

# $\eta^2$ -SO<sub>2</sub> linkage photo-isomer of an osmium coordination complex

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## Supporting Information Placeholder

**ABSTRACT:** We report the discovery of an  $\eta^2$ -SO<sub>2</sub> linkage photo-isomer in the osmium pentaammine coordination complex, [Os(NH<sub>3</sub>)<sub>5</sub>(SO<sub>2</sub>)] [Os(NH<sub>3</sub>)<sub>5</sub>(HSO<sub>3</sub>)]Cl<sub>4</sub> (**1**). Its dark and light-induced crystal structures are determined via synchrotron X-ray crystallography, at 100 K, where the photo-induced state is metastable in a single crystal that has been stimulated by 505 nm light for 2.5 hrs. The SO<sub>2</sub> photo-isomer in the [Os(NH<sub>3</sub>)<sub>5</sub>(SO<sub>2</sub>)]<sup>2+</sup> cation contrasts starkly with the photo-inactivity of the HSO<sub>3</sub> ligand in its companion [Os(NH<sub>3</sub>)<sub>5</sub>(HSO<sub>3</sub>)]<sup>+</sup> cation within the crystallographic asymmetric unit of this single crystal. Panchromatic optical absorption characteristics of this single crystal are revealed in both dark and light-induced states, using concerted absorption spectroscopy and optical microscopy. Its absorption halves across most of its visible spectrum, upon exposure to 505 nm light. The SO<sub>2</sub> ligand seems to be responsible for this photo-induced bleaching effect, judging from a comparison of the dark and light-induced crystal structures of **1**. The SO<sub>2</sub> photo-isomerism is found to be thermally reversible and so **1** presents a rare example of an osmium-based solid-state optical switch. Such switching in an osmium complex is significant because bottom-row transition metals stand to offer linkage photo-isomerism with the greatest photo-conversion levels and thermal stability. The demonstration of  $\eta^2$ -SO<sub>2</sub> bonding in this complex also represents a fundamental contribution to osmium coordination chemistry.

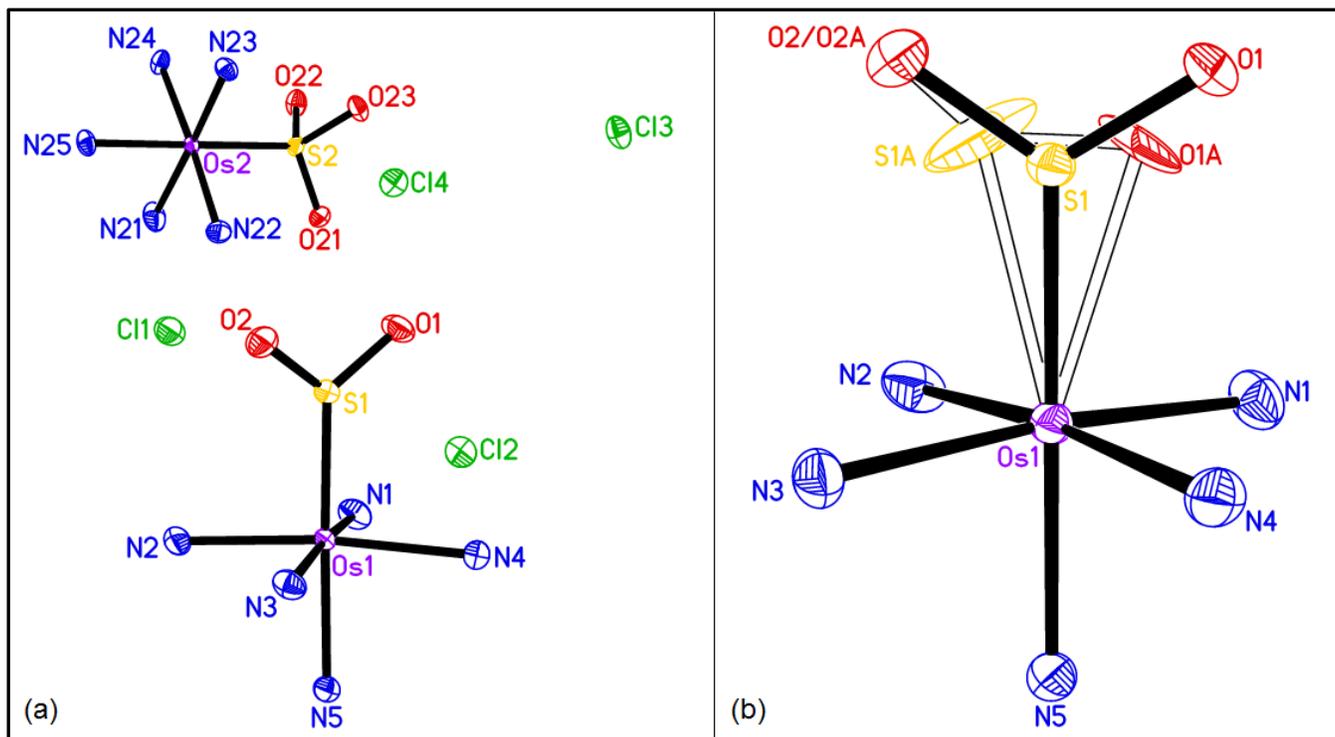
Taube and Harman have shown that the chemistry of osmium ammine complexes is rich and diverse.<sup>1,2</sup> In particular, they demonstrated that a large range of organic ligands can coordinate to osmium pentammine ions with  $\eta^2$ -configurations, with their early work on the [Os(NH<sub>3</sub>)<sub>5</sub>( $\eta^2$ -acetone)]<sup>2+</sup> complex<sup>3</sup> stemming to a large portfolio of research on the  $\eta^2$ -coordination of aromatic ligands to [Os(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup> ions.<sup>2</sup> These osmium pentaammine complexes support multiple oxidation states, especially where strong  $\pi$ -acceptors are coordinating ligands. This means that Os<sup>2+</sup>/Os<sup>3+</sup> redox couples can form in [Os(NH<sub>3</sub>)<sub>5</sub>( $\pi$ -acceptor)] complexes and cyclic voltammetry

studies have shown that their redox changes are often accompanied by  $\eta^2$ -to- $\eta^1$ -linkage isomerization of the  $\pi$ -acceptor.<sup>3,4</sup> Analogous research on osmium pentaammine complexes to which inorganic Lewis bases are coordinated is much less mature, despite the fact that the first endeavors in this area preceded the large portfolio of work on organic ligands. The discovery of [Os(NH<sub>3</sub>)<sub>5</sub>( $\eta^1$ -N<sub>2</sub>)]<sup>2+</sup> complexes offered a forerunner in this field.<sup>5</sup>  $\eta^1$ -to- $\eta^2$  N<sub>2</sub> photo-isomerization was suspected in these [Os(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>]<sup>2+</sup> salts, given their sensitivity to strong light<sup>5</sup> and modest electrochemical redox potentials; such photo-isomerization was later confirmed in single-crystals of [Os(NH<sub>3</sub>)<sub>5</sub>N<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> once stimulated by 325 nm light at 100 K<sup>6</sup>

Reports on osmium pentaammine chemistry involving neutral inorganic Lewis bases, other than N<sub>2</sub>, remain surprisingly scant. The most represented are the conflicting reports of [Os(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>2+</sup> ions which may be unstable<sup>7</sup> or long-lived.<sup>8</sup> One reported attempt to coordinate SO<sub>2</sub> to osmium pentaammine produced an impure compound.<sup>9</sup>

Interestingly, ruthenium SO<sub>2</sub> tetraammine coordination chemistry is rich in solid-state linkage photo-isomerization;<sup>10-17</sup> and pentaammines are a special case of tetraammine with NH<sub>3</sub> as the *trans* ligand. We thus wished to see if [Os(NH<sub>3</sub>)<sub>5</sub>(SO<sub>2</sub>)]<sup>2+</sup> ions could be synthesized; if so, might they present with  $\eta^1$ -to- $\eta^2$  linkage photo-isomerization in the solid state? If so, would their optical absorption properties suit solid-state optical switching in a similar way to that demonstrated for their Ru counterparts?

[Os(NH<sub>3</sub>)<sub>5</sub>(SO<sub>2</sub>)] [Os(NH<sub>3</sub>)<sub>5</sub>(HSO<sub>3</sub>)]Cl<sub>4</sub> (**1**) was synthesized from [Os(NH<sub>3</sub>)<sub>5</sub>(CF<sub>3</sub>SO<sub>3</sub>)](O<sub>3</sub>SCF<sub>3</sub>)<sub>2</sub> (10 mg, 13.8  $\mu$ mol), which was dissolved in deionized water (500  $\mu$ L), before HCl (200  $\mu$ L, 32 %) was added. Yellow crystals precipitated which were collected by filtration (see Supporting Information, S.2, for the associated crystal structure determination). These crystals were added to NaHSO<sub>3</sub> (aq) (3 mL, 0.04 M). This reaction mixture was heated to 75 °C for 30 min under continuous SO<sub>2</sub> (g) sparging. The yielding yellow solution was cooled to 297 K, while SO<sub>2</sub> sparging was maintained. HCl (80 mL, 32%) was added to this solution, and the resulting mixture was heated



**Figure 1.** (a) Crystallographic asymmetric unit of **1** in its dark state ( $\eta^1$ -SO<sub>2</sub> isomer) at 100 K; (b)  $\eta^2$ -SO<sub>2</sub> photo-isomer in the light-induced state of **1** (unshaded bonds), superimposed upon a dark state  $\eta^1$ -SO<sub>2</sub> configuration of **1** (shaded bonds). 9.3(3)% of the SO<sub>2</sub> ligands in the light-induced crystal structure of **1** have been photo-converted into their  $\eta^2$ -SO<sub>2</sub> photo-isomer by irradiating a single-crystal of **1** with 505 nm light for 2.5 hrs at 100 K. All atomic displacement parameters are shown at the 50% probability level.

to its boiling point and held there for 5 min; it was then left to cool overnight void of direct light. Single crystals of **1** formed which were collected by vacuum filtration, washed with CH<sub>3</sub>OH, and dried at 60 °C for 1h. Further synthetic details of **1** are provided in the Supporting Information, S.1.

The crystal structures of the dark and light-induced states of **1** were then determined using synchrotron-based X-ray crystallography, at the ChemMatCars beam line of the Advanced Photon Source, Argonne National Laboratory, IL, USA. A 0.1 x 0.1 x 0.05 mm single crystal of **1** was mounted onto a Huber three-circle diffractometer equipped with a Pilatus 3 x CdTe 1M shutterless pixel array detector and a 100 K nitrogen open-flow cryostream delivered by an Oxford cryojet. An X-ray beam of wavelength 0.41328 Å was used to capture a series of data frames over multiple  $\phi$  scans of crystal orientations, collected in 0.3° increments each with 0.6 s exposure time, using  $\omega$  and  $\kappa$  offsets spanning 20° and 45°, while maintaining a 130 mm sample-to-detector distance. For control purposes, the ambient lighting in the experimental hutch of the beam line was extinguished while data were being acquired for both dark and light-induced crystal structure determinations. Data for the dark-state crystal structure were first obtained. The crystal was then maintained at 100 K on the diffractometer and rotated continuously while being irradiated with 505 nm light for 2.5 hr, using a Thorlabs M505L3 light-emitting diode (LED) whose head power output was 1000 mA constant current and 3.3 V forward voltage. This light was switched off before acquiring data for the light-induced crystal structure. Further experimental details, as well as structure solution and refinement information, are given in the Supporting Information, S6-S9. A more detailed description of the specialist photo-

crystallography aspects of these experiments is given elsewhere.<sup>18,19</sup>

The dark and light-induced crystal structures of **1** are displayed in Figure 1. The crystallographic asymmetric unit (Figure 1a) shows that all atoms are ordered at 100 K, and two chloride ions support each cation locally. The angular geometry of the osmium pentaammine units in each cation is essentially identical: average N-Os<sub>1</sub>-N and N-Os<sub>2</sub>-N bond angles in the tetraammine equatorial plane are 89.82(6)° and 89.97(7)°, respectively; the NH<sub>3</sub> ligand *trans* to the SO<sub>2</sub> or SO<sub>3</sub>H group exhibits S-Os-N angles of 177.93(4)° and 177.75(4)°, respectively. The equatorial planes in both cations lie almost perfectly perpendicular to these near-linear *trans* axes (89.8(1)° and 90.0(1)°, respectively), evidencing highly regular octahedral coordination symmetry of both osmium centers. The relative orientation of these two *trans* axes (92.4(1)°) site the cations almost perpendicular to each other within the crystal lattice.

The relative coordination strengths of each ligand can be assessed by a comparison of bond lengths. Os<sub>1</sub>-N bond lengths in the equatorial plane range from 2.1238(13)-2.1396(15) Å while those of Os<sub>2</sub>-N span 2.1023(14)-2.1045(13) Å. These are classically shorter than the Os-N bond lengths for the ammine ligand *trans* to SO<sub>2</sub> or SO<sub>3</sub>H: 2.1447(12) Å and 2.1481(14) Å, respectively. Any *trans* influence in these cations appears to be negligible, given that this pair of Os-N<sub>trans</sub> bonds are similar in length despite the marked differences in sulfur coordination strength of the ligand opposite to this ammine, *cf.* Os<sub>1</sub>-S<sub>1</sub> is 2.0965(3) Å; Os<sub>2</sub>-S<sub>2</sub> is 2.2513(4) Å. The weaker coordination of S<sub>2</sub> to osmium, compared with that of S<sub>1</sub>, is expected given the greater bond connectivity in SO<sub>3</sub>H, compared with SO<sub>2</sub>, which will naturally place the electrons of S<sub>2</sub> in greater demand. The

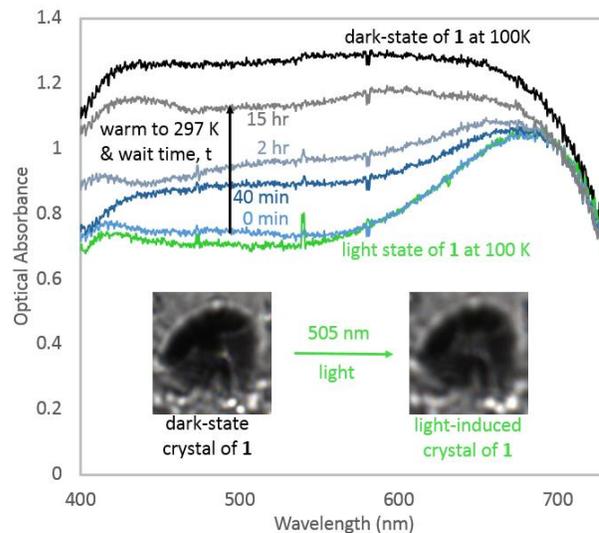
SO<sub>2</sub> ligand contains symmetrically delocalized S-O bonding (S1-O1: 1.4549(13) Å; S1-O2: 1.4514(13) Å) as anticipated for an S-bound η<sup>1</sup>-coordinated ligand, and supports a classical O1-S1-O2 angle of 113.13(8)° for a metal-coordinated sulfur dioxide ligand.<sup>10</sup> The delocalized portion of the SO<sub>3</sub>H ligand presents a similar bond geometry: S2-O21: 1.4653(13) Å; S2-O22: 1.4688(12) Å; O21-S2-O22: 112.39(8)°; cf. the σ-bonded S2-O23 1.6090(13) Å with average O-S-O angles of 102.85(9)°.

Figure 1b shows the crystal structure of **1** once irradiated with 505 nm light for 2.5 hr at 100 K. This features a light-induced metastable state whereby 9.3(3)% of the η<sup>1</sup>-SO<sub>2</sub> ligands in the crystal structure have been photo-converted into a η<sup>2</sup>-coordinated SO<sub>2</sub> species. Superimposed upon this light-induced state is the predominant (90.7(3)%) dark state structure that persists throughout the rest of the crystal lattice. Atomic displacement parameters of **1** are little altered by the formation of this η<sup>2</sup>-SO<sub>2</sub> ligand within its crystal lattice (see Figure 1 and Supporting Information). This suggests that the observed η<sup>1</sup>- to η<sup>2</sup>-SO<sub>2</sub> linkage photo-isomerization imposes little structural deformation on the residual dark state of **1**. A bond geometry comparison of the dark- and light-induced crystal structures of **1** (Table S1 in Supporting Information) bears further testament to this end.

This lack of structural deformation stands to reason considering that only 9.3(3)% of SO<sub>2</sub> ligands exist in the η<sup>2</sup>-SO<sub>2</sub> photo-converted form of **1**. This modest photo-conversion fraction is presumably a result of the strong σ-donating nature of the Os-N coordinative bonding from the NH<sub>3</sub> group that lies *trans* to the SO<sub>2</sub> ligand.<sup>1</sup> The act of varying the nature of this *trans* ligand and the counter-ions in ruthenium sulfur dioxide tetraammine complexes has been shown to influence the photo-conversion fraction of η<sup>2</sup>-SO<sub>2</sub> isomers, by virtue of their steric and electronic factors.<sup>10,12,15</sup> It is therefore anticipated that such chemical derivatization of **1** will yield osmium sulfur dioxide ammine complexes which exhibit higher η<sup>2</sup>-SO<sub>2</sub> photo-conversion fractions. Furthermore, osmium sulfur dioxide ammine complexes are expected to outstrip their ruthenium counterparts in producing linkage photo-isomers with higher conversion fractions. This is because third row transition metals afford maximum opportunity for overlap of their d orbitals with ligand bonding orbitals.<sup>6</sup> Moreover, the more diffuse nature of 5d orbitals in Os, compared with the 4d orbitals of Ru, means that osmium complexes will better support more diffuse ligand bonding types such as the 3-center 2-electron bonding observed for η<sup>2</sup>-SO<sub>2</sub> coordination herein.

The η<sup>2</sup>-SO<sub>2</sub> bonding in **1** is best qualified by the Os1-S1A and Os1-O1A separations (2.368(9) and 2.340(16) Å, respectively) since S1A is the most well resolved atom in this η<sup>2</sup>-SO<sub>2</sub> species; followed by O1A. While 9.3(3)% of 8 electrons (for an oxygen atom) is difficult to model accurately, an independent and anisotropic refinement of both S1A and O1A were possible; meanwhile, the position of O2A and O2 are so close that O2A could not be distinguished from O2. The somewhat oblate nature of the atomic displacement parameters for S1A and O1A indicate the presence of static or dynamic disorder in the η<sup>2</sup>-SO<sub>2</sub> ligand, which is not surprising given that this η<sup>2</sup>-SO<sub>2</sub> bonding exists as a minor species within a crystal lattice that is dominated by η<sup>1</sup>-SO<sub>2</sub> bound ligands; indeed, such structural manifestations have been observed in light-induced crystal structures of ruthenium-sulfur dioxide tetraammine complexes that host η<sup>2</sup>-SO<sub>2</sub> photo-isomers.<sup>10,14</sup> Atomic disorder is

well known to cause a foreshortening of true bond lengths and so the apparent S1A-O1A bond length (1.27(3) Å) yielded by this study is substantially shorter than its true value;<sup>10</sup> nonetheless, the η<sup>2</sup>-SO<sub>2</sub> configuration is qualitatively clear.



**Figure 2.** Optical absorption spectra of a single crystal of **1** in its dark and 505 nm photo-induced state at 100 K, together with microscopy images of the single crystal under these conditions (photo insets). The tail of the black arrow marks the optical absorption spectrum once the crystal has been warmed to 297 K, upon which the arrow tracks the progressive increase in optical absorption as a function of time lapse (0 – 15 hr), back towards its dark state optical properties.

If one is going to develop the solid-state photo-isomerization characteristics of osmium sulfur dioxide ammine complexes, then their optical properties in a single-crystal form also need to be determined. Moreover, while osmium stands to better stabilize sulfur dioxide photo-isomers than its ruthenium counterpart, where there is an already established field in linkage photo-isomerization,<sup>10-17</sup> this better opportunity can only be realized if the optical and structural properties are tuned in tandem. Indeed, corresponding osmium and ruthenium-based complexes will likely differ in their optical properties owing to their distinct charge-transfer bands that result from differences in valence d-orbital involvement.

Optical spectroscopy offers a convenient means by which the absorption effects of photo-isomerization can be tracked. Meanwhile, optical microscopy can monitor any photochromic changes associated with linkage photo-isomerization in single crystals of metal complexes upon light irradiation.

A concerted optical absorption spectroscopy and microscopy set up was custom built to probe the optical properties of **1**. This set up accounted for the single-crystal form of **1**, as well as the need to deliver external light (505 nm LED) and cryogenic conditions (100 K) to the sample which are compatible with the conditions that were used to access the photo-isomer of **1** by X-ray diffraction. The same crystal that was used for the synchrotron study was used for these optical measurements to ensure matching results. Further details of the experimental set up are given in the Supporting Information, S.5.

The dark-state single crystal of **1** at 100 K affords a panchromatic optical absorption spectrum in visible light (black line, Figure 2). Much narrower and blue-shifted optical absorption

bands are observed in osmium pentaammine solution chemistry; see for example, the solution-state UV/vis absorption spectrum of the  $[\text{Os}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)]^{2+}$  cation<sup>20</sup> which is the starting material for **1**, and its comparison to that of **1**, given in the Supporting Information, S.3. Corresponding photoluminescence spectroscopy on **1**, shown in the Supporting Information, S.4, also highlight the stark differences between single-crystal and solution-state based optical spectral data of **1**. As such, the single-crystal optical absorption spectroscopy results presented herein should be considered to refer exclusively to a solid-state phenomenon. The black crystal of **1** (left photo inset, Figure 2) undergoes photo-induced bleaching upon 2.5 hr of irradiation with 505 nm light at 100 K. A photo-stationary state appears to be achieved well before this exposure time, judging from the indistinguishable nature of two snapshots of the crystal that were taken after 45 min and 2.5 hr of irradiation. While its overarching panchromatic nature is maintained upon light irradiation (green line, Figure 2), the optical absorption of **1** is essentially halved where  $\lambda < 600$  nm, and reduced significantly throughout the visible spectrum; a charge-transfer band supports an absorption feature that peaks at 680-690 nm. This photo-bleaching effect is also manifested by a grey appearance of the light-induced single crystal shown in the right photo inset of Figure 2.

We have herein shown that the only difference between the dark and light-induced crystal structure of **1** is the 9.3(3)% photo-conversion of its  $\eta^1$ -SO<sub>2</sub> ligand to a  $\eta^2$ -SO<sub>2</sub> linkage photo-isomer. The formation of this  $\eta^2$ -SO<sub>2</sub> ligand is therefore wholly responsible for this change in optical absorption observed in the single crystal of **1**. The  $\eta^2$ -SO<sub>2</sub> photo-isomer in **1** appears to be metastable at 100 K, judging from the 3 hr of testing at 100 K, and its slow thermal decay once it has been warmed to 297 K; cf. the progressive recovery in its optical absorption, observed over a time evolution of 0-15 hr once at 297 K, shows that it has not reached its dark state by 15 hr (Figure 2). This contrasts starkly with metastable ruthenium sulfur dioxide complexes which return to their dark state within a few seconds or minutes once raised to room temperature. The much greater longevity of this thermal decay in **1**, relative to that observed in its ruthenium-based counterparts,<sup>10-12</sup> presumably owes its origins to the third row transition metal nature of osmium; the more diffuse 5d orbitals in Os, compared with the 4d orbitals of Ru, will better stabilize the bonding of an  $\eta^2$ -SO<sub>2</sub> photo-isomer.

In summary, we have discovered an osmium sulfur dioxide ammine complex and demonstrated that it exhibits solid-state  $\eta^2$ -SO<sub>2</sub> linkage photo-isomerization, as characterized by its dark- and light-induced crystal structures and solid-state optical absorption properties. The photo-isomerization process was found to be thermally reversible. **1** thus presents a rare example of an osmium-based solid-state optical switch.

In order to develop the solid-state photo-isomerization characteristics of this osmium sulfur dioxide ammine chemistry, the act of varying the nature of the counter-ions and the ligand that lies *trans* to SO<sub>2</sub> stands to produce chemical derivatives of **1** that will yield higher  $\eta^2$ -SO<sub>2</sub> photo-conversion fractions. This expectation arises because steric and electronic factors associated with these counter-ions and pendant ligands are known to influence the photo-conversion fraction of  $\eta^2$ -SO<sub>2</sub> isomers in ruthenium tetraammine complexes.<sup>10,12,15</sup> The existence of other types of SO<sub>2</sub> photo-isomers in this family of osmium complexes is also anticipated; especially the O-bound

$\eta^1$ -OSO species which is known in analogous Ru complexes.<sup>10-14,16</sup>

It would also be interesting to determine the dark- and light-induced structures of a series of osmium sulfur dioxide tetraammine complexes, where this *trans* ligand is systematically varied. This would offer important structural detail, by revealing the extent to which the coordination of  $\eta^2$ -SO<sub>2</sub> to osmium is stabilized by donation of the side-bound S-O electrons to the Os d $\sigma$ -orbital, compared with  $\pi$ -backbonding; such work on their Ru counterparts showed that donation into the Os d $\sigma$ -orbital dominated, countering original assumptions.<sup>14</sup> Meanwhile, the herein determination of the dark and light-induced crystal structures of an osmium sulfur dioxide complex offers a fundamental contribution to the structure and bonding of osmium coordination chemistry.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Further synthetic details of **1**, including the crystal structure determination of its reaction intermediate. Solution-state UV/vis absorption spectra of **1**. Solid-state and solution-state photoluminescence spectra of **1**. Crystal, data collection and structural refinement details for **1** determined in its dark and light-induced state, difference density maps to corroborate the structural model of the photo-isomer, and a dark versus light bond geometry comparison. Details of custom experimental set up for concerted optical spectroscopy and microscopy on a single crystal of **1**.

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### Author Contributions

J.M.C. performed all of the photo-crystallography and optical absorption spectroscopy work, with experimental assistance from S.G.W and Y-S.C. on beam line operation at the synchrotron and D.J.G. on setting up the optical spectroscopy apparatus. D.J.G. carried out the photoluminescence spectroscopy. J.M.C. was the PhD supervisor of J.d.J.V. who synthesized the material and determined the crystal structure of its reaction intermediate. J.M.C. drafted the paper.

### Notes

The authors declare no competing financial interests.

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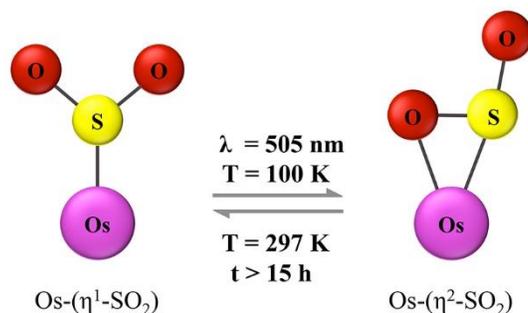
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## Table of Contents (TOC) graphic:



## Table of Contents (TOC) synopsis:

$\eta^2$ -SO<sub>2</sub> linkage photo-isomerism in the osmium pentaammine coordination complex [Os(NH<sub>3</sub>)<sub>5</sub>(SO<sub>2</sub>)] [Os(NH<sub>3</sub>)<sub>5</sub>(HSO<sub>3</sub>)]Cl<sub>4</sub> was discovered in the solid state by means of state-of-the-art *in situ* light-induced x-ray diffraction methods using synchrotron facilities, and a custom-built concerted optical absorption spectroscopy and microscopy apparatus. The corresponding Os-( $\eta^2$ -SO<sub>2</sub>) photo-isomer is the first structurally characterized example of its kind, which, considering the thermal reversibility of the isomerism, represents a rare example of an osmium-based solid-state optical switch.