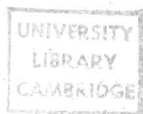


Ph.D. 9439

DESIGN AND SYNTHESIS OF MACROCYCLIC
LIGANDS DERIVED FROM 2,2'-BIPYRIDYL AND THEIR
TRANSITION METAL COMPLEXES

A thesis submitted to the University of Cambridge in
partial fulfilment of the requirements for the degree
of Doctor of Philosophy

by



KEVIN PETER WAINWRIGHT B.Sc.(Hons) (W. Aust.)

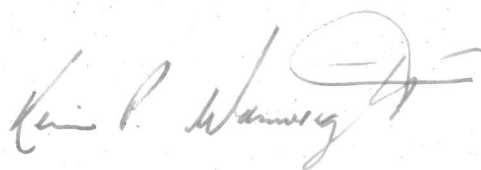
SIDNEY SUSSEX COLLEGE

1975

To all those who have contributed to my formal
education during the past twenty years-

PREFACE

The research work described in this thesis was carried out at the University Chemical Laboratory, Cambridge, during the period between August 1972 and July 1975, under the supervision of Professor J. Lewis, F.R.S. The results and conclusions presented represent original work performed by the author, except where specific reference is made to the contrary, and include nothing which is the outcome of work done in collaboration. Neither whole nor part of this thesis has been submitted previously in support of a degree at this or at any other university.



Kevin P. Wainwright

July 14th 1975

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And, by no means least of all, my dear wife for her patient acquiescence to the demands on my time during the past three years and for her assistance, together with that of Mrs. Wendy Lewis, in the preparation and typing of this thesis.

SUMMARY

Whilst α -diimines such as 2,2'-bipyridyl have been extensively studied in their capacity as simple bidentate ligands which form complexes of high redox stability with many of the transition metals, relatively little has been done to develop these compounds as multidentate or macrocyclic complexing agents. This thesis describes what is believed to be the first systematic approach towards the synthesis of macrocyclic derivatives of 2,2'-bipyridyl and in so doing correlates much of the classical co-ordination chemistry of bipyridyl with the rapidly developing area of macrocyclic ligand investigation.

Initial access to a multidentate system of this type has been gained by the reaction of 6,6'-dibromo-2,2'-bipyridyl either with hydrazine hydrate or with methylhydrazine. This gives, in excellent yield, the quadridentate ligands 6,6'-dihydrazino-2,2'-bipyridyl and 6,6'-di-N-methylhydrazino-2,2'-bipyridyl, respectively. Subsequent reaction of the nickel(II) complexes of these ligands with simple aliphatic carbonyl compounds such as acetone, under conditions expected to yield Curtis type macrocyclic products, gave instead a series of open chain, co-ordinated 6,6'-bis(N'-hydrazone)-2,2'-bipyridyl ligands. These ligands manifest imino-azo tautomerism, which has been investigated by n.m.r., and evidence for their reaction with oxygen to form azo-hydroperoxide compounds is presented. These results are described in Chapter Two.

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The spectral and magnetic properties of the transition metal complexes of these ligands are discussed in Chapter Four, and in so doing correlate this work, to some extent, with existing work.

Chapter Five describes the oxidative denitrogenation reaction that occurs when the complex dichloro-6,6'-dihydrazino-2,2'-bipyridyliron(II) is exposed to air. This reaction is peculiar to the iron(II) complexes of the ligand and yields a variety of iron(II) polypyridyl complexes. It has been studied by partial deuteration of the free reactant ligand in an attempt to elucidate the mechanism. The nature of the product suggests a novel way of preparing various polypyridyl species. The Mössbauer spectra for both the reactant and product are reported.

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ABBREVIATIONS

bipy	2,2'-bipyridyl
B.M.	Bohr Magneton
br	broad
d	doublet
DBBP	6,6'-dibromo-2,2'-bipyridyl
DHBP	6,6'-dihydrazino-2,2'-bipyridyl
DMeHBP	6,6'-di-N-methylhydrazino-2,2'-bipyridyl
DMF	dimethylformamide
en	ethylenediamine
e.p.r.	electron paramagnetic resonance
Et	Ethyl group
e.v.	electron volt
Hz	Hertz
I.R.	Infrared
kcal	kilocalorie
m	medium or multiplet
Me	Methyl group
m.p.	melting point
nm	nanometre
n.m.r.	nuclear magnetic resonance
Ph	Phenyl group
1,10-phen	1,10-phenanthroline
p.m.r.	proton magnetic resonance
q	quartet
R	hydrocarbon group
s	strong or singlet
sh	shoulder
s.o.	spin only
t	triplet
THF	Tetrahydrofuran
trien	triethylenetetramine
TMS	Tetramethylsilane
w	weak
δ	infrared bending absorption
ν	infrared stretching absorption

CHAPTER ONE

GENERAL INTRODUCTION

1.1 General

Principally because of its ability to form highly stable complexes with transition metals in a wide range of oxidation states, 2,2'-bipyridyl has been extensively examined, in the past¹⁻⁴, in its capacity as a simple bidentate ligand. It is the purpose of this thesis to describe work which has been directed towards structurally developing 2,2'-bipyridyl in such a way as to incorporate it as a part of the ring system of a quadridentate macrocyclic ligand. Such a ligand system might well be expected to have not only the potential for stabilising its complexes at various otherwise unstable oxidation levels, by virtue of the 2,2'-bipyridyl residue, but also, upon co-ordination, should manifest the dissociative stability characteristic of macrocyclic complexes in general.

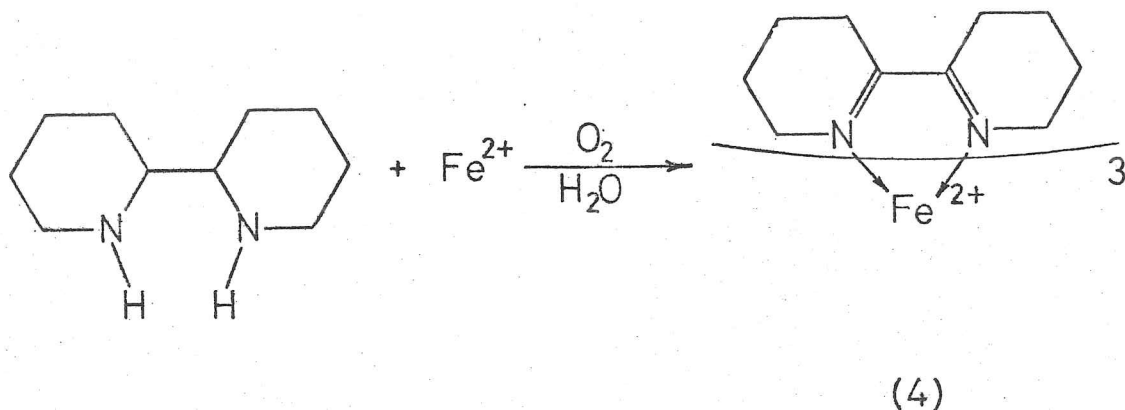
The significant chemical behaviour of transition metal complexes very often depends upon their facile redox properties. This is true to a large degree for the natural and synthetic complexes involving macrocyclic ligands. These substances undergo a diverse array of chemical reactions such as ligand oxidative dehydrogenation⁵⁻⁹, metal alkylation¹⁰⁻¹³ and carbonylation,¹⁴ ligand substitution¹⁵⁻¹⁷, and hydrogenation¹⁸⁻²⁰. The success of some of these reactions is closely linked with the ability of higher and lower oxidation states of the complexes to function as reactive intermediates. Accordingly, the availability of a macrocyclic ligand system containing an electron sink such as 2,2'-bipyridyl

may contribute to the study of such reactions by rendering the intermediates more thermodynamically accessible, and hence increasing the facility for the reaction to occur, and possibly by stabilising the otherwise reactive intermediates so as to permit their isolation and examination in the solid state.

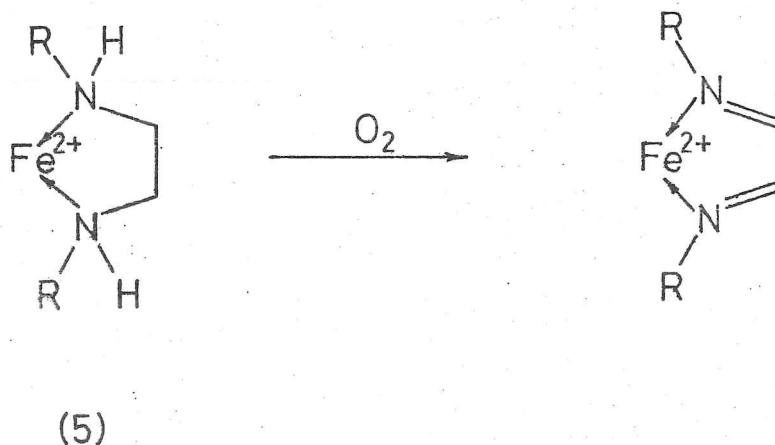
In the following sections the origin of the stability associated with complexes of 2,2'-bipyridyl (hereafter referred to simply as bipyridyl or bipy) and other α -diimine type ligands will be discussed and the so called "macrocyclic effect"; a term which describes the high dissociative stability of macrocyclic complexes, will be described both in terms of its proposed origin and in terms of its manifestations. Additionally, by way of introduction to the manner in which the synthetic work was approached, a review of the substituted bipyridyl compounds that are suitable for use as macrocyclic precursors, together with the more generally applicable techniques by which they might be cyclised, will be given.

1.2 The α -Diimine-Metal Chelate Ring

The fact that the α -diimine metal chelate ring system, which is formed when bipyridyl, amongst other ligands containing the α -diimine group, undergoes complexation, structure (1), constitutes a system of exceptional stability, is best exemplified by the ease with which a compound will undergo structural modification so as to adopt this functional grouping. For example, the

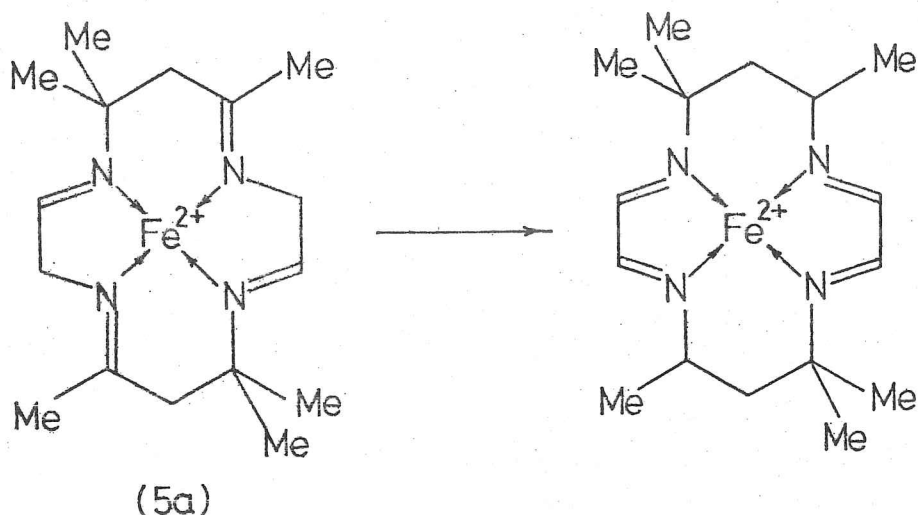


complexes and reflects the unusual resistance towards oxidation that iron(II) shows when forming part of an



α -diimine system. Finally, it is worth noting that tautomerism of complexes containing unconjugated imines, (5a), has been observed to occur in such a way as to produce the α -diimine ring⁵.

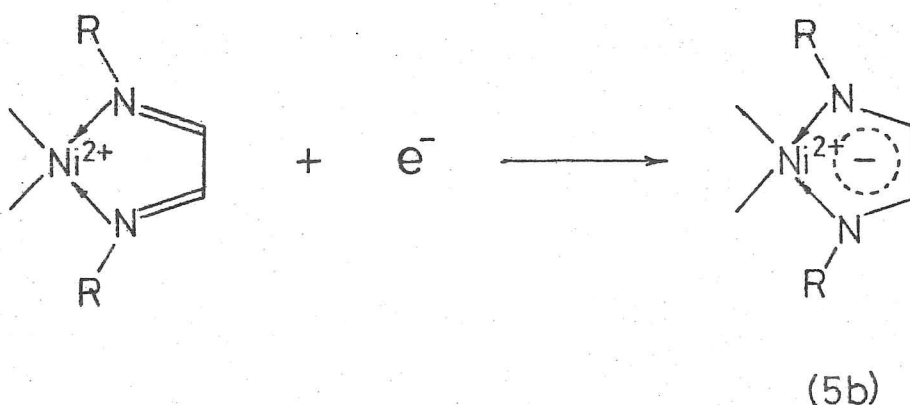
The origin of this stability apparently lies with the fact that the α -diimine group is not only a good sigma donor by way of the sp^2 orbitals on each nitrogen atom, but also, there is considered to be extensive bonding



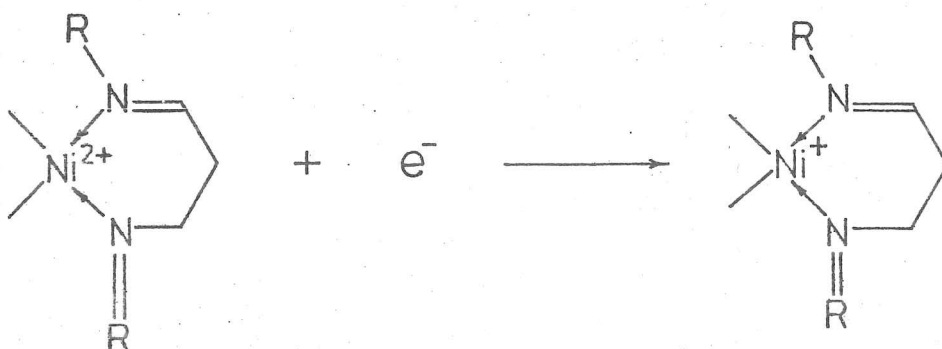
from the $d\pi$ orbitals on the metal to the $p\pi$ antibonding orbitals associated with the α -diimine system, or vice versa^{21,23}. Since the two imine moieties are in conjugation with one another this π bonding allows the metal chelate ring the facility to assume complete π electron delocalisation and hence aromatic character. It is this potential for aromaticity that is believed to account for its high stability²³.

Besides the unusual stability, the aromatic character of the metal chelate ring is further suggested, according to Busch²⁵, by an observed shift to lower energy in the imine carbon to nitrogen stretching frequency upon complexation of such ligands. This reduction in frequency is taken to indicate enhanced conjugation of the double bond as a result of participation of the metal atom in double bonding. The actual magnitude of the frequency shift suggests that iron(II) participates to a significantly greater degree in the double bonding than do cobalt(II) or nickel(II).

Recent electrochemical studies not only demonstrate the capacity that imine containing macrocycles have for stabilising reduced forms of the complex, but furthermore the manner in which the stabilisation is achieved provides additional evidence for the aromatic nature of the α -diimine metal-chelate ring. Characteristically, the electrolytic reduction of nickel(II) complexes containing α -diimine linkages produces a metal ion stabilised ligand radical anion (5b)²⁶. This has been shown by the nature



of the e.p.r. signal and it is suggested that the added electron goes into a low lying π antibonding orbital. In contrast complexes containing unconjugated imine groups in their chelate rings undergo reduction at the metal ion.

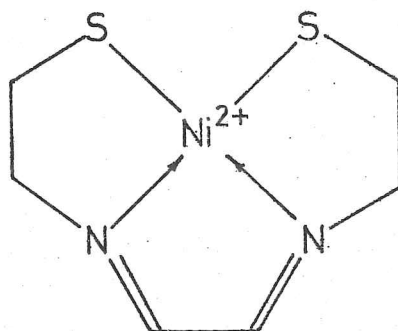


Also, it has been observed that the presence of an α -diimine group in the ligand contributes significantly towards lowering the reduction potential of the system. From the determination of the redox potentials of a large number of these ligand systems the authors are able to show that the α -diimine group has a much greater effect on the stability of iron(II) with respect to iron(III) than on the stability of nickel(II) with respect to nickel(III). This is consistent with the infrared findings mentioned above and also with synthetic observations for the two different metals with similar ligands. For example, the oxidative dehydrogenation reaction, referred to above, for an iron(II) species such as (5), where the iron(II) compound reacts in solution with molecular oxygen to yield a structure which ultimately contains the α -diimine group. This does not occur with the analogous nickel(II) complex. Instead the nickel(II) compounds produce complexes containing only isolated imines⁶.

The use of e.p.r. spectroscopy, in the manner described above, has shown unambiguously the potential that α -diimines have for forming radical anions. This observation largely clarifies rationalisation of the facility that this group has for stabilising metals in apparently very low oxidation states. Thus, the $M(\text{bipyridyl})_2$ complexes of Be, Mg, Ca and Sr in which the metal formally appears to be zerovalent²⁷ are now known from e.p.r. data to consist of metal²⁺ cations surrounded

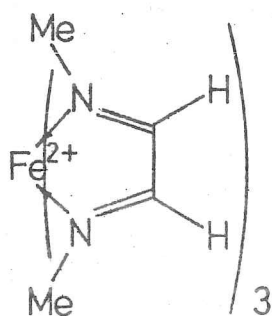
in a tetrahedral environment by two radical anions²⁸.

However, formation of a radical anion appears to represent the extreme case of electron delocalisation. There are other cases, for example compound (6), where e.p.r. shows

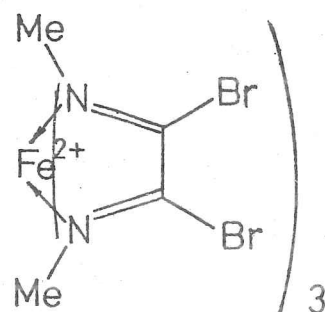
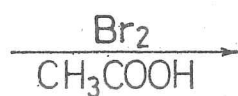


(6)

that the electron density, in excess of that which the metal will carry, is distributed between the metal and the ligand without complete transfer to the ligand or complete reduction of the metal²⁹. This appears to be the general situation for compounds having metals neither in their highest nor unusually low oxidation states and reflects the extent of the π bonding. It is evidenced, for example, by the fact that tris(glyoxal-bis-methylimine)iron(II), (7), undergoes electrophilic bromination on the ring to produce (8)^{30,31}. This reaction stands in strong contrast to the



(7)



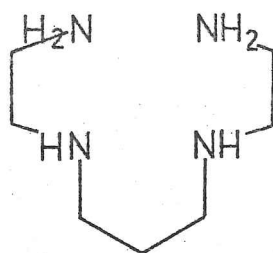
(8)

usual oxidation of iron(II) to iron(III) by bromine and clearly indicates the high electron density on the chelate ring. Thus in considering redox properties, such systems must be considered in their entirety as an electron sink to which, within limits, electrons may be added or subtracted with relative ease.

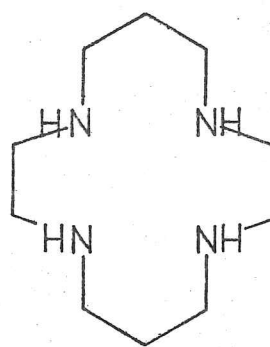
1.3 The Macrocyclic Effect

The enhanced stability of a cyclic tetramine metal complex when compared to an open chain tetramine complex has been termed the "macrocyclic effect"^{32,65}. Since the aim of this work was to implant an α -diimine group, in the form of a bipyridyl residue, into a macrocyclic system so as to take advantage of this stability, it is pertinent at this point to review what is known of its origin.

It appears that the stabilisation of metal complexes by cyclic ligands is both thermodynamic and kinetic in origin. Margerum and co-workers have determined the dissociation constants for the nickel(II) and copper(II) complexes of the open chain tetramine, 2,3,2-tet, (9), and have compared these with the dissociation constants for the corresponding complexes of the closely related macrocycle, cyclam, (10)^{32,33}. This comparison shows that the macrocyclic complex has a stability constant approximately 10^5 times greater than that for the open chain complex and leaves little doubt that the effect is thermodynamically real. Chemically the effect is manifested for instance,



(9)



(10)

by the fact that open chain complexes such as $\text{Ni}(2,3,2\text{-tet})^{2+}$ are destroyed in fractions of a second in strongly acidic solutions, yielding the protonated ligand and $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, whilst when $\text{Ni}(\text{cyclam})^{2+}$ is placed in 6M HCl nothing happens³⁴. That is, the rate of loss of the ligand is remarkably slow. The rates of dissociation for $\text{Cu}(2,3,2\text{-tet})^{2+}$ and $\text{Cu}(\text{cyclam})^{2+}$ have been measured and show that the linear tetradentate ligand dissociates some 10^7 times faster than does the macrocyclic complex³⁵. This huge effect on the dissociation rate is probably due to the fact that the mechanism by which the linear complex dissociates is not available to the macrocyclic complex.

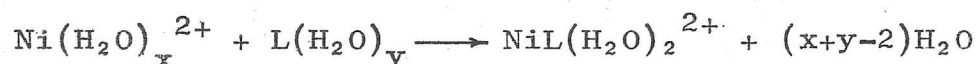
The usual mechanism of substitution at nickel(II) involves bond breaking in the rate determining step³⁶. In a polydentate ligand this normally occurs at a terminal position. In acidic media the dissociated groups are protonated quickly and the vacated site in the co-ordination sphere of the nickel atom is filled rapidly by solvent. A second atom then dissociates and the entire ligand is replaced by solvent in a sequence of $\text{S}_{\text{N}}1$ steps³⁶. From

the structure of a cyclic system it is obvious that a simple dissociative step cannot occur, because the ring has no end. It is not possible to extend the metal to nitrogen distance sufficiently to constitute bond rupture without additional bond rupture involving the ligand or extensive rearrangement within the co-ordination sphere. Accordingly, it has been suggested³⁴ that the process by which a macrocycle is displaced from nickel(II) involves nucleophilic addition at the metal which causes the macrocycle to develop an incipient fold, the extent of the folding being related to the flexibility of the particular macrocycle, and that in this folded conformation bond rupture occurs. Thus the rate determining step in this process is bimolecular and clearly involves a higher activation energy than that required in the dissociation of the non-cyclic complex.

As well as this kinetic stability, caused by the fact that the macrocyclic complex can only undergo dissociation by an energetically less favourable pathway than that followed by a linear tetramine, the determination of thermodynamic constants has shown that the enhanced stability of the macrocyclic complex is also due to its lower enthalpy of formation³³. Thus, a comparison of the values of ΔH^0 and ΔS^0 for $\text{Ni}(\text{cyclam})^{2+}$ and $\text{Ni}(2,3,2\text{-tet})^{2+}$ shows that the macrocyclic ligand has a more favourable ΔH^0 by 14 kcal mole⁻¹ and a less favourable ΔS^0 by 16 cal deg⁻¹ mole⁻¹. The authors rationalise their findings in the following way³⁷.

The relative enthalpy and entropy changes cannot be understood unless ligand solvation, which in the past has tended to be neglected³³, is taken into consideration. Thus, the non-cyclic ligand would be expected to suffer a much larger loss of configurational entropy upon co-ordination than the cyclic ligand where the geometry is already restricted. However, the experimental ΔS^0 differences are in the opposite direction. Also, considerations of bond strengths in various related compounds show that no more than 2 kcal mole⁻¹ of the enthalpy difference could be assigned to differences in nickel to nitrogen bond strengths in the two complexes.

By considering ligand solvation, however, these changes in enthalpy and entropy can be understood. The complexation reaction in aqueous solution may be represented as :-



where the free ligand L is hydrated primarily through hydrogen bonding. The nickel cation has six water molecules in its inner co-ordination sphere and additional water molecules associated with it in the outer hydration sphere. The complex will be less hydrated than the metal ion because of the ligand co-ordination, the decreased charge to radius ratio and the hydrophobic exterior presented by the bound ligand. The net heat of formation of the nickel complex is equal to the enthalpy of the nickel to nitrogen bond formation less the additional hydration enthalpy. The

release of water from the metal ion and the ligand results in a positive entropy contribution because the number of independent particles has been increased, but a negative contribution to the entropy change stems from the loss of configurational entropy of the ligand upon co-ordination. The major difference in the formation reactions of $\text{Ni}(2,3,2\text{-tet})^{2+}$ and $\text{Ni}(\text{cyclam})^{2+}$ is believed to be due to the magnitude of y in the above equation. The cyclic nature of cyclam is said to physically prevent it from having as large a hydration number as 2,3,2-tet, thus reducing the energy required from the system for solvent dissociation or conversely, the energy gained from the system on dissociation of its complex.

Since hydrogen bonding of the ligand to water is an important part of ligand solvation and that the average enthalpic value for a hydrogen bond of this type is $\Delta H^0 = -7 \text{ kcal mole}^{-1}$ the authors suggest that the cyclic ligand is solvated by the equivalent of at least two fewer water molecules than 2,3,2-tet.

In conclusion the dominant thermodynamic factor responsible for the "macrocyclic effect" in the tetramine ligands appears to be the lower degree of solvation of the macrocycle. A smaller, but important contributing factor, is the lower configurational entropy of the ligand because it is already cyclic. The latter factor tends to be obscured in the ΔS^0 value because the more solvated linear ligand releases additional solvent molecules in its reaction and so increases the entropy of the system.

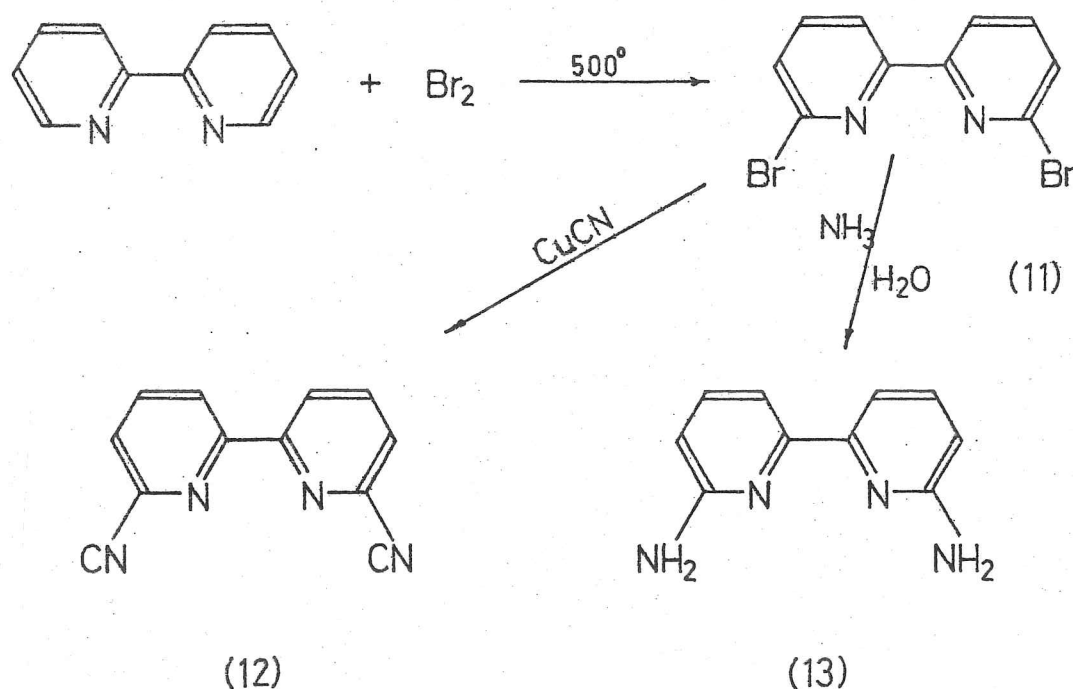
The kinetic factor is due to the fact that the cyclic complex is compelled to undergo dissociation by a less favourable mechanism.

1.4 Macrocyclic Precursors Containing the 2,2'-Bipyridyl Functionality

The majority of high yield macrocyclic tetramine forming reactions are metal template reactions. These are ligand reactions which are dependent on, or can be significantly enhanced by, a particular geometrical orientation imposed by metal co-ordination³⁸. The functional groupings at which reaction takes place to generate the macrocycle, are generally primary and secondary amines, aldehydes or ketones, forming part of a multidentate chelate. Accordingly, in selecting derivatives of bipyridyl suitable for use as macrocyclic precursors, the most obvious choice lies with compounds capable of structural development into quadridentate chelates having these functional groups at their terminal positions. This then only requires the formation of a single bridge to bring about ring closure. Alternatively, one could set about to co-ordinate two suitably substituted bipyridyl residues to a metal and effect ring closure by a double bridge forming reaction. To fulfill the requirements for chelation the 6,6'-disubstituted derivatives of bipyridyl are the obvious starting point.

At the time when this work was commenced, 6,6'-disubstituted derivatives of bipyridyl had been prepared

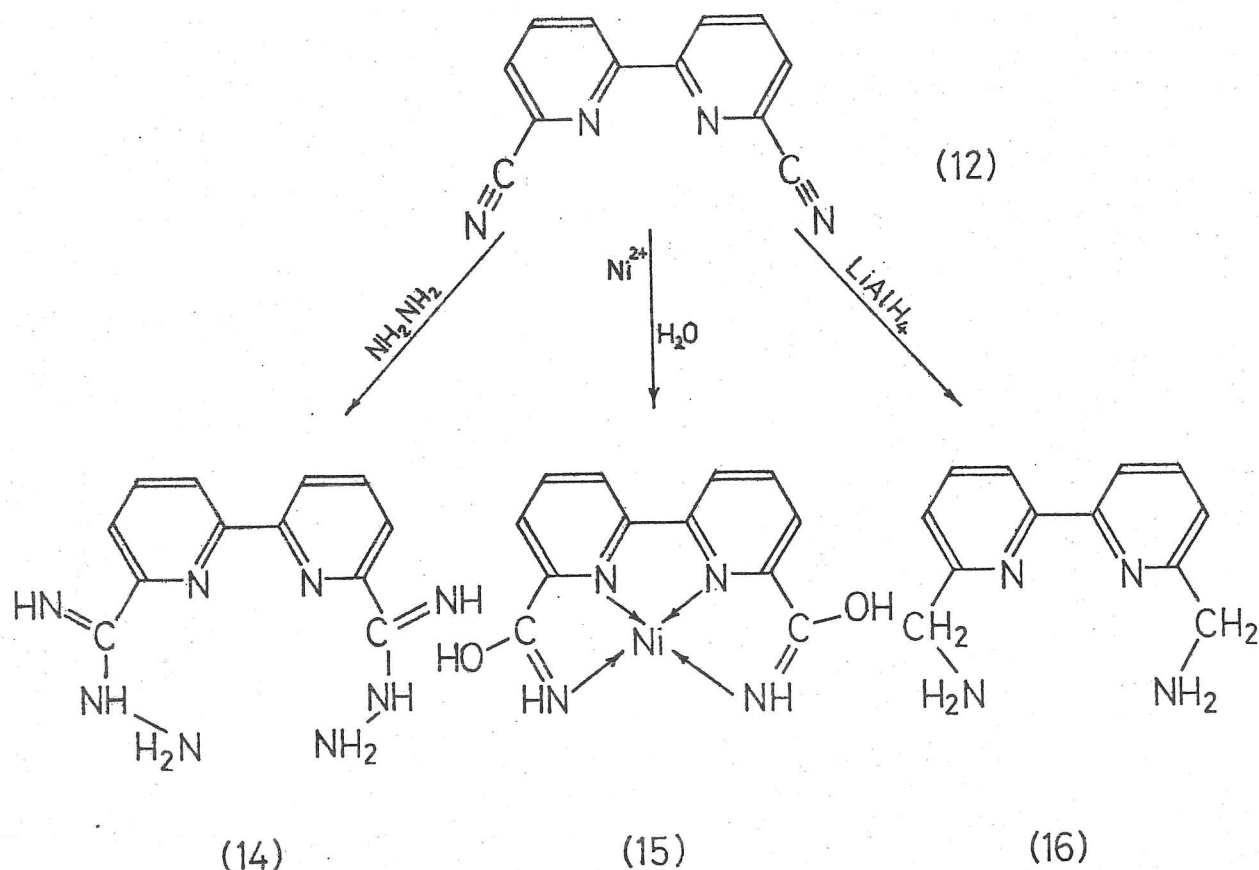
by the direct bromination of bipyridyl and the subsequent conversion of the 6,6'-dibromo-2,2'-bipyridyl, (11), into various other substituted derivatives³⁹. Of particular



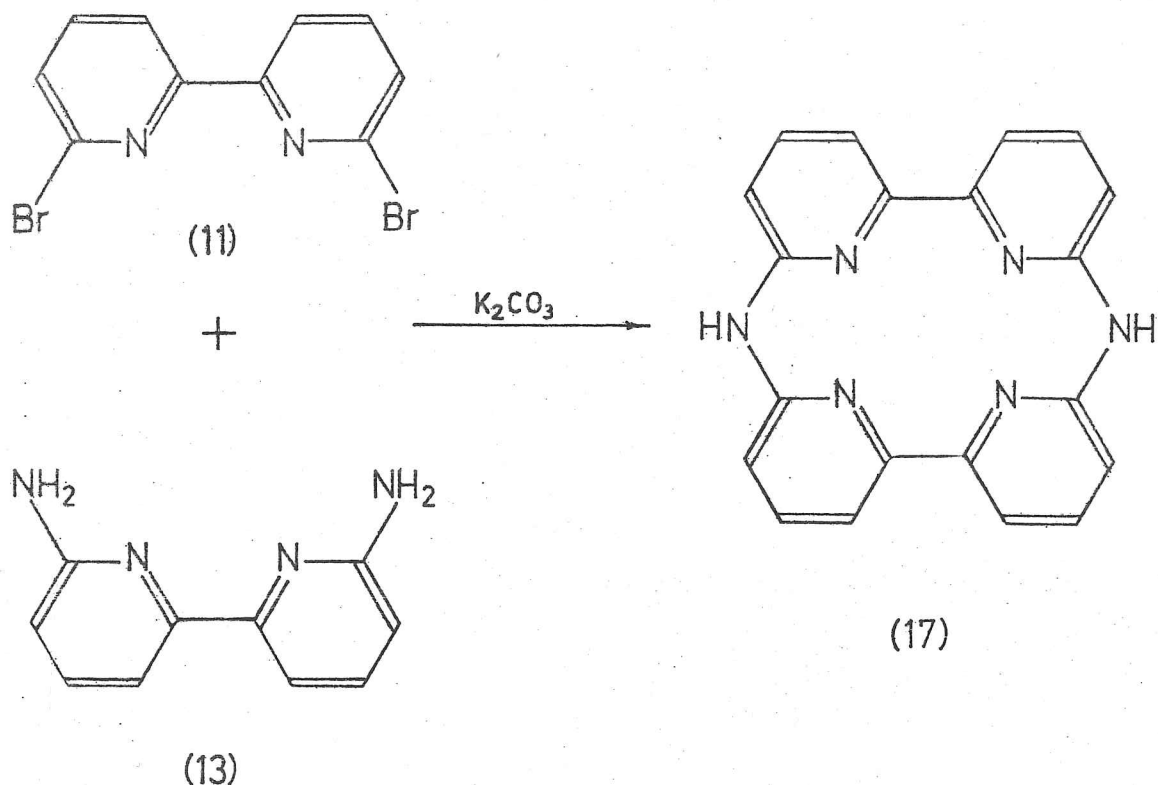
interest to this work are the 6,6'-dicyano, (12), and 6,6'-diamino, (13), compounds.

It should be noted, however, that the bromination reaction itself is a synthetically difficult, low yield reaction (c.a. 30%) and that the formation of both the dicyano and diamino compounds proceeds in less than 10% yield, thus multistage synthetic sequences originating from the latter two compounds are not really feasible. This is regrettable since one can envisage several ways in which the dicyano compound might be converted to form macrocyclic precursors, in addition to the formation of the dicarboxylic acid, which has already been reported³⁹. For example, reaction of the cyano group with hydrazine is

known to produce functional groupings of the type shown in (14)⁴⁰. Partial hydrolysis of metal complexes of (12)

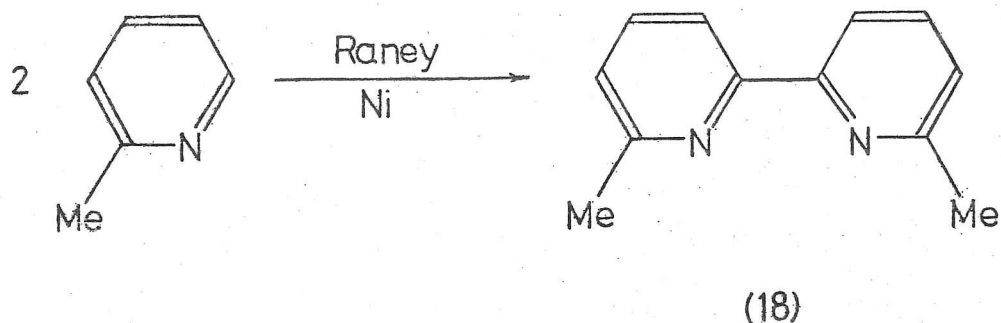


may readily occur, by analogy with the 2-cyano-1,10-phenanthroline⁴¹, to produce (15) where the ligand is able to bind as a tetradentate chelate. Reduction of the cyano group normally leads to amine formation⁴² and thus it may be possible to derive compound (16) which would also be a useful macrocyclic precursor. Similarly, were the diamine, (13), readily accessible it would be of interest to learn whether it would undergo cyclisation in conjunction with 6,6'-dibromo-2,2'-bipyridyl, (11), to form the macrocycle (17) in a manner as facile as that in which the analogous 1,10-phenanthroline compounds combine^{43,44}. Generally the reaction of a compound with two equivalent, like functional



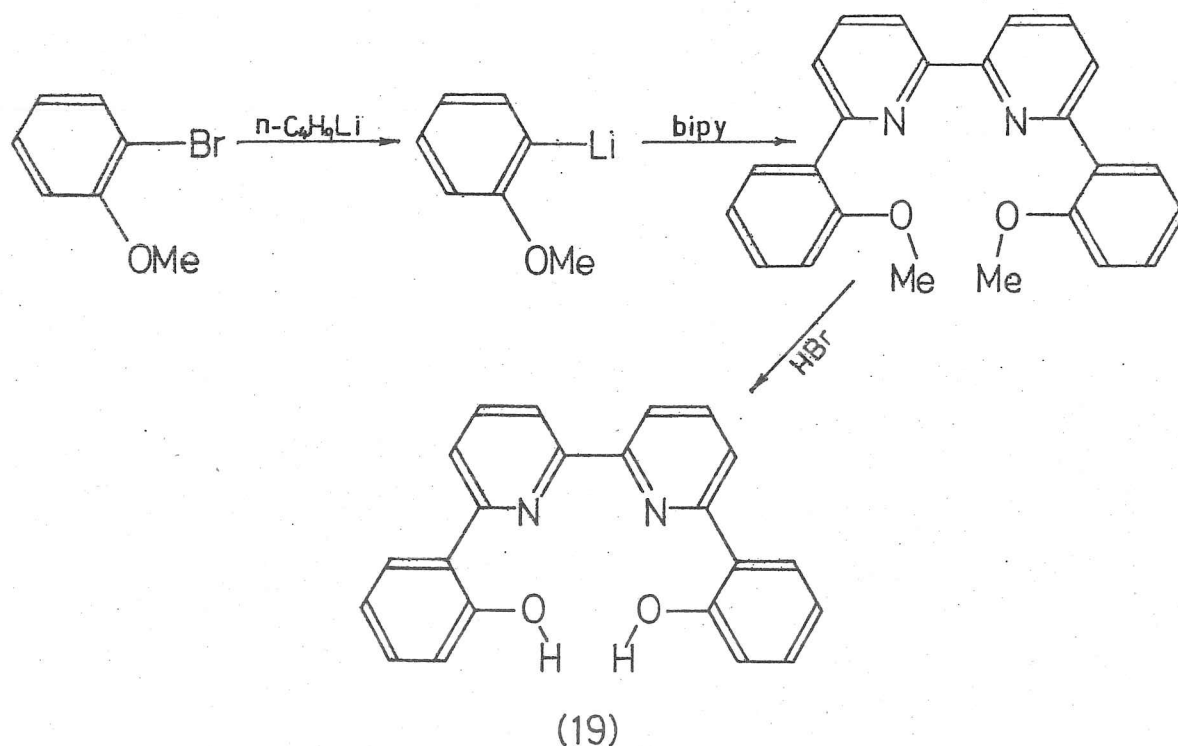
groups with another also having two equivalent, like functional groups (a reaction type which I propose to refer to as a "2 + 2" reaction) results in polymeric products rather than monomeric products. That is, in polymeric chains, rather than in discrete two component rings, for purely statistical reasons. This 1,10-phenanthroline system is quite remarkable in producing quantitative yields of the cyclic product without even having to resort to high dilution conditions or to metal template effects.

Some substituted bipyridyls, particularly alkylated bipyridyls, for example, 6,6'-dimethyl-2,2'-bipyridyl, (18), can be prepared by coupling substituted pyridines^{39,45,46}. Again the yields are generally mediocre, but moreover none of the derivatives prepared by this method are immediately



useful as macrocyclic precursors.

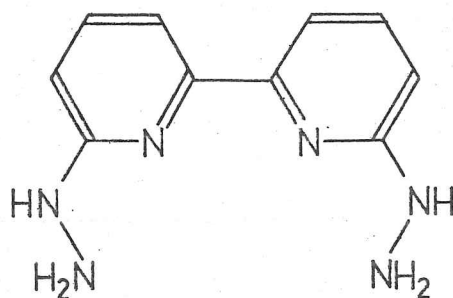
Only a single quadridentate ligand derived from bipyridyl, (19), appears to be recorded in the literature⁴⁷, and no attempts to study its metal complexes have been



reported. The synthetic sequence used is shown above. The ligand itself seems unlikely to be useful in its present form as a macrocyclic precursor, unless a method

for cyclising a compound such as this by reaction at aromatic alcohol functionalities is developed.

This brings considerations back to the dibromide, (11), and it was planned to look for a high yield synthesis, using this compound, that would convert it to a suitable macrocyclic precursor. One method that seemed promising was by reaction with hydrazine. In the case of 2-bromopyridine this reaction proceeds readily and in high yield to form the 2-hydrazino derivative⁴⁸. The corresponding product derived from (11) is shown as structure (20).

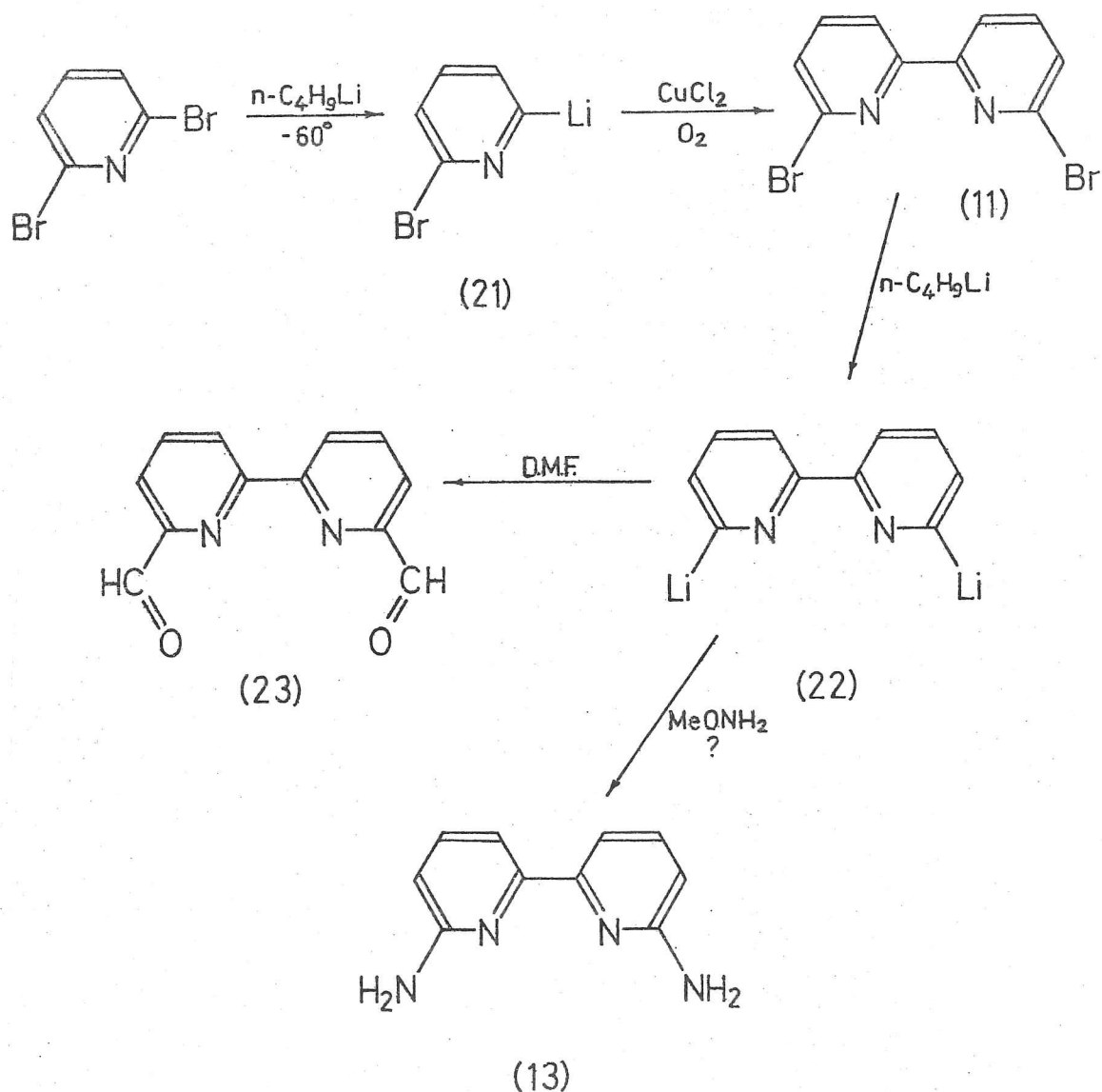


(20)

A study of molecular models shows that complexes of this compound may well prove to be highly reactive macrocyclic precursors. This is evident since, assuming no distortion of bond angles, the minimum N-N through-space distance between the terminal amines is approximately 65% greater than the corresponding distance between the bipyridyl nitrogens. Thus, upon complexation the ligand should bind strongly through the α -diimine group, but only relatively weakly, because of the geometry, at the two terminal co-ordination sites. As a result

the terminal amines are left in a state of unusually high lability and nucleophilicity, which should enable them to participate readily in a cyclisation reaction whilst still deriving the benefits of the metal template effect. Indeed it proved possible to synthesise 6,6'-dihydrazino-2,2'-bipyridyl, (20), efficaciously and the studies that were undertaken with it are described in subsequent chapters.

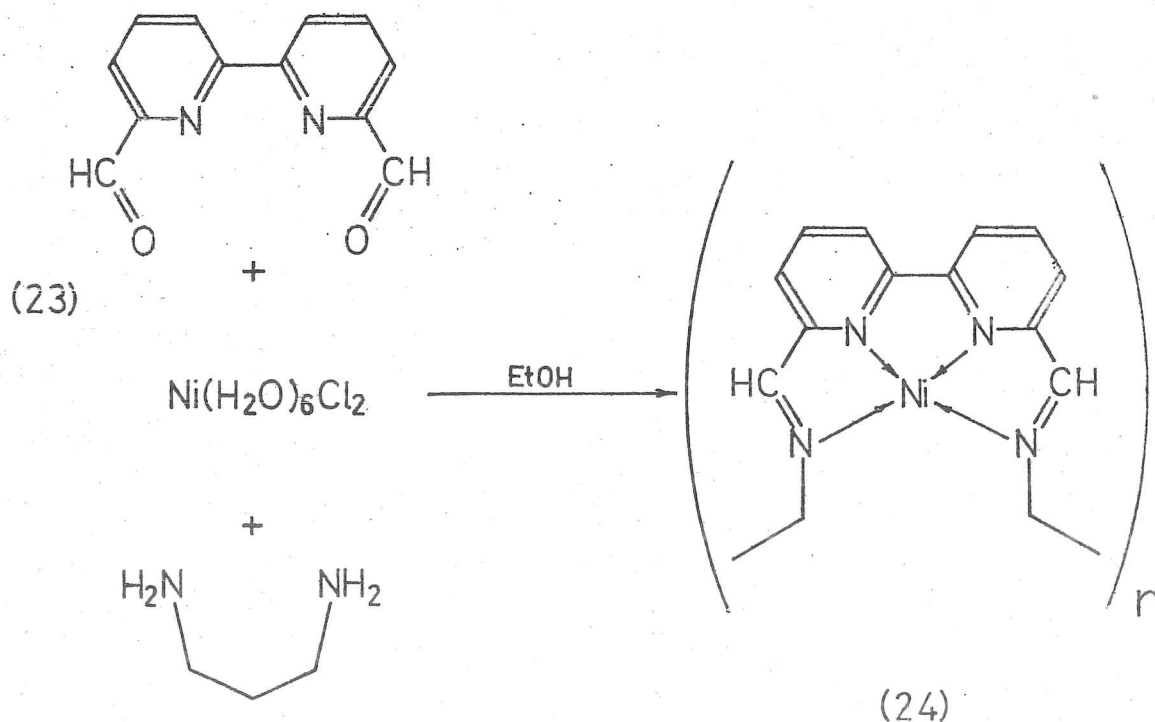
During the course of this work a publication by Holm and co-workers⁴⁹ appeared in the literature giving details of a procedure, of some considerable generality, for preparing 6,6' disubstituted bipyridyls. The procedure involves the dilithiation of 6,6'-dibromo-2,2'-bipyridyl, (11), (which itself they prepared in 50% yield from monolithiated 2,6-dibromopyridine, (21)) to give (22), and subsequent reactions of this species. This sequence provides a new method for the preparation of (11), which gives a higher yield, but which is still probably as laborious as the direct vapour phase bromination of bipyridyl (described in detail in Chapter Two) and not as suited to large scale preparations. Of direct interest to the search for macrocyclic precursors was the fact that the preparation of 6,6'-diformyl-2,2'-bipyridyl, (23), was described; proceeding in 48% yield by the reaction of dimethylformamide with (22). Also of interest is the potential that (22) must have for the formation of the diamino species, (13). This does not yet appear to have been investigated. Normally, reaction of organolithium reagents with methoxyamine yields the corresponding



organoamine together with lithium methoxide⁵⁰.

6,6'-Diformyl-2,2'-bipyridyl, (23), prepared by Holm's method, was investigated as a macrocyclic precursor in this work, however, it did not prove useful. Unlike the dihydrazine, (20), (*vide infra*) no nickel(II) complex of (23) could be isolated, although slight changes in the ligand field spectrum of aqueous nickel(II) on adding (23) suggested that some association in solution was occurring. The apparently lower stability constant for this association is probably due to a combination of the unfavourable

geometry and the fact that two nitrogen donors have been substituted by two less polarisable oxygen donors. As a consequence of this, even if the ligand does behave as a tetradentate in solution, any metal template effects must be severely compromised. Additionally, the only general way of cyclising a system about terminal aldehyde groups is by a "2 + 2", Schiff-base forming reaction, with an appropriate diamine.⁵¹ The pitfalls associated with this technique have already been mentioned. Reactions of this type were attempted, but even under high dilution conditions no purely monomeric compounds (as indicated by molecular weight studies of both complex and liberated ligand) could be obtained. The combination of millimolar amounts of (23), hexaaquanickel(II) chloride and 1,3-diaminopropane, for example, led to polymers containing an average of seventeen dialdehyde residues, (24).



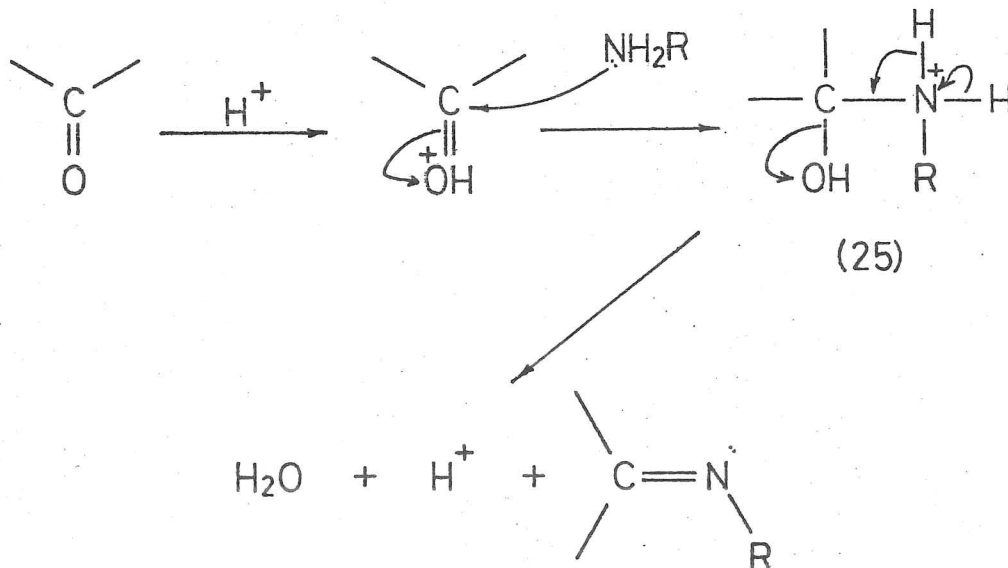
Thus the most expedient, immediately available synthetic route to macrocycles containing the bipyridyl moiety appeared to originate from 6,6'-dibromo-2,2'-bipyridyl by way of its dihydrazino derivative, (20). In cases where the absence of the active secondary amino proton was desired 6,6'-di-N-methylhydrazino-2,2'-bipyridyl (that is (20) with the secondary amines methylated) was prepared with equal ease from methylhydrazine and the dibromide, (11), and was found useful as a precursor.

1.5 Cyclisation Techniques Applicable to the 2,2'-Bipyridyl System

Having chosen to develop the macrocyclic system by way of 6,6'-dihydrazino-2,2'-bipyridyl (hereafter referred to as DHBP) the cyclisation reactions that are of interest are then those that involve reaction at co-ordinated primary amines. Often co-ordinated amines are relatively inert and do not participate as readily as their metal free counterparts in reactions which depend upon their nucleophilic properties⁵². This is one of the principal shortcomings of the metal template effect; that co-ordination tends to destroy the nucleophilicity, and hence the reactivity, of amines by involving the lone pair of electrons in the co-ordination bond. In the case of DHBP however, as already noted, one hopes that the strained geometry will result in the terminal amines being highly labile and so free to react in their nucleophilic capacity. On the other hand functional groups such as aldehydes and ketones

which react by nucleophilic attack at the acyl carbon have their reactivity enhanced by co-ordination. The participation of electrons on the oxygen in co-ordination bonding results in the acyl carbon becoming more electro-positive in character⁵².

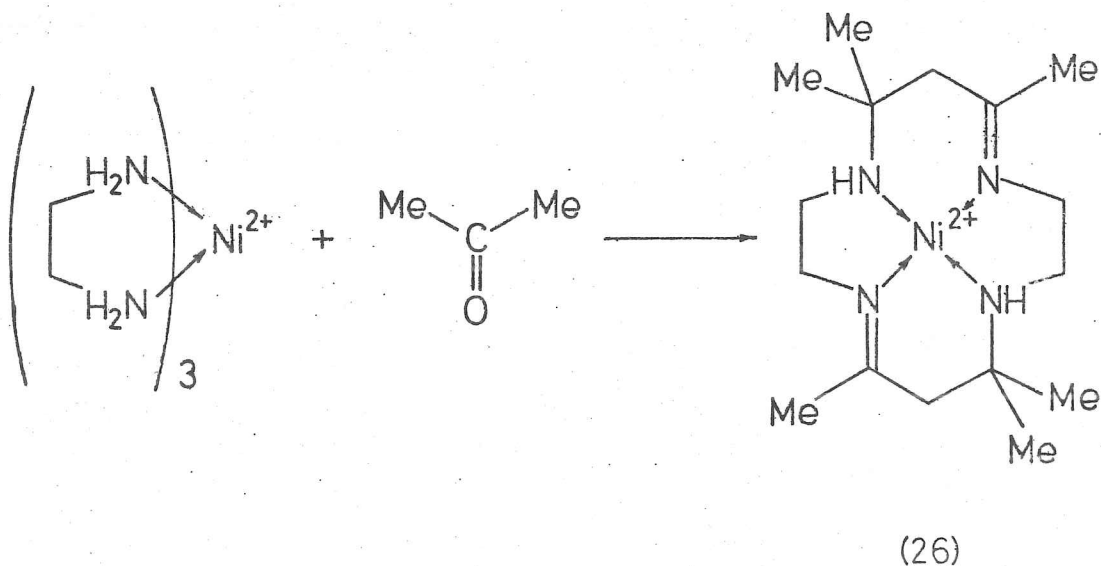
Although the individual cyclisation reactions may vary in procedure and detail the majority of those involving amines rely, at some stage in the process on the formation of a Schiff-base. The mechanism of Schiff-base formation is well established⁵⁴. Nucleophilic attack by a primary amino group at the carbonyl carbon of an aldehyde or ketone produces a carbinolamine, (25), which then dehydrates to produce the required imino linkage. The reaction is acid-



catalysed since protonation of the oxygen enhances the electrophilicity of the carbonyl carbon, however, if the pH is too low quarternisation of the amine occurs and inhibits the reaction. The reaction is fully reversible.

Probably the most extensively studied of all cyclisation reactions is applicable to the cyclisation of co-ordinated amines. This is the reaction first discovered by Curtis. The work which has been done in developing it is well summarised in his excellent review⁶. The details of this which are especially significant to this work are briefly reviewed.

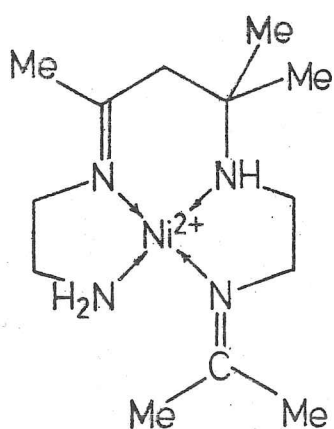
In the prototype reaction tris(ethylenediamine)-nickel(II) perchlorate was allowed to react with anhydrous acetone at room temperature over a period of days. Instead of the expected tetrakis(Schiff-base) complex, the product was found to be a fourteen membered macrocyclic complex in which the co-ordinated amines were linked by three-carbon bridges, (26).



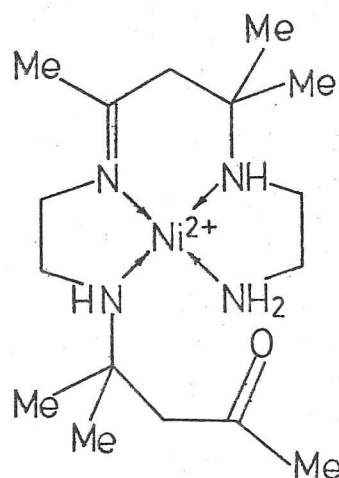
The formation of this type of three-carbon bridge is the characteristic feature of the Curtis Reaction and it can be produced by reaction of a variety of co-ordinated

amines with acetone.

Subsequent work showed that under certain conditions it was not always possible to effect closure of the two bridges. Instead, formation of compounds such as (27) and (28), believed to be intermediates in the ring closing process, occurred.



(27)

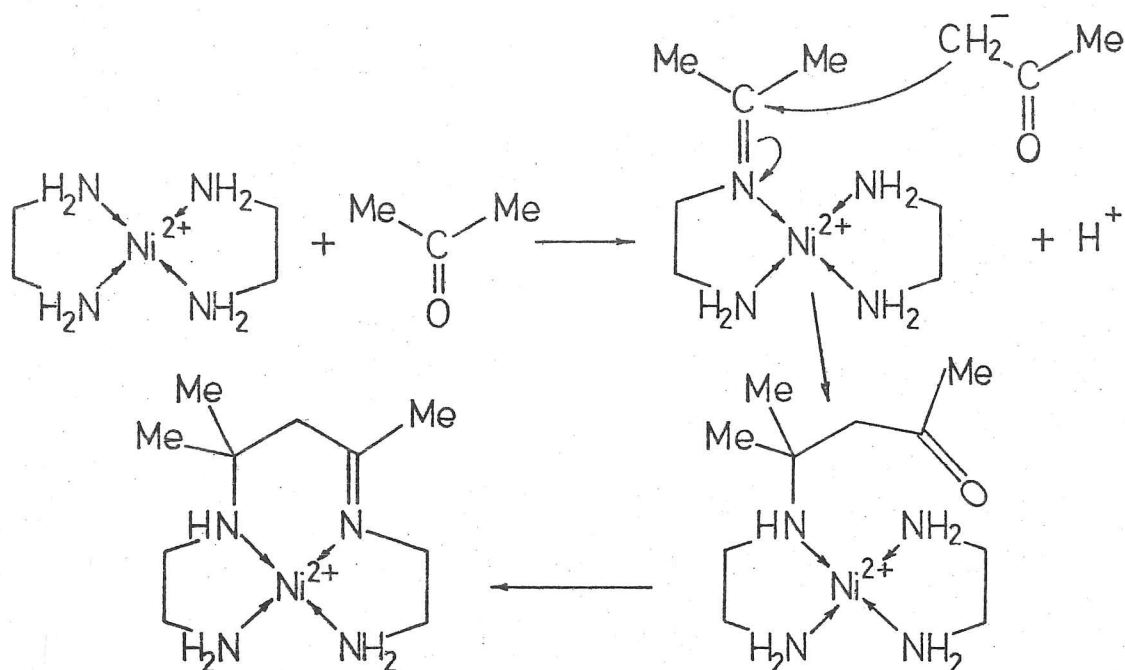


(28)

The formation of these intermediates has led to the proposal that the mechanism of the bridge forming reaction involves an internal Aldol condensation, which proceeds by attack of a carbanion, derived from a free acetone molecule, at the imino carbon of a condensed acetone, followed by a second Schiff-base condensation (see Scheme One). What is not fully understood is why carbanion formation occurs so readily under neutral conditions⁵⁵.

Diacetone alcohol, which is the Aldol product derived from acetone and corresponds in configuration to the preformed bridging unit, has been used instead of acetone in the Curtis Reaction and leads to the same

Scheme One



product. Since there are always acetone and mesityl oxide in equilibrium with diacetone alcohol⁶ it is not clear which species is actually reacting, however, there is no obvious mechanism by which diacetone alcohol could react directly. Mesityl oxide can react by Michael Addition of the amine, followed by imine formation⁶.

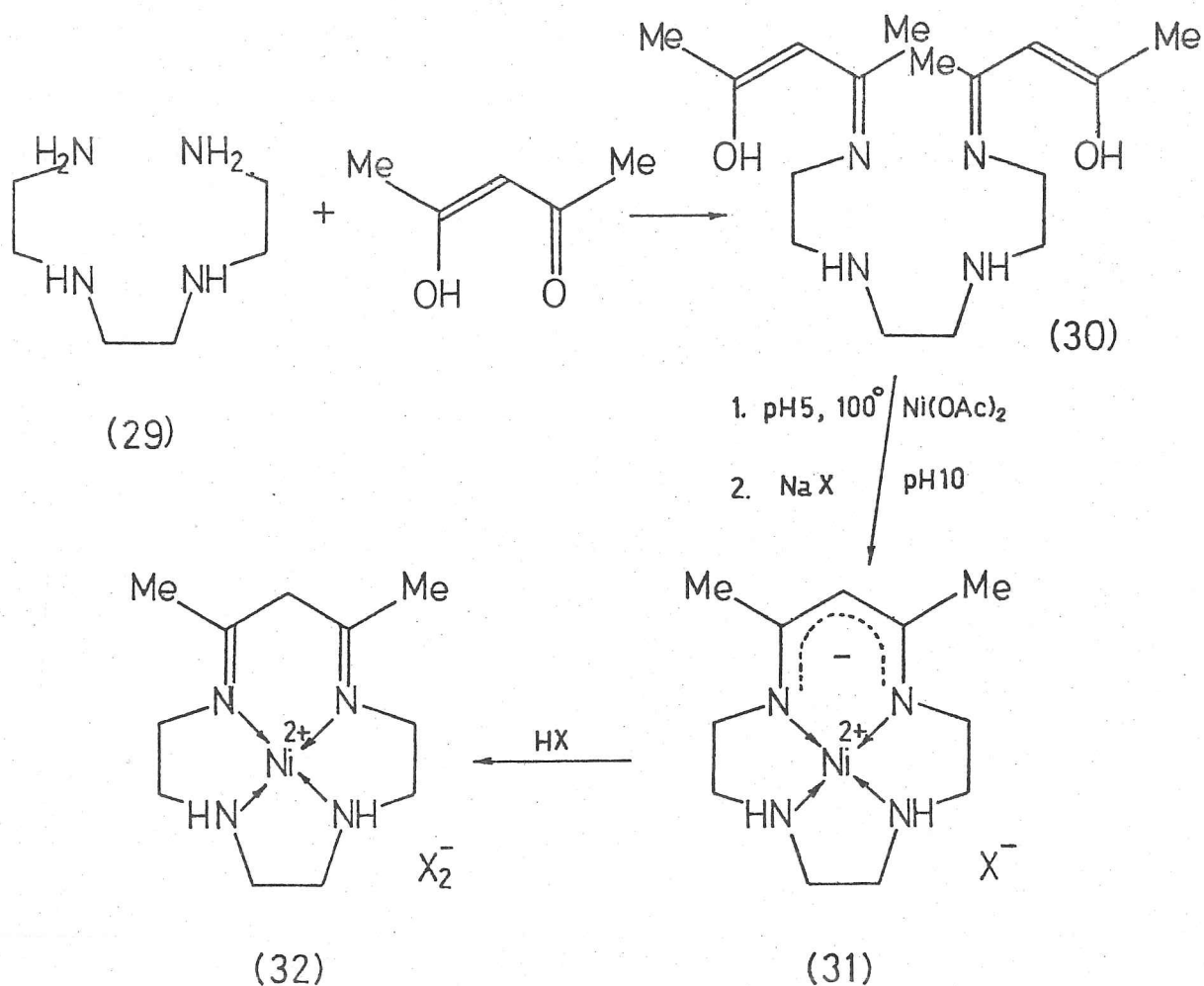
With the tetradentate ligand triethylenetetramine, (29), (hereafter referred to as *trien*) formation of only a single bridge is required and this proceeds without difficulty not only with acetone, but also with aldehydes and other α -methyl ketones, although more vigorous reaction conditions are required with these compounds. The *trien* system is closely analogous to the DHBP, (20), system since in both cases the single bridge forming reaction results in the formation of a thirteen membered macrocycle. Furthermore, the crystal structure of square-planar

Ni(trien)(ClO₄)₂ shows the trapezoidal disposition of the nitrogen donors⁵⁶ (that is, with the two outer nitrogen donors further apart (by 0.21Å) than the two inner ones) that is expected, but to a greater degree because of the unsaturation, in a square-planar nickel(II) complex of DHBP.

The Curtis Reaction proceeds at its best when the metal template ion is nickel(II). Copper(II) gives lower, but still reasonable yields, however, with other metal ions the reaction is generally unsuccessful. This observation is not only true with respect to this cyclisation reaction, but in many other cyclisation reactions nickel(II) seems to promote macrocycle formation to a greater extent than other metal ions⁵⁵.

Cummings and Sievers first reported in 1970 another method, which has now been shown to be of considerable generality, which also results in the linking of a coordinated tetramine by a three-carbon bridge⁵⁷. This reaction involves the synthesis of a Schiff-base macrocycle by the condensation of one equivalent of the tetramine with one equivalent of a β-diketone.

In the case of triethylenetetramine, (29), for example⁵⁸, the reaction proceeds in the following way : Trien, (29), reacts, in the absence of a metal, with two equivalents of acetylacetone to produce the potentially sexadentate ligand, (30). Under acidic conditions (30) reacts with nickel(II) acetate, presumably by acid hydrolysis of one Schiff-base linkage, followed by reaction at the



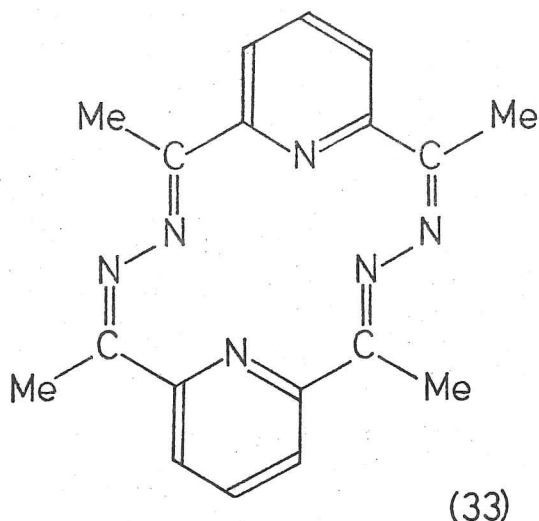
acyl group of the bound acetylacetonone, to produce a cyclic species. This species is precipitated from solution, as compound (31), by adjusting the pH to ten and adding an appropriate counterion. The ligand in (31) has undergone deprotonation at the γ carbon atom in the acetylacetonone residue so as to yield the charge delocalised structure shown. Alternatively, under acidic conditions protonation of the γ carbon atom can be effected so as to yield a complexed neutral macrocyclic ligand, (32)⁵⁹.

2,3,2-Tet^{60,61} and various tetramine compounds

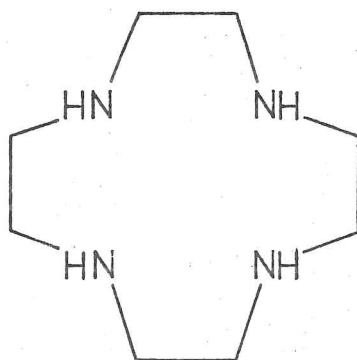
formed by generation of a single Curtis type bridge between two co-ordinated amines⁵² have been shown to undergo an analogous reaction so as to yield fourteen membered macrocyclic systems. Also, there has been a preliminary report of the formation of a neutral fifteen membered macrocyclic system, derived from 3,2,3-tet by this method⁶¹. Formation of sixteen membered systems and of the fifteen membered uninegative macrocyclic complex has been attempted, but unsuccessfully. This observation is attributed to the steric crowding associated with the adjacent six membered rings, particularly if one of those rings happens to be planar⁶¹.

Besides using nickel(II) as the template metal, copper(II) gives similar results⁵⁹. The relative acidities of the copper(II) analogues of the trien and 2,3,2-tet derived systems are 10^3 times less than the corresponding nickel(II) complexes, a fact which the authors relate to the steric strain introduced into the six membered ring by co-ordination to the slightly larger copper(II) ion. The strain is expected to be greater in the deprotonated, planar six membered ring since this ring system is more rigid than the protonated ring containing an sp^3 hybridised member which can bend out of the plane.

Hitherto the possibility of a macrocycle co-ordinating in anything other than a square-planar configuration has not been discussed. Surprisingly, even highly unsaturated macrocycles such as (33) have the potential to fold and bond across two faces of an octahedral co-ordination array.



rather than in the equatorial plane⁶². The smallest tetraza ring systems that have been observed to bond by square-planar co-ordination are thirteen membered rings⁶³. Macrocycles derived from DHPB by either the Curtis or Cummings type of reaction will be of this class. There are no known examples of twelve membered rings bonding around the equatorial plane⁶³, although the only system that has been studied to date is a fully saturated one; cyclen, (34), which can very readily fold⁶⁴.

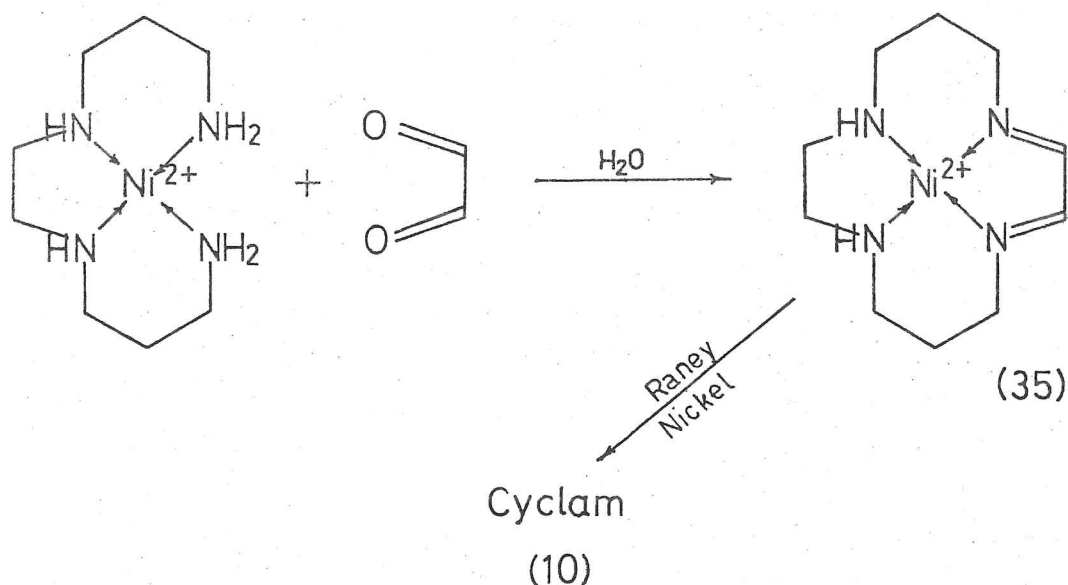


(34)

These observations were the motivation behind a crystal structure determination⁶³ of the thirteen membered

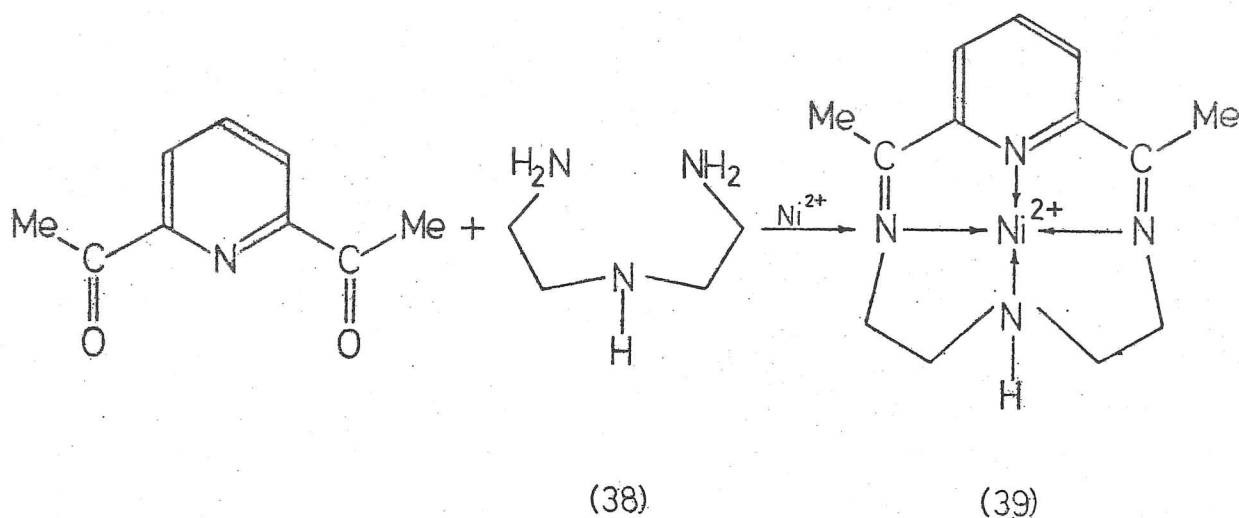
square-planar compound, (31). This was carried out in order to ascertain whether there was any reason why square-planar co-ordination should not extend to systems smaller than thirteen membered rings. The structure showed that the bond angles and distances adopted in the macrocyclic complex were very little different to those assumed when two sterically unopposed, comparable bidentate ligands co-ordinate to a metal in a trans disposition. The implication of this is that in the biologically occurring sixteen membered porphyrin ring and to a lesser extent in the fifteen membered corrin ring, the metal may in fact be straining to bridge the gap between the nitrogen donors. Accordingly, there seems no reason why unsaturated twelve membered macrocycles should not bond in a square-planar fashion. Relative to compound (31), thirteen membered macrocycles derived from DHBP should be considerably more strained due to the sp^2 bond angles in the five membered rings. The trapezoidal disposition of the nitrogen donors is already apparent in (31) which has sp^3 hybridisation throughout the five membered rings.

It was with respect to these two reactions, due to Curtis and Cummings respectively, that DHBP was studied in this work. The former involves reaction of the precursor with a monoketone, the latter with a β -diketone. There are also cyclisation reactions known which utilise the interaction of an α -diketone with a co-ordinated amine. For example, the most efficient means of preparing cyclam, (10), (20% yield) relies on the formation of (35) by a



reaction of this type⁶⁶. Such reactions generally only give poor yields because of the deactivation of the amine by the metal and because of the fact that they belong to the "2 + 2" category where the competing linear polymerisation tends to dominate the cyclisation process. A mitigating factor, upon which the success of the reaction probably lies, is the formation of the α -diimine system, since with diketones separated by more than one carbon atom cyclisation has not been recorded. Various reactions of this type were attempted with DHBP, but none were successful. Possibly in addition to the factors already discussed which tend to militate against success, is the fact that addition of an α -diketone to DHBP would lead to a twelve membered ring which even disregarding the metal would be a highly strained system.

Some amines, especially aromatic amines, for example, (36), deprotonate on co-ordination to a metal. Here the



the carbonyl groups towards attack by the terminal amines of the triamine, which due to metal template effects may be favourably positioned for attack. The reaction of DHBP with 2,6-diacetylpyridine was studied, but produced no monomeric products. It is not fully clear why this should be so, but it may be associated with the lability of the terminal amines obviating the metal template effects which are so necessary if "2 + 2" reactions are to give monomeric products. The similarity between this and the attempts to cyclise 6,6'-diformyl-2,2'-bipyridyl, (23), discussed in the previous section should be noted. In both cases it is possibly the lack of metal template orientation that leads to the polymerisation.

Those reactions that led to the formation of characterisable products and hence, or, to an understanding of the reactivity of the bipyridyl system, as well as to the ultimate objective, are the subject of the following chapters.

CHAPTER TWO

REACTIONS OF

6,6'-DIHYDRAZINO-2,2'-BIPYRIDYLNICKEL(II) PERCHLORATE

WITH ALIPHATIC CARBONYL COMPOUNDS

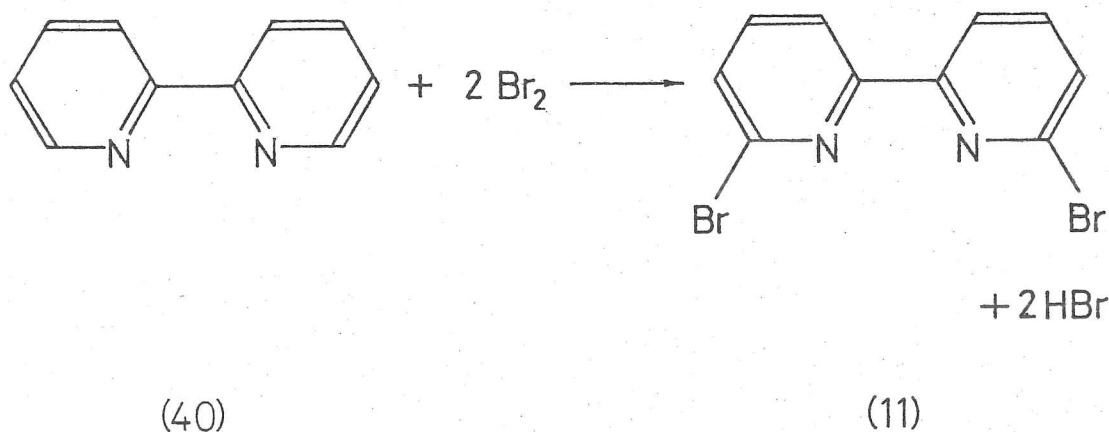
2.1 Preparation of 6,6'-Dibromo-2,2'-bipyridyl

Historically, the origins of 6,6'-dibromo-2,2'-bipyridyl (hereafter referred to as DBBP) lie with the Dutch workers den Hertog and Wibaut, who first observed that the orientation of the reaction between bromine and pyridine was temperature dependent.⁷⁰ They were able to demonstrate that the action of bromine vapour on pyridine vapour during their passage through a tube, packed with charcoal or pumice as a contact surface, at 300°, gave a mixture of 3-bromopyridine and 3,5-dibromopyridine in a combined yield of 50%; whereas at 500°, using otherwise identical reaction conditions, the bromination proceeded markedly more smoothly giving a mixture of 2-bromopyridine and 2,6-dibromopyridine in a combined yield of 80%. In both cases a molar ratio of bromine to pyridine of 1.5 : 1 was used. Presumably by altering this ratio the yield of a single desired product, at either of the temperatures, can be optimised; making this an excellent method for gaining access to certain specifically substituted pyridines.

Raising the temperature above 500° produced no further bromination products and only a decreased overall yield due to increased pyrolysis of the pyridine. Reaction at temperatures between 300° and 500° produced mixtures of all four compounds. Thus, for yields of the 2 and 2,6-disubstituted compound 500° was concluded to be the optimum temperature. Several different contact surfaces

were experimented with, but were found to have little effect on the overall yield. It appears from this that the function of the contact material is only to contain the rate of passage of the reactants down the tube, and that the packing density of the contact material determines the degree of compromise which is achieved between incomplete reaction and pyrolysis of the organic materials.

In order to prepare certain polypyridyl compounds Burstall substituted 2,2'-bipyridyl, (40), for pyridine in this reaction³⁹ and found that it was possible, although only in reduced yield, to generate 6-bromo-2,2'-bipyridyl and DBBP, (11), in an analogous fashion, according to the following reaction scheme :-



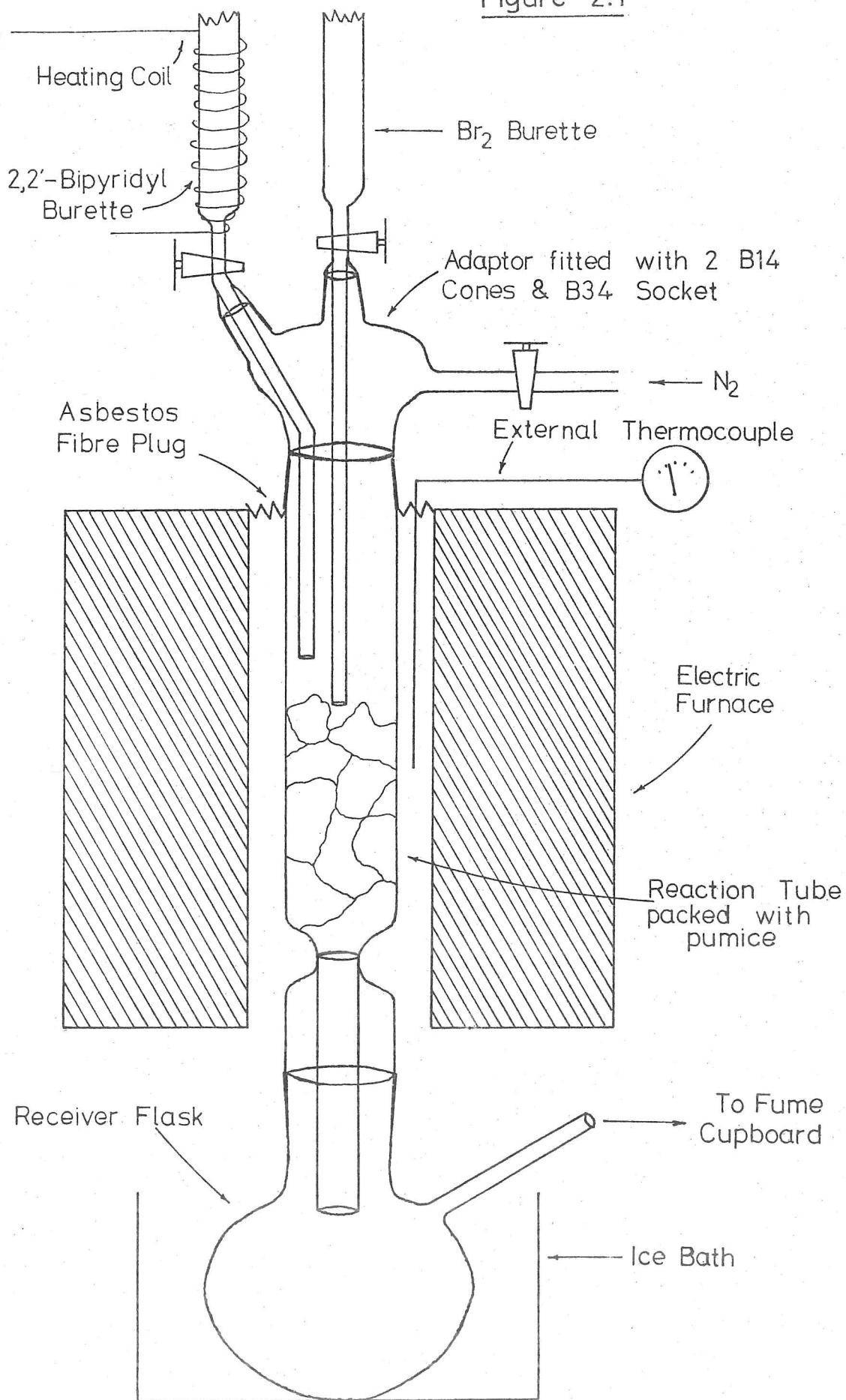
The procedure for the preparation of DBBP used in this work is basically the method used by Burstall, with slight adaptations to the apparatus and in the method of isolation of the compound. A general description of the

method and apparatus that was used will be given here, actual experimental details will be found in the experimental section of this chapter (Section 2.6).

The reaction is carried out by quantitatively dripping bromine and bipyridyl, which is a solid at room temperature and hence must be melted (m.p. $71-73^{\circ}71$), from separate burettes into an open tube. The tube is packed with pumice, and is held at 500° in a furnace; as the reaction proceeds the product condenses into a cooled receiving flask at the bottom of the tube.

The apparatus, which is shown in Figure 2.1, was constructed by T.W. Wingent Co. Ltd., and maintained by Mr. W.V. Titchener of these laboratories. The vertical pyrex reaction tube (3 cm diameter) is heated and held at 500° in an electrical furnace over a length of 60 cm, the lower 30 cm is packed with irregularly broken pumice each piece being approximately 1 cm^3 . The temperature is indicated by means of an external thermocouple. Because of the low thermal conductivity of the pumice it was found necessary to allow approximately three hours for the column to equilibrate, after the initial attainment of a recording of 500° by the external thermocouple, before commencing addition of the reactants. Failure to do this results in the formation of a viscous tarry product which rapidly blocks the tube forcing the abandonment of the preparation. Prior to the equilibration period dry nitrogen is passed through the heated tube, via the tap on the adaptor at the

Figure 2.1



Apparatus for the preparation of 6,6'-dibromo-2,2'-bipyridyl

top of the tube, until all traces of water are removed from within the system. The amount of pumice indicated, packed at the density which results from lumps of the specified volume settling under their own weight, is believed to lead to the optimum yield, based on experience gained over many runs. Bromine is introduced into the reaction tube by way of a concentric tube 5 mm in diameter which extends from the burette through an adaptor equipped with ground glass joints to a point just above the pumice level. In this way the bromine is preheated to 500° before reacting. Bipyridyl is contained just above its melting point in the electrically heated burette on the left of the diagram and enters the reaction tube by way of the short extension tube (3 mm diameter) on the burette. As the product forms during the reaction it collects in the receiving flask, which is cooled in an ice bath, at the bottom of the tube. Hydrogen bromide and excess bromine are vented to a fume cupboard by way of the side arm on the receiver flask.

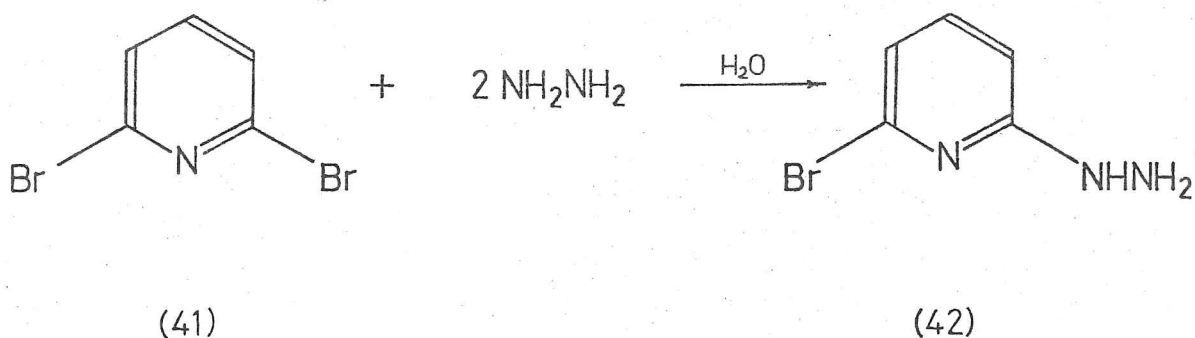
A molar ratio of bromine to bipyridyl of 2.5 : 1 was maintained at all times by monitoring the relative flow rates from the burettes. This molar ratio was chosen as it gives a 25% excess of bromine over that required for the dibromination reaction. An absolute flow rate of 30 g of bipyridyl per hour was used as this corresponds to the optimum molar flow rate of pyridine determined by den Hertog and Wibaut for the pyridine/bromine system.⁷⁰ Bringing together the desired stoichiometry and the optimised flow

rates, via the appropriate constants, shows that a flow rate of 0.5 ml per minute of bipyridyl and 0.4 ml per minute of bromine is required to be maintained from the burettes. Continued outlet adjustments are necessary because of the changing head of liquid.

Following this procedure, an average run using 50 g of bipyridyl gave 35 g of DBBP. Thus this reaction gives, in good yield, a product in which the bipyridyl moiety is activated towards further reactivity at the 6 and 6' positions.

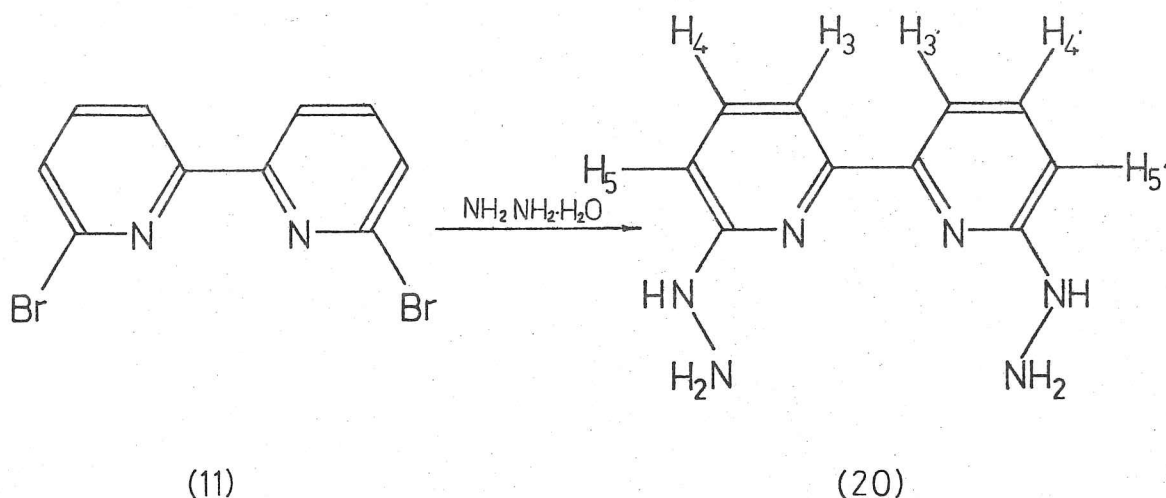
2.2 Preparation and Characterisation of 6,6'-Dihydrazino-2,2'-bipyridyl, 6,6'-Di-N-methylhydrazino-2,2'-bipyridyl and their Nickel(II) Complexes

In accordance with the reasons given in Chapter One it was proposed to prepare the quadridentate ligand 6,6'-dihydrazino-2,2'-bipyridyl from DBBP, by nucleophilic substitution of the two bromide groups with hydrazine. It was not clear initially whether this reaction would proceed to give the disubstituted product, since, for example, when 2,6-dibromopyridine, (41), (or 2,6-dichloropyridine) is treated with hydrazine hydrate, the standard way of introducing a hydrazine moiety^{48,72}, only the monosubstituted product, (42), results⁷³. However, this is probably rationalised by the fact that the introduction of the first hydrazine moiety, which behaves as a good electron donor to the system due to resonance effects⁷⁴, deactivates even



the meta position towards nucleophilic substitution to the extent where further nucleophilic substitution becomes unfavourable. In which case, in the bipyridyl system where the same resonance stabilisation effects cannot be transmitted into the second ring, the substitution of the first hydrazine should have no significant effect on the reactivity of the second site.

Indeed this was found to be the case and reaction of DBBP with refluxing hydrazine hydrate over a period of several hours gave virtually quantitative yields of the disubstituted product, (20). The structure of (20) was confirmed by elemental analysis, proton magnetic resonance, infrared and mass spectroscopy. The p.m.r. spectrum, in D_2O containing one drop of acetic acid, has a pattern of signals in the aromatic region which is analysable as repeated AX patterns by simple first order spin-spin splitting theory and which shows the equivalence of the two rings and confirms the expected substitution pattern. Thus, H_4 appears as a doublet of doublets with approximately equal coupling constants ($J_1 = 7 \text{ Hz}$, $J_2 = 8 \text{ Hz}$) and H_3 and

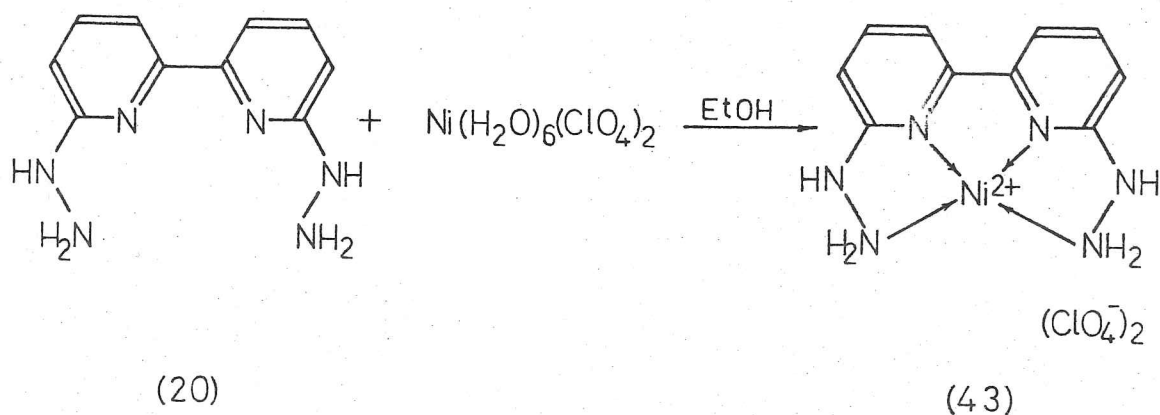


H₅ both appear as doublets with the appropriate coupling constants, split into further doublets by long range coupling ($J = 1$ Hz). Precise details of the spectrum are given in the experimental section (Section 2.6).

In contrast to some mono-hydrazines, for example 2-pyridylhydrazine⁴⁸, this dihydrazine is quite air stable over long periods of time. During its preparation, however, it was found essential to use highly purified DBBP as traces of impurity were sufficient to bring about its total decomposition.

Addition of hexaaquonickel(II) perchlorate to a refluxing solution of DHBP led to the precipitation of a 1 : 1 adduct of nickel perchlorate and the ligand. This was indicated by elemental analysis (Table 2.1). The product is orange in colour and diamagnetic, properties

which are strongly indicative of square-planar nickel(II)⁷⁵ and it was on this basis, together with the molar conductivity in water (Table 2.1) which was found to be in the normally observed range for 2 : 1 electrolytes⁷⁶, that the square-planar formulation shown for the product, (43), was made. The visible absorption spectrum for this



and other transition metal compounds mentioned in this chapter will be found described in detail in Chapter Four.

In a similar way 6,6'-di-N-methylhydrazino-2,2'-bipyridyl, (DMeHBP), was prepared by refluxing DBBP in methylhydrazine. In this case the use of a free hydrazine rather than a hydrated form resulted in the reaction being complete in a matter of minutes rather than hours. Completion of the reaction is indicated in both cases by complete dissolution of the DBBP. The p.m.r. spectrum of the product in D₂O, acidified with acetic acid, showed

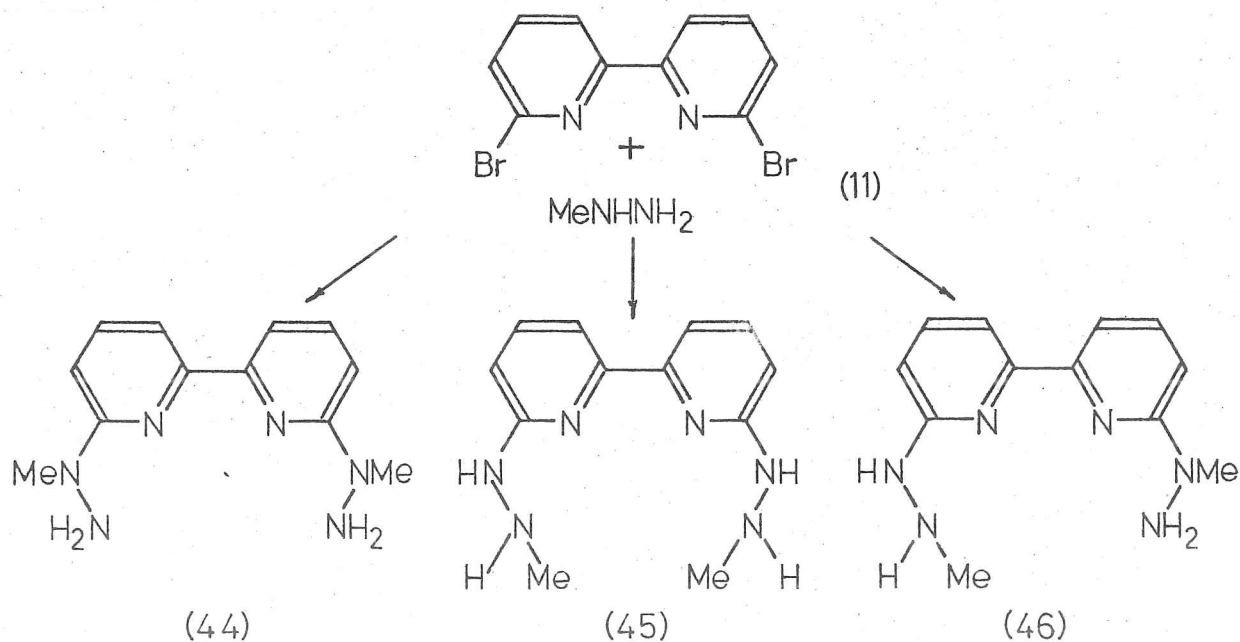
Table 2.1

Analytical and Conductivity Data

Compound	No.	<u>Found</u>			<u>Expected</u>			m.p.	Δ [*] $\text{cm}^2 \text{ ohm}^{-1} \text{ M}^{-1}$
		C	H	N (%)	C	H	N		
DHBP	20	55.2	5.60	38.9	55.5	5.59	38.9	208°	-
Ni(DHBP)(ClO ₄) ₂	43	25.7	2.67	17.5	25.4	2.55	17.7	-	222
Ni(DHBP)(H ₂ O)Cl ₂	48	33.2	3.48	24.0	34.7	3.50	24.0	-	215
DMeHBP	44	58.9	6.60	34.8	59.0	6.60	34.4	155-6°	-
Ni(DMeHBP)(ClO ₄) ₂	47	28.6	3.26	16.6	28.7	3.21	16.7	-	227
Ni(DMeHBP)(H ₂ O)Cl ₂	49	36.4	4.61	21.6	36.8	4.63	21.4	-	198
Ni(DMeHBP)ZnCl ₄	50	28.3	3.14	16.6	28.2	3.16	16.5	-	-

* 10⁻³ M in H₂O at 22°

only one resonance for the methyl protons, this occurring at $\delta 6.49\tau$ measured relative to the methyl resonance of the acetic acid taken as $\delta 7.90\tau$, which is its observed shift relative to internal TMS⁷⁷. The single methyl resonance indicated the formation of one or other of the two isomeric possibilities, (44) and (45), where both methyl groups are equivalent, but owing to the paucity of information available concerning the chemical shifts of substituted hydrazines, especially when in a protonated form, (as this most certainly is, being in acidified D_2O , most hydrazines have pK_a values between 6.3 and 8.0⁷⁸) does not distinguish between them. Owing to competing steric and electronic effects there is no a priori expected product. There is also the possibility of a third isomer forming, (46), but this would have shown two methyl resonances and is unlikely to form anyway



owing to the previously observed independence of the two reactive sites.

The problem of determining whether (44) or (45) is the product of the reaction was resolved by reacting it with various ketones and β -diketones (vide infra) the fact that bis(Schiff-base) adducts were formed in the conventional manner showed unequivocally that (44) is the correct structure.

Reaction of DMeHBP, (44), with hexaaquonickel(II) perchlorate in ethanol produced an orange diamagnetic product, (47), analogous to (43).

Although the hazards of working with perchlorates were appreciated it was only as the perchlorate salt that these metal complexes could be obtained in pure form. Reaction of DHBP and DMeHBP with hexaaquonickel(II) chloride, for example, precipitates products (48) and (49) which analyse approximately for $\text{Ni}(\text{ligand})(\text{H}_2\text{O})\text{Cl}_2$, but which could not be obtained in an analytically pure form. Further reaction of (49) with zinc chloride (vide infra) produces a pure, but highly insoluble zincate salt, (50). All perchlorate complexes were tested and found to be shock stable.

2.3 Condensation Reactions of Aldehydes and Ketones with 6,6'-Dihydrazino-2,2'-bipyridylnickel(II) Perchlorate

As outlined in the introductory chapter one of the most efficacious methods for generating macrocyclic complexes is via the reaction of acetone with an appropriately co-ordinated set of amino groups⁶. Indeed

this reaction is one of the few ways of inducing co-ordinated amine groups to cyclise, and is certainly the best documented and most generally applicable method. For this reason, initial attempts to effect cyclisation of DHBP, co-ordinated to nickel, were centred on this reaction. Nickel(II) was chosen as the template metal in accordance with the reasoning already given.

$\text{Ni}(\text{DHBP})(\text{C}_{10}\text{H}_8)_2$, (43), was refluxed in anhydrous acetone for periods of up to three days, following the general procedure of Curtis⁶, without any apparent sign of reaction. This reactant, (43), is almost totally insoluble in acetone and it was possible to recover virtually all of it unchanged simply by filtration. Since it seemed likely that the lack of reactivity was associated with this low solubility, water (5% by volume) was added on one occasion to increase the solubility. Although water is known to retard the desired reaction⁷⁹ it was thought that this may well be of secondary importance compared with the necessity of getting the reactant into solution.

The effect of adding the water was quite dramatic. The orange solid dissolved almost instantaneously to give an emerald green solution. Refluxing this solution for a further ten minutes followed by evaporation of the solvent and recrystallisation gave a quantitative yield of a green crystalline material.

The electronic absorption spectrum (see Chapter Four) of this material indicated that it was an octahedral complex of nickel(II) and the room temperature magnetic moment, $\mu_{\text{eff}} = 3.29$ B.M., was compatible with this assignment⁸⁰. The infrared spectrum showed a very broad intense band in the 3500 to 3200 cm^{-1} region which suggested that co-ordinated water molecules⁸¹ were occupying the additional two co-ordination sites. Assuming two co-ordinated water molecules, then, the elemental analysis (see Table 2.2) indicates that two molecules of acetone have been incorporated into the ligand accompanied by the loss of two molecules of water. The fact that the compound is a 2 : 1 electrolyte confirms the neutrality of the ligand system.

It was verified that the compound was monomeric by a mass spectroscopic determination of the molecular weight of the neutral derivative formed by deprotonation of the secondary amines. Such deprotonation reactions have been well studied⁸²⁻⁸⁵, and in this case it was carried out in the following way: The green crystalline material was dissolved in water and an equal volume of chloroform was added. As sodium hydroxide (2M in water) was added into the water layer a reddish brown colouration, due to the doubly deprotonated complex, began to develop in the chloroform layer upon mixing the two phases together. When the aqueous layer had been completely decolourised the chloroform layer was separated, dried over magnesium sulphate and evaporated to dryness. The

mass spectrum of the resulting oil was then recorded and showed the highest peak at the m/e value corresponding to the doubly deprotonated (and doubly deaquated) form of the monomeric material.

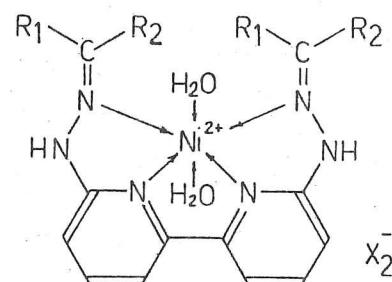
The matter of determining whether the two coordinated water molecules are arranged in a configuration cis to one another or trans to one another is discussed in Section 2.5. For the sake of clarity, all structural diagrams will show the water molecules bound trans to one another, although it will be seen later that this configuration is most improbable.

The above mentioned condensation reaction is not specific to acetone and series of analogous products were obtained by reacting various aqueous aldehydes and ketones with $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$. Thus the reaction appears to be a general one for these classes of compound.

Such a condensation reaction can lead to either of two isomeric products. A simple non-cyclic Schiff-base may be formed, where the acetone residues are bonded as N'-isopropylidene groups (Scheme One) or alternatively formation of the cyclic product (Scheme Two) may take place by the Aldol type of mechanism which has been discussed in Chapter One⁶.

Previous work with similar systems, for example with triethylenetetraminenickel(II) perchlorate, which is the closest analogy, as it preceeds the formation of a

Table 2.2
Analytical Data For
Compounds of the Type



Cmpd. No.	R ₁	R ₂	X	Derived From	C	<u>Found</u>		C	<u>Expected</u>		Δ^d cm ² ohm ⁻¹ M ⁻¹
						H	N (%)		H	N	
51	CH ₃	H	ClO ₄	Acetaldehyde	29.7	3.50	15.2	30.0	3.41	15.0	196
52	CH ₃ CH ₂	H	ClO ₄	Propionaldehyde	32.4	4.09	14.4	32.6	4.10	14.2	177
53	CH ₃ CH ₂ CH ₂	H	ClO ₄	Butyraldehyde	35.3	4.59	13.9	35.0	4.57	13.6	184 ^c
54	CH ₃	CH ₃	ClO ₄	Acetone	32.6	4.17	14.2	32.6	4.10	14.2	182
55	CH ₃ CH ₂	CH ₃	ClO ₄	Methyl Ethyl Ketone	34.7	4.57	13.6	35.0	4.57	13.6	194
56	CH ₃ CH ₂	CH ₃ CH ₂	ClO ₄	Diethyl Ketone	36.6	4.99	13.2	37.2	4.99	13.0	189
57	CH ₃ CH ₂ CH ₂	CH ₃	ClO ₄	Methyl n-Propyl Ketone	36.6	4.78	12.8	37.2	4.99	13.0	190 ^c
58 ^a	CH ₃	CH ₃	Cl	Acetone	44.7	4.45	19.6	45.1	4.73	19.6	- ^b

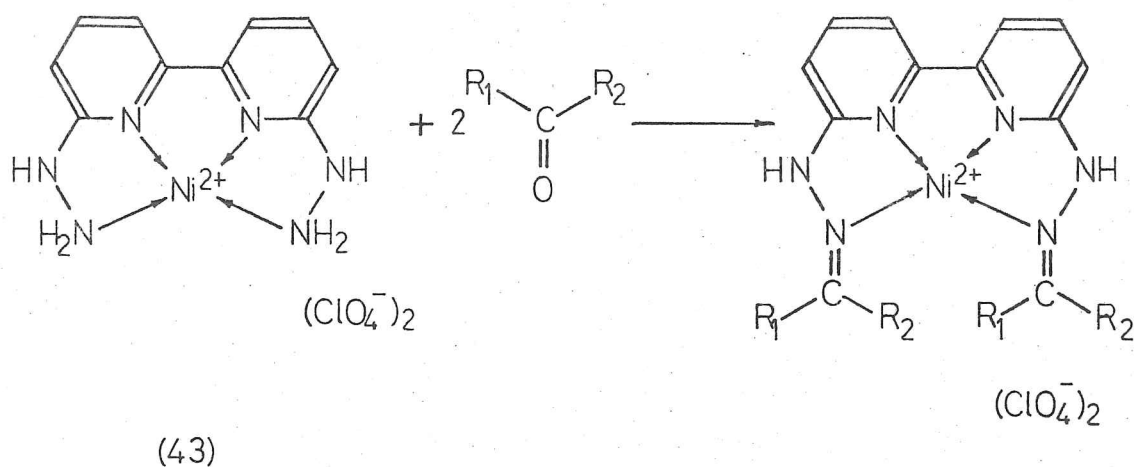
a Crystallises as the anhydrous compound

b Insufficiently soluble

c Methanol (20%) added to effect dissolution

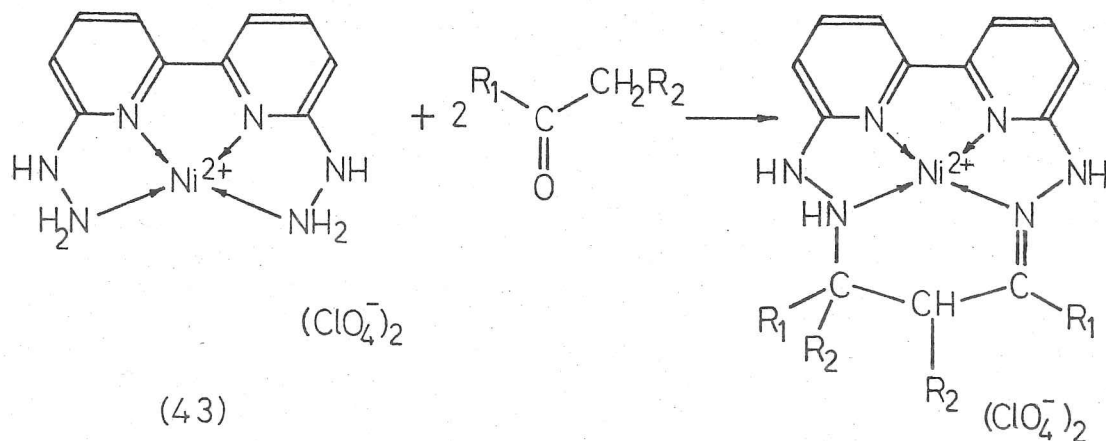
d 10⁻³ M in H₂O at 22°

Scheme One



thirteen membered macrocycle by a single bridge forming condensation,^{86,87} has shown that provided the reaction proceeds by the incorporation of two moles of acetone and

Scheme Two



loss of two moles of water, then it does so to produce the cyclic product. Thus the cyclic product is the expected product and there are no reported cases in which a nickel(II) complex having two N-isopropylidene groups disposed in a potentially cyclisable configuration

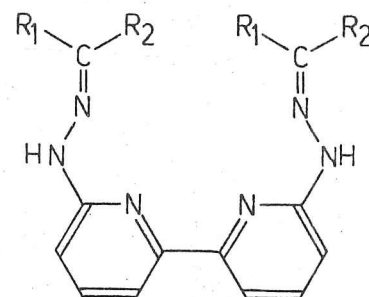
has been isolated. Curtis has synthesised a bis(N-isopropylidene) complex from tris(1,3-diaminopropane)-nickel(II) perchlorate and acetone⁸⁸, but here the N-isopropylidene groups are almost certainly disposed trans to one another, and cannot readily isomerise into a potentially cyclisable disposition. The only report which there has been on the formation of a complex with two potentially cyclisable N-isopropylidene groups was an early one by Curtis⁷⁹ which was later shown to be incorrect⁸⁹, perhaps reflecting the difficulties associated with determining between these two isomeric possibilities.

Whilst it was possible to characterise the products of this series of reactions within the bounds of the two isomeric alternatives, no definitive evidence in support of either isomer could be obtained by the application of spectroscopic or physical techniques. Chemically the complexes are totally resistant to hydrolysis of the imine moiety, even in 4M hydrochloric acid, hence blocking attempts to examine their degradation products, and proved totally inert towards hydrogenation either with sodium borohydride or catalytically over palladium or platinum, making it impossible to determine the degree of unsaturation of the molecule. Such inertness of an imine moiety is usually associated with its presence in a macrocyclic complex⁶, however, the alternative disposition as part of a linear hydrazone system would also be expected to result in greater stability than that characteristic of isolated imine groups, which readily undergo hydrolysis⁹⁰.

In order to apply magnetic resonance spectroscopy to the problem the paramagnetic nickel complexes were decomposed with sodium cyanide in a reaction which yields the free ligand and sodium tetracyanonickellate(II)²⁰. That the ligand was liberated from the metal unchanged was verified by recombining it with nickel perchlorate and regenerating the original complex. Analytical data for the series of ligands so formed is given in Table 2.3. These ligands show no tendency towards hydrolysis under acidic or basic conditions and indeed it was possible to isolate the acid salts of these compounds without difficulty.

The 100 MHz proton magnetic resonance spectrum of the ligand derived from the condensation of acetone with $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$, (62), was recorded in deuteromethanol and is shown in Fig. 2.2. The methyl/methylene region of the spectrum shows three singlet resonances together with a small multiplet, at the chemical shifts indicated. The close proximity of the signals made accurate integration impossible and assessments of relative intensity could only be made from the height of the signal. This data, as far as could be determined, was consistent with the spectrum reported by Busch⁹¹ for a metal macrocyclic complex containing the same bridging group as that which could exist in this situation, if Scheme Two is followed, where also three methyl resonances are observed. The p.m.r. spectrum recorded in deuteriochloroform, however, (Fig. 2.3), shows only two sharp

Table 2.3
Analytical Data
for Compounds of the Type



Cmpd. No.	R ₁	R ₂	Derived From	C	Found		N (%)	C	Expected		Melting Point
					H				H	N	
59	CH ₃	H	51	62.6	5.96	31.2	62.7	6.01	31.3	206-7°	
60	CH ₃ CH ₂	H	52	64.6	6.85	28.5	64.8	6.80	28.4	175-7°	
61	CH ₃ CH ₂ CH ₂	H	53	66.6	7.39	26.2	66.6	7.46	25.9	143-5°	
62	CH ₃	CH ₃	54	64.6	6.70	28.1	64.8	6.80	28.4	217-9°	
63	CH ₃ CH ₂	CH ₃	55	66.8	7.40	25.8	66.6	7.46	25.9	156-7°	
64	CH ₃ CH ₂	CH ₃ CH ₂	56	68.0	8.03	23.9	68.2	8.01	23.8	207-8°	
65	CH ₃ CH ₂ CH ₂	CH ₃	57	68.5	8.29	24.0	68.2	8.01	23.8	153-5°	
66 ^a	CH ₃ CH ₂	CH ₃	63	51.1	6.02	19.7	50.9	5.93	19.8	223-4°	
67 ^b	CH ₃	CH ₃	44	66.3	7.41	26.3	66.6	7.46	25.9	158-9°	

a 63 as its hydroperchlorate salt, formed during attempted acid hydrolysis.

b Derived directly from DMeHBP and acetone.

Figure 2.2

Compound: (62)
Solvent: CD₃OD

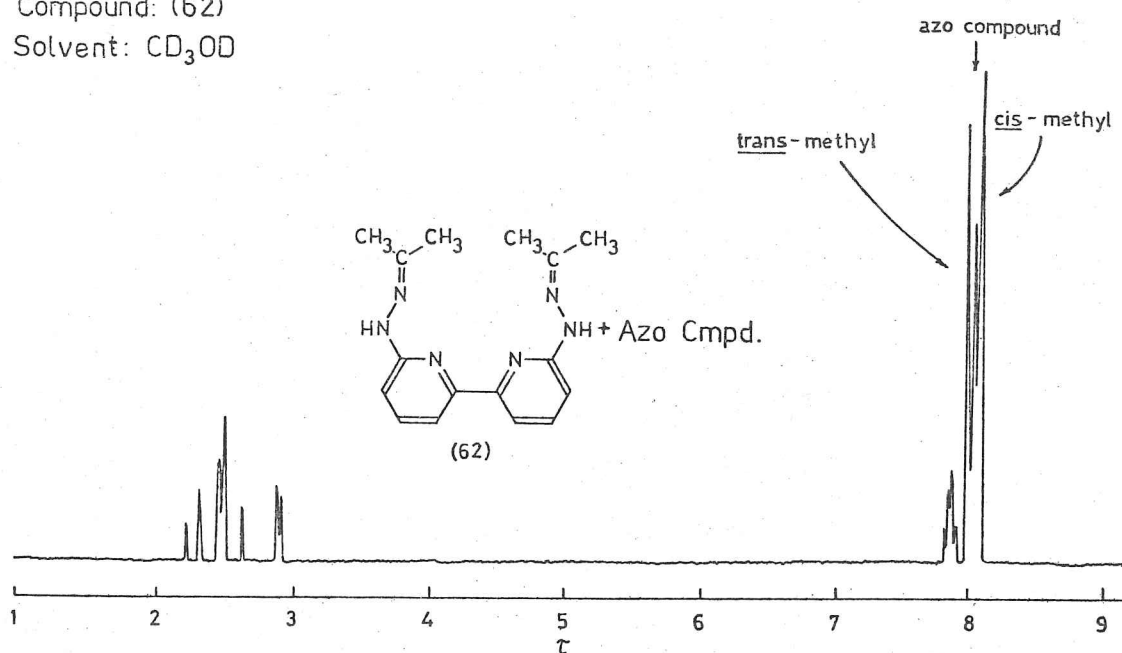


Figure 2.3

Compound: (62)
Solvent: CDCl₃

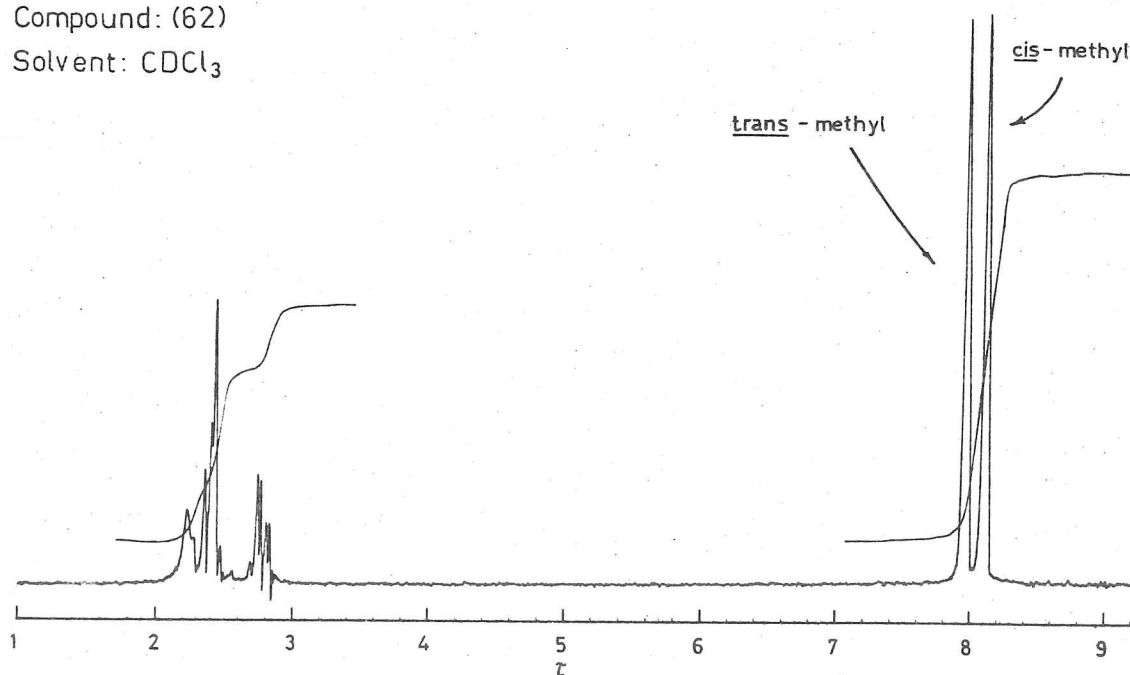


Fig. 2.2. ¹H-n.m.r. spectrum of bis(N¹-isopropylidene)-6,6'-dihydrazino-2,2'-bipyridyl, (62), in deuteromethanol.

Fig. 2.3. ¹H-n.m.r. spectrum of bis(N¹-isopropylidene)-6,6'-dihydrazino-2,2'-bipyridyl, (62), in deuteriochloroform.

singlets of equal intensity in the methyl/methylene region at 7.98 τ and 8.11 τ which is the precise pattern of signals expected for the simple non-cyclic species derived from Scheme One, where the two resonances correspond to the cis and trans environments of the methyl groups.

Definitive evidence supporting the non-cyclic formulation is afforded by the ^{13}C magnetic resonance spectrum of (62) recorded at 25.2 MHz in deuteriochloroform. Under proton decoupling two singlets occur in the methyl region of the spectrum (Fig. 2.4) at 15.4 and 24.9 p.p.m. downfield from the carbon of TMS; upon proton coupling these signals split into two quartets, $J = 128$ Hz, Fig. 2.5. This spectrum can only be rationalized in terms of the non-cyclic formulation as the macrocyclic alternative having a methylene group as a part of the bridging unit would require under the same spectral conditions a singlet splitting to a triplet upon proton coupling.

Further evidence in favour of the bis(hydrazone) type of structure is provided by the reaction of DMeHBP, (44), with acetone to yield a product in which two moles of acetone have been incorporated. The product from this reaction in contrast to the analogous product from DHBP, (62), would be expected to show either the presence or complete absence of any $\nu\text{N-H}$ bands in the infrared spectrum, depending upon which of the two possible isomers

Figure 2.4

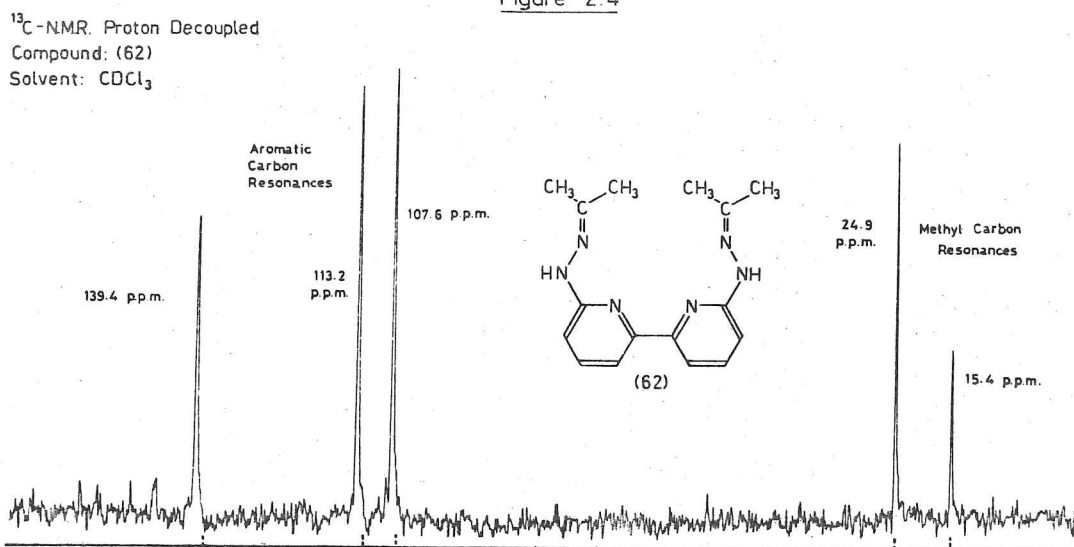


Figure 2.5

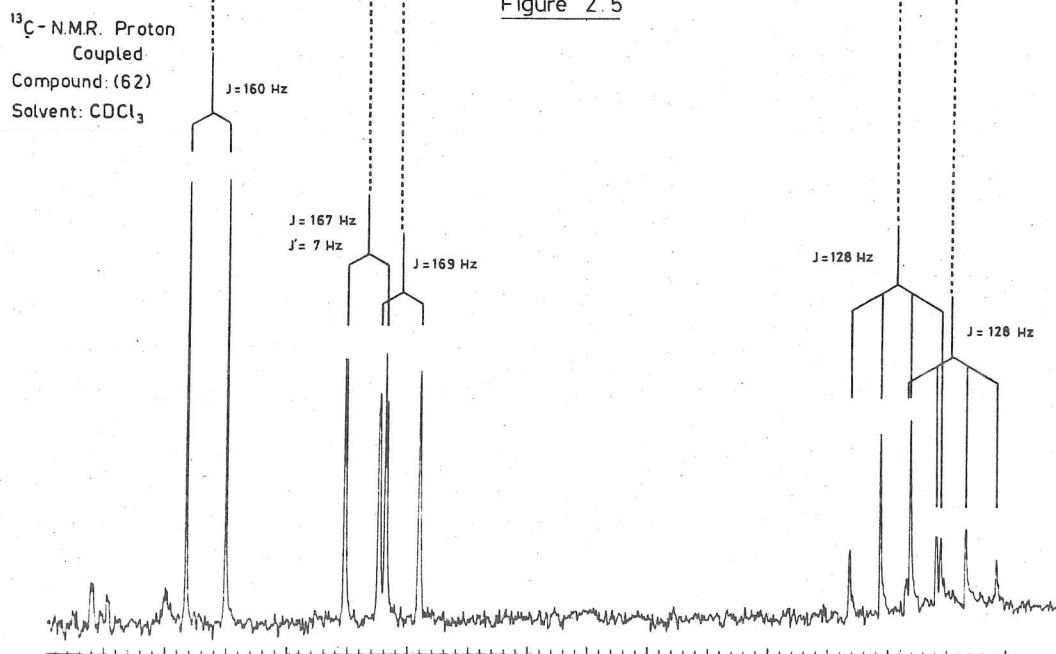
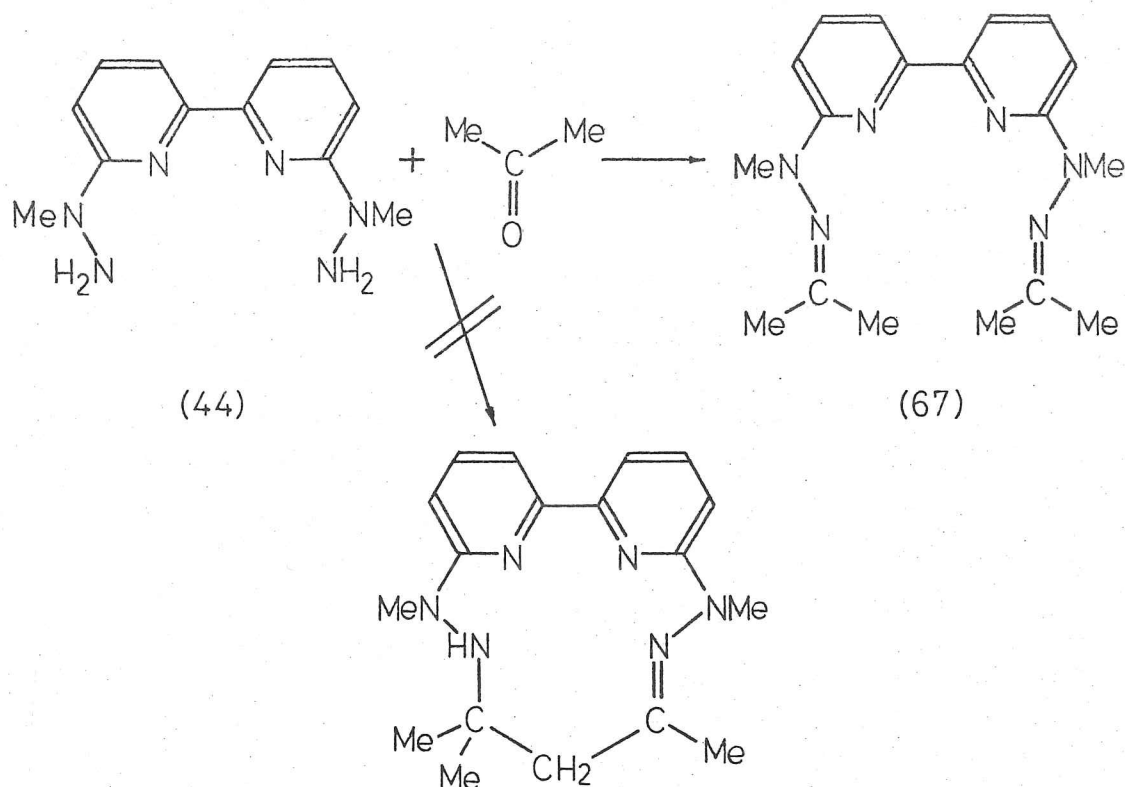


Fig. 2.4. ¹³C-n.m.r. of compound (62) under proton decoupling.

Fig. 2.5. ¹³C-n.m.r. of compound (62) proton coupled.



forms. The presence and frequency of ν N-H bands in the spectra of Curtis-type macrocycles have been well documented⁸⁹. In fact no ν N-H bands occur in the spectrum of the product, which unambiguously supports the bis(hydrazone) formulation, (67).

It was necessary to use nickel-free DMeHBP in the above reaction since its nickel complexes, (47) or (49), failed totally to react either in refluxing aqueous acetone or under more forcing conditions in a Carius tube. Addition of zinc chloride to the Carius tube in attempted reactions of (49) with acetone simply resulted in formation of the zincate salt, (50). The only factor to which this inertness can be attributed appears to be increased basicity of the terminal nitrogens,

brought about by the presence of the electron donating methyl groups, which results in the formation of stronger ligand to metal bonds, or in other words, to a more non-labile system.

Since it was later discovered that ligands (59) to (65) can also be produced in the absence of a metal, simply by reacting DHBP with the appropriate aldehyde or ketone (a fact which in itself suggests that the product is non-cyclic) the absence of a metal in the above reaction does not destroy the analogy between the two systems.

Returning to the infrared spectra of the free ligands, it is interesting to note that no $\nu\text{C}=\text{N}$ frequency, distinguishable from that in the bipyridyl residue (which occurs at c.a. 1580 cm^{-1} ⁹²) is observed. However, this observation is in accordance with the findings of Fabian⁹³ who after a comprehensive survey has concluded that the imine stretching frequency in hydrazone-type compounds is generally weak or unobservable and also with Abramvotich and Spenser⁹⁴ who were unable to find the $\nu\text{C}=\text{N}$ band in acetaldehyde phenylhydrazone.

No imino stretching frequency is seen in the infrared spectrum of the diaquated nickel perchlorate complexes owing to masking by the $\delta\text{O}-\text{H}$ absorption. However, its presence is confirmed in the water-free dichloro complex, (58), where it occurs at 1602 cm^{-1} .

Thus the reaction of $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ with aldehydes

and ketones produces the bis(hydrazone) type of compound shown in Scheme One and so represents an anomaly in the normally observed mode of reaction of these classes of compound. Attempts to produce the macrocyclic complex by extending the reaction time and by using more forcing conditions, for example, reaction in a Carius Tube at 150° for forty-eight hours in the presence of zinc chloride, have failed. This may be rationalised in the following way. The cyclisation reaction (Chapter One, Section 1.5) is a particular type of Aldol condensation which has been shown to proceed by attack of a carbanion derived from a free acetone molecule at the imino carbon of a condensed acetone residue followed by a second Schiff-base condensation⁶. In our case the lability of the terminal amines is probably high, for the reasons outlined in Chapter One, leading to ready formation of the bis(hydrazone) in a reaction which is known to be essentially irreversible, from the stability of the free ligands towards hydrolysis. Thus the free amine necessary for the second Schiff-base condensation, which is the ring closing reaction, is never available and hence the cyclisation is blocked. By implication suitable precursors for the Curtius cyclisation⁶ should be either sufficiently kinetically non-labile such that the Aldol condensation is a faster reaction than the irreversible blocking of the second amino site, or alternatively the imine forming reaction must be readily reversible under the prevailing reaction conditions.

It is not fully clear why water has such a dramatic effect on the course of the reaction since there appear to be a number of possible reasons. Firstly, there is the increase in solubility of the reactant brought about by the addition of water. Also there is the fact that Schiff-base condensations, as mentioned in Chapter One, are acid catalysed, thus addition of water, which is relatively acidic, should greatly effect the rate of reaction. This appears to be the most probable cause of the rate enhancement, but also there is the fact that $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ exists as an octahedral species in water, probably through co-ordination of two water molecules. This has been determined from its electronic spectrum in water (see Chapter Four) and it is possible that the observed rate enhancement reflects the greater lability of the octahedral species over the more inert square-planar molecule.

The failure of monoketones and aldehydes to bring about cyclisation of DHBP, following the anticipated in situ Aldol condensation, led into an examination of the reactivity of $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ with diacetone alcohol.

Diacetone alcohol is the Aldol product formed by the condensation of two moles of acetone under basic conditions⁹⁵ and was chosen for examination since by using it, instead of acetone, one is presenting the co-ordinated amine with the preformed bridge closing array, rather than relying on its assembly in situ. Previous work with diacetone alcohol and triethylenetetraminenickel(II)

has shown that it reacts to give the same product as that produced when acetone is used⁸⁶. However, as noted in Chapter One, it is not clear whether it is actually diacetone alcohol that is reacting or whether it is the acetone or mesityl oxide, which exist in equilibrium with it⁶, that are the reactive species.

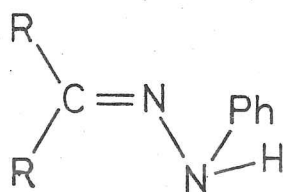
Reactions of $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ with diacetone alcohol under various conditions produced no characterisable products; only viscous tarry materials were obtained. The fact that the bis(N-isopropylidene) complex obtained from the reaction of acetone with $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ is not obtained, as neither is the bis(Schiff-base) which could form by the condensation of two moles of diacetone alcohol accompanied by retention of the tertiary alcohol, suggests that diacetone alcohol is possibly capable of reaction with the system at both the acyl and tertiary alcohol positions. The nature of the products obtained suggests that it does so in an intermolecular fashion to produce polymeric materials. This provides an illustration of the problems, referred to in Chapter One, inherent with such "2 + 2" approaches to cyclisation.

$\text{Ni}(\text{DMeHBP})(\text{ClO}_4)_2$ failed totally to react with diacetone alcohol again displaying its characteristic inertness.

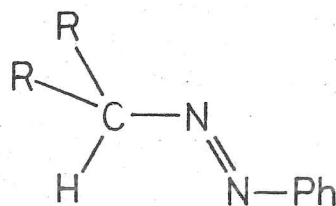
2.4 Configuration and Nature of the Free Ligand

The apparent solvent dependence of the p.m.r. spectrum of the hydrazone compound derived from acetone and DHBP, (62), mentioned in Section 2.3, is now studied in detail using data from the series of metal-free hydrazones, (59) to (65).

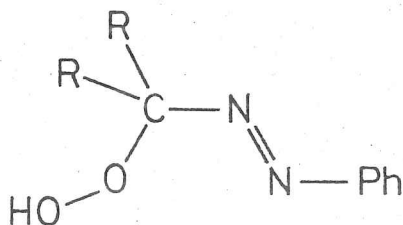
The instability of phenylhydrazones in neutral solutions is well known⁹⁶. Solutions of these compounds exhibit a spectral band at 405 to 413 nm ($\epsilon = 110$ to 135), characteristic of azo compounds which have a $n \rightarrow \pi^*$ transition usually seen at this wavelength⁹⁷. In view of this, early reports suggested that there was a simple tautomeric equilibrium between the phenylhydrazone, (68), and its corresponding phenylazoalkane^{98,99}, (69),



(68)



(69)



(70)

and that both forms could be isolated. Later work^{97,100}, however, refuted this and presented extensive spectroscopic and chemical evidence showing that this spectral change

only occurred in aerobic solutions of the phenylhydrazone and that the equilibrium product is a phenylazoalkane-hydroperoxide, (70). Quantitative oxygenation experiments showed that the formation of the bright yellow solution was accompanied by absorption of one mole of oxygen, and were used in support of the hydroperoxide formulation. More recently, p.m.r. work has been carried out which is in thorough agreement with the hydroperoxide formulation¹⁰¹.

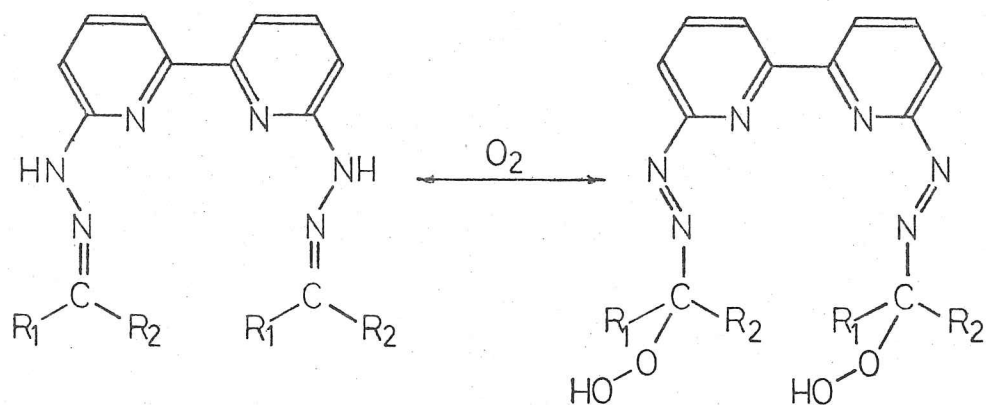
The above mentioned references do not make it clear whether this oxygen insertion is reversible or not. The studies carried out later in this work, however, with the co-ordinated ligand (Section 2.5) make it quite clear that the reaction is indeed reversible and hence defend the use of the terms "equilibrium product" and "equilibrium mixture".

This yellow colouration was observed in solutions of the bipyridyl hydrazones, (59) to (65), and their visible spectra all show a distinct shoulder at c.a. 410 nm on the much stronger $\pi \longrightarrow \pi^*$ absorption band ($\epsilon = 1.5 \times 10^4$) which occurs at c.a. 350 nm.

This observation led to an explanation for the "anomalous" third methyl peak which occurs in the p.m.r. spectrum of (62) when recorded in deuteromethanol. The equilibrium as it applies to the compounds under discussion is seen in Scheme Three.

The hydrazone, (62), (Scheme Three, $R_1 = R_2 = \text{Me}$)

Scheme Three

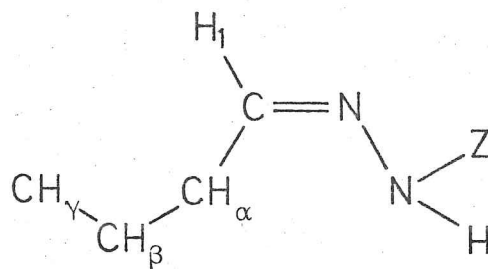


is expected to show two methyl resonances due to the cis and trans environments of the methyl groups. Loss of the imine bond in producing the azo-hydroperoxide, however, will bring about equivalence of the two methyl groups and hence a third resonance should be seen in the spectrum of the equilibrium mixture, due to this component. Work by Karabatsos and Taller¹⁰² on the proton magnetic resonance spectrum of acetonephenylhydrazone in d₆ benzene supports this suggestion as it has shown that the two methyl resonances at 8.16τ and 8.72τ have added to them a third resonance at 8.53τ upon introduction of oxygen to the system. The fact that no third signal appears in the deuteriochloroform solution spectrum of (62) is possibly due to deposition of the azo-hydroperoxide from solution, which appears to occur in this solvent. Characteristically solutions became cloudy and deposited a fine brown material from which no pure compound could be isolated.

Further evidence for the existence of the azo-hydroperoxide was gained from the mass spectrum of (62) where a metastable peak, usually more prominent in aged samples of the compound, at $m/e = 267$ corresponding to loss of oxygen from the azo-hydroperoxide of (62), $m/e = 328$, to reform (62), $m/e = 296$, occurs.

Complete proton magnetic resonance data for the series of hydrazones is given in Table 2.5 and representative spectra can be seen in Figures 2.2, 2.3, 2.6, 2.8 and 2.10. Two sets of signals are seen for each alkyl group bonded to the imino group corresponding to residence in either the cis or the trans environment relative to the secondary amine. If the problem of determining which signal corresponds to which disposition can be resolved, then it is possible in the case of unsymmetrical compounds to work out the concentration of a given substituent in a given position, from the relative intensity of the signals.

Karabatsos and Taller¹⁰²⁻¹⁰⁴, have studied this problem and by making the assumption that the more intense of the two signals in an unsymmetrical compound is associated with the sterically less hindered configuration (i.e. with the smaller group cis to the secondary amine) have compiled the following table (Table 2.4) applicable to such systems. The data relates to structure (71).



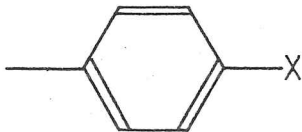
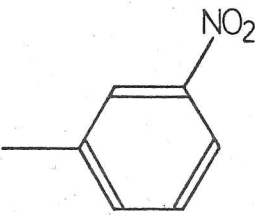
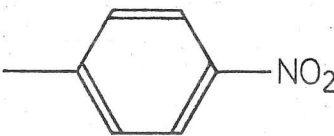
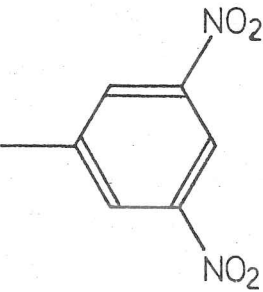
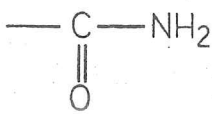
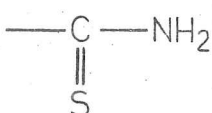
(71)

A "+" in the table indicates that when the designated hydrogen is cis to the secondary amine it resonates at higher field than it would were it trans. Conversely for a "-" entry.

The reason for these observed variations in the direction of the chemical shift, which are dependent upon the nature of Z, is thought to lie with the strength of the hydrogen bonding interaction between the secondary amino proton and the solvent. Thus the nature of Z effects the acidity of this proton and hence the degree of interaction with the solvent. The existence of such a hydrogen bond brings the cis substituent into closer association with the solvent than the trans substituent and thus may well account for their observed magnetic non-equivalence.

The p.m.r. spectra of the bipyridyl hydrazones, (59) to (65), see especially Fig. 2.6, show, upon making the same assumption about the relative intensity of the signals, that protons on a carbon α to the double bond in a cis position resonate at higher field than

Table 2.4

Z	H ₁	H _α	H _β	H _γ
H	-	+	+	*
Me	-	+	+	*
				
X = H, Cl, Me	-	+	+	*
	-	+	-	*
	-	+	no observed shift	
	-	+	-	-
	-	+	no observed shift	
	-	+	-	*

* Not determined

Table 2.5

Proton Magnetic Resonance Data

Cmpd. No.	Solvent	Hydroxylic + Amino	Aromatic + Imino Methine	Amino Methine	Methyl + Methylene
59	CDCl ₃	1.3-2.0τ, br m, (2H)	2.1-3.0τ, m, (7H)	3.37τ, q, J=5.5 Hz (1H)	8.09τ, d, J=6.0 Hz, <u>trans</u> -methyl } (3H) 8.12τ, d, J=6.0 Hz, <u>cis</u> -methyl } 8.15τ, d, J=5.5 Hz, azo compd., (3H)
60	CDCl ₃	1.3-2.2τ, br m, (2H)	2.25-3.0τ, m, (7.6H)	3.48τ, t, J=5.0 Hz (0.4H)	7.67τ, d of q, J ₁ =7.5 Hz J ₂ =5.0 Hz (4H) 8.80τ, t, J=7.5 Hz <u>cis</u> -methyl } (6H) 8.88τ, t, J=7.5 Hz <u>trans</u> -methyl }
61	CDCl ₃	1.3-2.2τ, br m, (2H)	2.25-3.2τ, m, (7.6H)	3.48τ, t, J=5.0 Hz (0.4H)	7.78τ, q, J=6.5 Hz (4H) 8.48τ, sextet J=7.0 Hz (4H) 9.00τ, t, J=11.5 Hz <u>cis</u> -methyl } (6H) 9.06τ, t, J=7.5 Hz <u>trans</u> -methyl }
62	CDCl ₃	2.2-2.3τ, s, (2H)	2.3-2.9τ, m, (6H)		7.98τ, s, } (12H) <u>trans</u> -methyl 8.11τ, s, } <u>cis</u> -methyl
	CD ₃ OD	---	2.2-3.0τ, m, (6H)		7.86τ, m, } (12H) 7.97τ, s, } 8.01τ, s, } 8.04τ, s, }

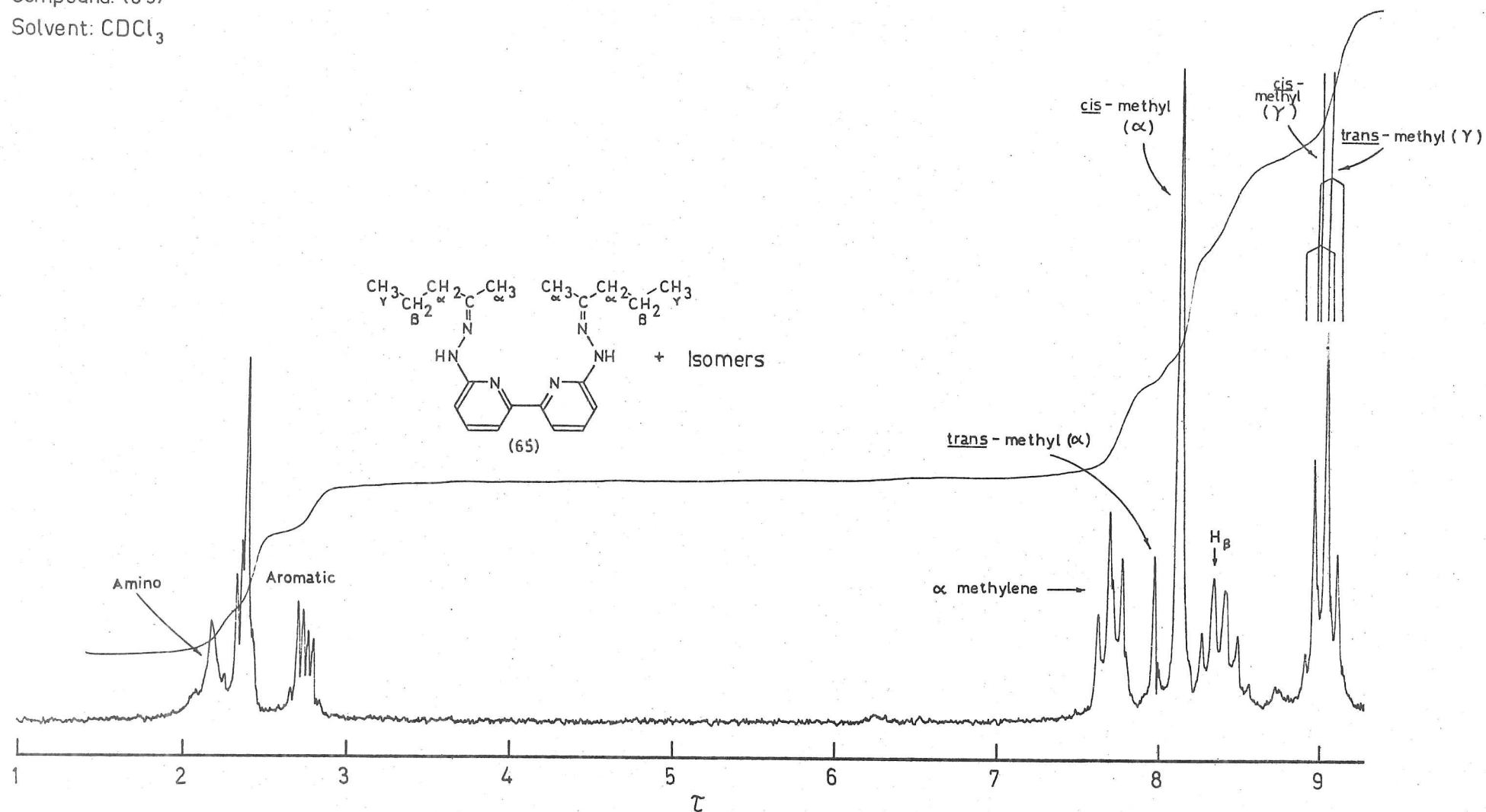
Table 2.5 (continued)

Cmpd. No.	Solvent	Hydroxylic + Amino	Aromatic + Imino Methine	Amino Methine	Methyl + Methylene
63	CDCl ₃	2.1 τ, s, (2H)	2.25-2.9 τ, m, (6H)		7.67 τ, q, J=7.5 Hz (4H) 7.98 τ, s, <u>trans</u> -methyl } (6H) 8.14 τ, s, <u>cis</u> -methyl } 8.79 τ, t, J=7.5 Hz <u>cis</u> -methyl } (6H) 8.88 τ, t, J=7.5 Hz <u>trans</u> -methyl }
64	CDCl ₃	2.06 τ, s, (2H)	2.25-2.9 τ, m, (6H)		7.67 τ, q, J=7.5 Hz, (4H), <u>trans</u> -methylene 7.69 τ, q, J=7.5 Hz, (4H), <u>cis</u> -methylene 8.86 τ, t, J=7.5 Hz, (12H)
65	CDCl ₃	2.19 τ, s, (2H)	2.25-2.9 τ, m, (6H)		7.70 τ, t, J=7.5 Hz <u>trans</u> -methylene } (4H) 7.71 τ, t, J=7.5 Hz <u>cis</u> -methylene } 7.98 τ, s, <u>trans</u> -methyl } (6H) 8.13 τ, s, <u>cis</u> -methyl } 8.39 τ, sextet, J=7.5 Hz, (4H) 8.99 τ, t, J=7.5 Hz <u>cis</u> -methyl } (6H) 9.04 τ, t, J=7.5 Hz <u>trans</u> -methyl }

Figure 2.6

Compound: (65)

Solvent: CDCl_3



^1H -n.m.r. spectrum of compound (65) recorded in deuteriochloroform

when in the trans configuration ("+" entry in Table 2.4) and that protons on carbons β and γ resonate at lower fields than when trans ("-" entry in Table 2.4). Thus the bipyridyl hydrazones show the same behaviour as compounds in Table 2.4 having Z groups that are strongly electron withdrawing. This is reasonable since the pyridine ring is often likened in its reactivity to a benzene ring carrying an electron withdrawing group¹⁰⁵.

In accordance with this, the concentration of substituents in a given position were determined from the integration values of the appropriate signals in the spectra of (59) to (65) and these values are tabulated (Table 2.6). It is not possible to make a determination of the amounts of syn isomer and of anti isomer present (where the syn isomer is that with the smaller of the two substituents cis to the secondary amine) because of the presence of an unknown concentration of the mixed syn-anti-isomer.

Evidence of the azo-hydroperoxide species is readily seen in the spectra of the aldehyde derivatives where the imino methine proton provides a convenient probe with which to monitor the tautomerism. This proton is normally resonant at 1.9 τ to 2.2 τ ¹⁰⁶ and in the systems under discussion is overlapped by the aromatic protons. However, formation of the azo-hydroperoxide brings the methine proton into an environment where, in the absence of the hydroperoxide, it is known to

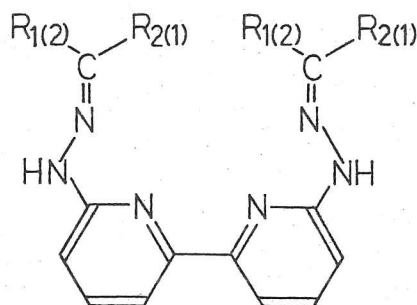
resonate at approximately $4.3\tau^{107}$. Accepting a downfield shift of approximately 1 p.p.m. for the presence of a hydroperoxide group; the presence of signals at c.a. 3.5τ exhibiting the appropriate coupling pattern must then arise from this methine proton and indicate the presence of the appropriate azo-hydroperoxide species. The intensity of this signal can be used to determine the percentage of the hydrazone which is present in the azo form. These results are also tabulated (Table 2.6) and correspond to the equilibrium mixture obtained after allowing an approximately 0.1 M solution to stand in an open 5 mm p.m.r. tube for ten minutes after preparation. In the case of the ketone derived compounds such determinations must be made on the basis of signals which appear in the methyl/methylene region of the spectrum and it is only in the case of the acetone derived compound that this region of the spectrum is sufficiently uncongested to make meaningful measurements of the small amounts that were present.

2.5 Configuration and Nature of the Co-ordinated Ligand

Summarising the conclusions of Section 2.4; we now know that an aerobic solution of an unsymmetrical ligand (i.e. one derived from an unsymmetrical carbonyl compound) of the type under discussion contains five distinct molecular species. There are the mono(azo-hydroperoxide) and bis(azo-hydroperoxide) forms of the ligand and in the hydrazone form there are configurational

Table 2.6

Isomeric Distribution Data for Compounds of the Type :



Cmpd. No.	R ₁ (2)	R ₂ (1)	% of Larger Group in <u>trans</u> Position (of material which is hydrazone)	% of Azo- hydroperoxide
(All values \pm 5%)				
59	CH ₃	H	78%	50%
60	CH ₃ CH ₂	H	63%	20%
61	CH ₃ CH ₂ CH ₂	H	60%	20%
62	CH ₃	CH ₃	-	15%
63	CH ₃ CH ₂	CH ₃	85%	< 15%
64	CH ₃ CH ₂	CH ₃ CH ₂	-	< 15%
65	CH ₃ CH ₂ CH ₂	CH ₃	83%	< 15%

isomers where a particular substituent is cis to the secondary amine on both arms of the ligand, or cis on one arm and trans on the other, or trans on both. For a symmetrical ligand there is only a single hydrazone species.

The question of which of these forms of the ligand co-ordinate to a metal and how they arrange themselves around a metal upon complexation is now considered.

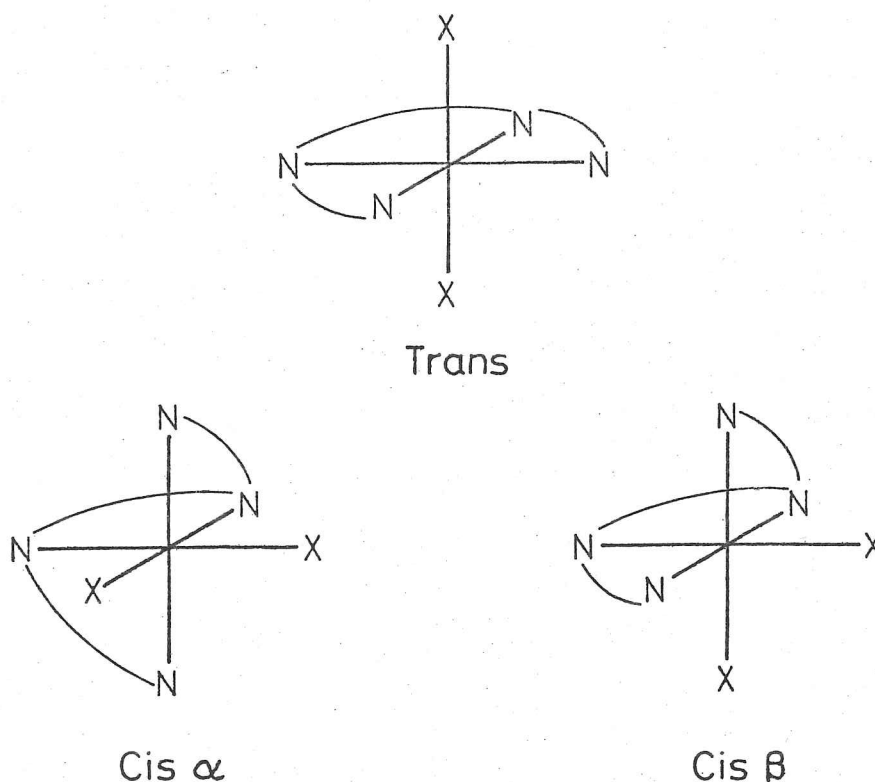
One can envisage three modes of co-ordination that may be adopted by such a ligand system; they are the trans bonding arrangement, the cis α arrangement and the cis β arrangement¹⁰⁸. These three dispositions are shown diagrammatically in Fig. 2.7.

The trans complex shows extreme steric hindrance at the point where the two arms of the ligand come together and given a six co-ordinate environment it seems very unlikely that such a configuration would be adopted. Indeed there is no evidence to suggest that it ever is (c.f. Chapter Six where attempts which have been made to put the ligand into a square-planar environment around palladium(II) are described).

Of the other two forms the cis β is certainly the more sterically hindered. This steric hindrance would be minimised in unsymmetrical compounds by disposing the sterically more bulky group cis to the secondary amine rather than trans; the position which it predominantly occupies in the free ligand. The cis α form is the least sterically hindered of the three forms.

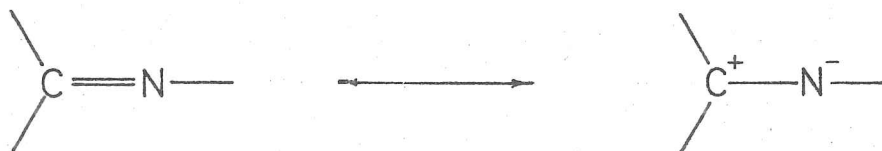
Since rotation about the imino linkage occurs considerably more easily than rotation about a doubly

Figure 2.7



Co-ordination modes for a linear quadridentate ligand

bonded carbon (a tendency which may be accounted for by the greater electronegativity of nitrogen compared to that of carbon causing a lowering of the double bond character of the imine linkage by polarisation¹⁰⁹) it is possible for the alkyl groups on the imine linkage to arrange themselves



in such a way as to minimise steric repulsions. Thus, were an unsymmetrical ligand to co-ordinate in the cis β configuration, for example, one would expect to observe a rearrangement that would move the more bulky substituent away from its free ligand trans position into a position cis to the secondary amine. Alternatively, should the unsymmetrical ligand co-ordinate so as to give the cis α complex, inspection of Fig. 2.7 shows that there should be no significant difference between the concentration of a given substituent in a given position in the complex and that in the free ligand.

Thus, by comparing the manner in which the more bulky substituent disposes itself in a metal complex, with that in the free ligand, using the p.m.r. technique already described, it should be possible to determine whether the cis α or cis β geometry is being adopted. As the series of nickel(II) complexes already described, (51) to (57), are paramagnetic the analogous series of zinc(II) complexes was prepared for this purpose.

It was also of interest to know whether co-ordination of the ligand occurs via the hydrazone form of the ligand or via its azo-hydroperoxide. In the event that only the hydrazone co-ordinates then it would also be possible to prove whether or not the oxygen insertion reaction is reversible by observing the yield of the reaction and relating this to the known concentration of hydrazone present.

The complexes were prepared by adding a solution of

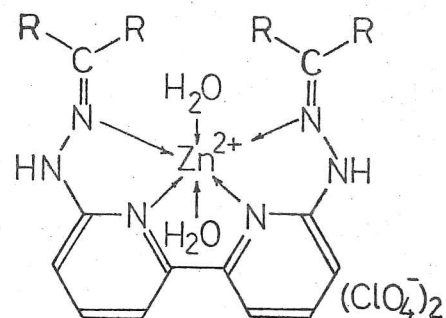
hexaaquozinc(II) perchlorate to a solution of the ligand (for experimental details see Section 2.6). As it was essential to provide the metal with the opportunity of combining with either form of the ligand if this last mentioned consideration was to be investigated, a solution of the ligand was exposed to the atmosphere in refluxing methanol for ten minutes before adding the stoichiometric amount of hexaaquozinc(II) perchlorate. In all cases virtually quantitative yields were obtained. This fact indicates one of the following possibilities; that both forms of the ligand co-ordinate, that there is an equilibrium which moves to favour the hydrazone, or that all of the hydrazone is converted to azo-hydroperoxide either by a shift in the position of the equilibrium, if one exists, or by irreversible reaction with oxygen.


The analysis of the zinc complexes (Table 2.7) shows that they are all $\text{Zn}(\text{ligand})(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ adducts. Conductivity measurements in methanol confirm them as 2 : 1 electrolytes⁷⁶.

The p.m.r. spectra of (72) to (78) were recorded in deuteromethanol and the data is tabulated in Table 2.8. The most immediate observation is the total absence of any co-ordinated azo-hydroperoxide. This is readily seen, for example, on comparison of the spectrum of the free acetaldehyde derived ligand (Fig. 2.8) where the quartet at 3.37 τ indicates a 50% abundance of the azo-hydroperoxide, with the spectrum of its zinc complex (Fig. 2.9) where this quartet is totally

Table 2.7

Analytical Data for
Compounds of the Type:



Cmpd. No.	Derived from	C	Found		N (%)	C	Expected		N	 cm ² ohm ⁻¹ M ⁻¹
			H				H			
72	59	29.8	3.46	14.6	29.6	3.55	14.8	183		
73	60	32.2	3.96	13.9	32.2	4.05	14.1	182		
74	61	34.6	4.37	13.6	34.6	4.52	13.5	177		
75	62	32.4	4.05	14.2	32.2	4.05	14.1	178		
76	63	34.4	4.42	13.3	34.6	4.52	13.5	177		
77	64	36.9	4.98	12.6	36.8	4.94	12.9	184		
78	65	37.0	4.93	12.6	36.8	4.94	12.9	183		
79	DHBP	23.5	2.90	16.3	23.3	3.12	16.3	187		

^a 10^{-3}M Solutions in methanol at 22° .

absent. This observation is perhaps an indication that oxygen is behaving as an electrophilic species rather than a nucleophilic species in the addition reaction, since co-ordination of the ligand drains electron density away from the imino carbon atoms, rendering them slightly electro-positive in character. Thus, co-ordination creates a situation where the ligand presents a less favourable site for electrophilic attack than that existing in the free

Table 2.8

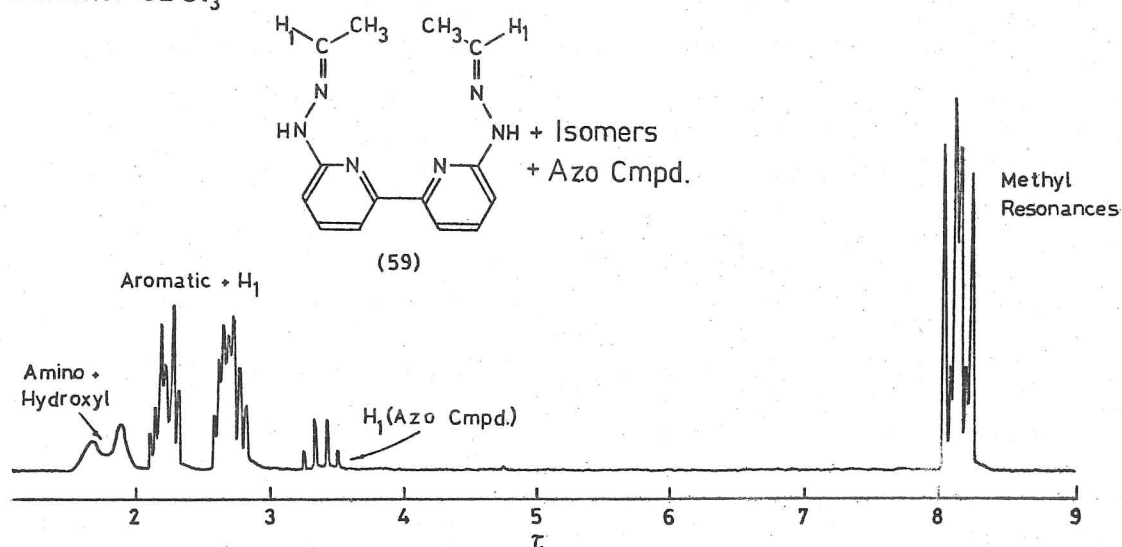
Proton Magnetic Resonance Data for $\text{Zn}(\text{ligand})(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ Compounds

Hydrazone derived from	Aromatic + Imino Methine	Methylene	Methyl
Acetaldehyde (72)	1.8 - 3.1 τ , m, (8H)		7.74 τ , 8-line multiplet, (6H)
Propionaldehyde (73)	1.8 - 3.1 τ , m, (8H)	7.41 τ , m, (4H)	8.68 τ , t, J=7.5Hz } (6H) <u>cis</u> -methyl 8.73 τ , t, J=7.5Hz } <u>trans</u> -methyl
Butyraldehyde (74)	1.8 - 3.1 τ , m, (8H)	7.47 τ , m, (4H) 8.26 τ , m, (4H)	8.91 τ , t, J=7.5Hz } (6H) <u>cis</u> -methyl 8.94 τ , t, J=7.5Hz } <u>trans</u> -methyl
Acetone (75)	1.8 - 2.3 τ , m, (4H) 2.8 τ , d, J=8.0Hz (2H)		7.65 τ , s, } (12H) <u>trans</u> -methyl 7.78 τ , s, } <u>cis</u> -methyl
Methyl Ethyl Ketone (76)	1.8 - 2.3 τ , m, (4H) 2.81 τ , d of d (2H) J ₁ =8.0Hz, J ₂ =1.0Hz	7.39 τ , q, J=8.0Hz (4H)	7.68 τ , s, } (6H) <u>trans</u> -methyl 7.80 τ , s, } <u>cis</u> -methyl 8.78 τ , t, J=8.0Hz, (6H)
Diethyl Ketone (77)	1.8 - 2.3 τ , m, (4H) 2.72 τ , d of d, (2H) J ₁ =8.0Hz, J ₂ =1.0Hz	7.30 τ , q, J=8.0Hz } (8H) 7.34 τ , q, J=8.0Hz }	8.72 τ , t, J=8.0Hz } (12H) <u>cis</u> -methyl 8.73 τ , t, J=8.0Hz } <u>trans</u> -methyl
Methyl n-Propyl Ketone (78)	1.8 - 2.3 τ , m, (4H) 2.76 τ , d of d, (2H) J ₁ =8.0Hz, J ₂ =1.0Hz	7.35 τ , t, J=8.0Hz } (4H) 7.39 τ , t, J=8.0Hz } 8.22 τ , sextet J=8.0Hz, (4H)	7.61 τ , s, } (6H) <u>trans</u> -methyl 7.77 τ , s, } <u>cis</u> -methyl 8.89 τ , t, J=8.0Hz } (6H) <u>cis</u> -methyl 8.92 τ , t, J=8.0Hz } <u>trans</u> -methyl

Figure 2.8

Compound: (59)

Solvent: CDCl_3

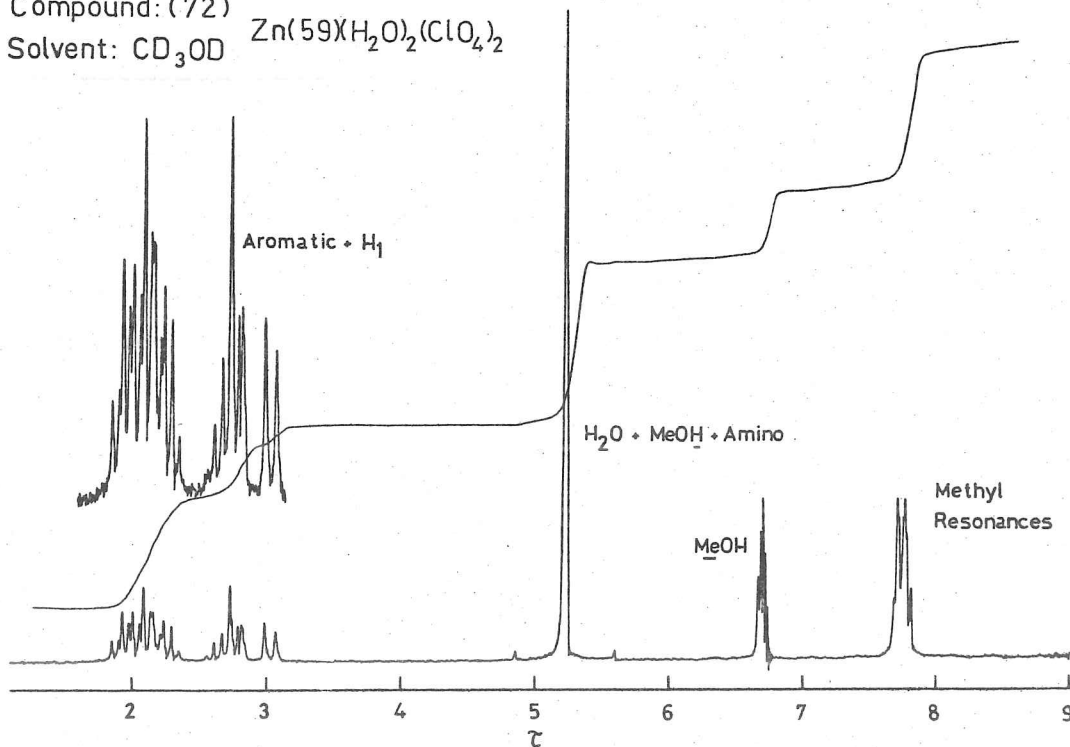


^1H -n.m.r. spectrum of compound (59) in oxygenated CDCl_3

Figure 2.9

Compound: (72)

Solvent: CD_3OD $\text{Zn}(59)(\text{H}_2\text{O})_2(\text{ClO}_4)_2$



^1H -n.m.r. spectrum of $\text{Zn}(59)(\text{H}_2\text{O})_2(\text{ClO}_4)_2$, (72), in CD_3OD

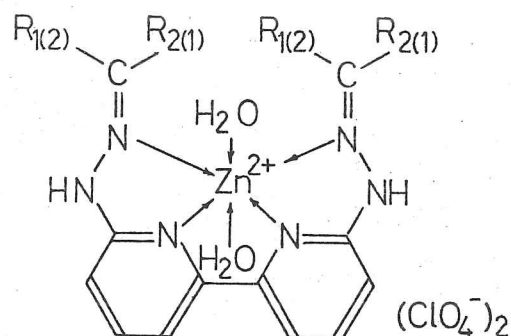
ligand and the reduced reactivity towards oxygen which is observed, suggests that it is in this electrophilic capacity that oxygen attacks. In a similar way electrophilic attack is also suggested by the fact that oxygen addition into the protonated metal-free ligands is not observed. The p.m.r. spectra of the free hydrazones dissolved in deuterated acetic acid show no indication of the presence of the azo-hydroperoxide species. Furthermore, it should be noted that conversion of the co-ordinated hydrazone to a co-ordinated azo-hydroperoxide would necessarily lengthen an already long terminal nitrogen to metal bond by increasing the relevant bond angle at the secondary amino position.

The total absence of any azo-hydroperoxide in the zinc complexes, in conjunction with the quantitative yields, shows that the oxygen addition reaction must be reversible.

Provided that there is no change in the orientation of the chemical shifts for the protons on cis or trans alkyl groups from that previously determined for the free ligand (and the data obtained is compatible with this) there is no marked change in the configuration of any of the ligands, with the exception of that derived from acetaldehyde, upon co-ordination. The disposition of the various alkyl groups as determined from the spectra is given in Table 2.9 and is essentially the same as that determined for the free ligand. Only in the case of the butyraldehyde derived complex, (74), is there a slight shift which is outside the bounds of experimental error (contrast Fig. 2.10 with Fig. 2.11 noting particularly the intensity reversal in

Table 2.9

Isomeric Distribution Data for Compounds of the Type:



Cmpd. No.	$R_1(2)$	$R_2(1)$	% of Larger Group <u>trans</u> to the Secondary Amine. (% for free ligand given in parentheses). (All values \pm 5%)	
72	CH ₃	H	<u>cis</u> α and <u>cis</u> β isomers present, no determination possible.	
73	CH ₃ CH ₂	H	60%	(63%)
74	CH ₃ CH ₂ CH ₂	H	45%	(60%)
75	CH ₃	CH ₃	-	-
76	CH ₃ CH ₂	CH ₃	76%	(85%)
77	CH ₃ CH ₂	CH ₃ CH ₂	-	-
78	CH ₃ CH ₂ CH ₂	CH ₃	85%	(83%)

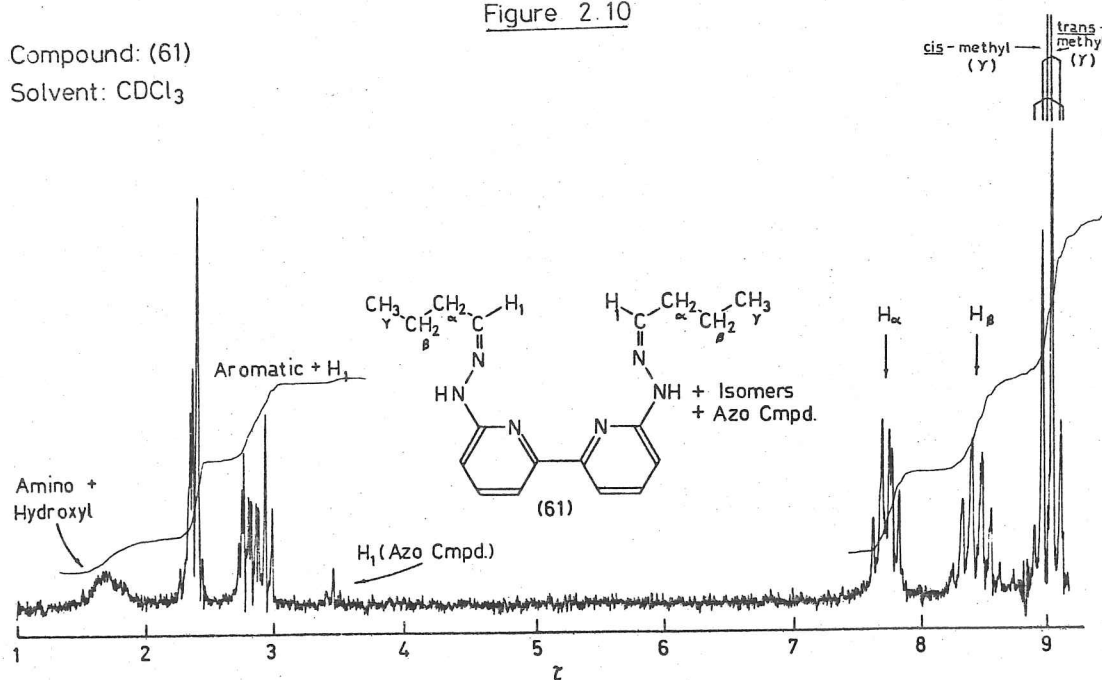
the two triplets due to the terminal methyl group).

In accordance with what has already been said the implication of this spectral data is that the cis α isomer exists predominantly in solution.

Figure 2.10

Compound: (61)

Solvent: CDCl_3

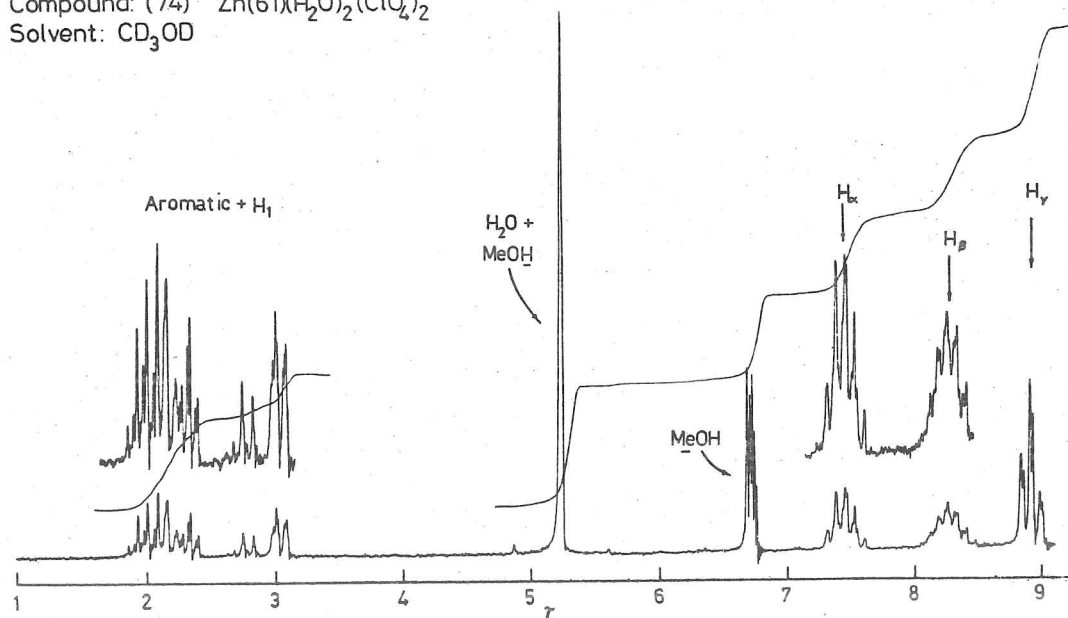


^1H -n.m.r. spectrum of compound (61) in deuterochloroform

Figure 2.11

Compound: (74) $\text{Zn}(61)(\text{H}_2\text{O})_2(\text{ClO}_4)_2$

Solvent: CD_3OD



^1H -n.m.r. spectrum of $\text{Zn}(61)(\text{H}_2\text{O})_2(\text{ClO}_4)_2$, (74), in CD_3OD

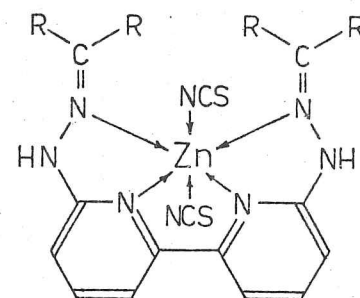
The spectrum of the acetaldehyde derived zinc complex, (72), (Fig. 2.9) is interesting as it shows the presence of eight signals in the methyl region instead of the four expected for a single azo-hydroperoxide free compound. The only conclusion from this seems to be that in this case, where both substituents on the imino group are relatively small, namely a proton and a methyl group, both the cis α and cis β forms of the complex are capable of existence. This contrasts quite reasonably with the other members of the series of compounds under study which all have bulkier imino substituents and which accordingly form only the cis α isomer.

In order to confirm these configurational assignments an analogous series of $\text{Zn}(\text{ligand})(\text{NCS})_2$ complexes was prepared by adding diisothiocyanatobis(pyridine)zinc(II) to a solution of the appropriate ligand. Analytical data is given in Table 2.10. The fact that the zinc does not co-ordinate any solvent molecules in the presence of the two isothiocyanate counterions strongly suggests that both counterions are co-ordinated, since in the presence of the less strongly co-ordinating perchlorate counterions it has been seen that octahedral geometry is probably assumed with the aid of two solvent molecules. The compounds proved to be too insoluble to permit conductivity determinations which may well have verified this.

By choosing this particular counterion one has a convenient means of probing the geometry of the complex,

Table 2.10

Analytical and Spectral Data
For Compounds of the Type :



Cmpd. No.	Derived from	Found			Expected			Infrared	
		C	H	N (%)	C	H	N	ν C \equiv N (cm ⁻¹ \pm 2)	ν C-S
80	59	42.8	3.63	25.2	42.7	3.59	24.9	2095, 2083 2068, 2056	812
81	60	45.5	4.36	23.7	45.2	4.22	23.5	2110 br	809
82	61	47.6	4.87	22.2	47.5	4.78	22.2	2122, 2106	829
83	62	45.3	4.34	23.6	45.2	4.22	23.5	2121, 2101	826
84	63	47.4	4.84	22.1	47.5	4.78	22.2	2125, 2108	828
85	64	49.7	5.29	21.2	49.5	5.29	21.0	2122, 2102	828
86	65	49.2	5.28	20.9	49.5	5.29	21.0	2099, 2086	813
87	DHBP	36.0	3.02	27.9	36.2	3.04	28.2	2123, 2096	815

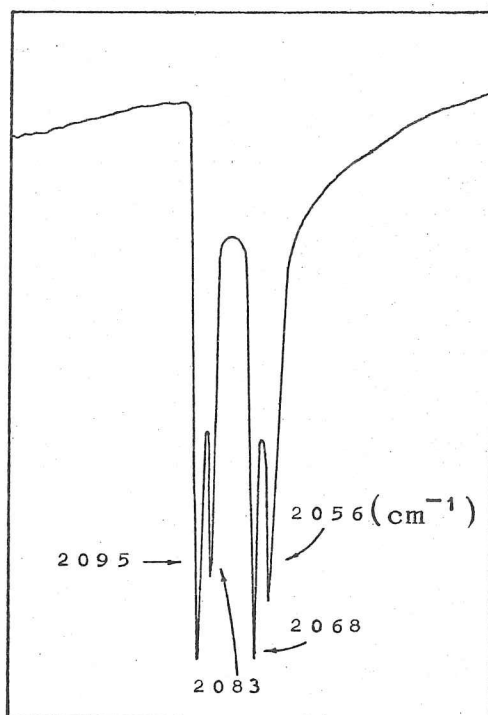
since disposition of the two isothiocyanate groups trans to one another leads to only a single $\nu\text{C}\equiv\text{N}$ frequency in the infrared spectrum whereas a cis disposition leads to a splitting of the $\nu\text{C}\equiv\text{N}$ absorption¹¹⁰.

Configurational assignments based on this technique, however, have to be treated with some caution since the coupling between the $\nu\text{C}\equiv\text{N}$ vibrations may be quite small and thus unobservable. Accordingly, the presence of two bands may be evidence for the cis isomer, but only one band is not necessarily evidence for the trans isomer. Also, with this series of compounds whose spectra have to be recorded in the solid state owing to their low solubility, solid state splitting has to be considered. Fortuitously, it seems that such complications are uncommon in complexes carrying large ligands such as bipyridyl. Several workers have looked for solid state effects in the infrared spectra of a number of bipyridyl isothiocyanate complexes in coming to this conclusion^{4,111-113}.

With the exception of the acetaldehyde derivative, (80), all the $\text{Zn}(\text{ligand})(\text{NCS})_2$ compounds, (81) to (86), show either a broad or a split band in the range 2125 to 2086 cm^{-1} , indicative of the expected cis geometry. In agreement with the p.m.r. spectra, the acetaldehyde derived compound shows a group of two split bands, one in the above mentioned range and one 30 cm^{-1} to lower frequency (see Fig. 2.12).

If one takes these observations in conjunction with

Figure 2.12



Infrared spectrum, in the $\nu \text{C}\equiv\text{N}$ region, of Zn(59)(NCS)_2 , (80)

the p.m.r. configurational determinations, they suggest that the absorptions in the range 2125 to 2080 cm^{-1} , shown by all compounds, originate from a complex of cis α stereochemistry whilst the lower frequency absorptions shown only by the acetaldehyde derivative, (80), originate from the complex having the cis β configuration.

It is difficult to know whether solid state splitting is being observed or not. Certainly if one ignores it, in accordance with what has been said above, then the conclusions drawn from the infrared spectra nicely confirm and complement those drawn from the p.m.r. spectra. In the case of the acetaldehyde derived compound at least one

of the bands must be split on molecular symmetry grounds (there is only one trans structure). If solid state effects were occurring, then this split band should show further splitting. The fact that there is no splitting beyond the doublet stage in either of the ν C \equiv N bands in this spectrum shows that no solid state effects are operating on one of the bands in this particular compound, but carries no implication concerning solid state effects on the constitution of these bands in the other members of the series.

The isothiocyanate complex prepared from DHBP, (87), shows much the same ν C \equiv N pattern as those compounds, (81) to (86), for which the cis α configuration alone has already been proposed. This is interesting because this is a case where steric hindrance does not preclude even the trans configuration (recall the square-planar Ni(DHBP)-(ClO₄)₂) and whereas a percentage of the more hindered acetaldehyde derivative adopts the cis β configuration here there is only the least hindered cis α form, at least in the solid state. Clearly there are more forces controlling the geometry of the complex than just intramolecular steric repulsions, probably intermolecular lattice packing factors have a significant effect on the geometry of the complex in the solid state.

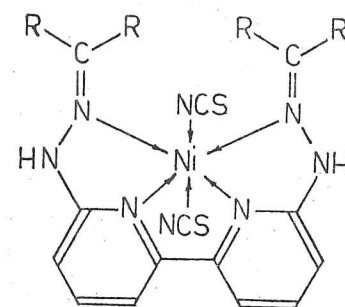
The ν C-S band confirms the expected mode of bonding of the isothiocyanate moiety, namely via the nitrogen atom,¹¹⁰ since it falls in the range 780 to 860 cm⁻¹ normally taken to be indicative of this bonding mode¹¹⁴.

In order to ascertain whether nickel(II) also undergoes complexation with these ligands to form predominantly the cis α product (in the solid state at least) the corresponding series of Ni(ligand)(NCS)₂ complexes were prepared and their infrared spectra examined. Preparation was effected by the reaction of diisothiocyanatotetra(pyridine)nickel(II) with the free ligand. Analytical data and details of their infrared spectra are given in Table 2.11. Molar conductivity values in water are between those expected for a non-electrolyte and a 1 : 1 electrolyte⁷⁶ and suggest that partial dissociation of the complexes occurs in solution by displacement of the co-ordinated anion by water molecules. Spectral and magnetic properties (see Chapter Four) confirm that they are all octahedral complexes in the solid state.

The solid state infrared spectra in the ν C \equiv N region, with the exception of the DHBP derivative, all show two groups of split bands analogous to Fig. 2.12 again probably indicating the presence of both cis α and cis β forms of the complex. Indeed, in the case of the methyl ethyl ketone derivative, (92), it was possible to separate two isomeric components by fractional crystallisation. The least soluble fraction precipitated as fine yellow crystals and showed only the higher frequency pair of absorptions at 2126 and 2108 cm⁻¹. In accordance with that which was determined for the zinc complexes this is believed to indicate that this compound has the cis α configuration. The green residual fraction consisted of a mixture of both

Table 2.11

Analytical and Spectral Data
For Compounds of the Type



Cmpd. No.	Derived from	C	<u>Found</u> H	N (%)	C	<u>Expected</u> H	N	Infrared ν C \equiv N ($\text{cm}^{-1} \pm 2$)		ν C-S	\bigwedge^c $\text{cm}^2 \text{ohm}^{-1} \text{M}^{-1}$
88	59	44.1	3.85	25.4	43.4	3.64	25.3	2116, 2090,	2102 2078	b	59
89	60	45.8	4.32	23.6	45.9	4.28	23.8	2120, 2081,	2109 2071	b	69
90	61	47.5	4.72	22.5	48.1	4.85	22.4	2114, 2075,	2104 2061	818	64
91	62	45.7	4.20	23.5	45.9	4.28	23.8	2117, 2088,	2106 2072	812	a
92	63	47.7	4.77	21.9	48.1	4.85	22.4	2126, 2085,	2108 2073	825	62
93	64	50.2	5.40	20.6	50.1	5.35	21.2	2124 2099,	br 2088	b	a
94	65	50.1	5.34	21.2	50.1	5.35	21.2	2103, 2073,	2092 2060	811	56
95	DHBP	35.5	3.08	28.5	36.8	3.09	28.6	2100,	2080	810	a

a Too insoluble.

b No band clearly resolved.

c 10^{-3}M solutions in water at 220

isomers, but showed predominantly the lower frequency pair of ν C \equiv N absorptions in its infrared spectrum and hence is thought to be mostly the cis β isomer.

Again, the infrared spectrum of the DHBP derivative suggests that it is predominantly in the cis α form in the solid state.

2.6 Experimental

General experimental methods relevant to the work as a whole are given in the Appendix.

Commercially available hydrazine hydrate "99-100%" was used without further purification. All aldehydes and ketones were distilled before use. Analytical grade nickel perchlorate and zinc perchlorate were used. Diisothiocyanatotetrapyridinenickel(II) and diisothiocyanatobis(pyridine)-zinc(II) were prepared by standard procedures¹¹⁵.

6,6'-Dibromo-2,2'-bipyridyl (11) : 2,2'-Bipyridyl (50 g) and bromine (127.5 g) were passed through a tube packed with pumice heated to 500°. The oily product which formed was collected and boiled with water (500 ml) until a solid grey material had fully separated from the oil. During this period sodium thiosulphate was added in sufficient quantity to reduce any free bromine that had been retained in the oil. The grey solid was collected by filtration, boiled with 2M sodium hydroxide (200 ml) for ten minutes, washed with water (2 x 50 ml) and triturated with acetone

(50 ml) to remove oily impurities. The solid was again collected by filtration and recrystallised, twice, from benzene, in the presence of activated charcoal, yielding the product as white needles (35 g, 35%), m.p. 218 - 219° (lit.³⁹ 218°). (Found : C, 38.1; H, 1.97; N, 8.9. Calc. for $C_{10}H_6Br_2N_2$: C, 38.2; H, 1.93; N, 8.9%).

P.M.R. (d_6 benzene, 100 MHz) : 1.85 τ , d, $J=8.0$ Hz, (2H); 3.10 to 3.41 τ , m, (4H).

I.R. (nujol) : 1570m, 1530m, 1414m, 1150m, 1131m, 1119m, 1070s, 982s, 782s.

Mass Spectrum (70 e.v.) : m/e of parent ion calculated : 312, 314, 316. Found : 312, 314, 316.

6,6'-Dihydrazino-2,2'-bipyridyl (20) : To hydrazine hydrate (100 ml), refluxing in a stream of nitrogen, 6,6'-dibromo-2,2'-bipyridyl (8.0 g) was added. The resulting suspension was refluxed with stirring for four hours during which time the dibromide dissolved completely. Upon cooling the solution the crude product crystallised as fine yellow needles. The crystals were collected by filtration and recrystallised (once) from water (600 ml) to give the pure product (5.3 g, 96%).

P.M.R. (D_2O + 1 drop of CH_3COOH) : 2.02 τ , d of d, $J=7.0$ Hz, $J'=8.0$ Hz, (2H); 2.37 τ , d of d, $J=7.0$ Hz, $J''=1.0$ Hz, (2H); 2.90 τ , d of d, $J'=8.0$ Hz, $J''=1.0$ Hz, (2H).
I.R. (nujol) : 3325m, 3243m br, 3178m br, 3111m br, 3078m br, 1578s, 1374s, 1305s, 1270s, 1166s, 1001s, 985s, 900m, 792s.

Mass Spectrum : m/e of parent ion calculated : 216.

Found : 216.

6,6'-Di-N-methylhydrazino-2,2'-bipyridyl (44) :

6,6'-Dibromo-2,2'-bipyridyl (3.0 g) was added to methylhydrazine (50 ml) which had been refluxing in a stream of nitrogen for ten minutes. The resulting solution was refluxed for one hour before removing 40 ml of the methylhydrazine by distillation. The residue was allowed to cool and was diluted with water (20 ml). The yellow crystalline material was collected by filtration and washed with water (2 x 10 ml). Recrystallisation, once, from methanol gave the pure product as yellow prisms (1.8 g, 77%).

P.M.R. (D_2O + 1 drop of CH_3COOH) : 1.92 τ , d of d, $J=7.0Hz$, $J'=8.0Hz$, (2H); 2.33 τ , d of d, $J=7.0Hz$, $J''=1.0Hz$, (2H); 2.79 τ , d of d, $J'=8.0Hz$, $J''=1.0Hz$, (2H); 6.49 τ , s, (6H).

I.R. (nujol) : 3310m, 3206w, 1633m, 1572s, 1390m, 1325w, 1127w, 974s, 911m, 790s.

Mass Spectrum : m/e of parent ion calculated : 244.

Found : 244.

6,6'-Dihydrazino-2,2'-bipyridylnickel(II) perchlorate (43) :

6,6'-Dihydrazino-2,2'-bipyridyl (1.0 g) was dissolved in refluxing ethanol (200 ml). To the refluxing solution hexaaquonickel(II) perchlorate (1.7 g) dissolved in ethanol (15 ml) was added dropwise over a period of ten minutes.

The fine orange crystals which were precipitated were collected by filtration and dried in vacuo to give the pure product (1.6 g, 72%).

CAUTION : This compound detonates violently upon being introduced into a flame, but has been found to be quite shock stable.

I.R. (nujol) : 3360s, 3269s, 3165s, 3080m, 1626s, 1572m, 1511m, 1399w, 1275m, 1231s, 1150 to 1030s, 935w, 794s.

Dichloro-6,6'-dihydrazino-2,2'-bipyridylnickel(II) monohydrate (48) : This compound was prepared in a manner analogous to compound (43) with the exception that hexaaquonickel(II) chloride (1.1 g) was substituted for hexaaquonickel(II) perchlorate. Yield : 1.4 g, 83%.

I.R. (nujol) : 3255m, 3225s, 3145m, 3073m, 1602s, 1582s, 1512s, 1353s, 1335m, 1284s, 1261s, 1186s, 1141s, 1089m, 1046m, 1025m, 994m, 879w, 826w, 811w, 789s.

6,6'-Di-N-methylhydrazino-2,2'-bipyridylnickel(II) perchlorate (47) : Reaction of 6,6'-di-N-methylhydrazino-2,2'-bipyridyl (0.2 g) with hexaaquonickel(II) perchlorate (0.3 g) in a manner analogous to that described for the DHBP compound, (43), gave the product as yellow crystals (0.4 g, 97%).

I.R. (nujol) : 3217m, 3177m, 3109m, 1630s, 1597m, 1561m, 1511m, 1317m, 1239s, 1080s br, 788s.

Dichloro-6,6'-di-N-methylhydrazino-2,2'-bipyridylnickel(II) monohydrate (49) : This compound was prepared in a manner analogous to compound (47) with the exception that hexaaquonickel(II) chloride (0.2 g) was substituted for hexaaquonickel(II)

perchlorate. Yield : 0.27 g, 84% .

I.R. (nujol) : 3305w, 3195m, 3105m, 1620s, 1594s,
1572s, 1294s, 1202, 1169m, 1086m, 1014s, 980m, 948m,
782s.

6,6'-Di-N-methylhydrazino-2,2'-bipyridylnickel(II) tetra-
chlorozincate (50) : The dichloro compound, (49), (1.5 g) was
dissolved in methanol (25 ml). To this solution a solution
of zinc chloride (1.8 g) in methanol (15 ml) was added and
the two were stirred together for ten minutes. The orange
material which precipitated was collected by filtration
and washed with methanol (2 x 10 ml) to yield the pure
product (1.8 g, 96%).

I.R. (nujol) : 3527m, 3455m, 3163s, 3145s, 1620s,
1591m, 1563m, 1318m, 1247m, 1229m, 1175m, 1160m,
1027m, 897m, 820w, 793s.

Diaquo-6,6'-bis(N'-hydrazone)-2,2'-bipyridylnickel(II)
perchlorate complexes (51) to (57) : 6,6'-Dihydrazino-
2,2'-bipyridylnickel(II) perchlorate was suspended in an
excess of the appropriate aldehyde or ketone and the
mixture brought to reflux. Sufficient water was then
added so as to render the solvent 10% aqueous, resulting in
rapid dissolution of the solid. The solution was refluxed
for a further ten minutes before evaporating it to dryness
under reduced pressure. Recrystallisation from an acetone
diethyl ether mixture gave the pure product. Yields were
essentially quantitative.

I.R. (nujol, generally observed pattern): 3400s,
3340s, 1610s, 1585s, 1510s, 1260s, 1080s, 790s.

Bis(N'-isopropylidene)-6,6'-dihydrazino-2,2'-bipyridyl-
nickel(II) chloride (58) : 6,6'-Dihydrazino-2,2'-bipyridyl-
nickel(II) perchlorate (0.24 g) and zinc chloride (0.5 g)
were dissolved in a mixture of methanol (60 ml) and acetone
(3 ml) and allowed to stand for three days. The yellow
crystals which formed were collected by filtration, washed
with methanol (2 x 10 ml) and dried in vacuo, yielding the
pure product (0.18 g, 84%).

I.R. (nujol) : 3312m, 1620sh, 1602s, 1580s, 1518s,
1378s, 1297w, 1191s, 1145s, 1128s, 795s, 789s.

6,6'-Bis(N'-hydrazone)-2,2'-bipyridyl ligands (59)
to (65) : The appropriate 6,6'-dihydrazone-2,2'-bipyridyl-
nickel(II) perchlorate complex (1 mmol) was dissolved in
methanol (30 ml) and brought to reflux. Sodium cyanide
(4 mmol) was added and refluxing continued for a further
fifteen minutes. The volume of methanol was then reduced
to approximately 5 ml under reduced pressure. In one case,
(62), the free ligand precipitated at this point; it was
collected by filtration and recrystallised from methanol,
under anaerobic conditions, to give the pure product. In
general the solution was now taken and applied to a 30 cm
alumina column packed in chloroform. Elution with chloroform
gave a single broad yellow band which was collected, dried
with magnesium sulphate, filtered and diluted with petroleum
ether to a point where precipitation commenced. The fine
crystals so formed were collected by filtration and
recrystallised from a mixture of chloroform and petrol.
Typically the yield was approximately 70%.

P.M.R. Data is presented in Table 2.5.

I.R. (nujol, general features of the spectra) :

3300m, 1570s, 795s.

Mass spectrum : All compounds show the calculated parent ion peak.

Bis(N'-isopropylidene)-6,6'-di-N-methylhydrazino-2,2'-bipyridyl (67) : 6,6'-Di-N-methylhydrazino-2,2'-bipyridyl (0.2 g) was refluxed in acetone (15 ml) for one hour. The solution was allowed to cool and set aside to slowly evaporate. When the volume had been reduced to c.a. 2 ml the white needles of the pure product which had formed were collected by filtration (0.21 g, 79%).

P.M.R. (CDCl₃) : 2.0 to 2.6τ, m, (4H); 3.36τ, d of d, J=8.0Hz, J'=1.0Hz, (2H); 6.70τ, s, (6H); 7.86τ, s, (6H); 7.99τ, s, (6H).

I.R. (nujol) : 1567s, 1404m, 1328m, 1286m, 1254w, 1096m, 982m, 925m, 804s, 791s.

Mass spectrum : ^m/e of parent ion calculated : 324.

Found : 324.

Diaquo-6,6'-bis(N'-hydrazone)-2,2'-bipyridylzinc(II) perchlorate complexes (72) to (78) : The appropriate dihydrazone ligand, (59) to (65), (1 mmol) was dissolved in methanol and refluxed under aerobic conditions for fifteen minutes. Hexaquo-zinc(II) perchlorate (1 mmol) in methanol (5 ml) was then added and the solution refluxed for a further ten minutes. The solution was then filtered and diethyl ether was added until the solution became cloudy, whereupon it was allowed to stand in the fridge overnight. The fine pale yellow crystals which formed were separated

by filtration and required no further purification. In all cases the yield was greater than 95%.

I.R. (nujol) : These compounds show the same general features as the corresponding nickel complexes, (51) to (57). P.M.R. data is presented in Table 2.8.

Diaquo-6,6'-dihydrazino-2,2'-bipyridylzinc(II) perchlorate (79) : Hexaaquozinc(II) perchlorate (0.18 g) was added to a solution of 6,6'-dihydrazino-2,2'-bipyridyl (0.1 g) in methanol (25 ml). The solution was refluxed for twenty minutes before it was filtered and allowed to cool. Diethyl ether was then added to the filtrate resulting in precipitation of the pure product as pale yellow crystals (0.23 g, 96%).

P.M.R. (CD_3OD) : 2.0 to 2.5 τ , m, (4H); 3.12 τ , d, $J=8.0\text{Hz}$, (2H).

I.R. (nujol) : 3500s, 3330s, 1625s, 1608s, 1589s, 1505s, 1280m, 1201s, 1160 to 1030s, 791s.

Diisothiocyanato-6,6'-bis(N'-hydrazone)-2,2'-bipyridylzinc(II) complexes (80) to (86) : Diisothiocyanatobis(pyridine)zinc(II) (1 mmol) was suspended in refluxing methanol, the appropriate hydrazone ligand, (59) to (65), (1 mmol) was then added and the suspension refluxed for fifteen minutes. The precipitated crystals were collected by filtration and washed with methanol (2 x 10 ml) to give the pure compound. In all cases the yield was greater than 95%.

Diisothiocyanato-6,6'-dihydrazino-2,2'-bipyridylzinc(II)

(87) : This compound was prepared by the method given above substituting DHBP (1 mmol) for the hydrazone. Yield 87%.

Diisothiocyanato-6,6'-bis(N'-hydrazone)-2,2'-bipyridyl-nickel(II) (88) to (94) : Diisothiocyanatotetra(pyridine) nickel(II) (1 mmol) was suspended in refluxing methanol. The appropriate hydrazone ligand, (59) to (65), (1 mmol) was added and the suspension refluxed for fifteen minutes. In the case of the symmetrical derivatives, (91) and (93), the product precipitated and was isolated by filtration and purified by washing with methanol (2 x 10 ml). The product in the other cases remained in solution and so the solution was filtered, and to it was added diethyl ether which precipitated the product. The product was then collected by filtration and washed with methanol (2 x 10 ml) in the usual way to yield the pure compound. In the case of the methyl ethyl ketone derivative, (92), two isomeric fractions were obtained during the crystallisation process. Yields were in all cases greater than 75%.

Diisothiocyanato-6,6'-dihydrazino-2,2'-bipyridyl-nickel(II) (95) : This compound was prepared in the manner described above for compounds (88) to (94), except that the hydrazone was substituted by DHBP (1 mmol). The product precipitated from solution without addition of diethyl ether, was collected by filtration and washed with methanol (2 x 10 ml) to yield the pure compound (82%).

CHAPTER THREE

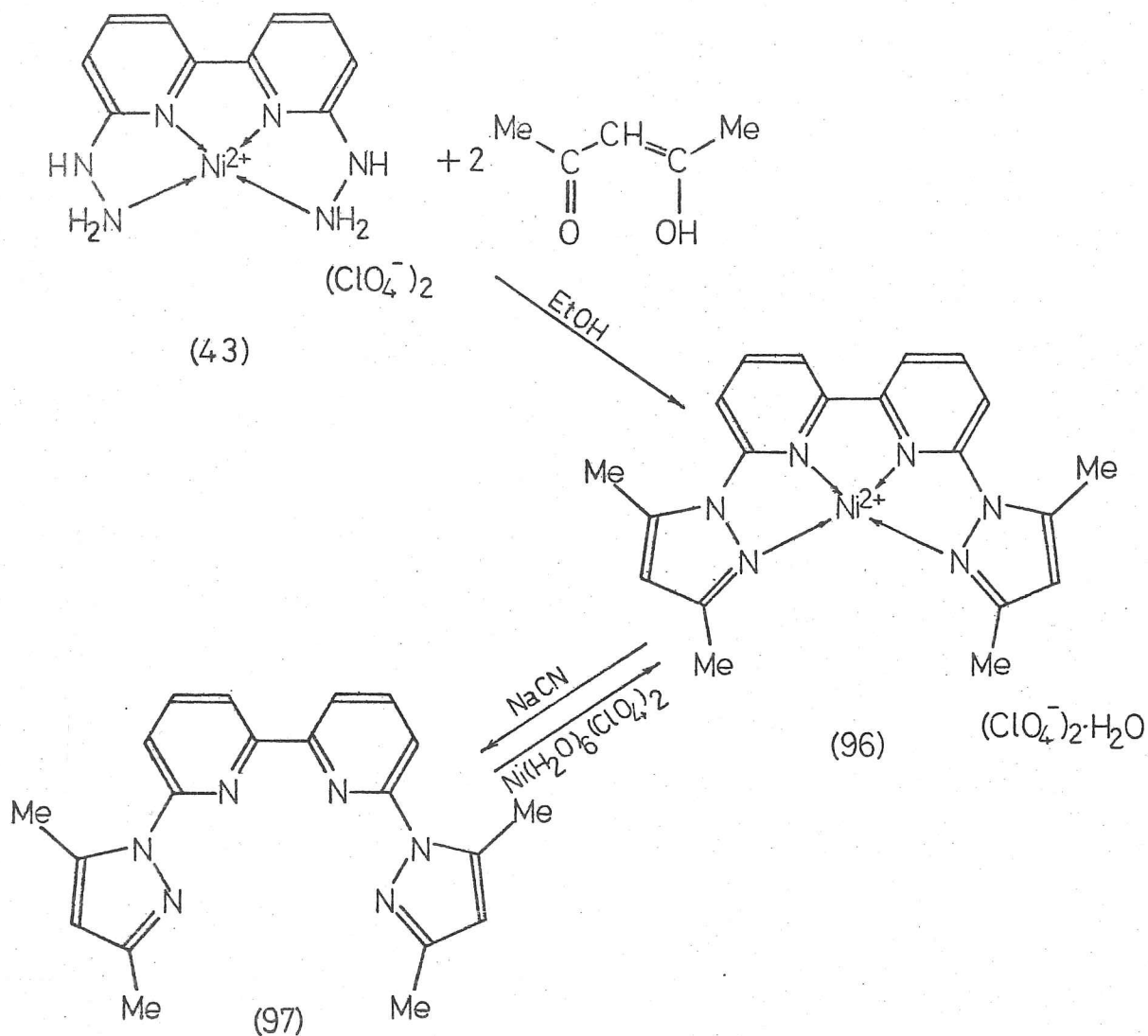
RING CLOSURES, MACROCYCLIC AND OTHERWISE,
EFFECTED BY REACTIONS WITH VARIOUS β -DIKETONES

3.1 Reaction of $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ with Acetylacetone and Benzoylacetone

The failure of simple aliphatic carbonyl compounds to bring about cyclisation of DHBP, by way of the Curtis type of reaction⁶, led to an investigation of the reactivity pattern of this system with β -diketones. As noted in Chapter One both the triethylenetetraminenickel(II) and triethylenetetraminecopper(II) systems are successfully converted to macrocyclic systems by reaction with acetylacetone^{58,59}.

Accordingly, $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ was suspended in a hot ethanolic solution of acetylacetone; the orange crystalline reactant gradually dissolved over a period of one hour to give an emerald green solution, the electronic spectrum of which indicated the formation of an octahedral nickel(II) complex (see Chapter Four). Addition of diethyl ether precipitated pale green crystals whose elemental analysis (Table 3.1) indicated that not one, but two moles of acetylacetone had condensed with the complex. Conductivity data showed that the compound was a 2 : 1 electrolyte in water and hence, by implication, that the ligand was neutral.

Reference to the literature¹¹⁶ shows that a method commonly employed in heterocyclic chemistry for the preparation of pyrazole ring systems involves the reaction of a hydrazine with a β -diketone and it became clear that it was a reaction of this type which had occurred to form (96), in preference to the formation of a macrocyclic species.



This was verified by decomposition of (96), which was paramagnetic, with sodium cyanide, so as to liberate the free ligand, (97), which was more amenable to spectroscopic techniques. Recombination of (97) with hexaaquanickel(II) perchlorate gave (96), confirming that the ligand was liberated unchanged.

Whichever way the metal complex, (96), is prepared the elemental analysis is consistent with the retention of only one molecule of water in the compound. Since the complex is known to be six co-ordinate from its electronic

spectrum and magnetic moment, $\mu_{\text{eff}} = 3.21$ B.M., the implication is that in the solid state at least one of the perchlorates is co-ordinated. Conductivity data indicates that in aqueous solution the complex is a normal 2 : 1 electrolyte⁷⁶, thus in water, any perchlorate anions that are co-ordinated in the solid state must be displaced. Generally the Cl-O stretching absorption in the infrared spectrum is split into two components upon lowering the symmetry of the perchlorate ion through co-ordination¹¹⁷. The ν Cl-O band in the solid state infrared spectrum of (96) shows no splitting, which tends to suggest that in the solid one perchlorate ion and the one water molecule are used to complete the inner co-ordination sphere, with the unsplit ν Cl-O band, arising from the ionic perchlorate, masking the splitting expected from the co-ordinated perchlorate.

When the reaction between $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ and acetylacetone is carried out in ethanol to which sufficient hydrochloric acid has been added to bring the solution to pH 2, the dichloro analogue of (96), $\text{Ni}(\text{ligand})(\text{H}_2\text{O})\text{Cl}_2$, (98), is obtained, which also contains only one water molecule. The conductance in water (Table 3.1) is somewhat low for a 2 : 1 electrolyte⁷⁶ suggesting that there is some interaction between the counterion and the complex in solution.

The p.m.r. spectrum of (97) in deuterochloroform showed the expected signals : two singlet methyl resonances at 7.20τ and 7.69τ , a singlet due to the methine protons

at 3.95 τ and a multiplet centred on 1.9 τ arising from the bipyridyl protons. The p.m.r. spectrum of 3,5-dimethyl-pyrazole in deuteriochloroform shows a single methyl resonance at 7.73 τ ¹¹⁸ (and a methine resonance at 4.20 τ) thus the lower field signal at 7.20 τ , in the spectrum of (97), was assigned to the methyl group on the carbon atom α to the nitrogen carrying the bipyridyl. The infrared spectrum was also compatible with the proposed formulation showing two ν C=N bands at 1586 and 1578 cm^{-1} both characteristic of C=N stretching in cyclic systems¹¹⁹. No ν N-H, ν O-H, or ν C=O bands were seen which may have indicated incomplete formation of the bis(pyrazole) system.

It was also found possible to synthesise the free ligand, (97), by reacting DHBP directly with acetylacetone. The product obtained in this way was identical in all respects to that derived by way of the metal complex.

The facile formation of (96) is readily accounted for in terms of the thermodynamic stability of the product, since the pyrazole ring is known to have considerable aromatic character; free pyrazole itself has a heat of combustion which indicates a resonance energy of 29.3 kcal mole⁻¹ (ref. 120) (c.f. benzene 36.0 kcal mole⁻¹ (ref. 121) and pyridine 31.9 kcal mole⁻¹ (ref. 122)).

In order to establish the generality of the reaction between $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ and β -diketones, benzoylacetone was substituted for acetylacetone. Reaction proceeded in the same general way as with acetylacetone except that in this case it was necessary to continue the refluxing for five

Table 3.1
Analytical and Conductance Data

Cmpd. No.	Molecular Formula	Found			Expected			Melting point	Δ^d cm ² ohm ⁻¹ M ⁻¹
		C	H	N (%)	C	H	N		
96	Ni(C ₂₀ H ₂₀ N ₆)(H ₂ O)(ClO ₄) ₂	39.0 38.8	3.82 3.68	13.7 ^a 13.4 ^b	38.7	3.58	13.6	-	191
97	C ₂₀ H ₂₀ N ₆	69.3	5.85	24.0	69.7	5.85	24.4	220°	-
98	Ni(C ₂₀ H ₂₀ N ₆)(H ₂ O)Cl ₂	48.7	4.28	17.5	48.8	4.51	17.1	-	162
99	Ni(C ₃₀ H ₂₄ N ₆)(H ₂ O) ₂ (ClO ₄) ₂	47.1	3.77	11.0	47.3	3.70	11.0	-	190
102	C ₃₀ H ₂₄ N ₆	76.8	5.15	18.0	76.9	5.16	17.9	231°	-
103	C ₃₀ H ₂₈ N ₆ O ₂	71.7	5.89	16.9	71.4	5.59	16.7	204°	-
105	Ni(C ₂₀ H ₂₀ N ₆)(NCS) ₂	50.6	3.99	21.7	50.9	3.88	21.6	-	c
106	Ni(C ₃₀ H ₂₄ N ₆)(NCS) ₂	59.4	3.88	17.2	59.7	3.76	17.4	-	c

a Prepared by reaction of Ni(DHBP)(ClO₄)₂ with acetylacetone.

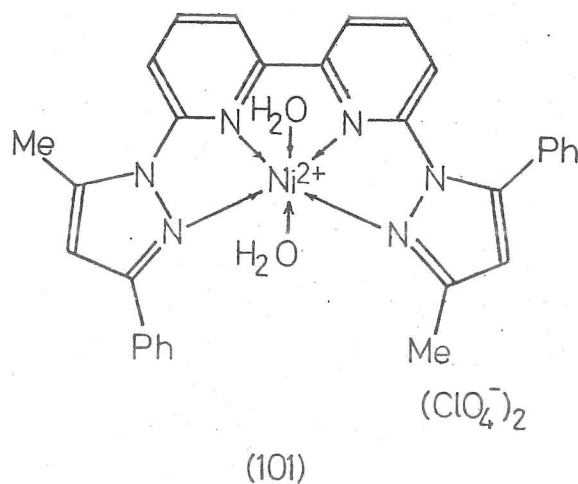
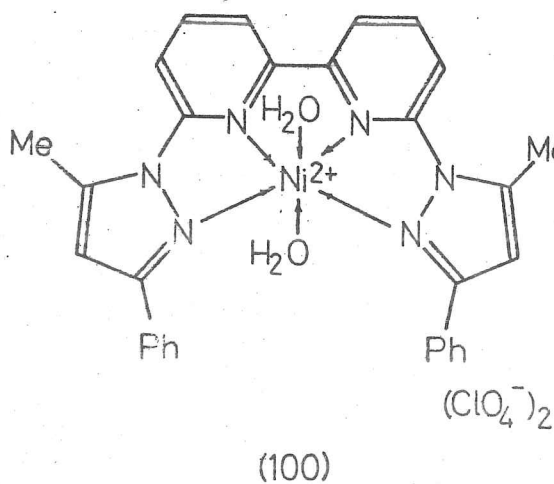
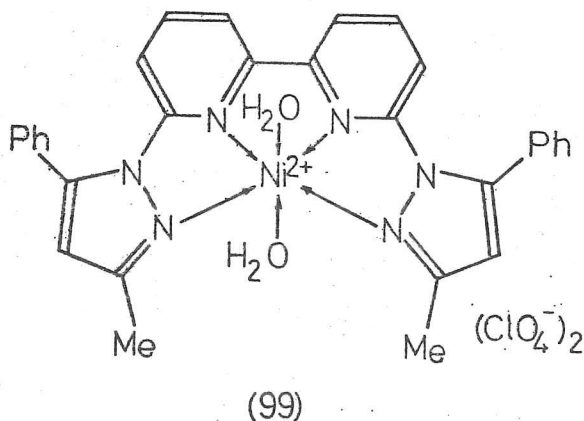
b Prepared by reaction of Ni(H₂O)₆(ClO₄)₂ with (97).

c Too insoluble.

d 10⁻³M in H₂O at 22°.

hours before complete dissolution of the reactant, which indicated the completion of the reaction, had been effected. This had been expected owing to the lower electrophilicity of the benzoyl carbon atom. Again, elemental analysis (Table 3.1) indicated the incorporation of two moles of the β -diketone into the ligand, but in this case showed that two water molecules are retained in the complex. The solid state infrared spectrum showed an unsplit ν Cl-O band suggesting that both water molecules are co-ordinated.

In this case where a non-symmetrical β -diketone has been used several different isomeric products are possible, (99), (100) and (101). It was of interest to ascertain



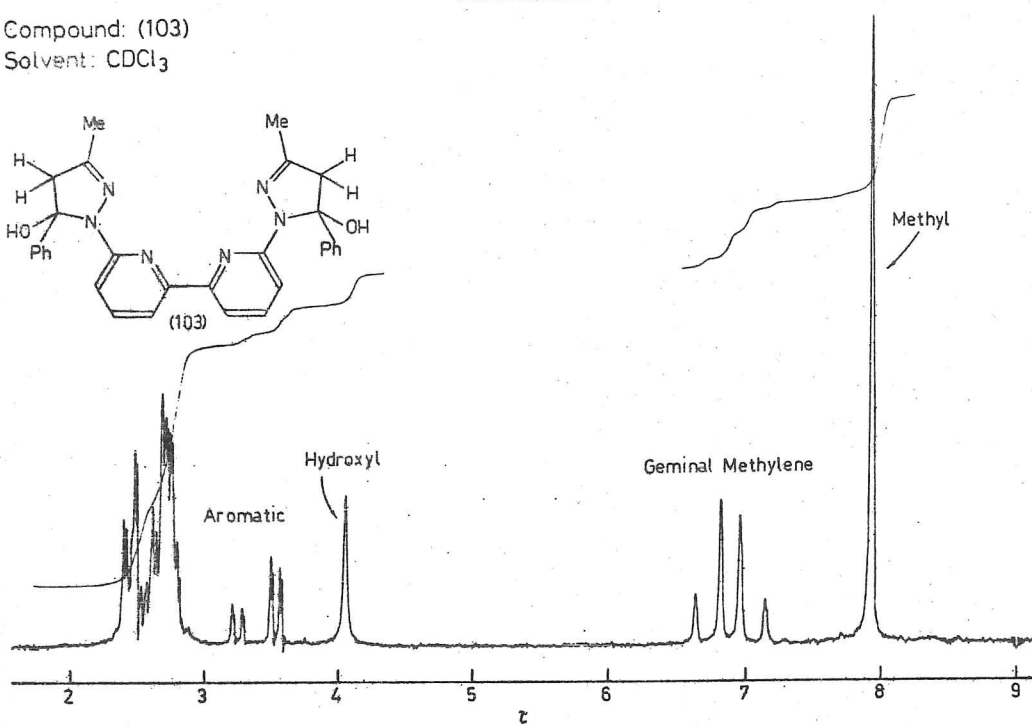
which of the isomers had formed, since this would convey information about the relative reactivities of the two nitrogen atoms in the $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ molecule, which could be compared with the reactivities at the corresponding sites in free DHBP.

In order to do this the nickel complex was decomposed with sodium cyanide, in the usual way, to yield the free ligand, (102). The p.m.r. spectrum of (102) was recorded in deuteriochloroform (Fig. 3.2) and showed a single methyl resonance at 7.63 τ indicating that either (99) or (100), exclusively, had been formed, since (101) has methyl groups in two different environments and hence would be expected to show two methyl resonances in the same manner as (97). The chemical shift of the observed signal strongly suggests, judging from those seen in compound (97), that the methyl group is on the carbon γ to the nitrogen carrying the bipyridyl residue and hence that (99) is the structure of its nickel complex. The downfield shift of 0.06 p.p.m. relative to the corresponding signal in the spectrum of (97) is consistent with the attachment of the phenyl group to the ring.


For comparative purposes the direct reaction of benzoylacetone with DHBP was examined. After refluxing the two together for three hours in methanol the product which had precipitated was collected by filtration. The p.m.r. spectrum of this product together with its elemental analysis (Table 3.1) showed that it was not the expected product, but rather that it was a hydrated intermediate

Cc1c[nH]c2c1c(O)c(c2)c3ccccc3-c4nc5ccc(cc5n4)-c6nc7c[nH]c8c7c(O)c(c8)c9ccccc9

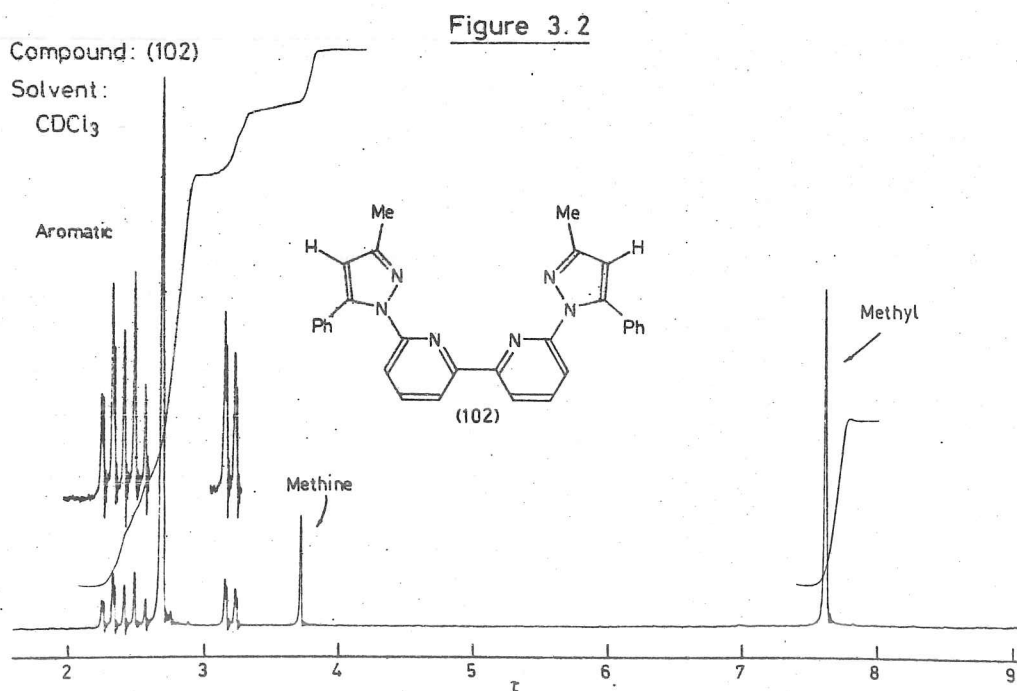
(103)

¹H-n.m.r. spectrum of compound (103) in deuterochloroform

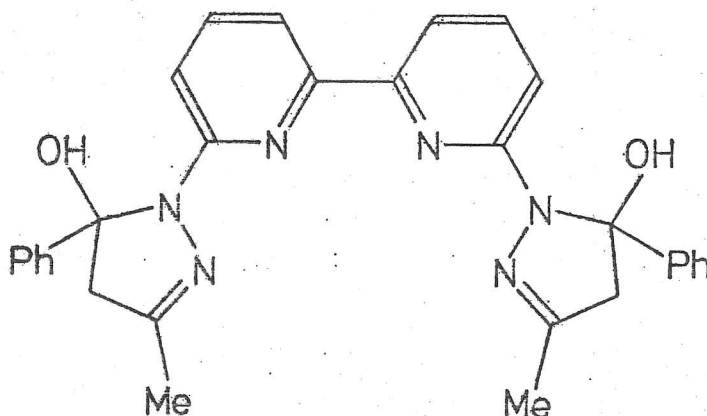
Aromatic



(102)

¹H-n.m.r. spectrum of compound (102) in deuteriochloroform

having structure (103). Structure (103), with the alcohol at the position α to the nitrogen carrying the bipyridyl residue is favoured since here the possibility



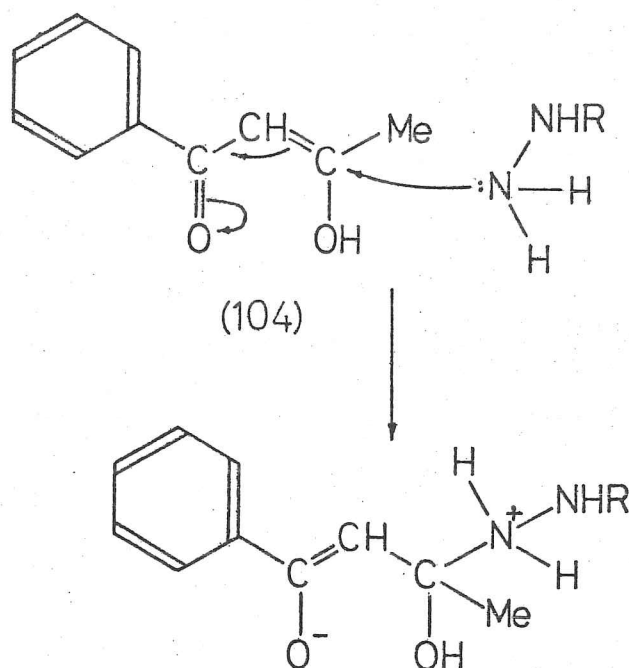
(103)

for intramolecular hydrogen bonding exists which may help to offset the tendency for the compound to dehydrate through to the aromatic product, and so explain its stability.

The infrared spectrum shows a very broad ν O-H band consistent with strong hydrogen bonding¹²³. If this structural assignment is correct then the dehydrated product derived from (103) should be identical to (102).

Compound (103) was readily dehydrated by stirring it in acetic acid for a few minutes. The dehydrated product was identical in all respects to (102), thus providing additional evidence for the proposed structure.

Since benzoylacetone exists almost entirely in its enol form, (104), due to the stabilisation obtained from the resulting conjugation,¹²⁴ and hence behaves as an



α,β -unsaturated ketone, there is little doubt that initial attack by the amine occurs at the terminal position of the conjugated system (i.e. on the carbon bearing the methyl group). From the structure of the product, it is obvious that attack at this position takes place by way of the terminal amine whether it be co-ordinated or not. So it appears as expected that the terminal amines in $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ are indeed quite labile and that they retain their basicity towards available electrophiles to an extent where they are still more basic than the adjacent secondary amine which, but for steric effects, would probably be the more basic, even in the free ligand.

Again, just as with the hydrazone ligands discussed in Chapter Two, we are dealing with facultative ligands which in principle can combine with a metal to form products

having trans, cis α or cis β stereochemistry (see Fig. 2.7). In order to establish which were the prevailing stereochemistries in the solid state, the perchlorate complexes of the two ligands, (96) and (99), were converted to their highly insoluble isothiocyanate complexes, (105) and (106), by methathesis with ammonium thiocyanate. These complexes have magnetic moments of 3.17 B.M. and 3.09 B.M. respectively, which are in the range generally found for octahedral nickel(II)⁸⁰; their elemental analysis indicated stoichiometries of Ni(ligand)(NCS)₂ suggesting that both anions are co-ordinated.

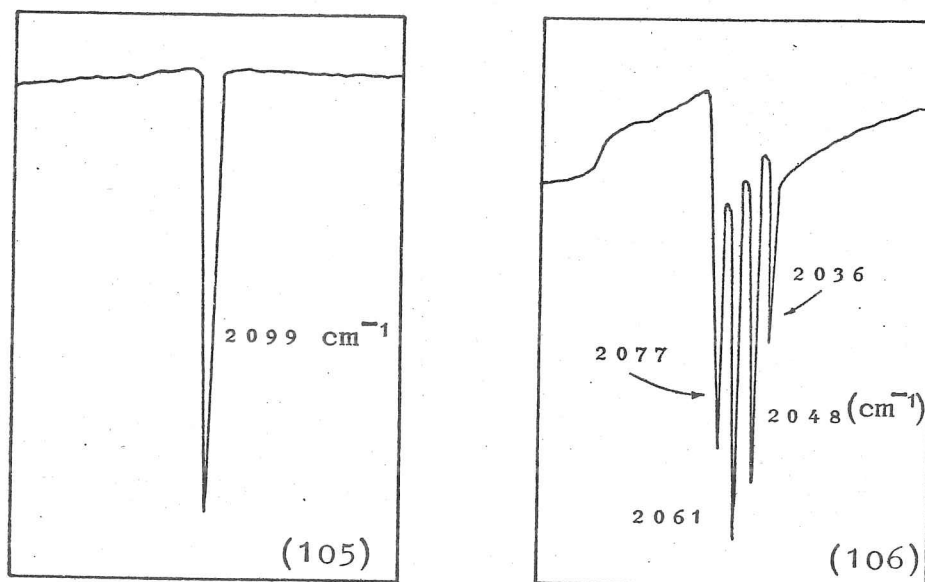
Molecular models indicate a high degree of steric strain associated with the trans bonding configuration arising from the interaction between the two methyl groups which are γ to the bipyridyl bearing nitrogens. One would expect this hindrance to be less than it was in the case of the hydrazone compounds discussed in Chapter Two owing to the increase in the relevant bond angle, at the secondary amine position, from c.a. 109° to c.a. 120° concomitant with the change in hybridisation (sp^3 to sp^2) at that point. Of the two cis arrangements the cis α is the least hindered, but the difference between the two is only slight.

The isothiocyanate complex derived from acetylacetone, (105), shows a single very sharp ν C \equiv N band at 2099 cm^{-1} (Fig. 3.3). As explained in Chapter Two this may indicate the trans structure, however, it may be a case where the resolution of the spectrometer is insufficient to distinguish between the two components of a split band; it should be

emphasised though, that this band is not at all broad and also that it does not occur at the frequencies which we shall see with the benzoylacetone derivative, (106), appear to be associated with the cis configurations. It was seen in Chapter Two that the frequencies of the $\nu \text{C}\equiv\text{N}$ bands remained fairly constant for a given stereochemistry as one imposed peripheral changes on the ligand.

The benzoylacetone derivative, (106), shows four $\nu \text{C}\equiv\text{N}$ bands in the infrared spectrum, all of which are extremely sharp, at 2077, 2061, 2048 and 2036 cm^{-1} (Fig. 3.3). This combination of bands can only be rationalised as arising from a mixture of the cis α and cis β isomers each of which would be expected to show a split band.

Figure 3.3



Infrared, in the $\nu \text{C}\equiv\text{N}$ region, of Compounds (105) and (106)

These stereochemical differences, which apparently occur in response to the substitution of a phenyl group for a methyl group on the periphery of the ligand, must surely

be an intermolecular lattice packing effect. It will be seen in Chapter Four that the solution electronic spectra of the nickel(II) perchlorate complexes of these two ligands, (96) and (99), show no evidence to suggest the presence of the trans bonded species in aqueous solution.

3.2 Formation of Thirteen Membered Macrocyclic Ligands from 6,6'-Di-N-methylhydrazino-2,2'-bipyridyl

It would appear that the reaction of β -diketones at both of the nitrogen nuclei in a given hydrazine residue of DHBP, to produce the substituted pyrazole derivatives described in the previous section must readily be blocked by converting the secondary amine to a tertiary amine. Thus it was anticipated that by using the methylated derivative, DMeHBP, (44), which already has a tertiary amine at the appropriate position, rather than DHBP, cyclisation to form a macrocyclic product may well result simply through lack of any alternative mode of reaction.

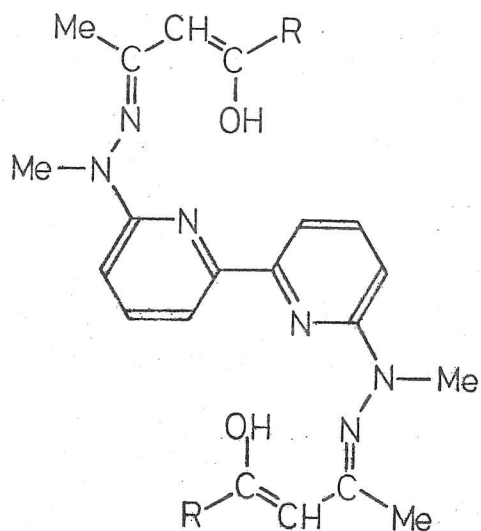
Since the nickel(II) complexes of DMeHBP have been found to be appreciably inert towards acyl compounds, initial investigations were carried out on the metal free system in an attempt to prepare the type of macrocyclic precursor used by Cummings⁵⁸ (c.f. page 30). The reaction of two moles of acetylacetone with DMeHBP under neutral conditions in refluxing ethanol gave the expected compound, (107), which has the structure shown. Two moles of acetylacetone are incorporated, bound simply as their monohydrazones.

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(107): R = Me

(108): R = Ph

Table 3.2

Analytical Data

Cmpd. No.	C	Found		N (%)	C	Expected		m.p.
		H				H	N	
107	64.8	7.00	20.9	64.7	6.91	20.6	230-3°	
108	72.2	6.30	16.0	72.2	6.06	15.8	224-6°	

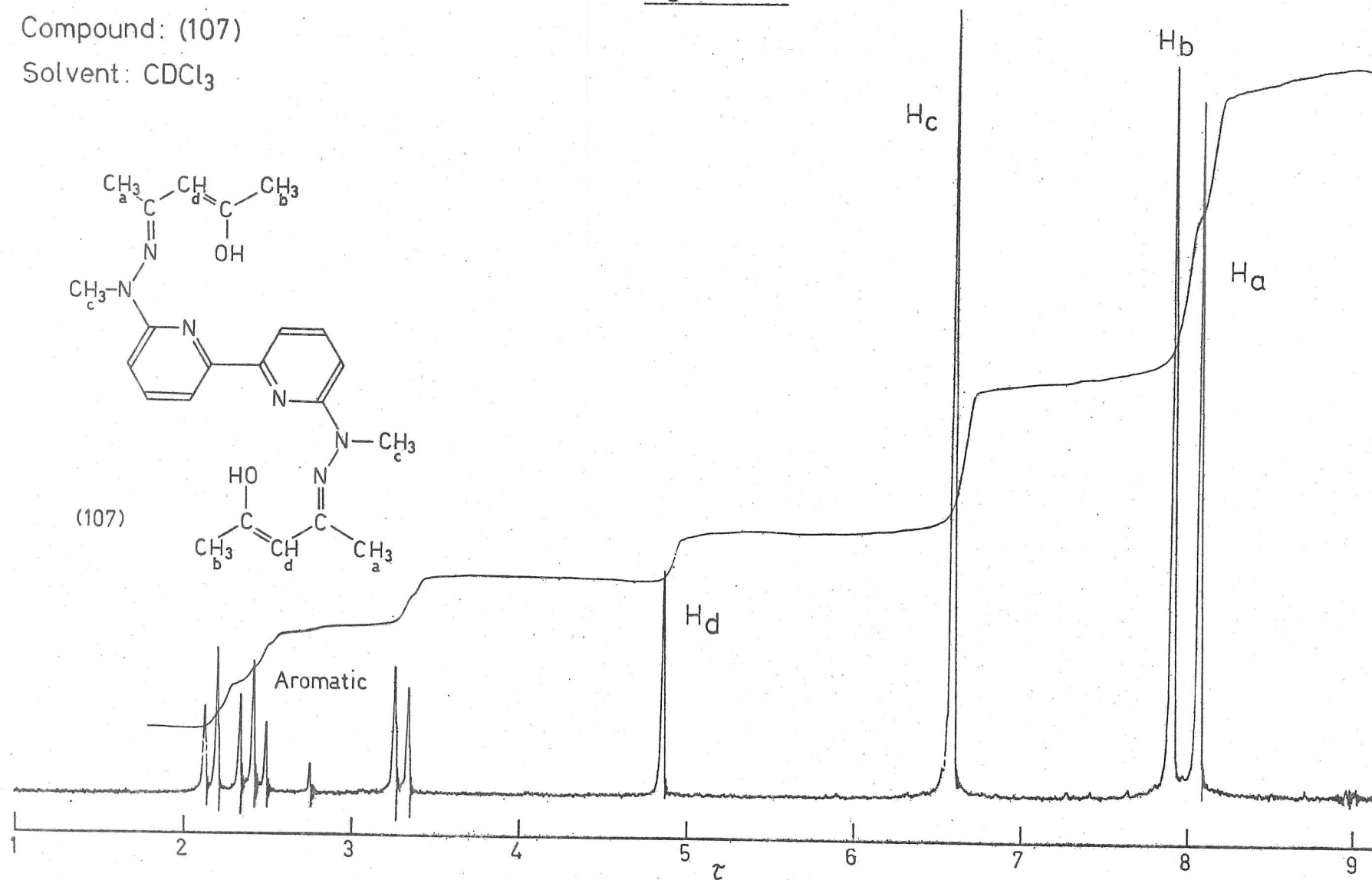
The stoichiometry was determined from the elemental analysis (see Table 3.2) while the exclusive formation of the particular isomer shown was determined from the p.m.r. spectrum, together with infrared and mass spectral data. As may be observed, several different configurationally unstable isomers are possible.

The p.m.r. spectrum of (107), (Fig. 3.4) in deuteriochloroform shows in addition to the resonances arising from the bipyridyl protons just four signals: A singlet at 4.85 τ , (2H); attributable to the methine proton; a singlet at 6.58 τ , (6H); arising from the nitrogen bound methyl groups and two singlets each integrating for six protons at 7.90 τ and 8.06 τ due to the methyl groups on

Figure 3.4

Compound: (107)

Solvent: CDCl_3



^1H -n.m.r. spectrum of Compound (107) recorded in deuteriochloroform

the acetylacetone residue. This data leads to the following conclusions concerning the structure of the compound. Firstly, the precise ratio 3 : 1 of either one of the signals at 7.90 τ or 8.06 τ to that at 4.85 τ , together with the absence of any methylene resonance, establishes that all of the acetylacetone residue exists in the enol form. This is readily rationalised, since acetylacetone itself exists 85% in the enol form¹²⁴, so as to take advantage of the hydrogen bonding and resonance stabilisation available in this configuration. In compound (107) several possibilities for hydrogen bonding leading to cyclic systems exist, which probably account for the total absence of any of the compound in the keto form. Secondly, the presence of only two methyl resonances from the acetylacetone residue shows that only one configuration exists about the imino double bond. Presumably this is the least sterically hindered configuration in which the methyl group on the imino carbon is cis to the tertiary nitrogen substituent. That only one configuration is adopted is quite reasonable in view of the relative steric bulk of the two imino substituents.

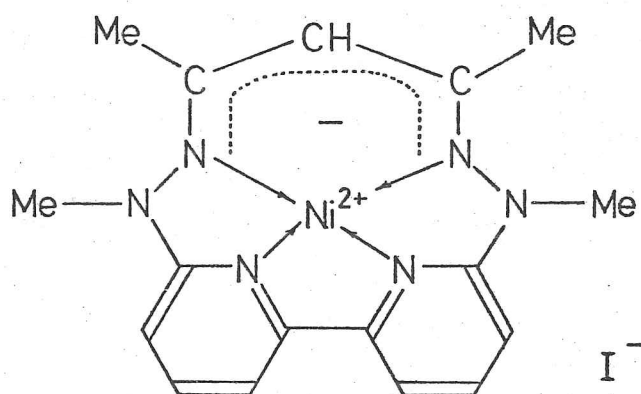
The solid state infrared spectrum of (107) confirms the presence of the hydrogen bonded hydroxyl groups by showing a broad ν O-H absorption centred on 3170 cm^{-1} . Also seen is the hydrazone ν C=N band, at 1610 cm^{-1} , some 30 cm^{-1} to higher frequency than that observed in the pyrazole derivatives, reflecting the placement of this moiety in a linear rather than a cyclic system.

Reaction of DMeHBP with benzoylacetone in a similar way produces (108). The structure which is indicated for this compound assumes that the primary amine of DMeHBP attacks, in the usual way, at the terminus of the conjugation existing in the enolic form of benzoylacetone.

The p.m.r. spectrum of (108) in deuterochloroform shows, besides the expected aromatic signals, a methine singlet at 4.12τ , an amino methyl singlet at 6.51τ and an imino methyl singlet at 7.90τ . The first two signals are both displaced downfield, relative to their position in (107), presumably, in the usual way, by the phenyl groups, by an amount which decreases with the distance of the proton from the phenyl group. If this downfield shift is also applied to the 7.90τ signal then it suggests that the imino methyl signal in (107) is that occurring at 8.06τ rather than that at 7.90τ , which then must arise from the olefinic methyl group.

Following the general procedure used by Cummings⁵⁸, which could be expected to lead to the rearrangement of (107) in such a way as to form the macrocyclic ligand corresponding to the overall condensation of one mole of acetylacetone with one mole of DMeHBP, (107) was refluxed with nickel(II) acetate in water, which had been acidified to pH 5 with acetic acid. After three hours at reflux the white, potentially sexadentate ligand had completely dissolved to yield a deep red solution. Addition of this solution to a saturated aqueous solution of sodium iodide

resulted in the precipitation of a red crystalline solid. Its observed diamagnetism and visible spectrum showed that it was a square-planar nickel(II) complex (see Chapter Four). Analytical data (Table 3.3) confirmed that it had the expected stoichiometry, namely that shown in structure (109). The molar conductivity in acetonitrile



(109)

was consistent with that normally observed for 1 : 1 electrolytes in this solvent¹²⁵.

In order to establish whether or not the compound was monomeric an attempt was made to obtain its mass spectrum; as its low solubility prohibited a solution molecular weight determination. At 265° the compound was found to have a sufficiently high vapour pressure for a spectrum to be obtained at 70 e.v. The highest peak in this spectrum had an m/e value of 365 corresponding to the mass of the cationic part of the molecule. The fact that the peak at $m/e = 365$ is the highest peak shows that the compound is in fact monomeric, however the fact that a spectrum is

Table 3.3

Analytical and Conductance Data

Cmpd. No.	Compound	C	Found		N (%)	C	Expected		Λ^a cm ² ohm ⁻¹ M ⁻¹
			H				H	N	
109	Ni(ADMeHBP)I	41.2	3.90	16.4		41.4	3.88	17.0	144
110	Ni(ADMeHBP)ClO ₄	43.7	4.05	17.8		43.9	4.11	18.0	138
111	Ni(ADMeHBP)PF ₆	39.8	3.78	16.5		39.9	3.75	16.5	130
112	Ni(HADMeHBP)(PF ₆) ₂	29.9	3.09	11.2		31.1	3.07	12.8	-
113	Cu(DMeHBP)(ClO ₄) ₂	28.6	3.20	16.2		28.4	3.18	16.6	198 ^b

a 10⁻³M in acetonitrile at 22°.

b Conductivity in water.

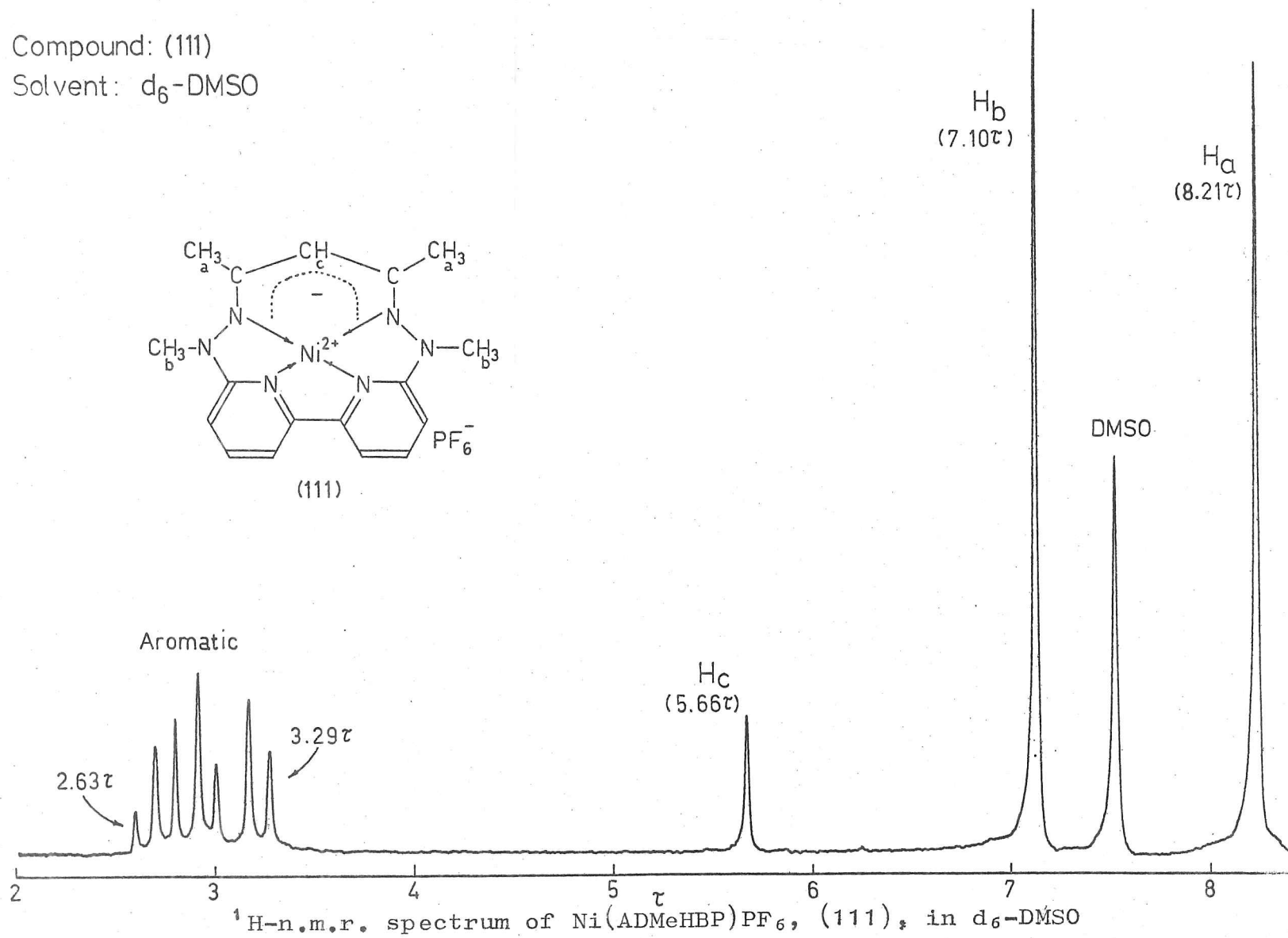
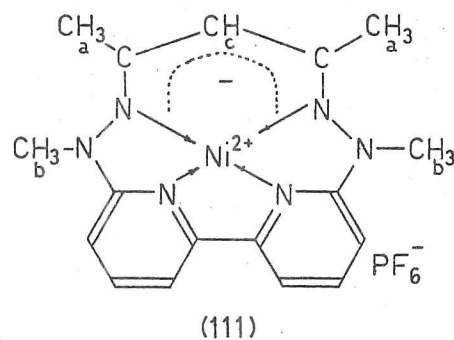
obtained at all is interesting and suggests that the macrocyclic complex may be undergoing reduction in the spectrometer, at this high temperature, to form a neutral species. Cummings⁵⁸ succeeded in obtaining a mass spectrum of the triethylenetetramine analogue of (109) under similar conditions, although the spectrum of that particular compound has as its highest mass peak that corresponding to the parent compound minus hydrogen halide. It should be noted though, that in that particular compound the two secondary amino groups provide a readily available source of protons which would facilitate the loss of the hydrogen halide. The mass spectrum of the 2,3,2-tet analogue of (109), however, shows a parent peak corresponding to the m/e value for the cation, in the same manner as (109)⁶¹.

Despite the low solubility of the macrocyclic species it was possible to record the p.m.r. spectra of (110) and (111) using pulse Fourier Transform techniques at 80 MHz in deuterated dimethylsulphoxide. The spectrum from (111) is shown in Fig. 3.5. The methine proton resonates at much the same chemical shift value, 5.66τ , as it does in the corresponding triethylenetetramine analogue ($\sim 5.3\tau$)⁵⁸. Similarly, the resonance due to the methyl protons on the acetylacetone residue are found to occur at approximately the same values; 8.21τ in (111), $\sim 8.0\tau$ in the triethylenetetramine analogue. The p.m.r. spectrum of the perchlorate salt, (110), also shows similar data to that of the trien analogue. Minor downfield shifts of the signals relative to (111) may indicate slightly less ion pairing in solution.

Figure 3.5

Compound: (111)

Solvent: d_6 -DMSO

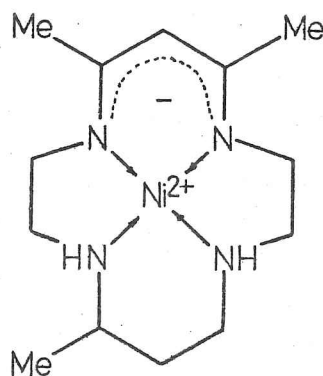


The rate of formation of this cyclic system decreases significantly if the pH is allowed to rise above five. This suggests that acid hydrolysis of one of the imine moieties is responsible for the initiation of the reaction. It then appears that the resulting free amine attacks the acyl group of the bound acetylacetone residue, which, because of the metal template effect, is favourably positioned for attack. Two observations support this suggestion; the first is that no cyclic product is obtained in the absence of a metal, hence supporting the requirement for favourable positioning of the bound acetylacetone residue, so as to avoid preferential recombination with a molecule of free acetylacetone. Secondly, attempts to cyclise the benzoyl-acetone derivative, (108), in the same manner as (107) gave no result. The compound did not react at all. This is reasonable in view of what has been suggested, since attack at the benzoyl carbon atom, which would be necessary for cyclisation, is known from Section 3.1 to be less favourable than attack at an acetyl carbon atom. Hence with (108) the primary amine formed in the initial hydrolysis step will always tend to recombine with the free benzoylacetone, rather than the bound benzoylacetone, thus avoiding cyclisation.

Once the cyclic product has formed the characteristic inertness of the imines in such systems towards hydrolysis⁶ prevents any further hydrolysis.

The final step in the reaction involves the deprotonation of the γ carbon atom in the acetylacetone residue to form

the delocalised π electron system. With compounds (109) to (111) the system is fully deprotonated under the prevailing reaction conditions, that is at pH 5, and it is only necessary to add an appropriate counterion to precipitate the 1 : 1 complex. With the triethylenetetramine system and those derived from 2,3,2-tet and 3,2,3-tet, however, it is necessary to bring the pH to ten before deprotonation occurs,^{58,60,61} and with systems such as (114) precipitation of a deprotonated product does not occur until pH 14 is reached⁵².

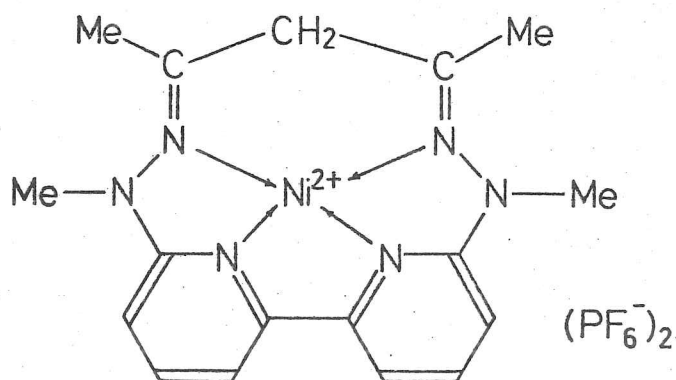


(114)

There seems little point in speculating on the reasons for this wide variation in the acidities of the γ protons in these systems until more information is accrued, however, perhaps it is worth noting that the facility of (109) to so readily stabilise a negative charge on the ligand may be due to delocalisation of that negative charge into the bipyridyl system by way of conjugation through the metal atom. This is borne out by the p.m.r. data from both (110) and (111) where the bipyridyl protons appear approximately 0.6 p.p.m. to higher field than they do in any case where they are part of a neutral co-ordinated ligand system (c.f. Table 2.8).

In accordance with Cummings who has named the ligand derived from acetylacetone and triethylenetetramine, "AT"⁵⁸, the macrocyclic ligand co-ordinated in compound (109) will hereafter be referred to as ADMeHBP.

If instead of precipitating the cyclic compound as its iodide, (109), or perchlorate salt, (110), by filtering the reaction solution into aqueous sodium iodide or sodium perchlorate respectively, hexafluorophosphoric acid is added, one initially obtains the bright red hexafluorophosphate salt, (111), of the co-ordinated uninegative macrocycle. By adding further HPF_6 the red precipitate is converted to a yellow precipitate; a process which is complete by the time the concentration of HPF_6 has reached 2M. The yellow product, (112), $[\text{Ni}(\text{HADMeHBP})(\text{PF}_6)_2]$, proved difficult



(112)

to purify owing to its high acidity and low solubility, however, elemental analysis indicated that protonation had occurred to yield a neutral ligand system.

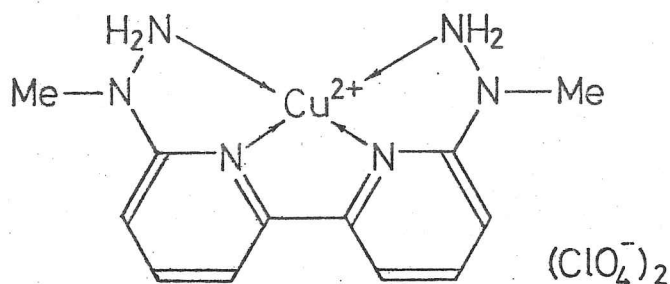
A comparison of the solid state infrared spectra of (111) and (112) in the $\nu \text{ C=N}$ region suggests that protonation

of the charge delocalised system has occurred to yield the structure shown, rather than protonation at one of the tertiary amines. Whereas (111) shows a broad unresolved band between 1605 and 1520 cm^{-1} , (112) shows a well resolved C=N stretching absorption at 1601 cm^{-1} . No band is seen in the spectrum of (112) in the region 2700 to 2250 cm^{-1} where the ν N-H characteristic of protonated tertiary amines generally occurs¹²⁶.

Attempts were made to remove the macrocycle from (110) by reacting it with sodium cyanide, however, the complex proved to be totally inert towards cyanide and the only products isolated were those in which partial metathesis had occurred to yield compounds containing varying amounts of ionic cyanide. This observation is in common with that of Cummings⁵³ who has found that the triethylenetetramine analogue, (31), shows total resistance towards demetallation.

As copper(II) macrocyclic complexes generally undergo demetallation more readily than their nickel(II) counterparts⁵³ an attempt was made to prepare the copper(II) analogue of (110) by reaction of copper(II) acetate, rather than nickel(II) acetate, with (107). Instead of cyclisation though, hydrolysis of both of the Schiff-base linkages of (107) resulted giving only the copper(II) complex of DMeHBP, (113).

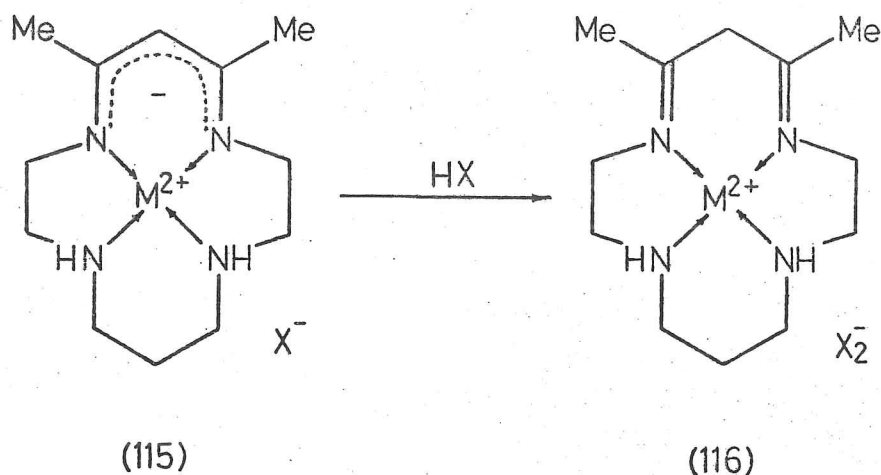
The fact that this cyclisation does not occur in the presence of copper(II) is interesting. As has already been noted in Chapter One, pK_a determinations have shown that



(113)

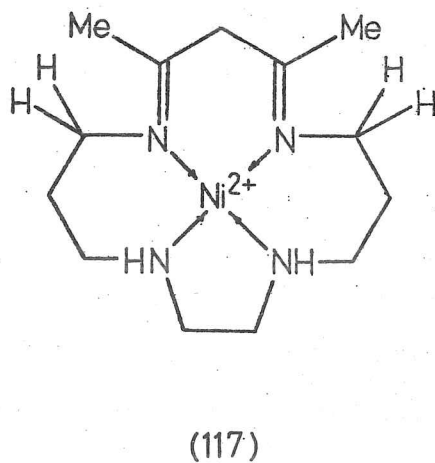
copper(II) prefers co-ordination with the protonated, more flexible, form of the ligand to a greater extent than nickel(II). The suggested reason for this is that the slightly more bulky copper(II) ion forms a less stable system, than nickel(II), when bound to the sterically constrained, deprotonated form of the ligand. As a corollary, it would seem that where a ligand approaches its strain limit, whether this be due to the required geometry or to intraligand repulsions, it will tend to form with nickel(II) whilst not with copper(II). This is evidenced by the fact, for example, that the fourteen membered rings (115) and (116) can be formed around both nickel(II) and copper(II), whereas, the fifteen membered ring, (117), in which there is interaction between the protons and methyl groups on the adjacent six membered rings, will only form about nickel(II) and will not undergo deprotonation to form a more constrained, planar, charge delocalised system⁶¹.

So it appears that in accordance with what was anticipated from molecular models as well as from a study



M = Ni, Cu

of the crystal structure of the triethylenetetramine analogue, (31),⁶³ that the reaction under study forms a macrocyclic system which exists under the influence of



virtually as much internal strain as such systems will tolerate. For this reason a determination of the crystal structure of the ADMeHBP complex would be interesting, so that a measure

of the trapezoidal distortion, in the plane of the nitrogen atoms, and of the departure of the internal angle at the γ carbon atom from 120° (128° in the trien analogue⁶³) can be made.

3.3 Experimental

Aquo-6,6'-bis(N-3,5-dimethylpyrazole)-2,2'-bipyridyl-nickel(II) perchlorate (96) : Acetylacetone (0.16 g) was added to a stirred refluxing suspension of 6,6'-dihydrazino-2,2'-bipyridylnickel(II) perchlorate (0.25 g) in ethanol (40 ml). After one hour the complete dissolution of the reactant marked the completion of the reaction. The green solution was filtered and was reduced in volume to c.a. 5 ml by evaporation under reduced pressure. Addition of diethyl ether precipitated the pure compound as pale green plates (0.28 g, 85%).

Alternatively : 6,6'-Bis(N-3,5-dimethylpyrazole)-
nickel(II) 2,2'-bipyridyl (97), (0.2 g) was suspended in ethanol (25 ml) and the suspension brought to reflux. Hexaaquonickel(II) perchlorate (0.25 g) was added and the suspension refluxed until all of the reactant had dissolved. The pure product was then isolated from the resulting solution in the manner described above. (0.31 g, 89%).

I.R. (nujol) : 3400s, 1604s, 1585m, 1566s, 1490s, 1426s, 1333s, 1310s, 1275m, 1194w, 1182w, 1150 to 1030s, 990m, 925w, 848w, 792s, 715m.

6,6'-Bis(N-3,5-dimethylpyrazole)-2,2'-bipyridyl (97) : Compound (96) (0.2 g) was dissolved in methanol (25 ml) and

the solution brought to reflux. Sodium cyanide (0.075 g) was then added and the solution refluxed for a further fifteen minutes before evaporating to dryness under reduced pressure. The resulting residue was extracted with hot chloroform (2 x 20 ml) and the extract filtered, before evaporating it to dryness under reduced pressure to yield the crude product. Recrystallisation, once, from a mixture of chloroform and petroleum ether gave the pure compound as white needles (0.1 g, 87%).

Alternatively : 6,6'-Dihydrazino-2,2'-bipyridyl (0.4 g) was suspended in refluxing methanol; to the suspension were added acetylacetone (0.4 ml) and glacial acetic acid (2 drops). The suspension was refluxed for one hour before collecting the white precipitate, which formed, by filtration. The precipitate was washed with methanol (2 x 10 ml) and dried in vacuo to give the pure product. (0.6 g, 94%).

P.M.R. (CDCl_3): 1.7 τ to 2.2 τ , m, (6H); 3.95 τ , s, (2H); 7.20 τ , s, (6H); 7.69 τ , s, (6H).

I.R. (nujol) : 1586m, 1578m, 1562s, 1282w, 1143w, 1095m, 1072m, 1041m, 982w, 968s, 793s, 770s, 697s.

Mass Spectrum : m/e of parent ion calculated : 344.

Found : 344.

Dichloro-6,6'-bis(N-3,5-dimethylpyrazole)-2,2'-bipyridylnickel(II) hydrate (98) : 6,6'-Dihydrazino-2,2'-bipyridyl (0.2 g) was suspended in ethanol (20 ml), concentrated aqueous hydrochloric acid (11.5 M) was added until the solution attained pH 2. Acetylacetone (0.13 g) was then

added and the solution refluxed for one hour. The solution was then filtered and reduced in volume, under reduced pressure, to c.a. 5 ml, whereupon bright green crystals of the pure product precipitated. The product was isolated by filtration, washed sparingly with water and dried in vacuo. Yield : (0.15 g, 72%).

I.R. (nujol) : 3400s, 1600m, 1560s, 1339m, 1307m, 1272m, 1196m, 1125s, 1028m, 990m, 919w, 850w, 803s, 796s.

Diaquo-6,6'-bis(N-3-methyl-5-phenylpyrazole)-2,2'-bipyridylnickel(II) perchlorate (99) : Benzoylacetone (0.26 g) and 6,6'-dihydrazino-2,2'-bipyridylnickel(II) perchlorate (0.25 g) were refluxed together in 95% ethanol (40 ml) until, after five hours, complete dissolution of the reactant marked the finish of the reaction. The pure product was isolated from the resulting green solution in the same manner as the acetylacetone derivative, (96). Yield : (0.36 g, 89%).

In the same manner as compound (96), compound (99) was also prepared by the direct interaction of hexaaquonickel(II) perchlorate with 6,6'-bis(N-3-methyl-5-phenylpyrazole)-2,2'-bipyridyl in ethanol.

I.R. (nujol) : 3400s, 1600m, 1581m, 1575m, 1481s, 1435s, 1335m, 1310m, 1279m, 1205m, 1150 to 1030s, 986m, 975m, 930m, 849m, 815m, 793m, 696s.

6,6'-Bis(N-3-methyl-5-phenylpyrazole)-2,2'-bipyridyl (102) : Compound (102) was prepared from its nickel complex, (99) in the same manner as that in which (97) was derived

from (96). Recrystallisation, once, from methanol gave the pure compound.

Alternatively; 6,6'-Dihydrazino-2,2'-bipyridyl (0.3 g) and benzoylacetone (0.45 g) were refluxed together for three hours. The white precipitate which had formed after this time was collected by filtration and recrystallised twice from methanol. This product was found to be 6,6'-bis(N-2,3-dehydro-3-methyl-5-hydroxyphenylpyrazolidine)-2,2'-bipyridyl, (103); it was dissolved in glacial acetic acid (10 ml) and stirred at room temperature for twenty minutes before adding ethanol (90 ml) and allowing the solution to cool overnight in the fridge. At the conclusion of this period the white crystals which had formed were collected by filtration and recrystallised once from methanol to yield the pure compound. (0.6 g, 92%).

P.M.R. (CDCl_3) : 2.31 τ , d of d, $J=8.0$ Hz, $J'=1.0$ Hz, (2H); 2.52 τ , t, $J=8.0$ Hz, (2H); 2.72 τ , s, (10H); 3.22 τ , d of d, $J=8.0$ Hz, $J'=1.0$ Hz, (2H); 3.74 τ , s, (2H); 7.63 τ , s, (6H).

I.R. (nujol) : 1584m, 1565s, 1556s, 1544s, 1194w, 1146w, 1105w, 1071w, 1017w, 992m, 971s, 909w, 810s.

Mass Spectrum : m/e of parent ion calculated : 468.

Found : 468.

6,6'-Bis(N-2,3-dehydro-3-methyl-5-hydroxyphenylpyrazolidine)-2,2'-bipyridyl (103) : This compound was isolated in the manner described above.

P.M.R. (CDCl_3) : 2.4 τ to 2.8 τ , m, (14H); 3.25 τ , d of d, $J=7.0$ Hz, $J'=1.0$ Hz, (2H); 4.05 τ , s, (2H); 6.73 τ ,

d, J=18 Hz, (2H); 7.05 τ , d, J=18 Hz, (2H); 7.94 τ , s, (6H).

I.R. (nujol) : 3400m br, 1572s br, 1309m, 1249w, 1211w, 1156w, 1091w, 1071m, 1034w, 1019w, 977w, 911w, 872m, 796s, 772s.

Mass Spectrum : m/e for parent ion calculated : 504.

Found : 504.

Diisothiocyanato-6,6'-bis(N-3,5-dimethylpyrazole)-2,2'-bipyridylnickel(II) (105) : The corresponding perchlorate salt, (96), (0.2 g) was dissolved in methanol (20 ml). Ammonium thiocyanate (0.08 g) was added to the solution which was then stirred for thirty minutes. The pale blue precipitate was isolated by filtration and purified by washing with methanol (2 x 10 ml). Yield : Quantitative.

I.R. (nujol) : 2099s, 1602s, 1585m, 1569s, 1551m, 1326w, 1305w, 1269w, 1192m, 1174w, 1127m, 1037w, 1017w, 990m, 819m, 811m, 787s.

Diisothiocyanato-6,6'-bis(N-3-methyl-5-phenylpyrazole)-2,2'-bipyridylnickel(II) (106) : The corresponding perchlorate salt, (99), was treated in the same way as described above for the preparation of the acetylacetone analogue, (105). The pale green product was obtained in quantitative yield.

I.R. (nujol) : 2077s, 2061s, 2048s, 2036s, 1600m, 1578m, 1565m, 1309m, 1278m, 1204m, 1175w, 1157w, 1036s, 1002w, 989m, 976m, 846w, 828m, 797s.

Bis(N'-acetylacetone monohydrazone)-6,6'-di-N-methyl-hydrazino-2,2'-bipyridyl (107) : 6,6'-Di-N-methylhydrazino-

2,2'-bipyridyl, (44), (0.45 g) was dissolved in ethanol (60 ml) and the solution brought to reflux. Acetylacetone (0.3 g) was added and the solution refluxed for one hour. As the reaction proceeded the crude product precipitated from the solution; it was isolated by filtration and purified by washing with methanol (2 x 10 ml). Yield : (0.7 g, 93%).

P.M.R. (CDCl₃) : 2.16τ, d, J=8.0 Hz, (2H); 2.41τ, t, J=8.0 Hz, (2H), 3.29τ, d, J=8.0 Hz, (2H); 4.85τ, s, (2H); 6.58τ, s, (6H); 7.90τ, s, (6H); 8.06τ, s, (6H).

I.R. (nujol) : 3170s br, 1610s, 1568s, 1301m, 1277m, 1216w, 1191w, 1120w, 1078w, 1015m, 978m, 874m, 788s.

Mass Spectrum : ^m/e of parent ion calculated : 408.

Found : 408.

Bis(N'-benzoylacetone monohydrazone)-6,6'-di-N-methylhydrazino-2,2'-bipyridyl (108) : 6,6'-Di-N-methylhydrazino-2,2'-bipyridyl, (44), (0.3 g) was dissolved in ethanol (30 ml) and the solution brought to reflux. Benzoylacetone (0.6 g) was added and the solution refluxed for four hours before cooling it and reducing the volume to c.a. 10 ml by evaporation under reduced pressure. The product was collected by filtration, washed with methanol (2 x 5 ml) and dried in vacuo (0.61 g, 93%).

P.M.R. (CDCl₃) : 2.0 to 2.7τ, m, (14H); 3.21τ, d, J=8.0 Hz, (2H); 4.12τ, s, (2H); 6.51τ, s, (6H); 7.90τ, s, (6H).

I.R. (nujol) : 1602s, 1571s, 1549s, 1537m, 1341m,

1284m, 1203m, 1127m, 1042w, 1069m, 1029w, 979m, 894m, 850s, 790s, 758s.

Mass Spectrum : m/e parent ion calculated : 532.

Found : 532.

Ni(ADMeHBP)I (109) : Compound (107) (0.1 g) was suspended in boiling water (15 ml). Nickel(II) acetate (0.08 g) was added and the pH adjusted to five with acetic acid. After refluxing, with stirring, for three hours the ligand had completely dissolved to yield a deep red solution. This reaction solution was filtered into an aqueous solution of sodium iodide (5 g NaI in 15 ml H₂O). The resulting flocculent red precipitate was collected by filtration and washed with water (2 x 10 ml) to give the product (0.1 g, 83%). Further purification for analytical purposes was effected by recrystallisation from a pyridine diethyl ether mixture.

I.R. (nujol) : 1605 to 1520m br, 1160m, 1080w, 1031m, 975w, 812m, 781s.

Mass Spectrum : m/e of parent cation calculated : 365.

Found : 365.

Ni(ADMeHBP)ClO₄ (110) : The reaction solution, prepared in the manner described above for compound (109), was filtered into an aqueous solution of sodium perchlorate. The resulting red precipitate was collected and purified in the same manner as (109).

I.R. (nujol) : 1605 to 1520m br, 1170m, 1090s, 990m, 787s.

P.M.R. (d₆-DMSO) : 2.50 to 3.13 τ , m, (6H); 5.51 τ , s, (1H); 6.97 τ , s, (6H); 8.09 τ , s, (6H).

Ni(ADMeHBP)PF₆ (111) : This compound was prepared in the same manner as (110) using, instead, an aqueous solution of ammonium hexafluorophosphate.

I.R. (nujol) : 1605 to 1520m br, 850s, 788s.

Ni(HADMeHBP)(PF₆)₂ (112) : Hexafluorophosphoric acid was added to the reaction solution, prepared in the manner described above for compound (109). Initially a red precipitate formed, but more acid was added until this was completely yellow in colour. The yellow precipitate was stirred for one hour. It was collected by filtration on an acid washed sinter and washed once with concentrated hydrochloric acid.

I.R. (nujol) : 1601s, 1565s, 1302s, 1169s, 1094w, 1065w, 1046m, 969m, 901m, 900 to 860s br.

6,6'-Di-N-methylhydrazino-2,2'-bipyridylcopper(II) perchlorate (113) : Compound (107) (0.15 g) was suspended in boiling water. The pH was adjusted to five with acetic acid before adding cupric acetate monohydrate (0.072 g). The resulting green solution was refluxed for three hours. At this stage the product was isolated and purified in the same manner as (110). Yield (0.18 g, 96%).

I.R. (nujol) : 3290s, 1630s, 1605m, 1520m, 1310m, 1220s, 1100s br, 1018m, 965w, 786s.

Ni(ADMeHBP)PF₆ (111) : This compound was prepared in the same manner as (110) using, instead, an aqueous solution of ammonium hexafluorophosphate.

I.R. (nujol) : 1605 to 1520m br, 850s, 788s.

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CHAPTER FOUR

SPECTRAL AND MAGNETIC PROPERTIES OF COMPLEXES FORMED FROM 2,2'-BIPYRIDYL DERIVED MULTIDENTATE LIGANDS

4.1 General

During the course of the preparative work described in Chapters Two and Three, the ligand field spectra and magnetic properties of the complexes that were formed provided valuable assistance in their structural characterisation. Additionally, measurement of these properties provides a means of gauging the ligand field strength of the particular ligand array that confronts the metal and hence gives an indication of the actual bonding situation within the inner co-ordination sphere. It is the purpose of this chapter to describe the ligand field properties of those ligands that have been discussed in previous chapters, in terms of the data derived from their spectral and magnetic properties.

Magnetic moments were determined by the Gouy method¹²⁷ on solid state samples (unless otherwise noted) using a Newport Variable Temperature Magnetic Susceptibility Apparatus, and are corrected for inner core and ligand diamagnetism¹²⁷. The apparatus was calibrated over the temperature range 80°K to 300°K using mercury tetrathiocyanatocobaltate(II) which was prepared in the recommended manner¹²⁸ ($10^6 \chi = 16.44 (\pm 0.08)$ c.g.s. units at 293°K, $\theta = + 2^\circ\text{K}$)¹²⁹. Visible spectra were recorded on a Unicam SP700A Spectrometer. Solution spectra were obtained using the solvents specified. Solid state spectra were obtained by transmittance through nujol mulls supported on calcium fluoride plates.

4.2 Spectral and Magnetic Properties of Nickel(II) Complexes

The Ni^{2+} ion has the $3d^8$ outer electron configuration

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4.2 Spectral and Magnetic Properties of Nickel(II) Complexes

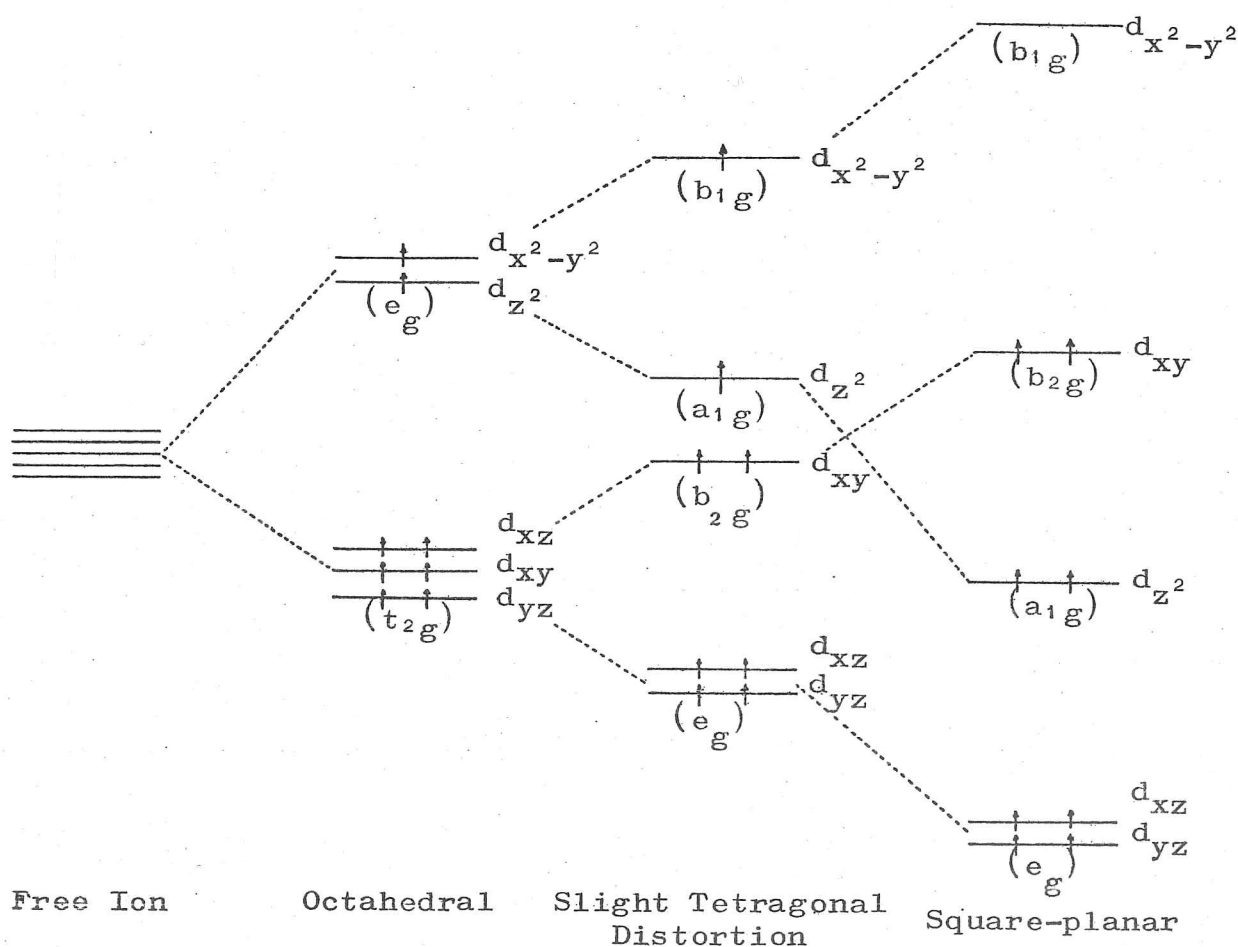
The Ni^{2+} ion has the $3d^8$ outer electron configuration

which gives rise to the singlet and triplet terms (in order of increasing energy) 3F , 1D , 3P , 1G , 1S .¹³⁰ The simple crystal field diagram for the orbital splitting of this ion in octahedral and tetragonal fields (the fields which are relevant to the compounds under discussion) is shown in Fig. 4.1.

It can readily be seen from this diagram that in

Figure 4.1

Orbital Splittings for Ni(II) in Various Ligand Fields

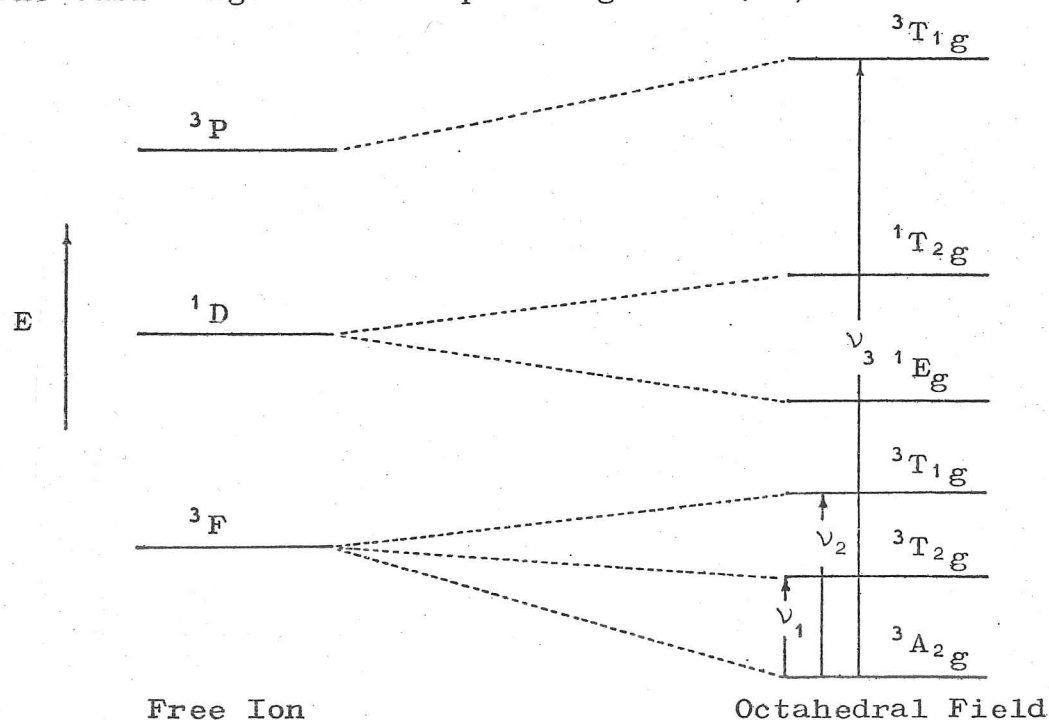


octahedral and in slightly tetragonally distorted octahedral fields two unpaired electrons are present and that the ground state makes no orbital contribution to the magnetic moment. In strong tetragonal fields the electrons pair and the complex becomes diamagnetic.

Under the influence of an octahedral field the low lying free ion terms split in the manner shown in Fig. 4.2. The spin allowed transitions and the energies involved are as follows :¹³⁰

Figure 4.2

The Cubic Ligand Field Splitting of Ni(II) Free Ion Terms



$${}^3A_{2g} \rightarrow {}^3T_{2g} \quad \nu_1 = 10Dq$$

$${}^3A_{2g} \rightarrow {}^3T_{1g}(F) \quad \nu_2 = 15Dq + \frac{15B}{2} - \frac{1}{2}[(15B - 6Dq)^2 + 64(Dq)^2]^{\frac{1}{2}}$$

$${}^3A_{2g} \rightarrow {}^3T_{1g}(P) \quad \nu_3 = 15Dq + \frac{15B}{2} + \frac{1}{2}[(15B - 6Dq)^2 + 64(Dq)^2]^{\frac{1}{2}}$$

These three transitions are generally observed in the regions $7,000$ to $13,000 \text{ cm}^{-1}$, $11,000$ to $20,000 \text{ cm}^{-1}$ and $20,000$ to $28,000 \text{ cm}^{-1}$, respectively and frequently the spin forbidden transitions ${}^3A_{2g} \rightarrow {}^1E_g$ and ${}^3A_{2g} \rightarrow {}^1T_{2g}$ are also observed in the ranges $11,000$ to $15,000 \text{ cm}^{-1}$ and $17,000$ to

22,000 cm^{-1} respectively¹³⁰. The ratio ν_2/ν_1 lies in most cases between 1.5 and 1.7. In the bipyridyl containing complexes of this work ν_3 is never observed due to the overlap of an intense charge transfer band.

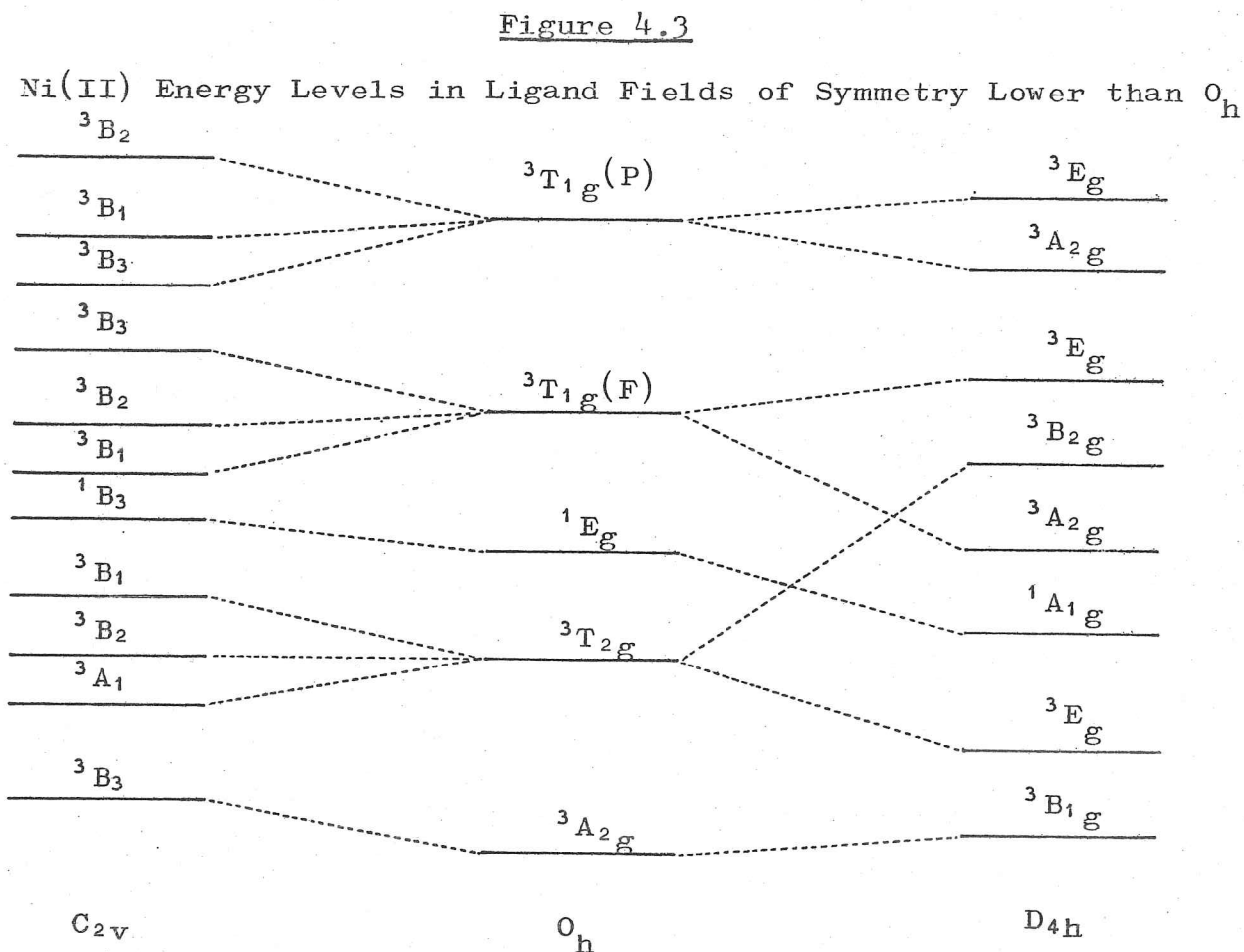
The best fit for the three observed bands using the equations for the transitions enables the values of Dq and B to be obtained for a given complex. Often this is simplified to $10Dq = \nu_1$ and $B = (\nu_2 + \nu_3 - 3\nu_1)/15$. Some representative values of $10Dq$ are given in Table 4.1.

Table 4.1

Compound	$10Dq$	ν_2/ν_1	Reference
$\text{Ni}(\text{EtOH})_6^{2+}$	8,180	1.64	131
$\text{Ni}(\text{MeOH})_6^{2+}$	8,430	1.69	131
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	8,500	1.59	132
$\text{Ni}(\text{NCS})_6^{2-}$	9,600	1.66	133
$\text{Ni}(\text{trien})(\text{H}_2\text{O})_2^{2+}$	10,200	1.70	134
$\text{Ni}(\text{CH}_3\text{CN})_6^{2+}$	10,600	1.65	135
$\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$	10,750	-	138
$\text{Ni}(\text{NH}_3)_6^{2+}$	10,800	1.64	132
$\text{Ni}(\text{en})_3^{2+}$	11,500	-	138
$\text{Ni}(\text{bipy})_3^{2+}$	12,650	1.52	136
$\text{Ni}(1,10\text{-phen})_3^{2+}$	12,700	1.52	136

Geometrical distortions and/or non-identical donor atoms cause departures from O_h symmetry. The orbital

triplets then undergo further splitting so that a large number of transitions are expected in the electronic spectra. Figure 4.3 shows the effect on the energy levels of



substituting two weaker ligands in the cis and trans positions of an octahedron¹³⁷. The largest splittings are observed for a trans distortion and are as much as 2,000 to 3,000 cm^{-1} ,¹³⁸ depending upon the difference in the axial and equatorial fields. Generally the splittings arising from a cis distortion are too small to be resolved. The mean value of the split ν_1 band corresponds approximately to the average ligand field strength.

As stated, octahedral compounds of nickel(II) are always paramagnetic. Although there is no orbital contribution to the magnetic moment from the ground state spin-orbit coupling introduces a slight orbital contribution from the ${}^3T_{2g}$ level, which augments the spin-only value of magnetic moment by about 10%. This additive contribution is proportional to the spin-orbit coupling constant, λ , and inversely proportional to the separation between the levels, $10Dq$. The magnetic moments are given by the relationship :-

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - \frac{4\lambda}{10Dq} \right) \quad (4.1)$$

where λ is, in general, 70 to 80% of the Ni^{2+} free ion value of -315 cm^{-1} .¹⁴⁰

Thus, the deviation of the magnetic moment from the spin only value affords a measure of the ligand field strength or of the spin-orbit coupling constant. Use of this method, though, is severely limited in accuracy by two facts : Firstly, the relative error in the small difference between μ_{eff} and $\mu_{\text{s.o.}}$ is large, often as high as $\pm 20\%$. Secondly, the value of the spin-orbit coupling constant for the complex (if $10Dq$ is being determined) is not known accurately.

Square-planar complexes of nickel(II) are stabilised by strong nickel to ligand covalent bonding (both σ and π bonding) and short nickel to ligand bond lengths are commonly

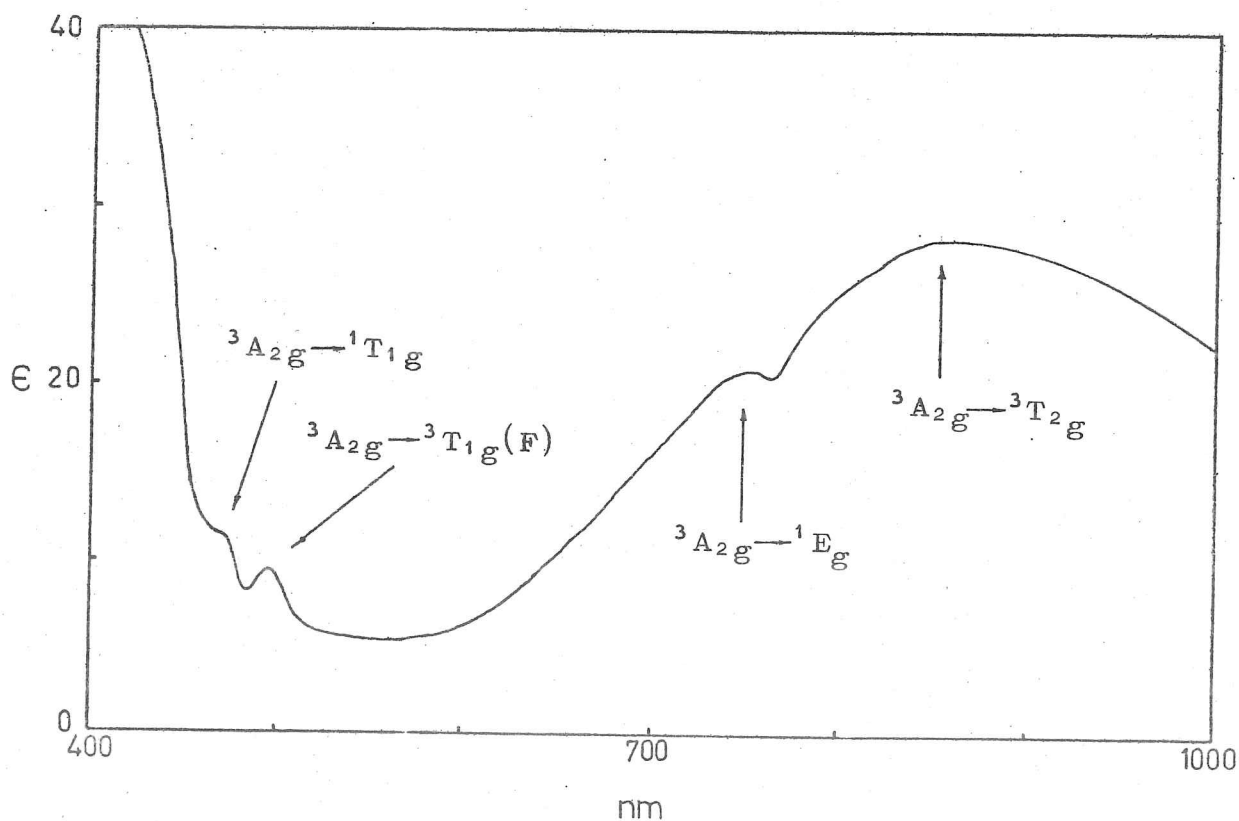
observed. The configuration $e_g^4, a_{1g}^2, b_{2g}^2$ ($^1A_{1g}$ term) is favoured if the separation between the $d_{x^2-y^2}$ and d_{xy} orbitals is greater than $10,000 \text{ cm}^{-1}$.¹³⁷ The compounds are generally orange or red and have a strong spectral band ($\epsilon = 50$ to 500) around $15,000$ to $23,000 \text{ cm}^{-1}$, believed to correspond to the transition $b_{2g} \rightarrow b_{1g}$ ($^1A_{1g} \rightarrow ^1A_{2g}$)¹³⁸.

4.2.1 Nickel(II) Complexes of DHBP and DMeHBP

Although solid samples of $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$, (43), and $\text{Ni}(\text{DMeHBP})(\text{ClO}_4)_2$, (47), are both orange and diamagnetic indicating square-planar geometry, in aqueous solution they both exhibit ligand field spectra characteristic of octahedral complexes (Fig. 4.4). The implication of this

Figure 4.4

Visible Spectrum of $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ in Aqueous Solution



is that two water molecules enter the inner co-ordination sphere to form a six co-ordinate diaquo species. Such square-planar to octahedral interconversion is commonly observed.¹³⁹

On examining the spectra in Fig. 4.4; firstly, no splitting of ν_1 is observed. This suggests that the two water molecules are mutually cis and that the ligand has rearranged to adopt either the cis α or cis β configuration. If the frequency of ν_1 is taken as the average ligand field strength, this gives a value for the DMeHBP complex (Table 4.2) which is a little higher than that for the DHBP complex.

Table 4.2

Electronic Spectral Properties in Aqueous Solution
(Frequency in cm^{-1} \pm 1%, extinction coefficient in parentheses)

Compound	$^3A_{2g} \rightarrow ^3T_{2g}$ (10Dq)	$^3A_{2g} \rightarrow ^1E_g$	$^3A_{2g} \rightarrow ^3T_{1g}$ (F)	$^3A_{2g} \rightarrow ^1T_{1g}$
NiDHBP(ClO ₄) ₂ ^a	11,560(28)	12,970(21)	19,380(6)	20,920(11)
NiDHBP(H ₂ O)Cl ₂ ^b	11,550(30)	12,970(22)	19,380(10)	20,880(15)
NiDHBP(NCS) ₂ ^{c,e}	10,340	12,640	18,450	19,920
NiDMeHBP(ClO ₄) ₂ ^a	11,950(33)	13,000(28)	19,960(17)	21,050(43)
NiDMeHBP(H ₂ O)Cl ₂ ^d	11,850(37)	13,020(13)	19,380(32)	21,140(37)

^a Diamagnetic, ^b $\mu_{\text{eff}} = 3.04$, ^c $\mu_{\text{eff}} = 3.12$, ^d $\mu_{\text{eff}} = 2.97$ B.M.,

^e Solid State

This suggests that DMeHBP is the more basic of the two ligands and is consistent with the observed chemical properties of

the two complexes where $\text{Ni}(\text{DMeHBP})(\text{ClO}_4)_2$ was found to be the less reactive of the two.

The relative magnitude of $10Dq$ for the two ligands is also borne out by the values for the corresponding chloride derivatives (Table 4.2).

The absolute value for $10Dq$ is somewhat higher than the $11,030 \text{ cm}^{-1}$ that is expected empirically using Jørgenson's f and g parameters¹⁴⁵ ($10Dq = f.g \text{ cm}^{-1} \times 10^3$) for a coordination sphere consisting of one bipyridyl, one ethylenediamine and two water molecules. Thus the strained geometry of the ligand does not produce an abnormally low field strength.

The magnetic moments of the two dichloro complexes, whilst indicative of predominantly octahedral geometry, gradually decreased over a period of time suggesting a slow transformation to a square-planar species possibly by loss of water.

The solid state spectrum (the solution spectrum not being obtained for solubility reasons) of $\text{Ni}(\text{DHBP})(\text{NCS})_2$ shows no splitting of ν_1 suggesting a cis configuration. This is in agreement with the determination based on the number of $\nu \text{ C}\equiv\text{N}$ absorptions in the infrared spectrum. The value of $10Dq$ suggested by ν_1 , however, is lower than that expected by comparison with the data for the other compounds in Table 4.2. The NCS^- group lies higher in the spectrochemical series than either H_2O or Cl^- and accordingly should lead to a higher value of $10Dq$, although inversions within

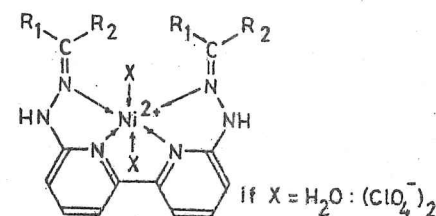
the spectrochemical series are frequently observed¹⁴¹. It is questionable, though, whether it is reasonable to closely compare solid state data with solution data. In previous cases discrepancies have been observed, which have been attributed to lattice packing effects¹⁴².

4.2.2 Nickel(II) 2,2'-Bipyridyl Dihydrazone Complexes

The solid state spectra of the diaquated nickel(II) dihydrazone complexes, (51) to (57), are similar to Fig. 4.4 and agree with the structural assignments already proposed. The data is tabulated in Table 4.3. Comparison of the average ligand field strengths in this series of compounds is interesting since ligand field strength is inversely proportional to the sixth power of the metal-ligand distance¹⁴³. As has already been discussed, the approach of the two terminal donors of the quadridentate hydrazone ligand towards the metal co-ordination sites is expected to be effected by the intramolecular steric repulsions existing between the alkyl groups attached to the imino carbon atoms. This is seen quite clearly by the difference in the value of $10Dq$ associated with those hydrazones that are derived from aldehydes and those derived from ketones. The sterically more crowded ketone derived hydrazones produce fields of the order of $1,300\text{ cm}^{-1}$ less than those of the less crowded aldehyde derivatives. This trend is also seen in the isothiocyanate derivatives, (88) to (94), (Table 4.3) and in the copper(II) complexes, (115) to (121), described in Section 4.3. It is paralleled by the increased departure

Table 4.3

Spectral and Magnetic Data for Compounds of the Type*
(Frequency in $\text{cm}^{-1} \pm 1\%$)



Cmpd. No.	R ₁	R ₂	X	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (10 Dq, ν_1)	${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2)	${}^3\text{A}_{2g} \rightarrow {}^1\text{T}_{2g}$	ν_2/ν_1	μ_{eff}^\dagger
51	CH ₃	H	H ₂ O	11,720	12,950	18,420	20,000	1.57	3.16
52	CH ₃ CH ₂	H	H ₂ O	11,450	13,040	17,890	19,840	1.57	3.14
53	CH ₃ CH ₂ CH ₂	H	H ₂ O	11,880	13,020	17,860	19,960	1.50	3.09
54	CH ₃	CH ₃	H ₂ O	10,470	12,900	16,180	19,920	1.55	3.29
55	CH ₃ CH ₂	CH ₃	H ₂ O	10,460	12,970	15,970	19,800	1.53	3.33
56	CH ₃ CH ₂	CH ₃ CH ₂	H ₂ O	10,420	12,920	15,950	19,960	1.58	3.31
57	CH ₃ CH ₂ CH ₂	CH ₃	H ₂ O	10,560	12,840	16,640	20,000	1.58	3.28
88	CH ₃	H	NCS	10,270	12,280	18,080	20,200	1.76	3.14
89	CH ₃ CH ₂	H	NCS	10,120	12,350	17,420	19,880	1.72	3.11
90	CH ₃ CH ₂ CH ₂	H	NCS	10,200	12,270	18,050	19,230	1.77	3.01
91	CH ₃	CH ₃	NCS	9,350	12,390	15,700	19,080	1.68	3.25
92	CH ₃ CH ₂	CH ₃	NCS	9,430	—	15,840	19,270	1.68	3.27
93	CH ₃ CH ₂	CH ₃ CH ₂	NCS	9,220	—	15,850	19,680	1.72	3.28
94	CH ₃ CH ₂ CH ₂	CH ₃	NCS	9,400	—	15,770	19,190	1.68	3.25

* Solid state data.

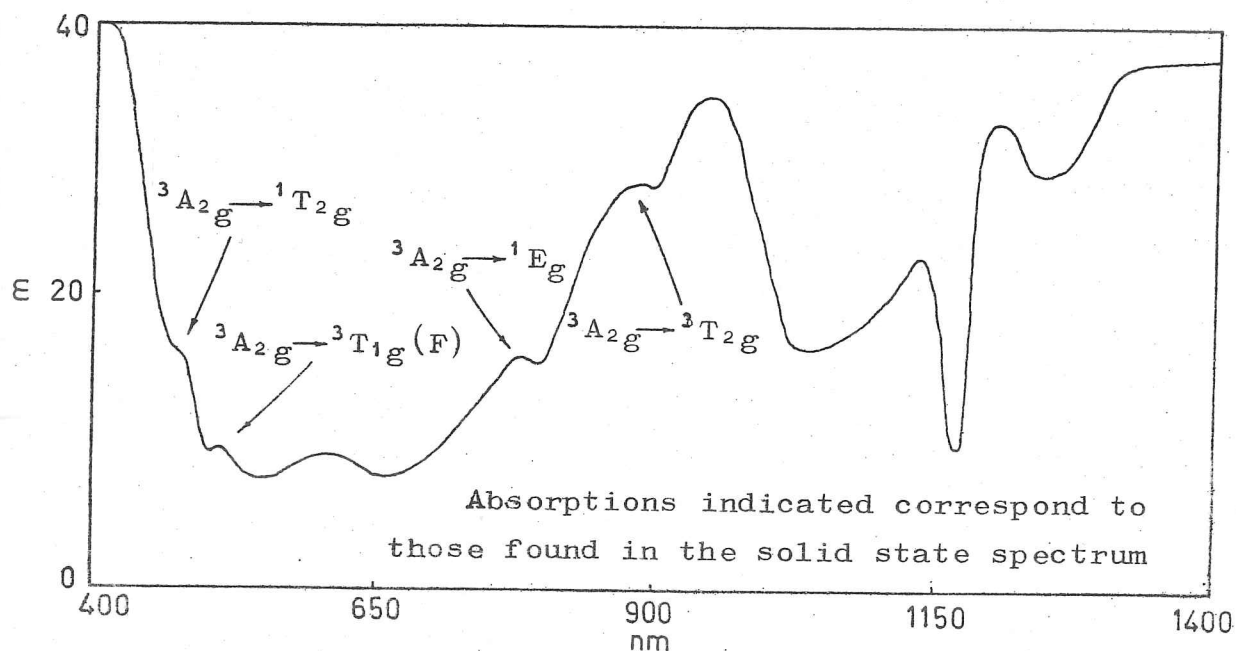
† B.M. at 22°

of the magnetic moment of the ketone derived compounds from the spin-only value, in accordance with equation 4.1.

When recorded in aqueous solution the spectra of (51) to (57) show several absorptions in the range 20,000 to 7,000 cm^{-1} superimposed upon the spectrum exhibited by the compound in the solid state (Fig. 4.5 is typical of the series). It is possible that these absorptions originate

Figure 4.5

Visible Spectrum of Compound (51) in Aqueous Solution



from an equilibrium concentration of a five co-ordinate species, as five co-ordinate nickel(II) complexes are known to exhibit similar low energy absorptions, although their origin is not well understood¹⁴⁴. Generally five co-ordinate nitrogen donor complexes are high spin and have magnetic moments in the range 3.2 to 3.4 B.M. The solution (methanol) magnetic moment of the acetaldehyde derived hydrazone, (51),

was determined and found to be 3.25 B.M. in contrast to its solid state value of 3.16 B.M. Although this is barely beyond the bounds of experimental error it is a shift in the direction expected due to the presence of a five co-ordinate species, perhaps more importantly though, it precludes the existence of any significant octahedral to square-planar equilibrium. It was verified from the spectra of the corresponding zinc complexes, (72) to (78), that none of these absorptions originate from within the ligand.

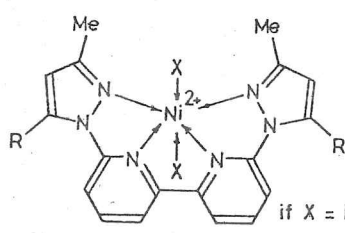
4.2.3 Nickel(II) 2,2'-Bipyridyl Bis(pyrazole) Complexes

This series of complexes showed spectra both in the solid state and in solution (methanol) indicative of six co-ordination with two monodentate ligands disposed *cis* to one another. The data is tabulated in Table 4.4. The

Table 4.4

Spectral and Magnetic Properties

(Frequency in $\text{cm}^{-1} \pm 1\%$, ϵ in parentheses)



	R	X
(96)	Me	H ₂ O
(99)	Ph	H ₂ O
(98)	Me	Cl
(105)	Me	NCS
(106)	Ph	NCS

Cmpd. No.	${}^3A_2g \rightarrow {}^3T_2g$ (10Dq)	${}^3A_2g \rightarrow {}^1E_g$	${}^3A_2g \rightarrow {}^3T_1g(F)$	${}^3A_2g \rightarrow {}^1T_2g$	ν_2/ν_1	μ_{eff}^\dagger
96	10,380(26)	12,850(8)	15,720 (5)	21,500(6)	1.51	3.21
99	10,410(24)	12,280(8)	16,230 (4)	21,510(7)	1.56	3.11
98	10,380(27)	12,770(8)	15,390 (5)	21,600(6)	1.48	3.18
105*	9,970	12,590	17,670	-	1.77	3.17
106*	10,250	12,260	17,450	-	1.70	3.09

* Solid state data

† B.M. at 22°

ligand field strengths are approximately the same as those observed for the ketone derived hydrazones of the previous section, which was to be expected in view of their structural similarity. The magnetic data is consistent with the proposed octahedral formulation.

4.2.4 Nickel(II) Macrocyclic Complexes

These complexes, (109) to (112), are all diamagnetic and show a single absorption band in the visible region of the spectrum. This is in accordance with what is normally observed for square-planar nickel(II). There is no indication of any octahedral species, formed through solvation, in equilibrium with the square-planar complex. This is a property frequently encountered with macrocyclic complexes, in contrast to similar open chain species⁵⁵.

Table 4.5

Electronic Spectral Data

(Frequency in $\text{cm}^{-1} \pm 1\%$, ϵ in parentheses)

Cmpd. No.	Compound	$^1A_1g \rightarrow ^1A_2g$	Solvent
109	Ni(ADMeHBP)I	20,080 (227)	CH ₃ CN
110	Ni(ADMeHBP)ClO ₄	20,100 (241)	CH ₃ CN
111	Ni(ADMeHBP)PF ₆	20,080 (253)	CH ₃ CN
112	Ni(HADMeHBP)(PF ₆) ₂	23,200 -	Solid state

4.3 Copper(II) Complexes of 2,2'-Bipyridyl Dihydrazone Ligands

In order to verify the ligand field determinations

made on the nickel(II) complexes of the dihydrazone ligands the corresponding series of copper(II) complexes, (115) to (121), was prepared. This was achieved by addition of the appropriate ligand to a methanolic solution of hexaaquo-copper(II) perchlorate. The resulting greenish-blue complexes were 2:1 electrolytes. This was indicated by their molar conductivity⁷⁶. Analytical data indicated that they were 1:1 metal to ligand complexes in varying degrees of hydration (Table 4.6).

Copper(II) has the outer sphere configuration $3d^9$. The ground term of an octahedrally co-ordinated copper(II) ion is ${}^2E_g(t_{2g}^6, e_g^3)$. Application of a tetragonal distortion, which may originate from the Jahn-Teller effect, if not through the bonding pattern, results in a partial loss of the degeneracy of the system. This splitting is shown in Fig. 4.6.

Figure 4.6

Term Splitting Diagram for a d^9 System

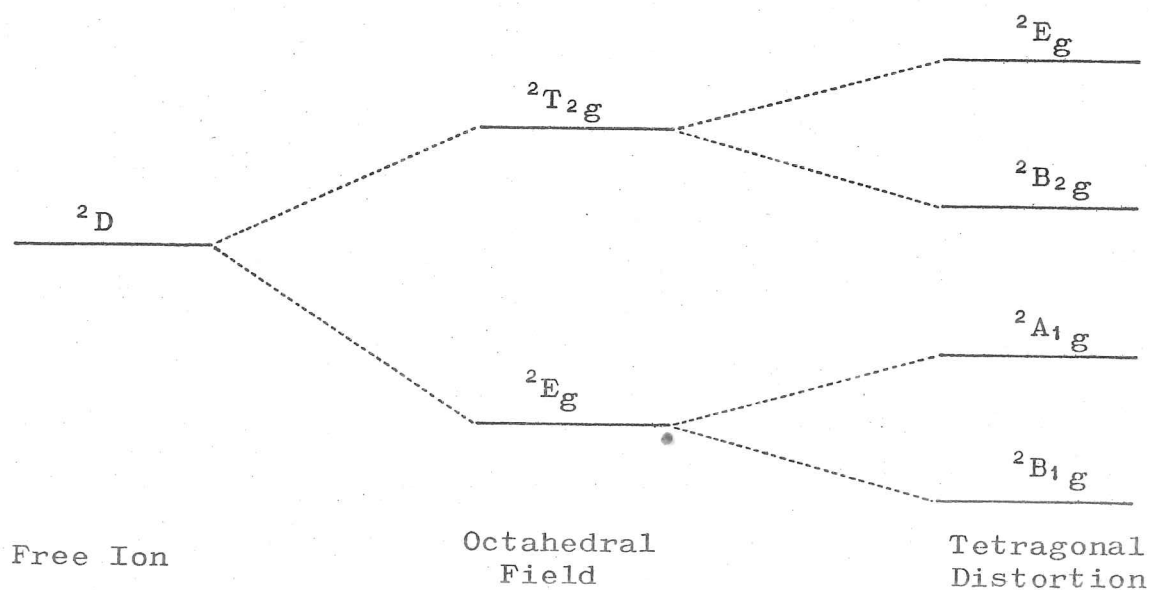
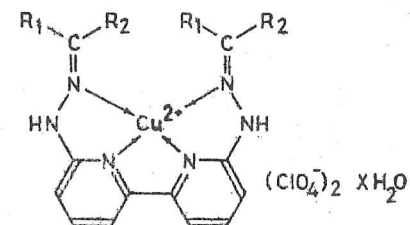


Table 4.6

Analytical and Conductance Data
for Compounds of the Type :



Cmpd. No.	R ₁	R ₂	X	C	<u>Found</u> H	N (%)	C	<u>Expected</u> H	N	Δ^* cm ² ohm ⁻¹ M ⁻¹
115	CH ₃	H	0	31.2	3.03	15.6	31.7	3.04	15.8	203
116	CH ₃ CH ₂	H	0	34.1	3.53	14.9	34.4	3.61	15.0	174
117	CH ₃ CH ₂ CH ₂	H	0	36.8	4.15	14.5	36.8	4.12	14.3	161
118	CH ₃	CH ₃	2	32.4	3.80	14.2	32.3	4.07	14.1	172
119	CH ₃ CH ₂	CH ₃	1	35.8	4.08	13.9	35.7	4.33	13.9	166
120	CH ₃ CH ₂	CH ₃ CH ₂	0	39.1	4.51	13.7	39.1	4.59	13.7	162
121	CH ₃ CH ₂ CH ₂	CH ₃	2	36.9	4.72	12.8	36.9	4.96	12.9	157
122	Cu(DHBP)(ClO ₄) ₂		-	24.8	2.88	17.6	25.1	2.53	17.6	**

* 10⁻³ M in methanol at 22°

** Too insoluble

The result of this is that copper(II) complexes normally give rise to a single absorption band in the visible region of the spectrum at about $16,000 \text{ cm}^{-1}$. The band can sometimes be resolved into two or three components originating from the transitions apparent from Fig. 4.6. However, generally these components are not resolved¹⁴⁶. The extinction coefficient of the absorption normally varies from 20 to 50 for centrosymmetric molecules to several hundred for acentric molecules.

The spectra of the complexes, (115) to (121), are typical of that shown in Fig. 4.7. The frequency of the absorption together with its extinction coefficient is given in Table 4.7.

Figure 4.7

Visible Spectrum of Compound (115) in Methanol

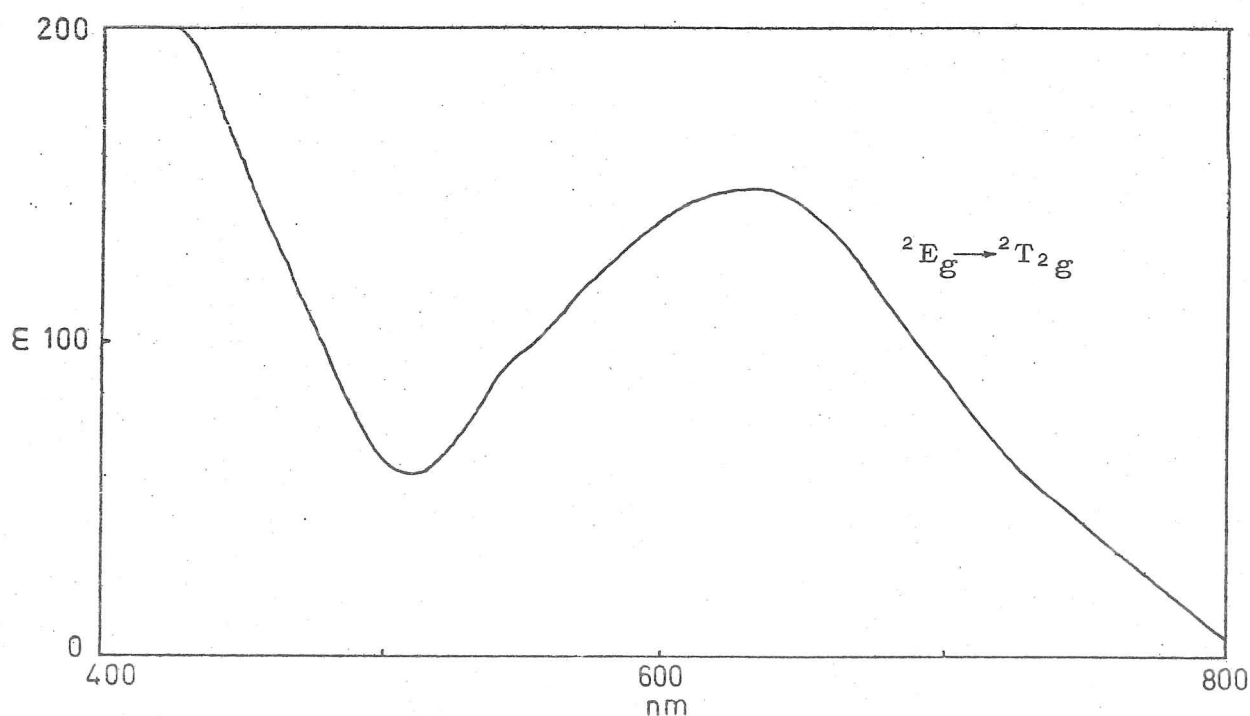


Table 4.7

Electronic Spectra of Copper(II) Complexes in Methanol
(Frequency in $\text{cm}^{-1} \pm 1\%$, ϵ in parentheses)

Cmpd. No.	Derived From	${}^2E_g \rightarrow {}^2T_{2g}$ (10Dq)	$\nu_{\text{calc.}}^{**}$	$\mu_{\text{eff}}^{\dagger}$
115	Acetaldehyde	15,870 (145)	15,820	1.90
116	Propionaldehyde	15,850 (109)	15,440	1.86
117	Butyraldehyde	15,850 (102)	16,040	1.91
118	Acetone	14,370 (93)	14,130	1.88
119	Methyl Ethyl Ketone	14,420 (96)	14,120	1.89
120	Diethyl Ketone	14,580 (90)	14,040	1.85
121	n-Propyl Methyl Ketone	14,510 (112)	14,260	1.87
122	DHBP*	17,890	15,590	1.84
113	DMeHBP*	17,700	16,110	1.83

* Solid state spectra.

** See text.

† B.M.
(at 22°)

By use of Jørgenson's parameter¹⁴⁵ ($g = 12.0$ for Cu^{2+} , 8.9 for Ni^{2+}) the value of 10Dq for the copper(II) complexes, (115) to (121), may be predicted from the value of 10Dq determined for the nickel(II) complexes. These expected values have been calculated and are compared with the observed values in Table 4.7. In all cases they agree to within 5%. This good correlation between ligand field strengths suggests that the copper(II) complexes are almost certainly solvated in solution and hence six co-ordinate. It is not

clear from the analytical data whether the complexes are four or six co-ordinate in the solid state.

Magnetically dilute, octahedral copper(II) complexes generally show magnetic moments corresponding to one unpaired electron, augmented by an orbital contribution from the upper orbital triplet, by spin-orbit coupling. Their magnetic moments are given by the equation¹⁴⁰ :

$$\mu_{\text{eff}} = \mu_{\text{s.o.}} \left(1 - \frac{2\lambda}{10Dq} \right) \quad (4.2)$$

where, in general, λ is 70 to 80% of its copper(II) free ion value of -830 cm^{-1} . All the complexes in Table 4.7 have magnetic moments within the range predicted by this relationship.

The copper complexes of DHBP and DMeHBP, (122) and (113), were isolated as their perchlorate salts by reaction of the free ligand with hexaaquocopper(II) perchlorate in methanol. They are 1:1 metal to ligand complexes with no tendency to hydrate in the solid state. The $\nu \text{ Cl-O}$ absorption in the infrared spectrum shows no splitting which would have suggested co-ordination of the perchlorate counterion. In view of this, it seems likely that the complexes are square-planar. Both compounds exhibit magnetic moments above 1.8 B.M. at room temperature (Table 4.7) and it was verified that these were essentially constant down to 80°K ; showing that there is no significant copper-copper interaction in this temperature range.

The electronic solid state spectra of $\text{Cu}(\text{DHBP})(\text{ClO}_4)_2$ and $\text{Cu}(\text{DMeHBP})(\text{ClO}_4)_2$ show a single band at c.a. $17,800 \text{ cm}^{-1}$. this does not correlate with the $10Dq$ value expected from the determination of $10Dq$ in the corresponding octahedral (through solvation) nickel(II) complexes and further suggests that the stereochemistry in these cases may well be square-planar rather than octahedral.

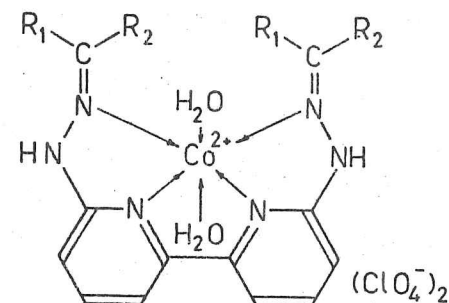
4.4 Cobalt(II) Complexes of 2,2'-Bipyridyl Dihydrazone Ligands

The cobalt(II) complexes of the series of dihydrazone ligands were prepared by the reaction of the appropriate free ligand with hexaaquocobalt(II) perchlorate in methanol. The orange-brown complexes thus obtained were air stable. Analytical data indicated the stoichiometry; $\text{Co}(\text{ligand})-(\text{H}_2\text{O})_2(\text{ClO}_4)_2$ and the conductivity measurements (Table 4.8) were in accord with a 2:1 electrolyte⁷⁶. The nature of the inner co-ordination sphere was determined by a study of the spectral and magnetic properties of the complexes. These were found to be consistent (vide infra) with a spin-free octahedral formulation involving co-ordination of the two water molecules and the ligand. An alternative means of synthesising this series of complexes involved initial formation of $\text{Co}(\text{DHBP})(\text{NCS})_2$, (130), followed by reaction with the appropriate acyl compound, in a fashion analogous to the method by which the corresponding nickel(II) complexes, (51) to (57), were prepared.

The ligand field spectrum of octahedral cobalt(II)

Table 4.8

Analytical and Conductance Data
for Compounds of the Type :



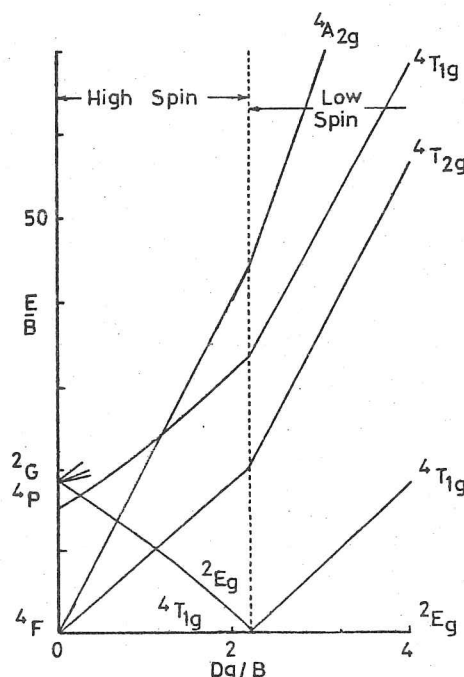
Cmpd. No.	R ₁	R ₂	C	Found		N (%)	C	Expected		* cm ² ohm ⁻¹ M ⁻¹
				H				H	N	
123	CH ₃	H	30.0	3.63	14.7	29.9	3.59	14.9		182
124	CH ₃ CH ₂	H	33.1	4.29	14.3	32.6	4.10	14.2		185
125	CH ₃ CH ₂ CH ₂	H	35.3	5.08	13.0	35.0	4.56	13.6		184
126	CH ₃	CH ₃	33.2	4.50	14.2	32.6	4.10	14.2		179
127	CH ₃ CH ₂	CH ₃	35.4	4.99	13.7	35.0	4.56	13.6		193
128	CH ₃ CH ₂	CH ₃ CH ₂	37.1	4.89	12.9	37.2	4.99	13.0		191
129	CH ₃ CH ₂ CH ₂	CH ₃	37.4	5.02	13.2	37.2	4.99	13.0		186
130	Co(DHBP)(NCS) ₂		36.7	3.10	28.8	36.8	3.09	28.6		**

* 10⁻³ M in methanol at 22°

** Too insoluble

(d^7 , 4F free ion ground term) complexes generally consists of two principal bands assigned in accordance with the term splitting diagram shown in Fig. 4.8.

Figure 4.8
Simplified Tanabe-Sugano Diagram for Cobalt(II) (d^7)



A band between 8,000 and 10,000 cm^{-1} ($\epsilon = 1$ to 10) is normally assigned to the $^4T_{1g}(F) \rightarrow ^4T_{2g}(\nu_1)$ transition¹⁴⁷. In addition a multiple band is generally observed near 20,000 cm^{-1} which is assigned as the $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)(\nu_3)$ transition mixed in with spin forbidden transitions to doublet terms. The $^4T_{1g}(F) \rightarrow ^4A_{2g}(\nu_2)$ transition is generally weak in intensity owing to the fact that it is formally a two electron transition. The assignment of this band is facilitated if ν_1 is observed since the transition energy ratio ν_2/ν_1 is almost invariably in the range 2.0 to 2.2 within the limits of Dq/B values found for octahedral cobalt(II).

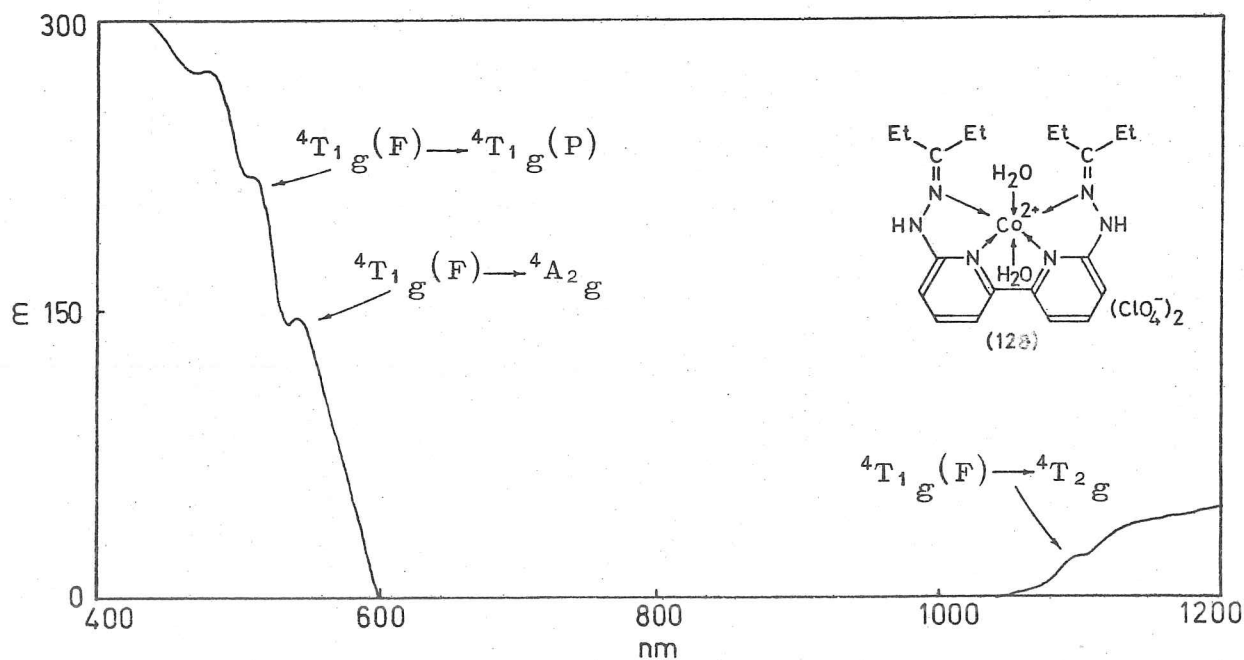
Approximate values of Dq and B may be obtained from

the more sensitive ν_3/ν_1 ratio. Considered in conjunction with the appropriate Tanabe-Sugano diagram, (Fig. 4.8) (or better, Figures A III 7 and A III 9 in reference 138) this gives the corresponding ratios of Dq/B and of E (the energy of the transition ν_3) to B , from which Dq and B may be evaluated.

A typical cobalt(II) dihydrazone solution spectrum (methanol) is shown in Fig. 4.9. The multiple band expected

Figure 4.9

Visible Spectrum of Compound (128) in Methanol



at c.a. $20,000\text{ cm}^{-1}$ occurs as a series of shoulders on the tail of the metal to ligand charge transfer band. The effect of this charge transfer band, besides making the frequency of the absorption maxima of the shoulders difficult to determine, is probably to shift the position of the maxima and to enhance the intensity of the peaks. At c.a. $9,000\text{ cm}^{-1}$ there is a peak which may be due to the $4T_{1g}(F) \rightarrow 4T_{2g}$ transition, but again this appears as a shoulder. The origin

of the broad area of absorption below $9,000\text{ cm}^{-1}$ is unknown, although, as in the case of the nickel(II) spectra, of which it is reminiscent, it may be due to a species of lower symmetry formed by dissociation in solution. The data for the other members of the series of complexes is tabulated in Table 4.9.

The ratio between the lowest energy component of the multiple band and the shoulder at c.a. $9,000\text{ cm}^{-1}$ was always found to be c.a. 2.06. This suggested that the $9,000\text{ cm}^{-1}$ band was due to the ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ transition and that the low energy component of the multiple band was the ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition enhanced by intensity stealing from the main band. Of the other two components of the multiple band one is probably a spin forbidden transition and the other the ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition.

By determining the value of B using both possible ratios of ν_3/ν_1 a much better agreement with the B value normally obtained (approximately 80% of the free ion value of $1,120\text{ cm}^{-1}$)¹⁴⁷ is found by assigning the lower energy band as ν_3 .

For all compounds the ratio ν_3/ν_1 falls within the limits 2.21 ± 0.04 which leads to a value of $900 \pm 40\text{ cm}^{-1}$ for B and $11,430 \pm 700\text{ cm}^{-1}$ for $10Dq$. Relating this back to the $10Dq$ values determined for the corresponding nickel(II) complexes, (51) to (57), (Table 4.3), by use of Jørgenson's parameters¹⁴⁵ ($\text{Co}^{2+} : g = 9.3$, $\text{Ni}^{2+} : g = 8.9$) the range $10,270$ to $11,610\text{ cm}^{-1}$ is spanned, which correlates quite reasonably. Similarly relating it to the copper(II) $10Dq$

Table 4.9

Spectral* and Magnetic Properties of Cobalt(II) Complexes
(Frequency in $\text{cm}^{-1} \pm 1\%$)

Cmpd. No.	Derived From	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}$ ν_1	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ ν_2	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ ν_3	Not Assigned	ν_3/ν_2	ν_2/ν_1	μ_{eff}^\dagger
123	Acetaldehyde	9,340	19,270	20,700	21,980	2.22	2.06	4.69
124	Propionaldehyde	9,090	18,940	20,280	21,600	2.23	2.08	4.74
125	Butyraldehyde	9,130	18,690	20,080	21,370	2.20	2.05	4.60
126	Acetone	9,050	18,660	20,040	21,460	2.21	2.06	4.70
127	Methyl Ethyl Ketone	9,070	18,800	19,960	21,320	2.20	2.07	4.76
128	Diethyl Ketone	9,040	18,620	19,880	21,140	2.20	2.06	4.67
129	n-Propyl Methyl Ketone	8,990	18,520	19,780	21,060	2.20	2.06	4.75
130	DHBP	-	-	-	-	-	-	4.79

* Solution Spectra in Methanol

† B.M. at 22°

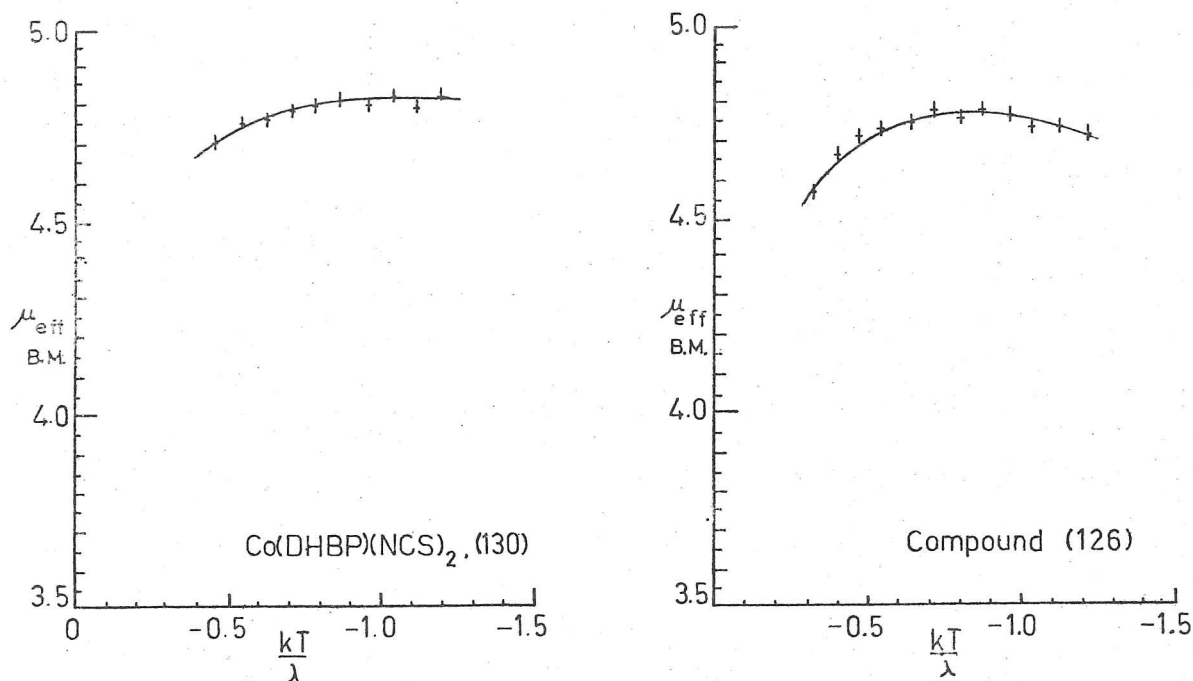
values for the corresponding compounds, (115) to (121), (Table 4.7), the range 13,850 to 15,650 cm^{-1} is spanned ($\text{Cu}^{2+} : g = 12.0$). Again this is quite a good correlation.

Since the ground state for octahedral cobalt(II) is an orbital triplet which will undergo splitting into a number of thermally accessible J states through spin-orbit coupling, one expects the magnetic moment of octahedral complexes to be temperature dependent. The absolute value of the magnetic moment does not unambiguously distinguish between tetrahedral and octahedral stereochemistry; complexes of both types can have moments of about 4.6 B.M. at room temperature¹⁴⁰. Tetrahedral complexes, however, have an orbital singlet ground term and hence the magnetic moment, corrected for temperature independent paramagnetism, is temperature independent. Thus by observing the variation of the magnetic moment with temperature, the stereochemistry may be deduced. Square-planar cobalt(II) complexes are usually spin-paired¹⁴⁰ and have moments corresponding to a single unpaired electron plus a temperature independent orbital contribution and are thus readily distinguished by the absolute value of the moment.

The cobalt(II) dihydrazone complexes, (123) to (129), have room temperature magnetic moments in the range 4.60 to 4.75 B.M. (Table 4.9). The moment of one compound, (126), was recorded in the range 300°K to 80°K and was found to vary from 4.70 ± 0.03 to 4.56 ± 0.03 B.M. through a maximum of 4.77 B.M., over that temperature range. This temperature variance is plotted against KT/λ in Fig. 4.10 and compares

Figure 4.10

Temperature Dependence of μ_{eff} for Compounds (130) and (126)



closely with the theoretical curve, seen for example in reference 148, for octahedral cobalt(II) with a ligand field that is approaching the strong field limit. A plot of the reciprocal molar susceptibility (corrected for the diamagnetism of the ligands and inner core) against temperature, gives θ as -4°K .

The cobalt(II) complex of DHBP, (130), was prepared as its diisothiocyanate derivative by reaction of the free ligand with diisothiocyanatotetrapyridinecobalt(II). Analytical data shows it to have the stoichiometry $\text{Co}(\text{DHBP})(\text{NCS})_2$. Owing to its low solubility it was only possible to obtain a solid state electronic spectrum and from this the peaks (which all appear as shoulders) could not be

sufficiently well resolved to make any definite assignments. Magnetically, however, the compound shows a temperature variable moment, $\mu_{\text{eff}} = 4.79 \pm 0.03$ at 300°K to 4.61 ± 0.03 at 93°K , and $\theta = -8^\circ\text{K}$, indicative of octahedral stereochemistry (Fig. 4.10). The infrared spectrum shows two $\nu \text{C}\equiv\text{N}$ bands suggesting mutually cis isothiocyanate groups.

4.5 Experimental

Analytical grade hexaaquocopper(II) perchlorate and hexaaquocobalt(II) perchlorate were used without further purification. Diisothiocyanatotetrapyridinecobalt(II) was prepared according to the published procedure¹¹⁵.

6,6'-Bis(N'-hydrazono)-2,2'-bipyridylcopper(II) perchlorate complexes (115) to (121) : The appropriate dihydrazono ligand (0.2 g) was dissolved in methanol (30 ml). Hexaaquocopper(II) perchlorate (one molar equivalent) dissolved in methanol (5 ml) was added dropwise to the stirred, refluxing solution over a period of ten minutes. On completion of the addition the solution was refluxed for a further fifteen minutes before cooling and filtering it. To the stirred filtrate diethyl ether was added until precipitation of the product was complete. Recrystallisation, once, from ethanol gave the pure product (>80%).

6,6'-Dihydrazino-2,2'-bipyridylcopper(II) perchlorate (122) : 6,6'-Dihydrazino-2,2'-bipyridyl (0.3 g) was dissolved in refluxing methanol (40 ml). Addition of hexaaquocopper(II) perchlorate (0.6 g) dissolved in methanol (5 ml) dropwise over a period of ten minutes led to the

precipitation of a fine grey crystalline product. This was collected by filtration and washed with methanol (2 x 10 ml) to yield the pure product (0.6 g, 96%).

I.R. (nujol) : 3394s, 3306s, 3246m, 3188m, 1621s, 1582m, 1302w, 1278w, 1215m, 1175 to 1050s br, 933w, 797s.

6,6'-Bis(N'-hydrazone)-2,2'-bipyridylcobalt(II) perchlorate complexes, (123) to (129) : These complexes were prepared from hexaaquocobalt(II) perchlorate and the free ligand by a procedure analogous to that described for the corresponding copper(II) complexes, (115) to (121). As a precaution against oxidation solutions of the complexes were handled under nitrogen. Yield : (>80%).

Diisothiocyanato-6,6'-dihydrazino-2,2'-bipyridylcobalt(II) (130) : Diisothiocyanatotetrapyridinecobalt(II) (0.66 g) was suspended in degassed acetonitrile which had been brought to reflux under an atmosphere of nitrogen. 6,6'-dihydrazino-2,2'-bipyridyl (0.3 g) was added and the resulting suspension stirred for twenty minutes before filtering to separate the pale brown crystalline material which had precipitated. The precipitate was washed with acetonitrile (2 x 10 ml) before drying in vacuo to give the pure product (0.52 g, 96%).

I.R. (nujol) : 3330s, 3305 to 3130s br, 2114s, 2095s, 1621s, 1604s, 1574s, 1409m, 1267m, 1184m, 1167w, 1124m, 1023m, 1007m, 810w, 789s.

CHAPTER FIVE

THE OXIDATIVE DENITROGENATION OF
DICHLORO-6,6'-DIHYDRAZINO-2,2'-BIPYRIDYLIRON(II)

5.1 Preparation of Dichloro-6,6'-dihydrazino-2,2'-bipyridyl-iron(II)

As a prelude to the study of macrocyclic complexes containing the biologically interesting element iron, the possibility of synthesising an iron(II) complex of the linear, quadridentate DHBP was considered. The formation of a complex of this type would enable its reactivity and potential for cyclisation to be studied and at the same time allow techniques for the synthetically more difficult introduction of iron(II) into macrocyclic systems to be developed.

The primary difficulty associated with preparing iron(II) amine complexes is related to the great tendency that iron has for forming hydroxo species, which will then oxidise to various oxo species in the presence of traces of water¹⁴⁹. This behaviour is observed with simple amines such as ammonia, linear polydentate amines such as trien and also with macrocyclic amine ligands. Thus, before attempting to introduce iron(II) into macrocyclic systems careful consideration was given to the source of iron(II) that was to be used. The required compound should be a monomeric, substitutionally labile, anhydrous iron(II) compound. Diiodotetracarbonyliron(II) was considered initially, but on examining the compound it was found that the carbonyl groups were so labile that the complex underwent spontaneous decomposition in the solid. This, together with the fact that the product is an intractable iodide

bridged polymer¹⁵⁰ rendered it unsuitable. Dichlorotetrapyridineiron(II)¹⁵¹, however (as well as the dibromo¹⁵² and diisothiocyanato¹¹⁵ derivatives) can readily be prepared as an anhydrous compound free from iron(III), and occurs as a stable, but substitutionally labile monomer. This substance was prepared according to published procedures¹⁵¹ and was used in the initial metallation studies.

The interaction of DHBP and dichlorotetrapyridine-iron(II) in acetonitrile (from which oxygen and water had been thoroughly removed, in the recommended manner¹⁵³) under an atmosphere of dry nitrogen, precipitated a fine orange-red crystalline compound, (131), in 90% yield. Analytical data indicated that it had the stoichiometry Fe(DHBP)Cl₂ (Table 5.1). The infrared spectrum (solid state) (Fig. 5.3)

Table 5.1
Analytical Data

Cmpd. No.	Compound	C	<u>Found</u>		N (%)	C	<u>Expected</u>	
			H				H	N
131	Fe(DHBP)Cl ₂	34.9	3.54	24.3	35.0	3.53	24.5	
132	Fe(DHBP)(NCS) ₂	37.1	3.41	28.9	37.1	3.12	28.9	
133	Fe(DHBP)Br ₂ *	28.8	2.64	15.4	27.8	2.80	19.5	
134	Fe(DMeHBP)Cl ₂	38.9	4.31	22.5	38.8	4.35	22.7	

* Partially denitrogenated

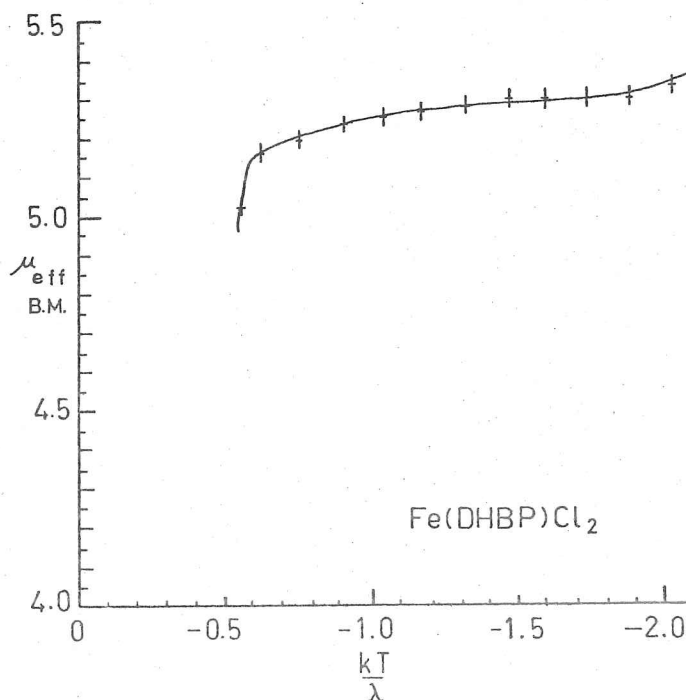
was consistent with this, particularly in the presence of the three strong ν N-H bands previously seen in complexes of this type with other metals. On the basis of its magnetic

properties and Mössbauer spectrum (vide infra) this compound, (131), was formulated as a six co-ordinate, high-spin iron(II) complex. Preparation of $\text{Fe}(\text{DHP})(\text{NCS})_2$, (132), in a similar manner, by the use of diisothiocyanatotetrapyridine-iron(II) and observation of the fact that it has two $\nu \text{C}\equiv\text{N}$ absorptions in the solid state infrared at 2095 and 2076 cm^{-1} suggests that the ligand is bound in the cis configuration.

Octahedral high-spin iron(II) has a $^5\text{T}_{2g}$ ground state and accordingly its complexes are expected to show a magnetic moment corresponding to four unpaired electrons, perturbed by a temperature dependent orbital contribution. A theoretical variation of magnetic moment with temperature may be seen plotted, for example, in reference 148. The magnetic moment of (131) was recorded over a temperature range and was found to vary from 5.33 ± 0.03 B.M. at 294°K to 5.05 ± 0.03 B.M. at 84°K (Fig. 5.1) in a manner approximately in accordance

Figure 5.1

Temperature Dependence of μ_{eff} shown by $\text{Fe}(\text{DHP})\text{Cl}_2$, (131)



with the theoretical curve. A plot of the reciprocal molar susceptibility, corrected for diamagnetism, against temperature gave a θ value of -8°K . The moment of the diisothiocyanate derivative (132) at room temperature was 5.38 B.M., that of the dibromo derivative, (133), was 5.34 B.M. and that of (134) was 5.36 B.M.

Of the various combinations of oxidation and spin-state in which iron may occur, Mössbauer spectroscopy is frequently able to distinguish high-spin iron(II) unambiguously, by the magnitude of the quadrupole splitting that some complexes of this species exhibit. This arises because, with few exceptions, only complexes of high-spin iron(II) ever show a quadrupole splitting of over 2.8 mm sec^{-1} (ref. 154); frequently it is over 3.0 mm sec^{-1} .

Accordingly, when the Mössbauer spectrum of (131) was recorded (Fig. 5.2) and was found to exhibit a quadrupole doublet with a splitting of 3.06 mm sec^{-1} at an isomer shift of 0.84 mm sec^{-1} , which is in the range normally expected for high-spin iron(II) (ref. 154), there was little doubt that the formulation indicated by the magnetic measurements was correct. The isomer shift, although it lies within the normally observed range for high-spin iron(II) (0.7 to 1.4 mm sec^{-1}) (ref. 154) is not diagnostic since signals due to iron in several other forms also fall within this range.

Furthermore, the magnitude of the quadrupole splitting is consistent with six rather than five co-ordination. Busch^{155,156} has correlated the magnitude of the quadrupole

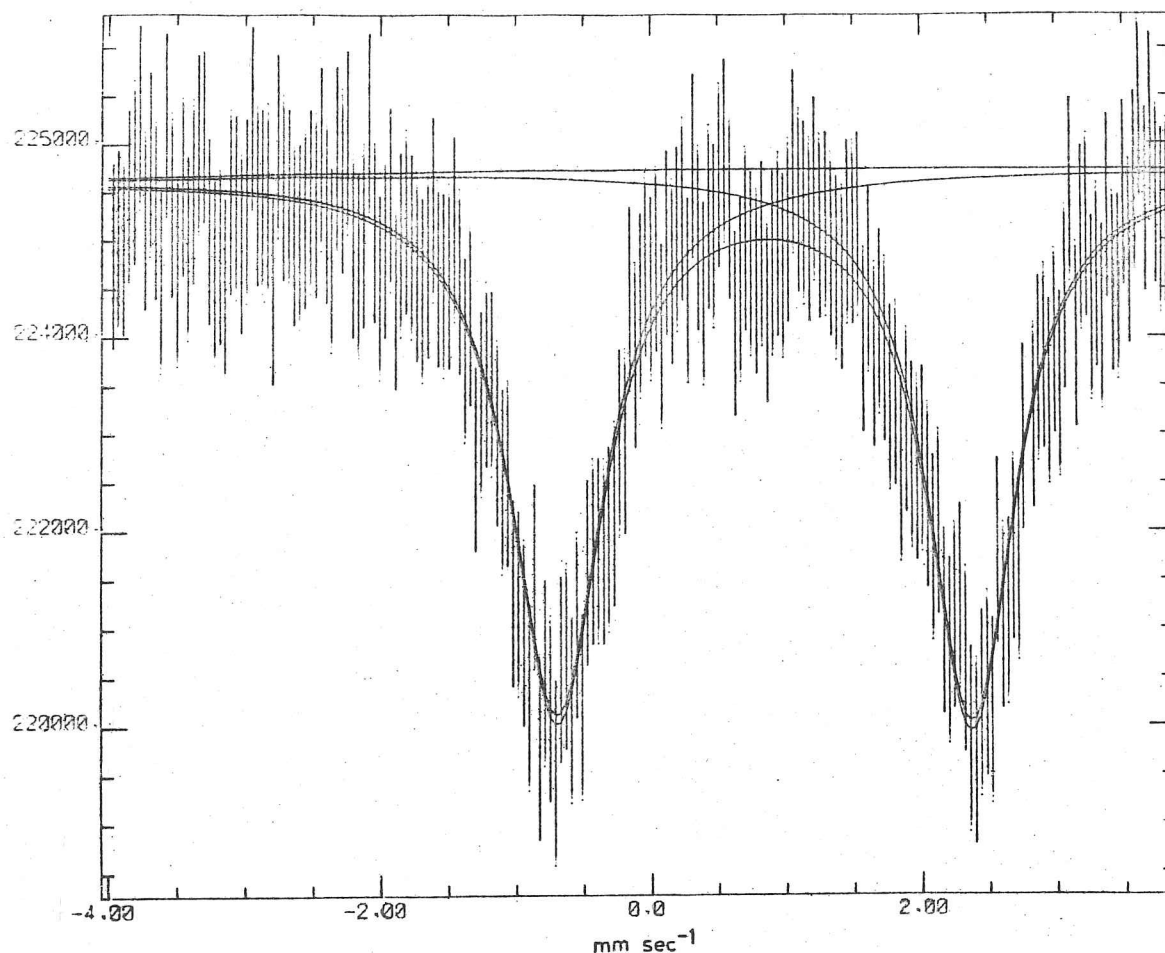


Figure 5.2 Mössbauer Spectrum of $\text{Fe}(\text{DHBP})\text{Cl}_2$, (131)

splitting in macrocyclic complexes of spin-free iron(II) with the co-ordination number of the iron. He suggests that whereas six co-ordinate species have splittings in the range 0 to 3.0 mm sec^{-1} , five co-ordinate species have somewhat larger splittings which are generally in the range 3.3 to 3.8 mm sec^{-1} .

5.2 The Oxidative Denitrogenation of $\text{Fe}(\text{DHBP})\text{Cl}_2$

The above mentioned characterisation of the orange-red $\text{Fe}(\text{DHBP})\text{Cl}_2$, (131), was carried out on freshly prepared

samples of the compound. On standing exposed to the air, or in pure oxygen, the compound undergoes reaction in the solid state to form a deep-red substance. For bulk samples of up to 1 g the process is essentially complete in about eight days. At the conclusion of this period the product analyses approximately as $\text{Fe}(\text{bipy})\text{Cl}_2(\text{H}_2\text{O})_{1.33}$ (Found : C, 39.2, 38.9; H, 2.97, 3.30; N, 9.07, 9.23; Cl, 23.5, 23.3. $\text{C}_{10}\text{H}_{10.66}\text{Cl}_2\text{FeN}_2\text{O}_{1.33}$ requires C, 39.1; H, 3.50; N, 9.13; Cl, 23.1%). The hydrogen analysis is somewhat low, but this is explicable and the reason will become obvious in due course. In contrast to the reactant the product is totally soluble in most polar solvents. A comparison of the infrared spectrum (Fig. 5.4) with that of the reactant (Fig. 5.3) shows, most significantly, that all the ν N-H absorptions have been lost. Contact with oxygen for more than about eight days gradually leads to the formation of insoluble components within the product. On storing under pure nitrogen, however, the initial compound, (131), is stable indefinitely.

The most obvious way in which this spontaneous change in elemental constitution can have occurred is by the loss of the two hydrazine moieties, as two moles of nitrogen, accompanied by the uptake of oxygen, in an oxidative process. The overall gas balance during the reaction was determined by allowing a weighed, solid sample of the compound, (131), to decompose, whilst measuring volumetrically the overall amount of gas that (as it turned out) was evolved. It is

Figure 5.3

Infrared Spectrum of $\text{Fe}(\text{DHBP})\text{Cl}_2$ before Denitrogenation

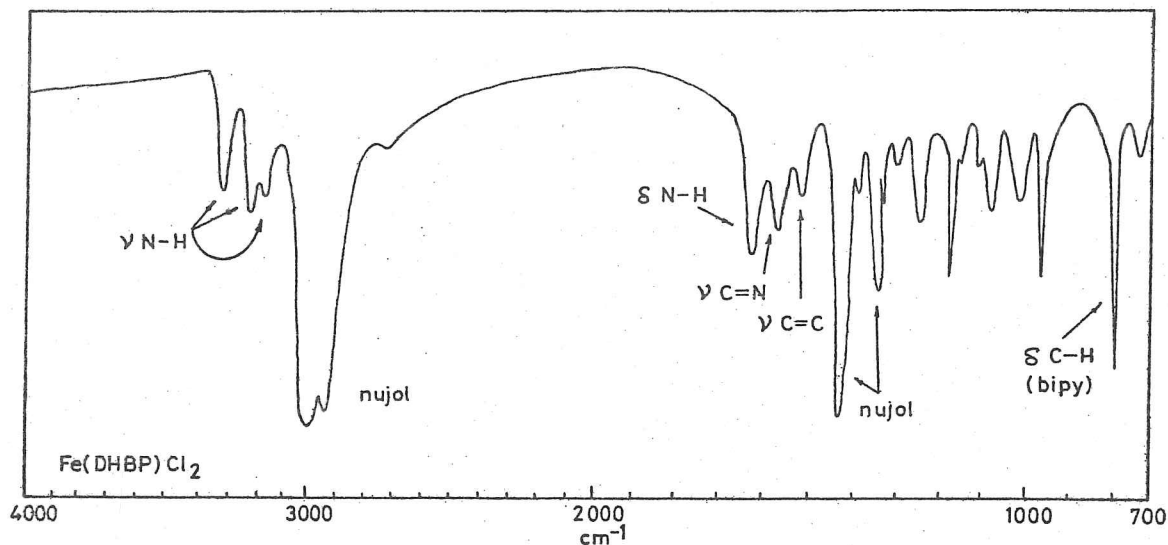
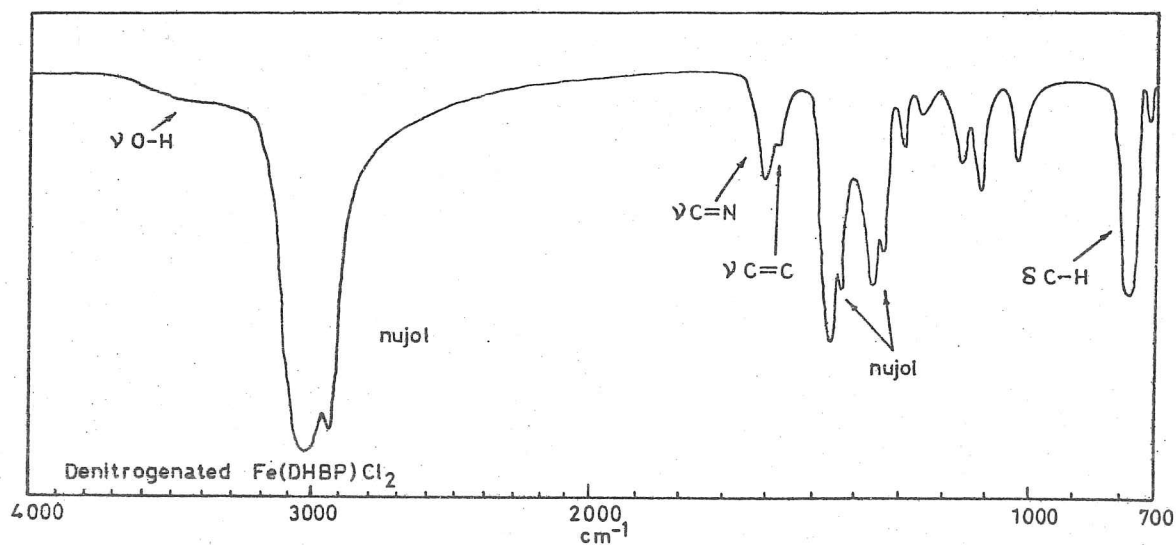


Figure 5.4

Infrared Spectrum of $\text{Fe}(\text{DHBP})\text{Cl}_2$ after Denitrogenation



then a simple matter to relate this volume, in terms of mole-equivalents, to the weight of material from which it was derived.

The experiment was performed in duplicate, allowing ten days for the reaction to go to completion. In both cases significant gas evolution had ceased after five days.

The overall amount of gas evolved corresponded to approximately one mole-equivalent; the actual results are detailed in Table 5.2.

Table 5.2

Wt. of Sample (g)	Gas Collected (ml. at S.T.P.)	Volume Expected for 1 mole-equiv. (ml. at S.T.P.)	Actual No. of mole-equivs. collected
0.2046	12.29	13.36	0.92
0.3128	20.84	20.43	1.02

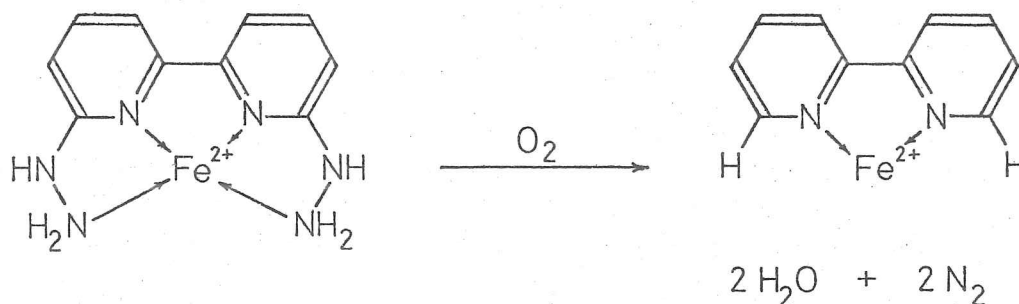
It was also noted during these gas evolution measurements that overall gas evolution only occurred during daylight hours, suggesting that a photochemical process may be involved, and also that there was a distinct period of gas uptake at the beginning of the decomposition, before any evolution occurred.

These measurements were verified semi-quantitatively by mass spectroscopy in an experiment expected to show that this overall evolution of one mole of gaseous products corresponded specifically to the uptake of one mole of oxygen and the evolution of two moles of nitrogen. A sample of (131) was placed in a calibrated flask, which was then evacuated, and a pressure of oxygen admitted such that if the reaction went as expected the ultimate nitrogen to oxygen ratio would be close to the atmospheric ratio for these gases. The experiment then simply involved comparing

the nitrogen to oxygen mass peak ratio in the mass spectrum of the gases in equilibrium with the sample after ten days, with the same ratio in the spectrum of the atmospheric gases. At the same time a check could be made for the presence of any other gaseous products formed during the reaction. That the sample had not been contaminated by the atmosphere through leakage into the low pressure system could be verified by the absence of any CO_2 peak in the spectrum of the sample gases.

The experiment was carried out and gave the expected results. The only gas detected as being formed during the reaction was nitrogen and this occurred in twice the volume of the one mole-equivalent of oxygen that was absorbed by the compound. These observations may be summarised in Scheme One.

Scheme One



Hydrazines as a class of compounds are known to be oxygen scavengers¹⁵⁷. However, in contrast to others, free DHBP is

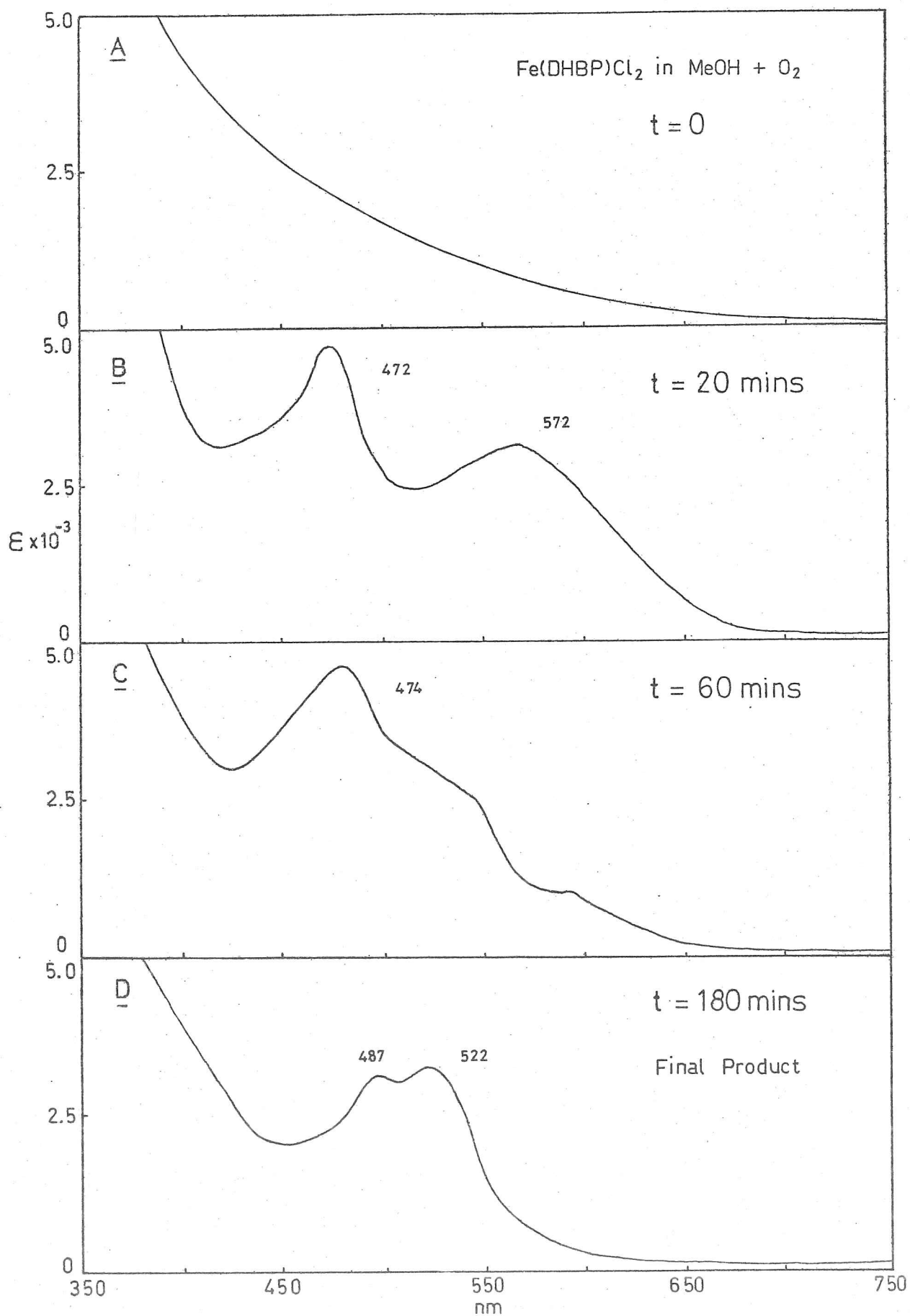
quite stable over long periods of time and, more particularly, its complexes with Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} are quite stable towards aerobic oxidation. Thus, so far, the decomposition reaction appears peculiar to the iron(II) species. In solution (methanol) the reaction of $\text{Fe}(\text{DHBP})\text{Cl}_2$ with oxygen is even more rapid and a series of visible spectra, representing the full course of the reaction over a three hour period is shown in Fig. 5.5. In pyridine, however, the reaction is completely prevented and solutions of $\text{Fe}(\text{DHBP})\text{Cl}_2$ will remain in equilibrium with oxygen indefinitely. This behaviour is reminiscent of iron(II) heme, the protein free active constituent of hemoglobin, which is rapidly oxidised to iron(III) in aqueous solution¹⁵⁸, but which remains as the iron(II) complex in pyridine¹⁵⁹. Perhaps an obvious suggestion is that in these situations oxidation requires initial co-ordination of oxygen to the iron and that in a good co-ordinating solvent such as pyridine access to the inner co-ordination sphere is totally blocked. In this respect it is worth noting that iron stands out amongst the other metals studied in conjunction with DHBP in its greater tendency to become seven co-ordinate¹⁶⁰.

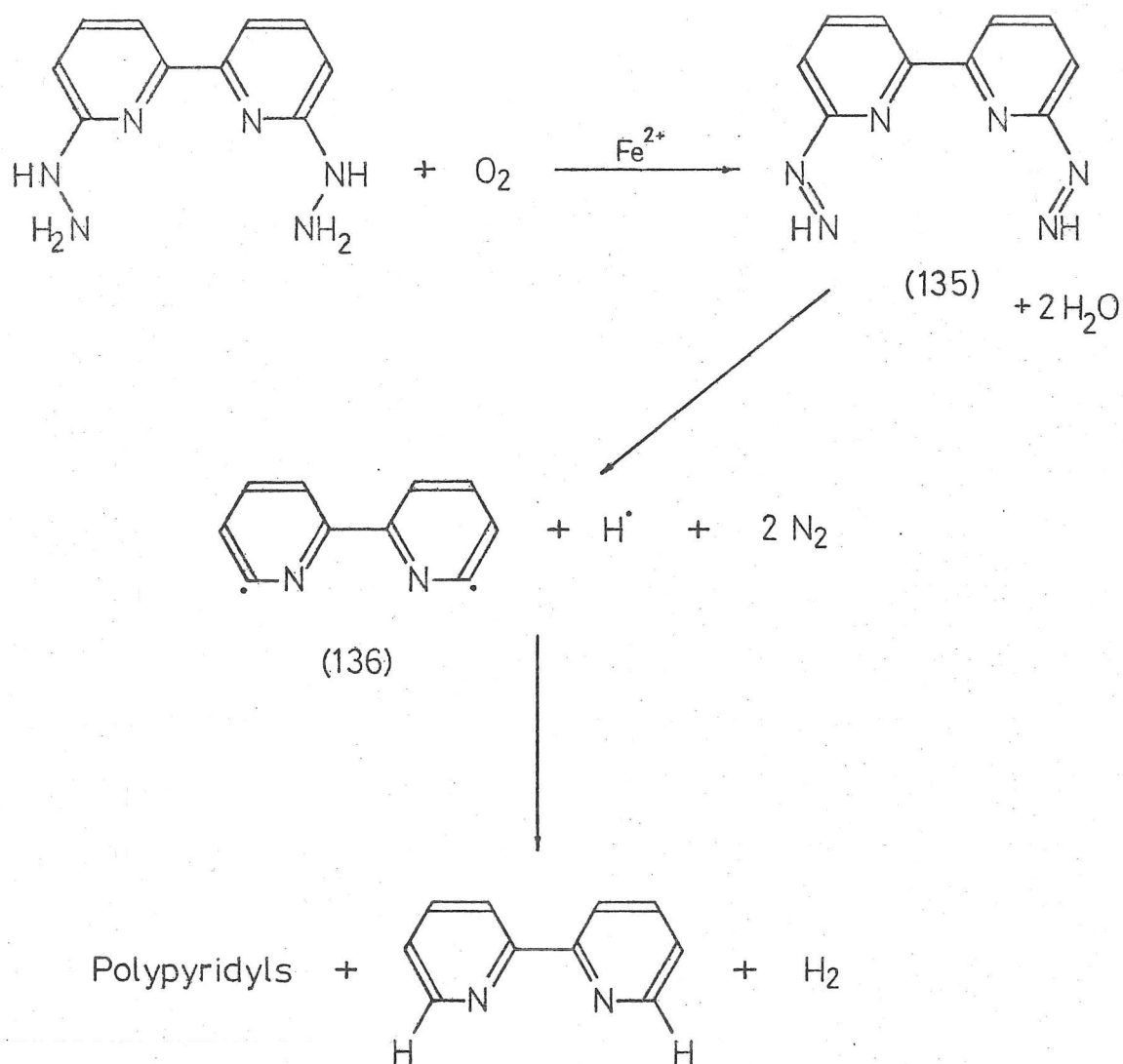
The process by which hydrazines react with oxygen is thought initially to involve a straight forward oxidation of the hydrazine to a diazene species¹⁶⁰. Thus, in the case of DHBP, compound (135) should be formed.

Diazenes are unstable and in a free radical reaction readily eliminate nitrogen^{161,162}. In so doing, in the

Figure 5.5

Electronic Spectra Shown by the System $\text{Fe}(\text{DHBP})\text{Cl}_2 + \text{O}_2$





case of (135), bipyridyl free radicals, (136), and hydrogen free radicals should be formed. Combination of these free radicals can then give rise to bipyridyl, various polypyridyl species, formed by coupling of the bipyridyl free radicals, and, for every molecule of coupled bipyridyl a molecule of hydrogen must be formed (or vice versa).

This mechanism is consistent with the ligand degradation that occurs in $Fe(DHBP)Cl_2$ for the following reasons:

Firstly, the overall gas balance is substantially correct and oxygen uptake precedes nitrogen evolution. Hydrogen may be formed in the reaction, but this will only be in small amounts (vide infra). It was not detected by mass spectroscopy because of instrument limitations in reaching such low m/e values. Secondly, the product from the denitrogenation reaction was further decomposed with hot 2M sodium hydroxide so as to isolate the free ligand. This was extracted from the inorganic residue with diethyl ether and subjected to mass spectroscopy, which showed that it was predominantly bipyridyl mixed in with various polypyridyl species. Mass peaks corresponding to as many as four coupled bipyridyl residues were detected in this way. The presence of these polypyridyls is precisely in agreement with the proposed free radical decomposition of the diazene, (135). Thirdly, there is a photochemical step in the reaction sequence.

One apparent inconsistency was the absence of any well defined ν O-H absorption in the infrared spectrum of the denitrogenated complex (Fig. 5.4) which should arise because of the formation of water during the reaction. Only a very broad area of low intensity absorption appeared in the region 3500 to 3200 cm^{-1} , the assignment of which was doubtful. This, however, was resolved by the following deuterium incorporation experiment.

The active protons in DHBP were replaced with deuterium by repeatedly dissolving it in deuterated acetic acid and

precipitating the product by the addition of deuterated sodium hydroxide. This was done until virtually complete replacement of the six protons was indicated by mass spectroscopy. Preparation and subsequent denitrogenation of deuterated $\text{Fe}(\text{DHBP})\text{Cl}_2$ gave a product showing a broad area of absorption in the region 2600 to 2300 cm^{-1} of its infrared spectrum. Using the usual ratio of $\nu_{\text{X-H}}/\nu_{\text{X-D}}$ of 1.4 (ref. 163) this area correlates with the broad area of absorption found in the infrared spectrum of the non-deuterated product and suggests that there is in fact water present in the compound. The broad nature of the absorption suggests that the water is strongly hydrogen bonded¹²³. Additionally, isolation of the free deuterated ligand from the product and comparison of its p.m.r. spectrum with that of non-deuterated bipyridyl (Fig. 5.6 and 5.7) shows that deuterium incorporation occurs exclusively at the 6 and 6' positions. This is obvious because of the absence of a resonance, due to the protons normally present in these positions, which is known to occur at 1.44 τ ¹⁶⁴. The remainder of the spectrum shows the expected perturbations in the coupling pattern, but apart from that is the same as for non-deuterated bipyridyl. Again this is in agreement with the proposed mode of ligand decomposition.

One further piece of evidence in support of the initial oxidation of the hydrazine moieties to diazenes comes from the compound $\text{Fe}(\text{DMeHBP})\text{Cl}_2$, (134). This is prepared in the same manner as $\text{Fe}(\text{DHBP})\text{Cl}_2$ using instead the methylated dihydrazine, DMeHBP, (44). In the presence of oxygen it is stable over

Figure 5.6

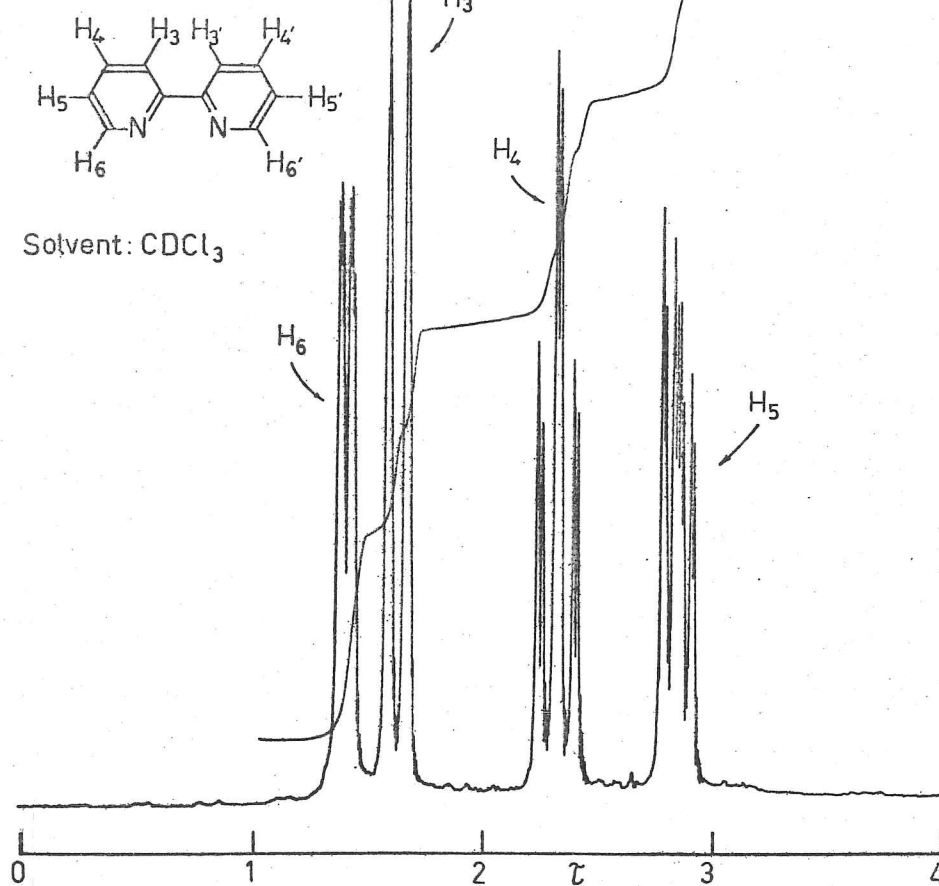
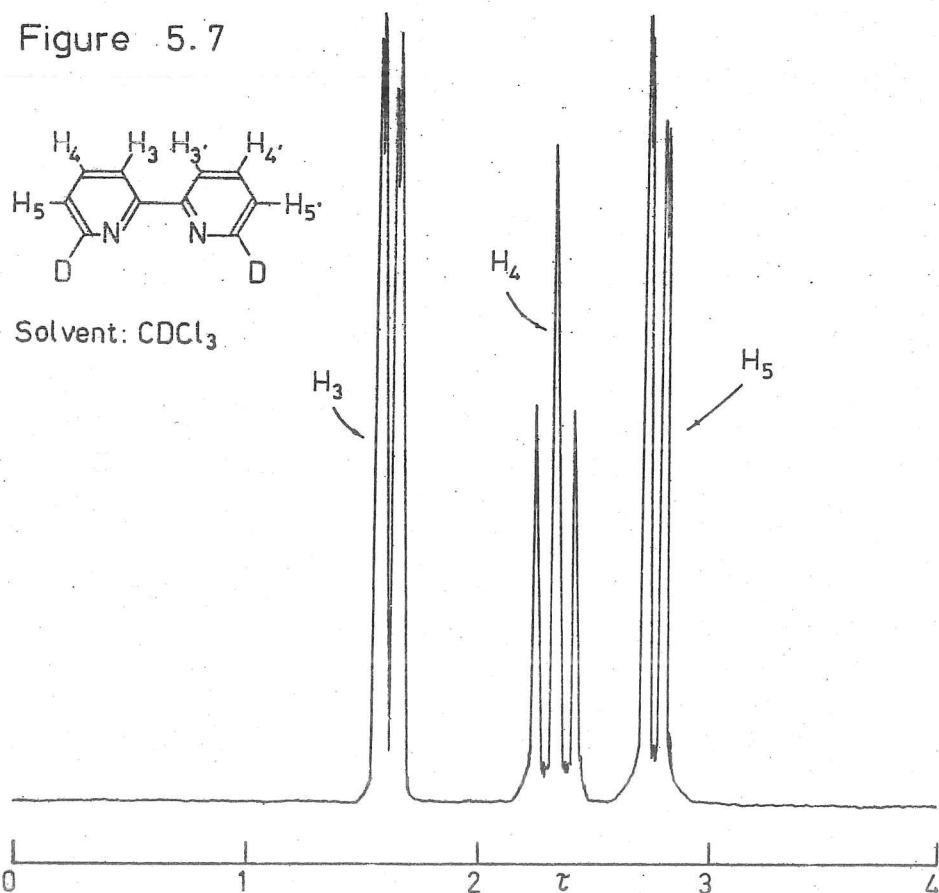


Figure 5.7



long periods of time. This is fully consistent, since for oxidation to a diazene to proceed elimination of a methyl group would have to be effected.

5.3 Nature of the Product

To this point the structural alterations undergone by the ligand alone have been considered. The precise nature of the inorganic product of the reaction is somewhat more complex and will now be discussed.

The spectral bands seen in the series of spectra in Fig. 5.5 have extinction coefficients of several thousand and accordingly, arise from fully allowed transitions. It is not likely that these bands arise from transitions within the diazene ligands since $\pi \rightarrow \pi^*$ transitions are not commonly seen at such low energies (c.a. $21,000 \text{ cm}^{-1}$) and any $n \rightarrow \pi^*$ bands, being symmetry forbidden, would not have the observed intensity. Certainly the spectral bands in the final product (Fig. 5.5) must be associated with transitions involving the metal since the ligand here is mostly bipyridyl, which is colourless. These bands are commonly accepted, in the case of iron(II), as arising from the excitation of an electron in a metal t_{2g} orbital to an empty π antibonding orbital associated with the ligand^{165,166}. As the π antibonding orbitals become lower lying in energy and this can happen, for example, by extending the conjugation in a polyene ligand¹⁶⁷, the energy of the charge transfer transition will decrease.

If the mechanism for the ligand degradation proposed

in the previous section is correct; the conjugation already present in the bipyridyl residue is extended in two stages; first to the mono(diazeno) and then, assuming that it doesn't decompose in a more rapid reaction, to the bis(diazeno), (135). As the progress of the reaction is monitored in the visible region of the spectrum the first band to appear is at 470 nm, eventually achieving a maximum extinction coefficient of c.a. 5×10^3 fifty minutes into the reaction. Also appearing rapidly in the first stages of the reaction is a band at 570 nm which achieves a maximum extinction coefficient of c.a. 3×10^3 after twenty minutes, and then decays completely in about the same period of time. It seems reasonable to speculate that the first formed band; the one at higher energy, is due to the mono(diazeno) complex and that the band at lower energy is due to the subsequent formation of the more highly conjugated bis(diazeno) complex (Fig. 5.5b). The bis(diazeno) complex then decomposes reforming a mono(diazeno) complex (Fig. 5.5c) which itself eventually decomposes through to the bipyridyl complex (Fig. 5.5d). The fact that one is able to make assignments in this manner suggests that the rate of oxidation to the diazeno is approximately equal to the rate of free radical decomposition of the diazeno, under the prevailing reaction conditions.

So far as the nature of the final complex is concerned Fig. 5.5d is of principal interest. Seen here is the characteristic "double humped" charge transfer band characteristic of all iron(II) α -diimine complexes²³. In

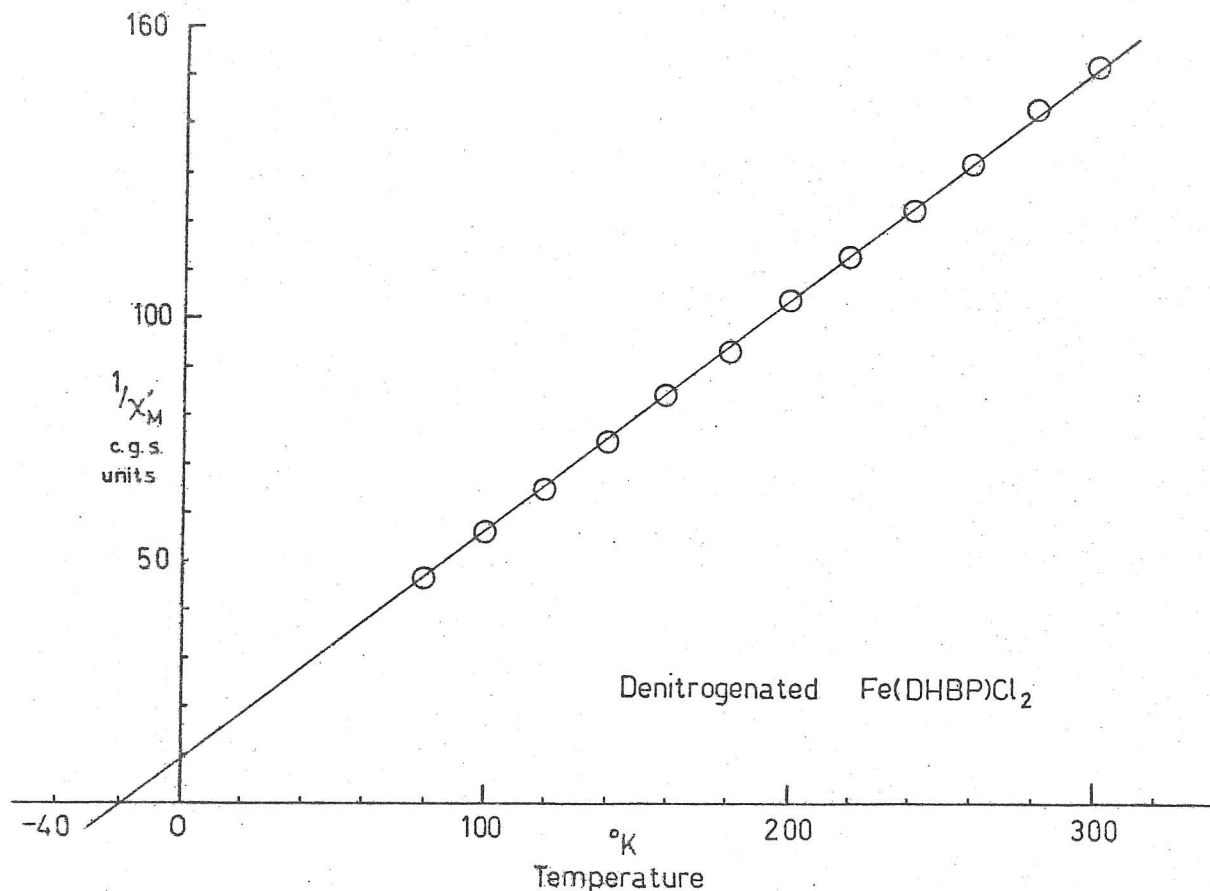
the case of tris(bipyridyl)iron(II) this band is known to have its maximum extinction coefficient of 8.78×10^3 at 522 nm (ref. 23). The band in spectrum 5.5d does indeed have its maximum at 522 nm, however, the apparent extinction coefficient is of the order of one-third of that which is expected. This suggests that only one-third of the iron originally introduced into the system as $\text{Fe}(\text{DHBP})\text{Cl}_2$ finishes up as tris(bipyridyl)iron(II), and is in accordance with the stoichiometry of the situation, if in fact the band is due to the tris(bipyridyl) species.

In a similar way the conductivity of the solution (methanol) was monitored during the course of the reaction and was found at all times to be in the range normally expected for 2:1 electrolytes.

After denitrogenation, allowing for the change in stoichiometry, the room temperature magnetic moment drops from 5.33 B.M., for the reactant, to approximately 3.95 B.M. The magnetic susceptibility was measured over the temperature range 300°K to 80°K and a plot of $1/\chi'_M$ against temperature shows Curie-Weiss behaviour with a θ value, extrapolated from 80°K , of -20°K (Fig. 5.8). No susceptibility maximum, indicative of antiferromagnetic behaviour, such as would be expected if oxo-bridged dimerisation had occurred¹⁶⁸, was observed. The absence of any iron(III) oxo-bridged compound was further verified by the absence of the ν Fe-O-Fe absorption which is normally seen in the infrared spectrum, at c.a. 850 cm^{-1} , of such compounds¹⁶⁹.

Figure 5.8

Temperature Dependence of $1/\chi'_M$ for Denitrogenated $\text{Fe}(\text{DHBP})\text{Cl}_2$



From the visible spectrum of the denitrogenation product it is known that the iron, at least that which is bound to the bipyridyl, is still iron(II). Thus, it seems probable that the reduction in magnetic moment is due to the partial formation of a spin-paired iron(II) species, and here it should be noted that tris(bipyridyl)iron(II) is well established as being spin-paired¹⁷⁵. Such species, having a $^1A_{1g}$ ground state, exhibit only a temperature independent magnetic moment, usually amounting to no more than 1 B.M. (ref. 170). A moment of 3.95 B.M. arising from a mixture of molecules having moments of 5.3 B.M. and 0.6 B.M., for instance, corresponds to between one-half and

one-third of the iron(II) being spin-paired. This is shown by the following relationships:-

$$\left(\frac{(0.6)^2 + (5.3)^2}{2} \right)^{\frac{1}{2}} = 3.77; \quad \left(\frac{(0.6)^2 + 2(5.3)^2}{3} \right)^{\frac{1}{2}} = 4.34$$

The Mössbauer spectrum of the denitrogenation product was recorded, but showed only a broad envelope of absorptions extending from -0.6 mm sec^{-1} to 2.0 mm sec^{-1} , corresponding to a mixture of various different iron species. Apart from this no useful information could be extracted from the spectrum owing to insufficient resolution of the overlapping absorptions.

Since the product was known to be an electrolyte, separation of the cationic and anionic components was carried out, by selective precipitation, in the following manner.

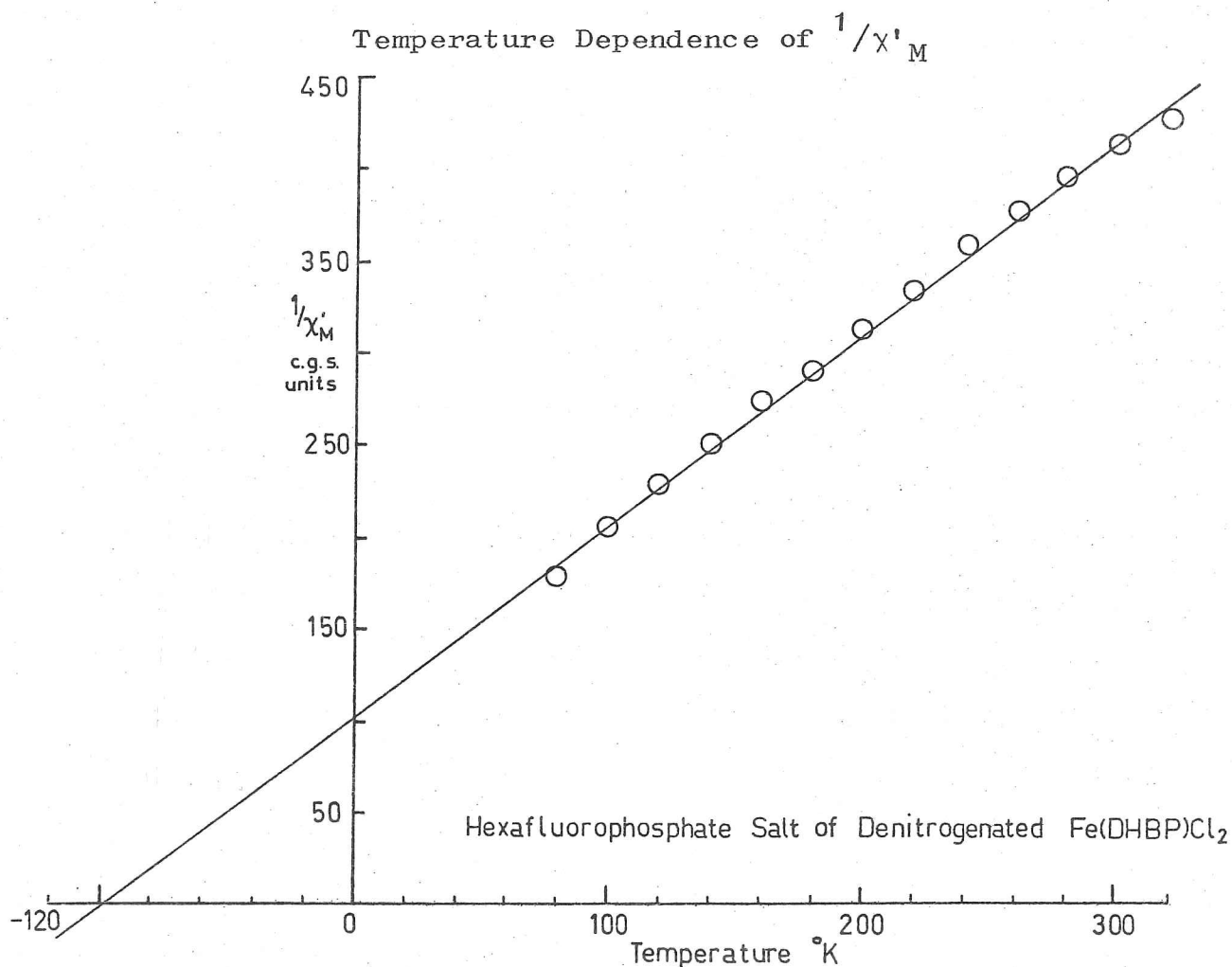
Addition of tetraphenylarsonium chloride to a solution of the dinitrogenation product in methanol resulted in precipitation, over a period of time, of the known compound $(\text{Ph}_4\text{As})^+(\text{FeCl}_4)^-$ (ref. 171). It is not fully clear whether the precipitation of this species is due to the presence of FeCl_4^{2-} or FeCl_4^- in the compound, as the ferrous species is notoriously difficult to isolate and purify, owing to its facile oxidation to the ferric state¹⁷¹. In the Mössbauer spectrum both FeCl_4^{2-} and FeCl_4^- have absorptions which fall within the envelope described above^{172,173}. In the visible spectrum FeCl_4^- shows several weak bands in the range 500 to 700 nm¹⁷¹, it was not possible to detect the presence or otherwise of these bands in the spectrum of the denitrogenation

product owing to the overlap of the tail of the 522 nm charge transfer band.

Addition of ammonium hexafluorophosphate to an aged aqueous solution of the denitrogenation product, after filtration, precipitated a deep-red compound which analysed as $\text{Fe}(\text{bipy})_3(\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$. The presence of water of hydration is substantiated by a broad ν O-H band in the infrared spectrum. The analytical data obtained for the compound is as follows : Found : C, 42.5; H, 3.00; N, 9.66; P, 7.36. $\text{C}_{30}\text{H}_{28}\text{F}_{12}\text{FeN}_6\text{O}_2\text{P}_2$ requires C, 42.4; H, 3.32; N, 9.88; P, 7.28%. As before the hydrogen figure is low and this is in accordance with the fact that some of the bipyridyl residues are now known to have coupled to form polypyridyls, wherein the overall hydrogen content is reduced.

An authentic sample of tris(bipyridyl)iron(II) hexafluorophosphate was prepared according to the method used previously by Burstall and Nyholm¹⁷⁴, for the preparation of the corresponding perchlorate salt. Measurement of its magnetic moment showed that, like the perchlorate salt, the iron is spin-paired; the compound having a room temperature magnetic moment of 0.84 B.M. In contrast, however, the hexafluorophosphate salt derived from the product of the denitrogenation reaction has a room temperature magnetic moment of 2.4 B.M., although this varied by as much as 0.2 B.M. for different samples of the compound. A plot of $1/\chi'_M$ against temperature (Fig. 5.9) is linear in the range 300°K to 80°K. Extrapolation from 80°K suggests a θ value of -100°K.

Figure 5.9



This marked difference in the magnetic properties of the two salts suggests that the presence of polypyridyl ligands, as well as bipyridyl ligands, in the salt derived from the denitrogenation product, may be leading to a simple mixture of molecules containing iron which is spin-paired, with molecules in which the iron is spin-free. The magnetic moment of the spin-free species would be approximately 5.3 B.M. The percentage of such a species necessary to give an overall moment of 2.4 B.M. is seen from the following expression:

$$\left(\frac{4(0.84)^2 + (5.3)^2}{5} \right)^{\frac{1}{2}} = 2.49$$

to be about 20%. It is quite reasonable to suspect that in

cases where a polypyridyl chain consisting of two or more bipyridyl residues binds two or three of these to the same iron centre, the overall ligand field strength is less than if three isolated bipyridyls were bound; because of the more restricted geometry. It is well established that in going from tris(bipyridyl)iron(II) to the more stereochemically restricted tris(6-methyl-2,2'-bipyridyl)iron(II) one goes through the crossover point between a spin-paired and a spin-free system¹⁷⁵; and it seems likely that substituting a polypyridyl for one or more bipyridyls will have the same effect. That polypyridyls do in fact lead to highly distorted geometries, upon co-ordination, is evident from a recent crystal structure, which shows that when the quadridentate ligand quarterpyridyl (two coupled bipyridyl residues) bonds in an equatorial fashion to cobalt(III), it does so only with extreme trapezoidal distortion¹⁷⁶.

The presence of the polypyridyl ligands may also account for the large, negative Weiss constant. Although there is no susceptibility maximum in the range studied, a figure of -100°K suggests that there may be some weak antiferromagnetic exchange¹⁷⁷. If a polypyridyl ligand bonds in such a way as to link several iron centres together, the effect may well be to make the unit magnetically non-dilute and to lead to antiferromagnetic coupling¹⁷⁸. However, it is also possible that there may be a thermal equilibrium between spin-paired and spin-free species, which could be the cause of the large Weiss constant.

In conclusion, the magnetic behaviour of the hexafluorophosphate salt of the denitrogenation product can be rationalised in terms of a mixture consisting of approximately 80% of the spin-paired tris(bipyridyl)iron(II) and 20% of a species which is stoichiometrically similar, but which is high-spin due to the co-ordination of polypyridyl rather than bipyridyl ligands. The high, negative θ value is explicable in terms of weak antiferromagnetic exchange between iron centres brought together by bridging polypyridyl ligands, or by a thermal equilibrium of spin states.

The Mössbauer spectrum of the hexafluorophosphate salt of the denitrogenation product is consistent with the above formulation, showing (Fig. 5.10) principally a quadrupole doublet with an isomer shift of 0.30 mm sec^{-1} and a splitting of 0.44 mm sec^{-1} . This is in good agreement with published data for tris(bipyridyl)iron(II) perchlorate (isomer shift : 0.32 mm sec^{-1} ; quadrupole splitting : 0.39 mm sec^{-1})¹⁷⁹. Superimposed upon the principal spectrum there are possibly weak absorptions, one underlying the stronger of the principal absorptions at c.a. 0.1 mm sec^{-1} and another at c.a. 2.1 mm sec^{-1} . These two absorptions could well be the quadrupole doublet expected of the high-spin iron(II) species in the mixture; the isomer shift of 1.1 mm sec^{-1} is in the expected region¹⁵² and the quadrupole splitting suggests a reasonably symmetrical molecule¹⁵⁴.

Returning to the nature of the denitrogenation product itself; the following conclusions can now be made : Since

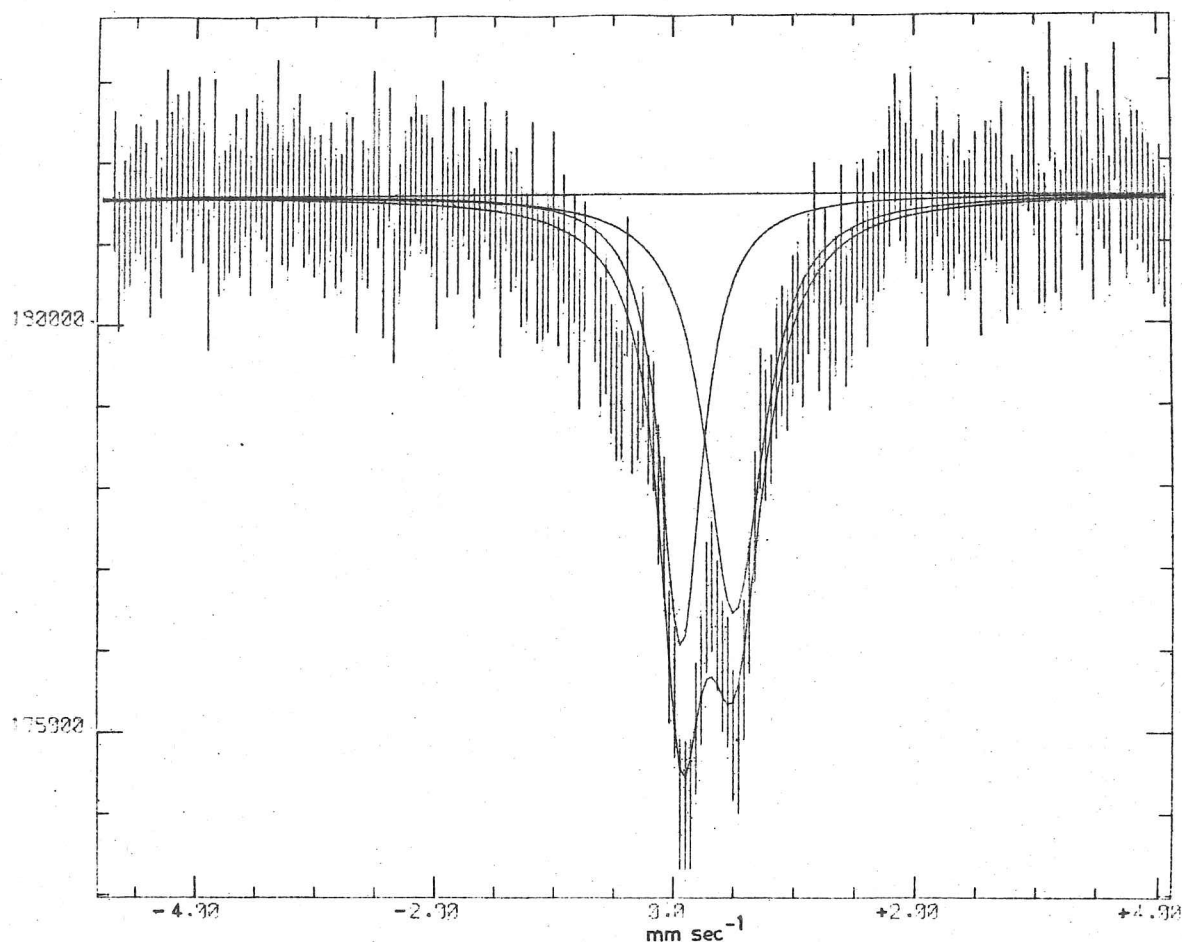
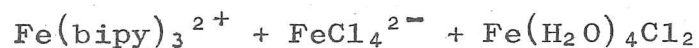


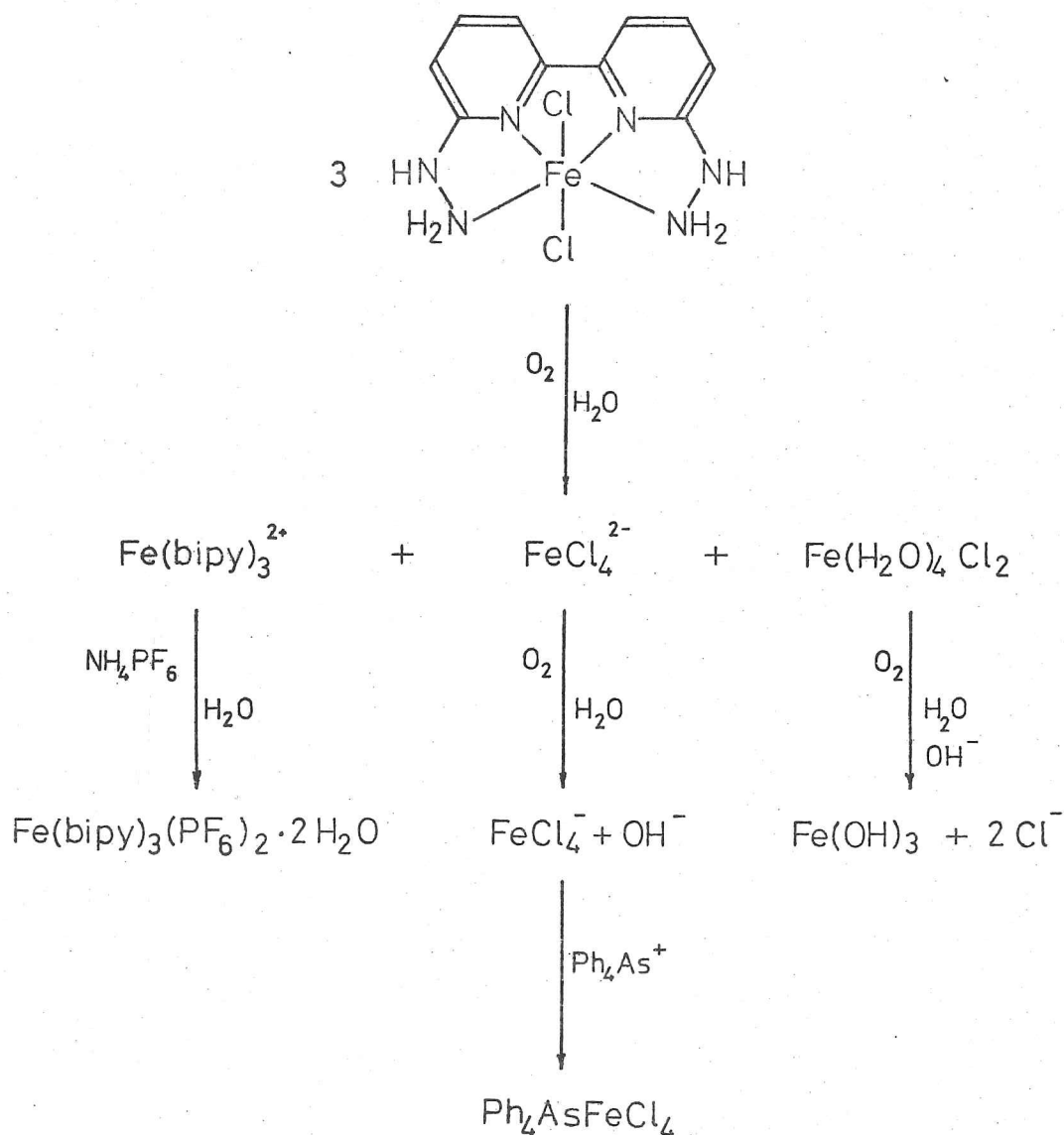
Figure 5.10 Mössbauer Spectrum of the Hexafluorophosphate salt of denitrogenated $\text{Fe}(\text{DHBP})\text{Cl}_2$.

three molecules of bipyridyl finish the reaction bound to one iron atom, clearly the overall stoichiometry, $\text{Fe}(\text{bipy})\text{-Cl}_2(\text{H}_2\text{O})_{1.33}$, represents a mixture of species. Multiplying this by three and including the species that are known to exist suggests the following mixture as the initial product formed upon denitrogenation:-



Subsequent reactions of this mixture, which may occur on prolonged exposure to air and moisture are shown in Scheme Two.

Scheme Two



This mixture is consistent with its observed physical, chemical and spectroscopic properties, in the following ways: The initial mixture suggests that one-third of the iron is low-spin, which is in accordance with the observed magnetic moment and, implicitly, with the extinction coefficient of the charge transfer band in the visible spectrum. The Mössbauer spectrum expected of the proposed mixture is in

accordance with that observed, in so far as that the expected absorptions would all fall within the absorption envelope. In the precipitation involving Ph_4As^+ it is not surprising that FeCl_4^- , arising from oxidation of FeCl_4^{2-} , is precipitated from a system that has been well aerated. Precipitation of the cationic species with ammonium hexafluorophosphate was only carried out after an aqueous solution of the product has been filtered so as to separate a fine brown suspension that had formed over a period of time (see experimental section). This fine brown suspension is quite likely an iron(III) hydroxide formed by the oxidation of the ferrous chloride under conditions which are already somewhat basic due to the release of hydroxide ion during the aerobic oxidation of the FeCl_4^{2-} to FeCl_4^- . Thus the only significant cationic species precipitated is the tris(bipyridyl)iron(II), which is resistant to oxidation.

One further point. The secondary oxidation of the two-thirds of a mole-equivalent of spin-free iron(II) will consume one-sixth of a mole-equivalent of molecular oxygen. It would seem, therefore, that the gas balance measurements described in the previous section should show a net gas evolution of only 0.83 mole-equivalents. The fact that an amount closer to one mole-equivalent is observed accounts for the small quantities of hydrogen expected to be produced, concomitant with polypyridyl formation, during the free radical decomposition of the diazene, (135).

5.4 Experimental

Dichloro-, dibromo- and diisothiocyanatotetrapyridineiron(II) were prepared according to published procedures^{151,152,115}. Acetonitrile was purified in the recommended manner¹⁵³. Analytical data may be seen in Table 5.1 for compounds (131) to (134), and otherwise within the text.

Dichloro-6,6'-dihydrazino-2,2'-bipyridyliron(II),
(131) : Dichlorotetrapyridineiron(II) (0.5 g) was added to dry degassed acetonitrile (40 ml) which had been heated to 50° in a stream of nitrogen. The suspension was stirred for ten minutes before adding 6,6'-dihydrazino-2,2'-bipyridyl (0.25 g), the resulting slurry was then stirred for one hour. The fine red precipitate which had completely formed by this time was collected by filtration under nitrogen and washed with degassed acetonitrile (2 x 5 ml) yielding the product (0.35 g, 89%).

I.R. (nujol) : 3315s, 3235s, 3175s, 1628m, 1597m,
1571m, 1560m, 1415m, 1312w, 1270m, 1186m, 1117m, 1075m,
1023m, 994s, 791s.

Diisothiocyanato-6,6'-dihydrazino-2,2'-bipyridyliron(II),
(132) : Compound (132) was prepared from diisothiocyanatotetrapyridineiron(II) (0.45 g) and DHBP (0.2 g) in a manner analogous to that used for the preparation of compound (131).
Yield : (0.33 g, 92%).

I.R. (nujol) : 3289s, 3247s, 3162s, 2095s, 2076s, 1616s,
1595s, 1568s, 1260m, 1186s, 1166m, 1153m, 1123m, 1023m,
1005m, 782s.

Dibromo-6,6'-dihydrazino-2,2'-bipyridyliron(II), (133):

Compound (133) was prepared from dibromotetrapyridineiron(II) (0.5 g) and DHP (0.2 g) in a manner analogous to the preparation of compound (131). Yield : (0.35 g, 87%).

I.R. (nujol) : 3310s, 3290 to 3110s br, 1621s, 1610s, 1575s, 1268s, 1182s, 1170s, 1120s, 1080w, 1025m, 1009w, 993m, 796s.

Dichloro-6,6'-di-N-methylhydrazino-2,2'-bipyridyliron(II),

(134) : Compound (134) was prepared from dichlorotetrapyridineiron(II), (0.19 g) and DMeHP (0.1 g) as described above for compound (131). Yield : (0.14 g, 92%).

I.R. (nujol) : 3400s br, 3210s br, 3160s br, 1625s, 1595m, 1563m, 1289m, 1224m, 1200s, 1122s, 1002s, 1068s, 783s.

Tetraphenylarsonium tetrachloroferrate(III) : A sample of the denitrogenated compound (0.2 g) was dissolved in degassed methanol (20 ml). Tetraphenylarsonium chloride (0.5 g) dissolved in degassed methanol (5 ml) was added and the solution allowed to stand at room temperature for three days. The solution was then filtered and the yellowish-white precipitate collected. Recrystallisation of this, once under nitrogen, from ethanol gave yellow needles of the pure compound (0.1 g). (Found : C, 49.8; H, 3.49. $C_{24}H_{20}AsCl_4Fe$ requires C, 49.6; H, 3.47%).

Tris(polypyridyl)iron(II) hexafluorophosphate dihydrate:

A sample of the denitrogenated compound (0.9 g) was dissolved in water and allowed to stand for two hours. This solution

was then filtered and a solution of ammonium hexafluorophosphate (1.1 g) in water (5 ml) was added to the filtrate, the resulting solution was allowed to stand overnight. The red crystalline product, which had precipitated, was collected by filtration and washed sparingly with methanol (5 ml).
Yield : (0.4 g).

I.R. (nujol) : 3400 to 3200s br, 1607s, 1518m, 1344m, 1161s, 1071w, 1049w, 1023w, 959m, 840s, 771s, 768s.

Tris(bipyridyl)iron(II) hexafluorophosphate : 2,2'-bipyridyl (2.0 g) was dissolved in hot distilled water (300 ml) and was treated with an excess of ferrous ammonium sulphate (2.0 g) and ammonium hexafluorophosphate (2.1 g). The red suspension was heated on a water bath for one hour and left to cool. The red crystalline precipitate (3.4 g) which separated was filtered off, washed with distilled water and dried in vacuo. (Found : C, 44.3; H, 3.05; N, 10.3. $C_{30}H_{24}F_{12}FeN_6P_2$ requires : C, 44.3; H, 2.97; N, 10.3%).

I.R. (nujol) : 1610s, 1320m, 1278w, 1246m, 1165s, 1130w, 1076m, 1051m, 864s, 840s br.

CHAPTER SIX

SECOND ROW TRANSITION METAL COMPLEXES
OF MULTIDENTATE LIGANDS DERIVED FROM
2,2'-BIPYRIDYL

6.1 Introduction

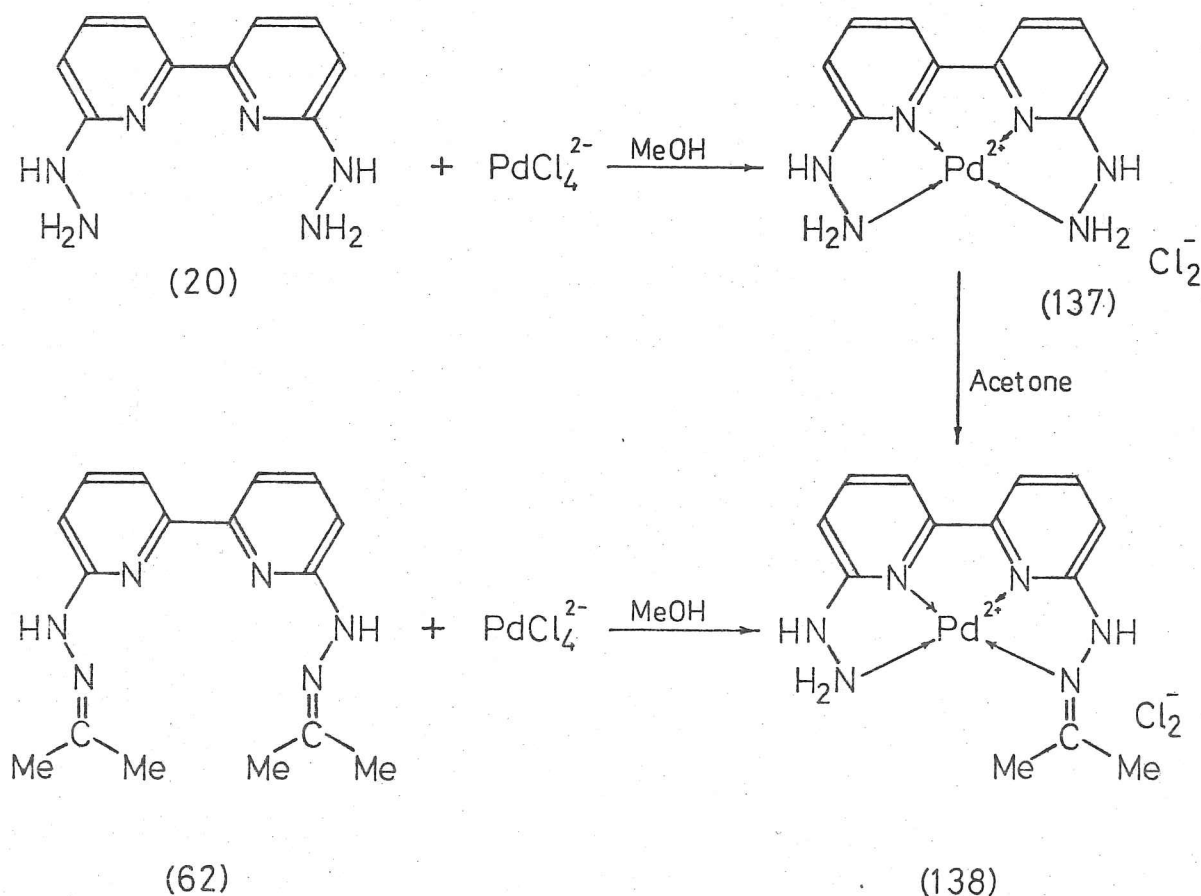
Except with respect to phthalocyanine¹⁸⁰ and porphyrin¹⁸¹ ligands, little has been reported concerning the co-ordination of macrocyclic ligands to second row transition metals. It is not clear whether this is due to fundamental chemical difficulties associated with the formation of such complexes or whether it is simply due to a paucity of effort applied in this direction. Some preliminary observations that have been made using the ligands under discussion, in conjunction with second row metals, are briefly reviewed in this chapter.

6.2 Palladium(II) Complexes

The interaction of DHBP with potassium tetrachloro-palladate in methanol leads to the precipitation of a highly insoluble orange complex, (137), which analyses as $\text{Pd}(\text{DHBP})\text{-Cl}_2$. (Found : C, 30.3; H, 3.19; N, 21.5. $\text{C}_{10}\text{H}_{12}\text{Cl}_2\text{N}_6\text{Pd}$ requires C, 30.5; H, 3.07; N, 21.4%). The similarity of its infrared spectrum in the ν N-H region, to that shown by $\text{Ni}(\text{DHBP})(\text{ClO}_4)_2$ suggests that the usual four nitrogen donors are co-ordinated. It is possible, however, that the two chlorides are co-ordinated and that the terminal amines of the DHBP are positioned away from the inner co-ordination sphere. Conductivity measurements, which may have resolved this matter, were not possible owing to the low solubility of the compound.

Reaction of this species, (137), with acetone does

not produce the bis(hydrazone) complex as was the case with the nickel(II) system. Instead, condensation with only one mole of acetone takes place, resulting in the mono(hydrazone) species, (138). (Found : C, 35.8; H, 3.87; N, 19.2. $C_{13}H_{16}Cl_2N_6Pd$ requires C, 36.0; H, 3.72; N, 19.4%). This



is interesting. Palladium(II) does not have the extreme facility for square-planar to octahedral interconversion that is shown by nickel(II)¹⁸² and thus it seems that if the ligand is to bind as a quadridentate, then it must do so in a trans configuration. When considering the chemistry of the nickel(II) bis(hydrazone) complexes in Chapter Two, the reason proposed for the fact that the ligands were never

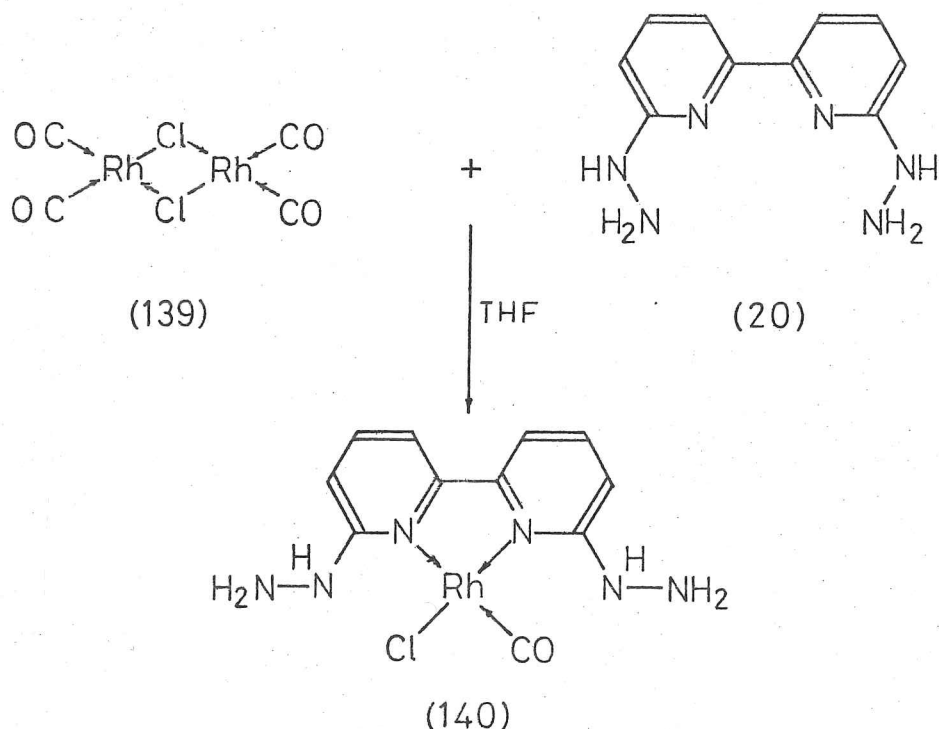
observed to bind in the trans configuration was that the steric interaction between the two opposing alkyl groups was excessive when the ligand was in this orientation. The manner in which the complex avoids this unfavourable steric interaction; by only forming the mono(hydrazone), where it does not exist, reflects not only evidence for the proposed interaction and the inability of the system to dissipate it by adopting octahedral stereochemistry, but also a preference for retaining four nitrogen donors in the inner co-ordination sphere. Displacement of the two terminal nitrogen donors by the chloride ions would leave them free to react in an unconstrained environment.

Whenever the preformed bis(hydrazone) ligand, (62), was reacted with K_2PdCl_4 in anhydrous methanol one imine group was always found to hydrolyse, so as to generate the same mono(hydrazone) complex, (138).

6.3 Rhodium(I) Complexes

Reaction of the rhodium dicarbonyl chloride dimer¹⁸³, (139), with DHP in tetrahydrofuran produces a red, crystalline compound, (140), which is a non-electrolyte and which analyses as $Rh(DHP)COCl$. (Found : C, 34.7; H, 3.33; N, 22.0; Cl, 9.26. $C_{11}H_{12}ClN_6ORh$ requires C, 34.5; H, 3.16; N, 22.0; Cl, 9.27%). The infrared spectrum shows a single $\nu C\equiv O$ absorption at 1985 cm^{-1} . Since a six co-ordinate rhodium(I) complex is unlikely¹⁸⁴ it is probable that the DHP is bonded through the α -diimine group alone, in a square-planar complex,

and that the terminal amines are not co-ordinated. The possibility of one terminal amine co-ordinating to form a five co-ordinate species, however, cannot be discounted.



Attempts to react the rhodium diethylene chloride dimer¹⁸⁵ with DHBP led to the formation of a pyrophoric material which could not be satisfactorily purified.

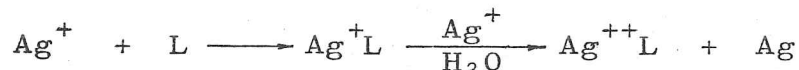
6.4 Ruthenium(II) Complexes

The formation of the ruthenium(II) analogue of $\text{Fe}(\text{DHBP})\text{Cl}_2$ was of interest in order to ascertain whether or not it would undergo oxidative denitrogenation. Accordingly, $\text{Ru}(\text{NH}_3)_6\text{Cl}_2$ (ref. 186) was reacted with DHBP in acetonitrile in a manner analogous to that used to prepare the iron(II) analogue. The yellow complex that resulted proved to be air-stable. Its analysis; as $\text{Ru}(\text{DHBP})(\text{NH}_3)_4\text{Cl}_2$, (Found :

C, 26.0; H, 5.53; N, 30.5. $C_{10}H_{24}Cl_2N_{10}Ru$ requires C, 26.3; H, 5.30; N, 30.7%) suggested, by analogy with the rhodium complex, (140), that the bipyridyl residue had simply displaced two amine groups and that the terminal amines of the DHBP were not co-ordinated.

6.5 Silver Complexes

Two reports concerning the interaction of cyclic tetramine ligands with silver have shown that ligands of this type have a propensity for stabilising silver in the +2 oxidation state^{187,188}. Excess silver(I) reacts with the first formed silver(I) complex, in the presence of trace amounts of water, in a manner which brings about disproportionation, as shown by the following equation:-



The orange coloured silver(II) complexes so formed, are stable and have the expected magnetic moment of c.a. 2.0 B.M.

The ability of the ligands under discussion to exhibit the same stabilising effect was of obvious interest. In the absence of water the reaction of silver(I) perchlorate with either DHBP or the bis(hydrazone) ligand, (62), derived from the condensation of acetone with DHBP, gave the expected 1 : 1 silver(I) to ligand adduct. Analytical data is given in Table 6.1.

When attempts were made to form the silver(II) complex by reacting two moles of silver(I) perchlorate with DHBP in

Table 6.1

Analytical Data

Compound	C	<u>Found</u>		N (%)	C	<u>Expected</u>	
		H				H	N
Ag(DHBP)ClO ₄	28.1	3.02	19.7		28.4	2.86	19.8
Ag(62)ClO ₄	37.6	4.04	16.4		38.1	4.00	16.7

water, the solution initially took on the orange colour characteristic of the silver(II) complexes referred to above. Within a few minutes, however, the orange colour had disappeared and the only products that could be isolated from the reaction mixture were silver metal and free bipyridyl. Thus, it appears that DHBP is too powerful a reducing agent to exist in association with silver(II). In contrast, reaction under the same conditions, of the bis(hydrazone), (62), showed no tendency to form the silver(II) species at all.

APPENDIX

General Experimental Techniques

In general, all synthetic work was carried out using standard techniques. Wherever the necessity to exclude oxygen and/or moisture from a reaction system arose the Schlenk Technique^{189,190} was employed, so as to enable the reaction to be conducted in an atmosphere of dry nitrogen.

The purification of solvents was effected using published procedures¹⁹¹. Where necessary, this was followed by a final distillation, from an appropriate drying agent, in a stream of nitrogen.

Elemental analyses were carried out, using standard Microanalytical techniques, by the Microanalytical Department of this Laboratory.

Proton magnetic resonance data was obtained in the continuous wave mode by use of either a Perkin-Elmer R12 (60 MHz) or a Varian Associates HA-100 (100 MHz) spectrometer, in the case of the latter instrument TMS was used as the lock. Alternatively, it was obtained in the pulsed Fourier Transform mode using either a Varian C.F.T. 20 (80 MHz) or a Varian XL-100FT (100 MHz) instrument, both of which employ the solvent deuterium as lock. Chemical shifts are quoted on the τ scale and relative areas of signals are shown in brackets. Signal multiplicities are abbreviated as follows: s = singlet,

d = doublet, m = multiplet, br = broad. ^{13}C magnetic resonance spectra were recorded using the XL-100FT instrument and signals are quoted in terms of their shift, in p.p.m., with respect to the carbon of TMS.

Infrared spectra were recorded on a Perkin-Elmer 257 or 457 grating spectrophotometer, in the range 4000 to 625 cm^{-1} , using nujol mulls, supported between sodium chloride discs. Absorbances are described using the abbreviations: s = strong, m = medium, w = weak, sh = shoulder, br = broad, and were calibrated against an appropriate polystyrene absorption.

Mass spectral determinations were made using an A.E.I. MS9 or MS12 spectrometer operating at 70 e.v. In cases where the volatility and thermal stability of a compound permitted it, mass spectroscopy was used as a means of verifying the molecular weight of the compound.

Mössbauer spectra of iron containing complexes were recorded at 80°K using a ^{57}Co in Pd source, in conjunction with a spectrometer which has been described in the literature¹⁹². Isomer shifts are quoted with respect to natural iron. All spectra were fitted without constraints to Lorentzian line shapes using a computer program written by Dr. A.J. Stone¹⁹³. The standard deviations in the isomer shift and quadrupole splitting values are believed to be less than 0.02 mm sec^{-1} (ref. 194).

Melting points were determined on a Koffler Block and are uncorrected.

Conductance measurements were made using a Wayne Kerr Universal Bridge. Determinations were made in the solvents specified.

Experimental details concerning the measurement of magnetic susceptibilities and the manner in which electronic spectra were recorded will be found in Section 4.1.

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