

# Lanthanide-based single-molecule

## magnets

## A rational design by chemical intuition



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I would like to dedicate this thesis to my loving parents Mr and Mrs Marcellus Izuogu, my late aunt Mrs. Ngozi Izuogu who first gave me the opportunity to pursue a higher education by providing the financial aid for my first year in undergraduate without which I might not have pursued a degree in the university. Having redefined my research during the COVID lockdown and completed my thesis at such extra ordinary time, I also wish to dedicate this piece of work to all the victims of COVID-19

### Declaration

I hereby declare that except where specific reference is made to the work of others, the contents of this dissertation are original and have not been submitted in whole or in part for consideration for any other degree or qualification in this, or any other university. This dissertation is my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text and Acknowledgements. This dissertation contains fewer than 52,000 words, including abstract, tables, and footnotes, but excluding table of contents, photographs, diagrams, figure captions, list of figures, list of nomenclatures (symbols and abbreviations), bibliography, appendices and acknowledgements, and has fewer than 75 figures.

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#### Abstract

A model complex of dysprosium,  $Dy(N_2O_2C_7H_{11})_3$  (Dy2) was built by successive capping of the peripheral aromatic ring of a butterfly-shaped dysprosium complex of a schiff base ligand, Dy(N4O5C14H11)3 (Dy1). The structural modifications were carried out in order to investigate the effect of the chemical surroundings like aromaticity on the observation of single-molecule magnet (SMM) behaviour in a lanthanide-based complex (Dy1). Experimental techniques were combined with theoretical tools to investigate the dynamics of magnetic properties of the Dy1 and compared with the theoretical results for Dy2 to gain insight on the contribution of covalency, crystal field effect and the role of aromaticity in stabilizing the excited magnetic levels of a single-molecule magnet. Dy1 showed frequency-dependent slow magnetic relaxation characteristics of a single-molecule magnet with and without applied dc field and a blocking temperature of about 8 K. The obtained results showed that despite f-electrons having weak interactions with ligand field, it is possible to tune the magnetic properties of lanthanide-based complexes using ring currents, control of covalency and peripheral ligand substitution. Furthermore, di-nuclear acetate bridged lanthanide complexes with two different structural motifs,  $\mathbf{Er1} = [\mathrm{Er}(\mathrm{CH}_3\mathrm{COO})(\mathrm{CH}_3\mathrm{COO})_2(\mathrm{H}_2\mathrm{O})_2]_2 \cdot 4\mathrm{H}_2\mathrm{O}$  and  $[Ln(CH_3COO)(CH_3COO)(CH_3COO)(H_2O)CH_3COOH]_2 \cdot 2CH_3COOH (Ln = Er (Er2),$  $Y_{0.8}Er_{0.2}$  (Er3)) were characterised. The solvent effects on the structure, electronic and magnetic properties were studied by experiments and theoretical methods. The tetraacetate-bridged erbium (Er2) showed a shorter intra-molecular Er – Er distance of 3.878 Å compared to the doubly-bridged counterpart (Er1) with Er – Er intra-molecular separation of 4.152 Å. Er2 exhibited weak ferromagnetic ordering at very low temperature in the dc magnetic measurement due to the short proximity of the Er centres. A field-induced slow magnetic relaxation for spin reversal characteristics of single-molecule magnet behaviour with relaxation dynamics dominated by Orbach process was observed for Er2. Er1 showed very fast slow magnetic relaxation dominated by quantum tunnelling of magnetization as evidenced in the Cole-Cole plot and the observed plateau in the susceptibility curve. The role of inter-molecular interactions between Er centres was investigated using

yttrium diluted sample (Er3). The enhanced magnetic property of Er2 and Er3 over **Er1** is attributed to the structural changes accompanying the choice of synthetic solvents used as well as the stronger interactions between Er and oxygen donor atoms of the acetate/acetic acid over that of water molecule as ligands. The present study presents an interesting result on solvent effects in the design of single-molecule magnets. In addition to the peripheral, aromatic, solvent effect and accompanying lanthanide-lanthanide coupling investigated, the role of hetero-metallic Pd-Ln bonding interaction was investigated using a set of tetranuclear acetate-bridged palladium-lanthanide complexes of the formula  $[Pd_2Ln_2(H_2O)_2(AcO)_{10}] \cdot 2AcOH (AcO = CH_3COO^-, Ln = Ce, Pr, Nd, Pm, Sm, Gd,$ Tb, Dy, Ho, Er, Tm and Yb) by theoretical means and compared with experimental results for the lanthanide series to establish an interesting alternating trend in the observation of slow magnetic relaxation between Kramers and non-Kramers ions along the series. The role of axial perturbation, electron-cloud distortion and utility of metal as a ligand to upset the electronic properties of lanthanide complexes and their implication to the observation of slow magnetic relaxation were investigated. Results showed that transition metal - lanthanide bonding interaction presents a unique way to control the ligand field of lanthanide at varying degrees while confirming the role of rigidity in SMM design.

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# Chapter 1

## General Introduction

The manifestation of physical and chemical properties of material arises from the overall behaviour of electrons in the atoms that make up such material. Millions of atoms therefore can combine in the right proportion to form a given material with characteristics identity which can be traced back to the electronic structure of the make-up atoms and ways in which they combine. A class of physical phenomena mediated by the magnetic field in which materials assert an attractive or repulsive influence on other materials is what is known today as magnetism. The causes of magnetism are electric current and the magnetic moments of elementary particles. The contributions from atomic nuclei are so negligible in the context of magnetic resonance (NMR) and magnetic resonance imaging (MRI). The observation of solid-state phenomena such as magnetism or superconductivity can be understood by studying pure metals, alloys, or well-defined compounds. However, practical applications that seek to use these solid-state phenomena are limited to designs by trial and error. Therefore, we must establish means of predicting with high precision how materials can be designed for optimum practical application and advancement.

As a prominent phenomenon in solid state chemistry, magnetic properties are exhibited by all forms of matter, from free atoms, ions, molecules or condensed aggregates because they develop a magnetic dipole moment in the presence of an external magnetic field.

Magnetic materials have contributed so much to the technological revolution particularly in storage devices, communication devices and medical equipment. Intermetallics consisting of lanthanoids like SmCo5 and Nd2Fe14B are one of the most powerful traditional magnets

which have been employed for various technological applications.[1, 2] These applications use giant magneto-resistance (GMR) or tunneling magneto resistance (TMR) effect for their magnetic random access memory (MRAM) application.[3, 4]

Molecule-base magnets such as the single-molecule magnets (SMMs), single-ion magnets (SIMs) and single-chain magnets (SCMs) are promising candidates for magnetic memory devices to overcome Moore's[5] limitation due to their potential for high-density information storage and quantum computing. Rather than encode data into binary digits in one of two definite states (0 or 1), the development of quantum computers that can encode data in an infinite number of superposition of states as quantum bits ( $\Psi = |0\rangle + |1\rangle$ ) has attracted much attention in recent time[6–10] Theoretically, a quantum computer would be able to solve certain problems much quicker than any classical computer that uses the best currently known algorithm.

With sharply defined sizes in sub-nano scale dimension, molecular magnets exhibiting superparamagnetic-like properties arising from their molecular origin rather than cooperative or destructive interactions in the bulk state are what we now know today as single-molecule magnets (SMMs).[11] They can act as small magnetic memories at such nano dimension and can be dissolved in solvents as well as fine-tuned with various ligand design, increasing the flexibility of fabrication.[12–15] SMM applications extend beyond storage device or quantum computing,[16, 17] to include information processing, spintronic,[18, 4] biomedical applications (e.g. MRI contrast agents)[19] or magnetic refrigeration.[20]

To be an active SMM, materials must show slow magnetic relaxation of the magnetization which is purely of molecular origin below a characteristic temperature known as the blocking temperature  $(T_B)$  and a large total spin ground state (S) with negative Ising type magnetic anisotropy otherwise called the axial zero-field splitting (D) whose effective energy  $(\Delta_{\text{eff}})$  value is expressed as  $S^2|D|$  or  $(S^2 - \frac{1}{4})|D|$  for integer and half-integer spins respectively.[21, 22] This expression is true for transition metals but differ for f-block ions whose spin-orbit coupling contribute to the magnetic anisotropy and so is best described by the *J*-term rather than the total spin (S). A positive *D* value describes a system in which the smallest  $m_j$  state is lower in energy than the larger  $m_j$  levels while a negative *D* indicates a system whose largest  $m_j$  state is lowest in energy.[23] The later scenario is favourable for the realisation of SMM behaviour because upon magnetisation and demagnetisation of the system, the magnetisation is retained (provided the thermal energy  $< \Delta_{\text{eff}}$ ) leading to a magnetic hysteresis effect of purely molecular origin which is the dominant attribute of SMM.

Despite the progress made so far in the field of SMM research, SMMs remains laboratory curiosities due to very low  $T_{\rm B}$  with 60 and 80 K been among the highest  $T_{\rm B}$  reported so far for a dysprosocenium complex.[24, 25] Therefore, the best way to increase the temperature for practical application must be found. Using series of ligands, SMM behaviour in complexes have been investigated using mono to polynuclear clusters involving d- and f-block[26] metal ions.[27] Although Long and Rinehart[2] had used the quadrupole moment approximation to show how molecular design can be used to enhance magnetic anisotropy, researchers are yet to fully understand how to rationally enhance the SMM behaviour when temperature is increased. The most promising reports are more like serendipity rather than design due to the complexity involved in the interaction of magnetic centres like the lanthanide ions and surrounding ligand field. Molecular designs that seek to maximize the total spin by turning to cluster chemistry is not so reliable due to destructive interactions between magnetic centres within the cluster system.[26] The implication is that parameters involved in maximising magnetic anisotropy of systems should be identified first to guarantee breakthrough in the field of SMMs.

The development of quantum mechanics undoubtedly is a landmark for solid state physics and chemistry as a whole because of its application to model problems. This has led to the use of multireference *ab initio* calculations, the principles of computational approach that can be applied to simple mononuclear complexes to elucidate and parameterise factors necessary to enhance SMM behaviour.[28]

Lanthanide SMMs are more promising than transition metal SMMs due to higher spin-orbit coupling and spin ground state for the single ion. Although quadrupole approximations of 4f-shell,[2] the Kramers doublet (odd numbers of spins)[29] and symmetry considerations[30] have been employed to further understand the factors for realising high  $T_{\rm B}$  SMMs, none of these approaches has yielded completely what the factors that cause this behaviour indeed is. Multi-parameter spin Hamiltonians of lanthanide complexes make the calculations quite complicated. The complexity of multiple electronic states, unquenchable spin-orbit coupling,[31, 32] and hyperfine interaction make it difficult to investigate lanthanoid SMMs with theoretical models like DFT at present.[33] Therefore, approaches are needed to solve this problem more directly and accurately. This is the crux of the present study.

In this thesis, multireference computational models was used to investigate dysprosiumbased complexes by looking at their electronic structures, magnetic moment, magnetic susceptibilities, spectroscopic states, magnetic structures and chemical environmental effects with the aim of mapping out parameters to enhance lanthanide-based single-molecule magnets and possibly drive this quantum phenomenon to or near room temperature for practical application. The success of which will also act as a test ground for new multireference techniques.

### 1.1 Electronic structure of materials

The term electronic structure in quantum chemistry is used to map both the wavefunction,  $(\Psi)$  and associated energies of electrons in each system. The electronic properties of molecular systems can be obtained from their auxiliary wavefunction, which is built as a determinant of molecular orbitals (MOs) as a linear combination of atomic orbitals (AOs) that make up the system. By solving the time-independent Schrödinger equation,  $(H\Psi = E\Psi)$ , we can find the wavefunction  $(\Psi)$  and associated energy (E) for a given system. Although this is not as straightforward as it sounds for large systems due to complexities arising from different types of interactions involving the electrons in orbitals and the nucleus. As computationally intensive as electronic structure calculations may be, along with nuclear dynamics, it remains a feasible method in studying quantum dynamics of large molecular systems. The Born-Oppenheimer approximation[34] which takes note of the great difference in masses of electrons and nuclei allows us to regard the nuclei as fixed in position and solve the Schr odinger equation for the electrons in the static electric potential arising from the nuclei in a particular arrangement. This means that we can extract the electronic contribution to magnetic moments by focusing on the electronic wavefunction of the total wavefunction in equation 1.1.[35] The solution can then be improved by considering the nuclear effect to the electrons.

$$\Psi_{total} = \Psi_{electronic} \times \Psi_{nuclear} \tag{1.1}$$

The non-relativistic time-dependent molecular Hamiltonian is then given by equation 1.2.

$$H = H_e + T_n \tag{1.2}$$

where  $H_e$  and  $T_n$  are given as

$$H_{e} = -\sum_{i}^{n} \frac{1}{2} \nabla_{\mathbf{r}_{i}}^{2} - \sum_{i,A} \frac{Z_{A}}{\mathbf{r}_{iA}} + \sum_{i>j} \frac{1}{\mathbf{r}_{ij}} + \sum_{B>A} \frac{Z_{A}Z_{B}}{\mathbf{R}_{AB}}$$
(1.3)

$$T_n = -\sum_A \frac{1}{2M_A} \nabla^2_{\mathbf{R}_A}$$
(1.4)

Where i, j refer to electrons and A, B refer to nuclei. By substituting equations 1.3 and 1.4 into 1.2, we have a more generalised equation 1.5 which defines the non-relativistic Hamiltonian in full.

$$\hat{H} = \underbrace{\sum_{A=1}^{N_n} -\frac{1}{2M_A} \nabla_{\mathbf{R}_A}^2}_{\hat{\mathbf{T}}_n} + \underbrace{\sum_{i=1}^{N} -\frac{1}{2} \nabla_{\mathbf{r}_i}^2}_{\hat{\mathbf{T}}_e} + \underbrace{\sum_{B>A} \frac{Z_A Z_B}{|\mathbf{R}_{AB}|}}_{\hat{\mathbf{V}}_{nn}} - \underbrace{\sum_{i,A} \frac{Z_A}{|\mathbf{r}_{iA}|}}_{\hat{\mathbf{V}}_{ne}} + \underbrace{\sum_{i< j} \frac{1}{|\mathbf{r}_{ij}|}}_{\hat{\mathbf{V}}_{ee}}$$
(1.5)

where  $N_n$  and N refer to the number of atomic nuclei and electrons respectively. By solving the Schrödinger equation for a given system, one can obtain an approximate solution to the total energy.

### 1.2 Classes of magnetic materials

It is possible to get information on the magnitude or direction of the magnetic moment generated within the particle(s) by simply specifying the position of the electron(s) within a particle system placed in a magnetic field. Depending on the alignment of the spins, the material could show a net attractive or repulsive force on the external magnetic field giving rise to magnetism. The type of magnetism observed in materials may include the following;

- 1. Diamagnetism: If S = 0, a zero net magnetic moment results, given rise to a weakly repelled material in a magnetic field and such materials are classed as diamagnetic.
- 2. Paramagnetism: These are materials with  $S \neq 0$ , leading to a non-zero net magnetic moments which are strongly attracted in a magnetic field with an induced dipole moment and spin aligned in the same direction as the applied field.

- 3. Ferromagnetism: This is observed for materials which are strongly attracted in a magnetic field with a permanent magnetic moment even in the absence of magnetic field. It also results when  $S \neq 0$ , leading to a non-zero net magnetic moments.
- 4. Antiferromagnetism: This also results when  $S \neq 0$ , leading to a zero net magnetic moments and possesses spin(s) which align antiparallel to another.
- 5. Ferrimagnetism: This is observed for materials with  $S \neq 0$ . In this type of materials the magnetic moments have opposing moments similar to that of antiferromagnetism, but does not lead to the cancellation of the antiparallel moments. A spontaneous magnetization would normally occur in the absence of field below the Neel temperature.[36]
- Metamagnetism: This is observed when a material shows a magnetization jump with a little change in applied magnetic field arising from exchange splitting of the Fermi surface[37] or field-induced spin flip.[38] FeCl<sub>2</sub> crystals were the first example of the observation of metamagnetism.[38]
- 7. **Superparamagnetism**: This is observed for single domain particles acting like single magnetic spin. This is mostly observed in nanoparticles with pure iron and cobalt nanoparticles embedded in non-magnetic matrices forming part of the most exciting observation of superparamagnetic behaviour.[39] Example of a class of material that exhibit superparamagnetic behaviour is the single-molecule magnet whose magnetic property is purely of molecular origin without collective long-range ordering.
- 8. **Spin glass**: Spin glass is an example of geometry frustration[22, 29, 37] observed below the freezing point above which the material is purely paramagnetic.

It is important to note that both ferromagnetism and antiferromagnetism are affected by temperature. Ferromagnets tend to lose their ferromagnetic properties above the Curie point while antiferromagnets lose their antiferromagnetic properties above the Néel temperature turning to paramagnets in both cases. When a material is magnetised, the dipole moment  $(\mathbf{m} = \mathbf{M}V)$  can interact with the external magnetic field **B** with energy described according to equation 1.6 below which can also refer to the Zeeman energy.

$$E = -\mu_0 \mathbf{m} \cdot \mathbf{B} \tag{1.6}$$

Where, **m** is dipole moment, **M** is magnetisation, V is the volume of the magnet and  $\mu_0$  is the magnetic field constant which ensures a correct energy dimension ( $\mu_0 = 4\pi \times 10^{-7}$ 

 $JA^{-2}m^{-1}$ ). If we consider a small particle placed in a uniform magnetic field (Figure 1.1), the magnetic energy can be expressed as in equation 1.7, where  $\theta$  is the angle the particle's spin makes to the magnetic field. By differentiating equation 1.7, the mechanical torque on the particle is obtained (equation 1.8) such that when  $\theta = 0$  or  $\mathbf{m} || \mathbf{B}$ , the obtained energy is minimum.



Fig. 1.1 Magnetized body in a uniform magnetic field

$$E = -\mu_0 m \cdot \mathbf{B} \cos \theta \tag{1.7}$$

$$\Gamma = -\frac{dE}{d\theta} = -\mu_0 m \cdot \mathbf{B} \sin \theta \qquad (1.8)$$

For a more extensive system, it might become necessary to compute the energy in a non-uniform field, so equation 1.7 becomes equation 1.9 or, in terms of atomic moments  $m_i = m(r_i)$  (equation 1.10).

$$E = -\mu_0 \int \mathbf{M}(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r}) dV \qquad (1.9)$$

$$E = -\mu_0 \sum_i m_i \cdot \mathbf{B}(r_i) \tag{1.10}$$

The orbital moment arising from the external magnetic field could be estimated by adding the kinetic term  $(\frac{1}{2}mev^2)$  to the magnetic energy equation described by equation 1.6 above and minimising the energy with respect to *m* to give equation 1.11.

$$E = \frac{\mu_0 \mathbf{B} e^2 R^2}{4m_e} \tag{1.11}$$

Quantum mechanics shows that subject to boundary condition  $(\psi(\phi + 2\pi) = \psi(\phi))$ , a rotating electron with mass,  $m_e$  and angular momentum  $(L = m_e R \mathbf{v})$  described by an angular wave function,  $\psi(\phi)$  will possess a quantised angular momentum in the units of  $\hbar = 1.054 \times 10^{-34}$  JS. Consequently, the moment is quantised in units of the Bohr magneton given by equation 1.12

$$\mu_B = \frac{e\hbar}{2m_e} \tag{1.12}$$

 $\mu_B$  is a critical quantity in magnetism and is of the correct order of magnitude for the moment of a single electron. If we assume that each electron in an atom possesses spin magnetic moment given by  $\mu_B$ , then the magnetisation of a single atom of Fe, for instance, will be much larger than experimental value of  $2.2\mu_B$ . The implication is that paired spins cancel out. Crystal fields can quench the moment resulting from the orbital if strong enough and so we observe that spin moment which fully survives in a crystal field contributes most of the magnetic moments observed in materials. For a given spin (*s*), we can then write the Hamiltonian if we apply field along the principal axis (equation 1.13).

$$H = -\mu_B \mathbf{BS}_z \tag{1.13}$$

The applied field causes a Zeeman splitting such that the up spin is energetically more favourable (Figure 1.2).



Fig. 1.2 Zeeman interaction of an electron with an external magnetic field  $(\mathbf{B})$ 

The probability, p of realizing the up and down spin state is then given by equation 1.14

$$p_{\pm} = \frac{1}{Z} \exp\left\{\pm \frac{\mu_0 \mu_B \mathbf{B}}{k_B T}\right\}$$
(1.14)

 $k_B$  is the Boltzmann constant and Z is the partition function.

### 1.3 Magnetic susceptibility

Magnetic susceptibility ( $\chi$ ) is a measure of the extent to which a material is magnetised in a magnetic field. It relates the magnetic moment to the magnetic flux density according to equation 1.15.

$$\chi_M = M_r \chi_m = \frac{M_r \chi_v}{\rho} \tag{1.15}$$

Where

 $\chi_m =$  mass magnetic susceptibility  $\chi_M =$  molar magnetic susceptibility  $M_r =$  relative molecular mass

ho = magnetic flux density

 $\chi_v =$  volume magnetic susceptibility

For a bulk sample, the magnetisation,  $\mathbf{M}$  is defined as the magnetic dipole moment per unit volume or unit mass given by equation 1.16.

$$\boldsymbol{\chi}\mathbf{B}_0 = \boldsymbol{\mu}_0\mathbf{M} \tag{1.16}$$

 $B_0$  is the ambient magnetic field and  $\chi$  magnetic susceptibility. The magnetic properties of the material are measured using a Superconducting Quantum Interference Device (SQUID), a device which consist of two superconductors separated by thin insulating layers to form two parallel Josephson junctions. During measurement, the SQUID magnetometer produces

an alternating magnetic flux in the pick-up coil to obtain the magnetic signal of the sample material when it is moved up and down the coil. A magnetic flux-to-voltage converter produces the voltage that is then amplified and read out by the magnetometer's electronics as bias signal.

#### 1.3.1 Magnetic anisotropy

The magnitude of the magnetic response measured in terms of the susceptibility is dependent on whether the system under investigation is isotropic or anisotropic such that the magnetisation is the same irrespective of direction or varies with direction respectively. This gives rise to the existence of an easy, intermediate and hard axis (Figure 1.3) which is a major determinant for the realisation of the single-molecule magnets. The easy axis corresponds to the energetically favourable direction of spontaneous magnetisation, the intermediate is less favourable while the hard axis is the energetically unfavourable direction of magnetisation.



Fig. 1.3 The Classical potential energy of a spin showing the axis of magnetisation for (a) uniaxial crystal field with negative D and (b) in addition to a transverse second-order term E[40]

By applying a transverse field **B** in the direction of the green arrow pointing down, the path integral can be converted in an area integral and the energy gap, the so-called tunnel splitting can be tuned in the hard-intermediate plane. The spin interacts with the magnetic field **B** via the Hamiltonian according to equation 1.13.

Depending on whether all spins are paired or not, the susceptibility values can either be less than zero ( $\chi < 0$ ) or greater than zero ( $\chi > 0$ ) for diamagnets and paramagnets

respectively. A linear relationship exists between the applied field and the observed magnetic moment for a paramagnetic material. However, ferromagnets do not show such linear relationship, and so an instantaneous differential term ( $\chi = \left(\frac{d\mathbf{M}}{dB}\right)$ ) is applied to account for their magnetic susceptibility.[41] The widespread occurrence of such small susceptibilities is an indication of the relativistic character of magnetic interactions. Susceptibilities, therefore, imply a competition between magnetic and mostly electrostatic forces. It is possible to get information on the dynamics of magnetization at different frequencies in an alternating current (*ac*) to obtain the *ac*-susceptibility with or without an applied direct current (*dc*) field.  $\chi$  can also be measured in the static mode (*dc*-susceptibility) for which a *dc* field is applied to probe the magnetic response at a specified temperature or temperature range.

#### 1.3.2 *dc*-susceptibility

Using a constant/static magnetic field (*dc*-magnetic field), the equilibrium value of magnetisation in a given sample can be measured to give a *dc* magnetisation curve. Force, torque or induction techniques can be used to measure the magnetic moment. The *dc*-susceptibility at constant field only varies with temperature when there is a unique interaction between magnetic centres leading to either ferromagnetism or antiferromagnetism or depopulation of  $m_j$  states if the crystal field allows it. The susceptibility calculated using the measured magnetisation from the *dc* measurement is termed *dc*-susceptibility.

#### 1.3.3 *ac*-susceptibility

To obtain information about magnetisation dynamics which are not available in *dc* measurements where the sample magnetic moment is constant during measurement, *ac* magnetic measurements are carried out. An essential tool for characterising SMM materials is *ac* magnetic measurements at different temperatures in which *ac*-field is applied to samples to measure the corresponding moment which is time-dependent and so gives information on the magnetisation dynamics. At low frequencies ( $\leq 1$  Hz), the measurement is like *dc* magnetometry and the magnetic moment follows the **M**(**B**) curve as would be measured in a *dc* experiment. If the *ac* field is small, the induced *ac* moment will be given by equation 1.17

$$\mathbf{M}_{AC} = \left(\frac{d\mathbf{M}}{dB}\right) \mathbf{B}_{AC} \sin\left(\omega t\right) \tag{1.17}$$

#### Where

 $\mathbf{B}_{AC} = \text{amplitude of the driving field}$   $\boldsymbol{\omega} = \text{driving frequency}$  $\boldsymbol{\chi} = \left(\frac{d\mathbf{M}}{dB}\right)$  is the slope of the  $\mathbf{M}(\mathbf{B})$  curve, called the susceptibility

The *dc*-susceptibility curve and that of the real part of *ac* show similar plot at low frequencies (the blue arrow in Figure 1.4) but vary at higher frequencies for all paramagnetic materials. This is due to the lagging of the magnetisation with the field drive leading to the observed susceptibility and a phase shift relative to the drive signal in an *ac*-field. Contrarily, single-molecule magnets show distinct relaxation processes that vary with frequency (*f*) and so, the *ac* susceptibility can deviate completely at all frequencies (high and low) when compared with their corresponding *dc* susceptibility. The frequency can then be converted to relaxation time.



Fig. 1.4 Schematic representation of frequency-dependent *ac* susceptibility plot of a magnetic material with varying external field (The blue line is the fit for the in-plane or real susceptibility ( $\chi'$ ) (blue bold circles). The red dotted lines is the fit for the out-of-phase or imaginary susceptibility ( $\chi''$ ) (red crosses)).[42]

 $\chi$  can also be regarded as the molar magnetic moment and second rank tensor. **B** is an axial vector. To obtain  $\chi$  which is diagonal with the principal value,  $\chi_u(u = x, y, z)$ , we choose the reference axes. In principle, the molar susceptibility is the algebraic sum of the diamagnetic and paramagnetic susceptibilities (i.e.  $\chi = \chi^D + \chi^P$  respectively). A diamagnetic material would have the negative  $\chi^D$  dominating while a paramagnet would be dominated by the positive  $\chi^P$ . The diamagnetic correction is usually applied following diamagnetic corrections from Pascal's Constants.[43] At higher frequency, *ac* moment no longer conforms to the *dc* magnetisation curve because of some dynamic effects in the sample, and so the magnetisation may lag behind the drive field. This effect is responsible for the two quantities usually measured in *ac* magnetometry;[44]

- 1. The magnitude of the susceptibility,  $\chi$
- 2. The phase shift relative to the drive signal,  $\phi$

This leads to measurement of two components of susceptibilities as;

- 1. In-phase or real component susceptibility,  $\chi'$
- 2. Out-of-plane, or imaginary component susceptibility,  $\chi''$
- $\chi^{'}$  and  $\chi^{"}$  are related by equations 1.18, 1.19, 1.20 and 1.21

$$\chi' = \chi \cos \phi \tag{1.18}$$

$$\chi'' = \chi \sin \phi \tag{1.19}$$

$$\chi = \sqrt{\chi'^2 + \chi''^2}$$
 (1.20)

$$\phi = \arctan\left(\frac{\chi''}{\chi'}\right)$$
 (1.21)

At low frequency where *ac* measurement is most like a *dc* measurement,  $\chi'$  represents the slope of the **M**(**B**) curve while  $\chi''$  indicates dissipative processes in the sample. Non-zero  $\chi''$  as observed in spin-glasses is attributed to relaxation and irreversibility while absorption due to permanent moment or irreversible domain wall movement is believed to be responsible for same observation in ferromagnets. To access information on thermodynamic phase changes, spin-glass behaviour, and other magnetic properties from *ac*-susceptibility, typical measurements are carried out and the following plots characterised;

- 1.  $\chi$  vs temperature
- 2.  $\chi$  vs driving frequency
- 3.  $\chi$  vs *dc* field bias

- 4.  $\chi$  vs *ac* field amplitude
- 5. Harmonic measurements and so forth.

In principle, an indication but not a conclusive evidence of SMM behaviour is the manifestation of a frequency dependent signal in the real and imaginary magnetic susceptibilities  $(\chi' \text{ and } \chi'')$  components of the dynamic susceptibility which is occasioned by the inability of the magnetization of materials to follow proportionately larger oscillating magnetic fields during practical *ac*-magnetization measurements. It is important to note that the peak maxima of the temperature dependent magnetic susceptibility  $(\chi'', \text{ not } \chi')$  corresponds to the point at which the angular frequency  $(\omega)$  of the oscillating magnetic field is equal to the rate of spin reversal  $(\frac{1}{\tau})$ . The real and imaginary magnetic susceptibilities follow the Cole-Cole model (equation 1.22 and 1.23). Where  $\chi_{adia}$  and  $\chi_{iso}$  are respectively the adiabatic and isothermal magnetic susceptibility,  $\tau$  is the relaxation time,  $\omega$  is the angular moment, and  $\alpha$  is the distribution of  $\tau$ ).

$$\chi'_{m} = \chi_{\text{adia}} + (\chi_{\text{iso}} - \chi_{\text{adia}}) \left( \frac{1 + (\omega \tau)^{(1-\alpha)} \sin \frac{\alpha \pi}{2}}{1 + 2(\omega \tau)^{(1-\alpha)} \sin \frac{\alpha \pi}{2} + (\omega \tau)^{(2-2\alpha)}} \right)$$
(1.22)

$$\chi_m'' = (\chi_{\rm iso} - \chi_{\rm adia}) \left( \frac{(\omega \tau)^{(1-\alpha)} \cos \frac{\alpha \pi}{2}}{1 + 2(\omega \tau)^{(1-\alpha)} \sin \frac{\alpha \pi}{2} + (\omega \tau)^{(2-2\alpha)}} \right)$$
(1.23)

Equations 1.22 and 1.23 are the basis for evaluating the slow magnetic response in SMMs. The out-of phase susceptibility is usually fitted to extract the relaxation time at different temperatures. Finally, by fitting the respective relaxation time insight on the mechanism of the spin dynamics is gained.

#### 1.4 Covalency and magnetic properties

The presence of d- or f-valence electrons in the crystal lattice of coordination complexes means that the ligand field (LF) or crystal field (CF) will directly have implications to the observed magnetic properties of such materials. Such effects are expected to vary on the basis of the covalent character of bonds formed between the magnetic metal centres and the organic ligands. The nature of these covalent interactions coupled with the electronic states and the symmetry of the molecule will have implications to the slow magnetic relaxation of SMMs. Few efforts have been made to understand how the f-orbitals can be influenced by the surrounding ligands.[45–47] Most of these efforts have only been rationalised using perturbation models.[48–51] The complex relationship between the anisotropy barrier ( $\Delta_{eff}$ ) and  $T_B$  and geometry which has seen random and non-correlating values for  $T_B$  and  $\Delta_{eff}$ means that more needs to be done to understand the best way to achieve high-performance SMM.[24, 25, 52–55] The contribution of covalency around the 4f orbitals with unpaired electrons deeply rooted within the core shell has become very important since the SMM behaviour is very sensitive to perturbations (for example changes in bond distances and little distortion in geometry) around the  $Ln^{3+}$  centre.

Although multireference computational methods like the Complete Active Space Self Consistent Field (CASSCF)[56–58] has been employed to rationalise the magnetic properties of lanthanide-based SMM, a reliable reproduction of the ligand field is still very challenging. This is due to the difficulties in accounting for the electrostatic field and covalent interactions between the deeply rooted f-orbitals and the crystal field environment created with the ligand. The ligand formal charge[59] and effective charge formalism[60] has been employed to account for the covalent and electrostatic contributions. However, both formalism leads to underestimation of the covalent and electronic characters especially for lanthanide complexes.[48] One reliable probe to circumvent this limitation could be the use of *ab initio* methods to understand the interplay between covalent and electrostatic contributions to the magnetic anisotropy tensor.

The degree of covalency for a series of imidodiphosphinochalcogenide complexes of the early lanthanides and actinides, M[N(EPR<sub>2</sub>)<sub>2</sub>]<sub>3</sub> (M = La, Ce, U, Pu; E = group 16 element; R = Ph, iPr) showed a greater covalency with soft acids as you descend the group 16 elements used as donor atoms. The trend was attributed to the increased *d*-orbital valence electron participation to the bonding molecular orbital.[61] It was also reported that the actinide containing complexes show higher degree of covalency compare to their lanthanide-based counterparts due to larger 5*f* vs 4*f* orbital participation.[61, 62] Izuogu *et. al*[63] reported a covalent interaction arising from the electron density donation from Pd<sup>2+</sup>  $d_{z^2}$  to hybrid *p*- and *d*-orbitals of the lanthanide using a La<sup>3+</sup>-model. Although the true nature of this interaction was not fully investigated they concluded that the interaction had some implication for the observed magnetic properties. Similar reports[64–66] for Pt<sup>2+</sup> showed even a much more interaction with stronger implication for the observed magnetic properties due to the more radially expanded 5*d*-orbitals of Pt<sup>2+</sup> compare to Pd<sup>2+</sup>. This shows

that more insight into the covalency for Ln containing complexes is needed as the race to high-performance SMM continues.

In this project, the effect of both covalent and electrostatic interactions (quadrupolar) will be investigated by carrying out structural perturbation involving the change of the  $Ln^{3+}$  centre or by ligand modifications to observe the effect of such variation on the electronic and magnetic properties across the lanthanide series. It is common knowledge that the ligand field effects in lanthanide-based complexes and their accompanying magnetic properties are strongly dependent on the the electrostatic interactions arising from the inner core f-orbital electrons.

#### 1.4.1 Ligand field effect

Lanthanide and actinide have been used to demonstrate the possibility of f-orbital participation in bonding.[61, 62, 67, 68] In some of the reports involving the actinide and cyclopentadienyl (Cp) ligand,[67, 68] there was a very large 5f contributions to the Cp-bonding orbitals for the later actinides which was attributed to a coincidental energy match of the 5f-orbitals with the Cp frontier orbitals which does not necessarily lead to metal to ligand bonding. Using spin densities as evidence, a contrasting report[69] on actinide dioxides, AnO<sub>2</sub> (An = Th - Es), showed an increased covalency in PuO<sub>2</sub>-CmO<sub>2</sub> when compared to the lighter actinides. Much of the debate on whether there is a genuine covalent character in coordination bonding involving f-orbitals have been focused on actinides complexes.[67–69] The lanthanide-based counterparts have not attracted much attention, probably due to the less radially expanded nature of the inner 4f-orbitals compare to the actinide 5f.

The preference of lanthanide ion for hard donor ligands in complex formation is strengthened by the high ionic character of coordination complexes involving lanthanide. The contracted and core nature of the  $4f^n$  electrons means they are unable to participate in bonding like  $\pi$ -backbonding that could introduce higher covalent character for the lanthanideligand (Ln-L) bond. Despite the small covalent character of the Ln-L interaction, the characteristics of Ln-based coordination complexes like orbital arrangement and bonding can be described by the ligand field theory (LFT). As an extension of point-charge based crystal field theory (CFT), LFT represents an application of molecular orbital theory (MOT) to metal complexes, allowing the incorporation of all forms of covalent interactions. The ligand field effect for lanthanide ions are very small compare to electronic and spin-orbit interactions. However, since the magnetic dipole-dipole interaction and accompanying j-coupling are significantly smaller than the ligand field effect, the LFT has become a crucial parameter to consider in the design of SMM.

In this thesis, theoretical treatment of covalency and ligand field effects will employ the *ab initio* computation of Slaters and Racah parameters and accompanying nephelauxetic effects as described in Chapter 3.

## Chapter 2

# Single-molecule magnets: Experimental perspectives

Nano-science opened a new window through which exceptional properties of materials which are absent in the bulk can be exploited for technological advancements. Dimensionality has become an intrinsic part of research with atom-science (for material less than 1 nm in size), nano-science (for materials between 1-100 nm in size), micro-science and mesoscopic-science (materials lager than 100 nm) been exploited for various forms of electronic properties not addressable in macro-science field. Nano-size materials have shown great promises for the observation of some quantum effects. DNA, biological and organic molecules, graphene, fullerenes, nano-tubes, polymers, inorganic materials, metals and their complexes are all candidates for nano-science research. However, for wider applicability of these materials, the ease of variation is key. Metal complexes possess enormous potential to tune material properties at such nano-dimension by metal and infinite ligand variations. The presence of unpaired spins and the different variations in molecular architecture opened a new research front in molecule-based magnets with quantum effect not observed independently in both pure metals and organic molecules.

Frontiers of molecular magnetism investigate electronic properties involving intimately related electron exchange and transfer which rely upon spin- and charge electronic effects, double exchange, spin crossover, valence tautomerism in small oligonuclear complexes and other kinds of spin dynamics.[70–72] By using mono-, di- and polynuclear complexes of transition and lanthanide metals researchers are now investigating new spin dynamics and corresponding quantum coherence that show promises for switchable bistable molecular nanomagnets for
potential applications in information data storage and processing, spintronics and medical imaging among others.[23, 26, 73]

However, one of the main targets of molecular magnetism continues to be the possibility of realising an SMM property with  $T_{\rm B}$  at nitrogen or near room temperature.

#### 2.1 Features of single-molecule magnet

Nano-size molecular magnets (SMMs, SIMs and SCMs) are different from classical or conventional magnets from viewpoints of their physical properties as well as their mechanism. They are composed of coordination compounds with superparamagnetic behaviour below a certain blocking temperature. The coordination architecture allows us to easily design and tune versatile compounds with cheap elements and light molecules. How suitable a material is as SMM can be quantified in some ways. To develop materials with enhanced SMM behaviour, these features are necessary and they include.

- Magnetic hysteresis: This is produced when a magnetization lags behind the applied magnetic field. After magnetization up to field saturation and upon reversal of field direction, a remnant magnetization is left at zero field, creating a loop (hysteresis loop). Most SMM show a butterfly-type hysteresis loop which shows different pathways for magnetization and demagnetization but with zero remnant magnetization at zero field when the external magnetic field is removed.
- 2. Coercive magnetic field  $(\mathbf{H}_c)$ , which is the field required to drive the residual magnetic induction (remnant magnetization) back to zero
- 3. Magnetic blocking temperature  $(T_B)$ , which is the temperature below which a material can exhibit magnetic hysteresis. This is also referred to as the temperature below which a slow magnetic relaxation for spin reversal is observed. For standard comparison of SMM properties,  $(T_B)$  can also be define as the temperature at which a molecular magnet can show a relaxation time of 100 seconds or portrays SMM behaviour.
- 4. Frequency dependence in ac magnetic susceptibilities are observed.
- 5. There are no peaks in the heat capacity measurements.
- 6. The Cole-Cole plots obtained by Debye model are semi-circles due to the singlerelaxation mechanism.

- 7. The presence of an Anisotropic energy barrier ( $\Delta$ ) or effective energy barrier ( $\Delta_{eff}$ )
- 8. SMMs and SCMs are composed of isolated molecules and chains, respectively.
- 9. There are no long-range magnetic orderings (LRO) at finite temperatures.

# 2.2 Factors affecting the observation of SMM behaviour in lanthanide materials

Reports over the years [14, 23, 26, 74, 75] have shown that the primary factor preventing the industrial application of SMM is the  $(T_{\rm B})$ . This is because the observed quantum phenomenon that gives rise to slow magnetic relaxation of spins collapses as more energy in the form of temperature enters the system. Maximising the spin state is also believed to enhance SMM behaviour provided there is no destructive coupling that lowers the total spin ground state, particularly for a cluster system. This is one of the reasons lanthanide-based SMM is now most preferred for SMM design because of the high spin state for a single ion. Therefore, we must consider interactions that might arise such as double exchange, couplings - antiferromagnetic coupling, ferromagnetic coupling among others in order to maximise the total spin state. Researchers have also argued that anisotropy of a single ion is an essential consideration towards SMM design. [28, 2, 76] This has diverted attention to lanthanide-based SMM due to the high intrisic anisotropy of a single lanthanide ion as portrayed by the quadrupole moment approximation. [2] Even though f-electrons rarely interact with coordinating ligands, the ligand field effect experienced by f-orbitals is enough to affect the magnetic property of SMM materials since the magnetic interaction is of the order of magnitude lower in energy than the ligand field. Therefore, it is possible to tune SMM behaviour by ligand variations and external stimuli like solvents.[74] QTM originates from the overlap of wave functions with different spin states.[77] Symmetry has been shown to affect SMM behaviour with higher symmetry favouring SMM because it minimises the mixing of the magnetic states  $(m_i \text{ states})$  which helps to give magnetic spins the time to relax over an energy barrier and through distinct  $m_i$  states rather than tunnel. [78–83] Lower symmetry increases mixing of the  $m_i$  states since the symmetry is such that different sets of spin states coexist, giving room for QTM and so not ideal for SMM design.

#### 2.3 Transition metal-based single-molecule magnets

The advent of single-molecule magnets could be traced back to the discovery made by Friedman *et al.*[84], Barbara *et al.*[85, 86] and Sessoli *et al.*[12, 87] when a  $Mn_{12}$ acetate cluster first synthesized by Lis[88] and later shown to exhibit macroscopic quantum tunnelling of magnetization[85] was reported to show step-wise magnetic hysteresis (Figure 2.1) different from that of a bulk magnet.



Fig. 2.1 Magnetization vs field plot showing magnetic hysteresis in Mn<sub>12</sub> acetate cluster.[85, 86]

The step-wise hysteresis loop arises because of quantum tunnelling of magnetisation at the different quantised energy level, indicating that spins are also quantised. This was the first observation of quantum phenomenon of spin in molecule-based magnets. Afterwards, research on molecular designs to observe this quantum phenomenon began. The magnetic spins in the Mn12 system exhibit slow magnetic relaxation induced by the combined effects of high-spin ground states ( $S_T$ ) arising from the Mn<sup>III</sup> and Mn<sup>IV</sup> centres as well as a negative zero-field splitting constant (D). This combined effects is responsible for the slow magnetic

relaxation of SMM. Early studies on molecular magnets focused on maximising the total spin state by increasing nuclearity using d-block metals and particularly the Mn<sup>III</sup>  $d^4$  metal whose anisotropy is mainly from the Jahn-Teller distortion.[15, 21, 89, 90] However, reports over the years have brought this assumption under challenge, questioning that this might not be the best approach to push  $T_{\rm B}$  and  $\Delta_{\rm eff}$  up particularly due to destructive coupling between magnetic centres. This is evident in reports which have shown systems with higher total spin ground state exhibiting lower  $T_{\rm B}$  and  $\Delta_{\rm eff}$  compare to some similar systems with lower total spin ground states.[89] Several theoreticians[28, 91, 92] pointed out that the often quoted  $\Delta_{\text{eff}} = S^2 |D|$  or  $(S^2 - \frac{1}{4})|D|$  relationship makes it difficult to understand the fundamental connection between S and  $\Delta_{eff}$  since D itself is inversely proportional to  $S^2$ . Detailed ab initio studies have been used to show the influence of structural distortions on the D value. [93, 94] This further confirms that maximising the total spin state might not be the best way to obtain a more negative D value due to the vibronic enhancement of low-symmetry perturbations that might arise from certain substituent of the ligands. The complexity in controlling the mutual alignment of anisotropy axes in polynuclear systems would also mean that single-ion complexes, the so-called single-ion magnets (SIM) would be well suited to understand the properties that dictate SMM behaviour compared to clusters. However, the d-block metals, especially the first-row transition metal (TM), appear to be poorly suited for SIM designs that would produce high  $T_{\rm B}$ , and  $\Delta_{\rm eff}$  due to lower spin-orbit coupling constants compared to f-block metals, smaller magnetic moments and the ease of quenching of the orbital contribution to the magnetic moment by ligand field which couples strongly with d-orbitals.[23] Although, the advantage of producing strongly coupled spin systems exist for d-block-based SMMs compared to lanthanides,[95] strategies that will allow us to couple the anisotropy of individual ions together to create polymetallic systems (SMMs) more rationally are not yet realised. In the light of this, researchers are now looking at lanthanide-based SMMs which have shown improvement especially for SIMs which are easier to study and control than d-block clusters.

#### 2.4 Lanthanide-based single-molecule magnets

Researchers are now turning to lanthanide-based SMM for new design after Ishikawa *et.* al[96] reported the first lanthanide-based double-decker phthalocyanine complex functioning as magnets at the single-molecule level in 2003. The terbium double-decker complex exhibits SMM behaviour below 50 K with  $\Delta_{eff}$  as high as 230 cm<sup>-1</sup>(331 K), which is by far higher than that for the Mn<sub>12</sub> cluster at 61 K.[13] The double-decker and multi-decker complexes

involving the phthalocyanine sandwich system have been extensively characterised with much higher  $\Delta_{\rm eff}$ , and most of the breakthroughs recorded in the field of molecular magnets till date are mostly lanthanide-based whether polynuclear or mononuclear.[26, 2, 96–101] This has been attributed to the large anisotropy arising from the unquenched orbital angular momentum of the f-orbitals.

In other to understand the mechanism of improved SMM behaviour observed in lanthanidebased SMMs, it is important to point out how the electronic structure which makes lanthanides (Ln) unique distinguishes them from the d-block transition counterparts. Two types of electronic structures are possible for lanthanides, [Xe]4 $f^n6s^2$  and [Xe]4 $f^n5d^16s^2$ , where  $1 \le n \le 14$ . In general, the most accessible oxidation state of Ln is the Ln<sup>3+</sup> with very few exceptions for Ln<sup>2+</sup> as found mostly for Eu<sup>2+</sup>. Remarkably, the 4f orbitals show strong angular dependence and reside deep in the core shell. Interestingly, Ln<sup>3+</sup> ions with 4f electrons except for Gd<sup>3+</sup> (4 $f^7$ , half-filled) and Lu<sup>3+</sup> (4 $f^{14}$ , full-filled) all present substantial unquenched orbital angular momentum and effective spin-orbital coupling under ligand field leading to large single-ion anisotropies. Such strong anisotropies of Ln<sup>3+</sup> ions are very crucial for their SMM behaviour, as observed in several discoveries of numerous Ln SMMs with high effective barriers surpassing those of transition metal SMMs.[26, 74]

The future development of single-molecule magnets therefore depends on elucidating factors that are required to create molecular designs/architecture which would help to extract the maximum anisotropy of incorporated ions to enhance SMM behaviour as well as help synthetic chemists to understand the fundamental physics of these new molecular architectures coupled with the various interactions necessary for the realisation of their slow magnetic relaxation. To do this, we are now looking up to theoretical models. High-level ab initio, DFT and multireference theoretical methods which can provide direct information for the relationship between the crystal structure and magnetic properties have been used as a valuable tool for predicting the local anisotropy and giving insights on the relationship between the electronic structure and relaxation processes in SMM.[102–106] It is now clear that to enhance SMM behaviour, a high spin S in a well-isolated ground state is needed coupled with high magnetic anisotropy. The lanthanide ions are well suited to extract the advantage of high magnetic anisotropy and spin state for a single ion; they, however, lag in terms of weak coupling involving f-electrons making it challenging to achieve a well isolated large spin ground state with multiple lanthanide centres.[107, 108] Surprisingly, the large magnetic anisotropy more than compensates for the weak exchange coupling. Significant breakthrough in SMM field were dysprosium-based complexes which

showed magnetic hysteresis up to 60 and 80 K.[24, 25] This validates the assumption that lanthanide-based SMM design is the way to go to enhance SMM behaviour.

#### 2.5 Magnetisation of single-ion magnet

SMMs owe their behavior on the large S and J ground state with 2S + 1 spin microstates (for transition-metal-based) and 2J + 1 microstates (for f-block-based) respectively. These correspond to the  $M_S$  (spin) and  $M_J$  (spin-orbit coupled) states in the absence of transverse anisotropy which can split up in zero field by spin-orbit coupling and crystal field interactions if S or  $J > \frac{1}{2}$ . This is termed zero-field splitting (ZFS). The spin-orbit coupling can promote the mixing of orbital angular momentum of the electronically excited state into the ground state, allowing ZFS in spin-only complexes.

The application of external field to an SMM material splits the  $m_s$  or  $m_j$  states into up and down spins. The  $-m_s$  or  $-m_j$  state is greatly stabilized in energy relative to the  $+m_s$ or  $+m_j$  state. The energy stabilization of the  $-m_s$  or  $-m_j$  state causes the sample to align their spins with the external field in the  $-m_s$  or  $-m_j$  state until saturation of the magnetization. If the external field is cycled to zero, the magnetization, **M** is frozen by the presence of the energy barrier between the up spin and the down spin and only very slowly tends to the equilibrium value ( $\mathbf{M} = 0$ ) with a remanent magnetization.[101] A negative field reduces the height of the barrier and unfreezes the spins, thus allowing a rapid reversal of the magnetization. A hysteresis loop is therefore observed, which has a molecular and dynamical origin. The width of the loop (i.e. the coercive field) depends on the temperature as well as the rate of sweep of the magnetic field.

# Chapter 3

# Single-molecule magnets: Theoretical perspectives

The electronic structure of materials at sub-nano dimensions has attracted much attention especially in electron transport through molecular electronics. [72, 109–112] Molecular bridge devices such as spintronics requires ultra-fine bottom-up fabrication techniques that are very challenging necessitating a superior understanding of the nature of interaction that exist at atomic/molecular level and the dynamics of such interactions as system size is scaled. The electronic properties of materials influence the magnetic behaviour at micro and macro level. However, for Ln-based single molecule magnets, the nature and magnitude of the energy splitting of the electronic states are determined by looking at the inter-electronic repulsion, spin-orbit coupling (SOC), the ligand field, interatomic exchange interactions (where they exist), and the applied magnetic field. The core nature of the 4f-electrons and the nature of their interactions make them more difficult to describe and predict the overall consequences of their interactions.

There have been a considerable improvement in accuracy of theoretical methods to model SMM behaviors.[24, 113] In this thesis, *ab initio* multireference SCF methods like CASSCF and RASSCF implemented in ORCA[114, 115] and Molcas[116, 117] quantum computational packages will be used to investigate various molecular variations built from an X-ray crystal structure of lanthanide complexes and their corresponding effect.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>The crystal structures that will be used in all the calculations were either synthesised as a private project carried out in Japan by David Izuogu or modified for structural variations. Some of the structures have been reported in literature but not the calculations and results reported in the thesis. Some other structures have not been reported anywhere nor used for any degree.

#### 3.1 Theories of single-molecule magnets

Single-molecule magnets have shown great promises in advancing emerging technologies like quantum information processing and storage, [118, 112, 119] magnetic refrigerating, [120-123] magnetic resonance imaging[19, 124] among others. However, their are still milestones that must be reached for practical applications, most important of which is a more fundamental understanding of how the chemical and structural features (especially for the Ln containing complexes) correlate with their reactivity and properties like their bonding, spectroscopic and magnetic properties. A fuller and probably more accurate description of these properties can be obtained through *ab initio* calculations.[48, 57, 125] The spectroscopic, bonding, ligand-field effects and magnetic properties of molecules with unpaired f-electrons have been computed for various compounds with reasonable accuracy. [43, 76, 118, 96–98, 126] Microscopic spin Hamiltonian parameters such as zerofield splitting parameters (D, E), anisotropic exchange interaction  $(J_x, J_y, J_z)$ , isotropic exchange interaction (J), double exchange interaction (B) and g-tensors can be computed reliably by ab initio methods using coordinates from single-crystal x-ray structures in order to describe the magnetic properties of various transition and lanthanide containing complexes. Computational tools hold overwhelming potential to predict new generation of SMMs as well as support in interpretation and rationalisation of observed SMM behaviours making it a veritable tool in the rational design of high performance SMMs.

## 3.2 Magnetic anisotropy and zero-field splitting parameter

The core nature of the f-electrons in lanthanide hypothetically means that the degeneracy is preserved as they do not significantly interact with the ligand donor atoms. This confers large magnetic anisotropy on the lanthanide ion as a result of large SOC and unquenched orbital angular moment. In a specified direction, the preferential alignment of the magnetic moment in response to magnetic field defines the term magnetic anisotropy. Therefore, the magnetisation axis is classed as easy (z-axis by definition or easy plane denoted as xy-plane), hard (axis or plane perpendicular to the easy axis or plane respectively) or intermediate (which lies in-between easy and hard axes) axes of magnetisation (Figure 1.3). At the heart of the development of zero-dimensional magnets popularly known as SMMs are the anisotropic axial (D) and rhombic (E) zero-field splitting parameters for any given total spin (S) or J state. These parameters which also have direct consequences for the symmetry around the magnetic centre essentially govern SMM behaviour and can be represented according to the simplified Hamiltonian similar to the giant spin Hamiltonian;[127]

$$\hat{H}_{zfs} = D\left(\hat{\mathbf{S}}_z^2 - \frac{1}{3}\hat{\mathbf{S}}^2\right) + E\left(\hat{\mathbf{S}}_x^2 - \hat{\mathbf{S}}_y^2\right)$$
(3.1)

 $\hat{\mathbf{S}}$  is a spin operator which describes the spin projection along a given axis. D and E help to lift the degeneracy of the spin multiplicity (2S+1) associated with a given S in the absence of an applied magnetic field, a phenomenon known as zero-field splitting (ZFS). Given that the ratio of E to D obeys the boundary relation,  $0 \le \frac{E}{D} \le \frac{1}{3}$ , D is evaluated as  $D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy})$  and  $E = \frac{1}{2}(D_{xx} - D_{yy})$ .  $D_{zz}, D_{xx} and D_{yy}$  are the main anisotropic D-tensors in the z, x and y-axes respectively. An axial symmetry has D and E values to be non-zero and zero respectively while a cubic symmetry holds zero values for both D and E. SMM behaviour is usually favoured when D < 0, generally referred to as easy-axis anisotropy. Under this condition, the spin state with the largest non-zero value  $(m_s = \pm S)$  component along the quantization axis is most stable. On the other hand, a D > 0 scenario (refer to as easy-plane anisotropy) implies that the lowest spin state ( $m_s = 0$  for non-Kramers systems (integer spin) or  $m_s = \pm \frac{1}{2}$  for Kramers system (half integer spin) of a given spin system is most stable.[128]Consequently, SMM behaviour is not favoured when D > 0. The anisotropic nature of the molecule helps to generate energy barriers when spins are reversed. It is important to note that the spin-orbit coupling (SOC) and spin-spin coupling (SSC) in a given system has direct consequences to the ZFS values (D and E). Their contributions to the ZFS can be obtained from the wavefunction of a multi-configuration based methods like CASSCF. The spin components of a system with  $S > \frac{1}{2}$  spin-orbit free state can show ZFS when:

- 1. The SOC is significantly large
- 2. The crystal field felt by the metal centre is anisotropic in nature (i.e. not corresponding to spherical or cubic symmetry)

In addition, the spin-spin coupling also contributes but to a very small extent.[129, 130]

#### 3.3 Spin-Orbit Coupling

The spin-orbit coupling (SOC) parameter is an important parameter to consider in the design of lanthanide-based single-molecule magnets. Time-dependent density functional theory (TD-DFT) has previously been used to access ground, and low lying excited states associated with molecular orbitals but without much accuracy.[131] The first-, second- or third-order SOC if accurately evaluated can provide information about the origin of the Dand in turn the slow relaxation dynamics for SMMs. Since the interaction due to SOC has a considerable effect in energy splitting of electronic levels compared to the ligand field, the explicit description of state mixing due to the spin-orbit coupling operator is required to evaluate the magnetic and spectroscopic properties of materials.[132] In-state (direct mixing of spin and orbital angular momenta in ground state) and out-of-state (mixing of excited state with the ground state (a term similar in a way to orbital hybridisation but with respect to electronic wavefucntion) spin-orbit coupling also known as first order and second order spin-orbit coupling (SOC) respectively give rise to ZFS. The SOC operator from the matrix elements can be fitted to a model matrix in a procedure analogous to the ab initio Ligand Field (AILF) method [133] and is expressed as in equation 3.2. Any splitting arising from SOC is of magnitude given by the SOC parameter,  $\lambda$  as defined in equation 3.3.

$$\hat{\mathbf{H}} = \zeta \sum_{i} \mathbf{l}_{i} \cdot \mathbf{s}_{i}$$
(3.2)

$$\lambda = \frac{\zeta}{2S} \tag{3.3}$$

 $\zeta$  is the single electron spin-orbit coupling constant and S is the total spin, l and s represent the one-electron orbital and spin moments respectively. For the lanthanide, the SOC splits the multiplets with the same L, S and different J-values with energies corresponding to  $E(^{2S+1}L_J) = (\frac{\lambda}{2}\{J(J+1) - L(L+1) - S(S+1)\})$ , such that the ground state J-value is given by J = L - S for n < 7 and J = L + S for n > 7 (n =number of f-electrons). The 2J + 1 degeneracy can then be removed by perturbations like magnetic field or ligand field. As mentioned in section 2.3, the height of the  $\Delta_{\text{eff}}$  or  $\Delta$  is not proportional to S for lanthanides as portrayed in  $S^2|D|$  due to the effect of SOC, this obscures the fundamental connection between D and S. By employing the theoretical argument based on second-order perturbation theory and exact eigenstates of the Born-Oppenheimer Hamiltonian, we arrive at equations 3.4, 3.5, and 3.6 which shows clearly that D is inversely proportional to  $S^2$ .[134, 135]

$$D_{kl}^{SOC-(0)} = -\frac{1}{S^2} \sum_{b(S_b=S)} \Delta_b^{-1} \left\langle OSS \left| \sum_i h_k^{SO}(i) S_{i,z} \right| bSS \right\rangle \times \left\langle bSS \left| \sum_i h_l^{SO}(i) S_{i,z} \right| OSS \right\rangle$$
(3.4)

$$D_{kl}^{SOC-(-1)} = -\frac{1}{S(2S-1)} \sum_{b(S_b=S-1)} \Delta_b^{-1} \left\langle OSS \left| \sum_i h_k^{SO}(i)S_{i,+1} \right| bS - 1S - 1 \right\rangle \times \left\langle bS - 1S - 1 \left| \sum_i h_l^{SO}(i)S_{i,-1} \right| OSS \right\rangle$$
(3.5)

$$D_{kl}^{SOC-(+1)} = -\frac{1}{(S+1)(2S-1)} \sum_{b(S_b=S+1)} \Delta_b^{-1} \left\langle OSS \left| \sum_i h_k^{SO}(i)S_{i,-1} \right| bS + 1S + 1 \right\rangle \times \left\langle bS + 1S + 1 \left| \sum_i h_l^{SO}(i)S_{i,+1} \right| OSS \right\rangle$$
(3.6)

All symbols have their usual meaning with the first term (equation 3.4) describing contributions from excited states of the same spin as the ground states (S' = S). The second term (equation 3.5) represents the states for which S' = S - 1 and the third term (equation 3.6) represents the states for which S' = S + 1.  $\Delta_b = E_b - E_0$  which is the energy difference between multiplet excited states (b) and the ground-state multiplet (0) in the absence of SOC. 0SS is the ground spin state and bSS is the excited spin state. k and l are the Cartesian components x, y, and z. The SOC appears as an effective one-electron operator of the form  $\hat{H}_{SO} = \sum_i h_k^{SO}(i)S_i$ . Excited state weightings of the same multiplicity have exact dependency (equation 3.4) while those from different multiplicity shows approximate dependency (equation 3.5, and 3.6) which makes  $S^2|D|$  to be largely independent of S. This further confirms that molecular designs that tend to maximize S by increasing nuclearity might not be the best way to enhance SMM but to find a better way to maximize |D|.

#### 3.4 Spin-spin coupling

The effect of the interaction between two spins for lanthanide complexes on the zero-field splitting D (ZFS) cannot be neglected. The spin-spin (SS) Hamiltonian is used to describe this interaction and is given by equation 3.7[32, 136]

$$\hat{H}_{SS} = \frac{g_e^2 \alpha^2}{8} \sum_{i \neq j} \left[ \frac{\hat{s}(i)\hat{s}(j)}{r_{ij}^3} - \frac{3(\hat{s}(i)\mathbf{r}_{ij})(\hat{s}(j)\mathbf{r}_{ij})}{r_{ij}^5} \right]$$
(3.7)

The first-order perturbation theory can be used to account for the contribution of the spin-spin interaction to the  $\mathbf{D}$  tensor by evaluating equation 3.8.[32, 137]

$$D_{kl}^{(SS)} = \frac{g_e^2 \alpha^2}{4S(2S-1)} \times \left\{ \Psi_0^{SS} \left| \sum_{i \neq j} \sum_{i \neq j} \frac{r_{ij}^2 \delta_{kl} - 3(r_{ij})_k(r_{ij})_l}{r_{ij}^5} \times \left\{ 2\hat{s}_z(i)\hat{s}_z(j) - \hat{s}_x(i)\hat{s}_x(j) - \hat{s}_y(i)\hat{s}_y(j) \right\} \right| \Psi_0^{SS} \right\}$$
(3.8)

Where  $\Psi_0^{SS}$  is the *N*-electron wavefunction of the state of interest,  $g_e$  the *g* factor of a free electron. If we take  $\Psi_0^{SS}$  to be a single determinant, then we can obtain a new form of expression for equation 3.8 as shown in equation 3.9.[32, 138]

$$D_{kl}^{(SS)} = \frac{g_e^2 \alpha^2}{4S(2S-1)} \sum_{\mu\nu} \sum_{\kappa\tau} \left( P_{\mu\nu}^{\alpha-\beta} P_{\kappa\tau}^{\alpha-\beta} - P_{\mu\kappa}^{\alpha-\beta} P_{\nu\tau}^{\alpha-\beta} \right) \times \left\langle \mu\nu \right| \left( 3r_{12,k}r_{12,l} - \delta_{kl}r_{12}^2 \right) \left|\kappa\tau\right\rangle$$
(3.9)

where  $P^{\alpha-\beta} = P^{\alpha} - P^{\beta}$  denotes the spin density matrix.

#### 3.5 Interelectronic Interactions and covalency

Electronic transition energies for metal complexes has been expressed in terms of parameters of interelectronic repulsion – Racah-parameters, A, B and C, (which is more suited for

transition metal complexes) or in terms of Slater-Condon parameters,  $F_0$ ,  $F_2$ ,  $F_4$ , and  $F_6$  (more suited for lanthanide-based complexes. A measure of these energies provides useful information towards the understanding of the extent of covalency in coordination compounds. The interelectronic interaction has been well studied for transition metal complexes due to the very strong ligand field interactions the transition metal complexes experience when ligands approach them. Such interactions have consequences to the electronic, spectroscopic and magnetic properties of the complexes and could vary greatly as ligands are varied. Such effect is not well pronounced for lanthanide-based complexes due to the core nature of the f-electrons when compared to the d-electrons. However the effect, especially on the magnetic properties of lanthanide-based compounds, becomes important when temperature is lowered and could lead to the depopulation of sublevels with observed deviation from Curie law for ferromagnets.

An understanding of the extent of interelectronic interactions on lanthanide-based complexes and by extension the covalency would provide useful insights on the splitting of the ground multiplets and magnetic properties of SMMs. The Racah, Slater-Codon and the nephelauxetic parameters are therefore useful in this regards.

#### 3.5.1 Racah and Slater-Condon Parameters

Depending on the number and spin of electrons in multi-electron atoms and the type of orbital they occupy, electrons will experience some electronic repulsion which can be expressed in three parameters A, B, and C. These parameters are called the Racah parameters. The Slater-Condon parameters are derived from the integral expression of one-and two-body operators over wavefucations which are constructed as Slater determinants of orthomormal orbitals. The Racah and Slater-Condon parameters are defined according to equation 3.10

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 1 & 0 & -49 \\ 0 & 1 & -5 \\ 0 & 0 & 35 \end{pmatrix} \begin{pmatrix} F_0 \\ F_2 \\ F_4 \end{pmatrix}$$
(3.10)

 $F_k$  are the Slater integrals which are related to unnormalized Slater-Condon parameters  $(F^k)$  by equation 3.11

$$\begin{pmatrix} F_0 \\ F_2 \\ F_4 \end{pmatrix} = \begin{pmatrix} F^0 \\ \frac{1}{49}F^2 \\ \frac{1}{441}F^4 \end{pmatrix}$$
(3.11)

By mapping the ligand field Hamiltonian of each system (e.g.  $Ln^{3+}$ ) to the energies and wavefunctions obtained from *ab initio* treatments, the unnormalized interelectronic parameter ( $F^2$ ) and the SOC constant can be obtained with insight on the energy splitting as well as the coordination environment.[133] The Slater Condon parameters[139] which are defined according to equation 3.11 are used to characterise f-interelectronic repulsion as opposed to the *B* and *C* Racah parameters used for d-block systems.  $F^2$ ,  $F^4$ ,  $F^6$  are the unnormalized inter-electronic repulsion parameters,  $F_2$ ,  $F_4$ ,  $F_6$  represent the normalised versions. The Racah parameters  $E^1$ ,  $E^2$ , and  $E^3$  are related to Slater-Condon ( $F_k$ ),(k=2,4,6) according to equations 3.12 - 3.14

$$E^{1} = \frac{(70F_{2} + 231F_{4} + 2002F_{6})}{9}$$
(3.12)

$$E^2 = \frac{(F_2 + 3F_4 + 7F_6)}{9} \tag{3.13}$$

$$E^{3} = \frac{(5F_{2} + 6F_{4} + 91F_{6})}{3} \tag{3.14}$$

 $E^3$  is responsible for the energy splitting observed for highest spin multiplicity  $(S_{\text{max}})$  for a given  $\text{Ln}^{3+}$  (e.g. 6 for  $\text{Dy}^{3+}$ ) while  $E^1$  and  $E^2$  are responsible for the energy splitting between terms of lower multiplicity (e.g. 4, and 2 for  $\text{Dy}^{3+}$ ).

#### 3.5.2 Nephelauxetic effects

The interaction between ligand donor atoms and a metal ion when a coordination complex is formed leads to a decrease in the Racah interelectronic repulsion parameter (B) when compared to the free metal ion as a result of electron cloud expansion of the metal ion when approached by a ligand field in the coordinated form. This effect is termed the Nephelauxetic effect. The electron cloud expansion is an indication of some covalent character when the ligand interacts with the metal centre. The interelectronic repulsion term is incorporated into the Hamiltonian for the free ion according to equation 3.15

$$\hat{H} = \sum_{k=1}^{n} \left\{ \frac{1}{2m} \mathbf{p}_{k}^{2} - \frac{Ze^{2}}{r_{k}} \right\} + \sum_{k=1}^{n} \zeta(r_{k}) \mathbf{l}_{k} \cdot \mathbf{s}_{k} + \sum_{k < l^{n}} \frac{e^{2}}{r_{kl}}$$
(3.15)

where the sum of the hydrogen-like terms for single electron and the sum of the singleelectron spin-orbit interaction are represented by the first and second term, and the third term is the interelectronic repulsion.

The nephelauxetic effect with respect to the Racah parameter, B and Slater-Condon parameter  $F_k$  are represented according to equations 3.16 and 3.17

$$\beta = \frac{B_{\text{complex}}}{B_{\text{free-ion}}}$$
(3.16)

$$\beta = \frac{F_{k(\text{complex})}}{F_{k(\text{free-ion})}}$$
(3.17)

#### 3.5.3 *Ab initio* treatment of crystal/ligand field effects of lanthanide

The crystal field splitting energy for f-block elements is usually very small compared to those of the transition metals due to the core nature of the f-electrons. However, such energy is significant enough to affect the magnetic properties of the complex. The implication is that we can carefully tune the crystal field by ligand selection to achieve different magnetic properties. Structural variation of lanthanide complexes will therefore be expected to affect the crystal field (CF) when the lanthanide ions are surrounded by different set of ligands leading to exciting electronic, magnetic and spectroscopic properties.[108, 121, 140–144]

The long magnetisation relaxation time observed in Tb<sup>III</sup> double-decker complex (TbPc2, Pc : phthalocyanine ligand) which was among the first lanthanide-based SMM reported by Ishikawa and coworkers[96] in 2003 stem from the ligand field. The splitting of the ground state with a total *J*-value of 6 by the ligand field is uniaxial and the lowest sub-energy level has the highest  $J_z$  value. For the Tb<sup>III</sup> ion, the ground state multiplet (<sup>7</sup>F6) is split by the ligand field from the Pc ligand into 7 energy levels  $|0\rangle, |\pm1\rangle, |\pm2\rangle, |\pm3\rangle, |\pm4\rangle, |\pm5\rangle, |\pm6\rangle$  in which the the energy gap for spin reversal ( 400 cm<sup>-1</sup>) lies between the  $|\pm5\rangle$  and  $|\pm6\rangle$ .[145] Figure 3.1 shows the various energy levels and sublevels arising from the ligand

field splitting of the TbPc<sub>2</sub> double-decker complex and the nuclear - angular momenta coupling contribution (I - J) to the magnetic behaviour.

Several theoretical approaches have been developed and applied to understand how the crystal/ligand field affects properties like the magnetic, including those that consider the electronic field effect,[146, 147] covalence splitting,[148, 149] and the hybrid versions of covalence splitting and electronic field effect.[150, 151]

The placement of a  $\text{Ln}^{3+}$  with partially filled 4f orbitals in a ligand field environment causes the f-orbital energies with 2J+1 fold degeneracy to split when the symmetry around the  $\text{Ln}^{3+}$  is lower than spherical. The ligand field effect can then be described by an operator ( $\hat{U}_C F$ ) and the potential created by the charge distribution ( $\rho(\mathbf{R})$  can be accounted for all *i*-electrons using equation 3.18

$$\hat{U}_{CF} = -e \sum_{j=1}^{nel.} \hat{U}_j = -e \sum_{j=1}^{nel.} \int \frac{\rho(\mathbf{R})}{|\mathbf{R} - r_i|} dv$$
(3.18)

The solution to equation 3.18 is the secular determinant with matrix element of the type  $\langle \Phi_l | \mathbf{U}_{CF} | \Phi_k \rangle$ , where  $\langle \Phi_l |$  and  $| \Phi_k \rangle$  which are many-electron functions can be expressed in spherical harmonics to identify the eigen functions of the free Ln<sup>3+</sup>. The decomposition of the free ion terms in linear combination of the mono-electronic functions to evaluate the matrix element using Stevens formalism by neglecting mixing between different *J* multiplets gives equation 3.19[48]

$$\hat{U}_{CF} = \hat{H}_{CF}^{Stev} = \sum_{k=2,4,6} \alpha^k \sum_{q=-k}^k A_k^q \left\langle r^k \right\rangle \hat{\mathbf{O}}_k^q(\theta,\phi)$$
(3.19)

where the product of  $A_k^q$  (the lattice sum) and  $\langle r^k \rangle$  (the radial expectation value) give the crystal field parameter  $\mathbf{B}_k^q$  of rank k=2,4,6 for nl = 4f, q is the projection of the operator parameter,  $\hat{\mathbf{O}}_k^q$  is the operator equivalent (Stevens operator) of the crystal field potential and  $\alpha^k$  is a number (which depends on k) for the different  $f^n$  configurations and k-values. The CF Hamiltonian is invariant under all symmetry operations of the metal site point group and it's projection on the ground atomic multiplet  $({}^{2S+1}L_J)$  of a given lanthanide transforms into equation 3.20



Fig. 3.1 Schematic of the electronic structure of the TbPc<sub>2</sub> double-decker complex (ER: Electron Repulsion; SOC: Spin-orbital coupling; LF: Ligand field; MDI: Magnetic dipoledipole interaction; *IJ*: nuclear spin - angular momenta coupling)[145]

$$\hat{H}_{CF} = \sum_{k,q} \alpha_n \mathbf{B}_k^q \mathbf{O}_k^q (\mathbf{J})$$
(3.20)

where  $O_k^q(J)$  is the Stevens operator acting on the eigenfunctions of the J ground state and  $\alpha_n$  is the projection coefficient. For lanthanide-based compounds, 27 independent crystalfield parameters (for low symmetry compounds) are deployed to describe the complexes. The  $B_k^q$  for values of  $k \ge 8$  essentially provides a quantitative assessment of the applicability of the crystal-field approach to lanthanide and is valid when the contribution to those higher ranks are negligible, else we assume that the covalent contribution of the ligand orbitals to the 4f orbitals is not small. A detailed description and implementation of the crystal-field formalism which will be employed to investigate the respective compounds in this thesis is presented in references [48, 57, 116] and [117]. It is difficult to obtain complexes that has a strict symmetry and so the closest symmetry is either assumed for compounds that show some high level of symmetry while majority adopt the low symmetry group  $(C_1)$ . The  $[Tb(Pc)_2]^-$  synthesised by Ishikawa and co-workers was assigned to a  $D_{4d}$  point group despite not having a strict symmetry with only three axial terms of the crystal-field parameter (  $B_k^0, k = 2, 4, 6$ ) included to model the crystal-field.[96, 100] Reu et. al[152] assigned a point group of  $C_4 v$  to the same compound to obtain a crystal field energy spectrum that is different from that of Ishikawa and cowokers. A comparison of the crystal-field spectrum of the ground atomic multiplet of  $Tb^{3+}$  in  $[Tb(Pc)_2]^-$  for Ishikawa and Reu's model ( $D_{4d}$  and  $C_{4V}$  respectively) and that obtained from the *ab initio* calculation using the experimental crystal structure from crystalographical information file (CIF) with  $C_1$  symmetry shows a significant deviation as the crystal structure is symmetrised from  $C_1$ through  $C_{4v}$  to  $D_{4d}$  indicating that such symmetrisation should be avoided. Therefore, the  $C_1$  symmetry should be used for lanthanide-based complexes where a strict symmetry is not well defined.

#### 3.6 Multireference methods

The unusually complex electronic structure (multiconfigurational) of lanthanide-based complexes arising from open f-shell and large relativistic and electron correlation effect makes it impracticable to obtain an accurate description of their electronic states by using static single-reference methods like Hatree-Fock (HF) which is a method of approximation for

the determination of the wavefunction and energy of a system in a stationary state as a single determinant. An accurate description of lanthanide systems will involve computation of multideterminants arising from multiple configurations involving the ground and excited states. To circumvent the challenges of using HF methods for multi-electron and multiconfigurational systems like lanthanides, the multireference method which allows the inclusion of large number of configuration state functions (CSFs) with variational treatment of a smaller number of CSFs to generate highly accurate result than those from HF methods have been developed. The multireference methods are able to capture a large number of dynamic and static correlation effects.

Attempts to accurately account for electron repulsion by including their correlation and exchange energies has seen methods like density functional theory (DFT), Moller-plesset pertubation theory (MP), coupled cluster theory (CC), and configuration interaction (CI) developed.[153–155] An exact answer would be one where a full configuration interaction (FCI) is carried out with complete basis set. However, this is almost impossible to get as FCI scales factorially or exponentially with the number of basis set functions and a complete basis set is an infinite number of them. To circumvent this problem, multiconfigurational self-consistent field (MCSCF) and multirefrence configuration interaction (MRCI) methods have been developed.[57, 156, 157] MR methods can still face the problem of exponential scaling with respect to the number of orbitals needed for the calculation, but with truncation and selection of certain spaces, methods like Complete Active Space Self Consistent Field (CASSCF), Restricted Active Space Self-Consistent Field (RASSCF) can now be used to more accurately compute large systems like lanthanide-based complexes.[57, 48, 158]

#### 3.6.1 Complete Active Space Self-Consistence Field and Restricted Active Space Self-Consistence Field

The complexity of the electronic structure of lanthanide-containing complexes makes it computationally cumbersome to accurately describe the  $Ln^{3+}$  systems using single-reference methods. The use of TD-DFT to calculate low-lying excited states which are responsible for the slow magnetic relaxation for SMMs is not reliable since TD-DFT is a monodeterminant method that is not able to describe the wavefunctions associated with systems with large magnetic anisotropy needed for the observation of SMM behaviour. This has necessitated the use of MR methods when dealing with lanthanide-based compounds. MCSCF remains the basis of MR methods and can be employed as a reference wave function to account for long-range correlation of electrons in bonds and orbitals. CASSCF has become the

most popular and widely used MCSCF-type methods. The molecular orbitals (MO) space in CASSCF is chosen such that the inactive orbitals comprise orbitals that are doubly occupied, partially occupied ones are designated active orbitals while anything else after the active orbitals are designated as virtual orbitals. These orbitals are defined in unitary transformation. Therefore, to thoroughly study the static correlation effects, the complete active space self-consistent field (CASSCF) method which is a variational multiconfiguration SCF method will be employed as implemented in ORCA[114] and MOLCAS[116, 117] program to provide a correct qualitative wavefunction for the systems under investigations. The systems under investigation possess  $Ln^{3+}$  with  $4f^n$  configuration as the magnetic centre, and so the f-orbitals will be chosen as active orbitals. The internal space generally comprises the active and inactive orbitals while the external space is the virtual orbitals. Concerning the unitary transformation, the wavefunction and energy are invariant within the three subspaces. This allows us to assign a fixed number of electron in each of the active or inactive subspace. By expanding a set of orthonormal MO  $\psi_i(r)$  in basis functions, a configuration state function (CSF) is constructed (equation 3.21) to define the CASSCF wavefunction according to equation 3.22

$$\psi_i(r) = \sum_{\mu} c_{\mu i} \phi_{\mu}(r) \qquad (3.21)$$

$$\left|\Psi_{I}^{SS}\right\rangle = \sum_{k} C_{kI} \left|\Phi_{k}^{S}\right\rangle$$
(3.22)

Where  $c_{\mu i}$  is the MO coefficient,  $|\Psi_I^{SS}\rangle$  is the CASSCF *N*-electron wavefunction for the state *I*, and *S* is the total spin and the spin projection ( $M_s = S$  or  $M_s \neq S$ ) in the active space. The right-hand ket,  $|\Phi_k^S\rangle$  is a representation of a set of configuration state functions (which could be linear combination of Slater determinants) adapted for *S* and built from a subset of the orbital wavefunction while  $C_{kI}$  is the expansion coefficients for the first set of variational parameters. The upper bound to the true CASSCF energy is given by the Rayleigh quotient according to equation 3.23

$$E(c,C) = \frac{\left\langle \Psi_{I}^{SS} \middle| \hat{\mathbf{H}}_{BO} \middle| \Psi_{I}^{SS} \right\rangle}{\left\langle \Psi_{I}^{SS} \middle| \Psi_{I}^{SS} \right\rangle}$$
(3.23)

As expected, the energy gradient with respect to the MO and configuration interaction (CI) vanishes at convergence as shown in equation 3.24 and 3.25 respectively.

$$\frac{\partial E(c,C)}{\partial c_{\mu i}} = 0 \tag{3.24}$$

$$\frac{\partial E(c,C)}{\partial C_{kI}} = 0 \tag{3.25}$$

The CASSCF wavefunction is constructed in a way to ensure a well-defined total spin symmetry such that the active space is made up of some  $n_{ele}$  number of electrons in  $n_{orb}$  number of orbitals, the so-called CAS( $n_{ele}$ , $n_{orb}$ ). A rule of thumb is that natural orbitals in the active space should have occupation number (indicated by N(occ) in the CASSCF iteration block) between 1.98 to 0.02. It is possible to obtain a converged CASSCF from multiple multiplicities and roots. To do so, the state average technique is employed in which the energy is transformed.

In CASSCF, full CI is computed but only for electrons in the active space (Figure 3.2). All possible arrangements of active electrons in the active-subspace are included in the MR calculation and so, the number (N) of the spin-adapted configurations increases factorially with the expansion of the active space. This can make CASSCF calculation very demanding of computational power and so a good understanding of the electronic structure of the system under investigation will be required to select the best active space that would yield higher accuracy without becoming impossibly computationally demanding.

Attempts to circumvent the restriction of the magnitude of CASSCF active space and to generate more electrons/holes while economising the unimportant configurations led to the utilization of the restricted active space SCF (RASSCF) which method is composed of three parts RAS1, RAS2 and RAS3 as shown in figure 3.3. The RAS2 subspace is treated in the same way as the CASSCF active space in which all possible orbital occupation are allowed and utilised. The RAS1 subspace is used to permit a limited number of holes with doubly occupied orbitals while the RAS3 subspace is only permitted to accept limited number of electrons in the unoccupied virtual space. The limitation of the electrons and holes help reduce the exponential scaling of the number of configurations as the active space is expanded and in turn circumvent the same problem for a traditional CASSCF. A RASSCF calculation that only utilises orbitals in the RAS2 subspace without having any

holes in RAS1 or electrons in RAS3 will therefore perform a traditional CASSCF calculation. The converged CASSCF orbitals can be used to carry out property calculations like the magnetic properties. Usually, a state-averaged CASSCF wavefunction is obtained with the ground state multiplet with the required number of configuration functions (CF). However, by including the CF of other multiplets for a given ion, insight can be drawn on any possible contribution of such configuration especially to the low lying excited states in Ln<sup>3+</sup> systems. For example, the ground state multiplicity of Dy<sup>3+</sup> (<sup>6</sup>H) has a total of 21 configurations which is usually enough to define the magnetic property of Dy<sup>3+</sup> complexes. However, in some case, the lower multiplicities (2S + 1 = 4 and 2) with 224 and 490 configurations respectively might become important in describing the electronic structure of the strongly correlated system. The inclusion of the configurations of these multiplicities scales up the calculation very quickly but provides more accurate results.



#### 3.6.2 Second-order N-Electron Valence Perturbation Theory

As a multireference (MR) electronic structure method, CASSCF has been used to compute the physical properties of Ln complexes including magnetic properties and anisotropy of SMMs.[81, 127, 138, 159, 160] Multireference configuration interaction (MRCI),[125]multireference coupled-cluster (MRCC)[161] or multireference perturbation theories (MRPTs) can be used to adequately account for the dynamic correlation with higher preference for MRCC and MRCI for more accuracy. However, the trade off between the very expensive computational cost and accuracy makes MRPT methods good compromises. Therefore, the wavefunction obtained from the CASSCF can be used for electron correlation dynamics by employing the second-order N-electron valence perturbation theory (NEVPT2).[162-164] The strongly correlated N-electron valence perturbation theory (SC-NEVPT2) option is one option that could be used. [163] Although CASPT2 method [165, 154] which is a partially contracted formalism that uses a Møller-Plesset zero-order Hamiltonian provides some level of accuracy for the ground state and excited energies at a reasonable cost, the choice of NEVPT2 over CASPT2 become necessary to avoid the intruder state problem [162, 164] to which CASPT2 is occasionally subjected leading to divergences in the perturbation series. This effect can be accounted for due to the one-electron nature of the zero-order Hamiltonian  $(\mathbf{H}_0)$  for the CASPT2 state energy. The NEVPT2 method, instead, includes a bielectronic zero-order Hamiltonian which tends to rectify the intruder state problem without the use of posteriori parameter. The dynamic correlation affects the spin-free state energies and alters the spacing between energy levels with different coupling. Since the coefficients of excited states mixing with the ground term are related to the inverse of the energy difference in perturbation theory, it is expected that the SOC matrix element will be altered appreciably by introducing the dynamic electron correlation (NEVPT2). This is very important when evaluating lanthanide-based SMMs since the observed slow magnetic relaxation is between the ground state and most of the low lying excited states.

#### 3.7 Restricted Active Space State Interaction (RASSI)

For large systems like the lanthanide-based complexes, the spin-orbit coupling term is very important and must be included to accurately describe the properties of the system. One way to do this for different electronic states is through the restricted active space state interaction (RASSI) based on mean field integrals. RASSI has been used in the past to compute matrix element and transition densities between RASSCF wave functions.[166]

A RASSI calculation utilises the RAS electronic wave functions which includes the spinorbit Hamiltonian. Each electronic state from the computed CASSCF wavefunction is different in energy and can be correlated by the use of multireference CI or PT2 through a level shift technique.[154, 167] A fuller description of how the RASSI uses the RASSCF wavefuction in its spin-free formalism (the so-called Graphical Unitary Group Approach -GUGA)[57, 168, 169] is presented in reference [58]. To compute molecular properties such as magnetism using the RASSI-SO calculations, a good understanding of the electronic structure of the system under investigation is necessary as the calculation is not a black box exercise. This will allow a proper selection of the needed states that needs to mix. The chosen state configurations are then used to run a CASSCF or RASSCF calculations with state-averaging and depending on whether a quantitative or qualitative treatment is most important, a dynamic correlation calculation with MRCI or MRPT is computed before invoking the RASSI-SO to obtain the final energies, wavefuctions and transition properties.

First, the Douglas-Kroll Hamiltonian[170, 171] was employed to account for the relativistic effects especially for the heavy lanthanide ions alongside the use of relativistic corrected basis sets (e.g. the ANO-RCC and the ANO-DK3). The RASSCF method is then used to obtain a spin-free eigenstates in which all electrons in the seven f-orbitals serve as the active space. The obtained RASSCF wavefuction is then used as the basis set for the RASSI calculation which requires  $\frac{N(N+1)}{2}$  sets of matrix elements to compute any given N-states. By employing the atomic mean field approximation, the spin-orbit coupling interaction is accounted for within the RASSI method. The obtained RASSI-SO eigenstates are used to compute the magnetic properties and parameters of the pseudo-spin Hamiltonian using the matrix element of the magnetic moment for the given compound as implemented within the SINGLE-ANISO module of MOLCAS software program.

The magnetic properties of lanthanides are strongly tied to the ground state and the low-lying excited multiplets which when accurately described by theoretical approach provide good match with experimental results.[57] The description of the magnetic properties from first principle which has been applied to both transition metals[172] and lanthanides[173, 174] provides a reliable way to compute the zero-field and Zeeman splitting in terms of pseudospin operators for the chosen multiplets and ensures the correct derivation of the crystal field parameters of the given complex *a priori*.

An understanding of the microscopic spin Hamiltonian parameters such as the magnetic exchange interaction (J), the zero-field splitting (D), the rhombic energy E and the landé

g-factor will allow us to rationally design high performance SMMs. The magnetic property of a mononuclear complex can be computed *ab initio* by first solving the complete electronic Schrödinger equation with the inclusion of the spin-orbit coupling according to equation 3.26

$$\hat{H}\Psi_i = E_i \Psi_i \tag{3.26}$$

One way to evaluate equation 3.26 is to first compute the eigenfunctions of the Hamiltonian with scalar-relativistic terms which is necessary especially for heavy atoms like lanthanides but without including the SOC. This can be done by running a CASSCF calculation as described in section 3.6.1. This is then followed by the inclusion of the SOC within a restricted active space state interaction (RASSI) as previously described in section 3.7 with the multiplet eigenstate ( $\Psi_i$ ) of equation 3.26 given as shown in equation 3.27.

$$\Psi_i = \sum_{rSM} c_{i,rSM}^{RASSI} \Psi_{rSM}^{CASSCF}$$
(3.27)

The admixture coefficients  $c_{i,rSM}^{RASSI}$  can be obtained by disgonalization of the SOC matrix with the restricted space. This approach is implemented in the MOLCAS software package.[116, 117] Finally we can compute the magnetic properties by using the matrix element of the magnetic moment operator ( $\hat{\mu}$ ) previously described in section 3.8 according to equations 3.28 and 3.29.

$$\left\langle \Psi_{i} \middle| \hat{\mathbf{S}}_{\alpha} \middle| \Psi_{j} \right\rangle = \sum_{rS} \sum_{MM'} \left( c_{i,rSM}^{RASSI} \right) * c_{j,rSM'}^{RASSI} \left( \hat{\mathbf{S}}_{\alpha} \right)_{MM'}$$
(3.28)

$$\left\langle \Psi_{i} | \mathbf{\hat{L}}_{\alpha} | \Psi_{j} \right\rangle = \sum_{rr' SM'} \sum_{SM'} (c_{i,rSM}^{RASSI}) * c_{j,r'SM}^{RASSI} \left\langle \Psi_{rSM}^{CASSCF} | \mathbf{\hat{L}}_{\alpha} | \Psi_{r'SM}^{CASSCF} \right\rangle$$
(3.29)

where *r* represents solutions with the same roots,  $\alpha$ , the cartesian components, *S*, the total spin and *M*, the spin projection. The matrix elements of the total spin can be expressed according to equations 3.30 - 3.32.

$$(\hat{\mathbf{S}}_z)_{MM'} = M \delta_{MM'} \tag{3.30}$$

$$(\mathbf{\hat{S}}_x)_{MM'} = \frac{1}{2}\sqrt{(S+M)(S-M+1)\delta_{M',M-1}} + \frac{1}{2}\sqrt{(S-M)(S+M+1)\delta_{M',M+1}} \quad (3.31)$$

$$(\mathbf{\hat{S}}_{y})_{MM'} = -\frac{i}{2}\sqrt{S+M}(S-M+1)\delta_{M',M-1} + \frac{i}{2}\sqrt{S-M}(S+M+1)\delta_{M',M-1} \quad (3.32)$$

The computation of the magnetic properties includes contributions from the excited states through their Zeeman admixture and thermal population. The 'SINGLE ANISO' programme implemented in Molcas package allows the non-pertubative calculation of the pseudospin Hamiltonian and the magnetic properties *ab initio* by the inclusion of the SOC through RASSI while accounting for the Crystal field acting on the ground state. Full description of the method is given in references [57] and [58] and the references therein.

#### 3.7.1 g-factor

The gyromagnetic tensor gives great insight in understanding the origin of the slow magnetic relaxation of molecular magnets. [29] The ground spin-orbital manifolds of lanthanides can be described by the combination of spin and orbital quantum numbers (J) and the microstates arising due to the corresponding crystal field splitting into 2J + 1 terms allowing us to obtain large magnetic anisotropy for the orientation of the magnetization. Low symetry cause J to no longer be a good quantum number as the orbital momentum is significantly quenched. The QTM between the  $\pm M_J$  level at the ground state which lanthanide ions face coupled with the weak exchange interactions for polynuclear lanthanide complexes limits their performance as SMMs. The QTM arises due to the existence of the intrinsic tunnelling split ( $\Delta_{tun}$ ) in the absence of any external field and is proportional to the  $\Delta_{tun}$ .

To achieve a high performance SMM, ground state QTM needs to be eliminated or reduce which implies ensuring a zero  $\Delta_{tun}$  or very small  $\Delta_{tun}$ . Previous reports have shown that a smaller  $\Delta_{tun}$  is observed for highly symmetric environment around the Ln and improves SMM behaviour.[82] The *g*-factor allows us to evaluate this since a highly symmetrical environment around the Ln ion would show very strong axiality with large  $g_z$  or  $g_{\parallel}$ , while a low symmetry would show a large transverse components with large  $g_x/g_y$  or  $g_{\perp}$  and QTM. A judicious analysis of the *g*-factor will therefore give insight on how to design high performance SMMs by looking at the magnitude and signs of the axial and transverse *g*-factors.

# 3.8 Ab initio treatment of pseudospin Hamiltonian of mononuclear complexes

Accurate solutions for many electron systems are now possible using ab initio methods which now allows us to make accurate predictions of unknown properties of compounds by computation.[57] The magnetization and the magnetic susceptibility are both computed as the expectation values of the eigenstates. For lanthanide complexes, the inclusion of the SOC in the matrix element of the magnetic moment operator becomes very important due to the unquenched orbital momentum of the f-electrons. This can be done both in the absence and in the presence of a magnetic field. The interplay between the SOC at a metal ion site and the ligand field generated by the surrounding ligands gives rise the the magnetic anisotropy which is necessary for the observation of SMM behaviour. The application of external magnetic field could split the degenerate energy levels into different manifold (Zeeman-splitting), as well, some group of degenerate ground energy levels in the absence of field could split into 2S+1 (or 2J+1 for  $Ln^{3+}$ ) manifolds, a term referred to as the Zero-field splitting. To describe the magnetic properties of a complex will therefore require an accurate description of the effective spin or the pseudospin Hamiltonian[175-181] using the Zeeman-spliting and the zero-field splitting tensors.[182-184] Similar spin Hamiltonian parameters are extracted experimentally from EPR spectroscopy. The Zeeman-splitting gtensor has been determined by DFT[185] and *ab initio* methods[186, 187] while the zerofield splitting **D** tensor have also be extracted by DFT[135, 188, 153] and *ab initio*[189–192] The Zeeman interaction is evaluated by using the matrix elements of the magnetic moment operator of any given complex according to equation 3.33[182]

$$\hat{\boldsymbol{\mu}} = -\boldsymbol{\mu}_B(g_e \hat{\mathbf{S}} + \hat{\mathbf{L}}) \tag{3.33}$$

where the spin free g-factor  $g_e = 2.0023$ ,  $\mu_B$  represents the Bohr magneton, while the  $\hat{S}$  and  $\hat{L}$  are the operators of the total spin and orbital momentum respectively and are given by equations 3.34 and 3.35

$$\hat{\mathbf{S}} = \sum_{i=1}^{N_{el}} \hat{\mathbf{s}}_i \tag{3.34}$$

$$\hat{\mathbf{L}} = \sum_{i=1}^{N_{el}} \hat{\mathbf{l}}_i$$
(3.35)

The  $\mu$  in turn becomes invariant in any coordinate system and so can be used to compute the isotropic Zeeman splitting. The Zeeman interaction in the presence of applied magnetic field is then expressed according to equation 3.36

$$\hat{H}_{Zee} = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} \tag{3.36}$$

 $\hat{\mu}$  reduces to  $-\mu_B(g_e \hat{\mathbf{S}})$ . On the other hand, the inclusion of SOC breaks the degeneracy of the ground state when the total spin quantum number is greater than half even without applied magnetic field - a term described as the zero-field splitting. The ZFS is then evaluated in the second order perturbation theory without field according to equation 3.37

$$H_{ZFS} = \mathbf{\hat{S}} \cdot \mathbf{D} \cdot \mathbf{\hat{S}}$$
(3.37)

The **D** term is a  $3 \times 3$  symmetric traceless matrix for the ZFS tensor. The form of the magnetic moment no longer has the  $g_e$  as shown for the isotropic case in equation 3.33. We can now rewrite this equation for a system with very weak SOC as;

$$\boldsymbol{\mu} = -\boldsymbol{\mu}_B \mathbf{g} \cdot \hat{\mathbf{S}} \tag{3.38}$$

For large SOC, the true total spin eigenstates can not be used as a model space for the construction of both the Zeeman spin Hamiltonian and the ZFS. The total angular momentum becomes an alternative. However, problem arises when a restricted manifold of crystal-field states that do not span the 2J+1 model space is considered. To circumvent this, the concept of pseudospin  $\tilde{S}$ , an abstract operator acting in the space of  $2\tilde{S}+1$  lowest spin-orbit states is used to replace the *S* operator.



Fig. 3.4 SMM description and magnetic anisotropy

The SMM behaviour can be modelled by using the Heisenberg Hamiltonian to account for the exchange coupling and magnetic anisotropy in clusters according to equation 3.39

$$\hat{\mathbf{H}} = \mu_B \sum_i \hat{\mathbf{S}}_i \cdot g_i \cdot \hat{\mathbf{B}} - \sum_{ij} J_{ij} \cdot \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j + \sum_i \hat{\mathbf{S}}_i \cdot D_i \cdot \hat{\mathbf{S}}_i$$
(3.39)

The first term in equation 3.22 designate the Zeeman interaction where  $\hat{\mathbf{B}}$  is the external magnetic field,  $\mu_B$  is the Bohr magneton and g is the Landé gyromagnetic tensor. The isotropic exchange interaction (J) between the spin vectors ( $\mathbf{S}_i, \mathbf{S}_j$ ) within the system is represented by the second term while the last term represents the ZFS parameter. Equation

3.39 is adequate for isotropic systems with axial or rhombic symmetry. In reality, systems may be distorted with lower symmetry and so cannot be described by the Hamiltonian above. The second and fourth order spin component may be added to the second order to fully describe the energy. Apart from Gd, the other members of the lanthanide series are characterized by strong magnetic anisotropy induced by the CF splitting of the J multiplets. The exchange interaction for the anisotropic lanthanide ion sites are formulated in terms of angular momenta  $\hat{J}_i$  (i=1,2). The magnetic anisotropic for the lanthanide systems are then described by the inclusion of the extended Steven's Operator systems described in section 3.5.3 in equation 3.39.[193, 101] For example using the Steven's formalism, the spin Hamiltonian for a single ion anisotropy is quite often described by equation 3.40

$$\hat{H}_{Anisotropy} = D[\hat{S}_z^2 - \frac{1}{3}S(S+1)] + B_4^0\hat{O}_4^0 + E(\hat{S}_x^2 - \hat{S}_y^2) + B_4^2\hat{O}_4^2 + B_4^4\hat{O}_4^4$$
(3.40)

where  $D = 3B_2^0$ , and  $E = B_2^2$ . The  $B_4^0$  is the fourth order axial term and have the same function as D.

#### 3.9 Magnetic exchange interaction

Multimetallic complexes show varying order of magnetic behaviour arising from suitable spins coupling.[194, 195] Experimental and theoretical methods have been used to understand the implication of these interactions for magnetism.[196] Leveraging on the vast magnetic properties of multimetallic complexes arising from the exchange interactions between metal ions, including superexchange interactions, [197] experimentalists have successfully isolated polynuclear compounds with 3d and 4f ions.[107, 198–201] Among the first reports of magnetic exchanges in SMMs was the Cu-Gd-Cu complex reported by Gatteschi et al. which shows some interesting ferromagnetic coupling.[202] The design of multimetallics could follow any of 3d - 3d, 3d - 4f or 4f - 4f pathways. However, as the number of nuclei increases, the observed interactions become more complicated to study. This is one of the disadvantages of transition metal clusters which usually show very strong exchange coupling that are difficult to characterise as higher nuclearity which may favour higher total spin ground state is targeted. The 4f - 4f pathways are usually less studied for magnetic coupling due to the core nature of the f-electrons. However, the 4f ions posses strong intrinsic magnetic anisotropy needed for SMM behaviour and so if we can better understand how to exploit chemical designs to access the 4f electrons for effective

coupling, then polynuclear complexes with enhanced SMM behaviour can be achieved with 4f ions. This has necessitated the use of computational methods. The magnetic exchange interaction (*J*) in large polynuclear transition metal complexes have been computed using DFT methods[203] leading to a very good numerical estimations by using suitable and carefully selected exchange-correlation functional and basis set. Noodleman *et al.*[204] Ruiz *et al.*[205] and Yamaguchi *et al.*[206] proposed different variants of equations 3.41, 3.42 and 3.43 respectively for computing the *J*-values by DFT methods.

$$J = \frac{(E_{BS} - E_{HS})}{2S_1 S_2 + S_2} \tag{3.41}$$

$$J = \frac{2(E_{BS} - E_{HS})}{S_{HS}(S_{HS} + 1)}$$
(3.42)

$$J = \frac{(E_{BS} - E_{HS})}{\langle S^2 \rangle_{HS} - \langle S^2_{BS} \rangle}$$
(3.43)

where the BS term represents the broken symmetry and HS represents high spin terms. The exchange interactions can be isotropic or anisotropic in nature. It could involve any of three different scenarios as;

- Heisenberg: Where two spins interact isotropically
- One Ising Spin: Where only the  $S_z$  component interacts with one isotropic spin of another
- Two Ising spins: Where two  $S_z$  components of spins interacts

Theoretical studies are able to compute them given that the exchange involves low-lying excited states which are closer to the ground state and so reasonable approximations will be able to extract the interactions with minimal margin of error.[207]

In isotropic exchange interaction, the *x*, *y* and *z*-components of the spins interact in the same way in space. Anisotropic exchange interactions arise when there is a synergistic perturbation of the SOC and the ground state coupling of one ion and the excited states of another.[184, 208] Different researchers have used different approach depending on choice to compute exchange interactions for complexes exhibiting exchange interactions. Computed *J*-values show transition metal complexes showing appreciable large exchange coupling ranging from -20 cm<sup>-1</sup> for a {Mn2<sup>III</sup>( $\mu$ -O)(OAc)} core[209] to -780 cm<sup>-1</sup> for a {Mn2<sup>IV</sup>( $\mu$ -O)3 core[210] On the other hand, 3*d*-4*f* exchange coupling were shown to be much lower compare to

3.10 Semi-*ab initio* calculation of the electronic structure and magnetic properties of polynuclear compounds

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3d-3d coupling due to the core nature of 4f-spins with complexes involving Cu<sup>II</sup>-Gd<sup>III</sup> showing higher J-values. Provided the structural parameters are maintained, the computed exchange values for the investigated 3d-4f complexes are of the order as  $J_{
m Cu^{II}-Gd^{III}}>$  $\begin{aligned} J_{\mathrm{Ni}^{\mathrm{II}}-\mathrm{Gd}^{\mathrm{III}}} > J_{\mathrm{Fe}^{\mathrm{II}}-\mathrm{Gd}^{\mathrm{III}}} > J_{\mathrm{Mn}^{\mathrm{II}}-\mathrm{Gd}^{\mathrm{III}}} > J_{\mathrm{Cr}^{\mathrm{III}}-\mathrm{Gd}^{\mathrm{III}}} [211] \ \mathsf{DFT} \ \mathsf{calculation} \ \mathsf{estimated} \ \mathsf{two} \ \mathsf{types} \ \mathsf{of} \ \mathsf{Gd}-\mathsf{Gd} \ \mathsf{interactions} \ \mathsf{in} \ \{\mathsf{Gd}^{\mathrm{III}}_{5}\}[\mathsf{Gd}^{\mathrm{III}}_{5}(\mu_{3}\text{-}\mathsf{OH})(\mathsf{NO}_{3})_{2}(\mathsf{dipp})_{6}(\mathsf{MeOH})_{7}(\mathsf{H}_{2}\mathsf{O})_{4}] \end{aligned}$ showing very weak coupling of about  $-1.3 \times 10^{-3}$  cm<sup>-1</sup> and  $1.0 \times 10^{-4}$  cm<sup>-1</sup>.[212] This further portrays the weak interaction showed by f-electrons. In polynuclear complexes, a high exchange coupling of the order of few hundred wavenumber is required to quench the ground state QTM effect making it difficult to design polynuclear complexes purely based on lanthanides. Although radical-bridged  $Gd^{3+}$  systems of dinuclear complexes (4f-2p)systems) were predicted to show very strong antiferromagnetic coupling of -54.4  $cm^{-1}$ among lower coupling constants including ferromagnetic coupling of +12.1 cm<sup>-1</sup>,[213, 214] mononuclear lanthanide complexes have been the focus of recent research against transition metal complexes due to their intrinsic magnetic anisotropy and unquenched orbital angular momentum. Encapsulation of lanthanide ions in fullerenes has also led to exceptionally strong ferromagnetic coupling of about  $+400 \text{ cm}^{-1}$ [215] while offering alternatives for novel SMMs.

# 3.10 Semi-*ab initio* calculation of the electronic structure and magnetic properties of polynu-clear compounds

One of the drawbacks of transition metal-based SMMs is the destructive effect[172] of the strong exchange interaction that exist in polynuclear complexes compare to lanthanide-based compounds. The zero-filed splitting on metal centres are usually much larger with weak exchange interactions making lanthanide-based compounds better candidates for enhanced polynuclear type SMM. The exchange interaction does not have a one-way effect as it can also help increase the spin ground state if they couple cooperatively. Therefore, to account for the contributions of each metal site to the magnetic property of a polynuclear lanthanide-based compound, the role of exchange coupling needs to be considered.

The polyaniso submodule implemented in MOLCAS[116, 117] provides a semi-*ab initio* method to incorporate the exchange interaction in elucidating the magnetic properties of polynuclear compounds including those containing lanthanides. It is usually difficult to

3.10 Semi-*ab initio* calculation of the electronic structure and magnetic properties of polynuclear compounds

account for the effect of neighbouring metal centres in a cluster/polynuclear complexes completely by computation. To circumvent this, individual fragment calculation in which all magnetic metal sites but one are replaced with a diamagnetic metal site can be carried out and used for further calculations that enable us to account for any interaction between magnetic centres. This can be done using the 'SINGLE ANISO' and 'POLY ANISO' submodules as implemented in MOLCAS. The obtained wavefuctions for each fragment computed under 'SINGLE ANISO' are combined in a separate 'POLY ANISO' job to compute the overall magnetic susceptibility in which the exchange interactions are simulated using Lines models[216]. The exchange interaction can then be computed using the Ising type Heisenberg Hamiltonian given by equation 3.44

$$\tilde{H}_{ex} = -\sum_{i=1}^{3} \tilde{J}_i \tilde{S}_{1z} \tilde{S}_{i+1z}$$
(3.44)

Where  $\tilde{S}_{1z}$  is the projection of the pseudo-spin on the anisotropy axis of each metal site. The method has been used to extract a J-value of -0.6 cm<sup>-1</sup> in a dysprosium triangle and proved how a toroidal arrangement of magnetic moments can lead to nonmagnetic ground state in a dysprosium(III) triangle.[173] The result showed that the state of maximal magetization was conserved at each dysprosium site at ground state and supports the Ising type exchange coupling.

For lanthanide-based compounds, the dominant dipole interaction becomes also important in elucidating the SMM behaviour due to the anisotropic nature of the lanthanide ions. The energy associated with the dipole-dipole interactions between two metal centres can be computed using information from already computed *ab initio* data for each metal site using equation 3.45

$$E_{dip} = \frac{\mu_{Bohr}^2}{r^3} [\overrightarrow{\mu}_1 \cdot \overrightarrow{\mu}_2 - 3(\overrightarrow{\mu}_1 \overrightarrow{n}_{12}) \cdot (\overrightarrow{\mu}_2 \overrightarrow{n}_{12})]$$
(3.45)

where  $\overrightarrow{\mu}_1$  and  $\overrightarrow{\mu}_2$  are the magnetic moments of metal centre 1 and 2 respectively. r is the distance separating the metal sites while  $\overrightarrow{n}_{12}$  is the directional vector that links the two interacting magnetic centres. From equation 3.45, we see that distance or separation and the angle between two interacting magnetic centre affects the dipolar magnet interaction.

### 3.11 Spin relaxation mechanism in single-ion magnets

The phenomenological classical method that considers the time evolution of magnetization with respect to the gyromagnetic ratio and damping parameter is not suitable to describe the spin relaxation of SMM materials due to the absent of quantum effects.[217] However, some formalism have been developed that could describe the relaxation pathway of SMM in several literature.[218–220] Multiconfigurational *ab initio* method has been used to estimate transition matrix elements which are proxies for the transition rates between pairs of states for the magnetic dipole operator over relativistic states. The largest matrix element connecting the two sides of the potential well can be used to identify relaxation pathways for SMM.[48, 57, 110, 221, 222]This procedure is already implemented in Molcas software package.

The mechanism of magnetisation of SMMs as well as the slow magnetic relaxation can be described by the double-well potential (Figure 3.5) and involves four main relaxation pathways. The spin reversal can follow one or combination of magnetic relaxation pathways depending on the electronic structure of the material as a result of the anisotropic-dependent nature of these pathways.



Fig. 3.5 The double-well potential for spin relaxation in single-molecule magnets

Usually, an easy axis is followed at the expense of the hard axis during spin reversal. In the absence of an applied magnetic field, half-integer spin states form degenerate pairs.

The degeneracy is broken when the material is magnetised (the Zeeman splitting under magnetisation, see Figure 1.2) such that the down spin state  $(-M_s)$  become stabilised at the expense of a destabilised up spin state  $(+M_s)$ . Consequently, only the  $(-M_s)$  state is populated at saturation of magnetisation. When the magnetic field is removed, with time the magnetisation is relaxed by either heat or tunnelling. If the temperature is enough to overcome the energy barrier, a one-phonon thermal relaxation that follows the Arrhenius law begins to take place and the relaxation time is described in equation 3.46.[219, 23] It is important to note that for lanthanide-based complexes, the  $(M_j)$  quantum number is preferred to  $(-M_s)$ .

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\Delta}{k_B T}\right) \tag{3.46}$$

Where  $\tau$  is the relaxation time at temperature T,  $\tau_0$  is the relaxation time at infinite temperature,  $k_B$  is the Boltzmann constant and  $\Delta$  is the energy barrier (the blue arrow on the left-hand side (LHS) of Figure 3.5). This process is known as the **Orbach relaxation** process.

However, when the relaxing spin at excited level is not degenerate with another state on the other side of the barrier, transition is observed between the up and down states (green arrow on the RHS of Figure 3.5), until the sub-levels are close in energy again (green arrow on the LHS of Figure 3.5). At such intermediate quantised sub-energy levels **thermally assisted quantum tunnelling of magnetisation (TA-QTM)**[23] will occur whose relaxation is also described by the Arrhenius law given by equation 3.47.

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\Delta_{\text{eff}}}{k_B T}\right)$$
(3.47)

and the energy barrier given as the effective energy barrier ( $\Delta_{eff}$ ) (the purple double-headed arrow on the LHS of Figure 3.5). The occurrence of this phenomenon at different quantised sub-levels caused the observed steps with the magnetic hysteresis reported by Sessoli *et. al* (Figure 2.1).[13] Alternatively, a relaxing spin can move to a virtual excited sub-level due to phonon scattering between the ground state and the virtual state such that the Arrhenius law cannot describe the relaxation process. This is known as the **Raman process**[23, 219]
and is a two-phonon process; the spin relaxation thus occurs via a virtual state and is described by equation 3.48

$$\tau^{-1} = CT^n \tag{3.48}$$

where C is the Raman constant and n is the exponent associated with the temperature T in relation to the relaxation time. It is possible to have some energy separation between the up spin  $(-M_s)$  and the down spin  $(+M_s)$  such that the spin reversal involves emission of a single lattice phonon as the spin relaxes from  $(-M_s)$  to  $(+M_s)$  state. This process is referred to as a **Direct process**[23, 219] and expressed according to equation 3.49

$$\tau^{-1} = AT^2 \tag{3.49}$$

where A is the direct process constant. SMMs can also show quantum tunnelling of magnetisation (QTM) if there is transverse anisotropy in the system. In this regime, **quantum tunnelling of magnetisation**, Q (QTM) in which  $\tau$  is fast and independent of temperature occurs.[23, 219] Molecular designs to realise SMMs aim to create unique environments around the magnetic centre to avoid relaxation being dominated by this fast relaxation process known as the QTM at the ground state. Relaxation via this pathway inhibits SMM behaviour and needs to be avoided. The overall relaxation process is obtained by fitting the temperature dependent relaxation rates using equation 3.50;

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{\Delta_{\text{eff}}}{k_B T}\right) + CT^n + AT^2 + \frac{1}{Q}$$
(3.50)

Where the first, second, and third terms represent **Orbach**, **Raman**, **Direct** processes respectively. The last term is the **QTM**. The relaxation time is usually in the region of milliseconds to picoseconds while reported energy barriers range from 0.9 cm<sup>-1</sup> to over 1200 cm<sup>-1</sup>.[23, 24, 26] Other quantities (C,A and Q) depends on the relaxation fit. Relaxation dynamics could be any one of them or combination of any.

#### 3.12 Motivation and research target

The holy grail for achieving high performance SMMs is the low blocking temperature  $(T_{\rm B})$  at which the slow magnetic relaxation is possible. The success of this research field will be dependent on understanding how molecular magnets can be tuned to achieve high  $T_{\rm B}$ . One of the ways to circumvent this challenge is to design a strongly coupled molecular architecture (polynuclear lanthanide-based complexes) which could withstand thermal interference on the magnetic centre by increasing the  $\Delta_{eff}.$  To do this, a complete understanding of the interaction between the magnetic centre (in this case,  ${\sf Ln}^{3+}$ ) and the ligand field generated by the direct coordination of ligand donor atoms and other peripheral atoms and substituents will be required. Experimental techniques like electron paramagnetic resonance (EPR), nuclear magnetic resonance, inelastic neutron scattering (INS), torque magnetometry, magnetic susceptibility measurements among others have been used to extract magnetic parameters to understand SMM behaviour and drive the phenomenon to higher temperature for practical applications. However, these techniques have shown myriads of limitations especially for lanthanide containing complexes with no rational approach for high-perfomance SMM design. In addition, extracting the g-tensors, multiple exchange interaction values for polynuclear systems and crystal field splitting parameters for lanthanides containing systems are extremely challenging using these experimental techniques. Even more challenging is the extraction of ZFS (D) values greater than 20  $cm^{-1}$ . This has made computational approaches indispensable as we see more advances in the development of computing hardware and methods like DFT[153, 203, 223] and ab initio [57, 224] Advances in computational methods provides us with the necessary tools to understand molecular systems. In this thesis, molecular designs with advantages for the realization of high performance single-molecule magnets (SMMs) will be investigated by looking at chemical intuitions that would become signatures to rationally design high performance SMMs. This will include aromaticity, chelation, solvent effect and the role of axial perturbation of heterobonds.

## Chapter 4

# The SMM behaviour of a butterfly-shaped mono-nuclear dysprosium complex

#### 4.1 Introduction

Dysprosium-based complexes are among the most promising SMM reports in the literature with the family of dysprosium metallocene setting a record high  $T_{\rm B}$  (> 80 K) that would allow practical application at liquid nitrogen temperature.[25] The dependency of the principal axis of magnetization on the coordinating apical water molecule in the archetype compound [Na{Dy(DOTA)(H<sub>2</sub>O)}]·4H<sub>2</sub>O(Na{DyDOTA}·4H<sub>2</sub>O)[225, 226] (Figure 4.1) necessitated further investigation into the overall effect of first coordination and peripheral ligands in the observed SMM behavior of lanthanide-based complexes. Although, the magnetic properties of the *f*-ions are very sensitive to ligand variations, the attribution of the overall magnetic properties of such complexes to a single donor atom remains questionable because any observed SMM behaviour could be lost if some other donor atom with the first coordination or even at a peripheral position is perturbed.

High performance SIM would require a large magnetic moment, very high Ising magnetic anisotropy (D), large  $\Delta_{\text{eff}}$  and  $T_{\text{B}}$ . Interestingly, these properties are affected by structural factors like the metal-ligand bonding and their associated directions, structural distortion around the metal ion (including first and peripheral coordination), the nature of the ligand

donor atom, coordination number, geometry, symmetry, arrangement of the ligands around the metal centre and covalency of the in-plane and axial metal-ligand interactions. Therefore a rational design of high performance SIM/SMM would require an understanding of how these structural factors could aid in fine tuning the magnitude, sign and direction of the ZFS parameters leading to the observation of the SMM property.



Fig. 4.1 Crystal structure of  $[Na{Dy(DOTA)(H_2O)}] \cdot 4H_2O(Na{DyDOTA} \cdot 4H_2O)$  showing the apical water molecule coordinated to  $Dy^{3+}$  (red:O, pale blue: N, grey: C, white: H, light green: Dy, purple: Na. The hydrogen atoms were assigned appropriate isotropic thermal parameters on their parent atoms. The crystal solvents were omitted for clarity)[225, 226]

In this chapter, the various structural variations built from a monometallic dysprosium compound with Schiff base ligand, obtained as a butterfly-shaped complex will be presented as well as the results from their magnetic property investigation using experimental and computational approaches. Insight on the magnetic property of the monometallic dysprosium complex as a molecular magnet exhibiting a slow magnetic relaxation stemming from the single ion behaviour is presented. The structural variation, inter-electronic interactions, ligand-field effects and computed wavefunctions of the dysprosium-based complexes were used to create insight on how structural variations including ligand chelate effect could affects the magnetic properties of such complex. In this thesis, some differences in the results with respect to the structural variation are shown and attempt to rationalise them for SMM designs were made.

#### 4.2 Single-crystal structural description of Dy1



(a) Schiff base ligand for Dy1 synthesis



(c) Crystal structure of **Dy1** 



(b) single ligand coordination of Dy1



(d) Crystal packing of **Dy1** 

Fig. 4.2 (a) Schiff base ligand showing the donor atoms (green mapped O and N), protonic hydrogen (green mapped hydrogen) and the hydrogen of the ligand involved in hydrogen bonding with the crystal solvent (black mapping) within the crystal lattice of **Dy1** (b) **Dy1** showing single ligand coordination to the metal centre. (c) Single-crystal structure of a butterfly-shaped Dy(N4O5C14H11)3 (**Dy1**) obtained from single-crystal X-ray machine (50 % probability). The crystal solvent (3 mols of DMF) was omitted for clarity (d) crystal packing of **Dy1** showing H-bonding network. The light blue circles show some of the H-bonds formed (red:O, pale blue: N, grey: C, white: H, bright turquoise blue: Dy. The hydrogen atoms were assigned appropriate isotropic thermal parameters on their parent atoms)

The tridentate Schiff base ligand (Figure 4.2a) was reacted with a dysprosium salt (see Appendix A for synthetic details) to form a butterfly-shaped complex of the dysprosium ion (Dy(N4O5C14H11)3), hereafter referred to as Dy1.<sup>1</sup>

The experimental crystal structure determination procedure is described in appendix A. The crystal structure was obtained from a single-crystal X-ray diffraction (SC-Xrd) machine and shows three ligands coordinated to the metal centre through three donor atoms (one oxygen of the carbonyl group, one nitrogen of the imine group, and one oxygen of the hydroxyl group which was deprotonated to give a unit negatively charged ligand) to form a neutral dysprosium complex with a coordination number of 9 (Figure 4.2b and 4.2c). **Dy1** crystallised in the triclinic space group  $P\overline{1}$  with two crystal structures packed within a unit cell (bounded box in Figure 4.2d). For clarity in the structural description, the crystal structure showing the atom numbering is presented in Figure 4.3.



Fig. 4.3 (a) Crystal structure showing atom numbering for **Dy1** (red:O, pale blue: N, grey: C, white: H, bright turquoise blue: Dy)

<sup>&</sup>lt;sup>1</sup>The crystal structure was synthesised in Japan by David Izuogu during his stay at Prof. Masahiro Yamashita's laboratory and has not been reported anywhere or used for any degree.



(b) 3 types of H-bonding interaction in **Dy1** 

Fig. 4.4 (a) Crystal packing showing H-bonding for **Dy1** (red and light blue lines) (b) 3 types of H-bonding interaction around a unit **Dy1** molecule showing the atoms involved (red:O, pale blue: N, grey: C, white: H, bright turquoise blue: Dy)

Geometry parameters and selected crystallographical data are presented in Table 4.1 and 4.2 respectively. The Dy-O bond distances are 2.282(3), 2.278(2) and 2.269(3) Å for the hydroxyl bonded oxygen and 2.399(4), 2.417(2) and 2.415(3) Å for the carbonyl bonded group respectively (Table 4.1 and Figure 4.3). On the other hand, the Dy-N bond distances were measured as 2.640(4), 2.596(5) and 2.582(3) (Table 4.1). By convention, two bonds are said to be significantly different if the difference in their bond lengths is greater than three times their corresponding weighted estimated standard deviations (WESDs), where  $WESDs = \sqrt{ESD_1^2 + ESD_2^2}$ . The WESD for Dy1–O12 (from OH group of one ligand) and Dy1-O11 (from CO of the same ligand) is 0.005 Å while the difference in their bond length is 0.117 Å which is by far greater than 3 times the WESD of 0.005 Å. This shows that the Dy–O bond for the negatively charged oxygen is substantially shorter than those involving the CO oxygen. In the same way, the Dy-N bond lengths are significantly longer than those of the Dy–O because of the lower electronegativity value of nitrogen compared to oxygen, making oxygen more strongly bonded to the Dy centre than nitrogen. The three ligands are arranged at approximately  $120^{\circ}$  from each other around the central Dy<sup>3+</sup> ion with true values of 122.9(3), 114.7(8) and  $121.9(2)^{\circ}$  to give a trigonal butterfly-shaped complex (Figure 4.2c). The discrepancies among the bond angles and distances for the same type of organic ligands show the extent of distortion and deviation of the structure from a strict symmetry. The tridentate nature of the organic ligand allows chellation with the central metal. It is expected that this should help to stabilise the complex further. The proximity of the hydroxyl donor atom to an aromatic ring (see the first green mapping of Figure 4.2a) should have strong donor effect on the ligand field and by extension to the magnetic properties of the complex. We shall see the extent of this in the subsequent section. As dimethylformamide (DMF) was used as synthetic solvent, the crystal structure crystallised with three molecules of DMF as crystal solvent which helped to stabilize the lattice structure through a 3-dimensional hydrogen bonding between DMF and the organic ligands of the complex (Figure 4.4). The H-bond network involves the amine functional hydrogen of the ligand and other hetero atoms of both DMF and neighboring molecules within the lattice (Figure 4.2d) and 4.4). The H-bonding interactions are such that around a unit molecule of **Dy1**, 3 types of H-bonding interactions exist resulting from each one of the three organic ligand. Two of the organic ligands of one Dy1 uses the H of the amine group to H-bond with the O of one DMF each (O18 ··· H6 and O16 ··· H10 with a bond distance of 2.244(2) and 2.065 (3) Å respectively). The third ligand then uses the same amine H to H-bond with the oxygen of the methoxy substituent of a second Dy1 molecule  $(O8 \cdots H2A \text{ with bond distance of } 2.203(2) \text{ Å}).$ 

| Bond type           | Bond distance (Å)    | Bond type            | Bond distance (Å)    | Bond type                 | Bond distance (Å)  |
|---------------------|----------------------|----------------------|----------------------|---------------------------|--------------------|
| C1 – H1             | 0.929                | C23 – C24            | 1.435(5)             | Dy1 – 06                  | 2.417(2)           |
| C1 – C2             | 1.35(1)              | C23 – O7             | 1.265(5)             | Dy1 – 07                  | 2.278(2)           |
| C1 – N1             | 1.330(9)             | C24 – C25            | 1.367(6)             | Dy1 – 011                 | 2.399(4)           |
| C2 – H2             | 0.929                | C24 – O8             | 1.375(6)             | Dy1 – 012                 | 2.282(3)           |
| C2 – C3             | 1.38(1)              | C25 – H25            | 0.929                | N2 – H2A                  | 0.859              |
| C3 – H3             | 0.931                | C25 – C26            | 1.396(7)             | N2 – N3                   | 1.384(6)           |
| C3 – C4             | 1.382(9)             | C26 – C27            | 1.371(5)             | N4 – O4                   | 1.231(7)           |
| C4 – H4             | 0.93                 | C26 – N8             | 1.439(6)             | N4 – O5                   | 1.223(7)           |
| C4 – C5             | 1.370(7)             | C27 – H27            | 0.93                 | N6 – H6                   | 0.862              |
| C5 – C6             | 1.488(7)             | C28 – H28            | 0.93                 | N6 – N7                   | 1.383(4)           |
| C5 – N1             | 1.330(7)             | C28 – C29            | 1.35(1)              | N8 – O9                   | 1.231(4)           |
| C6 – N2             | 1.328(6)             | C28 – N9             | 1.35(1)              | N8 – O10                  | 1.223(7)           |
| C6 – O1             | 1.242(6)             | C29 – H29            | 0.931                | N10 – H10                 | 0.862              |
| C7 – H7             | 0.929                | C29 – C30            | 1.35(1)              | N10 – N11                 | 1.386(7)           |
| C7 – C8             | 1.436(7)             | C30 – H30            | 0.93                 | N12 – O14                 | 1.233(7)           |
| C7 – N3             | 1.288(5)             | C30 – C31            | 1.39(1)              | N12 – O15                 | 1.219(8)           |
| C8 – C9             | 1.417(7)             | C31 – H31            | 0.93                 | N14 – C48                 | 1.32(1)            |
| C8 – C13            | 1.403(6)             | C31 – C32            | 1.374(8)             | N14 – C47                 | 1.48(2)            |
| C9 – C10            | 1.441(7)             | C32 – C33            | 1.487(8)             | N14 – C46                 | 1.41(2)            |
| C9 – O2             | 1.267(5)             | C32 – N9             | 1.31(1)              | C48 – H48                 | 0.93               |
| C10 – C11           | 1.363(6)             | C33 – N10            | 1.332(7)             | C48 – O17                 | 1.26(2)            |
| C10 – O3            | 1.368(6)             | C33 – O11            | 1.236(8)             | C47 – H47A                | 0.96               |
| C11 – H11           | 0.93                 | C34 – H34            | 0.931                | C47 – H47B                | 0.96               |
| C11 – C12           | 1.398(7)             | C34 – C35            | 1.439(7)             | C47 – H47C                | 0.96               |
| C12 – C13           | 1.367(7)             | C34 – N11            | 1.291(6)             | C46 – H46A                | 0.96               |
| C12 – N4            | 1.444(6)             | C35 – C36            | 1.425(7)             | C46 – H46B                | 0.96               |
| C13 – H13           | 0.929                | C35 – C40            | 1.393(7)             | C46 – H46C                | 0.96               |
| C14 – H14A          | 0.96                 | C36 – C37            | 1.448(7)             | C51 – H51A                | 0.96               |
| C14 – H14B          | 0.96                 | C36 - O12            | 1.267(5)             | C51 – H51B                | 0.96               |
| C14 – H14C          | 0.961                | C37 – C38            | 1.358(7)             | C51 – H51C                | 0.96               |
| C14 - 03            | 1 422(8)             | $C_{37} - 013$       | 1 359(6)             | C51 – N15                 | 1 34(1)            |
| C15 – H15           | 0.93                 | C38 – H38            | 0.931                | O18 - C50                 | 1.35(2)            |
| C15 - C16           | 1.372(7)             | $C_{38} - C_{39}$    | 1 400(9)             | N15 – C50                 | 1.00(2)<br>1.28(2) |
| C15 – N5            | 1.326(5)             | C39 - C40            | 1 371(7)             | N15 - C49                 | 1.23(2)<br>1 44(1) |
| C16 - H16           | 0.929                | C39 - N12            | 1.371(7)<br>1 452(7) | C50 - H50                 | 0.93               |
| C16 - C17           | 1 362(8)             | C40 - H40            | 0.931                | C49 – H49A                | 0.96               |
| $C_{10} = H_{17}$   | 0.929                | C41 - H41A           | 0.961                | C49 - H49B                | 0.96               |
| C17 - C18           | 1 386(5)             | C41 - H41R           | 0.96                 | C49 – H49C                | 0.96               |
| C18 - H18           | 0.93                 | C41 - H41C           | 0.959                | C43 – H43A                | 0.96               |
| $C_{10} = C_{10}$   | 1 370(7)             | $C_{41} = 013$       | 1 424(7)             | $C_{43} = H_{43}R$        | 0.058              |
| C10 = C19           | 1.370(7)<br>1.402(5) | $C_{41} = 013$       | 1.424(7)             | $C_{43} = H_{43}C_{43}$   | 0.950              |
| C19 = C20           | 1.492(3)<br>1.221(7) | $C_{42} = \Pi_{42R}$ | 0.90                 | $C_{43} = 1143C$          | 1.42(1)            |
| C19 = N5            | 1.331(7)<br>1.224(6) | $C_{42} = 1142B$     | 0.90                 | C43 = N13                 | 1.43(1)            |
| $C_{20} = 100$      | 1.324(0)             | C42 - H42C           | 0.90                 | C44 - H44A                | 0.959              |
| $C_{20} = 00$       | 0.031                | $D_{V1} = N2$        | 1.720(1)             | $C_{44} = \Pi_{44} D$     | 0.90               |
| $C_{21} = \Pi_{21}$ | 0.931<br>1 449(E)    |                      | 2.302(3)             | $C_{44} = \Pi_{44}C_{44}$ | 1 42(1)            |
| $C_{21} = C_{22}$   | 1.440(3)             | Dy1 = N7             | ∠.040(4)<br>2.506(5) | $C_{44} = N_{13}$         | 1.43(1)<br>0.020   |
| $C_{21} = INI$      | 1.202(U)             | Dy1 = N11            | ∠.390(5)<br>2.415(2) | $C_{45} = \Pi_{45}$       | 0.929<br>1 200(9)  |
| $C_{22} = C_{23}$   | 1.420(7)             | Dy1 = 01             | 2.413(3)             | C45 = 1013                | 1,209(0)           |
| C22 - C27           | 1.390(7)             | Dyr – O2             | 2.209(3)             | C45 - O16                 | 1.223(9)           |

Table 4.1 Geometry parameters for  $\ensuremath{\text{Dy1}}$ 

The shorter distance for O16  $\cdots$  H10 is due to the close proximity of the second DMF crystal solvent to the molecule. The shortest intermolecular Dy-Dy bond is 8.174(3) Å and is unlikely to facilitate inter-molecular magnetic coupling between any two or more dysprosium centres.

| Parameter                         | Dy1                           |
|-----------------------------------|-------------------------------|
| Radiation type, wave-length/ Å    | Mo K <sub>α</sub> , 0.71073   |
| Crystal dimensions /mm            | $0.134\times0.165\times0.314$ |
| Molecular formula                 | DyN12O15C42H33                |
| Sum molecular formula             | DyN15O18C51H54                |
| Formula mass / ${ m gmol}^{-1}$   | 1327.59                       |
| Space group                       | PĪ                            |
| Crystal system                    | Triclinic                     |
| a / Å                             | 14.0138(11)                   |
| <i>b</i> / Å                      | 14.9588(12)                   |
| <i>c</i> / Å                      | 16.0604(13)                   |
| α /°                              | 99.852(2)                     |
| β /°                              | 102.797(2)                    |
| γ /°                              | 113.600(2)                    |
| V /Å <sup>3</sup>                 | 2878.6(4)                     |
| Т /К                              | 496(2)                        |
| Ζ                                 | 2                             |
| $GOF$ on $F^2$                    | 1.004                         |
| $R_1$ , $wR_2[I \ge 2\sigma(I)]$  | 0.0313, 0.0725                |
| heta range for data collection /° | 1.55 to 22.53                 |
| $R_{ m int}/\%$                   | 3.39                          |

Table 4.2 Selected crystal data for Dy1

While high symmetry has been shown to support SMM behaviour of complexes, it is difficult to obtain real molecules with strict obedience to high symmetry especially when multidentate organic ligands with peripheral substituents are employed. As a way of simplicity, the symmetry of the first coordination sphere is usually used to investigate the role of symmetry in the SMM behaviour of metal complexes. While the computational

work done in this thesis will not attempt to approximate the symmetry, an understanding of approximate symmetry of the first coordination sphere will be important in the later discussion. As such, the SHAPE software (version 2.1)[227] was used to analyse the symmetry of the first coordination sphere of **Dy1**. Table 4.3 shows all possible symmetry for any central site with coordination number of 9.[227]

| Code<br>number | Symmetry   | symmetry code | Geometry                        |
|----------------|------------|---------------|---------------------------------|
| 1              | $E_{P-9}$  | Enneagon      |                                 |
| 2              | $C_{8v}$   | OPY-9         | Octagonal pyramid               |
| 3              | $D_{7h}$   | HBPY-9        | Heptagonal bipyramid            |
| 4              | $C_{3\nu}$ | JTC-9         | Johnson triangular<br>cupola J3 |
| 5              | $C_{4v}$   | JCCU-9        | Capped cube J8                  |
| 6              | $C_{4v}$   | CCU-9         | Spherical-relaxed               |
|                |            |               | capped cube                     |
| 7              | $C_{4 u}$  | JCSAPR-9      | Capped square an-               |
|                |            |               | tiprism J10                     |
| 8              | $C_{4v}$   | CSAPR-9       | Spherical capped                |
|                |            |               | square antiprism                |
| 9              | $D_{3h}$   | JTCTPR-9      | Tricapped trigonal              |
|                |            |               | prism J51                       |
| 10             | $D_{3h}$   | TCTPR-9       | Spherical tricapped             |
|                |            |               | trigonal prism                  |
| 11             | $C_{3v}$   | JTDIC-9       | Tridiminished icosahe-          |
|                |            |               | dron J63                        |
| 12             | $C_{2\nu}$ | HH-9          | Hula-hoop                       |
| 13             | $C_s$      | MFF-9         | Muffin                          |

Table 4.3 Possible geometries and symmetry around a central site with coordination number of 9

A SHAPE calculation was carried out on **Dy1** using the first coordination sphere of the nine donor atoms to ascertain how close the symmetry around the  $Dy^{3+}$  is to the listed possible symmetries for a nine coordinated site in Table 4.3. A perfect match (100 %

accuracy) would yield a match number of zero showing that there is no deviation from the strict symmetry. Therefore, the lower the match number the better the symmetry of the molecule could be described by the assigned group. Results from SHAPE calculations (Table 4.4) show a good approximation for a  $C_{4\nu}$  and  $D_{3h}$  symmetry and a large deviation for other symmetry groups listed with the  $D_{9h}$  having the worst match. It is important to also mention that the lower match number observed for  $D_{3h}$  (1.436),  $C_s$  (1.460), and  $C_{4\nu}$ (1.546) shows that the symmetry around the Dy3<sup>+</sup> centre could be described by any of these. However, we will prioritise the lowest match number to make a choice of  $C_{4\nu}$  (0.966) and  $D_{3h}$  (1.306).

| symmetry | symmetry name                      | Computed<br>match number |
|----------|------------------------------------|--------------------------|
| $C_{4v}$ | Spherical capped square antiprism  | 0.966                    |
| $D_{3h}$ | Spherical tricapped trigonal prism | 1.306                    |
| $D_{3h}$ | Tricapped trigonal prism J51       | 1.436                    |
| $C_s$    | Muffin                             | 1.460                    |
| $C_{4v}$ | Capped square antiprism J10        | 1.546                    |
| $C_{4v}$ | Spherical-relaxed capped cube      | 8.973                    |
| $C_{4v}$ | Capped cube J8                     | 9.764                    |
| $C_{2v}$ | Hula-hoop                          | 11.214                   |
| $C_{3v}$ | Tridiminished icosahedron J63      | 11.419                   |
| $C_{3v}$ | Johnson triangular cupola J3       | 13.789                   |
| $D_{7h}$ | Heptagonal bipyramid               | 17.831                   |
| $C_{8v}$ | Octagonal pyramid                  | 22.139                   |
| $D_{9h}$ | Enneagon                           | 34.007                   |

Table 4.4 computed Symmetry of the first coordination sphere of Dy1

Using the Diamond crystallographic structural visualisation software, the vertexes of the first coordination sphere of **Dy1** was connected to show the symmetry approximations for best match numbers ( $C_{4v}$  and  $D_{3h}$ ) and is presented in Figure 4.5. Figure 4.5c shows the staggered conformer with noticeable distortion from what would have been a strict  $D_{3h}$  spherical tricapped trigonal prism around Dy<sup>3+</sup> centre. In considering the  $C_{4v}$  symmetry, the SHAPE software has treated the oxygen and nitrogen atoms as identical which should

not be true for symmetry consideration and so, we will favour the  $D_{3h}$  as the closest symmetry of the first coordination sphere for **Dy1**.

To avoid deviation from the true symmetry which could lead to significant divergence in any obtained results, geometry optimisation will not be carried out for any of the structural variants presented in the next section. The symmetry of the first coordination sphere illustrated here will be maintained for all structural variants.



(a) Distorted symmetry lines (green lines) connecting the donor atoms in **Dy1** 



(c) Structural distortion from strict  $D_{3h}$  Spherical tricapped trigonal prism with staggered conformation



(b) Illustration of the distorted  $D_{3h}$ Spherical tricapped trigonal prism around **Dy1** 



(d) Illustration of the distorted  $C_{4\nu}$ Spherical capped square antiprism around **Dy1** 

Fig. 4.5 Distorted symmetry around **Dy1** ( $Dy(N4O_5C_{14}H_{11})_3$ ) with respect to the first coordination sphere (red:O, pale blue: N, grey: C, white: H, Bright Turquoise: Dy)

### 4.3 Structural variations of the butterfly-shaped dysprosium complex

To investigate the effects of aromatic ring and ligand field on  $Dy(N4O5C_{14}H_{11})_3$  (Dy1), structural variants (Figure 4.6) were built from the original experimental **Dy1** structure. First, the geometry of **Dy1** obtained from the single crystal X-ray diffraction as described in section 4.2 was used for the calculations without any further optimisation.  $Dy(N_2O_2C_7H_{11})_3$ (hereafter, Dy2) was obtained by deleting the aromatic components of the Dy1 ligands and using the methyl group to make up for the right configurations for the three carbon atoms linked to the aromatic rings. This allowed the comparison of the results from Dy1 and Dy2 to account for any aromatic and ligand field effects to the observed magnetic and electronic properties of Dy1. The structural modification of Dy1 to Dy2 was such that the structural integrity of the first coordination sphere up to the point of the aromatic ring attachment is identical in both structure. This allows the comparison of the peripheral substituent involving the aromatic ring. The crystal solvent was omitted for easy convergence. We do not expect the omission to have much effect on the magnetic properties of the complexes since the atom positions in the crystal struture with the crytal solvent is the same as without the crystal solvent. For this reason no structural optimisation was done to avoid a significant deviation from experimental data as previously reported.[48] The significant deviation which was observed when geometries are optimised could arise from the distortion which neighbouring crystals, solvent structures and counterions may cause in the experimental structure. These fragments are rarely included in theoretical computation due to prohibitive computational cost that may make it extremely difficult to obtain converged wavefunctions. Dimethylformamide (DMF) which was present as crystal solvent was also not included in the calculation. For **Dy1**, the reason for the exclusion of DMF crystal solvent in the computation was two-fold: (i) to reduce the computational cost (ii) the effect to the magnetic properties is expected to be minimal as the structural integrity of the molecule is still intact since the coordinates were obtained in the presence of the crystal solvent and no geometry optimisation was carried out on the molecule.

The synthetic procedure for **Dy1** and the coordinates of **Dy1** and **Dy2** used for the calculations are presented in the Appendix A and B respectively. The structural variation became necessary to draw insights on the effect of the ligand field, aromaticity and coordination environment on the magnetic properties of the **Dy1**. Peripheral ligands and the nature of the donor atoms can affect magnetic properties of SMMs.[228] We quantify

the extent to which this effect is felt by the metal centre in the above complexes using *ab initio* method.



Fig. 4.6 Structural variations of the complexes of Dy1 (Dy(N4O5C14H11)3) and Dy2 (Dy(N2O2C7H11)3) used for all computations (red:O, pale blue: N, grey: C, white: H, bright turquoise: Dy)

#### 4.4 Computational details for Dy1 and Dy2

*Ab initio* CASSCF-SO calculations for the structural variants described in section 4.3 were carried out using both the ORCA[114, 115] and MOLCAS[116, 117] quantum chemistry codes. Their computational procedures are described below.

#### 4.4.1 Computational details for the ORCA calculations

The Dy<sup>3+</sup> ion is a  $4f^9$  system with ground state spin multiplicity of 6, and so, for the calculation using ORCA code, a state averaged CAS(9,7) (representing 9 electrons in 7 f-orbitals) was carried out for Dy(N4O5C14H11)3 (Dy1) and Dy(N2O2C7H11)3 (Dy2) using the scalar relativistic Douglas-Kroll-Hess Hamiltonian (DKH)[170, 171] with DKH-DEF2-TZVP basis set (for O, N, C, H) and SARC2-DKH-QZVP basis set (for Dy) and their corresponding auxiliary basis sets of DEF2/JK and SARC2-DKH-QZVP/JK respectively as implemented in ORCA program package. The starting orbitals were chosen as a primitive model (PModel)-guess for CAS(9,7), and the convergence was set to very tight for the SCF procedure. The obtained wavefunction was used for NEVPT2 calculation before turning on the property flags to account for **g**-tensor, **D**-tensor, SOC, *ab initio* ligand field theory

(AILFT) and magnetic susceptibility. Due to convergence issues, the fragmentation method was adopted for **Dy1** and **Dy2** in which the Pmodel start orbitals were used to obtain converged SCF results for the ligand fragments and then the dysprosium ion fragment while ensuring the same basis functions. Afterwards, the two converged fragment orbitals were used as starting orbitals for the CAS(9,7) calculation for the full molecules (**Dy1** and **Dy2**). Rotation of the f-orbitals into the active space were carried out where necessary. First, we carried out separate calculations for each of the three spin allowed multiplicities, 6, 4 and 2 with 21, 224 and 490 roots respectively. Finally, a state average method was applied for a single calculation combining all three spin multiplicity.

#### 4.4.2 Computational details for the MOLCAS calculations

To account for the ligand field effect using the Stevens Operators as well as gain some insight about the ab initio blocking barrier, 'SINGLE ANISO' module implemented in the MOLCAS programme package was employed to obtain converged orbitals from the RASSCF/RASSI procedure. To ensure a high accuracy without exceeding computational capabilities in our group, the generally relativistically contracted all electron basis sets based on the Atomic Natural Orbital (ANO-RCC)[229-231] as obtained from the Basis Set Exchange Library, [232] were used. The polarised valence triple- $\zeta$  quality was employed for the dysprosium atom (Dy:ANO–RCC–VTZP), polarised valence double- $\zeta$  quality for nitrogen and oxygen atoms (N,O:ANO-RCC-VDZP), and the valence double- $\zeta$  quality was used for carbon and hydrogen atoms (C,H:ANO-RCC-VDZ). To speed up the calculation, the Cholesky decomposition of two-electron integral [116, 233, 234] was employed as implemented in MOLCAS package. The RASSCF calculation (RAS2 = 7 and number of electron= 9) in which the 9 f-electrons of Dy<sup>3+</sup> in the 7 f-orbitals were included in the active space was carried out for two different scenarios (spin multiplicity of 6 and combination of 6, 4 and 2) with the appropriate number of configuration interaction roots (CI-roots) before carrying out a RASSI calculation using the respective CI states. The state averaged RASSCF was computed with CI-roots of 21 for  $S = \frac{5}{2}$ , 224 for  $S = \frac{3}{2}$ and 490 for  $S = \frac{1}{2}$ . The obtained state averaged orbitals was used for the RASSI-SO calculations. However, only a total of 279 number of states were used for the RASSI procedure comprising of 21, 128 and 130 state configurations for the 6, 4 and 2 spin multiplicities respectively. These are enough to describe the effect of additional roots to the ground state multiplet and were included to compare any contribution of the 4 and 2 spin multiplicities to the ground state transitions to the low excited states for the

lanthanide complex. The spin-free eigenstates were obtained by state-averaged RASSCF procedure[235, 236] and then followed by the SO–RASSI energies computed using the SOC parameter obtained with the atomic mean-field integral (AMFI) approximation.[237] The inclusion of the SOC allows the generation of all possible *J*-multiplets and corresponding wavefunctions. The ligand orbitals have not been included in the active space as such inclusion would require consideration of electron transfer from lower energy ligand orbitals to very high energy molecular orbitals or the dysprosium virtual states. Such electronic excitation will have a large energy, making any accompany spin-orbit coupling negligible and so, the final energy levels are not expected to change significantly. This will also allow the assessment of the direct effect of the presence or absence of different donor and peripheral groups of the various structural variants. The obtained wavefunctions were then used to compute the crystal field parameters, magnetic properties, and blocking barrier using the 'SINGLE ANISO' module implemented in MOLCAS.[57]

#### 4.5 f-orbital splitting and structural effect

The f-orbital energies obtained from CAS(9,7) results for Dy1 and Dy2 using ORCA software are shown in Figure 4.7. The f-orbital energies for Dy1 and Dy2 show variations indicating broken degeneracy arising from coulombic interactions in the presence of ligand field. In comparing the f-orbitals of Dy1 and Dy2, we see some destabilization for Dy2 resulting from the repulsion between the ligand lone pairs as they approach the metal site. Overall, the coordinated centres are expected to be more stabilized when compared to the neutral dysprosium atom not experiencing any field effect from a ligand. The overall order of energy stabilisation of the f-orbitals is Dy1 > Dy2 as the f-orbital energies increases inversely in that order. The aromatic character of Dy1 ligand contributed to the further stabilisation of the f-orbitals of Dy1 compared to Dy2. It is important to note this ligand field effect as it will undoubtedly have a some effect on the SMM behaviour of the systems under study since the magnetic properties of f-electrons are sensitive to such ligand field effects.

Despite non-participation of the f-orbitals in bonding, the ligand field splits the orbitals according to Figure 4.7 such that the orbitals with ligands approaching the metal centre head-on to their lobes are less stabilised (for example,  $f_{x(x^2-3y^2)}$  of **Dy2** and **Dy1**) due to increased repulsion. As a result, their energies are higher than those situated at positions

such that the incoming ligands approach by the side of the orbital lobes and not head-on (for example,  $f_{z(x^2-y^2)}$  of **Dy2** and **Dy1**).



Fig. 4.7 Energy splitting of the seven f-orbitals of **Dy1** (Dy(N4O5C14H11)3) and **Dy2** (Dy(N2O2C7H11)3)

The splitting pattern of **Dy2** and **Dy1** are similar except for the energy values and the position of the  $f_{xz^2}$  and  $f_{xyz}$  orbitals which have their positions swapped when **Dy2** and **Dy1** are compared. This is attributed to the aromatic effect in which the aromatic ring present in **Dy1** is aligned so that it pushes the donor atom further in the *y*-axis. The implication is a lowering of orbitals without *y*-contribution and a slight increase in orbitals with *y*-contribution. Consequently, the  $f_{xyz}$  orbital become destabilized compared to  $f_{xz^2}$  orbital leading to the observed swap in Figure 4.7 from **Dy2** to **Dy1**. This effect is also felt for  $f_{z^3}$  of **Dy1** which tend to close the energy gap with  $f_{z(x^2-y^2)}$  that has a *y*-contribution.

#### 4.5.1 Electronic transitions computed for Dy1 and Dy2

The excited states obtained from the NEVPT2 calculation for **Dy1** and **Dy2** are shown in Figure 4.8. We observed the spin-free energy splitting for both systems into three regions of closely spaced states with energy gap ranging from  $6 \times 10^3$  to  $2 \times 10^4$  cm<sup>-1</sup> as would be expected.[160] These states are depicted in Figure 4.8 as lower splitting (below 1200 cm<sup>-1</sup>), intermediate splitting (6500 – 5700 cm<sup>-1</sup>) and higher splitting (26,600 – 25,400 cm<sup>-1</sup>).



Fig. 4.8 NEVPT2 excited energies (spin-free states) for Dy1 (Dy(N4O5C14H11)3) and Dy2 (Dy(N2O2C7H11)3). Only the excited states were shown. The ground state is 0 cm<sup>-1</sup>

However, a close look at each region (Figure 4.9 - 4.11) reveals very small variation in the gaps between similar states for systems **Dy1** and **Dy2**. The excited states for each region are closely packed suggesting a contribution from the ligand field.



Fig. 4.9 Expanded NEVPT2 excited energies (spin-free states) for Dy1 (Dy(N4O5C14H11)3) and Dy2 (Dy(N2O2C7H11)3) showing the lower excited sub spaces.

The splitting for each region is almost identical for Dy1 and Dy2 except for a relatively lower energy state (up to 18 cm<sup>-1</sup>) observed in Dy1 for each related excited state except for the first excited state which differs by 2.1 cm<sup>-1</sup>. Considering the structural differences between Dy1 and Dy2, this could be attributed to the contribution from the aromatic rings and their substituents which helps to make more electron density available for donation and hence more stabilization.



Fig. 4.10 Expanded NEVPT2 excited energies (spin-free states) for Dy1 (Dy(N4O5C14H11)3) and Dy2 (Dy(N2O2C7H11)3) showing the intermediate excited sub spaces

In other to understand and substantiate the factors contributing to the slow magnetic relaxation in the SMMs behaviour of **Dy1**, the identity of each state and their wavefunction contribution to the transition from the ground state  $\binom{6H_{15}}{2}$  was computed using MOLCAS software package and presented in section 4.5.3



Fig. 4.11 Expanded NEVPT2 excited energies (spin-free states) for Dy1 (Dy(N4O5C14H11)3) and Dy2 (Dy(N2O2C7H11)3) showing the higher excited sub spaces

#### 4.5.2 Ab initio ligand field theory (ALFT) of Dy1 and Dy2

Theoretical models for molecular magnetism like density functional theory (DFT),[45] ligand field,[160] spin-orbit coupling and *ab initio* calculations[57] have been employed to give more insight especially in the correlation between the electronic structure resulting from crystal-field splitting and magnetic relaxation dynamics of SMMs incorporating lanthanides. Neese *et al.* have used multireference *ab initio* ligand field theory to extract some periodic trend among lanthanide using the elpasolite complexes (Cs<sub>2</sub>NaLn<sup>III</sup>Cl<sub>6</sub>; where Ln<sup>III</sup> = Ce – Nd, Sm – Eu, Tb – Yb) and found their results compare with experimental results.[238] Although ligand field splitting is very weak for lanthanide compare to transition metal ions, its effect can affect the SOC arising from the unquenched total angular momentum of the

(NEVPT2).

f-electrons. Since single-molecule magnets are very sensitive to such small changes around the metal centre, one can tune the ligand field to enhance SMM behaviour. Magnetism, optical and luminescence properties of lanthanides and transition metal compounds have been rationalised by employing *ab initio* density functional theory (AIDFT) and *ab initio* ligand field theory (AILFT).[138, 239, 240, 191, 241, 135] The ligand field parameter are defined through *ab initio* theory[133] to gain insight on the effect of the ligand field to the magnetic properties of the compounds under investigation, the energies of electronic states arising from the  $4f^9$  Dy<sup>3+</sup> ion was obtained from CASSCF wavefunctions and further improved using the scalar relativistic second order N-electron valence perturbation theory

AILFT can be used to extract angular overlap as well as model ligand field and SOC parameters. [238] Since the quadrupole approximation of lanthanide ions has implications for the SMM behaviour, [2] the degree of covalency between the metal and participating ligand is expected to play a significant role in determining the SMM behaviour of materials. Therefore, AILFT as implemented in ORCA software was used to extract the nephelauxetic parameters to gain insight on the degree of covalency and by extension on how that affects the magnetic properties of Dy1 and Dy2. The order of the nephelauxetic parameter (Table 4.5) is  $Dy_3^+$  free ion >  $Dy_2$  >  $Dy_1$  which implies a higher interelectronic repulsion in the same order of magnitude with the free metal ion having the highest repulsion. This observation is justifiable since orbital overlap would lead to electron cloud expansion and a corresponding decrease of the charge density on the metal centre, especially as negatively charged ligands come in proximity. The nephelauxetic parameter for Ln ions tends to decrease across the period for a given ligand.[242] The relatively low involvement of lanthanide f-electrons in bonding makes it difficult to tune their properties by ligand field effectively. However, their magnetic properties are sensitive to such little contribution. AILFT then offers an excellent treatment of the fictitious pure f-orbitals assuming they are not too diluted by ligand orbitals. For this reason, a CAS(9,7) gives us a reliable means of investigating the low lying energy levels for the four systems. By introducing the dynamic correlation through NEVPT2 correction to the CAS-CI in ORCA program, the AI results were significantly improved. In computing the AILFT, the active space was rotated to match the model Hamiltonian of equation 4.1;

$$\hat{H} = V_{ee} + V_{LF} + \zeta \sum_{i=1}^{n} \hat{\mathbf{l}}_i \hat{\mathbf{s}}_i$$
(4.1)

where  $V_{ee}$  is the interelectronic repulsion term which can be expressed in terms of Racah parameters as  $E^1, E^2$ , and  $E^3$ .  $V_{LF}$  is the ligand field interaction term,  $\zeta$  is the SOC parameter, while  $\hat{\mathbf{l}}_i$  and  $\hat{\mathbf{s}}_i$  represent the monoelectronic orbital and spin vector operators in i = x, y, z sub-spaces. By mapping the ligand field Hamiltonian of each system to the energies and wavefunctions obtained from *ab initio* treatment, the unnormalized interelectronic parameter ( $F^2$  as defined in section 3.5) and the SOC constant were obtained as presented in Table 4.5. This gives insight on the energy splitting as well as the coordination environment.[133] Only the highest multiplicity (2S + 1 = 6) was included for the present study which yielded non-zero values of  $F^2$  for all systems with which the only needed Racah parameter was computed (Table 4.5). The consideration of only  $F^2$  term is in line with previous report[243] which shows that the nephelauxetic effect is predominantly given by the change in the second-order Slater integral and the conversion equations from  $F_k$  to  $E^k$  contains essentially  $F_2$ .[243, 244]

Table 4.5 *Ab initio* ligand field results of **Dy1**, **Dy2** and free  $Dy(3^+)$  ion with corresponding Slater Condon and Racah parameters

|          |             | NEVPT2      |             |             | CASSCF      |             | SOC         |
|----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| System   | $F^2$       | $F_2$       | $E^3$       | $F^2$       | $F_2$       | $E^3$       | constant    |
|          | $(cm^{-1})$ |
| Dy1      | 82316.1     | 365.8493    | 609.7488    | 111781.2    | 496.8053    | 828.0088    | 1936.61     |
| Dy2      | 82321.6     | 365.8737    | 609.7896    | 111777.8    | 496.7902    | 827.9837    | 1936.64     |
| Dy3(+)   | 83802.9     | 372.4573    | 620.7622    | 112551.8    | 500.2302    | 833.7170    | 1946.3      |
| free ion |             |             |             |             |             |             |             |
|          |             |             |             |             |             | <i>cc</i>   |             |

The SOC constant given above is proportional to the nephelauxetic effects as it follows the same trend with the complexes'  $F_k$  terms

# 4.5.3 *Ab initio* crystal field parameters of Dy1 and its model Dy2 complex

The total angular momentum (J) is a useful quantum number for understanding the electronic properties of lanthanide-based compounds. A qualitative model of the splitting of the *J* multiplet of a free  $Ln^{3+}$  ion by organic ligands can also be carried out using the Stevens crystal field operators to evaluate useful crystal field parameters (CFPs). The Stevens operator of the CFP is implemented in MOLCAS software and so this calculation

was carried out using MOLCAS. The 27 of the CF parameters (5 from second rank, 9 from fourth rank and 13 from sixth rank operators) are important for the  $Ln^{3+}$  ion. Although, information on higher ranked operators can be computed, their contributions are very negligible to give any physical meaning coupled with the complexity of operating on too many parameters. The splitting of the *J* multiplet of the valence 4f by the CF is very small and so does not impact the many electron wave function of the free ion due to the core-nature of the 4f electron. However, this has implication for the magnetic properties which can be computed from the energies of the 2J + 1 states. The CFPs for **Dy1** and **Dy2** were determined using *ab initio* calculations based on the RASSCF-RASSI-SO method (with 9 electrons in 7 active orbitals) from which the composition and the energies of the low-lying states were computed. Unlike the AILFT method which uses the Slater-Condon parameters ( $F^k$  and  $F_k$ ) in its modeling (as implemented in ORCA), the irreducible tensor operator (ITO) proposed by Chibotaru *et. al* which uses the many-electron energies and wavefunctions of the *J* states was used to determine the CFPs according to equation 4.2

$$\hat{H} = \sum_{k=2, even} \sum_{q=-k}^{k} B_k^q \hat{O}_k^q (\hat{\mathbf{J}}) + \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \hat{\mathbf{J}}$$
(4.2)

where  $B_k^q$  are the CFPs, k is rank of the ITO and is even (k = 2, 4, 6, ..), q is the component of the ITO and derives its value from k (q = -k through 0 to +k),  $O_k^q$  is the extended Steven operators,[57, 245]  $\hat{\mathbf{J}}$  is the pseudospin operator for dysprosium for which the expression - $\hat{O}_k^{-q}(\hat{\mathbf{J}}) = [\hat{O}_k^q(\hat{\mathbf{J}})]^*$  holds (\* denotes a complex conjugate).

A one-to-one correspondence of the computed and model states for the pseudospin Hamiltonian parameters was carried out and the eigenvectors of the magnetic moment operators were determined followed by the decomposition of the CFP using the ITO technique. The percentage contributions of the operator ranks of the evaluated CFPs ( $B_k^q$ ) using the 16 (2J + 1 manifolds) *ab initio* energy levels of Dy<sup>3+</sup> ion and the corresponding eigenfunctions are presented in Table 4.6. As expected, the 2<sup>nd</sup>-order operators contributed most for both **Dy1** and **Dy2**. As the symmetry of a metal complex increases, the number of CFPs required to define such complex is reduced.

|                        | Weight   | ing (%)  |  |
|------------------------|----------|----------|--|
| Operator               | Dv1      | Dv2      |  |
| Rank $(O_k)$           | Dyi      | Uyz      |  |
| <i>O</i> <sub>2</sub>  | 53.24497 | 53.43058 |  |
| $O_4$                  | 25.43602 | 25.30840 |  |
| <i>O</i> <sub>6</sub>  | 19.84256 | 19.68293 |  |
| $O_8$                  | 0.76911  | 0.73488  |  |
| $O_{10}$               | 0.51013  | 0.59987  |  |
| <i>O</i> <sub>12</sub> | 0.18848  | 0.23111  |  |
| $O_{14}$               | 0.00873  | 0.01224  |  |

Table 4.6 Contributions of the ranks of the individual irreducible tensor operators of the crystal field parameters for **Dy1** and **Dy2**. (Computed with combined RASSCF-RASSI-SO spin multiplicity of 2,4,6;  $J = \frac{15}{2}$ )

Table 4.6 shows that 3 rank operators (2,4 and 6) are sufficiently enough to describe all the systems here. Although, there are contributions from higher rank operators, these contributions are negligible and vanish as the even ranked operators increase beyond 6. Therefore the focus will be on the CFPs of rank 2, 4 and 6 as presented in Table 4.7. The extended Stevens operator acting in the Hilbert space of the Slater determinants may be computed with reference to either the one-electron (1), spin-free (L), or spin-orbit (J) manifolds. A q-value of zero in equation 4.2 represents uniaxial or diagonal contributions to the CFPs, anything else are transverse or off-diagonal contributions. Only the even integers of k are considered. The inclusion of the SOC (J-term) restores the over-parameterization of the CFPs for the spin-free term as such, we focus on the J-terms for other comparison. More also, a slight recovering of the over-estimated parameter was observed when all spin multiplicity (2,4 and 6) are employed for the RASSCF-RASSI wavefuction. For this reason, other studies in chapter 5 and 6 were restricted to the inclusion of all allowed spin multiplicities of the given  $Ln^{3+}$  in the RASSCF-RASSI procedure. The obtained CFPs  $(B_k^q)$ from molcas contains the operator equivalent factors which for the dysprosium ion ground multiplets is given as  $-\frac{2}{315}$ ,  $-\frac{8}{135135}$  and  $\frac{4}{3864861}$  for  $2^{nd}$ , 4th and  $6^{th}$  rank respectively and  $-\frac{2}{135}, -\frac{4}{10395}$  and  $\frac{2}{81081}$  respectively for the ground terms. We extracted the true CFPs using the corresponding operator equivalent factors and presented them in Table 4.7.

|   |    | $B_k^q$        |                           |                |                   |                      |  |  |
|---|----|----------------|---------------------------|----------------|-------------------|----------------------|--|--|
|   |    | RASSCF-RASSI-S | O spin multiplicity = $6$ | Combined RASSC | F-RASSI-SO spin m | nultiplicity = 2,4,6 |  |  |
| k |    | Dy1            | Dy1                       | Dy1            | Dy1               | Dy2                  |  |  |
| ĸ | Ч  | (L-Term based) | (J-Term based)            | (L-Term based) | (J-Term  based)   | (J-Term based)       |  |  |
| 2 | -2 | 225.6937       | 3.5438                    | 130.6807       | 11.4739           | -34.4059             |  |  |
| 2 | -1 | 508.3128       | -395.2132                 | -381.3014      | -389.4944         | 193.3250             |  |  |
| 2 | 0  | 329.3305       | 342.5405                  | 329.3305       | 338.2817          | 343.7280             |  |  |
| 2 | 1  | 203.2580       | 192.8005                  | -392.7589      | 175.0014          | -137.3888            |  |  |
| 2 | 2  | 27.1377        | -220.9820                 | 186.0827       | -216.7279         | -254.8224            |  |  |
| 4 | -4 | 238.6432       | -199.1552                 | 6.7308         | -202.7025         | -149.8309            |  |  |
| 4 | -3 | 270.0361       | 58.4459                   | 225.7014       | 40.7094           | -113.5134            |  |  |
| 4 | -2 | -65.1767       | -15.8784                  | -9.6933        | -18.5811          | -29.3919             |  |  |
| 4 | -1 | 68.0873        | 137.6688                  | -109.5373      | 140.2026          | 70.6080              |  |  |
| 4 | 0  | 98.0249        | 93.4121                   | 98.0249        | 92.3986           | 91.5540              |  |  |
| 4 | 1  | -116.0862      | 80.0675                   | 78.3783        | 77.1959           | -107.4323            |  |  |
| 4 | 2  | -45.4521       | 63.5135                   | -78.8201       | 61.3175           | 76.5202              |  |  |
| 4 | 3  | 324.0901       | 486.8238                  | -356.4446      | 478.3779          | -332.4321            |  |  |
| 4 | 4  | -32.5364       | 100.8445                  | 240.8002       | 85.6418           | 201.0133             |  |  |
| 6 | -6 | -130.9458      | 0.0002                    | 230.6754       | 154.5944          | -57.9729             |  |  |
| 6 | -5 | -445.9455      | 0.0000                    | -74.1891       | -57.9729          | -309.1889            |  |  |
| 6 | -4 | 146.3512       | -0.0002                   | -124.8647      | -164.2566         | -164.2566            |  |  |
| 6 | -3 | 29.1892        | 0.0002                    | -196.2160      | 144.9323          | 9.6622               |  |  |
| 6 | -2 | -139.0539      | -0.0001                   | -3.2432        | -67.6351          | -57.9729             |  |  |
| 6 | -1 | 247.7025       | -0.0001                   | -203.9187      | -135.2701         | 222.2295             |  |  |
| 6 | 0  | 12.5676        | 0.0000                    | 12.5676        | 19.3243           | 9.6622               |  |  |
| 6 | 1  | 53.9189        | 0.0002                    | -150.4053      | 154.5944          | -164.2566            |  |  |
| 6 | 2  | -120.8107      | 0.0002                    | -184.0539      | 135.2701          | 135.2701             |  |  |
| 6 | 3  | -196.6214      | -0.0001                   | 32.4324        | -96.6215          | 222.2295             |  |  |
| 6 | 4  | 109.4594       | -0.0001                   | 133.7837       | -67.6351          | 38.6486              |  |  |
| 6 | 5  | 173.9187       | 0.0005                    | 473.1076       | 492.7698          | -231.8917            |  |  |
| 6 | 6  | -212.8376      | -0.0002                   | 96.4864        | -193.2431         | -212.5674            |  |  |

Table 4.7 Crystal field parameters for Dy1 and Dy2

The  $|B_2^0|$  value for the ground multiplet is higher for **Dy2** compared to **Dy1** showing a slightly more symmetric system in the absence of the aromatic rings. **Dy1** and **Dy2** also show appreciable transverse contributions to the CFPs indicating possible competing uniaxial and transverse terms. This should have implication for the magnetic properties as will be discussed in the proceeding section. The closeness of the uniaxial and transverse contributions to the CFPs for both systems could cause the observation of competing easy axis and easy plane magnetic anisotropy. This might be due to the trigonal arrangement of the three coordinating ligands which tend to counter the effect of the other ligands lying between 114.67 (4) – 122.91(5)°from each other. This arrangement has implication for the overall quadrupole moment approximation of the Dy<sup>3+</sup> and by extension the SMM behaviour. The higher unaxial  $(|B_2^0|)$  contribution for **Dy2** compared to **Dy1** stems from the overall lesser peripheral distortion of the ligand for which the aromatic ring has contributed more for **Dy1**. The higher ranks CFPs also show significant contributions to the overall CFPs indicating that peripheral ligands contribute appreciably to the crystal field effect of the systems under investigation.

## 4.5.4 The effect of the crystal field splitting on the magnetic properties of Dy1

The crystal field contribution to the magnetic splitting of **Dy1** and **Dy2**, were investigated ab initio to ascertain the extent to which the peripheral ligands and aromaticity can affect the observation of SMM behaviour in **Dy1**. First, the spin-free energy states were extracted for each system followed by the inclusion of the spin-orbit contribution which allows the extraction of the eight Kramers pairs for each  $m_j$  state  $(|\pm \frac{15}{2}\rangle \longrightarrow |\pm \frac{1}{2}\rangle)$ . The inclusion of the 3 allowed spin multiplicities for dysprosium ion (6,4 and 2) in the RASSCF-RASSI-SO as described in the computational section above does not affect the absolute energy of the state. However, while such inclusion does not matter much for the ground state energy, the excited energies were more stabilised compared to results using only the ground state spin multiplicity of 6 (Table 4.8 and 4.9). For an anisotropic system, the direction of the applied magnetic field affects the resulting g-factor and so the z-axis of the crystal structure of **Dy1** was chosen as the magnetization axis which lies at the bisection of the butterfly shaped structure (Figure 4.12). Table 4.8 and 4.9 show the spin-free energies, RASSI-SO energies for the Kramers pairs and their corresponding g-factors and  $m_i$ -state assignments. Each RASSI-SO energy represents the energy of a Kramers pair  $(\pm m_i)$ . The inclusion of the SO interactions splits the Kramers doublets into two equal energies with the first excited states respectively 142.4283 and 143.0156 cm<sup>-1</sup> apart from the ground state for the ground state-only spin multiplicity and the inclusion of the 6.4 and 2 spin multiplicity for the RASSCF-RASSI-SO procedure.



Fig. 4.12 Structure of  $\mathbf{Dy1}$  showing the axis of magnetization

|  | RASSCF-RASSI-SO spin multiplicity=6; $J = \frac{15}{2}$ ; CSFs =21 (21)* |   |                |        |                       |                 |  |  |  |
|--|--|---|----------------|--------|-----------------------|-----------------|--|--|--|
|  |  |   |                | g-fa   | actor                 |                 |  |  |  |
| Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> )              | $\Psi_i$ contribution (for Kramers doublets)  | g <sub>x</sub> | $g_y$  | <i>g</i> <sub>z</sub> | $g_z$ angle (°) |  |  |  |
| 0.0000   | 0.0000   | $98.4\% \left \pm \frac{15}{2}\right\rangle$  | 0.0183         | 0.0135 | 19.8691               | 0.0000          |  |  |  |
| 14.5331  | 142.4283   | $86.3\% \left  \pm \frac{13}{2} \right\rangle$ , 10.3% $\left  \pm \frac{11}{2} \right\rangle$  | 0.3073         | 0.2467 | 17.3263               | 8.6567          |  |  |  |
| 186.8013   | 241.8101   | $\begin{array}{c} 29\% \left \pm\frac{1}{2}\right\rangle, \ 21.6\% \left \pm\frac{3}{2}\right\rangle \\ 12.1\% \left \pm\frac{9}{2}\right\rangle, \ 10\% \left \pm\frac{7}{2}\right\rangle \end{array}$   | 3.3559         | 2.3337 | 15.7758               | 77.1207         |  |  |  |
| 223.0127   | 287.6430   | $\begin{array}{c} 38.8\% \left  \pm \frac{11}{2} \right\rangle, \ 15.9\% \left  \pm \frac{1}{2} \right\rangle \\ 15.3\% \left  \pm \frac{9}{2} \right\rangle, \ 10.1\% \left  \pm \frac{5}{2} \right\rangle \end{array}$  | 10.0712        | 4.8393 | 0.6752                | 54.1318         |  |  |  |
| 279.7752   | 377.6652   | $\begin{array}{c} 25.3\% \left  \pm \frac{3}{2} \right\rangle, \ 20.9\% \left  \pm \frac{7}{2} \right\rangle, \ 17.4\% \left  \pm \frac{5}{2} \right\rangle \\ 14.4\% \left  \pm \frac{11}{2} \right\rangle, \ 13.8\% \left  \pm \frac{9}{2} \right\rangle \end{array}$ | 6.0777         | 1.0728 | 10.0774               | 0.9283          |  |  |  |
| 337.1472   | 415.8867   | $\begin{array}{c} 26.9\% \left  \pm \frac{5}{2} \right\rangle, \ 24.8\% \left  \pm \frac{1}{2} \right\rangle \\ 19.4\% \left  \pm \frac{3}{2} \right\rangle, \ 11.7\% \left  \pm \frac{7}{2} \right\rangle \end{array}$   | 10.0773        | 7.4691 | 1.8912                | 41.9944         |  |  |  |
| 424.2764   | 464.2833   | $\begin{array}{c} 34.9\% \left  \pm \frac{9}{2} \right\rangle, \ 24.9\% \left  \pm \frac{7}{2} \right\rangle, \ 11.8\% \left  \pm \frac{5}{2} \right\rangle \\ 10.5\% \left  \pm \frac{11}{2} \right\rangle, \ 9.5\% \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 2.2329         | 1.3710 | 12.0667               | 0.6375          |  |  |  |
| 467.0146   | 522.1780   | $\begin{array}{c} 26.4\% \left  \pm \frac{7}{2} \right\rangle, \ 23.1\% \left  \pm \frac{5}{2} \right\rangle, \ 18.6\% \left  \pm \frac{3}{2} \right\rangle \\ 14.9\% \left  \pm \frac{9}{2} \right\rangle, \ 14.6\% \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 0.6708         | 2.8526 | 16.8802               | 76.9571         |  |  |  |
| 537.9275   |  |   |                |        |                       |                 |  |  |  |
| 601.8654   |  |   |                |        |                       |                 |  |  |  |
| 634.8218   |  |   |                |        |                       |                 |  |  |  |

Table 4.8 Electronic structure of Dy1 calculated with RASSCF-RASSI-SO using MOLCAS software

\*The CSFs in the bracket represents the maximum number of states allowed

for the corresponding spin multiplicity (6)

\*\*Each energy value represents a degenerate of two states (Kramers doublet).

The sign of  $g_x \times g_y \times g_z$  is negative

|       | Combined RASSCF-RASSI-SO spin multiplicity=6,4,2; $J = \frac{15}{2}$ ; CSFs=21,128,130 (21,224,490)* |   |   |         |           |         |                 |  |
|-------|--|---|---|---------|-----------|---------|-----------------|--|
|       |  |   |   |         | g-f       | actor   |                 |  |
| State | Spin-free<br>state energies<br>$(cm^{-1})$   | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution (for Kramers doublets)  | $g_x$   | <i>gy</i> | $g_z$   | $g_z$ angle (°) |  |
| 0     | 0.0000   | 0.0000  | $98.5\% \left  \pm \frac{15}{2} \right\rangle$  | 0.0160  | 0.0119    | 19.7728 | 0.0000          |  |
| 1     | 14.5331  | 143.0156  | $86.7\% \left  \pm \frac{13}{2} \right\rangle$ , $10\% \left  \pm \frac{11}{2} \right\rangle$   | 0.2902  | 0.2300    | 17.2398 | 9.1378          |  |
| 2     | 186.8013   | 240.1283  | $\begin{array}{c} 29\% \left  \pm \frac{1}{2} \right\rangle, \ 21.4\% \left  \pm \frac{3}{2} \right\rangle, \ 13.7\% \left  \pm \frac{11}{2} \right\rangle \\ 10.6\% \left  \pm \frac{5}{2} \right\rangle, \ 10.3\% \left  \pm \frac{7}{2} \right\rangle \end{array}$   | 3.0444  | 2.2013    | 15.9929 | 77.4780         |  |
| 3     | 223.0127   | 286.4100  | $\begin{array}{c} 40.5\% \left  \pm \frac{11}{2} \right\rangle, \ 15.6\% \left  \pm \frac{1}{2} \right\rangle \\ 14.9\% \left  \pm \frac{9}{2} \right\rangle, \ 9.3\% \left  \pm \frac{5}{2} \right\rangle \end{array}$   | 10.2887 | 4.6888    | 0.4338  | 53.0048         |  |
| 4     | 279.7752   | 373.1423  | $\begin{array}{c} 24.6\% \left  \pm \frac{3}{2} \right\rangle, \ 20.8\% \left  \pm \frac{7}{2} \right\rangle, \ 17.5\% \left  \pm \frac{5}{2} \right\rangle \\ 14.4\% \left  \pm \frac{11}{2} \right\rangle, \ 14.2\% \left  \pm \frac{9}{2} \right\rangle \end{array}$ | 6.0158  | 1.0969    | 10.1237 | 2.9368          |  |
| 5     | 337.1472   | 410.7460  | $\begin{array}{c} 26\% \left  \pm \frac{5}{2} \right\rangle, \ 24.7\% \left  \pm \frac{1}{2} \right\rangle \\ 20\% \left  \pm \frac{3}{2} \right\rangle, \ 11.2\% \left  \pm \frac{7}{2} \right\rangle \end{array}$   | 10.0565 | 7.5015    | 1.8473  | 41.3629         |  |
| 6     | 424.2764   | 456.9879  | $\begin{array}{c} 35.1\% \left  \pm \frac{9}{2} \right\rangle, \ 25.1\% \left  \pm \frac{7}{2} \right\rangle, \ 12.4\% \left  \pm \frac{5}{2} \right\rangle \\ 9.9\% \left  \pm \frac{11}{2} \right\rangle, \ 9.1\% \left  \pm \frac{1}{2} \right\rangle \end{array}$   | 2.3085  | 1.4036    | 12.2093 | 0.7328          |  |
| 7     | 467.0146   | 512.8642  | $\begin{array}{c} 27\% \left  \pm \frac{7}{2} \right\rangle, \ 23.5\% \left  \pm \frac{5}{2} \right\rangle, \ 18.6\% \left  \pm \frac{3}{2} \right\rangle \\ 14.6\% \left  \pm \frac{1}{2} \right\rangle, \ 14.3\% \left  \pm \frac{9}{2} \right\rangle \end{array}$    | 0.6480  | 2.7109    | 16.9268 | 76.9142         |  |
| 8     | 537.9275   |   |   |         |           |         |                 |  |
| 9     | 601.8654   |   |   |         |           |         |                 |  |
| 10    | 634.8218   |   |   |         |           |         |                 |  |

Table 4.9 Electronic structure of Dy1 calculated with RASSCF-RASSI-SO using MOLCAS software

\*The CSFs in the bracket represents the maximum number of states allowed

for the corresponding spin multiplicity (6, 4 and 2)

\*\*Each energy value represents a degenerate of two states (Kramers doublet).

The sign of  $g_x \times g_y \times g_z$  is negative

For other excited states, it appears that the inclusion of the 3 spin multiplicity in the RASSCF-RASSI-SO procedure helps to stabilise the excited states. As such, we will now consider only situations where the RASSCF-RASSI-SO procedure includes all 3 spin multiplicities (Table 4.9 and 4.10).

The identity of the states were computed with the decomposition of the pseudospin for  $J = \frac{15}{2}$ . Easy axis (hard plane) and easy plane (hard axis) form the pathways for the unravelling of magnetic anisotropy and their contribution to the slow magnetic relaxation in SMM. If the energy is a minimum when the applied field is along an axis, it is referred to as easy axis anisotropy. On the other hand, if it is a minimum when the magnetic field is applied in a plane, it is referred to as easy plane anisotropy.[246] For the easy axis anisotropy, the identity of the minimum energy  $m_i$ -state must be that with the highest  $m_i$ . If the identity of the states contributing to the minimum energy is the lowest  $m_i$ value (usually the  $|\pm\frac{1}{2}\rangle$  state for the Kramers ions), the anisotropy is known as the easy plane or hard axis anisotropy. The lowest  $m_j$ -state in **Dy1** was 98.5 %  $|\pm \frac{15}{2}\rangle$  suggesting a possible magnetization along the easy axis. The symmetry of the first coordination sphere as presented in 4.5 is between a distorted  $D_{3h}$  and  $C_{4\nu}$  which is high enough to guarantee distinct mixing of states. However, the overall symmetry  $(C_1)$  of the molecule is far from that of the first coordination sphere leading to a terrible admixture of the  $m_i$ -state as the excited state energies increases. In principle, one would expect the order for a high symmetry compound with easy axis as the axis of magnetization to be  $\left|\pm\frac{15}{2}\right\rangle \longrightarrow \left|\pm\frac{13}{2}\right\rangle$  $\longrightarrow \left| \pm \frac{11}{2} \right\rangle \longrightarrow \left| \pm \frac{9}{2} \right\rangle \longrightarrow \left| \pm \frac{7}{2} \right\rangle \longrightarrow \left| \pm \frac{5}{2} \right\rangle \longrightarrow \left| \pm \frac{3}{2} \right\rangle \longrightarrow \left| \pm \frac{1}{2} \right\rangle \text{ with the lowest energy}$ and highest energy states belonging to  $\left|\pm\frac{15}{2}\right\rangle$  and  $\left|\pm\frac{1}{2}\right\rangle$  respectively. However, beyond  $\left|\pm\frac{13}{2}\right\rangle$  the mixing of the  $m_i$ -states no longer allowed the dominance of the higher Kramers pairs at a lower excited states in the order presented above for strict symmetry. This is attributed to the very low symmetry of the molecule when the coordination sphere is extended to include the peripheral ligands and is expected to have some implication for the slow magnetic relaxation of the system. The extracted g-factor shows appreciable axial anisotropy with  $g_z$ -value of 19.8691 at the ground state.

To ascertain the contribution of the aromatic ring to the crystal field splitting of the  $m_j$ -states in **Dy1** we looked at the results from **Dy2** (Table 4.10). The contribution of the  $m_j$ -states to the various state energies were comparable to those of **Dy1** as well as the distribution of the g-factors. The various excited state energies were higher for **Dy2** compared to **Dy1** for all  $m_j$  levels showing that **Dy2** would be expected to be a better SMM if it existed. The implication is that the inclusion of aromatic ring in **Dy1** seems to

impact negatively on the SMM ability of **Dy1**. For example, when the energy gaps between the ground state and the first excited state are compared, **Dy2** shows a higher energy gap of 174.1152  $cm^{-1}$  compared to 143.0156  $cm^{-1}$  for **Dy1**. This means that it will take a spin longer time to relax through the excited state in **Dy2** than in **Dy1**, making **Dy2** a better SMM.

The electronic structure presented in this section shows that **Dy1** and **Dy2** would have the propensity for SMM behaviour due to the anisotropic nature of the g-factor and the easy axis type magnetic anisotropy with  $|\pm \frac{15}{2}\rangle$  as the ground state. The low symmetry of **Dy1** and **Dy2** accounts for the admixture of the excited  $m_j$ -states which might have implication for slow magnetic relaxation due to complexity in determining a clear path for spin reversal as a result of the admixture.

|       | Combined RASSCF-RASSI-SO spin multiplicity=6,4,2; $J = \frac{15}{2}$ ; CSFs=21,128,130 (21,224,490)* |   |  |                |        |         |                 |  |
|-------|--|---|--|----------------|--------|---------|-----------------|--|
|       |  |   |  | g-factor       |        |         |                 |  |
| State | Spin-free<br>state energies<br>(cm <sup>-1</sup> )   | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution (for Kramers doublets)   | g <sub>x</sub> | gy     | $g_z$   | $g_z$ angle (°) |  |
| 0     | 0.0000   | 0.0000  | $98.6\% \left  \pm \frac{15}{2} \right\rangle$   | 0.0147         | 0.0107 | 19.7658 | 0.0000          |  |
| 1     | 13.3020  | 174.1152  | $84.8\% \left  \pm \frac{13}{2} \right\rangle$ , 10.2% $\left  \pm \frac{11}{2} \right\rangle$   | 0.4747         | 0.2982 | 17.0728 | 10.9529         |  |
| 2     | 229.8469   | 260.4896  | $ \begin{array}{c} 34.8\% \left  \pm \frac{1}{2} \right\rangle, \ 27.3\% \left  \pm \frac{3}{2} \right\rangle, \ 14.9\% \left  \pm \frac{5}{2} \right\rangle \\ 8\% \left  \pm \frac{7}{2} \right\rangle, \ 7.4\% \left  \pm \frac{11}{2} \right\rangle \end{array} $    | 2.0773         | 1.6635 | 16.6570 | 67.9732         |  |
| 3     | 269.5274   | 312.2480  | $\begin{array}{c} 46.8\% \left  \pm \frac{11}{2} \right\rangle, \ 17.3\% \left  \pm \frac{9}{2} \right\rangle \\ 8.2\% \left  \pm \frac{13}{2} \right\rangle, \ 8\% \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 0.1382         | 3.2892 | 11.3227 | 0.9398          |  |
| 4     | 296.6817   | 386.1393  | $\begin{array}{c} 24.4\% \left  \pm \frac{5}{2} \right\rangle, \ 20.9\% \left  \pm \frac{9}{2} \right\rangle, \ 20.6\% \left  \pm \frac{7}{2} \right\rangle \\ 15.4\% \left  \pm \frac{11}{2} \right\rangle, \ 13.2\% \left  \pm \frac{3}{2} \right\rangle \end{array}$  | 6.1251         | 2.1809 | 9.5002  | 49.3867         |  |
| 5     | 330.6834   | 428.7617  | $ \begin{array}{c} 30.9\% \left  \pm \frac{7}{2} \right\rangle, \ 30.6\% \left  \pm \frac{9}{2} \right\rangle, \ 12.9\% \left  \pm \frac{5}{2} \right\rangle \\ 11.5\% \left  \pm \frac{11}{2} \right\rangle, \ 9.3\% \left  \pm \frac{3}{2} \right\rangle \end{array} $ | 3.1458         | 0.6785 | 12.2759 | 48.2143         |  |
| 6     | 467.3750   | 452.3376  | $\begin{array}{c} 26.5\% \left  \pm \frac{1}{2} \right\rangle, \ 17.6\% \left  \pm \frac{5}{2} \right\rangle, \ 17.5\% \left  \pm \frac{7}{2} \right\rangle \\ 16.4\% \left  \pm \frac{5}{2} \right\rangle, \ 15\% \left  \pm \frac{9}{2} \right\rangle \end{array}$     | 0.6967         | 2.4919 | 15.8983 | 17.4227         |  |
| 7     | 483.2778   | 527.9922  | $\begin{array}{c} 26.1\% \left  \pm \frac{3}{2} \right\rangle, \ 24.3\% \left  \pm \frac{1}{2} \right\rangle, \ 23.9\% \left  \pm \frac{5}{2} \right\rangle \\ 14.9\% \left  \pm \frac{7}{2} \right\rangle, \ 8.4\% \left  \pm \frac{9}{2} \right\rangle \end{array}$    | 0.4919         | 0.7013 | 18.3939 | 73.2637         |  |
| 8     | 522.0509   |   |  |                |        |         |                 |  |
| 9     | 619.7565   |   |  |                |        |         |                 |  |
| 10    | 637.0277   |   |  |                |        |         |                 |  |

Table 4.10 Electronic structure of Dy2 calculated with RASSCF-RASSI-SO using MOLCAS software

\*The CSFs in the bracket represents the maximum number of states allowed

for the corresponding spin multiplicity (6,4 and 2)

\*\*Each energy value represents a degenerate of two states (Kramers doublet).

The sign of  $g_x \times g_y \times g_z$  is negative

#### 4.6 Magnetic properties

The magnetic susceptibility measurement of Dy1 was carried out for the direct current (dc) and alternating current (ac) regime using the solid polycrystalline sample on a Quantum Design MPMS-5S and a superconducting quantum interference device (SQUID) (MPMS-XL) magnetometer in applied dc fields. The diamagnetic contribution from the sample holder and that inherent in the sample was corrected using the Pascal's table.[43]. By applying an oscillating field of 3 Oe, the ac measurements were performed with the respective applied dc fields as presented below. The result shows a slow magnetic relaxation pathway for Dy1 which is of molecular origin with a butterfly-type hysteresis up to 10 K. The dynamic and static magnetic properties are presented below.

#### 4.6.1 Static magnetic properties of Dy1

Polycrystalline sample of Dy1 was used to measure the experimental static magnetic susceptibility ( $\chi_m$ ) at an applied dc field of 1000 Oe in the temperature regime of 2 – 300 K to understand the magnetic response as the temperature is varied. A plot of  $\chi_m T$  vs T (Figure 4.13) shows a room temperature value of 14.10 cm<sup>3</sup>Kmol<sup>-1</sup> which is close to the theoretical value of 14.18 cm<sup>3</sup>Kmol<sup>-1</sup>. The RASSCF-RASSI-SO computed  $\chi_m$  plot fits the experimental value with small difference below 100 K. The fit suggests accurate description of the system by the wavefunction obtained from the computational method employed. As the system is cooled to 2 K, the  $\chi_m T$  decreases to about 12.02 cm $^3$ Kmol $^{-1}$ . Such decrease in the  $\chi_m T$  value with decreasing temperature is usually attributed to either anti-ferromagnetic interaction or thermal depopulation of the magnetic  $m_i$  levels. For an anti-ferromagnetic interaction, there need to be closely interacting spin either between magnetic metal sites or between the spins of the metal and an unpaired spin of a ligand (radical). The ligands used do not posses any radical unpaired spins and the inter-molecular distances between the  $Dy^{3+}$  centres are too large to allow any interaction. The shortest inter-molecular distance between two dysprosium centres as described in section 4.2 is 8.174 (3) Å. This distance is too large to allow any strong intermolecular coupling between the metal sites. In addition, the core nature of the 4f electrons also makes it unlikely for the decrease in the  $\chi_m T$  value to be attributed to anti-ferromagnetic interaction. This leaves the thermal depopulation of the magnetic  $m_j$ -states split by the crystal field as the reason for the decrease in the  $\chi_m T$  value with decreasing temperature.



Fig. 4.13  $\chi_m T$  vs T plot for **Dy1** (Dy(N4O5C14H11)3) at a *dc* field of 1000 Oe and temperature range of 2 - 300 K.

A plot of the magnetization Vs field at a temperature of 2 K (Figure 4.14a) shows an opening of a butterfly-type hysteresis with the usual saturation of magnetization above 2 T field. The butterfly-type hysteresis is typical of molecules showing SMM behaviour with zero coercive field. The static magnetic response of **Dy1** also confirms it as a paramagnet. The wavefunction and g-factor computed from the RASSCF-RASSI-SO and presented in Table 4.9 showed an easy axis magnetic anisotropy for **Dy1**. Such uniaxial magnetic anisotropy can be tested experimentally by plotting the magnetization against the product of field and the reciprocal of temperature (M vs.  $HT^{-1}$ ) for different values of temperature. An isotropic system will show a perfect overlap of the temperature variant plots. On the other hand, the abrupt attainment of magnetic saturation from a perfect overlay of the plots. This phenomenon is attributed to the magnetic anisotropy of such system. Figure 4.14b therefore confirms the anisotropic nature of **Dy1** which does not show a perfect overlay of the temperature dependent M vs.  $HT^{-1}$  plots. Figure 4.14b also shows the
blocking temperature for **Dy1** to be about 8 K which is the temperature above which the hysteresis loop disappeared.



(a) M vs H plot for **Dy1** showing a butterflytype hysteresis at 2 K

(b) M vs  $HT^{-1}$  plot for **Dy1** from 2 to 8 K illustrating **Dy1** anisotropy

Fig. 4.14 Magnetization plots for Dy1 (Dy(N4O5C14H11)3) obtained from experiment

The static magnetic properties sheds some light on a possible SMM behaviour for **Dy1**. However, a dynamic investigation of the material by *ac* magnetic measurement needs to be carried out to confirm this as many permanent magnets are known for which a hysteresis loop were observed but were not characterised as SMM.

#### 4.6.2 Dynamic magnetic properties of Dy1

To ascertain the SMM behaviour of **Dy1**, the *ac* susceptibility measurements were carried out experimentally using a polycrystalline sample of **Dy1**. At first, a field scan at a temperature of 1.85 K from 0 – 3000 Oe (Figure 4.15) shows a frequency dependent inphase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) magnetic susceptibilities with double-wave slow magnetic relaxation at all applied *dc* field (0 – 3000 Oe). A weak relaxation peak between 0.1 and 1 Hz was triggered by applied field and gradually increases as the field is increased from 0 – 3000 Oe. The much stronger peak around 1000 Hz appeared at lower field with the slowest relaxation taking place at zero field. This shows that the frequency dependent nature of the slow magnetic relaxation around 1000 Hz is not field induced while that below 1 Hz was induced by field. To accurately measure the relaxation time around 1000 Hz, the susceptibility measurement was carried out with Physical Property Measurement System (PPMS) machine which has the capability to measure the relaxation time up to 10,000 Hz. The PPMS allows the complete recovery of the region with the maximum peak intensity at 2 K and field range of 0 - 5000 Oe (Figure 4.16. This clearly shows the field dynamics with the slow magnetic relaxation.



Fig. 4.15 Experimental field-dependent plot of (a) in-phase susceptibility ( $\chi'$ ) vs frequency (b) out-of-phase susceptibility ( $\chi''$ ) vs frequency for **Dy1** (Dy( $\eta^3$ -N4O5C14H11)3) at 1.85 K and field range of 0 - 3000 Oe

An optimum field (field at which the maximum intensity was observed) of 0 Oe and the butterfly-type hysteresis shown in Figure 4.14a shows that Dy1 exhibit SMM behaviour in the absence of any applied field. The application of dc field suppresses the slow magnetic relaxation at this frequency leading to flattening of the peak top above 5000 Oe.

The dynamic magnetic properties of Dy1 was then investigated at different temperature (1.85 – 9.5 K) in the presence of applied magnetic field of 800 Oe and 0 Oe as shown in Figure 4.17. The two measurements at 800 and 0 Oe shows similar pattern confirming that the splitting of the Kramers ground state in the presence of the crystal field was responsible for the observed slow relaxation. The implication is that unless the crystal field is strong enough to split the Kramers doublet, only a field induced slow magnetic relaxation is possible. This relaxation has a different pathway from the zero-field pathway. The observation of slow magnetic relaxation at zero field is an indication of a strong crystal field around the dysprosium ion in Dy1. A weak crystal field that is unable to split the Kramers doublet at zero field will not lead to a slow magnetic relaxation. The crystal field



Fig. 4.16 Higher frequency experimental field-dependent plot of (a) in-phase susceptibility ( $\chi'$ ) vs frequency (b) out-of-phase susceptibility ( $\chi''$ ) vs frequency for **Dy1** (Dy( $\eta^3$ -N4O5C14H11)3) at 2 K and field range of 0 - 5000 Oe

energy required to split the ground states of the  $Dy^{3+}$  ion in the absence of any external field is what we have discussed in preceding chapter as the zero-field splitting (ZFS) energy.



Fig. 4.17 Experimental temperature-dependent plot of (a) in-phase  $(\chi')$  (top) and out-ofphase  $(\chi'')$  (bottom) susceptibilities vs frequency at 0 Oe (b) in-phase  $(\chi')$  (top) and out-ofphase  $(\chi'')$  (bottom) susceptibilities vs frequency at 800 Oe for **Dy1** (Dy(N4O5C14H11)3) at temperature range of 1.85 - 9.5 K

#### 4.6.3 Spin relaxation dynamics of Dy1

To understand the mechanism of the slow magnetic relaxation of **Dy1**, the temperature dependent magnetic susceptibility graph (Figure 4.17) was fitted using the Dybye model described in equation 1.22 and 1.23. The obtained relaxation times at the various temperatures were then fitted using the Arrhenius equation given in equation 3.50 and presented in Figure 4.18. Figure 4.18 shows that at lower temperature (1.85 - 4.00 K), a competing QTM and thermally assisted QTM predominated the relaxation pathway due to lower thermal energy of the participating spins. As the temperature is increased, the spins gain more energy that allows them to attempt to transverse through an excited energy level. No individual relaxation type was able to fit the data at all temperature attesting to the competing relaxation process at all measured temperature. An attempt to use a single relaxation type equation to fit the curve gave fits that are outside the graph boundary further confirming that no single relaxation process occurs at the measured regions. Pairwise processes were then tried (QTM+Raman, QTM+Orbach, Raman+Orbach, Direct process+Orbach, Direct process+QTM and Direct process+Raman), but none provided a fit within range except for QTM+Orbach which shows appreciable fit (Figure 4.18a) with fit values of 10.54625  $cm^{-1}$ ,  $3.52 \times 10^{-5}$  s and  $2.01 \times 10^{-7}$  s for  $\Delta_{eff}$ ,  $\tau_0$  and QTM respectively . The same behaviour was observed for the fitting of the relaxation time at 800 Oe. However, only the sum fit is presented in Figure 4.18b.

The relaxation times at zero field and applied 800 Oe mimics each other with only a negligible difference in value. Detailed analysis shows the relaxation at 800 Oe to be a little slower but less probable than that at zero-field. This is in line with the observation in the frequency-dependent susceptibility plot at field range of 0 - 5000 Oe shown in 4.15 and 4.16. Results from the RASSCF-RASSI-SO calculation accounted for this phenomenon. At zero-field, the 4*f* degeneracy is split by the CF which is strong enough to cause a zero-field splitting of the degenerate states. However, the low symmetry of the complex means that the mixing of the magnetic levels causes a lack of well defined excited magnetic energy levels (see Table 4.9). In the presence of applied magnetic field, the degeneracy is further split. Figure 4.19 depicts the possible relaxation pathway computed for Dy1 at the RASSCF-RASSI-SO level but not the exact path taken as observed by the experiment. The various states are described in Table 4.9.





Fig. 4.18  $ln\tau$  vs  $T^{-1}$  plots for **Dy1** (Dy(N4O5C14H11)3) at (a) zero field (b) 800 Oe at temperature range of 1.85 – 9.5 K



Fig. 4.19 Pathway for the spin relaxation Dynamics of **Dy1** computed from RASSI-SO. State 0 to state 6 are as given in Table 4.9

The energy gap between the ground state (state 0) and the first excited state (state 1) was computed as 143.0156 cm<sup>-1</sup>. This is higher than the  $\Delta_{\text{eff}}$  extracted by experiment. The mixing of the  $m_j$ -states as a result of the distorted/low symmetry makes it difficult for spins to be excited into pure  $m_j$  levels. At this point, the vibronic energy of the molecule which helps to create additional excited virtual states begins to facilitate the relaxation through the Raman process in which the spin relaxes from the ground state, through an excited virtual state to the state of opposite sign. Table 4.11 shows the quantitative contributions to the relaxation processes extracted by fitting Figure 4.18. The process of spin reversal is therefore a competition among ground state QTM, Raman and Orbach (thermally assisted QTM) processes. The  $\Delta_{\text{eff}}$  extracted at zero field is about 40.90 cm<sup>-1</sup> which is slightly lower than that extracted at 800 Oe (44.04 cm<sup>-1</sup>).



(b) Plot of RASSI-SO energy vs magnetic moment for Dy2

Fig. 4.20 Spin relaxation dynamics with the most probable pathways computed from RASSI-SO. The states are arranged from state 0 (0 cm<sup>-</sup>) to state 6 as shown in Table 4.9 and 4.10 for **Dy1** and **Dy2** respectively.

|     |     | Orbach Process Raman proces |                      |                             |     |                       |               |  |
|-----|-----|-----------------------------|----------------------|-----------------------------|-----|-----------------------|---------------|--|
| Н   |     | $\Delta_{eff}$              | $	au_0$              | С                           | n   | ОТМ                   | Adi P Squara  |  |
| (Oe | 2)  | $cm^{-1}$                   | (s)                  | $\left(s^{-1}K^{-n}\right)$ |     | QIIVI                 | Auj. N-Square |  |
| 0   |     | 40.90                       | $2.57 	imes 10^{-7}$ | 749.17                      | 0.8 | $1.54 \times 10^{-4}$ | 0.99963       |  |
| 800 | ) מ | 44.03                       | $4.77 	imes 10^{-7}$ | 1466.08                     | 0.5 | $2.44 \times 10^{-4}$ | 0.99989       |  |

Table 4.11 Parameters of the fit of the relaxation time for 0 Oe and 800 Oe applied magnetic field

# 4.7 Conclusion

The effect of aromaticity and crystal field to the observation of slow magnetic relaxation characteristics of SMM behaviour was investigated for a mononuclear dysprosium complex of Schiff base ligand. The electronic and magnetic properties of **Dy1** were investigated using experiment and theoretical methods. A model complex, **Dy2** was built from the experimental crystal structure of **Dy1**. Results show that aromaticity could be detrimental to the observation of SMM properties in **Dy1**. Therefore, we propose that one way to rationally favour a uniaxial magnetization which promotes SMM behaviour would be to avoid the incorporation of aromatic rings at peripheral positions. This is in contrast with the molecular designs of the best performing lanthanide-based SMMs synthesized till date which have 5-member aromatic rings directly bonded to the metal centre as oppose to peripheral position like in **Dy1**.[24, 25, 247–251] This implies that the position of the aromatic ring can influence the magnetic response of material and inhibit or enhance the performance of materials as SMM. For **Dy1**, the aromatic ring is at a peripheral position and tend to inhibit the performance of the material as SMM when compared with results from **Dy2**.

# Chapter 5

# Magnetic exchanges and solvent effect on slow magnetic relaxation of Er complexes

# 5.1 Introduction

To be an SMM, a molecule would be required to show the uniaxial Ising-type magnetic anisotropy as described in chapter 4, with slow relaxation of magnetization purely of molecular origin which allows the spin to relax over an effective energy barrier ( $\Delta_{eff}$ ), separating the up and down spin, below a characteristic blocking temperature ( $T_B$ ).[41] A high spin state for a single ion is also expected to favour SMM behavior provided there are no magnetic coupled exchanges with neighboring atoms or ions that reduce the total spin ground state.

The complexity surrounding the coordination chemistry of lanthanides through unaccounted interactions with donor atoms makes it even more difficult to rationalize completely all factors affecting the observation of SMM behavior. The availability of many frontier orbitals for lanthanides also means that they can interact with more donor atoms in different fashions than their transition metal counterparts while forming strong interactions with hard base donors like oxygen. An advantage of individual molecules as qubits for data storage is their solution processability. It is important to understand the dynamics of SMMs when they are exposed to different solvent media. As such, computation of the magnetic properties of the

different compounds produced using different solvent will aid the understanding of how the magnetisation dynamics might change with structural differences occasioned by the solvent choice.

In chapter 4, we mentioned that the magnetic property of single-molecule magnets (SMMs) is very sensitive to myriads of factors like geometry, symmetry, nature of coordinating ligands, peripheral substitution, coordination number among others. Most of these factors have been well studied in the literature.[80, 83, 228, 252–255] However, little is said of molecular voids and their makeup as well as how they impact other factors that are directly linked to the magnetic properties of SMMs. In this chapter the discussion was extended to the factors that affect the observation of SMM behaviour by looking at some chemical intuition related to solvent voids within two structurally distinct dinuclear erbium complexes with similar molecular makeup. The structural changes caused by solvent choice and their implications on the observed slow magnetic relaxation gave us some insight on how molecular magnets might respond when exposed to certain environmental factors like moisture in the face of practical application.

#### 5.1.1 Solvent effect and magnetic properties

It has been proven that  $\Delta_{eff}$  is not the only factor to be considered to achieve improved SMM behavior. [256] Apart from the static electronic structure of molecule-based magnets, the dynamic coupling of the molecular spin to the environment (crystal lattice, solvent, peripheral ligands) helps to govern the SMM behavior. [257] The coupling of such molecular spin with its environment in the form of spin-phonon coupling gives rise to energy and angular momentum exchanges with implications for the magnetic relaxation, allowing spins to relax through any of the established relaxation pathways like spin-lattice relaxation, phononbottle-neck (PB), resonance phonon trapping (RPT), Orbach process, Raman process, Direct process, thermally activated quantum tunneling of magnetization (TA-QTM), and quantum tunneling of magnetization (QTM) in the ground state. [77, 182, 258-263] The implication is that lattices which are stabilized by crystal solvents must play a vital role in the mechanism of spin relaxation. Crystal lattices can collapse following loss of crystal solvents driving such compound from crystalline to powder state and affecting possible coupling of the molecule with the environment. Myriads of structures have also shown the role of crystal solvents in intermolecular stabilization through interactions like H-bonding.[63, 264, 265] It is now imperative to understand the role of lattice solvent in spin relaxation when spin

predominates at ultra low temperature where QTM is most probable.[266, 267]

Symmetry and structural parameters, ligand field, unquenchable orbital angular moment and minor changes, like presence and absence of solvent either as crystal solvents or as coordinated solvents can drastically influence the magnetic properties of such material. [30, 83, 268– 272] The magnetic anisotropy of single ions is also very sensitive to the first and second coordination spheres of lanthanide complexes. [273] Solvent-led structural variation involving transition metal complexes has been shown to slightly affect their magnetic properties, [272] dielectric properties and morphology, [274] as well as shape [275] and mechanical [276] properties. Cai-Ming Liu et al. [277] had investigated a [Cu3Tb2(H3L)2(OAc)2(hfac)4] · 2ROH system with varying R-group for the crystal solvent and found a correlation between the solvatomagnetic effects and the size of the R-group. The larger the R-group, the higher the observed effective energy barrier ( $\Delta_{eff}$ ). The presence of water as crystal solvents has been investigated and found to cause a lowered  $\Delta_{eff}$  while a dehydrated analogue showed increased  $\Delta_{eff}$  in a dinuclear dysprosium SMM.[273] The solvent effect is more pronounced for metal organic frameworks (MOFs)[276, 278, 279] where they take up available pores that usually hinders such properties like gas absorption. Most reports on the effect of solvent on magnetic properties have been focused on transition metal complexes.[272, 274, 275, 280-286] Solvent effects, especially when they form part of the secondary coordination sphere, have not received much attention for the lanthanide-based SMM except for few examples involving dysprosium.[273, 287] The low attention could be attributed to the fact that the 4f electrons of lanthanide responsible for the observed SMM behavior are deeply embedded inside the core shell, limiting their interactions with secondary coordination sphere and possibility to couple with the environment. However, since SMM behaviour is very sensitive to such changes in secondary coordination sphere as is with peripheral ligands substitutions, [228, 288] we expect similar changes as we tune the make-up of the crystal lattice with solvent molecules. Indeed, the manifestation of environmental effect as a prerequisite for making devices with SMMs has been investigated using surfaces. [289] In this thesis, the spin-lattice interaction leading to the SMM behaviour of di-nuclear erbium complexes was investigated. An attempt to correlate the observed discrepancy in the magnetic properties of the complexes with the lattice make-up (crystal solvent and coordinated solvent) is presented with implications to SMMs applications.

# 5.2 Crystal structure description of Er1 and Er2

 $[Er(CH_3COO)_3(H_2O)_2]_2 \cdot 4H_2O(Er1)$  and  $[Ln(CH_3COO)_3(H_2O)CH_3COOH]_2 \cdot 2CH_3COOH$ (Ln = Er (Er2), Y<sub>0.8</sub>Er<sub>0.2</sub> (Er3a), Y (Er4)) were synthesized and characterised as described in Appendix A.<sup>2</sup> The single crystal structure of Er1 and Er2 were determined at room temperature by using the single-crystal X-ray diffraction technique. Selected crystal data for Er1 and Er2 are listed in Table 5.1.

| Parameter                         | Er1   | Er2   |
|-----------------------------------|---|---|
| Radiation type,                   | M   | ο K <sub>α</sub> ,  |
| wave-length /Å                    | 0.  | 71073   |
| Crystal dimensions /mm            | 0.12	imes 0.08	imes 0.17  | 0.14 	imes 0.15 	imes 0.24                                      |
| Molecular formula                 | C <sub>12</sub> H <sub>26</sub> Er <sub>2</sub> O <sub>16</sub> | C16H30Er2O18  |
| Sum molecular formula             | C <sub>12</sub> H <sub>34</sub> Er <sub>2</sub> O <sub>20</sub> | C <sub>20</sub> H <sub>38</sub> Er <sub>2</sub> O <sub>22</sub> |
| Formula mass / ${ m gmol}^{-1}$   | 760.85  | 965.02  |
| Space group                       | $P\bar{1}$  | $P\bar{1}$  |
| Crystal system                    | Triclinic   | Triclinic   |
| a /Å                              | 8.8504(6)   | 8.465(3)  |
| b/Å                               | 9.2274(7)   | 8.800(3)  |
| <i>c</i> /Å                       | 10.4356(7)  | 14.031(5)   |
| $\alpha / ^{\circ}$               | 91.7110(10)   | 84.365(7)   |
| $\beta / ^{\circ}$                | 114.1910(10)  | 84.881(7)   |
| γ /°                              | 117.7020(10)  | 84.881(7)   |
| $V/Å^3$                           | 662.17(8)   | 941.7(6)  |
| T/K                               | 296(2)  | 296(2)  |
| Ζ                                 | 1   | 1   |
| $GOF$ on $F^2$                    | 1.158   | 1.3458  |
| $R_1$ , $wR_2[I \ge 2\sigma(I)]$  | 0.0185, 0.0453  | 0.0771, 0.1860  |
| heta range for data collection /° | 2.96 to 34.64   | 2.02 to 26.63   |
| $R_{\rm int}/\%$                  | 1.85  | 7.71  |

Table 5.1 Selected crystal data for Er1 and Er2

The crystal structure (Figure 5.1a and 5.2a) shows that **Er1** crystallises in the triclinic  $P\bar{1}$  space group with an asymmetric units as [Er(CH3COO)3H2O·2H2O] (Figure 5.2c). Two asymmetric units are fused together through two acetate bridging ligands to give the full structural motif as [Er( $\mu_2$ ,  $\eta^3$ -CH3COO)( $\eta^2$ -CH3COO)2(H2O)2]2·4H2O (Figure 5.1a) with a total of 4 waters of crystallization. Each Er centre in the asymmetric unit is

<sup>&</sup>lt;sup>2</sup>All syntheses and characterisation were carried out at Prof. M.Yamashita's Lab at Tohoku University, Japan by David Izuogu. All experiment were done in Japan while the theoretical results were obtained in Cambridge

coordinated to two water molecules at an angle of 75.89°as well as three acetate ligands in a dihapto( $\eta^2$ ) fashion to give a coordination number of eight. One of the already coordinated acetate in each of the two asymmetric units uses one of its coordinated oxygen to form a bridge with a second asymmetric units by coordinating to its Er leading to bridging via two acetate molecules with inversion centre as show in Figure 5.3a. The implication is that the bridging acetates are now coordinated in a trihapto( $\eta^3$ ) fashion. The Er – O bond distances varies with those involving the unbridged oxygen ranging from 2.374(5) – 2.449(5) Å while each bridging Er – O measures 2.553(3) and 2.344(5) Å. The difference in the bond length between the unbridged and bridging oxygen (upper and lower limits) is 0.179 Å which is greater than 3 times the weighted standard deviation (0.02121 Å), indicating significant differences in the bond lengths.



Fig. 5.1 (a) crystal structure of **Er1** with water as crystal solvent. The uncoordinated oxygen molecules are the water of crystallisation (b) crystal structure of **Er2** with acetic acid as crystal solvent. The uncoordinated acetic acid molecule is the crystallisation solvent (c) First coordination geometry around Er ion in complex **Er1** showing the distorted  $C_{4\nu}$  symmetry in a Spherical capped square antiprism geometry (d) first coordination geometry around Er ion in complex **Er2** showing the distorted  $C_s$  symmetry in a Muffin-type geometry (red: O, grey: C, light green: Er, light Blue: Er, light grey: Er, white: H; hydrogen atoms were omitted in the crystal structure for clarity)

For the acetate ligands, the longest Er - O distances observed for one site of the bridging is a trade-off for coordinating with a second Er centre. Surprisingly, the second site shows a compensated shortest Er - O distance of 2.344(5) Å. The Er - O bond distance for water ligand is much shorter (2.317(3) Å and 2.334(4) Å). Since the water ligands formed both intramolecular as well as intermolecular H-bonds with the water solvents and the acetate ligands, one would expect a longer bond length for the water ligands in comparison with the acetate ligands so as to compensate the H-bonding interactions. The increased bond length for the acetate Er - O distances is as a result of the strain within a four-member ring occasioned by the acute < O - Er - O bond angle of 53.60 °. This is expected to affect the crystal field effect of the ligand on the central metal ion.



Fig. 5.2 (a) Crystal structure with atom numbering for  $\mathbf{Er1}$  (b) Crystal structure and atom numbering for  $\mathbf{Er2}$  (c) Asymmetric unit of  $\mathbf{Er1}$  (d) Asymmetric unit of  $\mathbf{Er2}$ . (50 % probability, H atoms and crystal solvents were omitted for clarity)



Fig. 5.3 Inversion centre (yellow spots) for (a) complex Er1 (b) complex Er2

The intramolecular Er - Er distance for Er1 (Figure 5.2a) is only 4.152(3) Å which is close enough to induce intra-molecular interaction. On the other hand, the shortest intermolecular Er - Er distance (Figure 5.4a) was calculated as 6.208(3) Å between two adjacent molecules. The unit cell is made up of a single molecule surrounded by four water molecules as crystal solvents.



(b) Crystal packing for Er2

Fig. 5.4 Crystal packing showing the shortest Er - Er bond distances in (a) complex Er1 (b) complex Er2

The packing (Figure 5.6a) shows **Er1** arranged side by side in a slant manner and linked through intermolecular H-bonding to form a 1D chain in the *b*-direction (Figure 5.6a and 5.5). Each chain is separated by a channel of crystal solvent (H<sub>2</sub>O) which helped to link chains through H-bonding to form a 2D sheet. The 2D sheets are further linked via some other H-bonding interactions to give a 3D array of structure whose crystal lattice is stabilized by intra (1.842(3) Å) and inter-molecular(2.021 - 2.705 Å) H-bonding (Figure 5.6a and 5.5).



Fig. 5.5 Unit cell showing intra and inter molecular hydrogen bond interaction and length in complex **Er1** 



(b) 3D H-bonding in Er1

Fig. 5.6 Crystal packing showing the intra and inter molecular hydrogen bonding interaction in complex Er1 (a) Along the *b*-axis of Er1 (b) 3D network on a-c-plane of complex Er1

The solvent channels (Figure 5.7a) within the crystal lattice for **Er1** present a void volume of 18.26(2) Å<sup>3</sup> (2.8 % of the unit cell, calculated at a probe radius and grid space of 0.5 Å).

Considering only the atoms in the first coordination sphere places Er in an approximate  $C_{4\nu}$  symmetry with a spherical capped square antiprism as determined by SHAPE software[227] (Figure 5.1c and Table 5.2).



(a) Solvent accessible void for Er1



(b) Solvent accessible void for  $\ensuremath{\text{Er2}}$ 

Fig. 5.7 Solvent accessible voids in (a) complex Er1 (b) complex Er2. The yellow coloration represents the solvent accessible voids.

|   |   | Complex <b>Er1</b>                       |  |                                    |
|---|---|--|--|------------------------------------|
| $C_{4v}$                                | $C_s$                                   | $C_{4v}$                                 | $D_{3h}$                                 | $D_{3h}$                           |
| Spherical<br>capped square<br>antiprism | Muffin                                  | Capped square<br>antiprism J10           | Spherical<br>tricapped<br>trigonal prism | Tricapped<br>trigonal<br>prism J51 |
| 2.024                                   | 2.314                                   | 2.557                                    | 2.551                                    | 3.050                              |
|   |   |  |  |                                    |
|   |   | Complex Er2                              |  |                                    |
| $C_s$                                   | $C_{4v}$                                | $D_{3h}$                                 | $C_{4\nu}$                               | $D_{3h}$                           |
| Muffin                                  | Spherical<br>capped square<br>antiprism | Spherical<br>tricapped<br>trigonal prism | Capped square<br>antiprism J10           | Tricapped<br>trigonal<br>prism J51 |
| 1.435                                   | 1.933                                   | 2.318                                    | 2.600                                    | 3.388                              |

Table 5.2 Calculated geometries for **Er1** and **Er2** using SHAPE software.[227, 290, 291] The numbers represents the match number to a strict symmetry. The lower the number the better the geometry and symmetry description

Complex **Er2** crystallises in the triclinic  $P\overline{1}$  space group. The molecular structure (Figure 5.1b and 5.2b) is made up of two asymmetric units (Figure 5.2d) fused together via four acetate ligands.



Fig. 5.8 Unit cell showing intra and inter molecular hydrogen bond interaction and length in complex **Er2** 



(b) H-bonding in Er2

Fig. 5.9 Crystal packing showing the intra and inter molecular hydrogen bonding interaction in complex Er2 (a) Along the *a*-axis of Er1 (b) 2D network on a-b-plane of complex Er2

Two of each of the dihapto( $\eta^2$ ) and trihapto( $\eta^3$ ) bridging ligands are coplanar. In addition to the bridging acetates, each of the Er centre is further coordinated to a dihapto( $\eta^2$ )

acetate, a water molecule and a monohapto( $\eta^1$ ) acetic acid to bring the coordination number to nine. The Er – O bond distances for the acetate and acetic acid ligands within an asymmetric unit ranges from 2.398(3) - 2.414(5) Å while that involving water is measured as 2.332(3) Å. The  $\eta^3$  bridging ligands have the longest and shortest Er – O bond distances of 2.533(5) and 2.300(2) Å respectively for complex **Er2** while the  $\eta^2$  bridging counterparts have Er – O bond distances of 2.327(4) and 2.369(5) Å. The four bridging ligands further helps to shorten the Er – Er intramolecular distance from 4.152(3) Å in **Er1** to 3.878(5) Å in **Er2** (Figure 5.2b) thereby increasing the chances of intra-molecular coupling between the erbium centres. The shortest intermolecular Er – Er distances is slightly shorter in **Er2** (6.194(3) Å) (Figure 5.4b) compared to in **Er1** (6.208(3) Å) as measured along the H-bonded chain. Intra- (1.881(2)Å) and inter-molecular (1.863(3) - 2.707(3) Å) H-bonding were observed in **Er2** among the water, acetic acid and the acetate ligands in 2D fashion to form layers separated by non-polar interaction (Figure 5.9 and 5.8).

The non-polar interaction is as a result of alternate arrangements of the methyl group of the acetic acid crystal solvent separating each layer from the other. **Er2** does not show a 3D network of H-bonding as observed for **Er1**. The crystal packing shows a single molecule in the unit cell surrounded by two acetic acid molecules as crystal solvents. In a remarkable contrast to **Er1**, **Er2** shows solvent channels within the crystal lattice having void volume of 135 Å<sup>3</sup> (14.4 % of the unit cell volume, at a probe radius and grid space of 0.5 Å) (Figure 5.7b). **Er2** therefore shows a higher solvent accessible surface area than **Er1**. A symmetry operation around each Er ion while considering only the first coordinating atoms shows an appreciable shift from  $C_{4v}$  in **Er1** to  $C_s$  symmetry (Figure 5.1d and Table 5.2) around each Er in **Er2** with an approximate geometry of a Muffin as opposed to the distorted spherical capped square antiprism in **Er1** as determined using SHAPE 2.1 software.[227, 290, 291] The full molecule also possesses an inversion centre found between the two asymmetric units (Figure 5.3b).

Interestingly, **Er2** shows a unique structural convertibility to **Er1** in the presence of water. Stirring aqueous solution of **Er2** at room temperature for 1 hr leads to 100 % conversion of **Er2** to **Er1**. However, an attempt to convert the structure back to the original **Er2** was not possible in the presence of acetic acid. The implication is that **Er1** is more stable than **Er2** probably due to the sterric hindrance caused by having four acetate ion bridging two relatively small  $Er^{3+}$  ion. The implication is that any SMM behaviour observed for **Er2** could be permanently reversed by exposing **Er2** to smaller solvents like H<sub>2</sub>O. We keep

this in mind as we proceed to discuss the magnetic properties of **Er1** and **Er2** in the next section.

## 5.3 Computational details for the Er1 and Er2

Typical computational details for ab initio computation using MOLCAS software package for lanthanide-based complexes were already described in section 4.4.2 and so, only a brief description and specific details about the erbium complexes will be described here. Using the coordinates generated from the crystal structures obtained from the X-ray Diffraction measurement for Er1 and Er2 (see Appendix B), the RASSCF-RASSI-SO calculations were carried out using MOLCAS program. The basis sets employed were the ANO-RCC group with polarised valence triple- $\zeta$  quality for the erbium atom (Er:ANO-RCC-VTZP), polarised valence double- $\zeta$  quality for oxygen atoms (O:ANO-RCC-VDZP), and the valence double- $\zeta$  quality was used for carbon and hydrogen atoms (C,H:ANO-RCC-VDZ). All the basis sets were accessed from the EMSL Basis Set Exchange library.[232, 292] The calculation was sped up without compromising accuracy by employing the Resolution of Identity (RI) approximation. All calculation results were obtained under tightscf convergence. The fragment method was employed to compute the magnetic properties of the molecule by replacing one of the two  $Er^{3+}$  centre with a diamagnetic centre ( $_{30}Y^{3+}$ ,  $_{57}La^{3+}$ or  $_{71}Lu^{3+}$  can be used). In this case, only the magnetic contribution of one centre is computed without considering any possible interation from the spins of the second magnetic centre. As such, the RASSCF calculation considers only 11 electrons in 7 f-orbitals of one  $4f^{11}$  Er<sup>3+</sup> configuration. As already justified in chapter 4, all allowable spin multiplicity of 4 and 2 were included in the state averaged RASSCF procedure with 35 and 112 CI roots respectively. The converged RAS orbitals were then used for the RASSI-SO calculation with the same CI roots as in the RASSCF step. The RASSI-SO wavefunctions were then used to compute the magnetic properties and the crystal field parameters for the isolated magnetic centres of each fragment using the SINGLE ANISO module implemented in MOLCAS by substituting the second  $Er^{3+}$  centre with a diamagnetic  ${}_{39}Y^{3+}$ ,  ${}_{57}La^{3+}$  or  ${}_{71}Lu^{3+}$ ion. This process has been used before to accurately describe the magnetic properties of polynuclear complexes.[103, 173]  $_{71}Lu^{3+}$ ,  $_{57}La^{3+}$  or  $_{39}Y^{3+}$  are usually used to replace a lanthanide centre for this type of calculation. However, to maximise accuracy for our system, the  $_{71}Lu^{3+}$  was preferred for the  $Er^{3+}$  replacement as it is the closest in terms of ionic size and number of electrons in the f-orbital. Two different SINGLE ANISO jobs were carried out, one for each metal site, before combining the magnetic wavefucntions

obtained from both independent calculation under the POLY ANISO module implemented on MOLCAS to account for possible magnetic interactions. The results of the electronic properties of **Er1** and **Er2** computed using the description above are presented in the following sections.

## 5.4 Electronic properties of Er1 and Er2

Magnetic orbitals of lanthanide-based complexes are localised within the f-orbitals. The localised character combined with the core nature of the f-electrons give rise to very weak interactions between magnetic centres where they exist.[197, 293] The implication is that the magnetic contribution of a single metal site can be computed independently with reasonable accuracy by substituting other magnetic sites within the polynuclear complex with a diamagnetic metal. Therefore, the semi-*ab initio* technique (the POLY ANISO) implemted in MOLCAS programme which uses the fragment method to compute the electronic and magnetic properties of polynuclear complexes were used to obtained converged RASSI-SO wavefuctions for the **Er1** and **Er2** complexes as described in section 5.3.

Experimentally,  $Y^{3+}$  is widely used to annihilate the magnetic interactions in polynuclear lanthanide compounds through dilution. While the electronic structure of  $Y^{3+}$  is similar to those of the lanthanides, the number of shells differs considerable and could led to wide discrepancy in the electronic structure of complexes where they are substituted. Theoreticians also prefer to use  $Y^{3+}$  in computation because of the lower number of electrons compared to La<sup>3+</sup> and Lu<sup>3+</sup> which makes computation easy and faster. To confirm the effect of substituting one of the Er<sup>3+</sup> site with a diamagnetic Lu<sup>3+</sup>, La<sup>3+</sup> or  $Y^{3+}$ , the RASSI-SO for the **Er1** complex was computed for 3 different scenarios for the first site (Er1-X, where X is  $Y^{3+}$ , La<sup>3+</sup> or Lu<sup>3+</sup>) (See Table 5.3 to 5.5). The electronic structure in all 3 cases look identical with much of the similarity higher between  $Y^{3+}$  and Lu<sup>3+</sup> (Table 5.3 and 5.5 respectively) due to similar ionic size (ionic size for 9-coordination number,  $Y^{3+}$ :1.075 Å, La<sup>3+</sup>:1.216 Å and Lu<sup>3+</sup>:1.032 Å)[294] as the increasing effective nuclear charge across the lanthanide series causes the ionic size of Lu<sup>3+</sup> to be significantly smaller than early members of the lanthanide series.

|       |                                      |   |   |                | g-     | factor  |                             |
|-------|--------------------------------------|---|---|----------------|--------|---------|-----------------------------|
| State | Spin-free state energies $(cm^{-1})$ | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution (for Kramers doublets) (%) $ \pm m_j angle$   | g <sub>x</sub> | gy     | gz      | g <sub>z</sub> angle<br>(°) |
| 0     | 0.0000                               | 0.0000  | $41.9\% \left  \pm \frac{15}{2} \right\rangle$ , $35.6\% \left  \pm \frac{11}{2} \right\rangle$ , $14.1\% \left  \pm \frac{7}{2} \right\rangle$   | 3.8009         | 1.6093 | 13.1286 | 0.0000                      |
| 1     | 66.4041                              | 35.0175   | $30.3\% \left \pm\frac{9}{2}\right\rangle$ , 24.8% $\left \pm\frac{5}{2}\right\rangle$ , 11.2% $\left \pm\frac{13}{2}\right\rangle$   | 0.9523         | 5.0662 | 8.8317  | 117.498                     |
| 2     | 110.2258                             | 92.9549   | $ \begin{array}{c} 32.7\% \left  \pm \frac{13}{2} \right\rangle, \ 13.1\% \left  \pm \frac{15}{2} \right\rangle, \ 11.7\% \left  \pm \frac{7}{2} \right\rangle \\ 11.5\% \left  \pm \frac{3}{2} \right\rangle, \ 11.1\% \left  \pm \frac{1}{2} \right\rangle, \ 8.8\% \left  \pm \frac{11}{2} \right\rangle \end{array} $ | 0.0276         | 4.8706 | 9.7050  | 54.3212                     |
| 3     | 125.4751                             | 116.6639  | $\begin{array}{c} 25.9\% \left  \pm \frac{3}{2} \right\rangle, \ 23.3\% \left  \pm \frac{13}{2} \right\rangle \\ 22.2\% \left  \pm \frac{9}{2} \right\rangle, \ 12.7\% \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 1.8723         | 6.0569 | 7.6799  | 7.9005                      |
| 4     | 170.9790                             | 156.6671  | $\frac{36.8\%  \pm \frac{7}{2}\rangle, 20.8\%  \pm \frac{15}{2}\rangle}{13.5\%  \pm \frac{9}{2}\rangle, 9.1\%  \pm \frac{13}{2}\rangle}$  | 1.1012         | 3.5658 | 9.1689  | 47.0364                     |
| 5     | 189.0007                             | 216.6191  | $\begin{array}{c} 20.6\% \left  \pm \frac{5}{2} \right\rangle, \ 17\% \left  \pm \frac{7}{2} \right\rangle, \ 14.6\% \left  \pm \frac{11}{2} \right\rangle \\ 14.5\% \left  \pm \frac{1}{2} \right\rangle, \ 11.9\% \left  \pm \frac{3}{2} \right\rangle, \ 9\% \left  \pm \frac{13}{2} \right\rangle \end{array}$        | 4.1519         | 1.3882 | 9.1644  | 92.5943                     |
| 6     | 210.9422                             | 254.5867  | $\begin{array}{c} 22.6\% \left  \pm \frac{11}{2} \right\rangle, \ 20.6\% \left  \pm \frac{5}{2} \right\rangle, \ 18.4\% \left  \pm \frac{9}{2} \right\rangle \\ 13\% \left  \pm \frac{1}{2} \right\rangle, \ 12.7\% \left  \pm \frac{13}{2} \right\rangle \end{array}$  | 0.3904         | 1.3199 | 11.5997 | 100.100                     |
| 7     | 229.2507                             | 312.4678  | $36.1\% \left \pm \frac{3}{2}\right\rangle$ , $34\% \left \pm \frac{1}{2}\right\rangle$ , $11.3\% \left \pm \frac{5}{2}\right\rangle$   | 3.0001         | 1.6035 | 13.9476 | 74.7869                     |
| 8     | 296.4795                             |   |   |                |        |         |                             |
| 9     | 353.3588                             |   |   |                |        |         |                             |
| 10    | 399.7031                             |   |   |                |        |         |                             |
| 11    | 414.8483                             |   |   |                |        |         |                             |
| 12    | 448.8881                             |   |   |                |        |         |                             |

Table 5.3 Electronic structure of Er1 with Er-Y (site 1) centre calculated with RASSCF-RASSI-SO using MOLCAS software

\*\*Each energy value represents a degenerate of two states (Kramers doublet) The sign of  $g_x \times g_y \times g_x$  for the ground state is negative

|       |  |   |   |                | g-        | factor     |                 |
|-------|--|---|---|----------------|-----------|------------|-----------------|
| State | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution<br>(for Kramers doublets)<br>(%) $\left \pm m_j ight angle$   | g <sub>x</sub> | <i>gy</i> | <b>8</b> z | $g_z$ angle (°) |
| 0     | 0.0000   | 0.0000  | $41.7\% \left  \pm \frac{15}{2} \right\rangle$ , $35.9\% \left  \pm \frac{11}{2} \right\rangle$ , $14.2\% \left  \pm \frac{7}{2} \right\rangle$   | 3.8464         | 1.6203    | 13.0936    | 0.0000          |
| 1     | 66.4535  | 34.9973   | $29.9\% \left \pm\frac{9}{2}\right\rangle$ , $25.1\% \left \pm\frac{5}{2}\right\rangle$ , $11.3\% \left \pm\frac{13}{2}\right\rangle$   | 0.9393         | 5.0415    | 8.8290     | 116.0186        |
| 2     | 110.0098   | 92.6105   | $\begin{array}{c} 33.5\% \left  \pm \frac{13}{2} \right\rangle, \ 13.6\% \left  \pm \frac{15}{2} \right\rangle, \ 11.8\% \left  \pm \frac{3}{2} \right\rangle \\ 11\% \left  \pm \frac{7}{2} \right\rangle, \ 10.9\% \left  \pm \frac{1}{2} \right\rangle, \ 8.2\% \left  \pm \frac{11}{2} \right\rangle \end{array}$ | 0.0086         | 4.8020    | 9.7932     | 53.6703         |
| 3     | 124.9408   | 116.2139  | $ \begin{array}{c} 25.5\% \left  \pm \frac{3}{2} \right\rangle, \ 23.2\% \left  \pm \frac{13}{2} \right\rangle \\ 21.5\% \left  \pm \frac{9}{2} \right\rangle, \ 13.8\% \left  \pm \frac{1}{2} \right\rangle \end{array} $  | 1.8874         | 5.9288    | 7.8138     | 6.7656          |
| 4     | 170.6961   | 156.2135  | $ \begin{array}{c} 36.9\% \left  \pm \frac{7}{2} \right\rangle, \ 20.7\% \left  \pm \frac{15}{2} \right\rangle \\ 14\% \left  \pm \frac{9}{2} \right\rangle, \ 9.2\% \left  \pm \frac{13}{2} \right\rangle \end{array} $  | 1.0560         | 3.5949    | 9.1122     | 45.3850         |
| 5     | 188.6340   | 216.7419  | $ \begin{array}{c} 20.1\% \left  \pm \frac{5}{2} \right\rangle, \ 17\% \left  \pm \frac{7}{2} \right\rangle, \ 15\% \left  \pm \frac{1}{2} \right\rangle \\ 14.4\% \left  \pm \frac{11}{2} \right\rangle, \ 11.9\% \left  \pm \frac{3}{2} \right\rangle, \ 8.7\% \left  \pm \frac{13}{2} \right\rangle \end{array} $  | 4.1374         | 1.4188    | 9.1610     | 91.5841         |
| 6     | 210.5083   | 254.7444  | $\begin{array}{c} 23.2\% \left  \pm \frac{11}{2} \right\rangle, \ 20.1\% \left  \pm \frac{5}{2} \right\rangle, \ 18.4\% \left  \pm \frac{9}{2} \right\rangle \\ 12.7\% \left  \pm \frac{1}{2} \right\rangle, \ 12.3\% \left  \pm \frac{13}{2} \right\rangle \end{array}$  | 0.4068         | 1.3234    | 11.7014    | 99.9314         |
| 7     | 228.7502   | 312.0087  | $36\% \left \pm\frac{3}{2}\right\rangle$ , $32.8\% \left \pm\frac{1}{2}\right\rangle$ , $12.2\% \left \pm\frac{5}{2}\right\rangle$  | 2.9980         | 1.6176    | 13.9342    | 73.9335         |
| 8     | 295.8968   |   |   |                |           |            |                 |
| 9     | 353.7889   |   |   |                |           |            |                 |
| 10    | 399.5383   |   |   |                |           |            |                 |
| 11    | 414.3138   |   |   |                |           |            |                 |
| 12    | 448.2693   |   |   |                |           |            |                 |

number of states allowed for the corresponding spin multiplicity (4 2)

Table 5.4 Electronic structure of Er1 with Er-La (site 1) centre calculated with RASSCF-RASSI-SO using MOLCAS software

Continued on next page

\*\*Each energy value represents a degenerate of two states (Kramers doublet) The sign of  $g_x \times g_y \times g_x$  for the ground state is negative

|       |                                      |   |   |                | g-     | factor     |                            |
|-------|--------------------------------------|---|---|----------------|--------|------------|----------------------------|
| State | Spin-free state energies $(cm^{-1})$ | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution (for Kramers doublets) $(\%) \; ig  \pm m_j  angle$   | g <sub>x</sub> | gy     | <i>g</i> z | g <sub>z</sub> angl<br>(°) |
| 0     | 0.0000                               | 0.0000  | $42\% \left  \pm \frac{15}{2} \right\rangle$ , $35.4\% \left  \pm \frac{11}{2} \right\rangle$ , $14.1\% \left  \pm \frac{7}{2} \right\rangle$   | 3.7754         | 1.6032 | 13.1467    | 0.0000                     |
| 1     | 66.3101                              | 35.0892   | $30.3\%  \pm \frac{9}{2}\rangle$ , $25.1\%  \pm \frac{5}{2}\rangle$ , $11.1\%  \pm \frac{13}{2}\rangle$   | 0.9668         | 5.0703 | 8.8399     | 117.712                    |
| 2     | 110.2767                             | 93.0539   | $\begin{array}{c} 32.5\% \left  \pm \frac{13}{2} \right\rangle, \ 13.2\% \left  \pm \frac{15}{2} \right\rangle, \ 11.7\% \left  \pm \frac{7}{2} \right\rangle \\ 11.5\% \left  \pm \frac{3}{2} \right\rangle, \ 10.9\% \left  \pm \frac{1}{2} \right\rangle, \ 9\% \left  \pm \frac{11}{2} \right\rangle \end{array}$   | 0.0249         | 4.8603 | 9.7161     | 54.1222                    |
| 3     | 125.6711                             | 116.7451  | $\begin{array}{c} 26\% \left  \pm \frac{3}{2} \right\rangle, \ 23.2\% \left  \pm \frac{13}{2} \right\rangle \\ 22.1\% \left  \pm \frac{9}{2} \right\rangle, \ 12.8\% \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 1.8759         | 6.0464 | 7.6751     | 8.0975                     |
| 4     | 171.0632                             | 156.7364  | $ \begin{array}{c} 36.9\% \left  \pm \frac{7}{2} \right\rangle, \ 20.7\% \left  \pm \frac{15}{2} \right\rangle \\ 13.7\% \left  \pm \frac{9}{2} \right\rangle, \ 9.2\% \left  \pm \frac{13}{2} \right\rangle \end{array} $  | 1.1032         | 3.5614 | 9.1814     | 47.024                     |
| 5     | 189.0117                             | 216.6138  | $ \begin{array}{c} 20.8\% \left  \pm \frac{5}{2} \right\rangle, \ 16.9\% \left  \pm \frac{7}{2} \right\rangle, \ 14.8\% \left  \pm \frac{11}{2} \right\rangle \\ 14.7\% \left  \pm \frac{11}{2} \right\rangle, \ 11.6\% \left  \pm \frac{3}{2} \right\rangle, \ 9\% \left  \pm \frac{13}{2} \right\rangle \end{array} $ | 4.1486         | 1.3898 | 9.1583     | 92.5609                    |
| 6     | 211.0316                             | 254.6317  | $\begin{array}{c} 22.7\% \left  \pm \frac{11}{2} \right\rangle, \ 20.5\% \left  \pm \frac{5}{2} \right\rangle, \ 18.2\% \left  \pm \frac{9}{2} \right\rangle \\ 13\% \left  \pm \frac{1}{2} \right\rangle, \ 13\% \left  \pm \frac{13}{2} \right\rangle \end{array}$  | 0.3872         | 1.3311 | 11.5885    | 100.08                     |
| 7     | 229.1556                             | 312.4977  | $36.2\%  \pm \frac{3}{2}\rangle$ , $33.9\%  \pm \frac{1}{2}\rangle$ , $11.2\%  \pm \frac{5}{2}\rangle$  | 3.0077         | 1.6072 | 13.9383    | 74.732                     |
| 8     | 296.5931                             |   |   |                |        |            |                            |
| 9     | 353.3567                             |   |   |                |        |            |                            |
| 10    | 399.6641                             |   |   |                |        |            |                            |
| 11    | 414.9358                             |   |   |                |        |            |                            |
| 12    | 448.9663                             |   |   |                |        |            |                            |

Table 5.5 Electronic structure of Er1 with Er-Lu (site 1) centre calculated with RASSCF-RASSI-SO using MOLCAS software

\*\*Each energy value represents a degenerate of two states (Kramers doublet) The sign of  $g_x \times g_y \times g_x$  for the ground state is negative

However,  $_{71}Lu^{3+}$  was preferred over  $_{39}Y^{3+}$  substitutions because the ionic size of  $_{71}Lu^{3+}$  (1.032 Å)[294] is closer to that of  $Er^{3+}(1.062 \text{ Å})[294]$  in addition to the presence of valence f-electrons when compared with  $Er^{3+}$ . As a result, the electronic structure computation for the second site was computed using only the  $_{71}Lu^{3+}$ . The electronic structure of the second  $Er^{3+}$  site computed by replacing the first site with  $_{71}Lu^{3+}$  and shown in Table 5.6 was identical to that of the first site (Table 5.5). This is because both metal sites are related by symmetry through inversion when the entire crystal structure is considered. Therefore only the second site result of **Er1** (Table 5.6 will be describe in more detail to account for the electronic and magnetic properties of each **Er1** fragment.

To account for any additional effect from excited spin multiplicities other than the ground state spin multiplicity, all allowed spin multiplicity for  $Er^{3+}$  ion (4 and 2) were used for the RASSCF procedure using the maximum allowed number of configurations (35 for spin multiplicity of 4 and 112 for the spin multiplicity of 2). For the Kramers doublets, the ground state SOC  $(J = \frac{15}{2})$  was considered. For the spin-free states, the 13 states arising from the 7 f-orbital occupation ( $m_L = \pm 3 - \pm 1$  and 0) were considered while the low-lying 8 doublet states arising from the 16  $m_j$ -states ( $m_J = \pm \frac{15}{2} - \pm \frac{1}{2}$ ) were considered for the RASSI-SO energies. The spin-free states show a wider energy gap (66.31  $\text{cm}^{-1}$ ) between the ground state and the first excited state compared to the gap between the ground state and the first excited state for the RASSI-SO Kramers doublets. In the same way, other excited states differ by appreciable margins all due to the inclusion of the SO interaction and the CF which allowed the retrieval of low-lying excited states. The symmetry of the first coordination sphere around each  $Er^{3+}$  shows a highly distorted  $C_{4v}$  (Figure 5.1c). However, considering the full molecular structure with one metal site substituted with a  $Lu^{3+}$  centre, the symmetry is far from  $C_{4\nu}$  and is considered to be  $C_1$ . Such low symmetry is responsible for the high admixture of the  $m_i$ -states even in the ground state as presented in Table 5.6. We assume a good approximation to the assigned wavefunction pending the inclusion of the contribution from the magnetic exchange interaction in the proceeding section. The ground state  $g_z$ -value is by far larger than that of the ground state  $g_x$  and  $g_{\gamma}$ -values, indicating significant magnetic anisotropy for **Er1** at each site.

|       |  |   |   |                | g-        | factor    |                |
|-------|--|---|---|----------------|-----------|-----------|----------------|
| State | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution (for Kramers doublets) $(\%) \;   \pm m_j  angle$   | g <sub>x</sub> | <i>gy</i> | <i>Bz</i> | $g_z$ angl (°) |
| 0     | 0.0000   | 0.0000  | $42\% \left  \pm \frac{15}{2} \right\rangle$ , 35.4% $\left  \pm \frac{11}{2} \right\rangle$ , 14.1% $\left  \pm \frac{7}{2} \right\rangle$   | 3.7754         | 1.6032    | 13.1467   | 0.0000         |
| 1     | 66.3101  | 35.0892   | $30.3\%  \pm \frac{9}{2}\rangle$ , $25.1\%  \pm \frac{5}{2}\rangle$ , $11\%  \pm \frac{13}{2}\rangle$   | 0.9668         | 5.0704    | 8.8399    | 117.712        |
| 2     | 110.2768   | 93.0537   | $\begin{array}{c} 32.5\% \left  \pm \frac{13}{2} \right\rangle, \ 13.2\% \left  \pm \frac{15}{2} \right\rangle, \ 11.7\% \left  \pm \frac{7}{2} \right\rangle \\ 11.5\% \left  \pm \frac{3}{2} \right\rangle, \ 10.9\% \left  \pm \frac{1}{2} \right\rangle, \ 9\% \left  \pm \frac{11}{2} \right\rangle \end{array}$ | 0.0249         | 4.8603    | 9.7162    | 54.1222        |
| 3     | 125.6711   | 116.7450  | $\begin{array}{c} 26\% \left  \pm \frac{3}{2} \right\rangle, \ 23.3\% \left  \pm \frac{13}{2} \right\rangle \\ 21.1\% \left  \pm \frac{9}{2} \right\rangle, \ 12.8\% \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 1.8759         | 6.0464    | 7.6751    | 8.0975         |
| 4     | 171.0633   | 156.7363  | $ \begin{array}{c} 36.8\% \left  \pm \frac{7}{2} \right\rangle, \ 20.6\% \left  \pm \frac{15}{2} \right\rangle \\ 13.7\% \left  \pm \frac{9}{2} \right\rangle, \ 9.3\% \left  \pm \frac{13}{2} \right\rangle \end{array} $  | 1.1032         | 3.5614    | 9.1815    | 47.0243        |
| 5     | 189.0117   | 216.6136  | $\begin{array}{c} 20.8\% \left \pm\frac{5}{2}\right\rangle, \ 16.9\% \left \pm\frac{7}{2}\right\rangle, \ 14.7\% \left \pm\frac{1}{2}\right\rangle \\ 14.6\% \left \pm\frac{11}{2}\right\rangle, \ 11.7\% \left \pm\frac{3}{2}\right\rangle, \ 9\% \left \pm\frac{13}{2}\right\rangle \end{array}$                    | 4.1486         | 1.3897    | 9.1583    | 92.5609        |
| 6     | 211.0317   | 254.6313  | $\begin{array}{c} 22.6\% \left  \pm \frac{11}{2} \right\rangle, \ 20.5\% \left  \pm \frac{5}{2} \right\rangle, \ 18.2\% \left  \pm \frac{9}{2} \right\rangle \\ 13\% \left  \pm \frac{1}{2} \right\rangle, \ 13\% \left  \pm \frac{13}{2} \right\rangle \end{array}$  | 0.3872         | 1.3311    | 11.5885   | 100.08         |
| 7     | 229.1557   | 312.4972  | $36.2\% \left \pm\frac{3}{2}\right\rangle$ , $33.9\% \left \pm\frac{1}{2}\right\rangle$ , $11.2\% \left \pm\frac{5}{2}\right\rangle$  | 3.0077         | 1.6072    | 13.9383   | 74.732         |
| 8     | 296.5933   |   |   |                |           |           |                |
| 9     | 353.3565   |   |   |                |           |           |                |
| 10    | 399.6641   |   |   |                |           |           |                |
| 11    | 414.9357   |   |   |                |           |           |                |
| 12    | 448.9663   |   |   |                |           |           |                |

Table 5.6 Electronic structure of Er1 with Lu-Er (site 2) centre calculated with RASSCF-RASSI-SO using MOLCAS software

\*\*Each energy value represents a degenerate of two states (Kramers doublet) The sign of  $g_x \times g_y \times g_x$  for the ground state is negative

To understand how the electronic structure of **Er1** differs from **Er2**, a similar calculation as in **Er1** was carried out for **Er2** using only  $Lu^{3+}$  to substitute each  $Er^{3+}$  sites. The obtained results are presented in Table 5.7 and 5.8. The spin-free energy gap between the ground state and the first excited state is only 7.22 cm<sup>-1</sup> which is far lower than that for **Er1** (66.31 cm<sup>-1</sup>). However, the inclusion of the SO interaction led to energy gap of 51.15 cm<sup>-1</sup> between the ground state and the first excited state compared to 35.08 cm<sup>-1</sup> for **Er1**.



Fig. 5.10 RASSI-SO energies for **Er1** and **Er2**. The energies where computed from RASSCF orbital for which the configurations from spin multiplicities of 4 and 2 for the  $\text{Er}^{3+}$  was used for the RASSCF-RASSI-SO procedure. The composition of the states shown are as listed in Table 5.3 - 5.8

The higher energy gap for Er2 can be attributed to a stronger ligand field around the  $Er^{3+}$  in Er2 due to the replacement of one neutral water molecule in Er1 by a charged acetate anion in Er2 an effect that led to the shorter Er-O bond distances for Er2 as described in section 5.2. Er2 also shows a well stabilised excited states beyond the first excited

state compared to **Er1** (state 2 to state 7). The RASSI-SO energies of all considered cases showing the relative energies of states for spin reversal in **Er1** and **Er2** are shown in Figure 5.10. Although the symmetry around **Er2** considering only the first coordination sphere is the muffin type  $C_s$  compared to the highly distorted  $C_{4v}$  in **Er1**, the symmetry consideration goes beyond the first coordination sphere to include the peripheral ligands. The overall symmetry of the molecule favours the **Er2** over **Er1** due to the extra bridging acetate ligand which helped to position like-molecules at opposite distances in a slightly more symmetric fashion. The effect is a reduced admixture of the  $m_j$ -states for the ground state with 48 %  $\left|\pm\frac{15}{2}\right\rangle$  compared to 42 % for **Er1**. In addition, **Er2** shows more uniaxial anisotropy character with a ground state  $g_z$ ,  $g_x$  and  $g_y$ -values of 15.37, 0.58 and 0.50 respectively. The CFP for high symmetry is invariant with the orientation of the crystal axes. However, for low symmetry like our system, the orientation of the calculation of the g-factors and the CF parameters was taken to be the z-axis (principal axis) from the x-ray crystal structure (Figure 5.11).



Fig. 5.11 (a) Magnetization axis for **Er1** (b) Magnetization axis for **Er2**(red:O, grey: C, white: H, green:Er)

Again, the various excited states in **Er2** comprise highly mixed  $m_j$ -states signalling possible competing transverse and uniaxial magnetic anisotropy at each site of the metal ion(Table 5.7 and 5.8).

|       |  |   |   |                |        | g-factor  |                 |
|-------|--|---|---|----------------|--------|-----------|-----------------|
| State | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution (for Kramers doublets) $(\%) \; \ket{\pm m_j}$  | g <sub>x</sub> | gy     | <i>8z</i> | $g_z$ angle (°) |
| 0     | 0.0000   | 0.0000  | $48.1 \left  \pm \frac{15}{2} \right\rangle$ , 28.7 $\left  \pm \frac{11}{2} \right\rangle$ , 14.4 $\left  \pm \frac{7}{2} \right\rangle$   | 0.5875         | 0.5037 | 15.3729   | 0.0000          |
| 1     | 7.2205   | 51.1585   | $\begin{array}{c} 32.4 \left  \pm \frac{9}{2} \right\rangle, \ 17.5 \left  \pm \frac{5}{2} \right\rangle \\ 15 \left  \pm \frac{1}{2} \right\rangle, \ 12.8 \left  \pm \frac{13}{2} \right\rangle \end{array}$  | 5.9672         | 2.2767 | 9.3685    | 58.3361         |
| 2     | 77.9731  | 84.1281   | $\begin{array}{c} 29\left \pm\frac{1}{2}\right\rangle, \ 18.3\left \pm\frac{5}{2}\right\rangle\\ 17.1\left \pm\frac{13}{2}\right\rangle, \ 13.2\left \pm\frac{9}{2}\right\rangle\end{array}$  | 1.7892         | 4.5392 | 7.2372    | 106.7226        |
| 3     | 110.9171   | 113.1463  | $ \begin{array}{c} 28.1 \left  \pm \frac{15}{2} \right\rangle, 24.9 \left  \pm \frac{13}{2} \right\rangle \\ 15.5 \left  \pm \frac{1}{2} \right\rangle, 10.7 \left  \pm \frac{11}{2} \right\rangle \end{array} $  | 2.9561         | 0.4036 | 12.7952   | 34.2897         |
| 4     | 115.9978   | 157.9150  | $\begin{array}{c} 27.8 \left  \pm \frac{11}{2} \right\rangle, \ 17 \left  \pm \frac{9}{2} \right\rangle \\ 13 \left  \pm \frac{7}{2} \right\rangle, \ 12.3 \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 2.9612         | 1.6934 | 11.0043   | 12.0189         |
| 5     | 138.5163   | 207.4250  | $37.8 \left  \pm \frac{9}{2} \right\rangle$ , $26.8 \left  \pm \frac{7}{2} \right\rangle$ , $14.9 \left  \pm \frac{11}{2} \right\rangle$  | 1.4641         | 4.3961 | 8.2296    | 3.2156          |
| 6     | 189.8478   | 246.6475  | $\begin{array}{c} 21.2 \left  \pm \frac{7}{2} \right\rangle, \ 20.2 \left  \pm \frac{3}{2} \right\rangle, \ 15.3 \left  \pm \frac{9}{2} \right\rangle \\ 12.3 \left  \pm \frac{11}{2} \right\rangle, \ 12 \left  \pm \frac{1}{2} \right\rangle \end{array}$ | 2.3950         | 4.8573 | 7.2149    | 121.1275        |
| 7     | 222.6384   | 271.1463  | $37.9 \left  \pm \frac{5}{2} \right\rangle, 17.8 \left  \pm \frac{7}{2} \right\rangle, 14.9 \left  \pm \frac{3}{2} \right\rangle$ $9.5 \left  \pm \frac{9}{2} \right\rangle, 8 \left  \pm \frac{1}{2} \right\rangle$  | 6.8461         | 9.1378 | 0.8423    | 126.9425        |
| 8     | 250.6311   |   | · · · · · ·   |                |        |           |                 |
| 9     | 295.8135   |   |   |                |        |           |                 |
| 10    | 327.3857   |   |   |                |        |           |                 |
| 11    | 353.9319   |   |   |                |        |           |                 |
| 12    | 372.6403   |   |   |                |        |           |                 |

Table 5.7 Electronic structure of Er2 with Er-Lu (site 1) centre calculated with RASSCF-RASSI-SO using MOLCAS software

number of states allowed for the corresponding spin multiplicity (4 2) \*\*Each energy value represents a degenerate of two states (Kramers doublet) The sign of  $g_x \times g_y \times g_x$  for the ground state is negative

|       |  |   |   |                |        | g-factor  |                 |
|-------|--|---|---|----------------|--------|-----------|-----------------|
| State | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state**<br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i$ contribution<br>(for Kramers doublets)<br>(%) $\ket{\pm m_i}$  | g <sub>x</sub> | $g_y$  | <i>gz</i> | $g_z$ angle (°) |
| 0     | 0.0000   | 0.0000  | $48.2  \pm \frac{15}{2}\rangle, 28.8  \pm \frac{11}{2}\rangle, 14.4  \pm \frac{7}{2}\rangle$  | 0.5874         | 0.5037 | 15.3730   | 0.0000          |
| 1     | 7.2207   | 51.1584   | $32.3 \left  \pm \frac{9}{2} \right\rangle, \ 17.5 \left  \pm \frac{5}{2} \right\rangle$ $15 \left  \pm \frac{1}{2} \right\rangle, \ 12.8 \left  \pm \frac{13}{2} \right\rangle$  | 5.9662         | 2.2763 | 9.3691    | 58.3304         |
| 2     | 77.9668  | 84.1261   | $\begin{array}{c} 29\left \pm\frac{1}{2}\right\rangle, \ 18.2\left \pm\frac{5}{2}\right\rangle\\ 17\left \pm\frac{13}{2}\right\rangle, \ 13.2\left \pm\frac{9}{2}\right\rangle\end{array}$  | 1.7885         | 4.5394 | 7.2375    | 106.6904        |
| 3     | 110.9102   | 113.1402  | $ \begin{array}{c} 28.1 \left  \pm \frac{15}{2} \right\rangle, \ 24.9 \left  \pm \frac{13}{2} \right\rangle \\ 15.5 \left  \pm \frac{1}{2} \right\rangle, \ 10.7 \left  \pm \frac{11}{2} \right\rangle \end{array} $  | 2.9567         | 0.4038 | 12.7944   | 34.2947         |
| 4     | 115.9909   | 157.9075  | $\begin{array}{c} 27.8 \left  \pm \frac{11}{2} \right\rangle, \ 17 \left  \pm \frac{9}{2} \right\rangle \\ 13 \left  \pm \frac{7}{2} \right\rangle, \ 12.2 \left  \pm \frac{1}{2} \right\rangle \end{array}$  | 2.9609         | 1.6935 | 11.0049   | 12.0240         |
| 5     | 138.5090   | 207.4205  | $37.7  \pm \frac{9}{2}\rangle, 26.9  \pm \frac{7}{2}\rangle, 14.9  \pm \frac{11}{2}\rangle$   | 1.4640         | 4.3960 | 8.2287    | 3.2215          |
| 6     | 189.8378   | 246.6396  | $\begin{array}{c} 22.3 \left  \pm \frac{7}{2} \right\rangle, \ 20.2 \left  \pm \frac{3}{2} \right\rangle, \ 15.4 \left  \pm \frac{9}{2} \right\rangle \\ 12.3 \left  \pm \frac{11}{2} \right\rangle, \ 11.9 \left  \pm \frac{1}{2} \right\rangle \end{array}$ | 2.3944         | 4.8603 | 7.2122    | 121.0521        |
| 7     | 222.6288   | 271.1362  | $37.9 \left  \pm \frac{5}{2} \right\rangle, \ 17.8 \left  \pm \frac{7}{2} \right\rangle, \ 14.9 \left  \pm \frac{3}{2} \right\rangle \\9.5 \left  \pm \frac{9}{2} \right\rangle, \ 8.1 \left  \pm \frac{1}{2} \right\rangle$                                  | 6.8487         | 9.1349 | 0.8425    | 126.9300        |
| 8     | 250.6229   |   | · · · · · · ·   |                |        |           |                 |
| 9     | 295.7998   |   |   |                |        |           |                 |
| 10    | 327.3715   |   |   |                |        |           |                 |
| 11    | 353.9177   |   |   |                |        |           |                 |
| 12    | 372.6287   |   |   |                |        |           |                 |

Table 5.8 Electronic structure of Er2 with Lu-Er (site 2) centre calculated with RASSCF-RASSI-SO using MOLCAS software

number of states allowed for the corresponding spin multiplicity (4 2) \*\*Each energy value represents a degenerate of two states (Kramers doublet) The sign of  $g_x \times g_y \times g_x$  for the ground state is negative

A clearer picture of the uniaxial and transverse contribution was investigated by looking at the contribution of the various rank and order of the CF parameter using the Stevens formalism as shown in equation 4.2 and presented in section 5.4.1.

#### 5.4.1 Ab initio crystal field of Er1 and Er2

The effective pseudospin Hamiltonian presented in equation 4.2 was used to elucidate the properties of the energy levels presented in Table 5.3 – 5.8. The 16 *ab initio* energy levels and their corresponding eigenfuctions were used to evaluate the elements of the  $B_k^q$  values as presented in Table 5.9 and 5.10. The percentage contribution of the rank operators (Table 5.9) shows that only three rank operators are sufficient to describe the CF of the **Er1** and **Er2** with the 6th rank operator contributing the most (at 54.38 and 54.64 % for each metal site of **Er1** and **Er2** respectively), then the 2nd and 4th at 25.35 and 19.43 % for **Er1** and 23.82 and 20.83 % for **Er2** respectively.

| Table 5.9 Contributions    | of the r  | ranks of | the ind         | ividual i | rreducible | tensor | operators | of the |
|----------------------------|-----------|----------|-----------------|-----------|------------|--------|-----------|--------|
| crystal field parameters f | or site 1 | and 2 o  | of <b>Er1</b> ( | (Er-Lu, I | Er-La and  | Er-Y), | and Er2 ( | Er-Lu) |

|                        |  |          | Weight   | ing (%)  |          |          |  |  |  |  |
|------------------------|--|----------|----------|----------|----------|----------|--|--|--|--|
|                        | Combined RASSCF-RASSI-SO Spin multiplicity = 2,4; $J = \frac{15}{2}$ |          |          |          |          |          |  |  |  |  |
|                        |  | E        | r1       |          | E        | r2       |  |  |  |  |
| Operator               | Fr-Y   | Fr-1 a   | Fr-Lu    | Lu_Fr    | Fr-Lu    | Lu-Fr    |  |  |  |  |
| Rank $(O_k)$           |  | LI-La    | LI-LU    |          | LI-LU    |          |  |  |  |  |
| $O_2$                  | 25.35364   | 25.40016 | 25.32404 | 25.32398 | 23.82748 | 23.82752 |  |  |  |  |
| $O_4$                  | 19.43595   | 19.43795 | 19.43139 | 19.43142 | 20.83401 | 20.83502 |  |  |  |  |
| $O_6$                  | 54.38556   | 54.32247 | 54.41696 | 54.41698 | 54.64407 | 54.643   |  |  |  |  |
| $O_8$                  | 0.31142  | 0.3177   | 0.31221  | 0.31221  | 0.25293  | 0.25298  |  |  |  |  |
| $O_{10}$               | 0.2681   | 0.27593  | 0.2696   | 0.2696   | 0.24897  | 0.24896  |  |  |  |  |
| <i>O</i> <sub>12</sub> | 0.24175  | 0.24223  | 0.24224  | 0.24224  | 0.18947  | 0.18945  |  |  |  |  |
| $O_{14}$               | 0.00357  | 0.00356  | 0.00356  | 0.00356  | 0.00307  | 0.00307  |  |  |  |  |

These give a total contribution of the  $6^{th}$ ,  $4^{th}$  and  $2^{nd}$  rank operators to the CF parameters of **Er1** and **Er2** to be 99.16 and 99.29 % respectively. For this reason, the negligible contribution of the  $8^{th}$ ,  $10^{th}$  and other higher ranks will be ignored. The CF parameter for all
order of the  $6^{th}$ ,  $4^{th}$  and  $2^{nd}$  ranks are presented in Table 5.10. First, the CF parameter for **Er1** for which the second metal site was replaced by  $Y^{3+}$ , La<sup>3+</sup> and Lu<sup>3+</sup> were presented (Table 5.10). The results are similar with only a very small and negligible difference for both the diagonal and off-diagonal contributions.

|   |    |                | $B^q_k$ , comb | oined RASSCF-RAS | SI-SO Spin multiplic | tity = 2, 4    |                |
|---|----|----------------|----------------|------------------|----------------------|----------------|----------------|
|   |    |                | E              |                  | Er2                  |                |                |
| k | a  | Er-Y           | Er-La          | Er-Lu            | Lu-Er                | Er-Lu          | Lu-Er          |
| ĸ | Ч  | (J-Term based) | (J-Term based) | (J-Term based)   | (J-Term based)       | (J-Term based) | (J-Term based) |
| 2 | -2 | -148.5068      | -148.5146      | -148.0343        | -148.0343            | -0.6339        | -0.7245        |
| 2 | -1 | -89.0033       | -91.9091       | -89.4561         | -89.4561             | -40.0444       | -39.8829       |
| 2 | 0  | -231.1431      | -230.2493      | -231.0525        | -231.0525            | -227.7174      | -227.7174      |
| 2 | 1  | -146.7191      | -144.2031      | -147.0617        | -147.0617            | 190.6577       | 190.6223       |
| 2 | 2  | 222.8664       | 228.0206       | 221.7876         | 221.7836             | -42.0801       | -42.1155       |
| 4 | -4 | -86.0360       | -88.7387       | -85.1351         | -85.1351             | 63.5135        | 63.7387        |
| 4 | -3 | -4.0541        | -8.7838        | -2.0270          | -2.0270              | -13.5135       | -12.1622       |
| 4 | -2 | 74.0990        | 68.4684        | 73.4234          | 73.4234              | -47.9729       | -47.9729       |
| 4 | -1 | 256.5313       | 260.8106       | 257.8826         | 257.8826             | 124.5494       | 124.5494       |
| 4 | 0  | 16.2162        | 14.4144        | 16.2162          | 16.2162              | -46.8468       | -46.8468       |
| 4 | 1  | -262.1619      | -265.0898      | -262.1619        | -262.1619            | -101.5765      | -101.5765      |
| 4 | 2  | 87.8378        | 87.1621        | 87.1621          | 87.1621              | -33.3333       | -33.3333       |
| 4 | 3  | -63.9639       | -72.5225       | -63.2882         | -63.2882             | 523.4229       | 523.4229       |
| 4 | 4  | -71.1711       | -70.0450       | -71.3963         | -71.3963             | 66.4414        | 66.2162        |
| 6 | -6 | 33.8175        | 38.6486        | 33.8175          | 33.8175              | -53.1418       | -53.1418       |
| 6 | -5 | 144.9323       | 154.5944       | 144.9323         | 144.9323             | -628.0399      | -628.0399      |
| 6 | -4 | 72.4661        | 72.4661        | 72.4661          | 72.4661              | -111.1148      | -111.1148      |
| 6 | -3 | 24.1554        | 33.8175        | 24.1554          | 24.1554              | -38.6486       | -38.6486       |
| 6 | -2 | -217.3984      | -217.3984      | -217.3984        | -217.3984            | -53.1418       | -53.1418       |
| 6 | -1 | 62.8040        | 53.1418        | 62.8040          | 62.8040              | -48.3108       | -48.3108       |
| 6 | 0  | -9.6622        | -4.8311        | -9.6622          | -9.6622              | 9.6622         | 9.6622         |
| 6 | 1  | 154.5944       | 159.4255       | 154.5944         | 154.5944             | 183.5809       | 183.5809       |
| 6 | 2  | -72.4661       | -77.2972       | -72.4661         | -72.4661             | 111.1148       | 111.1148       |
| 6 | 3  | -48.3108       | -38.6486       | -48.3108         | -48.3108             | 0.0000         | 0.0000         |
| 6 | 4  | -53.1418       | -53.1418       | -53.1418         | -53.1418             | -86.9594       | -86.9594       |
| 6 | 5  | 429.9658       | 434.7969       | 429.9658         | 429.9658             | -154.5944      | -149.7634      |
| 6 | 6  | 159.4255       | 154.5944       | 159.4255         | 159.4255             | 86.9594        | 86.9594        |

Table 5.10 Crystal field parameters for Er1 (Er-Y, Er-La, Er-Lu & Lu-Er) and Er2 (Er-Lu & Lu-Er)

We therefore focus on the substitution with  $Lu^{3+}$  for both Er1 and Er2 complexes. The 2nd ranked uniaxial or diagonal CF parameter  $(|B_2^0|)$  shows a larger value when compared to the other individual transverse parameters, showing that the magnetic anisotropy has appreciable uniaxial contribution at the ground states. However, for the Er1 complex, we see appreciable off-diagonal contribution especially for the  $|B_2^{-2}|$ ,  $|B_2^{-1}|$ ,  $|B_2^1|$  and  $|B_2^2|$ values which are large enough to possibly counter the effect of the diagonal parameters in **Er1**. On the other hand, only  $|B_2^1|$  value of the off-diagonal values compares with the  $|B_2^0|$  value for **Er2**. The rhombic anisotropic contribution from the  $|B_2^2|$  is 221.7876 and 42.0801 for Er1 and Er2 respectively. For orthorhombic or lower symmetry, it is always preferable for the following relationship to exist for the rhombicity ratio  $\left(\frac{B_2^2}{\mu^0}\right)$  using the extended Stevens notation -  $0 \le \frac{B_2^2}{B_2^0} \le 1.$  [296] This standardisation allows useful comparison for the axial and rhombic energies for similar complexes. The rhombicity ratio of a single  $Er^{3+}$  site in **Er1** and **Er2** are on the opposite sides to each other with values of -0.9598 and 0.1849 respectively. The difference in the magnitude of the energy gap between the ground state and the first excited state is 35.09 cm<sup>-1</sup> for **Er1** and 51.16 cm<sup>-1</sup> for **Er2** with the  $g_z$  values of 13.14 for Er1 and 15.37 for Er2. As a result, one would expect Er2 to show better SMM behaviour compared to Er1 when the complexes are magnetised and allowed to relax. The absence of any symmetry in a given molecule is expected to lead to a significant off-diagonal CF parameter for all orders as seen for Er1. The role of the peripheral ligands or other atoms further away from the metal site in determining the ligand field and the magnetic properties of lanthanide-based complexes cannot be overemphasised. To account for the overall magnetic properties of **Er1** and **Er2**, the magnetic and electronic properties extracted from the two inversion related metal sites were combined using the the POLY ANISO module implemented in MOLCAS. The exchange interactions are computed and compared with experiments to identify their implication to the magnetic properties of Er1 and Er2 and are presented in the proceeding sections.

### 5.5 Magnetic properties of Er1, Er2 and Er3

The polycrystalline samples of  $\mathbf{Er1} = [\mathrm{Er}(\mathrm{CH}_3\mathrm{COO})(\mathrm{CH}_3\mathrm{COO})_2(\mathrm{H}_2\mathrm{O})_2]_2 \cdot 4\mathrm{H}_2\mathrm{O}$  and  $[\mathrm{Ln}(\mathrm{CH}_3\mathrm{COO})(\mathrm{CH}_3\mathrm{COO})(\mathrm{CH}_3\mathrm{COO})(\mathrm{H}_2\mathrm{O})\mathrm{CH}_3\mathrm{COOH}]_2 \cdot 2\mathrm{CH}_3\mathrm{COOH}$  (Ln = Er (Er2), Y<sub>1</sub> · 4 Er<sub>0</sub> · 4 (Er3a), Y (Er4)) were used to obtain the *dc* and *ac* magnetic susceptibility on a quantum design MPMS-XL superconducting quantum interference device (SQUID) magnetometer as well as a Quantum Design PPMS-6000 physical property measurement

system. The inherent diamagnetism of the samples and the sample holder were corrected using the Pascal's tables.[43] For the *ac* measurements, a 3 Oe oscillating magnetic field was used with applied *dc* field. The phase purity of the polycrystalline samples was ascertained by measuring the powder pattern and matching with the simulated pattern from the single crystal X-RD structure (Figure 5.12) prior to magnetic studies. For **Er3**, a simulated PXRD spectral was not presented as the single crystal obtained was essentially Y site given that the ICP-AES result shows only 20 % Er present. The single crystal structure was only able to identify the Y site, as such the diluted sample was compared with the simulated spectra of **Er2** to show that the crystal structure is essentially the same as **Er2** and so the magnetic properties of **Er3** should be the same as those of **Er2** in the absence of any possible inter- or intra-molecular interactions.



Fig. 5.12 The powder X-ray diffraction pattern of (a) complex **Er1**, simulated from the single crystal structure of **Er1** (b) complex **Er1**, experiment obtained using the polycrystalline powder of **Er1** at room temperature (c) complex 2, experiment obtained using the polycrystalline powder of **Er2** at room temperature (d) complex **Er2**, simulated from the single crystal structure of **Er2** (e) complex **Er3** (**Er3a**), experimental obtained using the polycrystalline powder of **Er3** (**Er3a**) at room temperature (radiation source for experiment is Cu  $K_{\alpha}$  :  $\lambda = 1.5402$  Å)

### 5.5.1 Static magnetic properties

The static magnetic susceptibility was measured at 1000 Oe and temperature range of 2 – 300 K. A plot of the product of molar susceptibility and temperature ( $\chi_m T$ ) vs Temperature (Figure 5.13a) for **Er2** shows a  $\chi_m T$  value for two uncoupled  $\text{Er}^{3+}$  at room temperature (RT) with a value of 22.79 cm<sup>3</sup>Kmol<sup>-1</sup> and remained fairly constant down to 230 K.



Fig. 5.13  $\chi_m T$  vs T for (a) complex **Er2** (inset: maximised region showing antiferromagnetic interaction below 4 K (b) complex **Er1** (inset: maximised region showing lesser antiferromagnetic interaction below 4 K when compared with **Er2** (c) complex **Er3a** (inset: maximised region showing approx. 100 % annihilation of the antiferromagnetic interaction below 4 K (d) complex **Er3b** (inset: maximised region showing incomplete annihilation of the antiferromagnetic interaction below 4 K. (A *dc* field of 1000 Oe was used in all cases of the magnetic susceptibility measurements. The red circles map out the region of antiferromagnetic coupling)

Below 230 K the  $\chi_m T$  decreases steadily down to 4 K reaching a minimum value of 12.55 cm<sup>3</sup>Kmol<sup>-1</sup> before rising again to 12.89 cm<sup>3</sup>Kmol<sup>-1</sup> at 2 K (inset of Figure 5.13a). The measured value of  $\chi_m T$  at 300 K corresponds to the theoretical value of two uncoupled Er<sup>3+</sup> (22.96 cm<sup>3</sup>Kmol<sup>-1</sup>).[184] The decrease in the  $\chi_m T$  value below 230 K can be attributed to either the depopulation of higher  $m_j$  states or antiferromagnetic coupling between the two closely spaced Er centers in **Er2**. To ascertain which phenomenon is taking place,

doped samples of Er2 using yttrium were prepared insitu during synthesis (Er3a) and by mixing already synthesized samples of Er2 and Er4 (Er3b). The  $\chi_m T$  values for Er3a (Figure 5.13c) and Er3b (Figure 5.13d) at RT correspond to the 13 % and 5 % of Er used respectively for doping. The insitu doping has the probability of giving complexes with any three of the lanthanide arrangements as Er - Er, Er - Y and Y - Y. A strongly stirred solution decreases the chances of forming Er - Er arrangement leading to mostly Er - Y and Y - Y arrangements for Er3a. This is because stirring ensures an evenly distributed  $Er^{3+}$  site over the entire solution compared to concentrating the  $Er^{3+}$  site in a part of the solution allowing for rapid reaction that ensures two Er sites per unit molecule in the absence of stirring. The implication is the annihilation of any intramolecular magnetic coupling between the two Er centres. On the other hand, doping after synthesis as in Er3b ensures that the Er – Er arrangement is still maintained. In both cases, we observed similar decrease in  $\chi_m T$  values down to 4 K confirming the depopulation of the higher  $m_J$  states in **Er2**. Furthermore, the slight increase below 4 K in the  $\chi_m T$  value recorded for Er2 (inset Figure 5.13a) is undoubtedly attributed to weak ferromagnetic coupling between the intramolecular Er centres occasioned by very low spin energies due to decreased thermal energy making it easier for the applied magnetic field to cause spin flip with parallel alignment. This agrees with the disappearance of such ferromagnetic coupling in Er3a (inset of Figure 5.13c) where the probability of Er – Er interaction is almost zero. In addition, we observed the weak ferromagnetic coupling below 4 K in Er3b (inset of Figure 5.13d) which despite the doping still has Er – Er arrangement.

On the other hand, **Er1** which has a longer Er - Er intramolecular distance does not show appreciable ferromagnetic exchange below 4 K as observed in **Er2** (inset of Figure 5.13b). The  $\chi_m T$  at RT (22.53 cm<sup>3</sup>Kmol<sup>-1</sup>) also corresponds to theoretical value for two uncoupled  $\text{Er}^{3+}$  (22.96 cm<sup>3</sup>Kmol<sup>-1</sup>)[184] and remained fairly constant down to 200 K. Further decrease in temperature down to 2 K shows depopulation of higher  $m_j$  states like that in **Er2** without appreciable ferromagnetic coupling below 4 K as observed in **Er2**. We attributed the lesser coupling to the longer intramolecular Er - Er distance of 4.152 Å observed in **Er1** compared to the 3.878 Å in **Er2** as described in the crystal structure description in section 5.2.

### 5.5.2 Magnetic exchange interaction

To understand and quantify the magnetic exchange interaction between the metal sites in both complexes, the POLY ANISO routine implemented in MOLCAS was used to

compute the overall magnetic and electronic properties of Er1 and Er2 using the obtained wavefunctions from the initial fragment calculations described in section 5.3 and 5.4 using the SINGLE ANISO routine. Magnetic exchanges, antisymmetric exchanges and dipole-dipole interactions are among the possible interactions that could exist between neighbouring magnetic sites in a polynuclear complex. To account for any magnetic exchanges in the complexes, the Lines model [216] which uses a quantitative statistical description of paramagnetic clusters with unquenched orbital angular momentum was employed. The interaction between highly anisotropic systems like the lanthanides is mainly of dipolar type, as such the dipolar coupling was also added to the exchange coupling in the Lines model when computing the exchange interaction using the POLY ANISO routine implemented in Molcas. First the intramagnetic exchange interaction  $(J_{ex})$  in the limit of -3 to +3 with incremental value of  $\pm 0.01$  were tested to see which produces a better match with the experiment (see Figure 5.14 and 5.15, fewer  $J_{ex}$  than calculated was shown for clarity). The POLY ANISO programme uses the given exchange coupling value to compute the magnetic property and compares the computed values with the experiment. In addition, it computes a standard deviation to show how much the computed values are from the experiment at all temperature. The computed standard deviation becomes less useful in the limit of ferromagnetic interaction at low temperature following either the depopulation or antiferromagnetic coupling. As a result, we used both direct inspection of the shape of the curve and standard deviation to decide which of the computed lines best fits the experiment.



Fig. 5.14 Extraction of the Er-Er exchange interaction by comparison between experimental and computed  $\chi_m T$  vs T for **Er1** at varying exchange interactions  $(J_{ex})$  and 1000 Oe

To extract these values, We compared the experimental plot with the calculated plots for  $J_{ex} = 0$  (no exchange coupling), -3 (extreme ferromagnetic exchange interaction within the limit of the measured samples) and +3 (extreme ferromagnetic exchange interaction within the limit of the measured sample) followed by comparison with  $J_{ex}$  between the +3, 0 and -3 boundary. The calculated  $\chi_m T$  vs T values for all  $J_{ex}$  at room temperature matches the experimental value at room temperature but began to deviate with decreasing temperature. However, the overall shape (slope) of the graphs remain the same with the experiment. For **Er1** and **Er2** the  $\chi_m T$  vs T for  $J_{ex} = 0$  follows the same downward trend as observed for the experiments with decreasing temperature. This is consistent with the depopulation of the  $m_j$  states with decreasing temperature as pointed out in the preceding section. We therefore focus on the plot below 4 K which shows varying degrees of agreement as the for  $J_{ex}$  is varied. This then allowed the extraction of  $J_{ex}$  values of 0.1 and 0.05 for **Er1** and **Er2** respectively.



Fig. 5.15 Extraction of the Er-Er exchange interaction by comparison between experimental and computed  $\chi_m T$  vs T for **Er2** at varying exchange interactions  $(J_{ex})$  and 1000 Oe

### 5.5.3 Dynamic magnetic properties of Er1, Er2, and Er3a

The out-of-phase *ac* susceptibility plots measured at 2 K for **Er1** (Figure 5.16), **Er2** (Figure 5.17 and **Er3** (Figure 5.19 show no peak maxima at zero field. A field scan from 200 – 4000 Oe at the same constant temperature showed field-induced frequency dependent slow magnetic relaxation for **Er2** with two relaxation maxima at around 0.25 Hz and above 1000 Hz (Figure 5.17). On the other hand we observed a very weak relaxation plateau for complex **Er1** (Figure 5.16) at all measured field which is indicative of a possible dominant QTM in the solid state. The slow magnetic relaxation is not well resolved for **Er1**.



Fig. 5.16 Out-of-phase magnetic susceptibility plot for complex  ${\sf Er1}$  at 2 K and field scan from 0 - 2800 Oe



Fig. 5.17 Out-of-phase magnetic susceptibility plot for complex  $\mbox{\rm Er2}$  at 2 K and field scan from 0 - 3000 Oe

A 0.045 M aqueous solution of  $\mathbf{Er2}$  showed a distinct relaxation pattern from solid state  $\mathbf{Er2}$  but a more resolved relaxation peak at the applied field (Figure 5.18) compared to

**Er1**. The relaxation pattern for the frozen aqueous solution of **Er2** follows more closely that of **Er1** and **Er3a** in terms of the position of the peak maxima. This is attributed to the structural conversion in aqueous solution with a possible asymmetric fragment that eliminates intramolecular interaction. The existence of the fragment of the asymmetric unit was confirmed as the base peak of the ESI-MS spectrum (see Appendix A).



Fig. 5.18 Out-of-phase magnetic susceptibility plot for 0.045 M aqueous solution of complex **Er2** at 2 K and field scan from 0 - 3000 Oe

To investigate the role of intermolecular interaction between nearest neighbour magnetic centres, we obtained a field scan of a 13 % doped sample of complex **Er4** with **Er2** (**Er3a**) prepared insitu during synthesis. **Er3a** showed an overall shift in the peak maxima from above 1000 Hz in **Er2** to about 500 Hz in **Er3a** (Figure 5.19) as well as the disappearance of the slowest relaxation around 0.2 Hz observed in **Er2**. This was attributed to a possible inter and/or intramolecular dipole interaction between the two Er centres in **Er2** which were absent in **Er3a** due to the substitution of one of the Er<sup>3+</sup> centre with  $\Upsilon^{3+}$ . To extract a useful physical meaning to the observed field dependent trend, temperature variation of the *ac* susceptibility was measured using the optimum fields (field at which susceptibility is maximum for each measured sample) and presented in the next section.



Fig. 5.19 Out-of-phase magnetic susceptibility plot for complex  $\mathbf{Er3a}$  at 2 K and field scan from 0 - 4000 Oe

### 5.5.4 Temperature dependent magnetic susceptibility of Er1 and Er2

Complex **Er1** shows a very fast and weak frequency dependency of magnetization at dc field of 1500 Oe (Figure 5.20) which is in accordance to the QTM dominated relaxation observed in the field scan (Figure 5.16). Moving on to **Er2** we observed two relaxation maxima, a slow step around 0.2 Hz and a fast step above 1000 Hz (Figure 5.21 and 5.22). It is worth mentioning that while the optimum field for the slowest step in **Er2** was 3000 Oe, that of the fastest step was 1500 Oe, we attributed the higher optimum field for the slowest step to the fact that the process might be dominated by phonon-bottleneck[297] which presupposes a phonon-lattice interaction type spin relaxation in which the relaxing spins reabsorb energy from the lattice well, leading to a prolonged equilibrium time thereby requiring more energy in the form of applied magnetic field to flip the spin. Another possible reason is the low symmetry around each  $Er^{3+}$  centre. A low symmetry allows very high mixing of the magnetic  $m_i$  states and produces a more complex state for spin reversal.



Fig. 5.20  $\chi_m''$  versus Frequency plots for **Er1** at dc and ac field of 1500 Oe and 3 Oe respectively from 2 – 10 K



Fig. 5.21  $\chi_m''$  versus Frequency plots for  $\rm Er2$  at dc and ac field of 3000 Oe and 3 Oe respectively from 1.85 – 10 K



Fig. 5.22  $\chi_m''$  versus Frequency plots for **Er2** (at higher frequency (10 – 10,000 Hz) at *dc* and *ac* field of 1500 Oe and 3 Oe respectively from 2 – 10 K

Although, complex **Er1** is dominated by QTM, the weak slow magnetic relaxation is not regarded as SMM behaviour but due to spin-lattice interaction which causes the spin to lag after re-absorption of energy from the closely packed crystal lattice (Figure 5.7a). The role of intermolecular interaction in the slow magnetic interaction for **Er2** is confirmed by using the doped sample (**Er3a**). The disappearance of the slowest step in **Er2** as observed in **Er3a** (Figure 5.23) is attributed to the reduction of the intramolecular interactions between magnetic centers ( $\text{Er}^{3+}$ ) by Y<sup>3+</sup> which reduced the intramolecular dipole interactions that dominated within the temperature range of 4 K and 2 K as observed in  $\chi_m T$  versus T plot (insets of Figure 5.13a and 5.13c). As expected, the relaxation time for the fastest step in **Er2** became slower in **Er3a** because of suppression of QTM and reduction of intermolecular dipolar interactions allowing spin relaxation through a higher energy state as well as competing tunneling. A similar observation was attributed to phonon bottleneck in the literature[76, 258, 259]



Fig. 5.23  $\chi_m''$  versus Frequency plot for **Er3a** at *dc* and *ac* field of 1500 Oe and 3 Oe respectively from 2 – 10 K



Fig. 5.24  $\chi_m''$  versus Frequency plots for 0.04 M aqueous solution of **Er1** at *dc* and *ac* field of 1500 Oe and 3 Oe respectively from 2 – 10 K

Previous reports have shown that choosing metal-ligand bonds with high local pseudosymmetry such as  $C_{3v}$  or  $C_{2v}$ , should favour SMM behaviour more than magnetic centres in very low symmetry. [23] In contrast to the reports, **Er1** with distorted high  $C_{3\nu}$  symmetry (Figure 5.1c) (considering the first coordination sphere) is not better SMM-behaved while **Er2** which is buried in a muffin type  $C_s$  symmetry shows slower magnetic behaviour that persisted in doped samples. The implication is that symmetry consideration that limits to the first coordination sphere is not a good factor to consider in molecular design for SMM. The overall symmetry of the molecule plays a vital role in determining the overall effect of symmetry on the SMM behaviour of a material. It has also been shown that the energy barrier of spin-reversal in hydrates can be remarkably increased by the removal of lattice water under 2 kOe dc field.[273] We attributed this effect to the fact that water as crystal solvent helps to build a compact lattice system that promotes spin-lattice interaction through a 3D H-bonding (Figure 5.6 for H-bonding in **Er1**). The acetic acid crystal solvent in Er2 only H-bond in 2D as opposed to 3D in Er1. We suggest that the 3D H-bonding network in **Er1** might have an implication for a continuous spin-lattice interaction leading to the inability to show SMM behaviour as much as Er2. This suggestion is further strengthened by the fact that a larger in size crystal solvent (acetic acid) found as crystal solvent in Er2 causes a less packed lattice system as portrayed in the solvent accessible void of 14.4 % of the unit cell of Er2 as opposed to only 2.8 % in Er1 (Figure 5.7). This is in accordance with previous report[277] that showed that crystal solvents with larger alkyl groups showed higher  $\Delta_{\rm eff}$  and therefore enhanced SMM behaviour. However, further investigation will be needed to satisfactory confirm this assertion of the role of the H-bonding.

The clarity in the observed slow magnetic relaxation dynamics for **Er1**, **Er2**, **Er3a** and aqueous solution of **Er2** are further shown in the Cole-Cole plots (Figure 5.25, 5.26, 5.27 and 5.28) extracted from the out-of-phase  $(\chi_m'')$  and in-phase  $(\chi_m')$  susceptibility responses. Again, we observed two relaxation waves for **Er2** and one well resolved peak for **Er3a**. The in-phase and out-of-phase susceptibilities as shown in the Cole-Cole plots (Figure 5.25) to Figure 5.28) were fitted using the Debye model[288, 298] (Equation 1.22 and 1.23) so as to extract information on the relaxation dynamics/pathways. The fits are presented in the next section.



Fig. 5.25  $\chi_m''$  versus  $\chi_m'$  plots for **Er1** at *dc* and *ac* field of 1500 Oe and 3 Oe respectively from 2 – 5 K



Fig. 5.26  $\chi_m''$  versus  $\chi_m'$  plots for **Er2** at *dc* and *ac* field of 3000 Oe and 3 Oe respectively from 1.85 – 5.5 K



Fig. 5.27  $\chi_m''$  versus  $\chi_m'$  plots for **Er3a** at *dc* and *ac* field of 1500 Oe and 3 Oe respectively from 2 – 5 K



Fig. 5.28  $\chi_m''$  versus  $\chi_m'$  plots for 0.04 M aqueous solution of **Er1** at *dc* and *ac* field of 1500 Oe and 3 Oe respectively from 2 – 10 K

#### 5.5.5 Mechanism of spin relaxation in Er1 and Er2

In section 5.4, the electronic structure of Er1 and Er2 were discussed with reference to a fragment of the metal site while the second metal site was replaced by  $Lu^{3+}$ . It was mentioned therein, that to account for the overall magnetic properties of each complex, the magnetic exchange coupling must be included. In this subsection, the effect of the exchange interaction which was initially discussed in section 5.5.2 was considered to understand the overall mechanism of the slow magnetic relaxation observed for both Er1 and Er2 from experiments. To do this, 4 RASSI-SO states were considered for each metal site leading to the generation of 16 exchange energies ( $4^2$  SO states). The choice of 4 SO states per site stem from the fact that the experimental  $\Delta_{eff}$  for each of the erbium complex did not exceed the third SO energies computed for a single site of the metal. Table 5.11 shows the new RASSI-SO magnetic levels calculated with the  $J_{ex}$  for Er1 and Er2. We present the absolute values along with the relative values to show the extent to which each RASSI-SO states were either stabilized of destabilized. The results show that the degeneracy of the Kramers doublets were lifted leading to the generation of 3-spaced levels. Each level is then split by very small amount compared to the 3-state splitting. The Er2 ground state was more stabilised (-0.1619 cm<sup>-1</sup>) compared to **Er1** (-0.0635 cm<sup>-1</sup>). This is attributed to the stronger magnetic exchange interaction facilitated by the closer proximity of the two  $Er^{3+}$  sites in Er2 compared to those in Er1. The extraction of the Zeeman energy (Table 5.12) allows the recovery of the low-lying excited doublets which are comparable to those calculated for the single sites.

In section 5.4.1, the CF parameters for each metal site was discussed and we saw that **Er1** exhibits more transverse anisotropy than **Er2**. This transverse anisotropy may split the two fold degeneracy of any non-zero magnetic levels by mixing states with different magnetic  $m_j$  values. This phenomenon is termed tunnel splitting. The computed tunnel splitting for **Er1** and **Er2** considering the effect of the magnetic exchanges are 0.01 and 0.0001 cm<sup>-1</sup> respectively. The relative magnitude of the computed tunnel splitting were in agreement with earlier results that confers higher admixture of the magnetic  $m_j$  states for **Er1** compared to **Er2**. The computed  $m_j$  levels for both the fragment and the incorporation of the exchange interaction for the full molecular motif show that the energy separation between the ground state and the first excited states, the tunnel splitting and the magnetic exchange  $J_{ex}$  are important energy scales that control the slow magnetic relaxation of the erbium dimmers presented in this thesis.

| Combined RASSCF-RASSI-SO spin multiplicity=4,2; $J = \frac{15}{2}$ ; CSFs=35,112 (35,112)* |                              |  |                              |                              |  |  |  |  |
|--|------------------------------|--|------------------------------|------------------------------|--|--|--|--|
|  | Total magnetic interact      | ion for <b>Er1</b> ( $J_{ex} = 0.05$ ) | Total magnetic interact      | ion for Er2, $(J_{ex}=0.1)$  |  |  |  |  |
| Coupled state  | Absolute value ( $cm^{-1}$ ) | Relative value (cm $^{-1}$ )           | Absolute value ( $cm^{-1}$ ) | Relative value (cm $^{-1}$ ) |  |  |  |  |
| 0  | -0.06354                     | 0                                      | -0.16191                     | 0                            |  |  |  |  |
| 1  | -0.05556                     | 0.00799                                | -0.16179                     | 0.00012                      |  |  |  |  |
| 2  | 0.05358                      | 0.11712                                | 0.1614                       | 0.32331                      |  |  |  |  |
| 3  | 0.06535                      | 0.1289                                 | 0.16225                      | 0.32416                      |  |  |  |  |
| 4  | 35.02362                     | 35.08717                               | 51.08763                     | 51.24954                     |  |  |  |  |
| 5  | 35.04505                     | 35.1086                                | 51.09472                     | 51.25664                     |  |  |  |  |
| 6  | 35.07562                     | 35.13916                               | 51.13712                     | 51.29903                     |  |  |  |  |
| 7  | 35.08738                     | 35.15093                               | 51.14218                     | 51.3041                      |  |  |  |  |
| 8  | 35.08966                     | 35.1532                                | 51.18076                     | 51.34267                     |  |  |  |  |
| 9  | 35.11509                     | 35.17864                               | 51.1849                      | 51.34681                     |  |  |  |  |
| 10   | 35.13447                     | 35.19802                               | 51.21594                     | 51.37785                     |  |  |  |  |
| 11   | 35.14268                     | 35.20623                               | 51.22421                     | 51.38612                     |  |  |  |  |
| 12   | 70.14292                     | 70.20647                               | 102.23558                    | 102.3975                     |  |  |  |  |
| 13   | 70.16026                     | 70.22381                               | 102.27732                    | 102.43924                    |  |  |  |  |
| 14   | 70.19587                     | 70.25941                               | 102.34929                    | 102.5112                     |  |  |  |  |
| 15   | 70.21453                     | 70.27807                               | 102.40544                    | 102.56736                    |  |  |  |  |

Table 5.11 The electronic structure showing the RASSI-SO states considering the magnetic interactions in Er1 and Er2

\*The CSFs is for the RASSI-SO calculation and the values in the bracket represents the maximum number of states allowed for the corresponding spin multiplicity (4 2)

| Combi | Combined RASSCF-RASSI-SO spin multiplicity=4,2; $J = \frac{15}{2}$ ; CSFs=35,112 (35,112)* |                             |  |  |  |  |  |
|-------|--|-----------------------------|--|--|--|--|--|
|       | Zeeman interaction for <b>Er1</b>  | Zeeman interaction for Er2, |  |  |  |  |  |
|       | tunneling split = 0.01   | tunneling split $= 0.0001$  |  |  |  |  |  |
| State | Zeeman Energy (cm $^{-1}$ )  | Zeeman Energy (cm $^{-1}$ ) |  |  |  |  |  |
| 0     | 0.00399  | 0.00006                     |  |  |  |  |  |
| 1     | 0.12301  | 0.32374                     |  |  |  |  |  |
| 2     | 35.09788   | 51.25309                    |  |  |  |  |  |
| 3     | 35.14505   | 51.30156                    |  |  |  |  |  |
| 4     | 35.16592   | 51.34474                    |  |  |  |  |  |
| 5     | 35.20212   | 51.38199                    |  |  |  |  |  |
| 6     | 70.21514   | 102.41837                   |  |  |  |  |  |
| 7     | 70.26874   | 102.53928                   |  |  |  |  |  |
|       |  |                             |  |  |  |  |  |

Table 5.12 Zeeman splitting energies between the 2  $\text{Er}^{3+}$  in **Er1** and **Er2** for the first 16 coupled states of the Kramers doublets. (The absolute values from 5.11 were used)

\*The CSFs is for the RASSI-SO calculation and the values in the bracket represents the maximum number of states allowed for the corresponding spin multiplicity (4 2)

The ongoing discussion provided a clearer picture for the understanding of the mechanism of the slow magnetic relaxation in both **Er1** and **Er2**. We now turn to the experimental results to elucidate this mechanism proper. The plots obtained from the Debye model fit (Figure 5.29 - 5.30) were fitted to understand the mechanism of the slow magnetic spin relaxation using equation 3.50, and the results are presented in Table 5.13. From the analyses of the plots of the natural logarithm of the relaxation time vs inverse temperature (Figure 5.29 - 5.30), no single relaxation process was sufficient to describe the spin dynamics for all the systems. The peak top of the relaxation dynamics necessary to fit **Er1** is outside the measured region (Figure 5.20. As such, an attempt to fit the curve gave undesirable fits and parameters. The data in figure 5.20 suggest a very fast spin relaxation, although we could not extract meaningful information to accurately describe its mechanism.



Fig. 5.29 Plot of  $ln\tau$  vs  $T^{-1}$  for **Er2** (the fastest process) under applied dc field of 1500 and ac field of 3 Oe



Fig. 5.30 Plot of  $ln\tau$  vs  $T^{-1}$  for **Er3a** under applied *dc* field of 3000 and *ac* field of 3 Oe (The fit for the aqueous solution of **Er2** was omitted due to over parameterisation arising from the inclusion of the frozen solvent lattice)

On the other hand, the 0.04 M solution of Er2 showed slow relaxation at a longer relaxation time compared to Er1 in the solid state given that the limit of the relaxation time is outside the measured frequency boundary for Er1. We attributed this to the reduction of intra dipolar interaction between  $Er^{3+}$  centres as complex **Er2** might have dissociated to produce mononuclear  $Er^{3+}$  complex with **Er1** asymmetric unit as evidence in the base peak of electrospray ionization - mass spectrum (ESI-MS) (See Appendix A) whose identity is predicted as ErC<sub>6</sub>H<sub>15</sub>O<sub>9</sub>. Although, the *ac* measurement for Er2 was carried out from 2 - 10K, we could not extract the relaxation time above 2.60K. As such, the relaxation time for Er2 was fitted with different processes from 2 - 2.60K and presented in Figure 5.29. No single independent relaxation process could fit the relaxation time as shown in Figure 5.29. Attempts to fit with a combination of different processes could not completely fit the relaxation time from 2 - 2.60K suggesting a complex process that cannot be described by a single relaxation mechanism. However, a combination of Orbach/TA-QTM and QTM gave the best fit possible with a competing TA-QTM (with pre-exponential factor of  $1.77 \times 10^{-12}$ and  $\Delta_{\rm eff}$  of 28.90 cm<sup>-1</sup>) and ground state QTM at optimal applied dc field of 1500 Oe. This is suggestive of the spin relaxing through a competitive thermally activated quantum tunnelling of magnetization (TA-QTM) and ground state QTM. The longer QTM could be attributed to the lag experienced by spins during tunnelling as a result of been trapped in a potential energy well while interacting with the crystal lattice. [299, 300] The relaxation processes that did not produce the best fits in Figure 5.29 - 5.30 are only presented for clarity and justification of the best modelled fits selected.

| Relaxation equation $\longrightarrow$  | $	au = rac{1}{A(H^4)T^n + 	au_0^{-1}\exp\left\{-rac{\Delta_{ m eff}}{k_{ m B}T} ight\} + CT^m + rac{1}{Q}}$ |                                |                       |                      |  |  |
|--|--|--------------------------------|-----------------------|----------------------|--|--|
| Relaxation Mechanism $\longrightarrow$ | Field  | Orbach process                 |                       | QTM                  |  |  |
| Sample                                 | H (Oe)   | $\Delta_{ m eff}~( m cm^{-1})$ | $	au_0$ (s)           | Q                    |  |  |
| Er2                                    | 1500   | 28.90                          | $1.77 	imes 10^{-12}$ | $1.77 	imes 10^{-4}$ |  |  |
| Er3a                                   | 1200   | 12.47                          | $1.09	imes10^{-7}$    | $6.28 	imes 10^{-4}$ |  |  |

Table 5.13 Parameters of the fit of the relaxation time for Er2 and Er3a

The spin therefore spends most of its time tunnelling (in agreement with the extracted tunnel splitting) than it does through the energy gap of 28.90 cm<sup>-1</sup>. The relaxation process for complex **Er2** (in the higher frequency regime) and **Er3a** follows similar pathways with competing QTM and Orbach processes (TA-QTM). For **Er3a**, the relaxation time was extracted within the temperature range of 2 - 3.75K even though the *ac* measurement

was carried out between 2 - 10K for the same reason given for **Er2** above. However, as expected **Er3a** which is a diamagnetic diluted sample of **Er2** with  $Y^{3+}$  shows a much slower relaxation time (Figure 5.30) with pre-exponential factor of  $1.09 \times 10^{-7}$  s against the faster  $1.77 \times 10^{-12}$  s fitted for the higher frequency regime in **Er2**. This is a confirmation that the relaxation pathway for **Er3a** is a slow magnetic relaxation characteristic of single-molecule magnet. A fit involving only the QTM or Orbach process did not give a better match with the plot. However, Orbach-only fit gave a closer result to the competing QTM+Orbach fit with a pre-exponetial factor of  $3.21 \times 10^{-7}$  s and  $\Delta_{\rm eff}$  of 9.77 cm<sup>-1</sup>. We could not fit the slowest step in **Er2** due to inconsistency in the relaxation dynamics occasioned by the spin-lattice interaction between the magnetic Er centres and the crystal lattice energy. This is further confirmed by the disappearance of this step in **Er3a** due to the reduction of intermolecular dipole interaction by reducing the number of magnetic centres closely packed together.

### 5.6 Conclusion

In this chapter, the effects of solvent in the primary and secondary coordination sphere on the structure of di-nuclear acetate bridged erbium complexes and the implication to the observed SMM behaviour were studied. Erbium was used due to its position on the lanthanide series by virtue of size which allows the flexibility for both crowded and few bridging between two lanthanids judging from previous structural report. [301] By changing the solvents used during synthesis, we determined accompanied structural changes by using single-crystal X-ray diffraction technique (SC-XRD), and further characterizing by powder-XRD, Fourier transform infrared (FT-IR) and elemental analyses. Furthermore, we studied the relationship between those structural changes and magnetic properties by using dc and ac magnetic susceptibility measurements and theoretical methods. The SMM behavior was clearly dependent on the solvent due to changes in the coordination environment, symmetry and crystal field. We show that the magnetic exchange interaction which is a function of distance of separation between magnetic sites can have far-reaching consequences to the slow magnetic relaxation of the erbium dimers and relate such consequences to the effect of the crystal field splitting energy. Results also show that a molecular design which does not factor in the role of symmetry beyond the first coordination sphere is unlikely to yield high performance SMM since the crystal field splitting especially of the 4<sup>th</sup> and 6<sup>th</sup> ranked can have non-negligible transverse contribution to the magnetic anisotropy.

### Chapter 6

## Electronic and magnetic properties of the heterometallic lanthanide series

### 6.1 Introduction

Despite the advantage of intrinsic magnetic anisotropy of  $Ln^{3+}$  ions, not all of them have shown potential as promising SMM precursors. For this reason, this chapter is set out to investigate trend in the magnetic property of a class of heterometallic palladium-lanthanide acetate bridged complexes across the lanthanide series as an extension of the dinuclear acetate-bridged erbium complexes discussed in chapter 5. This chapter will also investigate the role of heterometallic Pd-Ln bond in the observation of slow magnetic relaxation across the lanthanide series.

The effect of exchange interactions in SMM have been studied using single-chain magnet (SCM) type involving 3*d* metals, [302-304] 3*d*~3*d*, [305-307] 3*d*~5*d*, [308, 309] 3*d*~4*f*, [310] 3*d*~radical, [311, 312] and 4*f*~radical systems. [313]

### 6.1.1 The slow magnetic relaxation in heterometalic clusters

Molecular designs targeting high performance SMM have seen researchers incorporate magnetic[27, 198, 314] and non-magnetic[315–318] transition metals in lanthanide complexes to leverage on a combined effect of the intrinsic magnetic anisotropy of lanthanide

and higher exchange interactions involving d-electrons of the transition metals. Most of these molecular designs show the transition metals and the lanthanide within a molecule but separated by organic ligands which serve the purpose of bridging the metal centres. Recently, new reports have emerged in which a nonmagnetic palladium and platinum ions were incorporated within the crystal structure of lanthanide complexes such that the diamagnetic d-metals were shown to have possible bonding interaction with the lanthanide while pushing in some electron density to the lanthanide electron cloud. [63-66, 254] In chapter 5, we show that by placing two lanthanide centres next to each other, one can induce f - f interactions with implication for the slow magnetic relaxation. Such interaction could reduce or induce quantum tunnelling of magnetisation (QTM) depending on its nature (cooperative or destructive) and could speed up spin relaxation thereby degrading SMM behaviour or in most cases enhance the same behaviour. This phenomenon was also demonstrated by using multiple-decker complexes.[319–326] The rarity of Ln-Ln bonding interaction stems from the lack of participation of f-electrons in bonding due to their core character. However, a higher participation of d-orbitals in bonding interactions leading to many transition metal – transition metal (TM–TM) bonding interactions opens a new possibility of TM-Ln interaction. It was shown that  $d^8$  transition metals like Pt<sup>2+</sup> and Pd<sup>2+</sup> could in principle donate their electron density to lanthanide ions to initiate such TM-Ln bonding interactions.[63-66, 254, 327]Such electron density donation could set up perturbations with consequences for the SMM behaviour of such compounds. Such bonding integration can also affect the luminescence properties of lanthanide-containing compounds as demonstrated by Yoshida et al.[65] in a Pt-Ln heterobonded system.

Experimental results describing the compounds described in this chapter has been reported by our group with some calculations based on DFT methods.[63, 327]However, no investigation of the electronic and magnetic properties by multireference methods has been done on any of these systems, necessitating the need to better understand the factors affecting the observation of their SMM behaviour and how these factors might vary across the lanthanide series. Oftentimes, theoretical results obtained for lanthanide-based complexes deviate appreciably from experimental results due to approximations and complexity of lanthanide ions which sees their ionic size decrease with increasing atomic number as a result of increasing effective nuclear charge while the series is traversed from left to right makes it sometimes challenging to synthesize a complete set of molecular congeners with a uniform structural motif. This effect is mostly manifested by decreasing coordination number as the ionic size decreases causing the later members of the lanthanide series to differ structurally

from the early members. Such discrepancy makes it difficult to compare and rationalise electronic and magnetic properties of the lanthanide series including their SMM behaviour which could differ by changes in the coordination number and overall crystal structure due to changes in the crystal field. For this reason, the isostructural Pd-Ln-Ln-Pd acetato-bridged complexes (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, La and Y), hereafter known as Pd-Ln with the general formula [Pd2Ln2(H2O)2(CH3COO)10]  $\cdot$ 2CH3COOH previously synthesized and characterised experimentally[63, 327, 328] provided an avenue to use multi-reference method to investigate the electronic and magnetic properties of the complete series of isostructural lanthanide-based complexes. Although La and Lu are diamagnetic, they will serve the purpose of substitution when calculating the isolated properties of each lanthanide metal site for the early and later members of the series respectively.

On the other hand, Eu will not be investigated due to a *J* value of zero giving no magnetic properties. Pm is radioactive, but will be investigated to see how its electronic and magnetic properties compares with the other members. As a comparison, another set of isostructural Pt-Ln-Pt-Ln-Pt thioacetate-bridged complexes (Ln = Tb, Dy, Ho and Er), hereafter known as **Pt-Ln** with the general formula Ln<sub>2</sub>Pt<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>(SAc)<sub>12</sub> (SAc=thioacetate) were investigated for later members of the lanthanide series to confirm the extent to which the heterometallic bond interaction affected the observation of SMM behaviour in the **Pd-Ln** systems.

### 6.2 Crystal structure description of the Pd-Ln and Pt-Ln series

The crystal structure of the isostructural Pd-Ln-Ln-Pd acetato-bridged complexes (Ln = Ce, Pr,Nd, Sm, Gd, Tb, Dy, Ho, Er,Tm, Yb, Lu, La and Y), hereafter known as Pd-Ln with the general formula [Pd<sub>2</sub>Ln<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>COO)<sub>10</sub>] · 2CH<sub>3</sub>COOH were described in detail in references [63, 327] and [328]. As such, we will only present the crystal structure (Figure 6.1a) for easy reference with key crystal data necessary for the present discussion. Table 6.1 shows some structural parameters for the Pd-Ln series. The crystal structure which crystallised in the monoclinic space group  $P2_1/n$  placed each of the Pd<sup>2+</sup> in a square-planar pyramidal geometry and the Ln<sup>3+</sup> centre in a slightly distorted  $D_{3h}$  tricapped trigonal prism with a hetero Ln-Pd metallic bond (Figure 6.1a) with reference to the first coordination sphere. Pd-Dy shows a total coordination number of 9.



Fig. 6.1 Single crystal structures of (a) **Pd-Dy**[327] (b) **Pt-Dy**[65] obtained from singlecrystal xrd measurement (red:O, grey: C, white: H, yellow : S, bright turquoise: Dy, dark blue : Pd, purple : Pt)

|                    |  | Ta             | able 6.1 Selec | cted elementa   | al and crystal          | data of the            | Pd-Ln and I          | Pt-Ln series                     |                 |                             | 6.2 (                     |
|--------------------|--|----------------|----------------|-----------------|-------------------------|------------------------|----------------------|----------------------------------|-----------------|-----------------------------|---------------------------|
| Sample<br>code     | Crystal<br>system                                    | <i>a</i> (Å)   | b (Å)          | c (Å)           | α (°)                   | β (°)                  | γ (°)                | Cell<br>Volume (Å <sup>3</sup> ) | Pd/Pt-Ln<br>(Å) | Ln-Ln<br>(Å) <sup>[1]</sup> | Lan<br>(A) <sup>[2]</sup> |
| <b>Pd-Y</b> [327]  | $P2_1/n$   | 8.8515(16)     | 19.751(4)      | 11.650(2)       | 90                      | 90.659(4)              | 90                   | 2036.59(5)                       | 3.195(2)        | 4.034(3)                    | 8.491(2)                  |
| Pd-La              | No struc   | ctural data. D | iamagnetic and | l only used for | fragment substi         | itution for <b>Pd-</b> | Ce to Pd-Eu          |                                  |                 |                             | Icti                      |
| Pd-Ce              | No structural data. Pd-Nd used for Pd-Ce calculation |                |                |                 |                         |                        |                      |                                  |                 |                             | Ire                       |
| Pd-Pr              |  |                |                | No st           | ructural data. <b>I</b> | P <b>d-Nd</b> used for | <b>Pd-Pr</b> calcula | ition                            |                 |                             | des                       |
| Pd-Nd[328]         | $P2_1/n$   | 8.856(9)       | 19.98(2)       | 11.922(12)      | 90.00(1)                | 90.73(6)               | 90.00(1)             | 2109.34(8)                       | 3.221(2)        | 4.172(3)                    | 8.677(2)                  |
| Pd-Pm              |  |                |                | No str          | uctural data. <b>F</b>  | <b>Pd-Nd</b> used for  | Pd-Pm calcula        | ation                            |                 |                             | ptic                      |
| Pd-Sm              |  |                |                | No str          | uctural data. <b>F</b>  | <b>Pd-Nd</b> used for  | Pd-Sm calcula        | ation                            |                 |                             | n                         |
| Pd-Eu[327]         | $P2_1/n$   | 8.8303(5)      | 19.8110(11)    | 11.7809(6)      | 90                      | 90.678(2)              | 90                   | 2060.77(6)                       | 3.196(3)        | 4.102(5)                    | 8.573(2)                  |
| Pd-Gd[63]          | $P2_1/n$   | 8.8343(4)      | 19.8062(10)    | 11.7545(6)      | 90                      | 90.7250(10)            | 90                   | 2056.57(4)                       | 3.195(2)        | 4.089(4)                    | 8.5557(3)                 |
| Pd-Tb[327]         | $P2_1/n$   | 8.7229(4)      | 19.4527(8)     | 11.7072(5)      | 90                      | 90.8600(10)            | 90                   | 1986.3(8)                        | 3.190(3)        | 4.050(2)                    | 8.40(2)                   |
| Pd-Dy[327]         | $P2_1/n$   | 8.7318(9)      | 19.447(2)      | 11.6837(12)     | 90                      | 90.815(2)              | 90                   | 1983.78(10)                      | 3.191(3)        | 4.039(3)                    | 8. <del>47</del> 5(3)     |
| Pd-Ho[327]         | $P2_1/n$   | 8.7236(4)      | 19.4115(10)    | 11.6820(6)      | 90                      | 90.8620(10)            | 90                   | 1977.98(10)                      | 3.191(2)        | 4.023(5)                    | 8.458(3)                  |
| <b>Pd-Er</b> [327] | $P2_1/n$   | 8.7293(9)      | 19.390(2)      | 11.6462(12)     | 90                      | 90.905(2)              | 90                   | 1971.00(10)                      | 3.189(4)        | 4.006(2)                    | 8.445(5)                  |
| Pd-Tm[328]         | $P2_1/n$   | 8.7250(7)      | 19.3676(16)    | 11.5976(9)      | 90.00                   | 90.852(2)              | 90.00                | 1959.57(8)                       | 3.178(2)        | 3.992(3)                    | 8.4 5(5)                  |
| Pd-Yb[328]         | $P2_1/n$   | 8.7262(8)      | 19.3632(16)    | 11.5855(9)      | 90.00                   | 90.850(2)              | 90.00                | 1957.35(6)                       | 3.183(4)        | 3.98293)                    | 8.408(4)                  |
| Pd-Lu              |  |                | No structu     | ral data. Diam  | agnetic and onl         | y used for fragi       | ment substituti      | on for <b>Pd-Gd</b> to           | D Pd-Yb         |                             | l Se                      |
| <b>Pt-Tb</b> [65]  | $P\bar{1}$   | 8.430(2)       | 11.769(3)      | 12.695(4)       | 83.106(4)               | 73.907(4)              | 76.351(4)            | 1173.96(10)                      | 3.230(2)        | 7.872(4)                    | 8. 🖗 3(2)                 |
| <b>Pt-Dy</b> [65]  | $P\bar{1}$   | 8.356(2)       | 11.603(3)      | 12.742(3)       | 83.059(6)               | 74.106(6)              | 75.886(6)            | 1150.36(8)                       | 3.232(3)        | 7.876(3)                    | 8.356(4)                  |
| <b>Pt-Ho</b> [66]  | $P\bar{1}$   | 8.4429(5)      | 11.7813(7)     | 12.7014(7)      | 83.1550(10)             | 73.837(2)              | 76.1450(10)          | 1176.27(6)                       | 3.244(2)        | 7.905(3)                    | 8.443(4)                  |
| <b>Pt-Er</b> [66]  | $P\bar{1}$   | 8.3364(6)      | 11.5936(8)     | 12.7184(9)      | 82.957(2)               | 74.002(2)              | 75.934(2)            | 1144.14(8)                       | 3.239(3)        | 7.858(2)                    | 8.336(2)                  |
| [1] Intramolec     | [1] Intramolecular. [2] Intermolecular               |                |                |                 |                         |                        |                      |                                  |                 |                             |                           |

Table 6.1 Selected elemental and crystal data of the Pd-Ln and Pt-Ln series

To make a good comparison with our findings especially on the role of the diamagnetic palladium ion on the slow magnetic relaxation of the Pd-Ln series, heterometallic complexes with a Pt-Ln heterobonds and general formula as Ln2Pt3(H2O)2(SAc)12 (SAc=thioacetate, Ln=Tb,Dy,Ho and Er), hereafter known as Pt-Ln were also studied using computational methods. The crystal structure of Pt-Ln series as well as their properties based on experimental findings were reported in the literature.[65, 66] Therefore, only data necessary for our discussion in this thesis will be described here. The **Pt-Ln** system (Figure 6.1b) crystallised in the trinclinic  $P\bar{1}$  space group with the platinum ion embedded in a squareplanar pyramidal geometry as found in the Pd-Ln system. However, each lanthanide ion was found to be in a distorted  $C_{4\nu}$  local symmetry and a coordination number of 8 different to the Pd-Ln system. The Pd-Ln system is made up of 2  $Pd^{2+}$  and 2  $Ln^{3+}$  equally distributed across the two asymmetric units with inversion centre at the centre of the two bridging acetate ligands. On the other hand the Pt-Ln system is made up of 3  $Pt^{2+}$  and  $2 \text{ Ln}^{3+}$  distributed in such a way that the middle  $\text{Pt}^{2+}$  which is 3.938 Å (for the **Pt-Dy**) compound) away from each  $Ln^{3+}$  forms the inversion centre. Other relevant crystal data including the unit cell dimension, Ln-Ln, Pd-Ln, Pt-Ln intra- and inter-molecular distances for Pd-Ln and Pt-Ln systems are presented in Table 6.1.

## 6.3 Computational details for the Pd-Ln and Pt-Ln series

All the calculations in this section were carried out using MOLCAS program as detailed in section 4.4.2 and 5.3. However, specific details regarding the Pd-Ln and Pt-Ln series will be discussed here. The coordinates generated from the single-crystal xrd structure were used where they exist without geometry optimization. Structural optimisations were avoided to maximise accuracy with experimental results which could differ significantly by tiny structural variations since the single-molecule magnet behaviour is highly sensitive to such structural changes which is expected to affect the energy of states. Since no experimental structure has been reported for Pd-Ce, Pd-Pr, and Pd-Sm, the closest structure from the most similar ionic size (Nd<sup>3+</sup>) was used in their place and so Pd-Nd structure was deployed by substituting the Nd centre with the respective lanthanides.

| Sample                                 | Fragment      | A CR      | Term                     | RASSCF 2S+1                       | RASSI 2S+1                      | Davia Cat                      |
|--|---------------|-----------|--------------------------|-----------------------------------|---------------------------------|--------------------------------|
| code                                   | metal centres | 4T'       | symbol                   | & (number of CSFs) <sup>[3]</sup> | & (number of CSF)               | Basis Set                      |
| $Pd\text{-}Y^{[1]}$                    | diamagnetic   | $4f^0$    | ${}^{1}S_{0}$            |                                   |                                 |                                |
| $Pd-La^{[1]}$                          | diamagnetic   | $4f^0$    | ${}^{1}S_{0}$            |                                   |                                 | $\uparrow$                     |
| Pd-Ce                                  | Ce-La         | $4f^1$    | ${}^{2}F_{\frac{5}{2}}$  | 2 (7)                             | 2 (7)                           |                                |
| Pd-Pr                                  | Pr-La         | $4f^2$    | ${}^{3}H_{4}^{2}$        | 3,1 (21,28)                       | 3,1 (21,28)                     | <br>V · ANO_RCC_VT7P           |
| Pd-Nd                                  | Nd-La         | $4f^{3}$  | ${}^{4}I_{\frac{9}{2}}$  | 4,2 (35,112)                      | 4,2 (35,112)                    | $I_{a} \cdot ANO = RCC = VTZT$ |
| Pd-Pm                                  | Pm-La         | $4f^4$    | ${}^{5}I_{4}^{2}$        | 5,3,1 (35,210,196)                | 5,3,1 (35,120,130)              | $L_n : ANO - RCC - VTZP$       |
| Pd-Sm                                  | Sm-La         | $4f^{5}$  | ${}^{6}H_{5}$            | 6,4,2 (21,224,490)                | 6,4,2 (21,128,130)              | Pt : ANO-RCC-VTZP              |
| Pd-Gd                                  | Gd-Lu         | $4f^{7}$  | $8S_{\frac{7}{2}}^{2}$   | 8,6,4 (1,48,392) <sup>[2]</sup>   | 8,6,4 (1,48,120) <sup>[2]</sup> | Pd : ANO-RCC-VTZP              |
| Pd-Tb                                  | Tb-Lu         | $4f^{8}$  | $^{7}F_{6}^{2}$          | 7,5,3,1 (7,140,588,490)           | 7,5,3,1,(7,110,120,130)         | S : ANO-RCC-VDZP               |
| Pd-Dy                                  | Dy-Lu         | $4f^{9}$  | ${}^{6}H_{15}$           | 6,4,2 (21,224,490)                | 6,4,2 (21,128,130)              | O : ANO-RCC-VDZP               |
| Pd-Ho                                  | Ho-Lu         | $4f^{10}$ | $5I_{8}^{2}$             | 5,3,1 (35,210,196)                | 5,3,1 (35,120,130)              | C : ANO-RCC-VDZ                |
| Pd-Er                                  | Er-Lu         | $4f^{11}$ | ${}^{4}I_{15}$           | 4,2 (35,112)                      | 4,2 (35,112)                    | H : ANO-RCC-VDZ                |
| Pd-Tm                                  | Tm-Lu         | $4f^{12}$ | ${}^{3}H_{6}^{2}$        | 3,1 (21,28)                       | 3,1 (21,28)                     |                                |
| Pd-Yb                                  | Yb-Lu         | $4f^{13}$ | ${}^{2}F_{\frac{7}{2}}$  | 2 (7)                             | 2 (7)                           | $\downarrow$                   |
| $\mathbf{Pd}\text{-}\mathbf{Lu}^{[1]}$ | diamagnetic   | $4f^{14}$ | ${}^{1}S_{0}^{2}$        |                                   |                                 |                                |
| Pt-Tb                                  | Tb-Lu         | $4f^{8}$  | $^{7}F_{6}$              | 7,5,3,1 (7,140,588,490)           | 7,5,3,1,(7,110,120,130)         |                                |
| Pt-Dy                                  | Dy-Lu         | $4f^{9}$  | ${}^{6}H_{\frac{15}{2}}$ | 6,4,2 (21,224,490)                | 6,4,2 (21,128,130)              |                                |
| Pt-Ho                                  | Ho-Lu         | $4f^{10}$ | ${}^{5}I_{8}^{2}$        | 5,3,1 (35,210,196)                | 5,3,1 (35,120,130)              |                                |

Table 6.2 Computational data used for the Pd-Ln and Pt-Lnseries calculations

[1] Diamagnetic, see 4f configuration and corresponding term symbols.

Presented here for there role in isolating single magnetic centre through substitution.

[2] For RASSCF, all possible allowed multiplicities are included except for Pd-Gd for which

the inclusion of the spin multiplicity of 2 with 784 roots caused convergence issues with MOLCAS.

 $\left[3\right]$  For roots greater than 100, fewer roots are selected for the RASSI-SO as other excited states

are not necessarily important for the description of slow magnetic relaxation in lanthanides

To maintain high accuracy without exceeding existing computational capabilities in our group, the generally relativistic contracted all electron basis sets based on the ANO-RCC basis set obtained from the EMSL Basis Set Exchange library[232, 292] were employed for all atoms as presented in Table 6.2. The resolution of identity (RI) approximation was used with tight SCF convergence to speed up the calculation without compromising accuracy. As the Pd-Ln complexes contain two magnetic centres, the fragment method previously described in section 5.3 was used to first compute the magnetic properties of each isolated ion within the molecule by substituting the second lanthanide centre with either  $La^{3+}$  or  $Lu^{3+}$  as shown in Table 6.2. The choice of  $La^{3+}$  or  $Lu^{3+}$  depends on similarity in size and number of valence electrons.  $La^{3+}$  has no 4f electrons and so, are more comparable to early lanthanides with singly-filled orbitals while  $Lu^{3+}$  with fully filled 4f orbital is comparable to later lanthanides with doubly filled orbitals. More also, the ionic size decreases with increasing effective nuclear charge across the series making earlier members of the series to be comparable to  $La^{3+}$  while later members are comparable in size to  $Lu^{3+}$ . Without considering any possible magnetic exchanges, the isolated magnetic properties of each magnetic lanthanide site were computed by reading into the SINGLE ANISO module of molcas the converged RASSI-SO orbitals obtained from initial converged RASSCF states. The spin multiplicities as well as respective number of configuration state functions (CSFs) or roots used for both the RASSCF and the RASSI-SO procedures for each Pd-Ln and Pt-Ln compound are presented in Table 6.2. The overall magnetic property of each molecule was computed using the POLY ANISO module implemented in MOLCAS by combining the two fragments' magnetic data computed using the SINGLE ANISO module while factoring in a possible magnetic exchanges. For the Pt-Ln system, only the Pd-Tb, Pd-Dy, Pd-Ho and Pd-Er will be computed due to the availability of experimental data to compare with the computational results. The process is the same as detailed for Pd-Ln with successive SINGLE ANISO and POLY ANISO routine. Further details of the computations are presented in Table 6.2.

# 6.4 Electronic properties of the Pd-Ln and Pt-Ln series

The uniqueness in physical and chemical properties of the members of the lanthanide series made them interesting to study. Despite these similarities, the properties of their compound derivatives can still vary considerably. For example, there is a tendency to decreasing coordination number across the series as the size of the ions decreases with increasing effective nuclear charge. The magnetic properties of SMMs stem from the electronic structure of the isolated molecule as opposed to the long-range interactions that occur in classical magnets. As such, the understanding of the electronic structure of the  $Ln^{3+}$  will be useful in the rational design of SMMs. It was mentioned in the preceding section that the core nature of the 4f electrons means that the electronic properties have little dependency on the ligands coupled with very small crystal-field effects. At the molecular level, such a small effect on the electronic structure can have amplifying effects on the magnetic properties of lanthanide-containing complexes because of the smaller energy separation of the magnetic levels compared to the SO interaction energy. As a result, an understanding of how structural parameters could affect the electronic properties of a complete series of the lanthanide and how this effect could propagate the amplification of corresponding magnetic properties has become very important to design high performance single-molecule magnets. Izuogu et al. and Yoshida et al. showed by experiment that a hybrid heterometallic bond interaction involving Pd-Ln[63, 327] and Pt-Ln[64–66] bonding interaction could be a way to tune the magnetic properties of lanthanide-containing complexes. In the reports, [63, 327] all Kramers lanthanide ions of the Pd-Ln type showed slow magnetic relaxation characteristics of SMM behaviour, a property which was absent among the non-Kramers counterparts. Surprisingly, the derivative of the type, Pt-Ln with a heterometalic bonding interaction between the lanthanide and platinum ion showed slow magnetic relaxation for both Kramers and non-Kramers lanthanide ions. [64–66] This observation raises the question of the role of the heterometallic palladium- and platinum-lanthanide interaction in the observed magnetic properties. To understand how this interaction could possibly affect the SMM behaviour of compounds, the multireference RASSF-RASSI-SO method as implemented in the Molcas was used to study the electronic structure of the Pd-Ln series as presented below. The Pt-Ln series for some later members of the lanthanide series were also studied to better understand the reason the non-Kramers ions involving the Pd-Ln series did not show any slow magnetic relaxation. The electronic properties are presented for the Kramers and non-Kramers for better comparison.

### 6.4.1 Pd-Ln and Pt-Ln series of the Kramers ions

The results of the computed electronic properties of the Kramers ions, Pd-Ce, Pd-Nd, Pd-Sm, Pd-Dy, Pt-Dy, Pd-Er, Pt-Er and Pd-Yb are presented in Table 6.3 — 6.10. Pd-Gd will not be discussed in details due to the isotropic nature of the Gd<sup>3+</sup> which makes

it less important for SMM. The two magnetic metal centres in both the Pd-Ln and Pt-Ln samples are related by symmetry through inversion. This means that the electronic and magnetic properties at each site are expected to be the same. To confirm this, two separate calculations were done for Pd-Ce sample for site-1 (Ce-La) and site-2 (La-Ce) and presented in Table 6.3. The results show exact replication of site-1 result in site-2 calculation, as such, only site-1 results will be presented for other samples for all single ion contribution. For each sample, the spin-free energies were presented alongside the RASSI-SO coupled energies. As expected, the inclusion of the SO interaction caused each  $m_i$  state to split into a doublet, thereby presenting a possible route for the slow magnetic relaxation over an energy barrier for all Kramers ion-containing compounds. The distorted  $D_{3h}$  tricapped trigonal prism of the Pd-Ln system considering the first coordination sphere is advantageous to the observation of SMM behaviour as such high symmetry helps minimise the admixture of the magnetic levels leading to a well isolated ground state. This observation is in agreement with the high percentage contribution of the highest  $m_i$  states for each of the Kramers Pd-Ln system to their ground state energies as presented in Table 6.3 - 6.10. For instance the computed wavefunctions for the ground state energy of Pd-Ce is 82.2 %  $\left|\pm\frac{5}{2}\right\rangle$  and even higher for the Pd-Dy which has a percentage contribution of 94.6 %  $\left|\pm\frac{15}{2}\right\rangle$ . Note that only wavefunction contributing approximately 8% and above were included for all Kramers doublets presented in this chapter.

However, beyond the first coordination sphere, the symmetry of the compounds no longer obeys the  $D_{3h}$  geometry to any reasonable approximation due to the arrangement of other atoms within the molecule. The peripheral atoms are arranged such that the overall symmetry is significantly reduced. This affects the overall crystal-field leading to more mixing of the  $m_j$  states. The results show that the higher admixture is more pronounced for the excited states indicating that peripheral ligands can affect the electronic and magnetic properties of the Kramers ions of the **Pd-Ln** series via the excited  $m_j$  state admixture.

The energy gap between the ground state and the first excited state for the Pd-Ce is highest among the Kramers ions at 393.7836 cm<sup>-1</sup>. A high energy gap between the ground state and the excited state favours the observation of SMM behaviour, provided the spin is able to relax over such energy instead and not tunnel through the ground state.

|       |                |                         |  | $g-factor^{[2]}$ |        |        |             |
|-------|----------------|-------------------------|--|------------------|--------|--------|-------------|
|       | Spin-free      | RASSI-SO state $^{[1]}$ | $\Psi_i$ contribution <sup>[3]</sup>   |                  |        |        | a angla     |
| State | state energies | Kramers doublets        | (for Kramers doublets)   | $g_x$            | $g_y$  | $g_z$  | $g_z$ angle |
|       | $(cm^{-1})$    | $(cm^{-1})$             | (%) $ \pm m_j angle$   |                  |        |        | ()          |
|       |                |                         | Site-1   |                  |        |        |             |
| 0     | 0.0000         | 0.0000                  | $82.2 \left \pm\frac{5}{2}\right\rangle$ , $10.9 \left \pm\frac{3}{2}\right\rangle$  | 0.8461           | 1.6146 | 3.2113 | 0.0000      |
| 1     | 76.1639        | 393.7836                | $79 \left  \pm \frac{1}{2} \right\rangle$ , $11.1 \left  \pm \frac{3}{2} \right\rangle$ , $10 \left  \pm \frac{5}{2} \right\rangle$    | 0.5692           | 2.0224 | 2.5038 | 78.0969     |
| 2     | 136.9641       | 467.1009                | $78.1 \left  \pm \frac{3}{2} \right\rangle$ , $14.2 \left  \pm \frac{1}{2} \right\rangle$ , $7.8 \left  \pm \frac{5}{2} \right\rangle$ | 2.2380           | 1.7786 | 0.0138 | 69.7017     |
| 3     | 478.7539       |                         |  |                  |        |        |             |
| 4     | 513.5887       |                         |  |                  |        |        |             |
| 5     | 644.9347       |                         |  |                  |        |        |             |
| 6     | 1005.8008      |                         |  |                  |        |        |             |
|       |                |                         | Site-2   |                  |        |        |             |
| 0     | 0.0000         | 0.0000                  | $82.3 \left  \pm \frac{5}{2} \right\rangle$ , $10.9 \left  \pm \frac{3}{2} \right\rangle$  | 0.8461           | 1.6146 | 3.2113 | 0.0000      |
| 1     | 76.1643        | 393.7836                | $78.9 \left  \pm \frac{1}{2} \right\rangle$ , $11 \left  \pm \frac{3}{2} \right\rangle$ , $10 \left  \pm \frac{5}{2} \right\rangle$    | 0.5692           | 2.0224 | 2.5038 | 78.0968     |
| 2     | 136.9642       | 467.1010                | $78 \left  \pm \frac{3}{2} \right\rangle$ , 14.2 $\left  \pm \frac{1}{2} \right\rangle$ , 7.7 $\left  \pm \frac{5}{2} \right\rangle$   | 2.2380           | 1.7786 | 0.0138 | 69.7017     |
| 3     | 478.7540       |                         |  |                  |        |        |             |
| 4     | 513.5889       |                         |  |                  |        |        |             |
| 5     | 644.9341       |                         |  |                  |        |        |             |
| 6     | 1005.8014      |                         |  |                  |        |        |             |

Table 6.3 Electronic structure of Pd-Ce with Ce-La (site 1) and La-Ce (site-2) centres calculated from RASSCF-RASSI-SO

[1]Each energy value represents a degenerate of two states (Kramers doublet).

[2] The sign of  $g_x \times g_y \times g_z$  is positive

[3] Only the contributions that are greater than of equal to 8 % are included here.

|        |  |  |  |                       | g-fa      | actor <sup>[2]</sup> |                 |  |  |  |  |  |
|--------|--|--|--|-----------------------|-----------|----------------------|-----------------|--|--|--|--|--|
| State  | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state <sup>[1]</sup><br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i 	ext{ contribution}^{[3]} \ (	ext{for Kramers doublets}) \ (\%) ig   \pm m_j  angle$   | <i>g</i> <sub>x</sub> | <i>gy</i> | <i>Bz</i>            | $g_z$ angle (°) |  |  |  |  |  |
| 0      | 0.0000   | 0.0000   | $41.7 \left  \pm \frac{5}{2} \right\rangle, \ 33.6 \left  \pm \frac{9}{2} \right\rangle$ $9.2 \left  \pm \frac{3}{2} \right\rangle, \ 8 \left  \pm \frac{7}{2} \right\rangle$  | 1.8182                | 0.9431    | 3.8949               | 0.0000          |  |  |  |  |  |
| 1      | 40.6615  | 63.6244  | $\begin{array}{c} 42.3 \left  \pm \frac{3}{2} \right\rangle, \ 14.4 \left  \pm \frac{5}{2} \right\rangle \\ 13.5 \left  \pm \frac{7}{2} \right\rangle, \ 13.3 \left  \pm \frac{9}{2} \right\rangle \end{array}$  | 1.9476                | 0.0212    | 3.5306               | 46.0915         |  |  |  |  |  |
| 2      | 54.1724  | 173.7645   | $\begin{array}{c} 33.2 \left  \pm \frac{9}{2} \right\rangle, \ 28.2 \left  \pm \frac{5}{2} \right\rangle, \ 15.2 \left  \pm \frac{7}{2} \right\rangle \\ 12.6 \left  \pm \frac{1}{2} \right\rangle, \ 10.7 \left  \pm \frac{3}{2} \right\rangle \end{array}$ | 0.2966                | 1.4584    | 4.1081               | 27.3974         |  |  |  |  |  |
| 3      | 124.1738   | 221.0372   | $\begin{array}{c} 33.3 \left  \pm \frac{7}{2} \right\rangle, \ 30.5 \left  \pm \frac{1}{2} \right\rangle \\ 18.4 \left  \pm \frac{3}{2} \right\rangle, \ 14.4 \left  \pm \frac{9}{2} \right\rangle \end{array}$  | 1.8518                | 0.1337    | 2.8644               | 75.7731         |  |  |  |  |  |
| 4      | 192.3049   | 320.5860   | $\begin{array}{c} 32.8 \left  \pm \frac{1}{2} \right\rangle, \ 29.9 \left  \pm \frac{7}{2} \right\rangle \\ 19.4 \left  \pm \frac{3}{2} \right\rangle, \ 12.5 \left  \pm \frac{5}{2} \right\rangle \end{array}$  | 1.4083                | 1.7199    | 4.0940               | 36.6956         |  |  |  |  |  |
| 5      | 241.8102   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 6      | 286.7066   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 7      | 362.9009   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 8      | 448.4192   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 9      | 467.3964   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 10     | 489.9568   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 11     | 523.0425   |  |  |                       |           |                      |                 |  |  |  |  |  |
| 12     | 536.7022   |  |  |                       |           |                      |                 |  |  |  |  |  |
| [1]Eac | h energy value                                     | represents a degene  | [1] Each energy value represents a degenerate of two states (Kramers doublet)  |                       |           |                      |                 |  |  |  |  |  |

Table 6.4 Electronic structure of Pd-Nd with Nd-La (site 1) centres calculated with RASSCF-RASSI-SO

ramers doublet). ierate of two states (r

[1]Each energy value represents a deger [2] The sign of  $g_x \times g_y \times g_z$  is positive

[3] Only the contributions that are greater than of equal to 8 % are included here.
|   |  |  |   |                | g-f            | actor <sup>[2]</sup> |                 |  |  |  |
|---|--|--|---|----------------|----------------|----------------------|-----------------|--|--|--|
| State   | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state <sup>[1]</sup><br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i 	ext{ contribution}^{[3]}$ (for Kramers doublets) (%) $ig  \pm m_j ig angle$  | g <sub>x</sub> | g <sub>y</sub> | <b>g</b> z           | $g_z$ angle (°) |  |  |  |
| 0   | 0.0000   | 0.0000   | $63.1\left \pm\frac{5}{2}\right\rangle$ , $31.9\left \pm\frac{3}{2}\right\rangle$   | 0.2398         | 0.3210         | 0.9659               | 0.0000          |  |  |  |
| 1   | 6.0594   | 111.3614   | $41.8 \left  \pm \frac{1}{2} \right\rangle$ , $38.8 \left  \pm \frac{3}{2} \right\rangle$ , $19.4 \left  \pm \frac{5}{2} \right\rangle$ | 0.3555         | 0.5472         | 0.7796               | 1.8920          |  |  |  |
| 2   | 126.0959   | 240.7166   | $53.1 \left  \pm \frac{1}{2} \right\rangle$ , 28.4 $\left  \pm \frac{3}{2} \right\rangle$ , 17.5 $\left  \pm \frac{5}{2} \right\rangle$ | 0.3650         | 0.2195         | 1.3937               | 147.8205        |  |  |  |
| 3   | 151.4374   |  |   |                |                |                      |                 |  |  |  |
| 4   | 292.0831   |  |   |                |                |                      |                 |  |  |  |
| 5   | 331.2076   |  |   |                |                |                      |                 |  |  |  |
| 6   | 351.7696   |  |   |                |                |                      |                 |  |  |  |
| 7   | 409.1665   |  |   |                |                |                      |                 |  |  |  |
| 8   | 419.2650   |  |   |                |                |                      |                 |  |  |  |
| 9   | 459.7861   |  |   |                |                |                      |                 |  |  |  |
| 10  | 10 474.7804  |  |   |                |                |                      |                 |  |  |  |
| [1]Each energy value represents a degenerate of two states (Kramers doublet). |  |  |   |                |                |                      |                 |  |  |  |
| [2] T   | he sign of $g_x 	imes_x$                           | $g_y 	imes g_z$ is positive  |   |                |                |                      |                 |  |  |  |

Table 6.5 Electronic structure of Pd-Sm with Sm-La (site 1) centres calculated with RASSCF-RASSI-SO

[3] Only the contributions that are greater than of equal to 8 % are included here.

However, **Pd-Ce** does not posses high spin system  $(S = \frac{1}{2})$  and so the SOC effect will have a minimal effect compared to other lanthanide ions with higher spin state. The resultant magnetic behaviour when the spin couples with orbital moment is such that the *J* states are very far from each other energetically which means that the thermal energy in the form of kT - the Boltzmann distribution would not be able to populate all *J*-levels of  ${}^{2S+1}L$ .

The implication to the mechanism of slow magnetic relaxation will be discussed in the proceeding session of magnetic properties.

## 6.4.1.1 Anisotropic *g*-factor of the Kramers ions of the Pd-Ln and Pt-Ln series

The computed  $g_z$  value at the ground state is approximately two times either of the  $g_x$  and  $g_{y}$  showing some level of magnetic anisotropy but not as large as some of the later members of the series like the Pd-Dy system. This is partly due to the lesser SO contribution arising from the interaction of a single f-electron with the orbital moment. Pd-Nd (see Table 6.4) and Pd-Sm (see Table 6.5) show similar electronic properties as described for Pd-Ce (see Table 6.3) with a much more smaller anisotropic  $g_z$  value for **Pd-Sm** (see Table 6.5). On the other hand, the electronic properties of the later members of the series with the exception of Pd-Yb (Table 6.10) show distinct properties from those of the early members. For example, the anisotropic  $g_z$  values at the ground state are significantly high for Pd-Dy (19.5096) (Table 6.6), Pt-Dy (19.2555) (Table 6.7), Pd-Er (16.4695) (Table 6.8) and Pt-Er (16.6588) (Table 6.9) compare to those of Pd-Ce (3.2113), Pd-Nd (3.8949) and Pd-Sm (0.9659). The trend in these values is linked to the SO effect which for example is responsible for the small magnetic moment of  $\text{Sm}^{3+}$  when compared with  $\text{Ce}^{3+}$  despite having more electron spin. For the Pd-Ln Kramers ions, the sign of the g-factor is positive for the earlier members of the series - Pd-Ce, Pd-Nd and Pd-Sm showing that the dipole moment is parallel to their angular momentum. On the other hand, the later members of the Kramers ion - Pd-Gd, Pd-Dy, Pt-Dy, Pd-Er, Pt-Er and Pd-Yb show negative sign for the g-factors indicating antiparallel alignment of the dipole moment with the angular momentum.

|       |                     |                               |  |        | g-1    | factor <sup>[2]</sup> |             |
|-------|---------------------|-------------------------------|--|--------|--------|-----------------------|-------------|
| Ctata | Spin-free           | RASSI-SO state <sup>[1]</sup> | $\Psi_i$ contribution <sup>[3]</sup>   | _      | _      | _                     | $g_z$ angle |
| State | state energies      | Kramers doublets              | (for Kramers doublets)   | $g_x$  | $g_y$  | $g_z$                 | (°)         |
|       | (cm <sup>-1</sup> ) | (cm <sup>-1</sup> )           | (%) $ \pm m_j\rangle$  |        |        |                       |             |
| 0     | 0.0000              | 0.0000                        | $94.6\left \pm\frac{15}{2}\right\rangle$   | 0.0536 | 0.0378 | 19.5096               | 0.0000      |
| 1     | 10.3460             | 66.6393                       | $\begin{array}{c} 26.5 \left  \pm \frac{9}{2} \right\rangle, \ 21.9 \left  \pm \frac{11}{2} \right\rangle \\ 21.7 \left  \pm \frac{7}{2} \right\rangle, \ 15.7 \left  \pm \frac{13}{2} \right\rangle \end{array}$  | 0.3630 | 0.2469 | 18.6589               | 130.0660    |
| 2     | 81.2954             | 118.5702                      | $65.7 \left  \pm \frac{13}{2} \right\rangle$ , $10.5 \left  \pm \frac{9}{2} \right\rangle$ , $10.4 \left  \pm \frac{5}{2} \right\rangle$   | 3.2919 | 2.7845 | 14.0729               | 19.0418     |
| 3     | 100.7903            | 144.7121                      | $\begin{array}{c} 39.4 \left  \pm \frac{11}{2} \right\rangle, \ 19.6 \left  \pm \frac{7}{2} \right\rangle, \ 14.1 \left  \pm \frac{3}{2} \right\rangle \\ 11.1 \left  \pm \frac{13}{2} \right\rangle, \ 8.9 \left  \pm \frac{9}{2} \right\rangle \end{array}$      | 8.7769 | 7.2223 | 2.1093                | 33.0742     |
| 4     | 144.1241            | 166.2639                      | $32.3  \pm\frac{1}{2}\rangle, 22.6  \pm\frac{9}{2}\rangle, 14.7  \pm\frac{5}{2}\rangle 13.6  \pm\frac{11}{2}\rangle, 8.9  \pm\frac{3}{2}\rangle$   | 2.6370 | 3.4697 | 14.4746               | 73.4577     |
| 5     | 163.6176            | 227.0472                      | $\begin{array}{c} 28.2 \left  \pm \frac{7}{2} \right\rangle, \ 26.8 \left  \pm \frac{5}{2} \right\rangle \\ 23.2 \left  \pm \frac{3}{2} \right\rangle, \ 11.6 \left  \pm \frac{9}{2} \right\rangle \end{array}$  | 0.5588 | 0.3550 | 16.2755               | 114.7856    |
| 6     | 199.6045            | 264.7285                      | $22 \left  \pm \frac{5}{2} \right\rangle, 17.1 \left  \pm \frac{3}{2} \right\rangle, 16.5 \left  \pm \frac{7}{2} \right\rangle$ $16.2 \left  \pm \frac{9}{2} \right\rangle, 13.4 \left  \pm \frac{11}{2} \right\rangle, 10.7 \left  \pm \frac{1}{2} \right\rangle$ | 0.0642 | 0.2058 | 19.1495               | 48.4110     |
| 7     | 305.1889            | 511.0804                      | $45.1 \left  \pm \frac{1}{2} \right\rangle$ , $31.1 \left  \pm \frac{3}{2} \right\rangle$ , $15.2 \left  \pm \frac{5}{2} \right\rangle$  | 0.0005 | 0.0003 | 19.8088               | 122.7269    |
| 8     | 320.4301            |                               |  |        |        |                       |             |
| 9     | 560.4550            |                               |  |        |        |                       |             |
| 10    | 561.5112            |                               |  |        |        |                       |             |

Table 6.6 Electronic structure of **Pd-Dy** with Dy-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The sign of  $g_x \times g_y \times g_z$  is negative

[3] Only the contributions that are greater than of equal to 8 % are included here.

|       |  |   |  |                | g-f            | actor <sup>[2]</sup> |                 |
|-------|--|---|--|----------------|----------------|----------------------|-----------------|
| State | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | $\begin{array}{c} RASSI\text{-}SO \ state^{[1]} \\ Kramers \ doublets \\ (cm^{-1}) \end{array}$ | $\Psi_i 	ext{ contribution}^{[3]}$ (for Kramers doublets) (%) $ \pm m_j angle$   | g <sub>x</sub> | g <sub>y</sub> | $g_z$                | $g_z$ angle (°) |
| 0     | 0.0000   | 0.0000  | $91.2 \left  \pm \frac{15}{2} \right\rangle$   | 0.0687         | 0.1665         | 19.2555              | 0.0000          |
| 1     | 18.3524  | 39.0013   | $\frac{25.7 \left  \pm \frac{7}{2} \right\rangle, 24.9 \left  \pm \frac{5}{2} \right\rangle, 17.8 \left  \pm \frac{3}{2} \right\rangle}{13.9 \left  \pm \frac{9}{2} \right\rangle, 10 \left  \pm \frac{1}{2} \right\rangle}$   | 00.0102        | 0.1934         | 18.8112              | 107.0691        |
| 2     | 55.5824  | 106.9559  | $68.6 \left  \pm \frac{13}{2} \right\rangle$ , $8.3 \left  \pm \frac{9}{2} \right\rangle$ , $7.9 \left  \pm \frac{5}{2} \right\rangle$   | 0.4785         | 0.2777         | 14.8080              | 13.0459         |
| 3     | 91.4833  | 139.8811  | $ \begin{array}{c} 25.2 \left  \pm \frac{11}{2} \right\rangle, 22.4 \left  \pm \frac{9}{2} \right\rangle, 17.5 \left  \pm \frac{13}{2} \right\rangle \\ 14.1 \left  \pm \frac{1}{2} \right\rangle, 12 \left  \pm \frac{3}{2} \right\rangle \end{array} $   | 0.9048         | 1.2711         | 16.3796              | 14.2094         |
| 4     | 178.9147   | 179.9882  | $\begin{array}{c} 32.7 \left  \pm \frac{11}{2} \right\rangle, \ 18.2 \left  \pm \frac{1}{2} \right\rangle, \ 17.1 \left  \pm \frac{7}{2} \right\rangle \\ 12.1 \left  \pm \frac{3}{2} \right\rangle, \ 10.8 \left  \pm \frac{5}{2} \right\rangle \end{array}$  | 3.7488         | 6.5518         | 8.8649               | 41.6515         |
| 5     | 217.7920   | 235.3414  | $ \begin{array}{c} 31.9 \left  \pm \frac{1}{2} \right\rangle, \ 21.2 \left  \pm \frac{3}{2} \right\rangle, \ 14.3 \left  \pm \frac{5}{2} \right\rangle \\ 10.9 \left  \pm \frac{9}{2} \right\rangle, \ 9.5 \left  \pm \frac{11}{2} \right\rangle, \ 8.9 \left  \pm \frac{7}{2} \right\rangle \end{array} $ | 2.4711         | 3.1567         | 14.6921              | 104.4742        |
| 6     | 229.6834   | 360.2685  | $\begin{array}{c} 24.4 \left  \pm \frac{9}{2} \right\rangle, \ 18.9 \left  \pm \frac{5}{2} \right\rangle, \ 17.4 \left  \pm \frac{11}{2} \right\rangle \\ 17 \left  \pm \frac{7}{2} \right\rangle, \ 14 \left  \pm \frac{3}{2} \right\rangle \end{array}$  | 0.2369         | 0.1540         | 18.6809              | 26.6817         |
| 7     | 389.2562   | 431.2374  | $\begin{array}{c} 25.1 \left  \pm \frac{7}{2} \right\rangle, \ 22.5 \left  \pm \frac{5}{2} \right\rangle, \ 17.8 \left  \pm \frac{3}{2} \right\rangle \\ 17.3 \left  \pm \frac{1}{2} \right\rangle, \ 13.9 \left  \pm \frac{9}{2} \right\rangle \end{array}$   | 0.0447         | 0.1086         | 19.4934              | 126.6389        |
| 8     | 411.3831   |   |  |                |                |                      |                 |
| 9     | 489.8275   |   |  |                |                |                      |                 |
| 10    | 497.4070   |   |  |                |                |                      |                 |

Table 6.7 Electronic structure of **Pt-Dy** with Dy-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The sign of  $g_x \times g_y \times g_z$  is negative

[3] Only the contributions that are greater than of equal to 8 % are included here.

|       |                |                               |  |        | g-1    | factor <sup>[2]</sup> |              |
|-------|----------------|-------------------------------|--|--------|--------|-----------------------|--------------|
|       | Spin-free      | $RASSI\text{-}SO state^{[1]}$ | $\Psi_i$ contribution <sup>[3]</sup>   |        |        |                       | a anglo      |
| State | state energies | Kramers doublets              | (for Kramers doublets)   | $g_x$  | $g_y$  | $g_z$                 | $g_z$ aligie |
|       | $(cm^{-1})$    | $(cm^{-1})$                   | (%) $\left \pm m_{j}\right\rangle$   |        |        |                       | ()           |
| 0     | 0.0000         | 0.0000                        | 74.6 $\left \pm\frac{15}{2}\right\rangle$ , 12 $\left \pm\frac{11}{2}\right\rangle$ , 8.2 $\left \pm\frac{13}{2}\right\rangle$           | 0.1100 | 0.4465 | 16.4695               | 0.0000       |
| 1     | 5.9470         | 28.5485                       | $58.7 \left  \pm \frac{13}{2} \right\rangle$ , $11.5 \left  \pm \frac{15}{2} \right\rangle$ , $8.7 \left  \pm \frac{5}{2} \right\rangle$ | 0.4395 | 1.3114 | 14.6389               | 128.9007     |
| 2     | 14.3093        | 76.8201                       | $52.8 \left  \pm \frac{1}{2} \right\rangle$ , $16.6 \left  \pm \frac{13}{2} \right\rangle$ , $16.1 \left  \pm \frac{3}{2} \right\rangle$ | 2.4194 | 0.8479 | 11.5203               | 66.8116      |
| 3     | 36.7898        | 119.4594                      | $44.1 \left  \pm \frac{3}{2} \right\rangle$ , 25.5 $\left  \pm \frac{1}{2} \right\rangle$ , 11.2 $\left  \pm \frac{11}{2} \right\rangle$ | 4.2652 | 2.7791 | 10.6529               | 105.6756     |
| 4     | 72 5344        | 178 8948                      | $28.5 \left  \pm \frac{11}{2} \right\rangle$ , $25.5 \left  \pm \frac{5}{2} \right\rangle$   | 3 4426 | 1 7746 | 7 9790                | 16 1546      |
|       | 12.3344        | 170.0340                      | $21\left \pmrac{9}{2} ight angle$ , 9.5 $\left \pmrac{1}{2} ight angle$  | 3.4420 | 1.7740 | 1.5150                | 10.10+0      |
| 5     | 129.8571       | 206.6893                      | $27.2 \left  \pm \frac{11}{2} \right\rangle, 21.4 \left  \pm \frac{5}{2} \right\rangle, 19.3 \left  \pm \frac{3}{2} \right\rangle$       | 8.9728 | 6.4165 | 1.0212                | 103.5685     |
|       |                |                               | $12.5 \left  \pm \frac{7}{2} \right\rangle, 11.1 \left  \pm \frac{9}{2} \right\rangle$   |        |        |                       |              |
| 6     | 173.5366       | 275.4570                      | $39.5 \left  \pm \frac{7}{2} \right\rangle$ , $30 \left  \pm \frac{9}{2} \right\rangle$  | 2.1543 | 1.0806 | 13.5981               | 128.9950     |
|       |                |                               | $12.7 \left \pm\frac{5}{2}\right\rangle$ , $9.4 \left \pm\frac{11}{2}\right\rangle$  |        |        |                       |              |
| 7     | 198.2187       | 300.9464                      | $33\left \pm\frac{7}{2}\right\rangle$ , $30.6\left \pm\frac{9}{2}\right\rangle$ , $21.9\left \pm\frac{5}{2}\right\rangle$                | 1.3522 | 0.0819 | 14.6433               | 110.1267     |
| 8     | 242.3554       |                               |  |        |        |                       |              |
| 9     | 284.8220       |                               |  |        |        |                       |              |
| 10    | 318.7181       |                               |  |        |        |                       |              |
| 11    | 344.3283       |                               |  |        |        |                       |              |
| 12    | 369.0160       |                               |  |        |        |                       |              |

Table 6.8 Electronic structure of **Pd-Er** with Er-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The sign of  $g_x \times g_y \times g_z$  is negative

[3] Only the contributions that are greater than of equal to 8 % are included here.

|       |                |                               |   |                | <i>g</i> -1 | factor <sup>[2]</sup> |              |
|-------|----------------|-------------------------------|---|----------------|-------------|-----------------------|--------------|
|       | Spin-free      | $RASSI\text{-}SO state^{[1]}$ | $\Psi_i$ contribution <sup>[3]</sup>  |                |             |                       | a angle      |
| State | state energies | Kramers doublets              | (for Kramers doublets)  | g <sub>x</sub> | $g_y$       | $g_z$                 | $g_z$ aligie |
|       | $(cm^{-1})$    | $(cm^{-1})$                   | (%) $\left \pm m_{j} ight angle$  |                |             |                       | ()           |
| 0     | 0.0000         | 0.0000                        | 78.7 $\left \pm\frac{15}{2}\right\rangle$ , 17.1 $\left \pm\frac{11}{2}\right\rangle$   | 0.1912         | 0.5664      | 16.6588               | 0.0000       |
| 1     | 2.7084         | 27.5220                       | $30.8 \left \pm \frac{5}{2}\right\rangle, 25 \left \pm \frac{7}{2}\right\rangle$ $22.2 \left \pm \frac{9}{2}\right\rangle, 12.1 \left \pm \frac{1}{2}\right\rangle$   | 1.4686         | 0.9954      | 15.1748               | 103.3336     |
| 2     | 21.1226        | 50.7890                       | $\frac{1}{32.2 \left  \pm \frac{9}{2} \right\rangle, 22.4 \left  \pm \frac{7}{2} \right\rangle}{20.9 \left  \pm \frac{13}{2} \right\rangle, 12.8 \left  \pm \frac{11}{2} \right\rangle}$  | 2.1184         | 0.1631      | 13.3076               | 42.4882      |
| 3     | 24.4702        | 103.9828                      | $ \begin{array}{c} 28 \left  \pm \frac{3}{2} \right\rangle, 18 \left  \pm \frac{7}{2} \right\rangle, 17.4 \left  \pm \frac{5}{2} \right\rangle \\ 13.2 \left  \pm \frac{13}{2} \right\rangle, 12.6 \left  \pm \frac{1}{2} \right\rangle \end{array} $         | 6.1144         | 3.6762      | 9.1212                | 5.5716       |
| 4     | 49.3015        | 166.2644                      | $45\left \pm\frac{1}{2}\right\rangle$ , 24.5 $\left \pm\frac{5}{2}\right\rangle$ , 9.3 $\left \pm\frac{3}{2}\right\rangle$  | 1.5792         | 3.5436      | 8.9997                | 71.5296      |
| 5     | 104.8852       | 197.9826                      | $\begin{array}{c} 31\left \pm\frac{3}{2}\right\rangle, 18\left \pm\frac{13}{2}\right\rangle, 15.2\left \pm\frac{1}{2}\right\rangle\\ 13.8\left \pm\frac{11}{2}\right\rangle, 11.7\left \pm\frac{9}{2}\right\rangle \end{array}$                               | 5.2933         | 0.8518      | 7.5479                | 80.3577      |
| 6     | 167.7295       | 226.8142                      | $\begin{array}{c} 29.6 \left  \pm \frac{11}{2} \right\rangle, \ 18.3 \left  \pm \frac{1}{2} \right\rangle, \ 12.9 \left  \pm \frac{7}{2} \right\rangle \\ 12.2 \left  \pm \frac{3}{2} \right\rangle, \ 10.4 \left  \pm \frac{9}{2} \right\rangle \end{array}$ | 5.6657         | 7.8042      | 1.6296                | 78.7209      |
| 7     | 188.2160       | 237.0088                      | $32.2 \left  \pm \frac{13}{2} \right\rangle, \ 17.8 \left  \pm \frac{9}{2} \right\rangle, \ 14.6 \left  \pm \frac{11}{2} \right\rangle \\ 12.4 \left  \pm \frac{5}{2} \right\rangle, \ 9.7 \left  \pm \frac{7}{2} \right\rangle$                              | 6.5426         | 0.9079      | 10.1056               | 15.9047      |
| 8     | 215.5869       |                               |   |                |             |                       |              |
| 9     | 240.9090       |                               |   |                |             |                       |              |
| 10    | 248.3010       |                               |   |                |             |                       |              |
| 11    | 273.3110       |                               |   |                |             |                       |              |
| 12    | 288.0485       |                               |   |                |             |                       |              |

Table 6.9 Electronic structure of **Pt-Er** with Er-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The sign of  $g_x \times g_y \times g_z$  is negative

[3] Only the contributions that are greater than of equal to 8 % are included here.

|   |  |  |   |                | g-f            | $actor^{[2]}$ |                 |  |  |
|---|--|--|---|----------------|----------------|---------------|-----------------|--|--|
| State   | Spin-free<br>state energies<br>(cm <sup>-1</sup> ) | RASSI-SO state <sup>[1]</sup><br>Kramers doublets<br>(cm <sup>-1</sup> ) | $\Psi_i 	ext{ contribution}^{[3]}$ (for Kramers doublets) (%) $\ket{\pm m_j}$   | g <sub>x</sub> | g <sub>y</sub> | <i>8z</i>     | $g_z$ angle (°) |  |  |
| 0   | 0.0000   | 0.0000   | $42.3 \left  \pm \frac{7}{2} \right\rangle$ , $33.5 \left  \pm \frac{5}{2} \right\rangle$ , $20.2 \left  \pm \frac{3}{2} \right\rangle$ | 0.4269         | 1.4107         | 5.8562        | 0.0000          |  |  |
| 1   | 91.0109  | 56.7264  | 51.9 $\left \pm\frac{7}{2}\right\rangle$ , 40 $\left \pm\frac{5}{2}\right\rangle$   | 0.4463         | 0.8967         | 7.4335        | 143.1387        |  |  |
| 2   | 128.2131   | 251.0845   | $45.2 \left  \pm \frac{3}{2} \right\rangle$ , 29.8 $\left  \pm \frac{1}{2} \right\rangle$ , 19.8 $\left  \pm \frac{5}{2} \right\rangle$ | 1.3995         | 2.9030         | 3.7242        | 59.9253         |  |  |
| 3   | 160.7241   | 367.1005   | 63.4 $\left \pm\frac{1}{2}\right\rangle$ , 29.4 $\left \pm\frac{3}{2}\right\rangle$   | 0.8409         | 1.8526         | 6.9380        | 18.5113         |  |  |
| 4   | 414.9379   |  |   |                |                |               |                 |  |  |
| 5   | 417.5698   |  |   |                |                |               |                 |  |  |
| 6   | 451.0049   |  |   |                |                |               |                 |  |  |
| [1]Each energy value represents a degenerate of two states (Kramers doublet). |  |  |   |                |                |               |                 |  |  |

Table 6.10 Electronic structure of Pd-Yb with Yb-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The sign of  $g_x \times g_y \times g_z$  is negative

[3] Only the contributions that are greater than of equal to 8 % are included here.

Figure 6.2a and 6.2b shows the evolution of  $g_z$  values and angles for the Kramers ions. A comparison of the absolute value of the angle across the series is not useful since the  $g_z$ axes and values are function of the SO interaction which differs from one lanthanide ion to the other. But, it gives great insight when compounds of the same lanthanide ion with different ligands is considered as in Pd-Ln and Pt-Ln systems. The RASSI-SO energies, the  $g_z$  values and the angular separation between the ground and the first excited state  $g_z$ -axes for the Kramers ions of the Pd-Ln and Pt-Ln series are summarised in Figure 6.2. For the RASSI-SO energies, two prominent outliers exist, the first is the wider energy gap between the ground and first excited state in Pd-Ce compared to the other congeners as discussed at the beginning of this section. The second outlier lies with the Pd-Gd which shows overlap of the ground and the other 3 excited  $m_i$  states within the ground magnetic level of  $\frac{7}{2}$ . The reason for this is that the S = J due to an L-value of 0. The magnetic property from the SO consideration is the same as the spin-only magnetic moment. As a result, the magnet moment for all  $m_j$  states  $(m_j = \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$  and  $\frac{1}{2})$  are approximately the same. The first true excited state will therefore arise from the excited spin multiplicity of 6 and not that of 8. The energy separation of which was computed as 39705.9206  $cm^{-1}$ . This wide energy gap coupled with the isotropic nature of the quadrupole moment approximation make it currently difficult/impossible to realise gadolinium-based SMM. At this point, it is worth mentioning that the overall electronic structure and consequently the magnetic properties will need to factor in any possible exchange interaction between the magnetic lanthanide centres to fully describe the Pd-Ln and Pt-Ln systems. The results of which are presented in section 6.5. However, it is important to understand the individual contribution of each metal site to the electronic and magnetic properties of the systems and to what extent the intramolecular magnetic exchanges can affect the observation of SMM behaviour in clusters.





Fig. 6.2 (a)  $g_z$  values computed *ab initio* for the Kramers ions of the Pd-Ln and Pt-Ln series (b) The angular difference between the  $g_z$  axes of the ground state and the  $g_z$  axes of the first excited state computed *ab initio* for the Kramers ions of the Pd-Ln and Pt-Ln series. (c) The RASSI-SO energies computed for the Kramers ions of the Pd-Ln and Pt-Ln series

### 6.4.2 Pd-Ln and Pt-Ln series of the non-Kramers ions

The electronic properties of the non-Kramers ions of the Pd-Ln and Pt-Ln series are discussed separately in this section. The reason for the separate discussion stems from the lack of slow magnetic relaxation for all non-Kramers ions of the Pd-Ln series reported by Izuogu *et al.* [327] Although, there are no experimental results in the literature for the early members of the Pt-Ln series, we compare the electronic structure of the Pd-Ln and Pt-Ln series for the later members to gain insight on the factors responsible for the observation of slow magnetic relaxation for the non-Kramers ions of the Pt-Ln and not for the Pd-Ln systems. The earlier lanthanides for the Pd-Ln series are studied to elucidate any trend in their properties while limiting the study of the Pt-Ln series to those for which there are experimental results (i.e. Pt-Tb and Pt-Ho). The summary of the electronic structures of the non-Kramers ions of the Pd-Ln series are presented in Table 6.11 - 6.17.

## 6.4.2.1 Tunnelling splitting for non-Kramers ions of the Pd-Ln and Pt-Ln series

In low symmetry systems, the ground crystal-field multiplet of a non-Kramers ion can be described as a quasi doublet with unquenched orbital momentum. As expected, low symmetry around the non-Kramers ion would cause the magnetic levels to mix and vice verse for high symmetry. In the limit of the low symmetry of non-Kramers systems, the challenge becomes to assign the correct wavefunction contribution to the various ground and excited states such that one of the magnetic levels is assigned a singlet state and the others, quasi-doublets. To determine which of the magnetic levels is assigned a singlet state to the wavefunction, we compare the tunnelling splitting between each nearby quasi-doublets. The tunnelling splitting of particular interest is that within the ground state because of its role in the slow magnetic relaxation of non-Kramers-based SMM. The tunnelling split for the quasi doublet ground states are singlet, singlet, 0.7011, 0.0229, 2.7162, and 0.384 cm  $^{-1}$ for Pd-Pr (see Table 6.11), Pd-Pm (see Table 6.12), Pd-Tb (see Table 6.13), Pt-Tb (see Table 6.14), Pd-Ho (see Table 6.15), Pt-Ho (see Table 6.16) and Pd-Tm(see Table 6.17) respectively. The singlet states means that no quasi doublets were found at the ground state for Pd-Pr and Pd-Pm. This can be attributed to the weaker SO interaction which is manifested on the lower anisotropic  $g_z$  values, making it difficult to split the states into two quasi-degenerate states. On the other hand, Pd-Tb, Pt-Tb, Pd-Ho and Pt-Ho show relatively small tunnelling splitting which will be used to rationalise the magnetic behaviour of the complexes in the proceeding section.

|       |                |                                      |                        |  | 1      |        | [2]                  |                 |
|-------|----------------|--------------------------------------|------------------------|--|--------|--------|----------------------|-----------------|
|       |                |                                      |                        |  |        | g-f    | actor <sup>[3]</sup> |                 |
|       | Spin-free      | $RASSI\operatorname{-SO}state^{[1]}$ | $Tunnelling^{[2]}$     | $\Psi_i$ contribution $^{[4]}$   |        |        |                      | a angle         |
| State | state energies | non-Kramers states                   | splitting              | (non-Kramers quasi-doublets)   | $g_x$  | $g_y$  | $g_z$                | $g_z$ angle (°) |
|       | $(cm^{-1})$    | $(cm^{-1})$                          | $(cm^{-1})$            | (%) $\left \pm m_{j} ight angle$   |        |        |                      | ()              |
|       | 0.000          | 0.0000                               |                        | 27.6 $ \pm2\rangle$ , 24.4 $ \pm3\rangle$ , 24 $ \pm1\rangle$                          |        |        |                      |                 |
| 0     | 0.0000         | 0.0000                               | 32.2588 <sup>[5]</sup> | $16.8\left \pm4 ight angle$ , 7 $\left 0 ight angle$                                   | 0.0000 | 0.0000 | 3.4191               | 0.0000          |
| 1     | 10.3178        | 32.2588                              |                        | $51 \pm2 angle, 28 \pm4 angle, 17.4 \pm3 angle$  |        |        |                      |                 |
|       | 01 1020        | 10 2196                              |                        | 58.7 $ 0 angle$ , 24.8 $ \pm1 angle$ , 9.4 $ \pm2 angle$                               |        |        |                      |                 |
| 2     | 01.1030        | 49.3100                              | 26.3351 <sup>[5]</sup> | $6.8\ket{\pm3}$  | 0.0000 | 0.0000 | 3.0573               | 18.8100         |
| 3     | 118.3328       | 75.6537                              |                        | $43.8  \pm 1\rangle$ , $28.8  \pm 2\rangle$ , $15.6  \pm 3\rangle$ , $7  \pm 4\rangle$ |        |        |                      |                 |
|       | 166 1920       | 120 2002                             |                        | 76.4 $ \pm1 angle$ , 9.4 $ 0 angle$ , 8.8 $ \pm3 angle$                                |        |        |                      |                 |
| 4     | 100.1032       | 139.2003                             | —                      | $5.2\ket{\pm4}$  | _      | —      | —                    | —               |
| 5     | 220.4559       | 289.9740                             | 25 6407[5]             | $58\left \pm3 ight angle$ , $21.8\left \pm2 ight angle$ , $15.4\left 0 ight angle$     | 0.0000 | 0.0000 | E 0260               | 40.0425         |
| 6     | 261.9958       | 315.6236                             | 25.0497                | $39.4 \pm3 angle, 31.4 \pm2 angle, 20 \pm1 angle$                                      | 0.0000 | 0.0000 | 5.0200               | 49.9420         |
| 7     | 451.5643       | 442.7094                             | 4 7204                 | $66.8  \pm4\rangle$ , $15.6  \pm3\rangle$ , $15.6  \pm2\rangle$                        | 0.0000 | 0.0000 | 6 2107               | 122 6000        |
| 8     | 474.8281       | 447.4388                             | 4.7294                 | $68.2  \pm 4\rangle$ , $14.2  \pm 2\rangle$ , $13.8  \pm 3\rangle$                     | 0.0000 | 0.0000 | 0.5127               | 155.0002        |
| 9     | 661.5143       |                                      |                        |  |        |        |                      |                 |
| 10    | 665 8283       |                                      |                        |  |        |        |                      |                 |

Table 6.11 Electronic structure of **Pd-Pr** with Pr-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The tunnelling splitting energy for each quasi-doublet. State 4 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is positive

[4] Only the contributions that are greater than of equal to 5 % are included here.

|       |                |                                       |                        |   |                | g      | -factor <sup>[3]</sup> |                 |
|-------|----------------|---------------------------------------|------------------------|---|----------------|--------|------------------------|-----------------|
|       | Spin-free      | $RASSI\operatorname{-SO} state^{[1]}$ | $Tunnelling^{[2]}$     | $\Psi_i$ contribution <sup>[4]</sup>  |                |        |                        | a angle         |
| State | state energies | non-Kramers states                    | splitting              | (non-Kramers quasi-doublets)  | g <sub>x</sub> | $g_y$  | $g_z$                  | $g_z$ angle (°) |
|       | $(cm^{-1})$    | $(cm^{-1})$                           | $(cm^{-1})$            | (%) $\left \pm m_{j}\right\rangle$  |                |        |                        | ()              |
| 0     | 0.0000         | 0.0000                                | 40 6138 <sup>[5]</sup> | 43.8 $ \pm2 angle$ , 34.8 $ \pm4 angle$ , 15.8 $ \pm1 angle$                          | 0.0000         | 0 0000 | 3 1017                 | 0.000           |
| 1     | 9.1929         | 40.6138                               | 40.0130                | $58.8 \pm4 angle$ , $33.4 \pm2 angle$   | 0.0000         | 0.0000 | 5.1917                 | 0.0000          |
| 2     | 39.3922        | 92.8154                               | —                      | $45\left \pm3 ight angle$ , $36.4\left \pm1 ight angle$ , $14.4\left \pm2 ight angle$ | -              | _      | _                      | —               |
| 2     | 52 4602        | 106 5711                              |                        | $62.8 \pm3 angle, 23.4 \pm1 angle, 7.4 \pm2 angle$                                    |                |        |                        |                 |
| 3     | 52.4002        | 120.5711                              | 3.6911                 | $6.4\ket{\pm4}$   | 0.0000         | 0.0000 | 2.4472                 | 153.1923        |
| 4     | 63.2928        | 130.2622                              |                        | 54.8 $ 0\rangle$ , 34 $ \pm4\rangle$ , 8.8 $ \pm1\rangle$                             |                |        |                        |                 |
| F     | 150 7600       | 186 7476                              |                        | $37.8 \pm2 angle$ , $21.8 \pm3 angle$ , $21.6 \pm4 angle$                             |                |        |                        |                 |
| 5     | 159.7000       | 100.7470                              | 16.3607 <sup>[5]</sup> | $17\left 0 ight angle$  | 0.0000         | 0.0000 | 2.8251                 | 4.6833          |
| 6     | 219.4877       | 203.1084                              |                        | $55.4 \pm2\rangle$ , 29.4 $ \pm4\rangle$  | ]              |        |                        |                 |
| 7     | 263.8542       | 237.8617                              | 34 8216 <sup>[5]</sup> | 55.4 $ \pm1 angle$ , 34.6 $ \pm3 angle$   | 0.0000         | 0 0000 | 2 6708                 | 106 1310        |
| Q     | 308 8300       | 272 6823                              | 54.0210                | $46.2 \pm1 angle$ , 23.6 $ \pm3 angle$ , 21.2 $ 0 angle$                              | 0.0000         | 0.0000 | 2.0790                 | 100.1319        |
| 0     | 500.0200       | 212.0033                              |                        | $7.4\ket{\pm4}$   |                |        |                        |                 |
| 9     | 372.9420       |                                       |                        |   |                |        |                        |                 |
| 10    | 425.6211       |                                       |                        |   |                |        |                        |                 |
| 9     | 439.2472       |                                       |                        |   |                |        |                        |                 |
| 10    | 471.9395       |                                       |                        |   |                |        |                        |                 |

Table 6.12 Electronic structure of Pd-Pm with Pm-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The tunnelling splitting energy for each quasi-doublet. State 2 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is positive

[4] Only the contributions that are greater than of equal to 5 % are included here.

|       |                |                               |                        |   |        | Į      | g-factor <sup>[3]</sup> |              |
|-------|----------------|-------------------------------|------------------------|---|--------|--------|-------------------------|--------------|
|       | Spin-free      | RASSI-SO state <sup>[1]</sup> | $Tunnelling^{[2]}$     | $\Psi_i$ contribution <sup>[4]</sup>                                  |        |        |                         | a angla      |
| State | state energies | non-Kramers states            | splitting              | (non-Kramers quasi-doublets)  | $g_x$  | $g_y$  | $g_z$                   | $g_z$ aligie |
|       | $(cm^{-1})$    | $(cm^{-1})$                   | $(cm^{-1})$            | (%) $\left \pm m_{j} ight angle$                                      |        |        |                         | ()           |
| 0     | 0.0000         | 0.0000                        | 0 7011                 | $97.2\ket{\pm6}$  | 0 0000 | 0 0000 | 17 7370                 | 0.0000       |
| 1     | 59.3402        | 0.7011                        | 0.7011                 | $98\ket{\pm6}$  | 0.0000 | 0.0000 | 11.1510                 | 0.0000       |
| 2     | 79.7520        | 109.5224                      | 18 2051 <sup>[5]</sup> | 64.4 $ \pm5 angle$ , 18 $ \pm3 angle$ , 14.4 $ \pm1 angle$            | 0.0000 | 0 0000 | 12 27/2                 | 23 1151      |
| 3     | 429.4518       | 127.8175                      | 10.2931                | $\overline{77.4 \ket{\pm 5}}$ , $7.8 \ket{\pm 3}$ , $7.2 \ket{\pm 4}$ | 0.0000 | 0.0000 | 13.3743                 | 23.4431      |
| Λ     | 442 6765       | 160 5367                      |                        | $32.6  \pm 4 \rangle$ , $31  \pm 3 \rangle$ , $17.2  0 \rangle$       |        |        |                         |              |
| 4     | 442.0705       | 100.3307                      | —                      | $14.2\ket{\pm5}$  |        | _      | _                       | _            |
| 5     | 481 8200       | 218 0061                      |                        | 31.6 $ \pm5 angle$ , 26 $ \pm1 angle$ , 20.4 $ \pm3 angle$            |        |        |                         |              |
| J     | 401.0209       | 210.9001                      | 22.3016 <sup>[5]</sup> | $16.6 \ket{\pm 4}$  | 0.0000 | 0.0000 | 8.8157                  | 136.7173     |
| 6     | 689 0823       | 241 2077                      |                        | 68 $ \pm4 angle$ , 13.6 $ \pm1 angle$ , 8 $ \pm2 angle$               |        |        |                         |              |
|       | 005.0025       | 241.2011                      |                        | $6 \pm3 angle$  |        |        |                         |              |
| 7     |                | 321.1357                      | 4 1310                 | $48.4  \pm 4  angle$ , $47.6  \pm 2  angle$                           | 0 0000 | 0 0000 | 14 1185                 | 142 2483     |
| 8     |                | 325.2676                      | 4.1315                 | 84.8 $ \pm3 angle$ , 5.8 $ \pm5 angle$ , 5.2 $ \pm1 angle$            | 0.0000 | 0.0000 | 14.1105                 | 142.2405     |
| 9     |                | 399.8550                      | 0 7326                 | 69.9 $ 0 angle$ , 11.8 $ \pm2 angle$ , 10.2 $ \pm4 angle$             | 0.0000 | 0 0000 | 15 1/00                 | 151 /1/0     |
| 10    |                | 400.5876                      | 0.7520                 | 83.6 $ \pm1 angle$ , 6.6 $ \pm2 angle$                                | 0.0000 | 0.0000 | 13.1400                 | 131.4149     |
| 11    |                | 441 1367                      |                        | 47 $ \pm3 angle$ , 41 $ \pm1 angle$ , 5.5 $ 0 angle$                  |        |        |                         |              |
| 11    |                | 441.1307                      | 0.2277                 | $5.2\ket{\pm2}$   | 0.0000 | 0.0000 | 14.6732                 | 135.5423     |
| 12    |                | 441.3644                      |                        | $\overline{78.2 \pm2}$ , $9.2 \pm4\rangle$ , $8.8 \pm1\rangle$        |        |        |                         |              |

Table 6.13 Electronic structure of Pd-Tb with Tb-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The tunnelling splitting energy for each quasi-doublet. State 4 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is negative

 $\left[4\right]$  Only the contributions that are greater than of equal to 5 % are included here.

For each non-Kramers system, the RASSI-SO calculation allows the retrieval of the low-lying excited states relevant for the understanding of any possible slow magnetic relaxation. The extracted wavefunction contribution to each of the SO states shows that Pd-Pr and **Pd-Pm** have significant contribution of lower  $m_i$  states to their ground state energy (Table 6.11 and 6.12), a situation that rarely favours the observation of SMM behaviour. Note that only those wavefunction contributing up to 5% and above for the non-Kramers ions have been included in the tables. In general, the SO interaction is over 10 order of magnitude higher than the ligand field interaction, but the inhomogenous electric field (crystal-field) can break up the coupling of  $\mathbf{L}$  and  $\mathbf{S}$  vectors such that J is no longer a good quantum number. In addition, the previously degenerate 2L+1 sublevels of a given L in a free ion may be split by the crystal-field leading to a diminished contribution of the orbital motion to the magnetic moment. The implication is that the smaller the SO interaction in the first place, the higher the overall effect of the diminishing contribution to the magnetic moment making Pd-Pr and Pd-Pm more susceptible to quenching of the orbital angular moment. Both do not posses quasi-doublet at the ground state, making it more difficult for them to show SMM behaviour.

The later members of the series show highly improved tunnelling splitting at the ground state which should favour the observation of SMM behaviour. However, reports show that the non-Kramers **Pt-Ln** systems (**Pt-Tb** and **Pt-Ho**) showed SMM behaviour while the non-Kramers **Pd-Ln** did not despite having smaller tunnelling splitting compared to those of the **Pd-Pr** and **Pd-Pm**. Again, the established relationship between the tunnelling split and the wavefunction contribution is valid when the **Pd-Ln** and **Pt-Ln** are compared for the same lanthanide ion. **Pd-Tb** has a tunnelling splitting of 0.7011 cm<sup>-1</sup> and a 97.2%  $|\pm 6\rangle$  while **Pt-Tb** with a lower tunnelling split of 0.0229 cm<sup>-1</sup> has a 99%  $|\pm 6\rangle$  contribution. In the same way, the **Pt-Ho** tunnelling split of 0.3840 cm<sup>-1</sup> which is lower than the 2.7162 cm<sup>-1</sup> value for the **Pd-Ho** has a 59.2%  $|\pm 8\rangle$  compare to the 50.8%  $|\pm 8\rangle$  for **Pd-Ho**.

|       |                |                                |                    |   |        | g      | -factor <sup>[3]</sup> |              |
|-------|----------------|--------------------------------|--------------------|---|--------|--------|------------------------|--------------|
|       | Spin-free      | $RASSI\text{-}SO\ state^{[1]}$ | $Tunnelling^{[2]}$ | $\Psi_i$ contribution $^{[4]}$  |        |        |                        | a angla      |
| State | state energies | non-Kramers states             | splitting          | (non-Kramers quasi-doublets)  | $g_x$  | $g_y$  | $g_z$                  | $g_z$ aligie |
|       | $(cm^{-1})$    | $(cm^{-1})$                    | $(cm^{-1})$        | (%) $\left \pm m_{j}\right\rangle$  |        |        |                        | ()           |
| 0     | 0.0000         | 0.0000                         | 0 0220             | $99\ket{\pm6}$  | 0.0000 | 0 0000 | 17 9573                | 0.0000       |
| 1     | 119.2909       | 0.0229                         | 0.0229             | $99 \pm 6\rangle$   | 0.0000 | 0.0000 | 11.0515                | 0.0000       |
| 2     | 315.0178       | 198.2042                       | 1 7057             | 91 $ \pm5 angle$ , 6.8 $ \pm3 angle$  | 0.0000 | 0.0000 | 14 1004                | 0 2027       |
| 3     | 409.8848       | 199.9299                       | 1.7237             | $95 \pm 3 angle$  | 0.0000 | 0.0000 | 14.1904                | 0.3037       |
| 4     | 413.1363       | 261.1117                       | 0.7546             | $41.5  0\rangle$ , $30.2  \pm 2\rangle$ , $27.4  \pm 4\rangle$                    | 0.0000 | 0.0000 | 15 5104                | 20 2200      |
| 5     | 497.9469       | 270.8663                       | 9.7540             | $\overline{71.4\left \pm1 ight angle}$ , $24.8\left \pm3 ight angle$              | 0.0000 | 0.0000 | 15.5104                | 30.2209      |
| 6     | 723.0798       | 298.8609                       | _                  | 50.2 $ \pm2 angle$ , 40.2 $ \pm4 angle$   | _      | _      | _                      | _            |
| 7     |                | 201 7501                       |                    | $28\left \pm4 ight angle,\ 26.8\left \pm1 ight angle,\ 24.4\left \pm3 ight angle$ |        |        |                        |              |
| 1     |                | 521.7591                       | 6.4478             | $17\ket{\pm2}$  | 0.0000 | 0.0000 | 10.1351                | 165.1560     |
| 8     |                | 328.2069                       |                    | $52.8  \pm 4\rangle$ , $26  \pm 1\rangle$ , $13.8  \pm 3\rangle$                  |        |        |                        |              |
| 9     |                | 355.0795                       | 14 2201 [5]        | 48.2 $ 0 angle$ , 24 $ \pm4 angle$ , 21.4 $ \pm2 angle$                           | 0.0000 | 0.0000 | 12 0/60                | 94 0655      |
| 10    |                | 369.4096                       | 14.5501            | $45.6 \pm3 angle$ , $45.4 \pm1 angle$ , $7.8 \pm2 angle$                          | 0.0000 | 0.0000 | 13.0400                | 64.0055      |
| 11    |                | 200 2000                       |                    | $36.8 \pm2 angle$ , $35.6 \pm3 angle$ , $13.8 \pm4 angle$                         |        |        |                        |              |
| 11    |                | 399.3220                       | 2.8952             | $7\ket{\pm 1}$  | 0.0000 | 0.0000 | 15.7903                | 164.7292     |
| 12    |                | 402 2172                       |                    | $40 \pm3 angle$ , $32.6 \pm2 angle$ , $14 \pm1 angle$                             | ]      |        |                        |              |
| 12    |                | TU2.2112                       |                    | $10.6 \ket{\pm 4}$  |        |        |                        |              |

Table 6.14 Electronic structure of Pt-Tb with Tb-Lu (site 1) centres calculated with RASSCF-RASSI-SO

[2] The tunnelling splitting energy for each quasi-doublet. State 6 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is negative

[4] Only the contributions that are greater than of equal to 5 % are included here.

|       |                 |                                |                        |  |        | g      | $-factor^{[3]}$ |             |
|-------|-----------------|--------------------------------|------------------------|--|--------|--------|-----------------|-------------|
|       | Spin-free       | $RASSI\text{-}SO\ state^{[1]}$ | $Tunnelling^{[2]}$     | $\Psi_i$ contribution <sup>[4]</sup>                         |        |        |                 | a angla     |
| State | state energies  | non-Kramers states             | splitting              | (non-Kramers quasi-doublets)                                 | $g_x$  | $g_y$  | $g_z$           | $g_z$ angle |
|       | $(cm^{-1})$     | $(cm^{-1})$                    | $(cm^{-1})$            | (%) $\left \pm m_{j} ight angle$                             |        |        |                 | ()          |
| 0     | 0.0000          | 0.0000                         |                        | 50.8 $ \pm8 angle$ , 13.6 $ \pm5 angle$ , 11.8 $ \pm6 angle$ |        |        |                 |             |
| 0     | 0.0000          | 0.0000                         | 2.7162                 | $11\ket{\pm7}$ , $10\ket{\pm4}$                              | 0.0000 | 0.0000 | 16.9006         | 0.0000      |
| 1     | 22 8547         | 2 7162                         |                        | $61 \pm8 angle,\ 12.2 \pm7 angle,\ 10.6 \pm5 angle$          |        |        |                 |             |
| T     | 22.0347         | 2.7102                         |                        | $10 {\pm}6 angle$ , $5 {\pm}4 angle$                         |        |        |                 |             |
| 2     | <i>A</i> 1 0170 | 16 8442                        |                        | $36.2 \pm5 angle,\ 23 \pm4 angle,\ 14.6 \pm6 angle$          |        |        |                 |             |
| 2     | 41.9170         | 10.0442                        | 5.3882                 | 11.4 $ \pm3 angle$ , 7.6 $ \pm8 angle$                       | 0.0000 | 0.0000 | 16.0145         | 21.0867     |
| 3     | 70 2634         | 22 2324                        |                        | 31.6 $ \pm5 angle$ , 22.4 $ \pm4 angle$ , 19 $ \pm8 angle$   |        |        |                 |             |
| 5     | 79.2034         | 22.2324                        |                        | $12.2 \pm6 angle$ , $8 \pm3 angle$ , $5.4 \pm7 angle$        |        |        |                 |             |
| Λ     | 131 2111        | 75 6541                        |                        | 31 $ \pm3 angle$ , 28.8 $ \pm4 angle$ , 11.8 $ \pm6 angle$   |        |        |                 |             |
| 4     | 191.2111        | 15.0541                        | 0.3896                 | 9.8 $ \pm2 angle$ , 6.6 $ \pm7 angle$ , 5.2 $ \pm8 angle$    | 0.0000 | 0.0000 | 13.9375         | 11.3344     |
| 5     | 171 2407        | 76 0437                        |                        | $34.2 \pm4 angle$ , $24.2 \pm3 angle$ , $14.8 \pm6 angle$    |        |        |                 |             |
| 5     | 171.2407        | 10.0431                        |                        | $6.3\ket{0}$   |        |        |                 |             |
| 6     | 202 3510        | 04 2100                        |                        | 26.6 $ \pm3 angle$ , 22.8 $ \pm1 angle$ , 15.2 $ \pm4 angle$ |        |        |                 |             |
| 0     | 202.3319        | 94.2199                        | 15.6431 <sup>[5]</sup> | 14.4 $ \pm5 angle$ , 11.6 $ \pm6 angle$                      | 0.0000 | 0.0000 | 12.2120         | 102.4875    |
| 7     | 242.1343        | 109.8630                       |                        | 60.6 $ \pm2 angle$ , 8 $ \pm8 angle$ , 5 $ \pm3 angle$       |        |        |                 |             |
| 8     | 302 2764        | 150 6075                       |                        | 50.6 $ \pm3 angle$ , 10.6 $ \pm5 angle$ , 10.6 $ \pm7 angle$ |        |        |                 |             |
| 0     | 502.2704        | 150.0975                       | _                      | $9.4\left \pm4 ight angle,\ 8\left \pm6 ight angle$          |        | _      | _               | _           |
| 0     | 343 0361        | 172 1206                       |                        | $36.2 \pm7 angle$ , $18 \pm2 angle$ , $17.2 \pm8 angle$ ,    |        |        |                 |             |
| 9     | 5-5.0301        | 112.1290                       | 8.3714                 | 12.4 $ \pm6 angle$ , 7.2 $ \pm4 angle$                       | 0.0000 | 0.0000 | 14.1813         | 3.2747      |
| 10    | 347 5230        | 180 5010                       |                        | $55 \pm 7 angle$ , $15.8 \pm 8 angle$ , $7.8 \pm 2 angle$    |        |        |                 |             |
| 10    | JTI.J2J0        | 100.3010                       |                        | $7.2 \pm6 angle$ , $5.2 \pm4 angle$                          |        |        |                 |             |

Table 6.15 Electronic structure of Pd-Ho with Ho-Lu (site 1) centres calculated with RASSCF-RASSI-SO

Continued on next page

| 11 | 361 3183 | 100 1612 |        | 46.4 $ \pm1\rangle$ , 15 $ \pm6\rangle$ , 10.6 $ \pm3\rangle$                       |        |        |         |          |
|----|----------|----------|--------|---|--------|--------|---------|----------|
| 11 | 501.5105 | 190.1012 | 9.6369 | 10.3 $ 0 angle$ , 7.4 $ \pm2 angle$ , 6.8 $ \pm4 angle$                             | 0.0000 | 0.0000 | 14.1720 | 47.0366  |
| 12 | 368 2300 | 100 7081 |        | 42.4 $ \pm2\rangle$ , 14 $ \pm7\rangle$ , 11.4 $ \pm3\rangle$                       |        |        |         |          |
| 12 | 500.2500 | 199.7901 |        | $10.2\left \pm1 ight angle$ , $7\left \pm5 ight angle$ , $5.2\left \pm4 ight angle$ |        |        |         |          |
| 12 |          | 241 0622 |        | 25.8 $ 0 angle$ , 19.6 $ \pm5 angle$ , 18.4 $ \pm6 angle$                           |        |        |         |          |
| 15 |          | 241.0022 | 1.2934 | 13.2 $ \pm2 angle$ , 12.8 $ \pm7 angle$ , 5.8 $ \pm4 angle$                         | 0.0000 | 0.0000 | 17.6505 | 124.5340 |
| 1/ |          | 242 2556 |        | $\overline{34 \pm1\rangle}$ , 22.6 $ \pm6\rangle$ , 14.4 $ \pm5\rangle$             | ]      |        |         |          |
| 14 |          | 242.3330 |        | $11\left \pm7 ight angle$ , $10.4\left \pm4 ight angle$                             |        |        |         |          |
| 15 |          | 261 7046 |        | 52.4 $ \pm1\rangle$ , 11.4 $ \pm2\rangle$ , 10 $ \pm5\rangle$                       |        |        |         |          |
| 15 |          | 201.7040 | 0.5969 | $8.6\left \pm6 ight angle$ , $7\left \pm7 ight angle$ , $5.2\left \pm3 ight angle$  | 0.0000 | 0.0000 | 17.1558 | 123.0950 |
| 16 |          | 262 2015 |        | $\boxed{38.4 0\rangle, 14.2 \pm6\rangle, 12.8 \pm2\rangle}$                         | 1      |        |         |          |
| 10 |          | 202.3015 |        | 7.4 $ \pm5 angle$ , 7.2 $ \pm4 angle$ , 6.8 $ \pm3 angle$                           |        |        |         |          |

[2] The tunnelling splitting energy for each quasi-doublet. State 8 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is negative

[4] Only the contributions that are greater than of equal to 5 % are included here.

|       |                |                         |                    |   |        | g      | -factor <sup>[3]</sup> |             |
|-------|----------------|-------------------------|--------------------|---|--------|--------|------------------------|-------------|
|       | Spin-free      | RASSI-SO state $^{[1]}$ | $Tunnelling^{[2]}$ | $\Psi_i$ contribution $^{[4]}$  |        |        |                        | a angle     |
| State | state energies | non-Kramers states      | splitting          | (non-Kramers quasi-doublets)  | $g_x$  | $g_y$  | $g_z$                  | $g_z$ angle |
|       | $(cm^{-1})$    | $(cm^{-1})$             | $(cm^{-1})$        | (%) $ \pm m_j angle$  |        |        |                        | ()          |
| 0     | 0.0000         | 0.0000                  |                    | 59.2 $ \pm8 angle$ , 10 $ \pm7 angle$ , 7.6 $ \pm4 angle$                             |        |        |                        |             |
| 0     | 0.0000         | 0.0000                  | 0.3840             | $7 {\pm}1 angle$ , $6.6 {\pm}2 angle$ , $5.6 {\pm}5 angle$                            | 0.0000 | 0.0000 | 15.7119                | 0.0000      |
| 1     | 11 5146        | 0 3840                  |                    | $63 \pm 8 angle$ , $12.6 \pm 7 angle$ , $9.8 \pm 4 angle$                             |        |        |                        |             |
| T     | 11.5140        | 0.3040                  |                    | $5.6\ket{\pm2}$   |        |        |                        |             |
|       |                |                         |                    | $25\left \pm2 ight angle$ , $18.4\left \pm3 ight angle$ , $17\left \pm1 ight angle$   |        |        |                        |             |
| 2     | 49.2394        | 13.3842                 | 2 2717             | 16.5 $ 0 angle$ , 6.6 $ \pm5 angle$ , 5.4 $ \pm8 angle$                               | 0.0000 | 0 0000 | 12 6992                | 11 0912     |
|       |                |                         | 2.3717             | $5\ket{\pm4}$   | 0.0000 | 0.0000 | 13.0002                | 11.0015     |
| 3     | 53 2100        | 15 7550                 |                    | $28.6 \pm3 angle$ , $24.8 \pm1 angle$ , $13 \pm2 angle$                               |        |        |                        |             |
| J     | 55.2109        | 15.7559                 |                    | $12.8\left \pm8 ight angle$ , $9.6\left \pm7 ight angle$                              |        |        |                        |             |
|       |                |                         |                    | $22\left \pm3 ight angle$ , $19.5\left 0 ight angle$ , $15.4\left \pm6 ight angle$    |        |        |                        |             |
| 4     | 81.9196        | 28.8194                 | 8 5250             | 15.4 $ \pm2 angle$ , 10.4 $ \pm1 angle$ , 7.2 $ \pm5 angle$                           | 0 0000 | 0 0000 | 11 6354                | 100 1416    |
|       |                |                         | 0.3230             | $5\ket{\pm4}$   | 0.0000 | 0.0000 | 11.0354                | 100.1410    |
| 5     | 96 0362        | 37 3111                 |                    | $36 \pm4 angle, 25.2 \pm1 angle, 13.2 \pm8 angle$                                     |        |        |                        |             |
| 5     | 90.0302        | 57.5444                 |                    | 9.2 $ \pm2 angle$ , 8.4 $ \pm3 angle$   |        |        |                        |             |
| 6     | 115.5138       | 54.1340                 | 6 7777             | 37.8 $ \pm2 angle$ , 34.2 $ \pm5 angle$ , 16.6 $ \pm6 angle$                          | 0.0000 | 0 0000 | 11 2270                | 84 7504     |
| 7     | 192 7202       | 60 0117                 | 0.7777             | $\overline{33.4 \pm3\rangle, 32 \pm4\rangle, 10.6 \pm1\rangle}$                       | 0.0000 | 0.0000 | 11.5572                | 84.7504     |
| 1     | 103.7393       | 00.9117                 |                    | $8.6 {\pm}8 angle$ , $6.2 {\pm}5 angle$   |        |        |                        |             |
| 8     | 242 2641       | 108 1325                |                    | $28\left \pm6 ight angle$ , $24.6\left \pm7 ight angle$ , $20.8\left \pm1 ight angle$ |        |        |                        |             |
| 0     | 272.2041       | 100.1323                |                    | $8.8\left \pm4 ight angle$ , $5.6\left \pm2 ight angle$                               |        | _      |                        | —           |
| 0     | 271 0520       | 101 5907                |                    | $28.2  \pm 6\rangle$ , $25  \pm 7\rangle$ , $16.8  \pm 2\rangle$ ,                    |        |        |                        |             |
| 9     | 211.0339       | 121.3007                | 4.6341             | 9.6 $ 0 angle$ , 5.8 $ \pm4 angle$ , 5.6 $ \pm1 angle$                                | 0.0000 | 0.0000 | 11.2525                | 109.5095    |
|       |                |                         |                    |   |        |        |                        |             |

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| 10          | 276 6466       | 106 0147   |        | 34 $ \pm5 angle$ , 20.1 $ 0 angle$ , 20 $ \pm1 angle$                            |        |        |         |          |  |  |  |  |
|-------------|----------------|--|--------|--|--------|--------|---------|----------|--|--|--|--|
| 10 270.0400 |                | 120.2147   |        | 12.4 $ \pm3 angle$ , 6.4 $ \pm7 angle$   |        |        |         |          |  |  |  |  |
|             |                |  |        | $25.8 \pm4 angle$ , $17.6 \pm1 angle$ , $16.2 \pm3 angle$                        |        |        |         |          |  |  |  |  |
| 11          | 282.0339       | 171.0182   | 1 6797 | 14.8 $ \pm7 angle$ , 6.2 $ \pm2 angle$ , 6.2 $ \pm5 angle$                       | 0.0000 | 0 0000 | 15 0072 | 61 5116  |  |  |  |  |
|             |                |  | 1.0707 | 5.2 $ 0 angle$ , 5.2 $ \pm7 angle$   | 0.0000 | 0.0000 | 15.9975 | 01.5110  |  |  |  |  |
| 10          | 200 0100       | 172 6070   |        | $28.4 \pm5\rangle$ , 19.4 $ \pm2\rangle$ , 15.6 $ \pm4\rangle$                   |        |        |         |          |  |  |  |  |
| 12          | 209.0100       | 172.0970   |        | 12.2 $ 0 angle$ , 12.2 $ \pm7 angle$ , 5.4 $ \pm6 angle$                         |        |        |         |          |  |  |  |  |
| 12          | 10             | 104 0712   |        | $23.6 \pm2 angle$ , $23.2 \pm4 angle$ , $17.4 \pm5 angle$                        |        |        |         |          |  |  |  |  |
| 15          |                | 194.2715   | 2.0430 | 13.8 $ \pm6 angle$ , 13 $ \pm1 angle$ , 7.2 $ \pm3 angle$                        | 0.0000 | 0.0000 | 17.2896 | 111.2829 |  |  |  |  |
|             |                |  |        | $\overline{37.4  \pm 3\rangle, 15.4  \pm 5\rangle, 7.6  \pm 4\rangle}$           |        |        |         |          |  |  |  |  |
| 14          |                | 196.3143   |        | $7\left \pm1 ight angle$ , $7\left \pm2 ight angle$ , $6.8\left \pm7 ight angle$ |        |        |         |          |  |  |  |  |
|             |                |  |        | $5\ket{\pm 6}$   |        |        |         |          |  |  |  |  |
| 15          |                | 205 5154   |        | $38.2 \pm6 angle$ , $33.6 \pm7 angle$ , $13.6 \pm5 angle$                        |        |        |         |          |  |  |  |  |
| 15          |                | 205.5154   | 1.4078 | $10\ket{\pm8}$   | 0.0000 | 0.0000 | 18.1735 | 11.0635  |  |  |  |  |
| 16          |                | 206 0222   |        | $\overline{34 \pm6}$ , $33.2 \pm7\rangle$ , $9.8 \pm5\rangle$                    |        |        |         |          |  |  |  |  |
| 10          |                | 200.9232   |        | $9\ket{\pm8}$ , $8\ket{\pm4}$  |        |        |         |          |  |  |  |  |
| [1] Ea      | ich energy val | [1] Each energy value represents a single states (non-Kramers). Two states within a lager row represent possible quasi-doublets. |        |  |        |        |         |          |  |  |  |  |

[1] Each energy value represents a single states (non-Kramers). Two states within a lager row represent possible quasi-dol [2] The tunnelling splitting energy for each quasi-doublet. State 8 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is positive

[4] Only the contributions that are greater than of equal to 5 % are included here.

|                      |             |                                |                    |   |        | g      | -factor <sup>[3]</sup> |              |
|----------------------|-------------|--------------------------------|--------------------|---|--------|--------|------------------------|--------------|
|                      | Spin-free   | $RASSI\text{-}SO\ state^{[1]}$ | $Tunnelling^{[2]}$ | $\Psi_i$ contribution <sup>[4]</sup>  |        |        |                        | a anglo      |
| State state energies |             | non-Kramers states             | splitting          | (non-Kramers quasi-doublets)  | $g_x$  | $g_y$  | $g_z$                  | $g_z$ aligie |
|                      | $(cm^{-1})$ | $(cm^{-1})$                    | $(cm^{-1})$        | (%) $\left \pm m_{j} ight angle$  |        |        |                        | ()           |
| 0                    | 0.0000      | 0.0000                         | 0 1251             | $98.4\ket{\pm6}$  | 0.0000 | 0 0000 | 13 9503                | 0.0000       |
| 1                    | 2.1424      | 0.1251                         | 0.1251             | $98.4 \pm6 angle$   | 0.0000 | 0.0000 | 13.0505                | 0.0000       |
|                      | 212 0072    | 226 0208                       |                    | 33.8 $ \pm1 angle$ , 26.2 $ \pm3 angle$ , 20.8 $ \pm2 angle$                          |        |        |                        |              |
| Ζ                    | 213.0075    | 220.0296                       | 4.8684             | 13.9 0 angle  | 0.0000 | 0.0000 | 13.0338                | 81.5482      |
| 3                    | 235 3774    | 230 8082                       |                    | $33.2 \pm2 angle$ , $27.2 \pm1 angle$ , $19.8 0 angle$                                |        |        |                        |              |
| 5                    | 255.5774    | 230.0902                       |                    | 12.6 $ \pm3 angle$ , 6.6 $ \pm4 angle$  |        |        |                        |              |
| 4                    | 303.3393    | 274.4508                       | 3 4702             | 77 $ \pm5 angle$ , 8.6 $ \pm3 angle$ , 5.2 $ \pm2 angle$                              | 0,0000 | 0 0000 | 10 0316                | 0.0026       |
| 5                    | 322.0052    | 277.9211                       | 5.4702             | $75.6 \pm5 angle$ , $21.4 \pm4 angle$   | 0.0000 | 0.0000 | 10.9510                | 0.9920       |
| 6                    | 3/2 0712    | 302 0045                       |                    | $39\left \pm3 ight angle$ , $29\left \pm4 ight angle$ , $13.2\left \pm5 ight angle$   |        |        |                        |              |
| 0                    | 545.9715    | 502.0945                       | —                  | 9.6 $ \pm1 angle$ , 7.4 $ \pm2 angle$   |        | —      | _                      | _            |
| 7                    | 407 3520    | 331 2562                       |                    | 34.8 $ \pm3 angle$ , 28 $ \pm4 angle$ , 14.6 $ \pm2 angle$                            |        |        |                        |              |
| '                    | 407.3320    | 551.2502                       | 10.5219            | 12.2 $ \pm5 angle$ , 9.4 $ \pm1 angle$  | 0.0000 | 0.0000 | 8.4606                 | 103.3093     |
| 8                    | 412.2106    | 341.7781                       |                    | 44.2 $ \pm4\rangle$ , 32.8 $ \pm2\rangle$ , 13.4 $ \pm1\rangle$                       |        |        |                        |              |
| 0                    | 475 4052    | 103 2483                       |                    | $35\left \pm3 ight angle$ , $22.2\left \pm4 ight angle$ , $21.8\left \pm2 ight angle$ |        |        |                        |              |
| 9                    | 475.4952    | 403.2403                       | 1.7121             | $9\left \pm1 ight angle$ , 7.8 $\left \pm5 ight angle$                                | 0.0000 | 0.0000 | 13.0503                | 150.6263     |
| 10 402 7062          |             | 404 9604                       |                    | $31 \pm4 angle$ , $30.8 \pm3 angle$ , $20.6 \pm2 angle$                               |        |        |                        |              |
| 10                   | 403.7003    | 404.9004                       |                    | 9.6 $ \pm1 angle$ , 5.8 $ \pm5 angle$   |        |        |                        |              |
| 11                   |             | 472.0313                       | 1 3705             | $\overline{53\left 0 ight angle}$ , $41.8\left \pm2 ight angle$                       | 0.0000 | 0.0000 | 12 /202                | 126 2167     |
| 12                   |             | 473.4108                       | 1.3793             | 85.2 $ \pm1 angle$ , 10 $ \pm3 angle$   | 0.0000 | 0.0000 | 10.4020                | 120.3107     |

Table 6.17 Electronic structure of Pd-Tm with Tm-Lu (site 1) centres calculated with RASSCF-RASSI-SO

Continued on next page

[2] The tunnelling splitting energy for each quasi-doublet. State 6 is singlet and so no tunnelling splitting was calculated.

[3] The sign of  $g_x \times g_y \times g_z$  is negative

[4] Only the contributions that are greater than of equal to 5 % are included here.

The differences in the tunnelling splitting gap is expected to have consequences for the slow magnetic relaxation of the systems and might have contributed to the discrepancies observed in the slow magnetic relaxation of the non-Kramer **Pd-Ln** and **Pt-Ln**. We will look at this in more detail under the magnetic property section below.

## 6.4.2.2 Anisotropic *g*-factor of the non-Kramers ions of the Pd-Ln and Pt-Ln series

Recall that it was mentioned in the introductory chapter that many factors contribute to the magnetic properties of SMM. This means that while one factor might favour the observation of SMM behaviour, the other might not. However, there are criteria which must be met for some other factors to make significant contribution. One of such criteria is the anisotropic g-factor. Although, there are materials with anisotropic g-factors but no SMM behaviour but no report has shown the lack of anisotropic g-factor for lanthanide-based SMM. The  $g_z$  values at the ground and excited states for all non-Kramers doublets are non-zero while the  $g_x = g_y = 0$  for all ground and excited states at the same time for all the non-Kramers system reported in this thesis. The anisotropic g-factors (Figure 6.3a) follow similar trend observed for the Kramers ions except for the singlet excited states for which no  $g_z$  was computed but plotted at a constant value of 2.0 in Figure 6.3a. The product of  $g_x \times g_y \times g_z$ is positive for Pd-Pr, Pd-Pm and Pt-Ho but negative for Pd-Tb, Pt-Tb, Pd-Ho and **Pd-Tm**. The angular separation of the ground  $g_z$  axis and that of the first excited state axis shows similar trend reported for the Kramers ions in which the angular separation is lower for the Pt-Ln system compare to the Pd-Ln system of the same lanthanide (see Figure 6.3b. However, the trend for the earlier members of the Pd-Ln non-Kramers series differ from those of the Kramers. While the Kramers ions show a decreasing angle of separation as you move from left to right of the lanthanide series, a spike is observed on moving from Pd-Pr to Pd-Pm. It is not clear at this point while Pd-Pm shows such jump as no experimental data was found to support our result due to the radioactive nature of Pm<sup>3+</sup>.

Figure 6.3c summarises the RASSI-SO energies for all the non-Kramers systems investigated and shows clearly the large tunnelling splitting for **Pd-Pr** and **Pd-Pm**. The figure also shows the extent to which the quasi-doublets attempt to reach a true doublet both at the ground state as well as for the excited state. Having discussed the electronic properties of both the Kramers and non-Kramers ions, the next section will look at the contribution of the crystal-field to the observed splitting and the overall electronic structure discussed until now.





Fig. 6.3 (a)  $g_z$  values computed *ab initio* for the non-Kramers ions of the Pd-Ln and Pt-Ln series (b) The angular difference between the  $g_z$  axes of the ground state and the  $g_z$  axes of the first excited state computed *ab initio* for the non-Kramers ions of the Pd-Ln and Pt-Ln series. (c) The RASSI-SO energies computed for the non-Kramers ions of the Pd-Ln and Pt-Ln series

# 6.4.3 *Ab initio* crystal field parameters of the Kramers and non-Kramers Pd-Ln and Pt-Ln series

First, to ascertain which CFP is necessary to describe the **Pd-Ln** and **Pt-Ln** systems, the contributions of the extended Stevens operators to the CF were extracted and presented in Table 6.18 and 6.19. Generally, the lower the local site symmetry, the greater the number of the non-zero ZFS (crystal field) parameters needed to describe the system.[329]

The obtained results show that the local site symmetry is largely affected by the quadrupole moment approximation of the magnetic ion which grouped lanthanide ions into prolate, oblate and spherical forms (see Figure 6.4).[2] For example, although the Pd-Ln systems are isostructural, 99.15 % of the CF experienced by the Gd<sup>3+</sup> in Pd-Gd are contributed by the  $2^{nd}$  ranked operator.

|                     | Weighting (%)          |              |                       |         |                        |                        |                        |  |  |  |
|---------------------|------------------------|--------------|-----------------------|---------|------------------------|------------------------|------------------------|--|--|--|
|                     | Operator Ranks $(O_k)$ |              |                       |         |                        |                        |                        |  |  |  |
| $Tm	ext{-}Ln^{[1]}$ | <i>O</i> <sub>2</sub>  | $O_4$        | <i>O</i> <sub>6</sub> | $O_8$   | <i>O</i> <sub>10</sub> | <i>O</i> <sub>12</sub> | <i>O</i> <sub>14</sub> |  |  |  |
| Pd-Ce (site-1)      | 51.86398               | 48.13602     |                       |         |                        |                        |                        |  |  |  |
| Pd-Ce (site-2)      | 51.86404               | 48.13596     |                       |         |                        |                        |                        |  |  |  |
| Pd-Nd (site-1)      | 19.76067               | 27.26839     | 47.17107              | 5.79987 |                        |                        |                        |  |  |  |
| Pd-Nd (site-2)      | 19.76071               | 27.26835     | 47.1711               | 5.79984 |                        |                        |                        |  |  |  |
| Pd-Sm (site-1)      | 63.28724               | 36.71276     |                       |         |                        |                        |                        |  |  |  |
| Pd-Gd (site-1)      | 99.15418               | 0.83922      | 0.0066                |         |                        |                        |                        |  |  |  |
| Pd-Dy (site-1)      | 50.70304               | 29.93108     | 17.90045              | 0.86307 | 0.45091                | 0.1424                 | 0.00906                |  |  |  |
| Pt-Dy (site-1)      | 48.08429               | 37.38163     | 13.26621              | 0.86258 | 0.36584                | 0.03414                | 0.00531                |  |  |  |
| Pd-Er (site-1)      | 29.88723               | 29.68615     | 39.92017              | 0.21581 | 0.13747                | 0.15188                | 0.0013                 |  |  |  |
| Pt-Er (site-1)      | 28.92936               | 37.90949     | 32.54464              | 0.21173 | 0.27604                | 0.12656                | 0.00218                |  |  |  |
| Pd-Yb (site-1)      | 52.73156               | 33.14955     | 14.11889              |         |                        |                        |                        |  |  |  |
| [1] TM represent    | s either Pd            | or Pt. Ln is | the lanthan           | ide     |                        |                        |                        |  |  |  |

Table 6.18 Contributions of the ranks of the individual irreducible tensor operators of the crystal field parameters for Kramers ions of the Pd-Ln and Pt-Ln series

|               | Weighting (%) |                        |              |          |         |         |         |         |  |  |  |  |  |
|---------------|---------------|------------------------|--------------|----------|---------|---------|---------|---------|--|--|--|--|--|
|               |               | Operator Kanks $(O_k)$ |              |          |         |         |         |         |  |  |  |  |  |
| $Tm-Ln^{[1]}$ |               |                        |              |          |         |         |         |         |  |  |  |  |  |
| (site-1)      | 02            | 04                     | 06           | 08       | 010     | 012     | 014     | 016     |  |  |  |  |  |
| Pd-Pr         | 38.55485      | 35.10375               | 24.55518     | 1.78623  |         |         |         |         |  |  |  |  |  |
| Pd-Pm         | 28.2583       | 28.8801                | 34.04389     | 8.81772  |         |         |         |         |  |  |  |  |  |
| Pd-Tb         | 62.96618      | 29.17897               | 6.73922      | 0.88209  | 0.19924 | 0.03431 |         |         |  |  |  |  |  |
| Pt-Tb         | 56.86373      | 36.56594               | 5.22371      | 1.13946  | 0.17758 | 0.02958 |         |         |  |  |  |  |  |
| Pd-Ho         | 29.25883      | 26.71886               | 44.76535     | 0.48925  | 0.24571 | 0.51028 | 0.00674 | 0.00498 |  |  |  |  |  |
| Pt-Ho         | 28.5802       | 34.75124               | 35.97671     | 0.38372  | 0.1784  | 0.12741 | 0.00189 | 0.00042 |  |  |  |  |  |
| Pd-Tm         | 52.64427      | 26.9496                | 19.9375      | 0.27534  | 0.18371 | 0.00958 |         |         |  |  |  |  |  |
| [1] TM rep    | resents eithe | er Pd or Pt.           | Ln is the la | nthanide |         |         |         |         |  |  |  |  |  |

Table 6.19 Contributions of the ranks of the individual irreducible tensor operators of the crystal field parameters for non-Kramers ions of the Pd-Ln and Pt-Ln series

As you move from the spherical through the prolate to the oblate forms, the contribution from the 2<sup>nd</sup> rank to the CFP is highest for the spherical ion (Pd-Gd), followed by the two extreme cases of prolate and oblate forms (prolate – Pd-Sm, Pd-Yb and Pd-Tm; oblate – Pd-Ce and Pd-Tb, Pt-Tb Pd-Dy, Pt-Dy). The extreme cases are then followed by the less oblate Pd-Pr and less prolate Pd-Pm, Pd-Er & Pt-Er. Finally the mid point of the prolate and oblate (Pd-Ho, Pt-Ho and Pd-Nd) shows the least 2<sup>nd</sup> ranked contribution. This has allowed us to for the first time correlate the rank operator contribution to the quadrupole approximation of the lanthanide ions.



Fig. 6.4 Quadrupole approximations of the 4f-shell electron distribution for the tripositive lanthanides. Values are calculated using the total angular momentum quantum number (J), the Stevens coefficient of second order  $(\alpha)$  and the radius of the 4f shell squared  $\langle r^2 \rangle$ .[330] Europium is not depicted due to a J = 0 ground state. (Key: from left to right – extreme oblate  $\rightarrow$  mild oblate  $\rightarrow$  mild prolate  $\rightarrow$  extreme prolate  $\rightarrow$  spherical).[2, 331]

The rank operator weighting which is a measure of how much of the SO–CF splitting arises from the said operator shows that the 2<sup>nd</sup>, 4<sup>th</sup> and 6<sup>th</sup> ranked operators are mostly enough to fully describe the CF splitting of the Pd-Ln and Pt-Ln system with the exception of Pd-Ce and Pd-Sm which only needed 2<sup>nd</sup> and 4<sup>th</sup> ranked operators. Pd-Gd is spherical and so only needed the 2<sup>nd</sup> ranked operator. Using this information, the CFP arising from the respective rank operator necessary to describe the systems were extracted and presented in Table 6.20 and 6.21 for the Kramers and non-Kramers systems respectively. The rank operator contributions for the Pd-Ln and the Pt-Ln systems show that the 2<sup>nd</sup> ranked has a higher contribution to the Pd-Ln systems when compared with the Pt-Ln counterparts (i.e. Pd-Tb vs Pt-Tb, Pd-Dy vs Pt-Dy, Pd-Ho vs Pt-Ho and Pd-Er vs Pt-Er).

|   |    |           |           |           |           | В         | 9<br>k    |           |           |           |           |
|---|----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|   |    | Pd-Ce     | Pd-Ce     | Pd-Nd     | Pd-Nd     | Pd-Sm     | Pd-Dy     | Pt-Dy     | Pd-Er     | Pt-Er     | Pd-Yb     |
| k | q  | (site-1)  | (site-2)  | (site-1)  | (site-2)  | (site-1)  | (site-1)  | (site-1)  | (site-1)  | (site-1)  | (site-1)  |
|   |    | (J-Term)  |
| 2 | -2 | -100.5713 | -100.5708 | -47.3124  | -47.3124  | -10.6237  | 278.5403  | -40.3641  | -308.6055 | -178.4357 | 79.4840   |
| 2 | -1 | 74.2611   | 74.2606   | -873.1524 | -873.1524 | 646.9024  | -306.3611 | 546.1139  | 148.5343  | -154.1295 | 223.1539  |
| 2 | 0  | 320.6516  | 320.6511  | 104.7478  | 104.7494  | -142.2244 | 259.0938  | 181.5046  | -303.0221 | -175.1636 | -226.2746 |
| 2 | 1  | -33.8296  | -33.8294  | -63.3751  | -63.3736  | 52.2517   | -113.3795 | -452.9527 | 84.5145   | -28.4327  | 343.6118  |
| 2 | 2  | -224.8647 | -224.8650 | -10.1837  | -10.1822  | 248.1948  | -162.6881 | -212.3053 | -187.4132 | 383.5716  | 179.0019  |
| 4 | -4 | -748.2085 | -748.2101 | 12.4009   | 12.4009   | -79.2979  | 372.2969  | -76.3513  | -10.1351  | 49.3243   | -47.8574  |
| 4 | -3 | -473.8687 | -473.8718 | 1090.6615 | 1090.6615 | 1854.1562 | 165.8782  | -692.5669 | 170.4953  | 182.2070  | 571.0031  |
| 4 | -2 | -127.9184 | -127.9184 | -92.1995  | -92.1995  | 171.3256  | -230.2363 | 247.1281  | 111.7116  | -70.2702  | -88.7387  |
| 4 | -1 | 56.9961   | 56.9961   | 98.5889   | 98.5889   | 468.3187  | 227.7025  | -391.2158 | 13.9640   | 224.9998  | 314.8530  |
| 4 | 0  | -73.9163  | -73.9163  | 2.0611    | 2.0611    | 33.9357   | -16.5540  | 53.2094   | -103.8287 | -32.2072  | -36.3710  |
| 4 | 1  | 152.6522  | 152.6537  | -52.7983  | -52.7983  | 253.4701  | 18.0743   | 398.1415  | 61.0360   | 13.9640   | 234.5747  |
| 4 | 2  | 254.0018  | 254.0034  | 305.3165  | 305.3165  | -133.6957 | 84.2905   | 156.5877  | 52.7027   | 482.6572  | -10.6087  |
| 4 | 3  | 196.2434  | 196.2387  | 1176.4717 | 1176.4717 | 112.5019  | 434.2901  | -148.9863 | -288.9637 | 39.4144   | -170.8880 |
| 4 | 4  | -239.6331 | -239.6300 | -260.1442 | -260.1442 | -50.6876  | 381.4185  | -280.5740 | 225.4502  | -218.9187 | -72.8459  |
| 6 | -6 | -         | -         | 94.7669   | 94.7669   | -         | 77.2972   | -9.6622   | 48.3108   | 9.6622    | 42.9729   |
| 6 | -5 | -         | -         | 23.9550   | 23.9550   | -         | -367.1618 | -328.5132 | -333.3443 | 96.6215   | 25.1351   |
| 6 | -4 | _         | -         | -12.1091  | -12.1091  | -         | 0.0000    | 57.9729   | 86.9594   | -14.4932  | -60.6080  |
| 6 | -3 | -         | -         | 23.9550   | 23.9550   | -         | -96.6215  | 19.3243   | -57.9729  | 4.8311    | 220.2701  |
| 6 | -2 | -         | -         | -184.7954 | -184.7954 | -         | -193.2431 | -67.6351  | 101.4526  | 24.1554   | 78.4459   |
| 6 | -1 | _         | -         | -290.6184 | -290.6184 | -         | -38.6486  | 0.0000    | -72.4661  | -125.6080 | -83.2432  |
| 6 | 0  | -         | -         | 25.2712   | 25.2712   | -         | -28.9865  | 0.0000    | 19.3243   | -14.4932  | 1.3514    |
| 6 | 1  | -         | -         | -222.1757 | -222.1757 | -         | -57.9729  | 77.2972   | -57.9729  | -48.3108  | -151.4188 |
| 6 | 2  | _         | -         | 78.9724   | 78.9724   | -         | -19.3243  | 19.3243   | 67.6351   | -9.6622   | 58.8513   |
| 6 | 3  | -         | -         | -139.7811 | -139.7811 | -         | -28.9865  | -125.6080 | -82.1283  | -19.3243  | 6.1486    |
| 6 | 4  | -         | -         | 78.4459   | 78.4459   | -         | 38.6486   | 86.9594   | 111.1148  | 67.6351   | -45.3378  |
| 6 | 5  | -         | -         | 244.2879  | 244.2879  | -         | 251.2160  | 714.9993  | -14.4932  | 183.5809  | 260.0673  |
| 6 | 6  | -         | -         | 141.6238  | 141.6238  | -         | -86.9594  | 38.6486   | 53.1418   | 24.1554   | -3.0405   |

Table 6.20 Crystal field parameters for Kramers ions of the Pd-Ln and Pt-Ln series

 $D_{3h}$  symmetry compare to a lower  $C_{4\nu}$  for the Pt-Ln

The reason for this is due to the lower symmetry (triniclic) of the Pt-Ln system when compared to the slightly higher symmetry for the Pd-Ln (monoclinic). Also, considering the first coordination sphere of each system, the Pd-Ln systems are placed in a distorted

|   |    |           |           |           | $B_k^q$ (site-1) |           |           |           |
|---|----|-----------|-----------|-----------|------------------|-----------|-----------|-----------|
| k |    | Pd-Pr     | Pd-Pm     | Pd-Tb     | Pt-Tb            | Pd-Ho     | Pt-Ho     | Pd-Tm     |
| ĸ | q  | (J-Term)  | (J-Term)  | (J-Term)  | (J-Term)         | (J-Term)  | (J-Term)  | (J-Term)  |
| 2 | -2 | -307.3522 | 44.4779   | -290.5997 | 26.5320          | -193.6440 | -59.3505  | -102.4244 |
| 2 | -1 | -187.4179 | -233.5970 | 80.3385   | -92.5591         | 554.6790  | -728.2305 | -191.5224 |
| 2 | 0  | -211.2141 | -146.2203 | 320.0878  | 280.7323         | 206.6490  | 16.3125   | 280.9214  |
| 2 | 1  | -184.2390 | -169.6999 | -69.5129  | -11.4553         | 206.2305  | 274.7970  | -43.0551  |
| 2 | 2  | -173.7912 | 493.1692  | -25.6123  | 73.6164          | 64.4940   | -239.2875 | 245.9982  |
| 4 | -4 | -69.5190  | 29.0025   | -173.5594 | -178.1332        | 276.2760  | 12.0120   | -35.9574  |
| 4 | -3 | 435.8314  | -461.1940 | 268.9558  | -83.3902         | 551.6511  | -726.1254 | 25.3601   |
| 4 | -2 | -399.6086 | 23.5799   | 90.0875   | 159.1846         | 5.1051    | -9.6096   | -5.6968   |
| 4 | -1 | -344.5732 | -438.9637 | 29.8931   | -79.5515         | -188.2881 | -200.9007 | -44.4108  |
| 4 | 0  | 1.6607    | -6.2814   | -40.1841  | -102.1754        | -9.0090   | 60.9609   | -78.2855  |
| 4 | 1  | -462.2261 | -82.6400  | -82.4101  | -4.0021          | -34.2342  | 117.4173  | -70.1384  |
| 4 | 2  | -365.4412 | 411.2125  | -122.1041 | -182.5436        | 61.8618   | 61.5615   | 81.9609   |
| 4 | 3  | 119.1911  | 584.0744  | -165.3102 | 81.3483          | -945.6447 | 1012.3113 | 416.2975  |
| 4 | 4  | -68.1033  | -106.7597 | 591.2453  | 289.2112         | 186.1860  | 84.0840   | -133.1711 |
| 6 | -6 | -21.3136  | -15.4654  | -133.7837 | -205.1349        | -100.4864 | -85.0269  | 33.8919   |
| 6 | -5 | -34.1017  | -131.4561 | -169.4593 | -115.9458        | 108.2161  | -23.1892  | 51.7297   |
| 6 | -4 | 101.1575  | -40.6379  | 0.0000    | -115.9458        | 0.0000    | -77.2972  | -80.2702  |
| 6 | -3 | 538.9055  | -379.0675 | -115.9458 | 35.6756          | 108.2161  | 193.2431  | 153.4053  |
| 6 | -2 | 109.6829  | 115.8262  | 205.1349  | 17.8378          | -100.4864 | 30.9189   | -51.7297  |
| 6 | -1 | -48.3654  | 224.5777  | -151.6215 | -8.9189          | -131.4053 | -23.1892  | 46.3783   |
| 6 | 0  | 2.4593    | -16.2881  | -17.8378  | -17.8378         | 15.4594   | 7.7297    | 19.6216   |
| 6 | 1  | 378.2339  | 157.1222  | -71.3513  | 26.7567          | -154.5944 | 46.3783   | -23.1892  |
| 6 | 2  | 13.1160   | 0.6581    | 26.7567   | -35.6756         | -77.2972  | 54.1081   | 80.2702   |
| 6 | 3  | 164.4424  | 31.0954   | -187.2971 | 115.9458         | -131.4053 | -146.8647 | 121.2972  |
| 6 | 4  | -43.4469  | 75.6819   | 231.8917  | 98.1080          | 15.4594   | -69.5675  | -83.8378  |
| 6 | 5  | -552.8413 | -218.9839 | -8.9189   | 151.6215         | -154.5944 | 15.4594   | 233.6754  |
| 6 | 6  | -14.2637  | -8.2263   | 71.3513   | 115.9458         | 23.1892   | 30.9189   | -49.9459  |

Table 6.21 Crystal field parameters for non-Kramers ions of the Pd-Ln and Pt-Ln series

The diagonal or uniaxial CF parameter  $(|B_2^0|)$  contributes significantly to the total CF for all the Kramers ions showing some degree of axiality across the system. However, as expected for a low-symmetry system, there are significant contribution for the off-diagonal contribution including the  $|B_2^2|$  and  $|B_2^{-1}|$  terms. This is in agreement with the mixing of the  $m_j$  states as reported in the electronic structure section for the contributing wavefunctions. The significant contribution of the uniaxial terms for the Krammers ions is in line with previous experimental report which claims the existence of axial perturbation occasioned by the Pd-Ln bond axis (Figure 6.5).[63, 327]. The Pd-Ln bond interaction helps set up

some axial perturbation and increased the CF effect around the  $Ln^{3+}$ . To confirm the role of the Pd-Ln bond, the CFPs of **Er1** (see Table 5.10) were compared with those of **Pd-Er** (Table 6.20) which share approximate coordination number and geometry. The uniaxial term ( $B_2^0$ ) is largest for **Pd-Er** confirming the additional contribution to the CFP and the existence of a Pd-Ln interaction. In section 4.5.2, the trend in the interelectronic repulsion was established for the dysprosium complexes and shown that the free ion will experience the largest interelectronic repulsion. The implication is that the effect of the ligand field is less neutralised for a multi-electron system allowing a single-electron and single-spin system like the **Pd-Ce** to experience a larger field-effect around similar ligands. The lesser magnitude for **Pd-Yb** compared to **Pd-Ce** is attributed to the extra repulsive effect of the paired valence electron. This description is also true when the later members of the series of **Pd-Ln** are compared (see Table 6.20 and 6.21).



Fig. 6.5 (a) Contour maps of the local orbital locator (LOL) for Pd-La system in the Pd–La plane. The blue region (midway) represents critical regions with high electron density in a bonding environment (right and left denote the atomic nuclei). n is the principal quantum number. (b) LOL isosurface showing the degree of the polarizing power and the polarizability of the La and Pd, respectively. (c) LOL topology of the gradient paths associated with the Pd–La critical points in the Pd-La system. This defines the corresponding bond paths and interatomic surfaces.[63]

### 6.5 Magnetic properties of the Kramers and non-Kramers Pd-Ln and Pt-Ln series

One of the drawbacks of theoretical studies is that oftentimes there are hardly experimental data to compare obtained results from calculations. Therefore, bench marking theoretical results with those of the experiments provides the opportunity to both validate such theoretical predictions and establish the best way to accurately predict properties for which there are no experimental data. In this section, we leverage on available experimental data combined with theoretical results from the preceding sections of this chapter to describe the magnetic properties of the Pd-Ln and Pt-Ln systems. The results presented in this section were computed using the POLYANISO routine implemented in MOLCAS. The summary of the magnetic data for all Pd-Ln and Pt-Ln are presented in Table 6.22.

### 6.5.1 Static magnetic properties of the Pd-Ln and Pt-Ln series

The calculated  $\chi_m T$  are in agreement with the experiments showing that the multireference methods used to describe the systems are correct. A key observation in the  $\chi_m T$  value of lanthanide-based complexes is the tendency to decrease with decreasing temperature even for mononuclear SIMs. This observation is generally attributed to the depopulation of the magnetic  $m_j$  levels. For cluster system where magnetic exchange interaction might exist, the natural depopulation of the magnetic levels with decreasing temperature could make it challenging to quantify the exchange interaction especially for antiferromagnetic coupling which has the same downward trend as the thermal depopulation. The idea of incorporating clusters to enhance SMM behaviour especially for transition metals is not straightforward as magnetic response. This idea has been utilized extensively in the design of transition-metal-based SMMs. However, as was mentioned in the preceeding section, despite the advantage of large unquenched intrinsic orbital momentum, the core nature of 4f electrons makes it difficult to design lanthanide-based clusters that could leverage on exchange coupling to enhance SMM behaviour.

#### 6.5.1.1 Magnetic exchange interactions for the Pd-Ln

The experimental data presented in Table 6.22 enabled the computation of the exchange energies  $(J_{ex})$  for the Pd-Ln systems. The extracted  $J_{ex}$  values as presented in Table 6.22 show weak exchange interaction mostly for the later members of the series. Pd-Ce and

**Pd-Nd** (Figure 6.6) shows  $J_{ex}$  of about zero. Beyond **Pd-Sm**, the intramolecular forces between the Ln-Ln sites sets in while aiding depopulation of the magnetic levels. For example, we calculated a  $J_{ex}$  value of -0.01 cm<sup>-1</sup> for **Pd-Gd** which is very close to the -0.018 cm<sup>-1</sup> extracted from experiment.[63]

| Sample<br>code     | A <sup>Ln<sup>3+</sup></sup>   | 4f <sup>n</sup>  | $^{2S+1}L_J$                   | J <sub>ex</sub>          | Exptl $\chi_m T^{[a]}$<br>(cm <sup>3</sup> Kmol <sup>-1</sup> ) | RASSI-SO $\chi_m T^{[a]}$<br>(cm <sup>3</sup> Kmol <sup>-1</sup> ) | Exptl $\chi_m T^{[b]}$<br>(cm <sup>3</sup> Kmol <sup>-1</sup> ) | RASSI-SO $\chi_m T^{[b]}$<br>(cm <sup>3</sup> Kmol <sup>-1</sup> ) |
|--------------------|--------------------------------|------------------|--------------------------------|--------------------------|---|--|---|--|
| Pd-Y               | 39Y <sup>3+</sup>              | $4f^0$           | ${}^{1}S_{0}$                  |                          |   |  |   |  |
| Pd-La              | $57^{La^{3+}}$                 | $4f^0$           | ${}^{1}S_{0}$                  |                          |   |  |   |  |
| Pd-Ce[327]         | <sub>58</sub> Ce <sup>3+</sup> | $4f^1$           | ${}^{2}F_{\frac{5}{2}}$        | pprox 0                  | 0.64  | 0.85   | 1.42  | 1.39   |
| Pd-Pr              | 59Pr <sup>3+</sup>             | $4f^2$           | ${}^{3}H_{4}^{2}$              | $pprox 0^{[c]}$          | $7.23	imes10^{-6}$  |  |   | 3.09   |
| Pd-Nd[327]         | 60 <sup>Nd<sup>3+</sup></sup>  | $4f^3$           | ${}^{4}I_{\frac{9}{2}}$        | pprox 0                  | 1.05  | 1.25   | 3.42  | 3.20   |
| Pd-Pm              | <sub>61</sub> Pm <sup>3+</sup> | $4f^4$           | ${}^{5}I_{4}^{2}$              | $pprox 0^{[c]}$          |   | 0.03   |   | 1.90   |
| Pd-Sm[327]         | $_{62}^{Sm^{3+}}$              | 4f <sup>5</sup>  | ${}^{6}H_{\frac{5}{2}}$        | pprox 0                  | 0.02  | 0.07   | 0.18  | 0.60   |
| <b>Pd-Gd</b> [63]  | 64 <sup>Gd<sup>3+</sup></sup>  | 4f <sup>7</sup>  | ${}^{8}S_{\frac{7}{2}}$        | -0.01 (expt.= $-0.018$ ) | 15.39   | 15.17  | 15.78   | 15.81  |
| Pd-Tb[327]         | <sub>65</sub> Tb <sup>3+</sup> | 4f <sup>8</sup>  | $^{7}F_{6}$                    | -0.03                    | 12.16   | 15.93  | 24.40   | 23.33  |
| <b>Pt-Tb</b> [65]  | $_{65}^{3+}$                   | 4f <sup>8</sup>  | $^{7}F_{6}$                    | 0                        | 17.82   | 19.99  | 23.60   | 23.26  |
| <b>Pd-Dy</b> [327] | 66 <sup>Dy<sup>3+</sup></sup>  | 4f <sup>9</sup>  | ${}^{6}H_{\frac{15}{2}}$       | -0.03                    | 15.73   | 20.95  | 26.98   | 27.91  |
| <b>Pt-Dy</b> [65]  | 66 <sup>Dy<sup>3+</sup></sup>  | 4f <sup>9</sup>  | ${}^{6}H_{\underline{15}}^{2}$ | 0                        | 20.20   | 23.51  | 27.8  | 27.87  |
| Pd-Ho[327]         | <sub>67</sub> Ho <sup>3+</sup> | $4f^{10}$        | ${}^{5}I_{8}^{2}$              | -0.03                    | 13.71   | 13.97  | 28.20   | 27.64  |
| <b>Pt-Ho</b> [66]  | 67 <sup>Ho<sup>3+</sup></sup>  | $4f^{10}$        | ${}^{5}I_{8}$                  | 0                        | 13.52   | 16.45  | 27.7  | 27.67  |
| <b>Pd-Er</b> [327] | 68 <sup>Er<sup>3+</sup></sup>  | $4f^{11}$        | ${}^{4}I_{\frac{15}{2}}$       | +0.06                    | 15.36   | 18.64  | 22.63   | 22.63  |
| <b>Pt-Er</b> [66]  | 68 <sup>Er<sup>3+</sup></sup>  | 4f <sup>11</sup> | ${}^{4}I_{\underline{15}}^{2}$ | 0                        | 16.60   | 17.61  | 24.5  | 22.68  |
| Pd-Tm              | <sub>69</sub> Tm <sup>3+</sup> | $4f^{12}$        | ${}^{3}H_{6}^{2}$              | $+0.065^{[c]}$           |   | 9.03   |   | 14.06  |
| <b>Pd-Yb</b> [327] | $_{70}^{70}$ Yb <sup>3+</sup>  | 4f <sup>13</sup> | ${}^{2}F_{\frac{7}{2}}$        | +0.07                    | 2.33  | 2.52   | 4.90  | 4.99   |
| Pd-Lu              | 71 <sup>Lu<sup>3+</sup></sup>  | $4f^{14}$        | ${}^{1}S_{0}^{2}$              |                          |   |  |   |  |
| [a] Measured       | or calculated                  | d at 2 l         | К. [b] Ме                      | asured or calculated     | d at room tempe   | erature. [c] Estimatio   | n   |  |

Table 6.22 Electronic and magnetic properties of the  $\mathsf{Pd}\text{-}\mathsf{Ln}$  and  $\mathsf{Pt}\text{-}\mathsf{Ln}$  series



(b)  $\chi_m T$  vs T for Pd-Nd

Fig. 6.6 Comparison of the experimental and theoretical  $\chi_m T$  vs T plot for (a) Pd-Ce (b) Pd-Nd at temperature range of 2-300 K. Inset: Maximised region of antiferromagnetic coupling. The theoretical values were obtained at different  $J_{ex}$
**Pd-Gd** serves as a good example to demonstrated the role of thermal depopulation of magnetic states. This is because the electronic spins are mostly populating the ground state which was calculated to be essentially quasi-degenerate with the first actual excited state about 40,000 cm<sup>-1</sup> away from the ground state. Such wide gap makes it impossible for higher magnetic levels to be occupied at higher temperature and so, it is expected that the room temperature value of the  $\chi_m T$  should be equal to those at lower temperature regime in the absence of any magnetic exchange interaction. The negligible decrease in the  $\chi_m T$  value for Pd-Gd (Figure 6.7) indicates a possible antiferromagnetic coupling between the two Gd<sup>3+</sup> sites which was calculated to be -0.01 cm<sup>-1</sup> which is close to the value extracted from micro-squid.



Fig. 6.7 (a) Comparison of the experimental and theoretical  $\chi_m T$  vs T plot for Pd-Gd at temperature range of 2-300 K. Inset: Maximised region of antiferromagnetic coupling. The theoretical values were obtained at different  $J_{ex}$  (b) Experimental  $\chi_m T$  vs T plot for Pd-Gd (Complex 1) adapted from reference [63]



(b)  $\chi_m T$  vs T for Pt-Tb

Fig. 6.8 Comparison of the experimental and theoretical  $\chi_m T$  vs T plot for (a) Pd-Tb (b) Pt-Tb at temperature range of 2-300 K. Inset: Maximised region of antiferromagnetic coupling. The theoretical values were obtained at different  $J_{ex}$ 

The lack of quantifiable  $J_{ex}$  (which is a function of distance of separation between the coupled sites) for the early members of the series can be attributed to the increased Ln-Ln intramolecular distances from the right to the left of the lanthanide series as presented in Table 6.1. As such, it is expected that the exchange interaction should increase further from Pd-Gd to Pd-Yb. The  $\chi_m T$  values for Pd-Tb, Pd-Dy, and Pd-Ho show thermal depopulation of the magnetic levels which was ascertained with the  $\chi_m T$  vs T for which  $J_{ex} = 0$ . Previous reports[63, 327] had attributed the decreasing  $\chi_m T$  values to only depopulation of the magnetic levels. However, we found that in addition to the thermal depopulation of the  $m_i$  states, antiferromagnetic coupling sets in at very low temperature  $(\approx 10$  K). Our calculation therefore allowed us to reveal the hidden magnetic interaction which was not possible by experiment alone. Furthermore, the  $\chi_m T$  vs T plot of Pd-Tb and Pt-Tb were compared to confirm the exchange interaction in Pd-Ln system (Figure 6.8). No magnetic exchange interactions were found for all the Pt-Ln series because of the increased intramolecular distance of separation between the lanthanide sites. Unlike the Pd-**Tb**, **Pt-Tb** did not show a significant depopulation of the magnetic levels with decreasing temperature further confirming the role of the magnetic exchange in Pd-Tb. A similar trend was also observed for Pd-Dy and Pt-Dy (Figure 6.9). For each system, neutral, ferromagnetic as well as antiferromagnetic coupling were computed and compared with the experiment to confirm the accuracy of the results. Pd-Ho showed a very interesting  $\chi_m T$ vs T in which inclusion of a positive  $J_{ex}$  did not produce a visible ferromagnetic interaction (Figure 6.10). Pd-Er which follows Pd-Ho in the series showed ferromagnetic coupling following the depopulation of the  $m_i$  states below 5 K. The lack of ferromagnetic response of Pd-Ho even when a positive  $J_{ex}$  was used in the computation followed by the transition to ferromagnetic coupling as observed for Pd-Er show that Pd-Ho serves as a pivot point between the two magnetic exchanges in our system. This is further confirmed with the ferromagnetic coupling computed and obtained from experiment for the Pd-Yb system for which we have extracted  $J_{ex}$  and presented in Table 6.22. As the intramolecular Ln-Ln distance decreases the exchange interaction increases.

Furthermore, we focused on the Pd-Er system and compared the calculated  $J_{ex}$  with those obtained for Er1 and Er2 in chapter 5 and found that the Ln-Ln distance is inversely proportional to the ferromagnetic  $J_{ex}$ . The  $J_{ex}$  are +0.05, +0.06, +0.07 and +0.1 for Er1, Pd-Er, Pd-Yb and Er2 with Ln-Ln intramolecular distances of 4.152, 4.006, 3.982 and 3.878 Å respectively. This trend in Ln-Ln distances with the computed  $J_{ex}$  is as expected.



(b)  $\chi_m T$  vs T for Pt-Dy

Fig. 6.9 Comparison of the experimental and theoretical  $\chi_m T$  vs T plot for (a) Pd-Dy (b) Pt-Dy at temperature range of 2-300 K. Inset: Maximised region of antiferromagnetic coupling. The theoretical values were obtained at different  $J_{ex}$ 



Fig. 6.10 Comparison of the experimental and theoretical  $\chi_m T$  vs T plot for Pd-Ho at temperature range of 2-300 K. Inset: Maximised region of antiferromagnetic coupling. The theoretical values were obtained at different  $J_{ex}$ 

The results of **Er1** and **Er2** presented in chapter 5 allowed for a useful comparison with the **Pd-Er**. **Er1** is bridged in the same way as **Pd-Er** by two acetato ligands with each having a monohapto ( $\eta^1$ ) and dihapto ( $\eta^2$ ) oxygen bridges. Excluding the Pd-Er bonding interaction, both complexes (**Er1** and **Pd-Er**) would have coordination number of 8. However, results presented in the following section coupled with those previously reported in the literature[327] continued to support the existence of Pd-Er bonding interaction through which the electron deficient  $d^8 \text{ Pd}^{2+}$  pushes in electron density into the hybrid frontier orbitals of the lanthanide ion leading to some level of axial perturbation. A Pd-Ln interaction means that the Pd centre is in a square pyramidal geometry with a low spin state. A square pyramidal geometry, like a square planner, is a  $d^8$  system but differs in the identity of the HOMO ( $d_{z^2}$  for square pyramidal and  $d_{xy}$  for square planner)(Figure 6.11). For orbital overlap to happen, the energy and symmetry must agree. In a square pyramidal arrangement, the  $d_{z^2}$  orbital has the right symmetry and appreciable energy match to interact with the frontier orbitals of the lanthanide. Although the  $d_{x^2-y^2}$  is empty, the HOMO was able to interact with the frontier orbitals as shown in our previous report using local orbital locator (Figure 6.5)[63]



Fig. 6.11 Schematic representation of geometry transformation from octehedral to square planner

Despite, having exact bridging composition the Er-Er distance for Er1 (4.152 Å) is higher than that of Pd-Er (4.006 Å). This infers a stronger interaction for Pd-Er compared to Er1. The increased interaction was attributed to the slightly higher electron density supplied to the Er-centre by the  $Pd^{2+}$  in Pd-Er, thereby providing more electron density for increased interaction. This is also similar in a way with the increased interaction observed in Er2 as a result of having 4-bridging ligands between the two Er-centres. The description above continues to support the perturbative nature of the Pd-Ln bond and it's effect on the magnetic properties of the series.



(b)  $\chi_m T$  vs T for **Pt-Yb** 

Fig. 6.12 Comparison of the experimental and theoretical  $\chi_m T$  vs T plot for (a) Pd-Er (b) Pt-Yb at temperature range of 2-300 K. Inset: Maximised region of antiferromagnetic coupling. The theoretical values were obtained at different  $J_{ex}$ 

#### 6.5.2 Dynamics of the spin reversal for Pd-Ln and Pt-Ln series

In Table 6.3 – 6.17, the SOC-CF split magnetic levels were computed for both Kramers and non-Kramers Pd-Ln and Pt-Ln systems. The  $g_z$  values shows appreciable anisotropy for the systems at varying degrees. The computed CF parameters in Table 6.20 and 6.21 also shows appreciable negative diagonal  $(B_2^0)$  term which implies a ZFS that is less than zero and supports the occupation of the low lying states by the higher  $m_i$  values. It is important to note that a negative D is not the sole criteria that needs to be satisfied for a system to show SMM behaviour. In fact, the results presented in this thesis shows that SMM behaviour does not just happen with just a single criteria satisfied. We show that in addition to satisfying certain structural parameters, like higher symmetry, negative Dvalue, isolated ground and excited states among others, the magnitude and the extent to which opposing factors are present in a system also affects the probability of an outcome for SMM. For example, we see that despite Pd-Tb and Pd-Ho satisfying a negative D value and appreciable anisotropic  $g_z$  value and been placed in a relatively higher symmetry environment than the **Pt-Tb** and **Pt-Ho** respectively, the later counterparts show slow magnetic relaxation characteristics of SMM behaviour while the former did not even with applied magnetic field despite their Kramers counterparts exhibiting field induced slow magnetic relaxation as shown by experiments. [63–66, 327]

Kramers ions can show slow magnetic relaxation that is field-dependent as a manifestation of electro-nuclear spin entanglement.[332, 333] For SMM to be used for applications like information storage, the spin must remain in one of two states for a long time and be able to switch to the other state as quickly as possible when needed. This might sound contradictory since fast relaxations are accompany by short lifetimes. However, Kramers doublets are able to achieve such long lifetime owing to Kramers theorem and time-reversal symmetry which makes it difficult if not impossible for the relaxation within Kramers doublet to be affected by electric field.[182] Although, hyperfine interactions and transverse magnetic fields created by intermolecular interactions split the Kramers doublets to produce new relaxation channels for QTM and direct mechanisms, it was not surprising to see all the Kramers ions presented in this thesis to show slow magnetic relaxation characteristics of SMM.

Non-Kramers systems on the other hand are affected by electric fields which can help to remove level degeneracy for  $E \neq 0$  states, thereby mixing  $\pm m_j$  sublevels directly and making non-Kramers systems poorer SMM candidates. Table 6.11 to 6.17 shows that non-Kramers ions display intrinsic tunneling gap in the absence of applied field which favours QTM. The role of magnetic exchange and dipolar interactions can not also be overemphasised as they can also affect the relaxation dynamics by affecting the tunneling split. Table 6.23 compares the tunnelling splitting for a single metal site and that of two magnetic centres, whether coupled or uncoupled and we see a reduction in the tunnelling splitting for all non-Kramers ions indicating that a lower tunnelling splitting is good for a slow magnetic relaxation and is supported by either dipolar coupling or magnetic exchanges between metal sites in clusters. For the Kramers ions, we have recorded the relative values to allow for comparison, but the absolute values are negative near the ground state showing that the ground states are more stabilised with these type of interactions compare to a single site with no intrinsic tunnelling split due to the doublet nature of the ground state in the absence of field. This is the reason diamagnetic metals are used to dilute magnetic centres in systems with possible dipolar or magnetic exchanges to ensure any observed SMM behaviours is not as a result of such interactions.

|        | Ground state tunnelling splitting |                                |  |  |  |  |
|--------|-----------------------------------|--------------------------------|--|--|--|--|
| Sample | One metal site <sup>[1]</sup>     | Two metal sites <sup>[2]</sup> |  |  |  |  |
| Pd-Ce  | 0                                 | 0.000850                       |  |  |  |  |
| Pd-Pr  | 32.25883                          | 32.258000                      |  |  |  |  |
| Pd-Nd  | 0                                 | 0.000573                       |  |  |  |  |
| Pd-Pm  | 40.61377                          | 40.192073                      |  |  |  |  |
| Pd-Sm  | 0                                 | 0.000062                       |  |  |  |  |
| Pd-Gd  | 0                                 | 0.000007                       |  |  |  |  |
| Pd-Tb  | 0.70111                           | 0.491368                       |  |  |  |  |
| Pt-Tb  | 0.02286                           | 0.021641                       |  |  |  |  |
| Pd-Dy  | 0                                 | 0.000004                       |  |  |  |  |
| Pt-Dy  | 0                                 | 0.000007                       |  |  |  |  |
| Pd-Ho  | 2.71616                           | 2.712068                       |  |  |  |  |
| Pt-Ho  | 0.38404                           | 0.378956                       |  |  |  |  |
| Pd-Er  | 0                                 | 0.000003                       |  |  |  |  |
| Pt-Er  | 0                                 | 0.000153                       |  |  |  |  |
| Pd-Tm  | 0.12509                           | 0.078960                       |  |  |  |  |
| Pd-Yb  | 0                                 | 0.018990                       |  |  |  |  |

Table 6.23 Ground state tunnelling splitting of the Pd-Ln and Pt-Ln series for the isolated single sites and the coupled centres

Continued on next page

[1] Computed for a single metal site with the second site substituted with  $La^{3+}$  or  $Lu^{3+}$ [2] Computed for the full molecule with the two magnetic metal sites unchanged.

The computed SO-CF split states and assigned wavefunction were compared with the relaxation mechanisms for the Pd-Ln and Pt-Ln obtained from experiment as presented in Table 6.24 to better understand behaviour of our systems. The experimental results shows that most of the Pd-Ln and Pt-Ln systems show a combined direct and Orbach processes with the exception of diluted sample of Pd-Dy with yttrium. It is important to note at this point that the method of fitting experimental results from *ac* data is not so reliable because of too many parameters combinations of which may give good fit with different data. For this reason, we can rely on computational results to better understand and give accurate description of the relaxation mechanism.

# 6.5.2.1 Mechanism of the slow magnetic relaxation for the Pd-Ln and Pt-Ln series

From the experiment, **Pd-Ce** was fitted to a combined direct and Orbach processes with  $\Delta_{\text{eff}}$  of 33.53 cm<sup>-1</sup> (Figure 6.13b and Table 6.24). On the other hand the first excited magnetic level computed for **Pd-Ce** even with the inclusion of the dipolar interactions is about 393 cm<sup>-1</sup>. The reason for this difference are in two-folds, (i) the contribution to the direct process minimising the chances of the spin going through the excited state. (ii) increased chance of spin-phonon interaction that created a different relaxation pathway other than the distinct excited  $m_i$  levels.



(a) Pd-Gd relaxation time plot



(b) Pd-Ln relaxation time plot

Fig. 6.13  $ln\tau$  vs  $T^{-1}$  plots for (a) Pd-Gd and (b) other Pd-Ln systems





Pd-Nd shows a better agreement between the experiment and the computed results with experimental  $\Delta_{\rm eff}$  value of 41.92 cm<sup>-1</sup> (Figure 6.13b and Table 6.24) against 63.62 cm<sup>-1</sup> computed. Again, we attributed the discrepancy to the same reason as in Pd-Ce. Similar argument can be made for all other systems due to the complex spin-phonon interaction taking place. Although, the Orbach mechanism had been used to define what I would call a pseudo  $\Delta_{\rm eff}$ , an ideal Orbach process is a two-phonon process in which the energy to be transferred to the lattice is the difference between the energies absorbed and emitted for a specific low-lying excited state. The large phonon energy needed to make this process happen makes this process more probable at higher temperature. We argue that although most of the relaxation data from the experiments were not fitted with Raman process equation, it is most probable than the Orbach due to the low energy extracted for the Orbach process from our calculations. A Raman process is more probable to couple the vibronic motion of the bonds to create virtual states for spin reversal. This is because the Raman mechanism is driven by inelastic dispersion of phonons rather the elastic dispersion observed for Orbach. The Raman process is a two-phonon process in which the energy to be transferred to the lattice is the difference between the energies absorbed and emitted for a virtual excited state at any energy less than the Debye temperature. However, the inclusion of the direct process also helped mitigate the competing Orbach process.

| Debye equation $\longrightarrow$       | $	au=rac{1}{A(H^4)T^n}+	au_0^{-1}\exp\left\{-rac{\Delta_{	ext{eff}}}{k_{	ext{B}}T} ight\}+CT^m+Q$ |                        |                |                                |                      |      |            |  |
|--|---|------------------------|----------------|--------------------------------|----------------------|------|------------|--|
| Relaxation Mechanism $\longrightarrow$ | Direct Process  |                        | Orbach process |                                | Raman process        |      | (RASSI-SO) |  |
| Sample                                 | H (Oe)  | A (s $^{-1}$ K $^{-2}$ | n              | $\Delta_{ m eff}~( m cm^{-1})$ | $	au_0$ (s)          | С    | m          | Energy <sup>[1]</sup> (cm <sup><math>-1</math></sup> ) |
| <b>Pd-Ce</b> [327]                     | 2600  | $6.24 	imes 10^{-11}$  | 1.70           | 33.53                          | $8.91 	imes 10^{-9}$ | -    | _          | 393.7836   |
| <b>Pd-Nd</b> [327]                     | 1400  | $3.36 \times 10^{-10}$ | 2              | 41.92                          | $1.43 	imes 10^{-9}$ | _    | -          | 63.6244  |
| <b>Pd-Sm</b> [327]                     | 2600  | $3.59 \times 10^{-11}$ | 2              | 18.50                          | $2.06 	imes 10^{-9}$ | _    | -          | 111.3614   |
| <b>Pd-Dy</b> [327]                     | 2000  | $1.22\times10^{-10}$   | 2              | 33.19                          | $1.17\times10^{-10}$ | _    | -          | 66.6393  |
| <b>Pd-Dy-Y</b> [327]                   | 2000  | $5.40 	imes 10^{-12}$  | 2              | 16.01                          | $1.46 	imes 10^{-7}$ | _    | -          | 66.6393  |
| <b>Pd-Dy-Y</b> [327]                   | 800   | -                      | _              | 24.30                          | $1.06 	imes 10^{-8}$ | 6.58 | 5.44       | 66.6393  |
| <b>Pd-Er</b> [327]                     | 800   | $3.73 	imes 10^{-9}$   | 2              | 22.24                          | $3.01\times10^{-10}$ | _    | -          | 28.5485  |
| Pd-Er-Y[327]                           | 600   | $3.63 	imes 10^{-9}$   | 2              | 20.83                          | $8.10\times10^{-10}$ | _    | -          | 28.5485  |
| <b>Pd-Gd</b> (> 10 Hz)[63]             | 3000  | $1.01\times10^{-10}$   | 2              | 20.71                          | $1.03 	imes 10^{-6}$ | _    | -          | $0.9558^{[2]}$   |
| <b>Pd-Gd</b> (< 10 Hz)[63]             | 3000  | _                      | _              | 5.10                           | 0.6                  | -    | -          | $0.9558^{[2]}$   |
| <b>Pt-Tb</b> [65]                      | 3000  | _                      | _              | 22.6                           | $1.60 	imes 10^{-6}$ | -    | -          | 198.2042   |
| <b>Pt-Ho</b> [66]                      | 3000  | 172.9                  | 2              | 29.26                          | $1.16\times10^{-10}$ | -    | -          | 28.8194 <sup>[3]</sup>                                 |

Table 6.24 Parameters of the fit of the experimental relaxation time for the Pd-Ln and Pt-Ln series

 $\left[1\right]$  The nearest excited state to the experimental value computed.

[2] Although the most visible first excited state is about 40,000 cm<sup>-1</sup>, the 4 doublets from the  $J = \frac{7}{2}$  state were split to a very small

ratio despite the degeneracy of the isotropic gadolinium ion

 $\left[ 3\right]$  Represents the third quasi-excited doublet

### 6.6 Conclusion

The computation of the electronic structure as well as the CFPs for the Pd-Ln and Pt-Ln series allowed the investigation of the magnetic behaviour of the two series. Experiments showed that the Kramers ions of the Pd-Ln series all showed slow magnetic relaxation (Figure 6.13, 6.14 and Table 6.24) characteristics of SMM while the non-Kramers ions did not show any such property. On the other hand, both non-Kramers and Kramers ions of the **Pt-Ln** congeners showed the field-induced slow magnetic relaxation. The multireference method was employed to better understand the magnetic behaviour of the series and compared with experimental data (Figure 6.13, 6.14 and Table 6.24). Results showed that SMM behaviour is not a one-way switch that turns on with a single factor. In addition, the observation of these factors is as important as the magnitude at which each factor influences the property. The lack or presence of the slow magnetic relaxation for the series was greatly influenced by the choice of  $Pt^{2+}$  or  $Pd^{2+}$ , the coordination number, the symmetry considering the first coordination sphere as well as the overall symmetry of the full molecule. Despite the Pd-Ln series being favoured by most of these factors, the choice of the TM and the ligand field was not sufficient enough to create a better quasi-doublet required for slow magnetic relaxation for the non-Kramers ions. This confirms the earlier argument that the more radially expanded  $5d_z$  orbital of Pt<sup>2+</sup> set up softer but stronger axial perturbation in the system to produce favourable CF for slow spin relaxation compared to  $Pd^{2+}$ . This will open a new research front in the rational design of SMM materials by utilising polarizing metals to upset axial perturbation for SMM behaviour as well as understand how non-SMM materials could be made to show SMM in a rational fashion. The chapter finished by providing insights to the relaxation mechanisms of systems showing slow magnetic relaxation and showed that while the direct process is probable given the competing diagonal and off-diagonal terms of the CFP, the spin-phonon interaction which combines a direct, Orbach and Raman processes could best describe the relaxation mechanism and proposed a possible competing Raman process based on the magnitude of the computed excited states and the wavefunction contributions to each state.

## Chapter 7

### **General Conclusion**

### 7.1 Conclusion

Most of the physics used to describe the SMM behaviour are tied to theories developed in the 1960's. While they are still relevant, advances in the present day technology means that some of these theories can be modernised for easy, more reliable and accurate predictions of electronic and magnetic properties of materials like the SMMs. However, such development will require a good understanding of the properties of materials which can become candidates for SMMs. This would require insight in the CF splitting of lanthanide and the consequences to the slow magnetic relaxation which would enable rational design of SMM by ligand design, choice of metal as well as other lattice composition like solvent molecules. In this thesis, three different class of compounds were used to investigate different factors for the observation of SMM behaviour in lanthanide-based complexes. In chapter 4, the Schiff base ligand was used to investigate the role of aromaticity and ligand field through ligand modifications. In chapter 5, the dinuclear erbium acetate complexes were used to investigate the role of synthetic solvents in tuning the structural architecture of the later members of the lanthanide series and how any structural changes arising from it could affect the SMM behaviour. Chapter 6 extended the discussion in chapter 5 by looking at the Pd-Ln and Pt-Ln series with a view of understanding the role of heterometallic bond as axial pertubation to induce SMM behaviour across the lanthanide series.

The flexibility of design and diversity of Schiff base ligands from aliphatic to aromatic made them ideal candidates for high performance SMM. As a result this thesis started off in chapter 4 by investigating through experimental and theoretical methods the slow magnetic

#### 7.1 Conclusion

relaxation of a mononuclear dysprosium complex of a novel Schiff base ligand and how structural design involving aromaticity could affect the slow magnetic relaxation of the mononucelar dysprosium complex. The interplay between the magnetic properties and the CF occasioned by the ligand modifications showed that aromatic character at peripheral position inhibits the observation of SMM behaviour in **Dy1**. This is in line with the well established anisotropic behaviour of aromatic systems known as ring current which shows that external magnetic field applied in the perpendicular direction to the plane of an aromatic ring reinforces the magnetic moment in the direction parallel to the applied magnetic field compared to the magnetic moment perpendicular to the applied field direction.[334–337] The  $Dy^{3+}$  in **Dy1** is aligned in a plane slightly parallel to the plane of the aromatic ring, a position that feels opposing ring current from the aromatic centre when field is applied. The trigonal arrangement of the three Schiff base ligands results in a possible counter current which minimises this effect compared to Dy2 for which the aromatic ring was removed. Furthermore, Dy2 shows similar electronic properties to Dy1 signifying the importance of the structural similarity through chelation. The theoretical results supported the experimental results allowing us to describe the mechanism of spin reversal in Dy1 as one involving a competing Raman and Orbach relaxation process. The results show that SMM behaviour can be inhibited by incorporating aromatic ring at peripheral position with the metal centre placed parallel to the aromatic ring.

Chapter 5 followed with an extension to what was investigated in chapter 4 by looking beyond ligands that are directly coordinated to the magnetic lanthanide centre to investigate structural variations effected by changing the solvent medium and this time on dinuclear erbium complexes and the implication to the slow magnetic relaxation of the compounds. In addition, the role of magnetic exchange interactions between two erbium ions in a unit molecule to the observed slow magnetic relaxation was discussed. Results presented in the thesis shows that the SMM behaviour of the erbium complexes was dependent on the coordination environment, symmetry and the overall CF. The structural changes were induced by the choice of synthetic solvent and allowed us to study the possible effect of solvent when they interact with materials showing SMM behaviour. This study is important to better understand how the electronic properties of SMM material might be affected on exposure to moisture and other solvents in the environment, an insight that would support SMM application design.

Finally in chapter 6, multireference method was used to probe the complete series of isostructural Pd-Ln complexes which show SMM behaviour for the Kramers ions and none

for the non-Kramers ions. In contrast, the Pt-Ln counterparts showed SMM behaviour even for the non-Kramers ions. Results presented in this thesis show that the CF is affected by the coordination number and the extent of TM-Ln bonding interaction with implication for the Slow magnetic relaxation of the systems under investigation. The CFPs show that in a given material, there is always a competing uniaxial and transverse terms to the overall CF effect around a central metal. Although SMM behaviour is favoured with large negative uniaxial contribution, such contribution could be suppressed if there is appreciable off-diagonal terms to the CFPs. We see that the radially expanded  ${\rm Pt}^{2+}$ increased the probability of slow magnetic relaxation in the Pt-Ln series compared to the  $Pd^{2+}$  by stabilising the ground state of the later members of the lanthanide series. This is made possible by a stronger but softer interaction between the Pt and Ln centre which outweighs the decreased symmetry contribution to the  $m_i$  admixtures. Although previous experimental report argued for a possible combination of Direct and Orbach processes for spin reversal, the results from our calculations show a possible route for additional Raman process considering the stability of both the ground and excited states. In addition to the symmetry or geometry, we found that the percentage contribution of the extended Stenvens operators is related to the quadrupole moment approximation. The contribution from the second-order ranked operator which provides insight on the uniaxial anisotropy also depends on whether the  $Ln^{3+}$  is extremely or minimally prolate, oblate of just spherical. The magnetic axis which corresponds to the TM-Ln bond axis help to set up some axial perturbation with implication for the slow magnetic relaxation. In addition, the coordination number, the splitting of Kramers doublets, quadrupole moment and the effective nuclear charge combined to determine the overall magnetic properties of the systems investigated.

The results presented in this thesis will aid in the rational design of SMMs using chemical intuition of both the ligands and the metal ions. The effect of aromaticity, choice of synthetic solvent, heterometallic interactions involving transition metals and lanthanides, Ln-Ln exchange interactions and coordination number on the realisation of SMM behaviour were presented.

#### 7.1.1 Future Work

As the frontiers of molecular magnets continues, the need to rationally design SMM materials through in-depth understanding of material behaviour becomes very important. Schiff base ligands can help push this frontier further due to their versatility and easy of synthesis. To fully understand the role of aromaticity across the lanthanide series, my future work will be

focusing on synthesis, characterising and carrying out computational work on the rest of the lanthanide series apart from dysprosium using the chelate Schiff base ligand. This will provide more insight on how the quadrupole moment approximation, ionic size and nuclear charge affect the trend in the observed electronic and magnetic properties of the series and in turn give us some insights on the rational design of SMM materials. My future work will also investigate expanded solvent effect in which the solvent molecules which were not included in the current calculations will be included to better understand the role of crystal solvent in modulating SMM behaviour through structural distortion or conversion.

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# Appendix A

# Experimental protocol

# Synthesis of Dy(N4O5C14H11)3 (Dy1)

The synthesis of **Dy1** involves first, the synthesis of the organic ligand followed by the complexion with the dysprosium metal salt as described below. All chemical precursors were obtained from Wako Pure Chemical Industry Ltd and used without further purification.

## Synthesis of C10H15NO2 precursor ligand

2-picolinic acid (2.46 g, 0.02 mol) in anhydrous ethanol (12 mL) were stirred in an iced-water bath with a drop-wise addition of 98 % conc. sulfuric acid (2.5 mL). Upon complete addition of the conc. acid, the entire mixture was reflux for 24 hrs. The obtained product was cooled to room temperature and then poured into 20 mL of ice-water. The resulting solution was neutralised by adding a solution of K<sub>2</sub>CO<sub>3</sub> until pH 7, filtered and extracted from ether (4  $\times$  15 mL). The extract was dried with MgSO4 and evapourated to dryness to obtained the product as an ester (ethylpyridine-2-carboxylate) as white solid. 2.8 % of hydrazine hydrate (1.9 mL, 0.04 mol) was added to the crude ester product in ethanol (10 mL) and refluxed for 8 hrs. The final white solid product (pyridine-2-carboxylhydrzine – C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub>) was evaporated to dryness and recrystallised from anhydrous ethanol to obtain a colourless needle of pyridine-2-carboxylhydrazine in 80 % yield. Analyses: Calculated for C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub> (%): C, 66.27; H, 8.34; N, 7.73. Found (%): C, 66.25 ; H, 8.30; N, 7.78.

### Synthesis of C14H12N4O5 complex ligand

To a solution of pyridine-2-carboxylhydrzine (137.15 mg, 1 mmol) in ethanol (10 mL), ethanolic solution (10 mL) of 2-hydroxy-3-methoxy-5-nitrobenzaldehyde (197.14 mg, 1 mmol) was added and refluxed for 2 hrs. The resulting yellow product, N'-(2-hydroxy-3-methoxy-5-nitrobenzylidene)picolinohydrazide (C14H12N4O5) was recrystallised from warm ethanol with few drops of DMF to give a block-shaped yellow crystal suitable for single-crystal XRD measurement of in 95 % yield. Elemental analyses: calculated (%) - C, 53.17; H, 3.82; N, 17.72. Found (%) - C, 53.15; H, 3.75; N, 17.66.

### Synthesis of dysprosium complex, Dy1

A solution of N'-(2-hydroxy-3-methoxy-5-nitrobenzylidene)picolinohydrazide (94.8 mg, 0.3 mmol) in DMF was refluxed with a methanolic solution of dysprosium acetate tetrahydrate (33.95 mg, 0.1 mmol) for 4 hrs. The resulting golden-yellow solution was evaporated and recrystallised from DMF and few drops of methanol. Block-shaped crystals suitable for single-crystal XRD measurement were obtained after 3 weeks. Elemental analyses: Calculated (%) - C,46.14; H, 4.10; N, 15.83. Found (%) - C,46.02; H, 4.16; N, 15.92.

# Synthesis of Er1, Er2, Er3a and Y4

The hydrated Erbium Acetate, Yttrium Acetate and glacial acetic acid (99 %) were obtained from Wako Pure Chemical Industry LTD. All chemicals were used as received without further purification. Complex Er1 was synthesised under reflux without nitrogen flow, while complex Er2, Er3a and Y4 were obtained under reflux and continuous nitrogen flow after creating initial vacuum. All syntheses were carried out in the fume hood. The compounds were synthesis following modified procedures used to synthesis the same set of complexes in the literature.[301]

### synthesis of Er1

**Er1** was synthesised by refluxing Er(CH<sub>3</sub>COO)<sub>3</sub>·4H<sub>2</sub>O (207.50 mg, 0.50 mmols) in water (10 mL) for 1 hr. The resulting pink solution was cooled at room temperature and kept on standing for 2 days for crystals to appear. The clear pink hexagonal shaped crystals of [Er( $\mu_2$ ,  $\eta^3$ -CH<sub>3</sub>COO)( $\eta^2$ -CH<sub>3</sub>COO)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O (**Er1**) (380 mg, yield 91 %,) suitable for single-crystal X-ray diffraction measurement were collected under gravity

filtration and washed with cold water and dried under vacuum in a desiccator. Anal. Calc. For C<sub>12</sub>H<sub>34</sub>Er<sub>2</sub>O<sub>20</sub> (%): C, 17.30 ; H, 4.11. Found (%): C, 17.56 ; H, 4.05 . IR spectrum (ATR, v /cm<sup>-1</sup>): 3284, 1701, 1661, 1541, 1455, 1415, 1350, 1050, 1019, 967, 943, 682, 605

## Synthesis of Er2

**Er2** was synthesised by refluxing  $Er(CH_3COO)_3 \cdot 4H_2O$  (207.50 mg, 0.50 mmols) in glacial acetic acid (99 %, 10 mL) for 2 hr under nitrogen flow. The resulting pink solution was cooled at room temperature and kept on standing in an airtight vial pretreated with nitrogen flow for 14 days for crystals to appear. The pink needle shaped crystals of  $[Er(\mu_2, \eta^2-CH_3COO)(\mu_2, \eta^3-CH_3COO)(\eta^2-CH_3COO)(H_2O)CH_3COOH]_2 \cdot 2CH_3COOH$  (**Er2**) (449.50 mg, yield 93 %) suitable for single-crystal X-ray diffraction measurement were collected under gravity filtration and washed with acetic acid and dried under vacuum. Anal. Calc. For  $Er_2C_{20}H_{38}O_{22}$  (%): C, 24.89; H, 3.97. Found (%): C, 24.52; H, 3.95. IR spectrum (ATR,  $v / cm^{-1}$ ): 3314, 3019, 1751, 1720, 1698, 1590, 1542, 1466, 1392, 1317, 1054, 1014, 957, 881, 683, 619, 605

# Synthesis of (Er3a)

**3a** was synthesised by refluxing a mixture of Er(CH<sub>3</sub>COO)<sub>3</sub>·4H<sub>2</sub>O (18.90 mg, 0.045 mmols) and Y(CH<sub>3</sub>COO)<sub>3</sub>·4H<sub>2</sub>O (153.70 mg, 0.454 mmols) in glacial acetic acid (99 %, 10 mL) for 2 hr under nitrogen flow. The resulting light-pink solution was cooled at room temperature and kept on standing in an airtight vial pre-treated with nitrogen flow for 14 days for crystals to appear. The clear transparent needle-shaped crystals of [Y<sub>0.8</sub>Er<sub>0.2</sub>( $\mu_2$ ,  $\eta^2$ -CH<sub>3</sub>COO)( $\mu_2$ ,  $\eta^3$ -CH<sub>3</sub>COO)( $\eta^2$ -CH<sub>3</sub>COO)(H<sub>2</sub>O)CH<sub>3</sub>COOH]<sub>2</sub> · 2CH<sub>3</sub>COOH **3a** (332 mg, yield 79 %,) suitable for single-crystal X-ray diffraction measurement were collected under gravity filtration and washed with acetic acid and dried under vacuum. The Er<sup>III</sup> to Y<sup>III</sup> ratio was determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES). ICP-AES (mg/L): Er:Y; 0.2:0.80. Anal. Calc. For Er<sub>0</sub>·4Y<sub>1</sub>·6C<sub>20</sub>H<sub>38</sub>O<sub>22</sub> (%): C, 28.88; H, 4.60. Found (%): C, 28.38; H, 4.20. IR spectrum (ATR,  $\nu$  /cm<sup>-1</sup>): 3277, 3176, 1697, 1657, 1539, 1454, 1412, 1351, 1051, 1924, 964, 944, 682, 602

### Synthesis of Y4

Y4 was synthesised by refluxing Y(CH<sub>3</sub>COO)<sub>3</sub>·4H<sub>2</sub>O (169.05 mg, 0.50 mmols) in glacial acetic acid (99 %, 10 mL) for 2 hr under nitrogen flow. The resulting colourless solution was cooled at room temperature and kept on standing in an airtight vial pre-treated with nitrogen flow for 14 days for crystals to appear. The transparent colourless needle shaped crystals of [Y( $\mu$ 2,  $\eta^2$ -CH<sub>3</sub>COO)( $\mu$ 2,  $\eta^3$ -CH<sub>3</sub>COO)( $\eta^2$ -CH<sub>3</sub>COO)(H<sub>2</sub>O)CH<sub>3</sub>COOH]<sub>2</sub>·2CH<sub>3</sub>COOH Y4 (357.8 mg, yield 89 %,) suitable for single-crystal X-ray diffraction measurement were collected under gravity filtration and washed with acetic acid and dried under vacuum. Anal. Calc. For Y<sub>2</sub>C<sub>2</sub>OH<sub>3</sub>BO<sub>2</sub>2 (%): C, 29.72; H, 4.74. Found (%): C, 29.54; H, 4.68. IR spectrum (ATR,  $\nu$  /cm<sup>-1</sup>): 3400, 3266, 3019, 2940, 1687, 1620, 1541, 1410, 1346, 1280, 1051, 1024, 954, 690, 624

### Electrospray Mass spectrum of Er2



Fig. A.1 ESI-MS for Er2

## Characterization and instrumental procedures

The diffraction data for all the single-crystal analyses were collected on a Brucker APEX-II diffractometer equipped with an APEX II CCD detector and Japan thermal Engineering Co., Ltd Cryo system DX-CS190LD. Details of all crystallographical data are contained in the crystallographic information file (CIF). The crystal structures were solved by intrinsic phasing method. Then all atoms with the exception of hydrogen were located followed by anisotropic refinement. The hydrogen atoms were then assigned appropriate isotropic thermal parameters on their parent atoms. Final structural refinements were carried out using SHELXL-97 programs. The crystal structure visualization was done by either mercury 2021.3.0 or diamond 4.0 visualization software. The powder patterns were acquired on a Bruker D2 Phaser with Cu K $\alpha$  radiation (K $\alpha$ :  $\lambda = 1.5402$  Å) at standard condition. Diffraction data were collected in the range of 5.0  $^\circ \leq 2\theta \leq$  50.0  $^\circ$  with a scan width of 0.02 °, stripped of K $\alpha$  and smoothened using EVAC SUIT software. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed at Research and Analytical Centre for Giant Molecules, Graduate School of Science, Tohoku University, Japan on a SHIMADZU ICPE-9000 spectrometer with 5% HNO3(ag) solution. Elemental analyses were performed at Research and Analytical Centre for Giant Molecules, Graduate School of Science, Tohoku University, Japan on J-SCIENCE LAB CO., Ltd. JM-11 microanalyzer. FT-IR spectra of the polycrystalline samples were acquired on a JASCO FT/IR 6700 spectrometer using ATR method.

# Appendix B

# Coordination geometries used for the calculations

# Coordinates for the Dy n systems

Below are the coordinates of all the **Dyn** (where n = 1,2,3 and 5) molecular systems used in the computation as constructed from the single-crystal structures or modified for used in the calculations. These coordinates are either supplied as a separate file and read in by a line of code in the input files or included within the input file.

### Dy1 coordinates

| 103 |                   |                   |                  |
|-----|-------------------|-------------------|------------------|
| Dy1 | coordinates       |                   |                  |
| Dy  | 7.02358000000000  | 3.94433000000000  | 4.11790000000000 |
| С   | 10.89957000000000 | -1.17615000000000 | 6.28474000000000 |
| Н   | 10.92473000000000 | -1.70673000000000 | 7.04748000000000 |
| С   | 11.64616000000000 | -1.55062000000000 | 5.22080000000000 |
| Н   | 12.16348000000000 | -2.32186000000000 | 5.25976000000000 |
| С   | 11.63488000000000 | -0.7787400000000  | 4.07894000000000 |
| Н   | 12.16138000000000 | -1.0025200000000  | 3.34467000000000 |
| С   | 10.8193000000000  | 0.33658000000000  | 4.05346000000000 |
| Н   | 10.75956000000000 | 0.8680700000000   | 3.29222000000000 |
| С   | 10.10135000000000 | 0.63709000000000  | 5.1803400000000  |
| С   | 9.2238700000000   | 1.83926000000000  | 5.18933000000000 |
| С   | 7.70527000000000  | 3.75459000000000  | 7.63339000000000 |
|     |                   |                   |                  |

| Н | 8.1520300000000   | 3.34458000000000  | 8.33769000000000  |
|---|-------------------|-------------------|-------------------|
| С | 6.79049000000000  | 4.81272000000000  | 7.95857000000000  |
| С | 6.04264000000000  | 5.50069000000000  | 6.97105000000000  |
| С | 5.23835000000000  | 6.60921000000000  | 7.41911000000000  |
| С | 5.09143000000000  | 6.90674000000000  | 8.74079000000000  |
| Н | 4.5551300000000   | 7.61709000000000  | 9.01052000000000  |
| С | 5.76429000000000  | 6.12185000000000  | 9.68185000000000  |
| С | 6.62426000000000  | 5.12399000000000  | 9.31622000000000  |
| Η | 7.09706000000000  | 4.65452000000000  | 9.96357000000000  |
| С | 4.00484000000000  | 8.51656000000000  | 6.71331000000000  |
| Н | 3.23959000000000  | 8.34536000000000  | 7.26776000000000  |
| Η | 3.72595000000000  | 8.95387000000000  | 5.90562000000000  |
| Н | 4.6212300000000   | 9.08137000000000  | 7.18684000000000  |
| С | 7.43554000000000  | 1.14866000000000  | -2.14287000000000 |
| Н | 8.05480000000000  | 1.12095000000000  | -2.83667000000000 |
| С | 6.2887500000000   | 0.40694000000000  | -2.27324000000000 |
| Н | 6.1420300000000   | -0.11660000000000 | -3.02698000000000 |
| С | 5.37018000000000  | 0.45280000000000  | -1.26923000000000 |
| Н | 4.58667000000000  | -0.04393000000000 | -1.32618000000000 |
| С | 5.61882000000000  | 1.24859000000000  | -0.16184000000000 |
| Н | 5.00116000000000  | 1.31240000000000  | 0.53047000000000  |
| С | 6.80171000000000  | 1.93768000000000  | -0.11988000000000 |
| С | 7.14172000000000  | 2.77331000000000  | 1.06844000000000  |
| С | 9.59975000000000  | 5.06695000000000  | 1.80270000000000  |
| Н | 10.09577000000000 | 4.9093800000000   | 1.03097000000000  |
| С | 10.04375000000000 | 6.11929000000000  | 2.69282000000000  |
| С | 9.4058100000000   | 6.37059000000000  | 3.94557000000000  |
| С | 9.78841000000000  | 7.57440000000000  | 4.62589000000000  |
| С | 10.81963000000000 | 8.35480000000000  | 4.18233000000000  |
| Н | 11.06930000000000 | 9.11427000000000  | 4.65586000000000  |
| С | 11.49661000000000 | 8.00399000000000  | 3.01350000000000  |
| С | 11.10038000000000 | 6.91937000000000  | 2.2747300000000   |
| Н | 11.54366000000000 | 6.71746000000000  | 1.48202000000000  |
| С | 2.3653100000000   | 8.71173000000000  | 2.98053000000000  |
| Н | 1.4504000000000   | 8.8201500000000   | 3.10191000000000  |
| С | 3.10556000000000  | 9.8020800000000   | 2.68083000000000  |
| Н | 2.70197000000000  | 10.63310000000000 | 2.56694000000000  |
| С | 4.43733000000000  | 9.66257000000000  | 2.54896000000000  |
| Н | 4.97209000000000  | 10.40260000000000 | 2.37364000000000  |
| С | 5.00535000000000  | 8.4052600000000   | 2.67633000000000  |
| Н | 5.92344000000000  | 8.28408000000000  | 2.58792000000000  |
| С | 4.17536000000000  | 7.34229000000000  | 2.94007000000000  |

| С | 4.75761000000000  | 5.99094000000000  | 3.15136000000000  |
|---|-------------------|-------------------|-------------------|
| С | 3.55655000000000  | 2.92384000000000  | 4.20481000000000  |
| Η | 2.65858000000000  | 3.15267000000000  | 4.11939000000000  |
| С | 3.86772000000000  | 1.59011000000000  | 4.64687000000000  |
| С | 5.20328000000000  | 1.1663600000000   | 4.90461000000000  |
| С | 5.38152000000000  | -0.20714000000000 | 5.32869000000000  |
| С | 4.32838000000000  | -1.04356000000000 | 5.51900000000000  |
| Η | 4.46443000000000  | -1.92284000000000 | 5.79173000000000  |
| С | 3.03231000000000  | -0.56038000000000 | 5.30022000000000  |
| С | 2.80283000000000  | 0.71991000000000  | 4.86715000000000  |
| Η | 1.92995000000000  | 1.00944000000000  | 4.72180000000000  |
| С | 6.97102000000000  | -1.8994900000000  | 5.84118000000000  |
| Η | 6.58034000000000  | -2.1041800000000  | 6.69533000000000  |
| Η | 7.92176000000000  | -2.02555000000000 | 5.88614000000000  |
| Н | 6.60198000000000  | -2.4805000000000  | 5.17285000000000  |
| С | 7.79376000000000  | 8.36770000000000  | 5.53848000000000  |
| Н | 7.8227500000000   | 9.1905400000000   | 5.04547000000000  |
| Н | 7.34776000000000  | 8.5120800000000   | 6.37615000000000  |
| Η | 7.31739000000000  | 7.70598000000000  | 5.03199000000000  |
| Ν | 10.13450000000000 | -0.0882100000000  | 6.29523000000000  |
| Ν | 8.8281400000000   | 2.2522500000000   | 6.38814000000000  |
| Н | 9.10453000000000  | 1.86601000000000  | 7.10442000000000  |
| Ν | 7.95674000000000  | 3.32608000000000  | 6.44508000000000  |
| Ν | 5.51627000000000  | 6.35320000000000  | 11.08595000000000 |
| Ν | 7.71148000000000  | 1.9064700000000   | -1.09091000000000 |
| Ν | 8.2529300000000   | 3.48600000000000  | 0.96953000000000  |
| Η | 8.7637200000000   | 3.42174000000000  | 0.2787200000000   |
| Ν | 8.56655000000000  | 4.33838000000000  | 2.01249000000000  |
| Ν | 12.64441000000000 | 8.7693500000000   | 2.60590000000000  |
| Ν | 2.88389000000000  | 7.47590000000000  | 3.11390000000000  |
| Ν | 3.90642000000000  | 5.05286000000000  | 3.56345000000000  |
| Η | 3.05954000000000  | 5.2050700000000   | 3.60840000000000  |
| Ν | 4.43776000000000  | 3.82321000000000  | 3.92009000000000  |
| Ν | 1.90038000000000  | -1.44200000000000 | 5.52200000000000  |
| 0 | 8.8993900000000   | 2.4233100000000   | 4.14232000000000  |
| 0 | 6.04086000000000  | 5.18386000000000  | 5.74453000000000  |
| 0 | 4.6406100000000   | 7.2861700000000   | 6.39113000000000  |
| 0 | 4.68427000000000  | 7.2006900000000   | 11.40963000000000 |
| 0 | 6.13802000000000  | 5.69384000000000  | 11.90714000000000 |
| 0 | 6.42548000000000  | 2.79428000000000  | 2.07768000000000  |
| 0 | 8.55467000000000  | 5.59471000000000  | 4.46900000000000  |
| 0 | 9.12486000000000  | 7.91104000000000  | 5.78274000000000  |

|          | 0          | 13.00763000000000 | 9.71046000000000  | 3.31170000000000   |
|----------|------------|-------------------|-------------------|--------------------|
|          | 0          | 13.24303000000000 | 8.43698000000000  | 1.59291000000000   |
|          | 0          | 5.96096000000000  | 5.76919000000000  | 2.97888000000000   |
|          | 0          | 6.21739000000000  | 1.91728000000000  | 4.78818000000000   |
|          | 0          | 6.68647000000000  | -0.54553000000000 | 5.5040200000000    |
|          | 0          | 2.13030000000000  | -2.5797400000000  | 5.93708000000000   |
|          | 0          | 0.96481000000000  | -1.06527000000000 | 5.71775000000000   |
| Dv2 coor | dinat      | <b>es</b>         |                   |                    |
|          | annat      |                   |                   |                    |
|          | 67<br>Dv/2 | Coordinatos       |                   |                    |
|          | C Dyz      |                   | 0 6371000000000   | 5 18030000000000   |
|          | C          | 9 22390000000000  | 1 83930000000000  | 5 189300000000000  |
|          | C          | 7 705300000000000 | 3 75460000000000  | 7 633400000000000  |
|          | C          | 6 79050000000000  | 4 8127000000000   | 7 958600000000000  |
|          | C          | 6 042600000000000 | 5 50070000000000  | 6 9711000000000000 |
|          | C          | 5 23830000000000  | 6 60920000000000  | 7 4191000000000000 |
|          | C          | 6 62430000000000  | 5 124000000000000 | 9 316200000000000  |
|          | C          | 6.80170000000000  | 1.93770000000000  | -0.119900000000000 |
|          | С          | 7.14170000000000  | 2.77330000000000  | 1.06840000000000   |
|          | С          | 9.59980000000000  | 5.06690000000000  | 1.80270000000000   |
|          | C          | 10.04370000000000 | 6.11930000000000  | 2.69280000000000   |
|          | С          | 9.40580000000000  | 6.37060000000000  | 3.94560000000000   |
|          | С          | 9.78840000000000  | 7.57440000000000  | 4.62590000000000   |
|          | С          | 11.10040000000000 | 6.91940000000000  | 2.2747000000000    |
|          | С          | 4.17540000000000  | 7.34230000000000  | 2.94010000000000   |
|          | С          | 4.75760000000000  | 5.99090000000000  | 3.15140000000000   |
|          | С          | 3.55660000000000  | 2.92380000000000  | 4.20480000000000   |
|          | С          | 3.86770000000000  | 1.59010000000000  | 4.64690000000000   |
|          | С          | 5.20330000000000  | 1.16640000000000  | 4.90460000000000   |
|          | С          | 5.38150000000000  | -0.20710000000000 | 5.32870000000000   |
|          | С          | 2.80280000000000  | 0.71990000000000  | 4.86710000000000   |
|          | Dy         | 7.02360000000000  | 3.94430000000000  | 4.11790000000000   |
|          | Ν          | 8.82810000000000  | 2.25230000000000  | 6.38810000000000   |
|          | Ν          | 7.95670000000000  | 3.32610000000000  | 6.44510000000000   |
|          | Ν          | 8.25290000000000  | 3.48600000000000  | 0.96950000000000   |
|          | Ν          | 8.56660000000000  | 4.33840000000000  | 2.01250000000000   |
|          | Ν          | 3.90640000000000  | 5.05290000000000  | 3.56340000000000   |
|          | Ν          | 4.43780000000000  | 3.82320000000000  | 3.92010000000000   |

O8.89940000000002.42330000000004.1423000000000O6.04090000000005.18390000000005.74450000000000

| 0 | 6.42550000000000 | 2.79430000000000 | 2.07770000000000  |
|---|------------------|------------------|-------------------|
| 0 | 8.55470000000000 | 5.59470000000000 | 4.469000000000000 |
| 0 | 5.96100000000000 | 5.7692000000000  | 2.97890000000000  |
| 0 | 6.21740000000000 | 1.91730000000000 | 4.78820000000000  |
| Η | 3.24006000000000 | 4.8911000000000  | 2.80827000000000  |
| Η | 2.12591000000000 | 1.15575000000000 | 5.57191000000000  |
| Η | 3.17323000000000 | -0.2063100000000 | 5.2541500000000   |
| Н | 2.29113000000000 | 0.5417200000000  | 3.94441000000000  |
| Н | 2.56116000000000 | 3.17859000000000 | 4.10881000000000  |
| Н | 8.17646000000000 | 4.0533200000000  | 0.12528000000000  |

# Coordinates for the Er\_n systems

The coordinates below were used for the calculations carried out in chapter 5 for **Er1** and **Er2** systems. Note that for the SINGLE-ANISO job, one of the Er-centre was replaced by Lu or Y or La by changing one of the Er label in the coordinate files below to either Lu, Y or La as discussed in the text.

### Er1 coordinates

| Er | -1.468767 | 3.805721  | 3.757264 |
|----|-----------|-----------|----------|
| Er | 1.753301  | 1.766787  | 5.400763 |
| 0  | 0.157923  | 1.838974  | 3.684549 |
| 0  | -1.351191 | 2.016745  | 2.138766 |
| 0  | -3.748592 | 3.551352  | 2.900988 |
| 0  | 0.528467  | 4.578329  | 2.662605 |
| 0  | -2.732804 | 4.991666  | 5.294896 |
| 0  | -2.349100 | 2.160817  | 5.159632 |
| 0  | -0.632712 | 6.099813  | 3.717976 |
| 0  | -2.361306 | 4.818202  | 1.804406 |
| 0  | 0.126610  | 3.733534  | 5.473478 |
| 0  | 1.635724  | 3.555763  | 7.019261 |
| 0  | 4.033126  | 2.021156  | 6.257039 |
| 0  | -0.243933 | 0.994179  | 6.495422 |
| 0  | 3.017338  | 0.580842  | 3.863131 |
| 0  | 2.633634  | 3.411691  | 3.998395 |
| 0  | 0.917246  | -0.527305 | 5.440051 |
| 0  | 2.645839  | 0.754306  | 7.353621 |
| С  | -3.506747 | 4.294662  | 1.907617 |
| С  | -0.385937 | 1.385093  | 2.631834 |
| С  | 0.382283  | 5.774590  | 3.044128 |

| С | -4.543395 | 4.544844  | 0.852612  |
|---|-----------|-----------|-----------|
| С | 0.126744  | 0.137663  | 1.989123  |
| С | 1.426681  | 6.795463  | 2.702534  |
| С | 3.791281  | 1.277846  | 7.250410  |
| С | 0.670471  | 4.187415  | 6.526193  |
| С | -0.097749 | -0.202082 | 6.113899  |
| С | 4.827929  | 1.027664  | 8.305415  |
| С | 0.157790  | 5.434845  | 7.168904  |
| С | -1.142147 | -1.222955 | 6.455493  |
| Н | -4.846590 | 5.454112  | 0.910308  |
| Н | -5.286340 | 3.951123  | 0.987235  |
| Н | -4.161919 | 4.388850  | -0.014653 |
| Н | -0.534627 | -0.204277 | 1.382862  |
| Н | 0.310577  | -0.518053 | 2.664986  |
| Η | 0.932781  | 0.334435  | 1.505580  |
| Н | 2.267974  | 6.532453  | 3.082592  |
| Н | 1.168170  | 7.649175  | 3.056949  |
| Н | 1.512155  | 6.858582  | 1.748267  |
| Н | -3.165929 | 2.065673  | 5.449026  |
| Н | -1.819310 | 1.673247  | 5.824505  |
| Н | -2.936292 | 5.779877  | 5.229233  |
| Н | -2.863922 | 4.670831  | 5.971034  |
| Η | 5.131123  | 0.118396  | 8.247719  |
| Н | 5.570874  | 1.621385  | 8.170792  |
| Η | 4.446453  | 1.183658  | 9.172680  |
| Η | 0.819160  | 5.776785  | 7.775165  |
| Η | -0.026043 | 6.090561  | 6.493041  |
| Η | -0.648247 | 5.238073  | 7.652447  |
| Н | -1.983440 | -0.959945 | 6.075435  |
| Н | -0.883636 | -2.076667 | 6.101078  |
| Н | -1.227621 | -1.286074 | 7.409760  |
| Н | 3.450463  | 3.506835  | 3.709001  |
| Н | 2.103844  | 3.899261  | 3.333522  |
| Н | 3.220826  | -0.207369 | 3.928794  |
| Н | 3.148456  | 0.901677  | 3.186993  |

### Er2 coordinates

| Н | 7.606249 | 6.816318 | 11.108860 |
|---|----------|----------|-----------|
| Н | 6.638739 | 6.690365 | 9.839993  |
| Н | 7.303202 | 8.099748 | 10.202527 |
| Н | 8.185105 | 6.250331 | 3.600236  |

| Н | 8.667136  | 4.885618  | 2.917000  |
|---|-----------|-----------|-----------|
| Н | 9.611883  | 6.176360  | 2.879352  |
| Н | 7.750877  | 3.692202  | 9.365911  |
| Н | 6.931821  | 2.923141  | 8.226720  |
| Η | 7.211549  | 4.492758  | 8.088678  |
| Н | 13.471451 | 9.420699  | 10.282005 |
| Н | 13.278457 | 8.776261  | 11.733533 |
| Н | 12.088251 | 9.609690  | 11.064241 |
| Н | 12.166049 | 6.058397  | 10.622229 |
| Н | 9.998060  | 8.644338  | 6.196533  |
| Н | 11.330380 | 9.044835  | 7.074979  |
| Н | 14.288854 | 2.098878  | 2.834732  |
| Н | 15.256364 | 2.224831  | 4.103599  |
| Н | 14.591902 | 0.815448  | 3.741066  |
| Η | 13.709998 | 2.664865  | 10.343357 |
| Н | 13.227967 | 4.029578  | 11.026593 |
| Н | 12.283220 | 2.738836  | 11.064241 |
| Η | 14.144227 | 5.222994  | 4.577682  |
| Н | 14.963282 | 5.992055  | 5.716873  |
| Η | 14.683555 | 4.422438  | 5.854915  |
| Η | 8.423653  | -0.505503 | 3.661587  |
| Η | 8.616647  | 0.138935  | 2.210059  |
| Η | 9.806853  | -0.694494 | 2.879352  |
| Η | 9.729055  | 2.856799  | 3.321364  |
| Η | 11.897043 | 0.270858  | 7.747060  |
| Η | 10.564724 | -0.129639 | 6.868614  |
| С | 7.437097  | 7.131520  | 10.195555 |
| С | 8.604694  | 6.801228  | 9.340813  |
| С | 8.962774  | 5.678501  | 3.413392  |
| С | 12.321229 | 7.775400  | 10.279217 |
| С | 9.590934  | 5.254047  | 4.707357  |
| С | 7.576186  | 3.636234  | 8.402409  |
| С | 8.808208  | 3.358908  | 7.706624  |
| С | 12.832500 | 8.997217  | 10.889946 |
| С | 14.458007 | 1.783676  | 3.748038  |
| С | 13.290410 | 2.113968  | 4.602780  |
| С | 12.932330 | 3.236695  | 10.530201 |
| С | 12.304169 | 3.661149  | 9.236236  |
| С | 14.318918 | 5.278962  | 5.541184  |
| С | 13.086896 | 5.556288  | 6.236969  |
| С | 9.062603  | -0.082021 | 3.053647  |
| С | 9.573875  | 1.139796  | 3.664376  |

| 0  | 9.820299  | 6.091941 | 5.564888  |
|----|-----------|----------|-----------|
| 0  | 9.863000  | 4.023841 | 4.791018  |
| 0  | 11.762214 | 7.804668 | 9.230658  |
| 0  | 12.657581 | 6.687051 | 10.882974 |
| 0  | 9.555948  | 6.196518 | 9.792585  |
| 0  | 8.539581  | 7.071223 | 8.134692  |
| 0  | 9.711808  | 4.192966 | 7.675948  |
| 0  | 8.936998  | 2.268167 | 7.111232  |
| 0  | 10.678865 | 8.405105 | 6.815628  |
| 0  | 12.074805 | 2.823255 | 8.378705  |
| 0  | 12.032104 | 4.891355 | 9.152574  |
| 0  | 10.132889 | 1.110528 | 4.712934  |
| 0  | 9.237523  | 2.228145 | 3.060619  |
| 0  | 12.339156 | 2.718678 | 4.151008  |
| 0  | 13.355523 | 1.843973 | 5.808901  |
| 0  | 12.183296 | 4.722230 | 6.267645  |
| 0  | 12.958105 | 6.647029 | 6.832360  |
| 0  | 11.216238 | 0.510091 | 7.127965  |
| Er | 11.147015 | 2.668870 | 6.249797  |
| Er | 10.748089 | 6.246326 | 7.693796  |

# Coordinates for the Pd-Ln and Pt-Ln systems

The coordinates below were used for the calculations carried out in chapter 6 for Pd-Ln and Pt-Ln systems. Note that for the SINGLE-ANISO job, one of the Ln-centre was replaced by Lu or La by changing one of the two lanthanide label in the coordinate files below to either La or Lu.

#### Pd-Ce, Pd-Pr, Pd-Nd, Pd-Pm, and Pd-Sm coordinates

The original coordinates were obtained for Pd-Nd. However, the same coordinate system was used for Pd-Ce, Pd-Pr, Pd-Pm, and Pd-Sm due to similarity in the ionic size of the early  $Ln^{3+}$  and the lack of experimental crystal structure for Pd-Ce, Pd-Pr, Pd-Pm, and Pd-Sm. For each case, the Nd (now label Ln in the coordinate file below) was replace with the appropriate lanthanide ion.

| 80    |             |           |          |
|-------|-------------|-----------|----------|
| Pd-Nd | coordinates |           |          |
| Ln    | 3.772205    | -1.203375 | 4.358568 |
| Ln    | 4.931902    | 1.203375  | 7.562465 |
| С     | 0.447504    | -2.347650 | 1.159916 |

| С | 0.885807  | 3.728268  | 7.212225  |
|---|-----------|-----------|-----------|
| С | 1.817569  | -2.415582 | 1.782194  |
| С | 2.211177  | 3.332664  | 7.797547  |
| С | 2.232467  | -5.590404 | 5.362080  |
| С | 2.549012  | 0.275724  | 11.587243 |
| С | 2.923944  | -4.533462 | 4.541913  |
| С | 3.259791  | 1.128870  | 10.572764 |
| С | 3.688168  | 1.758240  | 4.267730  |
| С | 3.690284  | 3.252744  | 4.171169  |
| С | 5.013823  | -3.252744 | 7.749863  |
| С | 5.015939  | -1.758240 | 7.653303  |
| С | 5.444316  | -1.128870 | 1.348269  |
| С | 5.780163  | 4.533462  | 7.379119  |
| С | 6.155095  | -0.275724 | 0.333789  |
| С | 6.471640  | 5.590404  | 6.558952  |
| С | 6.492930  | -3.332664 | 4.123485  |
| С | 6.886538  | 2.415582  | 10.138838 |
| С | 7.818300  | -3.728268 | 4.708808  |
| С | 8.256603  | 2.347650  | 10.761116 |
| Η | 0.088279  | -1.464534 | 1.273166  |
| Η | -0.129146 | -2.985012 | 1.586689  |
| Η | 0.367241  | 4.189806  | 7.876226  |
| Η | 0.414771  | 2.943054  | 6.926120  |
| Η | 0.510808  | -2.549448 | 0.222923  |
| Н | 1.028232  | 4.307688  | 6.460007  |
| Η | 1.281875  | -5.512482 | 5.250023  |
| Η | 1.298672  | 0.055944  | 5.043789  |
| Н | 1.441641  | -0.821178 | 6.264503  |
| Н | 1.612018  | 0.247752  | 11.381010 |
| Η | 2.456235  | -5.474520 | 6.288345  |
| Η | 2.517810  | -6.459534 | 5.070015  |
| Η | 2.673360  | 0.647352  | 12.462247 |
| Η | 2.800220  | 3.582414  | 4.313030  |
| Η | 2.908869  | -0.615384 | 11.563401 |
| Η | 3.994521  | 3.516480  | 3.299742  |
| Η | 4.276015  | 3.614382  | 4.838747  |
| Η | 4.428092  | -3.614382 | 7.082285  |
| Н | 4.709586  | -3.516480 | 8.621291  |
| Η | 5.795238  | 0.615384  | 0.357631  |
| Η | 5.903888  | -3.582414 | 7.608003  |
| Н | 6.030747  | -0.647352 | -0.541215 |
| Н | 6.186298  | 6.459534  | 6.851017  |

| Н  | 6.247872 | 5.474520  | 5.632688  |
|----|----------|-----------|-----------|
| Н  | 7.092089 | -0.247752 | 0.540023  |
| Н  | 7.262466 | 0.821178  | 5.656530  |
| Н  | 7.405435 | -0.055944 | 6.877244  |
| Н  | 7.422232 | 5.512482  | 6.671010  |
| Н  | 7.675875 | -4.307688 | 5.461025  |
| Н  | 8.193299 | 2.549448  | 11.698109 |
| Н  | 8.289336 | -2.943054 | 4.994913  |
| Н  | 8.336866 | -4.189806 | 4.044806  |
| Н  | 8.615828 | 1.464534  | 10.647866 |
| Н  | 8.833253 | 2.985012  | 10.334343 |
| 0  | 1.705378 | -0.525074 | 5.513477  |
| 0  | 2.133586 | -1.567431 | 2.627396  |
| 0  | 2.551899 | 3.940655  | 8.858519  |
| 0  | 2.569997 | -3.361235 | 1.391184  |
| 0  | 2.879323 | -3.350047 | 4.916234  |
| 0  | 2.898563 | 2.465332  | 7.228914  |
| 0  | 2.967284 | 1.069529  | 3.503591  |
| 0  | 3.521852 | -4.940055 | 3.489286  |
| 0  | 3.534917 | 2.306092  | 10.943508 |
| 0  | 3.537978 | 0.649550  | 9.452187  |
| 0  | 4.266848 | -1.162237 | 6.809294  |
| 0  | 4.437259 | 1.162237  | 5.111739  |
| 0  | 5.166129 | -0.649550 | 2.468846  |
| 0  | 5.169190 | -2.306092 | 0.977525  |
| 0  | 5.182255 | 4.940055  | 8.431746  |
| 0  | 5.736823 | -1.069529 | 8.417441  |
| 0  | 5.805544 | -2.465332 | 4.692118  |
| 0  | 5.824785 | 3.350047  | 7.004799  |
| 0  | 6.134110 | 3.361235  | 10.529848 |
| 0  | 6.152208 | -3.940655 | 3.062513  |
| 0  | 6.570521 | 1.567431  | 9.293637  |
| 0  | 6.998730 | 0.525074  | 6.407555  |
| Pd | 4.348605 | -3.586130 | 2.269407  |
| Pd | 4.355502 | 3.586130  | 9.651625  |

### Pd-Gd coordinates

| 80    |             |           |          |
|-------|-------------|-----------|----------|
| Pd-Gd | coordinates |           |          |
| Gd    | 3.732952    | 11.079588 | 4.319903 |
| Gd    | 4.952614    | 8.726612  | 7.433656 |

| С | 0.431333  | 12.198639 | 1.169479  |
|---|-----------|-----------|-----------|
| С | 0.947157  | 6.276585  | 7.041557  |
| С | 1.796420  | 12.287766 | 1.783015  |
| С | 2.185058  | 15.400113 | 5.349045  |
| С | 2.259223  | 6.652506  | 7.656268  |
| С | 2.568861  | 9.677309  | 11.391549 |
| С | 2.896059  | 14.368210 | 4.523945  |
| С | 3.295211  | 8.803658  | 10.400724 |
| С | 3.716379  | 8.185704  | 4.205423  |
| С | 3.748950  | 6.692911  | 4.074959  |
| С | 4.936617  | 13.113289 | 7.678600  |
| С | 4.969188  | 11.620496 | 7.548136  |
| С | 5.390356  | 11.002542 | 1.352835  |
| С | 5.789508  | 5.437990  | 7.229614  |
| С | 6.116705  | 10.128891 | 0.362010  |
| С | 6.426344  | 13.153694 | 4.097291  |
| С | 6.500509  | 4.406087  | 6.404514  |
| С | 6.889147  | 7.518434  | 9.970544  |
| С | 7.738409  | 13.529615 | 4.712002  |
| С | 8.254234  | 7.607561  | 10.584080 |
| Н | 0.199803  | 11.275670 | 1.035489  |
| Н | -0.210376 | 12.606646 | 1.754806  |
| Н | 0.356818  | 7.033182  | 7.058012  |
| Н | 0.430543  | 12.654181 | 0.324398  |
| Н | 0.555676  | 5.555639  | 7.539908  |
| Н | 1.086752  | 5.999298  | 6.133007  |
| Н | 1.237890  | 15.316134 | 5.219756  |
| Н | 1.329782  | 9.883294  | 5.218580  |
| Н | 1.468959  | 10.754767 | 6.088344  |
| Н | 1.636165  | 9.710980  | 11.165881 |
| Н | 2.394180  | 15.268600 | 6.276400  |
| Н | 2.468526  | 16.276735 | 5.078713  |
| Η | 2.671654  | 9.314856  | 12.274242 |
| Η | 2.878114  | 6.336003  | 4.266542  |
| Н | 2.936695  | 10.564627 | 11.365692 |
| Н | 4.003212  | 6.454841  | 3.180513  |
| Н | 4.299566  | 13.474158 | 7.058012  |
| Н | 4.386001  | 6.332042  | 4.695547  |
| Н | 4.682355  | 13.351359 | 8.573046  |
| Н | 5.748871  | 9.241573  | 0.387867  |
| Н | 5.807453  | 13.470197 | 7.487017  |
| Н | 6.013913  | 10.491344 | -0.520683 |

| Н  | 6.217041 | 3.529465  | 6.674846  |
|----|----------|-----------|-----------|
| Н  | 6.291386 | 4.537600  | 5.477158  |
| Н  | 7.049402 | 10.095220 | 0.587678  |
| Н  | 7.216608 | 9.051433  | 5.665215  |
| Н  | 7.355785 | 9.922906  | 6.534979  |
| Н  | 7.447677 | 4.490066  | 6.533803  |
| Н  | 7.598815 | 13.806902 | 5.620552  |
| Н  | 8.129891 | 14.250561 | 4.213651  |
| Н  | 8.255024 | 7.152019  | 11.429161 |
| Н  | 8.328749 | 12.773018 | 4.695547  |
| Н  | 8.485764 | 8.530530  | 10.718070 |
| Н  | 8.895943 | 7.199554  | 9.998753  |
| 0  | 1.724633 | 10.428955 | 5.431320  |
| 0  | 2.127539 | 11.446003 | 2.633973  |
| 0  | 2.525125 | 13.223807 | 1.373991  |
| 0  | 2.589655 | 6.013360  | 8.701160  |
| 0  | 2.871864 | 13.177659 | 4.900059  |
| 0  | 2.949209 | 7.517047  | 7.095624  |
| 0  | 2.961627 | 8.871791  | 3.461423  |
| 0  | 3.472984 | 14.785328 | 3.473177  |
| 0  | 3.562474 | 7.639251  | 10.782715 |
| 0  | 3.589372 | 9.281780  | 9.285429  |
| 0  | 4.223533 | 11.014624 | 6.713515  |
| 0  | 4.462034 | 8.791576  | 5.040044  |
| 0  | 5.096195 | 10.524420 | 2.468130  |
| 0  | 5.123093 | 12.166949 | 0.970844  |
| 0  | 5.212583 | 5.020872  | 8.280382  |
| 0  | 5.723940 | 10.934409 | 8.292136  |
| 0  | 5.736358 | 12.289153 | 4.657935  |
| 0  | 5.813703 | 6.628541  | 6.853500  |
| 0  | 6.095912 | 13.792840 | 3.052399  |
| 0  | 6.160442 | 6.582393  | 10.379568 |
| 0  | 6.558028 | 8.360197  | 9.119586  |
| 0  | 6.960934 | 9.377245  | 6.322239  |
| Pd | 4.305086 | 13.446627 | 2.251512  |
| Pd | 4.380481 | 6.359573  | 9.502047  |

### Pd-Tb coordinates

| 80    |             |           |          |
|-------|-------------|-----------|----------|
| Pd-Tb | coordinates |           |          |
| С     | 0.384501    | 11.995897 | 1.174100 |

| С | 0.824343  | 6.165728  | 7.029382  |
|---|-----------|-----------|-----------|
| С | 1.760854  | 12.077792 | 1.763257  |
| С | 2.145536  | 6.529299  | 7.632235  |
| С | 2.177227  | 15.213957 | 5.288600  |
| С | 2.506061  | 9.619749  | 11.333400 |
| С | 2.882956  | 14.169736 | 4.471998  |
| С | 3.205582  | 8.716949  | 10.349170 |
| С | 3.644279  | 8.008093  | 4.193866  |
| С | 3.651189  | 6.508873  | 4.082192  |
| С | 4.895995  | 12.943827 | 7.623689  |
| С | 4.902905  | 11.444607 | 7.512015  |
| С | 5.341601  | 10.735751 | 1.356712  |
| С | 5.664228  | 5.282964  | 7.233883  |
| С | 6.041123  | 9.832951  | 0.372481  |
| С | 6.369956  | 4.238743  | 6.417281  |
| С | 6.401647  | 12.923401 | 4.073647  |
| С | 6.786329  | 7.374908  | 9.942624  |
| С | 7.722840  | 13.286972 | 4.676500  |
| С | 8.162682  | 7.456803  | 10.531781 |
| Н | 0.057351  | 11.074422 | 1.234970  |
| Η | -0.217816 | 12.589787 | 1.668088  |
| Η | 0.263754  | 5.734656  | 7.707152  |
| Η | 0.379109  | 6.975738  | 6.705129  |
| Н | 0.415185  | 12.270763 | 0.234118  |
| Η | 0.965543  | 5.547910  | 6.281376  |
| Η | 1.208943  | 15.118638 | 5.175170  |
| Η | 1.249620  | 9.631032  | 5.080352  |
| Η | 1.289306  | 10.640627 | 5.923176  |
| Η | 1.563400  | 9.708843  | 11.081958 |
| Η | 2.408141  | 15.099186 | 6.234552  |
| Η | 2.454733  | 16.104890 | 4.990217  |
| Η | 2.570196  | 9.234197  | 12.232646 |
| Η | 2.729394  | 6.178178  | 4.067794  |
| Η | 2.930985  | 10.502513 | 11.325440 |
| Н | 4.105851  | 6.244317  | 3.255406  |
| Н | 4.124643  | 6.125655  | 4.850917  |
| Η | 4.422541  | 13.327045 | 6.854964  |
| Η | 4.441333  | 13.208383 | 8.450476  |
| Н | 5.616198  | 8.950187  | 0.380441  |
| Н | 5.817789  | 13.274522 | 7.638088  |
| Н | 5.976988  | 10.218503 | -0.526765 |
| Н | 6.092450  | 3.347810  | 6.715664  |

| Н  | 6.139042 | 4.353514  | 5.471329  |
|----|----------|-----------|-----------|
| Н  | 6.983783 | 9.743857  | 0.623923  |
| Н  | 7.257878 | 8.812073  | 5.782705  |
| Н  | 7.297564 | 9.821668  | 6.625529  |
| Н  | 7.338240 | 4.334062  | 6.530711  |
| Н  | 7.581641 | 13.904790 | 5.424505  |
| Н  | 8.131999 | 7.181937  | 11.471764 |
| Н  | 8.168074 | 12.476962 | 5.000752  |
| Н  | 8.283429 | 13.718044 | 3.998729  |
| Н  | 8.489832 | 8.378278  | 10.470911 |
| Н  | 8.764999 | 6.862913  | 10.037793 |
| 0  | 1.691823 | 10.239707 | 5.391495  |
| 0  | 2.111509 | 11.228487 | 2.606197  |
| 0  | 2.446923 | 5.931517  | 8.718189  |
| 0  | 2.489222 | 13.037589 | 1.356126  |
| 0  | 2.823732 | 12.975340 | 4.837807  |
| 0  | 2.883850 | 7.350397  | 7.044833  |
| 0  | 2.917722 | 8.696913  | 3.434388  |
| 0  | 3.462811 | 9.141407  | 9.205037  |
| 0  | 3.489767 | 7.554262  | 10.779712 |
| 0  | 3.500839 | 14.586024 | 3.434974  |
| 0  | 4.146889 | 10.842351 | 6.675396  |
| 0  | 4.400295 | 8.610349  | 5.030485  |
| 0  | 5.046345 | 4.866676  | 8.270907  |
| 0  | 5.057417 | 11.898438 | 0.926169  |
| 0  | 5.084372 | 10.311293 | 2.500844  |
| 0  | 5.629462 | 10.755787 | 8.271493  |
| 0  | 5.663334 | 12.102303 | 4.661048  |
| 0  | 5.723452 | 6.477360  | 6.868075  |
| 0  | 6.057962 | 6.415111  | 10.349755 |
| 0  | 6.100260 | 13.521183 | 2.987692  |
| 0  | 6.435674 | 8.224213  | 9.099684  |
| 0  | 6.855360 | 9.212993  | 6.314386  |
| Pd | 4.260489 | 6.231672  | 9.497684  |
| Pd | 4.286695 | 13.221028 | 2.208197  |
| Tb | 3.688468 | 10.888260 | 4.300858  |
| Tb | 4.858716 | 8.564440  | 7.405023  |

### Pt-Tb coordinates

95 Pt-Tb

| С | 10.340484 | 14.573408 | 6.591210  |
|---|-----------|-----------|-----------|
| С | 10.521352 | 7.137972  | 7.070970  |
| С | 10.742985 | 15.883118 | 7.297455  |
| С | 10.797508 | 12.047896 | 10.333089 |
| С | 11.214085 | 13.612955 | 0.037748  |
| С | 11.374815 | 17.013411 | 2.326954  |
| С | 11.501361 | 11.047683 | 4.681915  |
| С | 12.129708 | 12.876886 | -0.891329 |
| С | 12.442341 | 18.024886 | 2.569269  |
| С | 12.641083 | 10.163592 | 4.349493  |
| С | 4.862275  | 13.423259 | 7.827138  |
| С | 5.061017  | 5.561965  | 9.607362  |
| С | 5.373650  | 10.709965 | 13.067960 |
| С | 6.001997  | 12.539168 | 7.494716  |
| С | 6.128543  | 6.573440  | 9.849677  |
| С | 6.289273  | 9.973896  | 12.138883 |
| С | 6.705850  | 11.538955 | 1.843542  |
| С | 6.760373  | 7.703733  | 4.879176  |
| С | 6.982006  | 16.448879 | 5.105661  |
| С | 7.162874  | 9.013443  | 5.585421  |
| С | 7.645498  | 12.708642 | 1.799706  |
| С | 7.802169  | 15.955357 | 3.982976  |
| С | 9.701189  | 7.631494  | 8.193655  |
| С | 9.857860  | 10.878209 | 10.376925 |
| Н | 10.306834 | 16.624398 | 6.871273  |
| Н | 10.381649 | 12.804602 | 10.755618 |
| Η | 10.480237 | 15.844499 | 8.219226  |
| Н | 10.978854 | 6.334594  | 7.335202  |
| Н | 10.996741 | 12.263139 | 9.419842  |
| Η | 11.171398 | 7.805539  | 6.831090  |
| Н | 11.606414 | 11.826908 | 10.797019 |
| Η | 11.695561 | 15.996418 | 7.240225  |
| Н | 11.789549 | 12.929655 | -1.786312 |
| Η | 12.045553 | 18.880115 | 2.740960  |
| Н | 12.187332 | 11.957067 | -0.623444 |
| Н | 12.376399 | 9.547941  | 3.660295  |
| Η | 12.904224 | 9.675313  | 5.131232  |
| Н | 12.970723 | 17.759409 | 3.327873  |
| Н | 13.004958 | 13.274520 | -0.858452 |
| Н | 13.010646 | 18.085863 | 1.794835  |
| Н | 13.289209 | 14.115446 | 4.396981  |
| Н | 13.377033 | 10.695498 | 4.038988  |

| Н  | 13.471893 | 13.886514 | 2.812802  |
|----|-----------|-----------|-----------|
| Н  | 4.031465  | 9.700337  | 9.363829  |
| Н  | 4.126325  | 12.891353 | 8.137642  |
| Н  | 4.214149  | 9.471405  | 7.779649  |
| Н  | 4.492712  | 5.500987  | 10.381795 |
| Н  | 4.498400  | 10.312331 | 13.035083 |
| Н  | 4.532635  | 5.827442  | 8.848758  |
| Н  | 4.599133  | 13.911538 | 7.045399  |
| Н  | 5.126959  | 14.038910 | 8.516336  |
| Н  | 5.316026  | 11.629783 | 12.800074 |
| Н  | 5.457805  | 4.706736  | 9.435671  |
| Н  | 5.713809  | 10.657196 | 13.962943 |
| Н  | 5.807797  | 7.590433  | 4.936406  |
| Н  | 5.896944  | 11.759943 | 1.379612  |
| Н  | 6.331960  | 15.781312 | 5.345541  |
| Н  | 6.506617  | 11.323712 | 2.756789  |
| Н  | 6.524504  | 17.252257 | 4.841428  |
| Н  | 7.023121  | 7.742352  | 3.957405  |
| Н  | 7.121708  | 10.782249 | 1.421013  |
| Н  | 7.196524  | 6.962453  | 5.305358  |
| Н  | 7.542604  | 16.632647 | 5.860612  |
| Н  | 9.960754  | 6.954204  | 6.316018  |
| Tb | 10.419367 | 13.974123 | 3.267599  |
| 0  | 10.820534 | 14.298821 | 5.516014  |
| 0  | 11.054429 | 11.805593 | 3.778409  |
| 0  | 11.087924 | 16.196605 | 3.201236  |
| 0  | 11.472639 | 13.675379 | 1.239581  |
| 0  | 12.918458 | 13.996161 | 3.551923  |
| 0  | 4.584900  | 9.590690  | 8.624708  |
| 0  | 6.030719  | 9.911472  | 10.937050 |
| 0  | 6.415434  | 7.390246  | 8.975395  |
| 0  | 6.448928  | 11.781258 | 8.398222  |
| 0  | 6.682824  | 9.288030  | 6.660617  |
| 0  | 8.479423  | 14.915541 | 4.096219  |
| 0  | 8.727831  | 10.975683 | 9.893513  |
| 0  | 8.775527  | 12.611167 | 2.283118  |
| 0  | 9.023935  | 8.671310  | 8.080412  |
| Pt | 8.666782  | 7.990318  | 11.209806 |
| Pt | 8.751679  | 11.793425 | 6.088315  |
| Pt | 8.836576  | 15.596533 | 0.966824  |
| S  | 10.449070 | 9.457273  | 11.148923 |
| S  | 10.566398 | 17.129356 | 0.831664  |

| S  | 10.890092 | 10.950815 | 6.249047  |
|----|-----------|-----------|-----------|
| S  | 6.613266  | 12.636036 | 5.927584  |
| S  | 6.936960  | 6.457495  | 11.344967 |
| S  | 7.054288  | 14.129578 | 1.027708  |
| S  | 7.667523  | 9.266395  | 12.868263 |
| S  | 7.773815  | 16.894518 | 2.561963  |
| S  | 8.275747  | 9.989502  | 4.735492  |
| S  | 9.227611  | 13.597349 | 7.441139  |
| S  | 9.729543  | 6.692333  | 9.614668  |
| S  | 9.835835  | 14.320455 | -0.691633 |
| Tb | 7.083991  | 9.612727  | 8.909032  |
|    |           |           |           |

# Pd-Dy coordinates

| 80    |             |           |           |
|-------|-------------|-----------|-----------|
| Pd-Dy | coordinates |           |           |
| Dy    | 4.876582    | 10.879819 | 7.387090  |
| Dy    | 3.689029    | 8.567181  | 4.295428  |
| Pd    | 4.287038    | 6.232180  | 2.204608  |
| Pd    | 4.278574    | 13.214820 | 9.477910  |
| С     | 6.043183    | 9.624320  | 0.375009  |
| С     | 5.340284    | 8.715756  | 1.356340  |
| С     | 0.394516    | 7.467648  | 1.177598  |
| С     | 1.765764    | 7.372358  | 1.766397  |
| С     | 2.174028    | 4.251114  | 5.292181  |
| С     | 2.882492    | 5.298335  | 4.472068  |
| С     | 7.719405    | 6.191925  | 4.691699  |
| С     | 6.398376    | 6.547805  | 4.071358  |
| С     | 3.664433    | 12.928366 | 4.072526  |
| С     | 3.646330    | 11.427835 | 4.178837  |
| С     | 8.171096    | 11.979352 | 10.504920 |
| С     | 6.799847    | 12.074642 | 9.916121  |
| С     | 2.522428    | 9.822680  | 11.307509 |
| С     | 3.225327    | 10.731244 | 10.326178 |
| С     | 4.919281    | 8.019165  | 7.503681  |
| С     | 0.846207    | 13.255075 | 6.990819  |
| С     | 2.167235    | 12.899195 | 7.611160  |
| С     | 4.901179    | 6.518634  | 7.609992  |
| С     | 6.391583    | 15.195886 | 6.390337  |
| С     | 5.683119    | 14.148665 | 7.210450  |
| Н     | 5.665222    | 10.505269 | 0.427580  |

| Н | 5.930982  | 9.282053  | -0.515199 |
|---|-----------|-----------|-----------|
| Н | 6.977954  | 9.663214  | 0.587631  |
| Н | 0.091797  | 8.377768  | 1.219655  |
| Н | -0.207183 | 6.907574  | 1.674105  |
| Н | 0.418023  | 7.179832  | 0.261688  |
| Н | 2.298712  | 4.437805  | 6.225614  |
| Н | 2.535797  | 3.385723  | 5.088905  |
| Н | 1.236538  | 4.264727  | 5.086568  |
| Н | 8.210949  | 6.993141  | 4.879788  |
| Н | 8.221393  | 5.643519  | 4.084208  |
| Н | 7.569826  | 5.709639  | 5.508307  |
| Н | 1.220679  | 9.859629  | 5.035165  |
| Н | 1.183017  | 8.887279  | 5.841259  |
| Н | 2.818599  | 13.280356 | 4.359916  |
| Н | 4.362908  | 13.280356 | 4.629782  |
| Н | 3.824090  | 13.183121 | 3.161289  |
| Н | 5.747012  | 6.166644  | 7.322602  |
| Н | 4.202703  | 6.166644  | 7.052736  |
| Н | 4.741522  | 6.263879  | 8.521229  |
| Н | 7.344932  | 9.587371  | 6.647353  |
| Н | 7.382595  | 10.559721 | 5.841259  |
| Н | 0.354663  | 12.453859 | 6.802730  |
| Н | 0.344218  | 13.803481 | 7.598310  |
| Н | 0.995786  | 13.737361 | 6.174211  |
| Н | 2.900390  | 8.941731  | 11.254938 |
| Н | 2.634630  | 10.164947 | 12.197717 |
| Η | 1.587658  | 9.783786  | 11.094887 |
| Η | 8.473814  | 11.069232 | 10.462863 |
| Η | 8.772794  | 12.539426 | 10.008413 |
| Η | 8.147588  | 12.267168 | 11.420830 |
| Η | 6.266899  | 15.009195 | 5.456904  |
| Н | 6.029815  | 16.061277 | 6.593613  |
| Η | 7.329073  | 15.182273 | 6.595950  |
| 0 | 5.062600  | 7.552437  | 0.927592  |
| 0 | 5.073379  | 9.141840  | 2.502395  |
| 0 | 2.492088  | 6.421788  | 1.348163  |
| 0 | 2.114356  | 8.220052  | 2.612211  |
| 0 | 3.490123  | 4.871668  | 3.435829  |
| 0 | 2.830106  | 6.487519  | 4.840067  |
| 0 | 6.100260  | 5.934058  | 2.991893  |
| 0 | 5.661785  | 7.365357  | 4.658988  |
| 0 | 1.708184  | 9.215155  | 5.384473  |

| 0 | 4.416834 | 10.822450 | 5.012968  |
|---|----------|-----------|-----------|
| 0 | 2.915703 | 10.746996 | 3.426483  |
| 0 | 3.503012 | 11.894563 | 10.754926 |
| 0 | 3.492233 | 10.305160 | 9.180123  |
| 0 | 4.148778 | 8.624550  | 6.669550  |
| 0 | 5.649909 | 8.700004  | 8.256035  |
| 0 | 6.857428 | 10.231845 | 6.298045  |
| 0 | 2.465351 | 13.512942 | 8.690625  |
| 0 | 2.903827 | 12.081643 | 7.023530  |
| 0 | 6.073524 | 13.025212 | 10.334355 |
| 0 | 6.451256 | 11.226948 | 9.070307  |
| 0 | 5.075489 | 14.575332 | 8.246689  |
| 0 | 5.735506 | 12.959481 | 6.842451  |

# Pt-Dy coordinates

| 95    |             |           |           |
|-------|-------------|-----------|-----------|
| Pt-Dy | coordinates |           |           |
| С     | 10.087606   | 5.201403  | 4.696735  |
| С     | 10.757617   | 6.956179  | -0.818473 |
| С     | 11.081284   | 12.164986 | 2.571643  |
| С     | 11.188246   | 4.226938  | 4.367634  |
| С     | 3.486673    | 7.736153  | 7.866634  |
| С     | 3.593636    | -0.201896 | 9.662625  |
| С     | 3.917302    | 5.006912  | 13.052740 |
| С     | 4.587313    | 6.761687  | 7.537532  |
| С     | 4.707274    | 0.801355  | 9.906087  |
| С     | 4.858251    | 4.243266  | 12.187778 |
| С     | 5.318178    | 5.706067  | 1.857162  |
| С     | 5.387792    | 1.888686  | 4.969560  |
| С     | 5.554016    | 10.571221 | 5.084562  |
| С     | 5.784011    | 3.207322  | 5.625316  |
| С     | 6.270102    | 6.873592  | 1.829023  |
| С     | 6.407852    | 10.102381 | 3.947998  |
| С     | 8.267068    | 1.860710  | 8.286270  |
| С     | 8.404818    | 5.089498  | 10.405245 |
| С     | 8.890909    | 8.755769  | 6.608952  |
| С     | 9.120904    | 1.391870  | 7.149706  |
| С     | 9.287128    | 10.074405 | 7.264708  |
| С     | 9.356741    | 6.257023  | 10.377106 |
| С     | 9.816669    | 7.719824  | 0.046490  |
| С     | 9.967646    | 11.161735 | 2.328181  |
| Dy | 5.651823  | 3.831434  | 8.953527  |
|----|-----------|-----------|-----------|
| Н  | 10.150411 | 10.370918 | 6.906244  |
| Н  | 10.261613 | 5.946501  | 10.591206 |
| Н  | 10.334095 | 6.777675  | -1.683435 |
| Н  | 10.796026 | 12.812059 | 3.250645  |
| Н  | 10.803144 | 3.427543  | 3.952892  |
| Н  | 10.984678 | 6.106988  | -0.385379 |
| Н  | 11.285348 | 12.636345 | 1.736043  |
| Н  | 11.573976 | 7.480406  | -0.956720 |
| Н  | 11.658322 | 3.975351  | 5.189776  |
| Н  | 11.721722 | 7.564838  | 4.102150  |
| Н  | 11.819954 | 4.646587  | 3.746133  |
| Н  | 11.882583 | 11.694803 | 2.884840  |
| Н  | 12.069542 | 8.225312  | 2.899522  |
| Н  | 2.605378  | 3.737778  | 9.334746  |
| Н  | 2.792337  | 0.268288  | 9.349428  |
| Н  | 2.854965  | 7.316503  | 8.488135  |
| Н  | 2.953198  | 4.398253  | 8.132118  |
| Н  | 3.016598  | 7.987739  | 7.044491  |
| Н  | 3.100944  | 4.482684  | 13.190988 |
| Н  | 3.389571  | -0.673255 | 10.498225 |
| Н  | 3.690242  | 5.856102  | 12.619647 |
| Н  | 3.871776  | 8.535547  | 8.281376  |
| Н  | 3.878894  | -0.848968 | 8.983623  |
| Н  | 4.340824  | 5.185415  | 13.917703 |
| Н  | 4.413307  | 6.016589  | 1.643062  |
| Н  | 4.524509  | 1.592172  | 5.328024  |
| Н  | 4.712545  | 10.067382 | 5.089455  |
| Н  | 5.313234  | 2.013594  | 4.000606  |
| Н  | 5.322118  | 5.302188  | 2.750263  |
| Н  | 5.363017  | 11.525953 | 4.976900  |
| Н  | 5.599050  | 5.039734  | 1.195288  |
| Н  | 6.026954  | 10.425634 | 5.929950  |
| Н  | 6.069573  | 1.211100  | 5.160414  |
| Н  | 8.605347  | 10.751991 | 7.073854  |
| Н  | 8.647966  | 1.537456  | 6.304318  |
| Н  | 9.075869  | 6.923356  | 11.038980 |
| Н  | 9.311903  | 0.437137  | 7.257368  |
| Н  | 9.352802  | 6.660903  | 9.484005  |
| Н  | 9.361686  | 9.949496  | 8.233662  |
| Dy | 9.023097  | 8.131656  | 3.280741  |
| 0  | 10.100384 | 7.829190  | 1.271140  |

| $\cap$ | 11 /01000 | 0 176601  | 2 572620  |
|--------|-----------|-----------|-----------|
| 0      | 11.491002 | 0.1/0001  | 5.575650  |
| 0      | 3.183038  | 3.786409  | 8.660638  |
| 0      | 4.574536  | 4.133900  | 10.963128 |
| 0      | 5.000078  | 1.605761  | 9.011762  |
| 0      | 5.024067  | 6.013403  | 8.429411  |
| 0      | 5.274628  | 3.479074  | 6.720283  |
| 0      | 7.051943  | 9.051182  | 4.099703  |
| 0      | 7.277382  | 5.194565  | 9.908534  |
| 0      | 7.397538  | 6.768525  | 2.325734  |
| 0      | 7.622976  | 2.911909  | 8.134565  |
| 0      | 9.400292  | 8.484016  | 5.513985  |
| 0      | 9.650852  | 5.949688  | 3.804857  |
| 0      | 9.674841  | 10.357329 | 3.222506  |
| Pt     | 7.220154  | 2.229671  | 11.282197 |
| Pt     | 7.337460  | 5.981545  | 6.117134  |
| Pt     | 7.454765  | 9.733419  | 0.952071  |
| S      | 5.182445  | 6.804545  | 5.926769  |
| S      | 5.460325  | 0.726373  | 11.446136 |
| S      | 5.647628  | 8.280141  | 1.047253  |
| S      | 6.234835  | 3.548646  | 12.914738 |
| S      | 6.399357  | 11.058793 | 2.533962  |
| S      | 6.897098  | 4.158117  | 4.763779  |
| S      | 7.777822  | 7.804974  | 7.470489  |
| S      | 8.275562  | 0.904298  | 9.700306  |
| S      | 8.440085  | 8.414444  | -0.680470 |
| S      | 9.027292  | 3.682949  | 11.187015 |
| S      | 9.214595  | 11.236718 | 0.788132  |
| S      | 9.492474  | 5.158546  | 6.307499  |

### Pd-Ho coordinates

| 80    |             |           |           |
|-------|-------------|-----------|-----------|
| Pd-Ho | coordinates |           |           |
| С     | 0.287600    | 7.465275  | 7.034104  |
| С     | 0.748325    | 13.224473 | 12.824216 |
| С     | 1.667631    | 7.367829  | 7.616736  |
| С     | 2.077235    | 12.877395 | 13.441657 |
| С     | 2.080394    | 4.248207  | 11.144418 |
| С     | 2.424862    | 9.786890  | 17.123991 |
| С     | 2.790693    | 5.288663  | 10.319529 |
| С     | 3.127762    | 10.701948 | 16.153093 |
| С     | 3.564503    | 11.416874 | 10.027862 |

| С      | 3.587127  | 12.910200 | 9.915728  |
|--------|-----------|-----------|-----------|
| С      | 4.784981  | 6.501300  | 13.445628 |
| С      | 4.807605  | 7.994626  | 13.333494 |
| С      | 5.244346  | 8.709552  | 7.208263  |
| С      | 5.581415  | 14.122837 | 13.041827 |
| С      | 5.947246  | 9.624610  | 6.237365  |
| С      | 6.291714  | 15.163293 | 12.216938 |
| С      | 6.294873  | 6.534105  | 9.919699  |
| С      | 6.704477  | 12.043671 | 15.744619 |
| С      | 7.623783  | 6.187027  | 10.537140 |
| С      | 8.084508  | 11.946225 | 16.327252 |
| Н      | -0.007486 | 8.399356  | 7.049289  |
| Н      | 0.216150  | 13.741401 | 13.464317 |
| Н      | 0.271152  | 12.400066 | 12.591771 |
| Н      | 0.300647  | 7.141491  | 6.108995  |
| Н      | -0.329268 | 6.918259  | 7.563239  |
| Н      | 0.893975  | 13.756930 | 12.014745 |
| Н      | 1.113186  | 4.330706  | 11.012543 |
| Н      | 1.178936  | 9.789219  | 10.933115 |
| Н      | 1.243389  | 8.824468  | 11.867569 |
| Н      | 1.474889  | 9.730985  | 16.890260 |
| Н      | 2.292953  | 4.381176  | 12.091838 |
| н      | 2 373326  | 3,354307  | 10.866535 |
| н      | 2 517618  | 10 142509 | 18 032631 |
| н      | 2 668602  | 13 252231 | 9 911055  |
| н      | 2 825944  | 8 894349  | 17 079487 |
| н      | 4 034965  | 13 168762 | 9 082895  |
| ц      | 4.034903  | 13 287172 | 10 678476 |
| и<br>П | 4.300084  | 6 12/328  | 12 682880 |
| п      | 4.300084  | 6 2/2720  | 14 279461 |
| п      | 4.337143  | 10 517151 | 6 201060  |
| п      | 5.546164  | 6 150260  | 0.201009  |
| п      | 5.703306  | 0.109209  | I3.43030I |
| н      | 5.854490  | 9.268991  | 5.328725  |
| н      | 5.998782  | 16.057193 | 12.494821 |
| Н      | 6.079155  | 15.030324 | 11.269518 |
| H      | 6.897219  | 9.680515  | 6.4/1096  |
| H      | /.128719  | 10.587032 | 11.493787 |
| H      | 7.193172  | 9.622281  | 12.428241 |
| H      | 1.258922  | 15.080794 | 12.348813 |
| Н      | 7.478133  | 5.654570  | 11.346611 |
| Η      | 8.071461  | 12.270009 | 17.252361 |
| Н      | 8.100956  | 7.011434  | 10.769585 |

| Н  | 8.155958 | 5.670099  | 9.897038  |
|----|----------|-----------|-----------|
| Н  | 8.379594 | 11.012144 | 16.312067 |
| Н  | 8.701376 | 12.493241 | 15.798117 |
| Но | 3.591761 | 8.556007  | 10.141165 |
| Но | 4.780347 | 10.855493 | 13.220191 |
| 0  | 1.616458 | 9.193481  | 11.220810 |
| 0  | 2.031042 | 8.212812  | 8.464170  |
| 0  | 2.367147 | 13.484781 | 14.524105 |
| 0  | 2.392545 | 6.410454  | 7.194597  |
| 0  | 2.736709 | 6.483829  | 10.678009 |
| 0  | 2.816763 | 12.051047 | 12.859959 |
| 0  | 2.829570 | 10.726601 | 9.272122  |
| 0  | 3.392448 | 10.280525 | 15.004298 |
| 0  | 3.402232 | 4.861610  | 9.280766  |
| 0  | 3.404174 | 11.862562 | 16.590534 |
| 0  | 4.049601 | 8.612883  | 12.499260 |
| 0  | 4.322507 | 10.798617 | 10.862096 |
| 0  | 4.967934 | 7.548938  | 6.770822  |
| 0  | 4.969876 | 14.549890 | 14.080590 |
| 0  | 4.979660 | 9.130975  | 8.357058  |
| 0  | 5.542538 | 8.684899  | 14.089234 |
| 0  | 5.555345 | 7.360453  | 10.501397 |
| 0  | 5.635399 | 12.927671 | 12.683347 |
| 0  | 5.979563 | 13.001046 | 16.166759 |
| 0  | 6.004961 | 5.926719  | 8.837251  |
| 0  | 6.341066 | 11.198688 | 14.897186 |
| 0  | 6.755650 | 10.218019 | 12.140546 |
| Pd | 4.180349 | 13.188950 | 15.312551 |
| Pd | 4.191759 | 6.222550  | 8.048805  |

#### Pt-Ho coordinates

| 95    |          |           |           |
|-------|----------|-----------|-----------|
| Pt-Ho |          |           |           |
| С     | 2.103641 | 2.002490  | 7.880456  |
| С     | 2.246218 | -5.858063 | 9.603925  |
| С     | 2.582100 | -0.742895 | 13.048428 |
| С     | 3.231134 | 1.064143  | 7.549160  |
| С     | 3.364350 | -4.899568 | 9.846307  |
| С     | 3.529616 | -1.489479 | 12.142236 |
| С     | 3.990377 | -3.716418 | 4.906102  |
| С     | 3.998752 | 0.121874  | 1.856231  |

| С | 4.235224  | 4.948391  | 5.131432  |
|---|-----------|-----------|-----------|
| С | 4.392256  | -2.434366 | 5.591835  |
| С | 4.917258  | 1.295462  | 1.795331  |
| С | 5.075480  | 4.491049  | 3.979204  |
| С | 6.903120  | -3.803934 | 8.200790  |
| С | 7.061342  | -0.608348 | 10.384663 |
| С | 7.586345  | 3.121481  | 6.588159  |
| С | 7.743376  | -4.261277 | 7.048563  |
| С | 7.979849  | 0.565240  | 10.323763 |
| С | 7.988223  | 4.403533  | 7.273893  |
| С | 8.448984  | 2.176593  | 0.037758  |
| С | 8.614250  | 5.586682  | 2.333687  |
| С | 8.747466  | -0.377029 | 4.630834  |
| С | 9.396501  | 1.430010  | -0.868434 |
| С | 9.732383  | 6.545177  | 2.576069  |
| С | 9.874960  | -1.315375 | 4.299538  |
| Н | 10.171433 | 1.971795  | -1.037736 |
| Н | 10.354050 | -0.983205 | 3.537070  |
| Н | 10.470374 | -1.378283 | 5.049826  |
| Н | 10.555339 | 6.059893  | 2.672291  |
| Н | 10.645098 | 2.585751  | 2.850119  |
| Н | 10.751531 | 2.323433  | 4.080298  |
| Н | 1.227069  | -1.636318 | 8.099696  |
| Н | 1.333502  | -1.898637 | 9.329876  |
| Н | 1.423261  | -5.372779 | 9.507703  |
| Н | 1.508226  | 2.065398  | 7.130169  |
| Н | 1.624551  | 1.670319  | 8.642924  |
| Н | 1.807167  | -1.284681 | 13.217730 |
| Н | 2.176062  | -6.463638 | 10.345687 |
| Н | 2.312733  | 0.076281  | 12.625782 |
| Н | 2.419889  | -6.356309 | 8.801264  |
| Н | 2.459335  | 2.871647  | 8.080208  |
| Н | 3.021734  | -0.545046 | 13.879103 |
| Н | 3.095658  | -3.950067 | 5.164318  |
| Н | 3.182004  | 0.330459  | 1.397045  |
| Н | 3.452887  | 4.396052  | 5.194768  |
| Н | 3.806665  | -0.086041 | 2.773385  |
| Н | 3.972018  | 5.861359  | 4.992580  |
| Н | 4.027223  | -3.595141 | 3.953626  |
| Н | 4.417943  | -0.633759 | 1.438457  |
| Н | 4.591030  | -4.419184 | 5.161882  |
| Н | 4.742004  | 4.880980  | 5.943837  |

| Н  | 7.236596  | -4.193866 | 6.236157  |
|----|-----------|-----------|-----------|
| Н  | 7.387570  | 5.106298  | 7.018113  |
| Н  | 7.560658  | 1.320874  | 10.741537 |
| Н  | 7.951377  | 4.282255  | 8.226368  |
| Н  | 8.006582  | -5.174245 | 7.187415  |
| Н  | 8.171936  | 0.773155  | 9.406610  |
| Н  | 8.525714  | -3.708938 | 6.985227  |
| Н  | 8.796596  | 0.356655  | 10.782949 |
| Н  | 8.882942  | 4.637182  | 7.015677  |
| Н  | 8.956866  | 1.232160  | -1.699109 |
| Н  | 9.519266  | -2.184533 | 4.099786  |
| Н  | 9.558711  | 7.043424  | 3.378730  |
| Н  | 9.665868  | 0.610833  | -0.445788 |
| Н  | 9.802539  | 7.150752  | 1.834307  |
| Но | 7.676621  | 2.532610  | 3.264604  |
| Но | 4.301979  | -1.845496 | 8.915390  |
| 0  | 10.141103 | 2.553517  | 3.535852  |
| 0  | 1.837497  | -1.866403 | 8.644142  |
| 0  | 3.256183  | -1.557115 | 10.923019 |
| 0  | 3.631902  | -4.045922 | 8.980310  |
| 0  | 3.695857  | 0.331402  | 8.409068  |
| 0  | 3.891155  | -2.154851 | 6.694125  |
| 0  | 5.740041  | 3.456740  | 4.096132  |
| 0  | 5.935726  | -0.515752 | 9.876757  |
| 0  | 6.042874  | 1.202867  | 2.303237  |
| 0  | 6.238560  | -2.769625 | 8.083862  |
| 0  | 8.087445  | 2.841965  | 5.485869  |
| 0  | 8.282743  | 0.355712  | 3.770926  |
| 0  | 8.346699  | 4.733036  | 3.199684  |
| 0  | 8.722418  | 2.244229  | 1.256975  |
| Pt | 5.890980  | -3.487431 | 11.217896 |
| Pt | 5.989300  | 0.343557  | 6.089997  |
| Pt | 6.087621  | 4.174545  | 0.962098  |
| S  | 3.843250  | 1.187639  | 5.940549  |
| S  | 4.158912  | -5.018088 | 11.348466 |
| S  | 4.304471  | 2.693748  | 1.025556  |
| S  | 4.884105  | -2.215083 | 12.873158 |
| S  | 5.017477  | 5.454047  | 2.567786  |
| S  | 5.510004  | -1.476039 | 4.748493  |
| S  | 6.468596  | 2.163153  | 7.431502  |
| S  | 6.961123  | -4.766933 | 9.612208  |
| S  | 7.094495  | 2.902198  | -0.693163 |

| S | 7.674130 | -2.006634 | 11.154439 |
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| S | 7.819689 | 5.705203  | 0.831528  |
| S | 8.135350 | -0.500525 | 6.239446  |

### Pd-Er coordinates

| 80    |             |           |           |
|-------|-------------|-----------|-----------|
| Pd-Er | coordinates |           |           |
| Er    | 3.673228    | 10.839980 | 4.292137  |
| Er    | 4.872125    | 8.550020  | 7.352610  |
| С     | 0.372126    | 11.922911 | 1.199409  |
| С     | 0.849699    | 6.183471  | 6.941434  |
| С     | 1.756291    | 12.022382 | 1.771166  |
| С     | 2.157952    | 15.132732 | 5.300689  |
| С     | 2.175368    | 6.535012  | 7.569086  |
| С     | 2.517042    | 9.618410  | 11.248826 |
| С     | 2.864991    | 14.089550 | 4.473912  |
| С     | 3.223726    | 8.700293  | 10.278818 |
| С     | 3.652792    | 7.996824  | 4.171148  |
| С     | 3.679928    | 6.500110  | 4.055865  |
| С     | 4.865425    | 12.889890 | 7.588882  |
| С     | 4.892561    | 11.393176 | 7.473599  |
| С     | 5.321628    | 10.689707 | 1.365929  |
| С     | 5.680362    | 5.300450  | 7.170835  |
| С     | 6.028311    | 9.771591  | 0.395921  |
| С     | 6.369986    | 12.854988 | 4.075662  |
| С     | 6.387402    | 4.257268  | 6.344058  |
| С     | 6.789063    | 7.367618  | 9.873581  |
| С     | 7.695654    | 13.206529 | 4.703313  |
| С     | 8.173227    | 7.467089  | 10.445338 |
| Н     | 8.794459    | 7.034692  | 9.856114  |
| Н     | 0.131833    | 10.998008 | 1.103922  |
| Н     | -0.249106   | 12.355308 | 1.788633  |
| Н     | 0.302675    | 5.725867  | 7.585388  |
| Н     | 0.349911    | 12.349491 | 0.340027  |
| Н     | 0.407248    | 6.986217  | 6.657302  |
| Н     | 0.996106    | 5.611466  | 6.183361  |
| Н     | 1.131058    | 10.848705 | 5.708255  |
| Н     | 1.209428    | 15.058274 | 5.167939  |
| Н     | 1.495552    | 9.299444  | 5.456729  |
| Н     | 1.600314    | 9.720207  | 10.982161 |
| Н     | 2.362378    | 14.998165 | 6.229940  |

| Н | 2.450249 | 16.006445 | 5.032860  |
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| Н | 2.553729 | 9.241274  | 12.131498 |
| Н | 2.796043 | 6.152447  | 4.196767  |
| Н | 2.948251 | 10.476417 | 11.249990 |
| Н | 3.984465 | 6.253275  | 3.179016  |
| Н | 4.270041 | 13.251126 | 6.928625  |
| Н | 4.275312 | 6.138874  | 4.716123  |
| Н | 4.560888 | 13.136725 | 8.465731  |
| Н | 5.597102 | 8.913583  | 0.394757  |
| Н | 5.749310 | 13.237553 | 7.447980  |
| Н | 5.991624 | 10.148726 | -0.486750 |
| Н | 6.095104 | 3.383555  | 6.611887  |
| Н | 6.182975 | 4.391835  | 5.414807  |
| Н | 6.945040 | 9.669793  | 0.662586  |
| Н | 7.049802 | 10.090556 | 6.188019  |
| Н | 7.335925 | 4.331726  | 6.476808  |
| Н | 7.414295 | 8.541295  | 5.936492  |
| Н | 7.549248 | 13.778534 | 5.461386  |
| Н | 8.138106 | 12.403783 | 4.987445  |
| Н | 8.195442 | 7.040509  | 11.304721 |
| Н | 8.242678 | 13.664133 | 4.059359  |
| Н | 8.413520 | 8.391992  | 10.540825 |
| 0 | 6.839762 | 9.187952  | 6.277217  |
| 0 | 1.705591 | 10.202049 | 5.367530  |
| 0 | 2.118149 | 11.184540 | 2.625891  |
| 0 | 2.464670 | 5.920349  | 8.651349  |
| 0 | 2.470012 | 12.982381 | 1.350325  |
| 0 | 2.821815 | 12.896871 | 4.830940  |
| 0 | 2.907815 | 8.679352  | 3.420761  |
| 0 | 2.915948 | 7.360444  | 6.995233  |
| 0 | 3.474176 | 14.525243 | 3.431591  |
| 0 | 3.493451 | 7.541547  | 10.721552 |
| 0 | 3.495801 | 9.121444  | 9.136003  |
| 0 | 4.133117 | 10.779483 | 6.644376  |
| 0 | 4.412236 | 8.610517  | 5.000371  |
| 0 | 5.049552 | 10.268556 | 2.508744  |
| 0 | 5.051902 | 11.848453 | 0.923196  |
| 0 | 5.071177 | 4.864757  | 8.213157  |
| 0 | 5.629405 | 12.029556 | 4.649515  |
| 0 | 5.637538 | 10.710648 | 8.223986  |
| 0 | 5.723538 | 6.493129  | 6.813807  |
| 0 | 6.075341 | 6.407619  | 10.294422 |

| 0  | 6.080683 | 13.469651 | 2.993399 |
|----|----------|-----------|----------|
| 0  | 6.427204 | 8.205460  | 9.018857 |
| Pd | 4.271985 | 13.172597 | 2.202371 |
| Pd | 4.273368 | 6.217404  | 9.442376 |

### Pt-Er coordinates

| Pt-Er | coordinates |           |           |
|-------|-------------|-----------|-----------|
| С     | 10.088523   | 5.227452  | 4.671712  |
| С     | 10.730421   | 6.962488  | -0.826214 |
| С     | 11.047158   | 12.145570 | 2.576276  |
| С     | 11.177085   | 4.261898  | 4.340982  |
| С     | 3.482257    | 7.713500  | 7.863072  |
| С     | 3.612183    | -0.170173 | 9.627779  |
| С     | 3.928921    | 5.012909  | 13.030269 |
| С     | 4.570819    | 6.747945  | 7.532342  |
| С     | 4.705018    | 0.822056  | 9.877962  |
| С     | 4.875001    | 4.236399  | 12.136932 |
| С     | 5.341475    | 5.696282  | 1.866000  |
| С     | 5.367336    | 1.904288  | 4.973152  |
| С     | 5.562364    | 10.560034 | 5.100074  |
| С     | 5.776391    | 3.206089  | 5.623628  |
| С     | 6.262928    | 6.876369  | 1.815963  |
| С     | 6.416575    | 10.095246 | 3.946791  |
| С     | 8.242766    | 1.880152  | 8.257263  |
| С     | 8.396414    | 5.099029  | 10.388091 |
| С     | 8.882950    | 8.769308  | 6.580426  |
| С     | 9.096977    | 1.415364  | 7.103980  |
| С     | 9.292006    | 10.071110 | 7.230902  |
| С     | 9.317866    | 6.279115  | 10.338055 |
| С     | 9.784340    | 7.738998  | 0.067122  |
| С     | 9.954324    | 11.153342 | 2.326093  |
| Er    | 9.013367    | 8.132467  | 3.272883  |
| Н     | 10.129465   | 10.386887 | 6.831830  |
| Н     | 10.233349   | 5.986999  | 10.530879 |
| Н     | 10.284811   | 6.757724  | -1.674396 |
| Н     | 10.731603   | 12.829706 | 3.203564  |
| Н     | 10.801264   | 3.504596  | 3.844277  |
| Н     | 10.988136   | 6.127597  | -0.381987 |
| Н     | 11.301906   | 12.570727 | 1.730535  |
| Н     | 11.530913   | 7.500935  | -0.999512 |

| Н  | 11.588509 | 3.936861  | 5.168417  |
|----|-----------|-----------|-----------|
| Н  | 11.817576 | 8.061904  | 2.816696  |
| Н  | 11.824547 | 11.687000 | 2.957042  |
| Н  | 11.854646 | 4.708153  | 3.791800  |
| Н  | 11.894096 | 7.987425  | 4.185991  |
| Н  | 2.765245  | 3.987973  | 8.018064  |
| Н  | 2.804695  | 7.267245  | 8.412255  |
| Н  | 2.834794  | 0.288398  | 9.247012  |
| Н  | 2.841765  | 3.913494  | 9.387359  |
| Н  | 3.070833  | 8.038536  | 7.035637  |
| Н  | 3.128429  | 4.474463  | 13.203567 |
| Н  | 3.357435  | -0.595329 | 10.473520 |
| Н  | 3.671205  | 5.847801  | 12.586041 |
| Н  | 3.858077  | 8.470802  | 8.359777  |
| Н  | 3.927738  | -0.854309 | 9.000490  |
| Н  | 4.374531  | 5.217674  | 13.878451 |
| Н  | 4.425992  | 5.988399  | 1.673176  |
| Н  | 4.529877  | 1.588511  | 5.372225  |
| Н  | 4.717355  | 10.064159 | 5.101295  |
| Н  | 5.238601  | 2.044812  | 4.012693  |
| Н  | 5.374936  | 5.293016  | 2.758116  |
| Н  | 5.378854  | 11.518125 | 5.004883  |
| Н  | 5.620748  | 5.035532  | 1.197218  |
| Н  | 6.036156  | 10.400137 | 5.943375  |
| Н  | 6.069228  | 1.234616  | 5.114719  |
| Н  | 8.590113  | 10.740782 | 7.089335  |
| Н  | 8.623185  | 1.575261  | 6.260680  |
| Н  | 9.038593  | 6.939866  | 11.006837 |
| Н  | 9.280487  | 0.457273  | 7.199172  |
| Н  | 9.284405  | 6.682382  | 9.445938  |
| Н  | 9.420741  | 9.930586  | 8.191361  |
| Er | 5.645975  | 3.842931  | 8.931171  |
| 0  | 10.073505 | 7.833848  | 1.277765  |
| 0  | 11.445310 | 8.176123  | 3.561143  |
| 0  | 3.214031  | 3.799274  | 8.642911  |
| 0  | 4.585836  | 4.141549  | 10.926290 |
| 0  | 5.002510  | 1.643892  | 8.989507  |
| 0  | 5.033318  | 6.006789  | 8.415916  |
| 0  | 5.262093  | 3.506778  | 6.721993  |
| 0  | 7.074261  | 9.044803  | 4.077375  |
| 0  | 7.260761  | 5.183248  | 9.877962  |
| 0  | 7.398580  | 6.792150  | 2.326093  |

| 0  | 7.585080 | 2.930594  | 8.126680  |
|----|----------|-----------|-----------|
| 0  | 9.397249 | 8.468620  | 5.482061  |
| 0  | 9.626023 | 5.968609  | 3.788139  |
| 0  | 9.656832 | 10.331506 | 3.214548  |
| Pt | 7.223751 | 2.234946  | 11.258118 |
| Pt | 7.329671 | 5.987699  | 6.102027  |
| Pt | 7.435590 | 9.740452  | 0.945936  |
| S  | 5.174918 | 6.801843  | 5.920309  |
| S  | 5.466350 | 0.732637  | 11.413110 |
| S  | 5.640183 | 8.278734  | 1.042470  |
| S  | 6.238256 | 3.556836  | 12.888214 |
| S  | 6.387225 | 11.056679 | 2.537711  |
| S  | 6.888773 | 4.154645  | 4.766782  |
| S  | 7.770568 | 7.820753  | 7.437273  |
| S  | 8.272116 | 0.918719  | 9.666343  |
| S  | 8.421085 | 8.418562  | -0.684159 |
| S  | 9.019159 | 3.696664  | 11.161584 |
| S  | 9.192991 | 11.242761 | 0.790945  |
| S  | 9.484423 | 5.173555  | 6.283746  |

### Pd-Tm coordinates

| 80    |             |           |           |
|-------|-------------|-----------|-----------|
| Pd-Tm | coordinates |           |           |
| С     | 10.048287   | -4.385793 | 7.118979  |
| С     | 10.388998   | 0.074759  | 0.401233  |
| С     | 10.717479   | 3.148591  | 4.069148  |
| С     | 10.760310   | -5.418667 | 6.293322  |
| С     | 11.170310   | -2.318302 | 9.818602  |
| С     | 12.034280   | 3.495852  | 4.701147  |
| С     | 12.556970   | -2.200159 | 10.387981 |
| С     | 4.720578    | 2.200159  | 1.208336  |
| С     | 5.243267    | -3.495852 | 6.895171  |
| С     | 6.107238    | 2.318302  | 1.777716  |
| С     | 6.517238    | 5.418667  | 5.302996  |
| С     | 6.560069    | -3.148591 | 7.527170  |
| С     | 6.888550    | -0.074759 | 11.195085 |
| С     | 7.229261    | 4.385793  | 4.477338  |
| С     | 7.602694    | -0.981163 | 10.226793 |
| С     | 8.024558    | -1.696989 | 4.153801  |
| С     | 8.064041    | -3.188294 | 4.021603  |
| С     | 9.213507    | 3.188294  | 7.574715  |

| С | 9.252990  | 1.696989  | 7.442517  |
|---|-----------|-----------|-----------|
| С | 9.674853  | 0.981163  | 1.369525  |
| Н | 10.128690 | 3.540397  | 7.579353  |
| Н | 10.376119 | 0.476443  | -0.492844 |
| Н | 10.461421 | -6.313838 | 6.561197  |
| Н | 10.557147 | -5.275734 | 5.345902  |
| Н | 11.296313 | -0.772767 | 5.452589  |
| Н | 11.317389 | -0.046482 | 0.691141  |
| Н | 11.726664 | -5.341584 | 6.435956  |
| Н | 11.792436 | -0.046482 | 6.648169  |
| Н | 11.891996 | 4.156287  | 5.409682  |
| Н | 12.435157 | 2.688223  | 5.084985  |
| Н | 12.533966 | -2.393835 | 11.348157 |
| Н | 12.635051 | 3.867710  | 4.022763  |
| Н | 12.892369 | -1.289882 | 10.246506 |
| Н | 13.149074 | -2.839290 | 9.940364  |
| Н | 4.128474  | 2.839290  | 1.655954  |
| Н | 4.385179  | 1.289882  | 1.349811  |
| Н | 4.642496  | -3.867710 | 7.573555  |
| Н | 4.743582  | 2.393835  | 0.248161  |
| Н | 4.842391  | -2.688223 | 6.511332  |
| Н | 5.385552  | -4.156287 | 6.186636  |
| Н | 5.485112  | 0.046482  | 4.948149  |
| Н | 5.550884  | 5.341584  | 5.160361  |
| Η | 5.960158  | 0.046482  | 10.905177 |
| Η | 5.981235  | 0.772767  | 6.143729  |
| Н | 6.720401  | 5.275734  | 6.250415  |
| Η | 6.816126  | 6.313838  | 5.035121  |
| Н | 6.901428  | -0.476443 | 12.089161 |
| Η | 7.148858  | -3.540397 | 4.016964  |
| Η | 7.339235  | 0.794072  | 11.221757 |
| Н | 8.510997  | -3.430002 | 3.184349  |
| Η | 8.556230  | -3.571385 | 4.777683  |
| Н | 8.721318  | 3.571385  | 6.818635  |
| Н | 8.766551  | 3.430002  | 8.411969  |
| Н | 9.938312  | -0.794072 | 0.374561  |
| 0 | 10.092723 | -3.189069 | 6.771090  |
| 0 | 10.432349 | 3.762931  | 3.001127  |
| 0 | 10.455321 | -3.276223 | 10.256943 |
| 0 | 10.798126 | -1.482009 | 8.972071  |
| 0 | 11.200602 | -0.513629 | 6.256213  |
| 0 | 6.076946  | 0.513629  | 5.340104  |

| 0  | 6.479422 | 1.482009  | 2.624247  |
|----|----------|-----------|-----------|
| 0  | 6.822227 | 3.276223  | 1.339375  |
| 0  | 6.845198 | -3.762931 | 8.595191  |
| 0  | 7.184825 | 3.189069  | 4.825228  |
| 0  | 7.280796 | -1.007890 | 3.417435  |
| 0  | 7.298819 | -2.314428 | 6.957791  |
| 0  | 7.824960 | 4.818078  | 3.435989  |
| 0  | 7.869147 | -2.145543 | 10.673251 |
| 0  | 7.876248 | -0.573281 | 9.081076  |
| 0  | 8.489564 | 1.077032  | 6.620338  |
| 0  | 8.787983 | -1.077032 | 4.975980  |
| 0  | 9.401300 | 0.573281  | 2.515241  |
| 0  | 9.408400 | 2.145543  | 0.923067  |
| 0  | 9.452588 | -4.818078 | 8.160329  |
| 0  | 9.978729 | 2.314428  | 4.638527  |
| 0  | 9.996752 | 1.007890  | 8.178883  |
| Pd | 8.622091 | 3.469609  | 2.197038  |
| Pd | 8.655457 | -3.469609 | 9.399279  |
| Tm | 8.030158 | 1.141584  | 4.278276  |
| Τm | 9.247390 | -1.141584 | 7.318042  |

### Pd-Yb coordinates

| С | 0.581955  | -3.181374 | 1.770070  |
|---|-----------|-----------|-----------|
| С | -0.581955 | 3.181374  | -1.770070 |
| С | 0.613480  | -1.684598 | 1.644960  |
| С | -0.613480 | 1.684598  | -1.644960 |
| С | 1.042012  | -0.989460 | -4.418223 |
| С | -1.042012 | 0.989460  | 4.418223  |
| С | 1.415012  | 4.372211  | 1.319443  |
| С | -1.415012 | -4.372211 | -1.319443 |
| С | 1.751652  | -0.081325 | -5.372764 |
| С | -1.751652 | 0.081325  | 5.372764  |
| С | 2.060524  | -3.146520 | -1.723733 |
| С | -2.060524 | 3.146520  | 1.723733  |
| С | 2.128955  | 5.396524  | 0.486537  |
| С | -2.128955 | -5.396524 | -0.486537 |
| С | 2.534541  | 2.306157  | 4.027835  |
| С | -2.534541 | -2.306157 | -4.027835 |
| С | 3.385410  | -3.493121 | -1.093551 |
| С | -3.385410 | 3.493121  | 1.093551  |
| С | 3.916461  | 2.184169  | 4.578086  |

| С | -3.916461 | -2.184169 | -4.578086 |
|---|-----------|-----------|-----------|
| Н | 0.058842  | -3.560892 | 1.033313  |
| Н | -0.058842 | 3.560892  | -1.033313 |
| Н | 0.169611  | -3.429223 | 2.624985  |
| Н | -0.169611 | 3.429223  | -2.624985 |
| Н | 1.362546  | 0.817127  | -5.319476 |
| Н | -1.362546 | -0.817127 | 5.319476  |
| Н | 1.496976  | -3.531848 | 1.735317  |
| Н | -1.496976 | 3.531848  | -1.735317 |
| Н | 1.655245  | -0.424054 | -6.285601 |
| Н | -1.655245 | 0.424054  | 6.285601  |
| Н | 1.875889  | 5.286154  | -0.454102 |
| Н | -1.875889 | -5.286154 | 0.454102  |
| Н | 1.879281  | 6.294976  | 0.787727  |
| Н | -1.879281 | -6.294976 | -0.787727 |
| Н | 2.702827  | -0.038726 | -5.138762 |
| Н | -2.702827 | 0.038726  | 5.138762  |
| Н | 2.836099  | 0.912007  | -0.240952 |
| Н | -2.836099 | -0.912007 | 0.240952  |
| Н | 3.011120  | -0.118116 | 0.784252  |
| Н | -3.011120 | 0.118116  | -0.784252 |
| Η | 3.097044  | 5.276472  | 0.580370  |
| Н | -3.097044 | -5.276472 | -0.580370 |
| Н | 3.245589  | -4.143725 | -0.374170 |
| Н | -3.245589 | 4.143725  | 0.374170  |
| Η | 3.794456  | -2.681803 | -0.726331 |
| Н | -3.794456 | 2.681803  | 0.726331  |
| Н | 3.911966  | 2.426209  | 5.527992  |
| Н | -3.911966 | -2.426209 | -5.527992 |
| Н | 3.978392  | -3.878449 | -1.772386 |
| Н | -3.978392 | 3.878449  | 1.772386  |
| Н | 4.227736  | 1.260544  | 4.477303  |
| Н | -4.227736 | -1.260544 | -4.477303 |
| Н | 4.516188  | 2.786364  | 4.091548  |
| Н | -4.516188 | -2.786364 | -4.091548 |
| 0 | 0.151787  | 1.059167  | -0.820163 |
| 0 | -0.151787 | -1.059167 | 0.820163  |
| 0 | 0.753561  | -0.577023 | -3.267910 |
| 0 | -0.753561 | 0.577023  | 3.267910  |
| 0 | 0.759040  | -2.145443 | -4.872325 |
| 0 | -0.759040 | 2.145443  | 4.872325  |
| 0 | 0.816650  | 4.815628  | 2.360865  |

| 0  | -0.816650 | -4.815628 | -2.360865 |
|----|-----------|-----------|-----------|
| 0  | 1.326237  | -2.296476 | -1.166531 |
| 0  | -1.326237 | 2.296476  | 1.166531  |
| 0  | 1.357417  | -1.001077 | 2.378241  |
| 0  | -1.357417 | 1.001077  | -2.378241 |
| 0  | 1.435926  | 3.173628  | 0.968441  |
| 0  | -1.435926 | -3.173628 | -0.968441 |
| 0  | 1.784915  | -3.758397 | -2.791798 |
| 0  | -1.784915 | 3.758397  | 2.791798  |
| 0  | 1.814327  | 3.270444  | 4.459927  |
| 0  | -1.814327 | -3.270444 | -4.459927 |
| 0  | 2.154666  | 1.490966  | 3.164810  |
| 0  | -2.154666 | -1.490966 | -3.164810 |
| 0  | 2.555172  | 0.522806  | 0.461052  |
| 0  | -2.555172 | -0.522806 | -0.461052 |
| Pd | 0.018742  | 3.469111  | 3.600841  |
| Pd | -0.018742 | -3.469111 | -3.600841 |
| Yb | 0.610506  | 1.137433  | 1.516028  |
| Yb | -0.610506 | -1.137433 | -1.516028 |

# Appendix C

## Input files for calculations

## Input files used for calculations with ORCA programming software

### Typical input files for computing the magnetic properties of Dy1

Below is a standard input file for computing the magnetic properties using CASSCF in ORCA.

#With the converged CASSCF orbitals, we compute the g-tensor (ground state), #magnetization and the susceptibility. Note that in the input below there are two "rel" #blocks. The global takes care of picture change effect and general settings regarding the #spin-orbit coupling operator, while the "rel" block in CASSCF sets the properties to be #computed. More refined options are documented in the ORCA manual. The ab initio #ligand field theory (AILFT) is available for CASSCF calculations with a single set of f-orbitals. #The analysis is enabled by adding "actorbs forbs" in the CASSCF block #we include a NEVPT2 keyword herein to compare the results with pure casscf calculation

```
%pal
nprocs 8
end
%maxcore 4500
%basis
newgto Dy "SARC2-DKH-QZVP" end
newAuxJKgto Dy "SARC2-DKH-QZVP/JK" end
end
%rel
picturechange 2 #second order DKH SOC
```

```
fpFWtrafo false #recommended option for g-tensor
end
%scf
MaxIter 1000
end
%casscf ci
Maxiter 200 end
end
%casscf
              9
       nel
       norb 7
       nroots 21
       mult
       etol
             1e-7 # resets energy convergence but is usualloverwritten by tightscf.
#
       cistep accci #for faster ci calculation, but this can not bused for NEVPT2 in
               #property calculation with cassof. It is still under development
       trafostep ri # RI is mandatory for NEVPT2 calcualtion
       actorbs forbs #for ab initio ligand field analysis
       rel
               dosoc true
               dossc true
               domagnetization true
               dosusceptibility true
               gtensor true
       end
end
*xyzfile 0 6 cas9_7merged_Dy1.xyz
```

## Input files used for calculations with MOLCAS programming software

### Sample SINGLE-ANISO input file for mono-nuclear system

Below is a sample input files used for the caluculation of the electronic and magnetic properties of the mono-nuclear systems. The input files below was used for **Dy2**.

```
&gateway
coord=Dy2.xyz
Basis=Dy.ANO-RCC-VTZP-2,N.ANO-RCC-VDZP,C.ANO-RCC-VDZ,O.ANO-RCC-VDZP,H.ANO-RC-VDZ
Group=Nosym
AngM
7.023600000000 3.944300000000 4.117900000000 Angstrom
AMFI
&SEWARD
HIGH CHOLESKY
&RASSCF
Spin
6
```

nActel 900 Inactive 153 Ras1 0 Ras2 7 Ras3 0 CIROOT 21 21 1 ORBA FULL махо 1 >> COPY \$Project.JobIph 1\_IPH >> COPY \$Project.RasOrb 1.RasOrb &RASSCF FILEORB 1.RasOrb Spin 4 Nactel 900 CiRoot 224 224 1 ORBA FULL MAXO 1 >> COPY \$Project.JobIph 2\_IPH >> COPY \$Project.RasOrb 2.RasOrb &RASSCF FILEORB 2.RasOrb Spin 2 Nactel 900 CiRoot 490 490 1 ORBA

FULL MAXO 1 >> COPY \$Project.JobIph 3\_IPH >> COPY \$Project.RaSOLD 3.RaSOLD &RASSI Nr of JobIph 3 21 128 130 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21

```
22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42
    44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62
 43
                                                                    63
    65 66 67
                  69
                     70
                         71
                            72
                                73
                                   74 75 76 77 78 79 80 81 82 83
 64
              68
                                                                    84
 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100101 102 103 104 105
 106 107 108 109 110 111 112 113 114115 116 117 118 119 120121 122 123 124 125
 126 127 128
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42
 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63
 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84
 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100101 102 103 104 105
 106 107 108 109 110 111 112 113 114115 116 117 118 119 120121 122 123 124 125
126 127 128 129 130
Spin
IPHN
 1_IPH
 2_IPH
 3_IPH
MEES
EJob
PROP
 3
'ANGMOM' 1
'ANGMOM' 2
'ANGMOM' 3
EPRG
7.0D-1
&SINGLE_ANISO
MLTP
8
2 2 2 2 2 2 2 2 2
XFIE
0.1
HINT
0 10.0 201
TINT
0 330 300 0.0001
TMAG
12 1.0 1.2 1.8 2.5 2.9 3.6 4 6 8 10 15 20
CRYS
Dv
UBAR
PLOT
```

### Sample SINGLE-ANISO input file for cluster system (site-1)

Below is a typical input file used to compute the magnetic properties of each multi-nuclear system. Here the coordinates are included within the input file and the unit of Angstrom is specified because by default, coordinates within the input files will be treated in Bohr unit

while coordinates in a separate files linked to the input files are treated in Angstrom by default and so Angstrom will not need to be specified therein. The sample input below is for the **Pd-Dy** system for which the second Dy site has been replaced by Lu.

| &seward       |                      |           |           |          |  |  |
|---------------|----------------------|-----------|-----------|----------|--|--|
| Basis Se      | Basis Set            |           |           |          |  |  |
| Dy.ANO-R      | CC-VTZP-2            |           |           |          |  |  |
| Dy1           | 4.876582             | 10.879819 | 7.387090  | Angstrom |  |  |
| End of B      | asis Set             |           |           |          |  |  |
|               |                      |           |           |          |  |  |
| Basis Se      | t                    |           |           |          |  |  |
| Lu.ANO-R      | CC-VTZP-2            |           |           |          |  |  |
| Lu2           | 3.689029             | 8.567181  | 4.295428  | Angstrom |  |  |
| End of B      | asis Set             |           |           |          |  |  |
|               |                      |           |           |          |  |  |
| Basis Se      | t                    |           |           |          |  |  |
| Pd.ANO-R      | CC-VTZP              |           |           |          |  |  |
| Pd3           | 4.287038             | 6.232180  | 2.204608  | Angstrom |  |  |
| Pd4           | 4.278574             | 13.214820 | 9.477910  | Angstrom |  |  |
| End of B      | asis Set             |           |           |          |  |  |
|               |                      |           |           |          |  |  |
| Basis Se      | t                    |           |           |          |  |  |
| C.ANO-RC      | C-VDZ                | 0 (24220  | 0 275000  | <b>D</b> |  |  |
| 06            | 6.043183<br>E 340294 | 9.024320  | 1 256240  | Angstrom |  |  |
| C0            | 0.204516             | 8./15/50  | 1 177500  | Angstrom |  |  |
| C?            | 1 765764             | 7.407040  | 1 766307  | Angstrom |  |  |
| C9            | 2 17/028             | 1.572556  | 5 202101  | Angstrom |  |  |
| C10           | 2 882492             | 5 208335  | 1 472068  | Angstrom |  |  |
| C11           | 7 719405             | 6 191925  | 4 691699  | Angstrom |  |  |
| C12           | 6 398376             | 6 547805  | 4 071358  | Angstrom |  |  |
| C13           | 3.664433             | 12.928366 | 4.072526  | Angstrom |  |  |
| C14           | 3,646330             | 11,427835 | 4.178837  | Angstrom |  |  |
| C15           | 8.171096             | 11.979352 | 10.504920 | Angstrom |  |  |
| C16           | 6.799847             | 12.074642 | 9.916121  | Angstrom |  |  |
| C17           | 2.522428             | 9.822680  | 11.307509 | Angstrom |  |  |
| C18           | 3.225327             | 10.731244 | 10.326178 | Angstrom |  |  |
| C19           | 4.919281             | 8.019165  | 7.503681  | Angstrom |  |  |
| C20           | 0.846207             | 13.255075 | 6.990819  | Angstrom |  |  |
| C21           | 2.167235             | 12.899195 | 7.611160  | Angstrom |  |  |
| C22           | 4.901179             | 6.518634  | 7.609992  | Angstrom |  |  |
| C23           | 6.391583             | 15.195886 | 6.390337  | Angstrom |  |  |
| C24           | 5.683119             | 14.148665 | 7.210450  | Angstrom |  |  |
| End of B      | asis                 |           |           |          |  |  |
|               |                      |           |           |          |  |  |
| Basis Set     |                      |           |           |          |  |  |
| H.ANO-RCC-VDZ |                      |           |           |          |  |  |
| H25           | 5.665222             | 10.505269 | 0.427580  | Angstrom |  |  |
| H26           | 5.930982             | 9.282053  | -0.515199 | Angstrom |  |  |
| H27           | 6.977954             | 9.663214  | 0.587631  | Angstrom |  |  |
| H28           | 0.091797             | 8.377768  | 1.219655  | Angstrom |  |  |

| H29                | -0.207183            | 6.907574  | 1.674105  | Angstrom    |
|--------------------|----------------------|-----------|-----------|-------------|
| H30                | 0.418023             | 7.179832  | 0.261688  | Angstrom    |
| H31                | 2.298712             | 4.437805  | 6.225614  | Angstrom    |
| H32                | 2.535797             | 3.385723  | 5.088905  | Angstrom    |
| H33                | 1.236538             | 4.264727  | 5.086568  | Angstrom    |
| H34                | 8.210949             | 6.993141  | 4.879788  | Angstrom    |
| H35                | 8.221393             | 5.643519  | 4.084208  | Angstrom    |
| H36                | 7.569826             | 5.709639  | 5.508307  | Angstrom    |
| H37                | 1.220679             | 9.859629  | 5.035165  | Angstrom    |
| H38                | 1.183017             | 8.887279  | 5.841259  | Angstrom    |
| H39                | 2.818599             | 13.280356 | 4.359916  | Angstrom    |
| H40                | 4.362908             | 13.280356 | 4.629782  | Angstrom    |
| H41                | 3.824090             | 13.183121 | 3.161289  | Angstrom    |
| H42                | 5.747012             | 6.166644  | 7.322602  | Angstrom    |
| H43                | 4.202703             | 6.166644  | 7.052736  | Angstrom    |
| H44                | 4.741522             | 6.263879  | 8.521229  | Angstrom    |
| H45                | 7.344932             | 9.587371  | 6.647353  | Angstrom    |
| H46                | 7.382595             | 10.559721 | 5.841259  | Angstrom    |
| H47                | 0.354663             | 12.453859 | 6.802730  | Angstrom    |
| H48                | 0.344218             | 13.803481 | 7.598310  | Angstrom    |
| H49                | 0.995786             | 13.737361 | 6.174211  | Angstrom    |
| H50                | 2.900390             | 8.941731  | 11.254938 | Angstrom    |
| H51                | 2.634630             | 10.164947 | 12.197717 | Angstrom    |
| H52                | 1.587658             | 9.783786  | 11.094887 | Angstrom    |
| Н53                | 8.473814             | 11.069232 | 10.462863 | Angstrom    |
| H54                | 8.772794             | 12.539426 | 10.008413 | Angstrom    |
| Н55                | 8.147588             | 12.267168 | 11.420830 | Angstrom    |
| H56                | 6.266899             | 15.009195 | 5.456904  | Angstrom    |
| Н57                | 6.029815             | 16.061277 | 6.593613  | Angstrom    |
| H58                | 7.329073             | 15.182273 | 6.595950  | Angstrom    |
| End of             | Basis Set            |           |           |             |
|                    |                      |           |           |             |
| Basis              | Set                  |           |           |             |
| O.ANO-             | RCC-VDZP             |           |           |             |
| 059                | 5.062600             | 7.552437  | 0.927592  | Angstrom    |
| 060                | 5.073379             | 9.141840  | 2.502395  | Angstrom    |
| 061                | 2.492088             | 6.421788  | 1.348163  | Angstrom    |
| 062                | 2.114356             | 8.220052  | 2.612211  | Angstrom    |
| 063                | 3.490123             | 4.8/1668  | 3.435829  | Angstrom    |
| 064                | 2.830106             | 6.48/519  | 4.840067  | Angstrom    |
| 065                | 6.100260             | 5.934058  | 2.991893  | Angstrom    |
| 066                | 5.001/85             | /.36535/  | 4.658988  | Angstrom    |
| 067                | 1./00104             | 9.215155  | 5.304473  | Angstrom    |
| 068                | 4.410834             | 10.822450 | 2 426492  | Angstrom    |
| 070                | 2.910/U3             | 11 00/EC2 | 3.420403  | Angstrom    |
| 070                | 3.003012             | 10 205100 | LU./04920 | Angstrom    |
| 071                | 3.492233<br>A 140770 | TO.302100 | 9.10U123  | Angstrom    |
| 072                | 4.140//0<br>5 6/0000 | 0.024000  | 0.009000  | Angstrom    |
| 074                | 5.049909             | 10 2210/5 | 6 200015  | Angstrom    |
| 075                | 0.0J/420<br>2 165351 | 13 512040 | 8 690625  | Angstrom    |
| 076                | 2 903827             | 12.081643 | 7.023530  | Angstrom    |
| 077                | 6 073524             | 13 025212 | 10 334355 | Angstrom    |
| $\bigcirc$ $i$ $i$ | 0.0/0024             | 10.020212 | TO.004000 | 1111YOCLOID |

```
078 6.451256 11.226948 9.070307
                                           Angstrom
                   14.575332 8.246689
079
        5.075489
                                           Angstrom
    5.735506 12.959481 6.842451
080
                                           Angstrom
End of Basis Set
AngM
4.876582 10.879819 7.387090 Angstrom
AMFI
End of Input
&RASSCF
Spin
6
nActel
900
Inactive
275
Ras1
0
Ras2
7
Ras3
0
CIROOT
21 21 1
ORBA
FULL
MAXO
1
>> COPY $Project.JobIph 1_IPH
>> COPY $Project.RasOrb 1.RasOrb
&RASSCF
FILEORB
 1.RasOrb
Spin
 4
Nactel
 900
CiRoot
224 224 1
ORBA
FULL
MAXO
1
>> COPY $Project.JobIph 2_IPH
>> COPY $Project.RasOrb 2.RasOrb
&RASSCF
FILEORB
2.RasOrb
Spin
 2
Nactel
 900
```

```
Dy
ABCC
8.732 19.447 11.684 90.000 90.815 90.000
4.876582 10.879819 7.387090
UBAR
PLOT
```

### Sample POLY-ANISO input file for cluster system

The input file was used for the POLYANISO calculation on **Pd-Dy** using the anisoinput files obtained from the initial SINGLE-ANISO job as described above. Note that, by using the SYMM keyword only one anisoinput file is needed since the second dysprosium site is equivalent to the first site and are related through inversion.

```
>>COPY $CurrDir/anisoinputfile/9_pd-Dy-site-1-single_aniso.aniso $WorkDir/aniso_1.input
>>COPY $CurrDir/anisoinputfile/9_pd-Dy-site-2-single_aniso.aniso $WorkDir/aniso_2.input
>>FOREACH J in (-0.3, -0.28, -0.26, -0.24, -0.22, -0.20, -0.19, -0.18, -0.17, -0.16, -0.15,
-0.14, -0.13, -0.12, -0.11, -0.1, -0.09, -0.08, -0.07, -0.06, -0.05, -0.04, -0.03, -0.02,
-0.01,\ 0.0,\ 0.01,\ 0.02,\ 0.03,\ 0.04,\ 0.05,\ 0.06,\ 0.07,\ 0.08,\ 0.09,\ 0.10, 0.12,\ 0.14,\ 0.16,
0.18, 0.20, 0.22, 0.24, 0.26, 0.28, 0.30)
&poly_aniso
NNEQ
1 T F
2
   # (To compute properties for the ground state doublet alone, 9 was replaced by 2
9
    # and the MLTP section is also changed from 8 to 2 below.)
SYMM
1
1.0
       0.0
              0.0
0.0
       1.0
              0.0
       0.0
0.0
              1.0
-1.0
       0.0
               0.0
       -1.0
0.0
               0.0
0.0
       0.0
               -1.0
PAIR
1
1 2 $J
PRLV
3
MLTP
8
2 2 2 2 2 2 2 2 2
XFIE
0.1
TEXP
159
              15.73119
2.00022
              16.14172
2.24856
2.49948
              16.46987
2.75004
              16.78617
```

| 2.99991  | 17.04691 |
|----------|----------|
| 3.24946  | 17.26124 |
| 3.52736  | 17.47125 |
| 3.75788  | 17.63479 |
| 4 00393  | 17 78374 |
| 4.000000 | 10 10201 |
| 4.25559  | 18.18201 |
| 4.49696  | 18.10956 |
| 4.74899  | 18.24464 |
| 4.99884  | 18.36846 |
| 5.24796  | 18.49296 |
| 5.496    | 18.62748 |
| 5.74612  | 18.74512 |
| 5.99648  | 18.84627 |
| 6.24412  | 18.91374 |
| 6.496    | 19.01082 |
| 6 74593  | 19 08696 |
| 6.00673  | 10 16294 |
| 0.99073  | 19.10204 |
| 7.24554  | 19.24188 |
| 7.49703  | 19.31681 |
| 7.74535  | 19.38088 |
| 7.99644  | 19.45059 |
| 8.23702  | 19.49474 |
| 8.49854  | 19.58346 |
| 8.74903  | 19.64847 |
| 8.99841  | 19.71146 |
| 9.2489   | 19.7761  |
| 9,49898  | 19,83951 |
| 9.74864  | 19,90189 |
| 9 99915  | 19 9639  |
| 10 50312 | 20 0889  |
| 11 00626 | 20.0000  |
| 11.00020 | 20.21139 |
| 11.5104  | 20.32949 |
| 11.99698 | 20.41505 |
| 12.50177 | 20.52834 |
| 13.00325 | 20.64744 |
| 13.50424 | 20.75813 |
| 14.00405 | 20.8607  |
| 14.49841 | 20.95703 |
| 14.99918 | 21.04987 |
| 15.49917 | 21.13838 |
| 15.99854 | 21.22115 |
| 16.49951 | 21.30289 |
| 16 99889 | 21 38112 |
| 17 40963 | 21.50112 |
| 10,00042 | 21.43074 |
| 10.00043 | 21.53903 |
| 18.499/3 | 21.61538 |
| 18.99915 | 21.68946 |
| 19.49991 | 21.76056 |
| 20.00003 | 21.82814 |
| 20.49859 | 21.89413 |
| 20.99906 | 21.95867 |
| 21.4988  | 22.02156 |
|          | 00.00460 |

| 22.49859 | 22.14504 |
|----------|----------|
| 22.9987  | 22.20656 |
| 23.49727 | 22.26434 |
| 23.99777 | 22.32576 |
| 24.49792 | 22.38255 |
| 24.99595 | 22.43713 |
| 25.50067 | 22.49368 |
| 26.00101 | 22.54773 |
| 26.50156 | 22.60128 |
| 27.00091 | 22.65291 |
| 27.50012 | 22.70325 |
| 28.00005 | 22.75312 |
| 28.49998 | 22.80149 |
| 28.99989 | 22.84963 |
| 29.50244 | 22.89854 |
| 29.99963 | 22.94172 |
| 31.00266 | 23.03452 |
| 32.00063 | 23.11864 |
| 33.00063 | 23.2008  |
| 33.99879 | 23.27704 |
| 35.00151 | 23.35655 |
| 36.0036  | 23.43153 |
| 37.00282 | 23.50431 |
| 38.00514 | 23.57243 |
| 39.00316 | 23.64117 |
| 40.00451 | 23.70303 |
| 41.00467 | 23.76843 |
| 42.00591 | 23.82912 |
| 43.00645 | 23.88094 |
| 44.0069  | 24.02689 |
| 45.00859 | 23.98979 |
| 46.01023 | 24.04245 |
| 47.0119  | 24.09663 |
| 48.01274 | 24.14787 |
| 49.01188 | 24.20653 |
| 50.01106 | 24.25365 |
| 52.01546 | 24.33997 |
| 54.02257 | 24.42237 |
| 56.02697 | 24.49029 |
| 58.02815 | 24.55941 |
| 60.03356 | 24.62581 |
| 62.0345  | 24.68751 |
| 64.04255 | 24.74956 |
| 66.04078 | 24.80818 |
| 68.04543 | 24.86913 |
| 70.0435  | 24.93093 |
| 72.04813 | 24.98364 |
| 74.0489  | 25.03216 |
| 76.05231 | 25.07598 |
| 78.05622 | 25.1151  |
| 80.05991 | 25.14731 |
| 82.03926 | 25.17552 |
| 84.06423 | 25.22347 |

| 0.0.0007 | 05 050   |
|----------|----------|
| 86.0657  | 25.259   |
| 88.06335 | 25.2917  |
| 90.06925 | 25.33766 |
| 92.07699 | 25.36927 |
| 94.07819 | 25.39892 |
| 96.07629 | 25.42431 |
| 98.06763 | 25.44992 |
| 100.0832 | 25.47068 |
| 105.0455 | 25.55483 |
| 110.0474 | 25.60752 |
| 115.0482 | 25.65519 |
| 120.0526 | 25.7042  |
| 125.0548 | 25.75054 |
| 130.0564 | 25.80155 |
| 135.0594 | 25.84373 |
| 140.064  | 25.88106 |
| 145.0629 | 25.91262 |
| 150.0637 | 25.94465 |
| 155.0627 | 25.97875 |
| 160.0623 | 26.01095 |
| 165.0683 | 26.03907 |
| 170.0679 | 26.06673 |
| 175 0695 | 26 09356 |
| 180 0674 | 26 11558 |
| 185 0729 | 26 13561 |
| 100.0705 | 26 15752 |
| 105 065  | 26.17060 |
| 195.065  | 26.17969 |
| 200.0717 | 26.19908 |
| 205.0696 | 26.21799 |
| 210.0378 | 26.23488 |
| 215.0628 | 26.26474 |
| 220.0693 | 26.28227 |
| 225.0666 | 26.29544 |
| 230.0668 | 26.31148 |
| 235.0663 | 26.32408 |
| 240.0629 | 26.33984 |
| 245.0577 | 26.35629 |
| 250.0704 | 26.37107 |
| 255.0667 | 26.38792 |
| 260.0685 | 26.40795 |
| 265.061  | 26.41899 |
| 270.0551 | 26.43258 |
| 275.0602 | 26.44636 |
| 280.0576 | 26.46525 |
| 285.057  | 26.48031 |
| 290.0617 | 26.49585 |
| 295.058  | 26.51526 |
| 300.0576 | 26.52647 |
| 299.9921 | 26.51403 |
| UBAR     |          |
| PLOT     |          |
| COOR     |          |
| 1        |          |

4.876582 10.879819 7.387090 Angstrom 3.689029 8.567181 4.295428 Angstrom >>ENDDO