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# Photocrystallography of $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$ reveals an O-bonded Metastable State.

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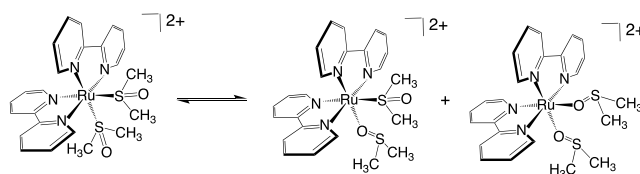
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We report the first instance of observing the phototriggered isomerization of dmsO ligands on a bis sulfoxide complex,  $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]$ , in the crystalline solid state. The solid-state UV-vis spectrum of the crystal demonstrates an increase in optical density around 550 nm after irradiation, which is consistent with the solution isomerization results. Digital images of the crystal before and after irradiation display a notable color change (pale orange to red) and cleavage occurs along planes,  $(\bar{1}01)$  and  $(100)$ , during irradiation. Single crystal X-ray diffraction data also confirms that isomerization is occurring throughout the lattice and a structure that contains a mix of the S,S and O,O/S,O isomer was attained from a crystal irradiated *ex situ*. *In situ* irradiation XRD studies reveal that the percent of the O bonded isomer increases as a function of 405 nm exposure time.

## Introduction

Photocrystallography has emerged as an indispensable tool for the structural characterization of metastable states of photochromic compounds.<sup>1</sup> Irradiation of single crystals of these compounds or complexes yields a mixture of ground state and metastable state isomers. While complete conversion of a single crystal can be achieved, it is much more common to observe partial conversion, and thus the isomerization is modelled as a disorder in the crystal. Success of this experiment requires that the solid-state photochemistry mimic the solution photochemistry. Moreover, crystal engineering to manage density, moduli, molecular structural changes, and heat dissipation is often required for photocrystallography to be successful. Indeed, irradiation of many crystalline materials can yield explosions (termed photosalient),<sup>2-4</sup> dramatic cracking or cleaving of planes,<sup>5,6</sup> and even disintegration of the crystal.<sup>7</sup> In stark contrast, other crystalline samples simply change color upon irradiation without any significant or substantial photochemistry beyond the surface of the crystal, revealing a complicated relationship between crystal structure and molecular photochemistry. Nevertheless, photocrystallography has yielded the molecular structures of metastable states of a wide range of transition metal complexes with  $\text{NO}^+$ ,<sup>8-11</sup>  $\text{N}_2$ ,<sup>12</sup>  $\text{SO}_2$ ,<sup>13-15</sup>  $\text{NO}_2^-$ <sup>16-18</sup> ligands as well as diarylethenes,<sup>19</sup> fulgides, spiro-compounds, and has recently been employed to observe

reaction intermediates in C–H bond activation.<sup>20-22</sup> We have created a large family of photochromic ruthenium sulfoxides by conjoining the electrochemistry of  $[\text{Ru}(\text{NH}_3)_5(\text{dmsO})]^{2+}$  (dmsO is dimethylsulfoxide) with the photochemistry of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy is 2,2'-bipyridine).<sup>23-25</sup> In 1982, Henry Taube first proposed an ECEC (Electrochemical-Chemical – Electrochemical-Chemical) mechanism to explain the peculiar cyclic voltammogram of  $[\text{Ru}(\text{NH}_3)_5(\text{dmsO})]^{2+}$ , where oxidation of  $\text{Ru}^{2+}$  to produce  $\text{Ru}^{3+}$  triggers intramolecular S  $\rightarrow$  O isomerization of the sulfoxide, and reduction of  $\text{Ru}^{3+}$  to yield  $\text{Ru}^{2+}$  prompts intramolecular O  $\rightarrow$  S isomerization.<sup>26</sup> While the ground state S-bonded isomer is well characterized by infrared spectroscopy and single crystal X-ray diffraction,<sup>27,28</sup> evidence for the formation of the isomerization product was provided by comparison of the O-bonded  $\text{Ru}^{3+/2+}$  coupled with other O-bonded coordination complexes and from its reactivity with exogenous ligands. Despite claims of X-ray data of the O-bonded isomer in  $[\text{Ru}(\text{NH}_3)_5(\text{dmsO})]^{3+}$ , the O-bonded structure produced from isomerization to our knowledge has not been reported.<sup>29,30</sup>



Scheme 1. Proposed isomerization products of S,S- $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$  to yield a mixture of O,O bonded and S,O bonded isomers upon visible light irradiation.

The MLCT (Metal-to-Ligand Charge-Transfer) transition in ruthenium polypyridine complexes yields an excited state best formulated as an oxidized ruthenium ion and a reduced bipyridine ligand (e.g.,  $[\text{Ru}(\text{bpy})_2(\text{bpy}^-)]^{2+}$ ).<sup>31</sup> The phototriggered S  $\rightarrow$  O isomerization in ruthenium polypyridine sulfoxides is

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activated by the formation of  $\text{Ru}^{3+}$  in the MLCT state of these heteroleptic complexes (Scheme 1). Characterization of the metastable state of these photochromic complexes has included  $^1\text{H}$  NMR spectroscopy,<sup>32</sup> infrared spectroscopy,<sup>33, 34</sup> DFT calculations,<sup>35-41</sup> and X-ray absorption spectroscopy.<sup>42</sup> While these techniques reflect molecular structure, none of these data provide the molecular structure of the metastable state. While there are many structures of S-bonded or O-bonded sulfoxides, we do not know of any X-ray diffraction study that characterizes the conversion of an S-bonded sulfoxide to an O-bonded sulfoxide.<sup>43, 44</sup> Herein, we report the structure of the metastable state of a photochromic ruthenium sulfoxide complex and show that the structure is unequivocally an O-bonded sulfoxide (Scheme 1).

## Results and Discussion

We chose to investigate  $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][\text{B}(\text{Ph})_4]_2$  as the large size, flexibility, weak basicity, and lack of functional groups capable of forming strong non-covalent interaction with the metal complex would increase the likelihood of observing isomerization of the dmsO ligands in the single crystalline phase. As expected, the tetraphenylborate salt exhibits a limited number of short contacts to the dmsO. For dmsO1 (containing S1), and dmsO2 (containing S2; Figure 1, left), three short contacts to the anion were observed (contacts not shown); however, for dmsO2 two of these contacts were to a symmetry related dmsO2.

Our previous investigations of bis sulfoxides have revealed that solvent and the nature of the chelate (if any) can be important in the quantum yield of isomerization and product distribution (one sulfoxide isomerization vs two sulfoxide isomerizations) following visible light irradiation.<sup>22</sup> These studies have demonstrated the presence of separate one isomerization (S,O-product isomer) and two isomerization (O,O-product isomer) reaction pathways. We are interested in

capturing the mechanistic details of isomerization within a crystalline environment and correlating these structural changes with electronic spectroscopic results within photochromic crystals.

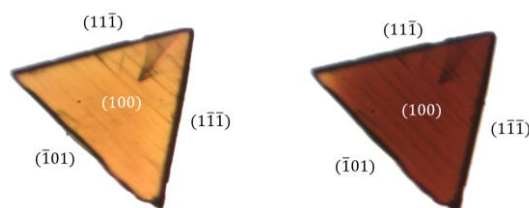


Figure 2. Digital images of the irradiated crystal before (left) and after 600 seconds of irradiation with 405 nm light (right).

Previous reports establish that the S,S-, S,O- and O,O-isomers each feature unique absorption maxima in solution. Thus, irradiation of solutions of this complex at much lower concentrations than those present in a crystal show a distinct darkening of the solution from colorless or pale yellow to a deep burgundy or purple color.

The solid-state UV-visible spectra of the crystal during irradiation demonstrates similar features to that seen in the solution data (Figure S1). Prior to irradiation, the crystal of the S,S-isomer absorbs at  $\sim 460$  nm. As the crystal is irradiated with 405 nm light, a new broad absorption feature appears at  $\sim 550$  nm, which is indicative of the formation of the bis O-bonded isomer. These changes in the optical density of the crystal are consistent with the solution isomerization results and are suggestive of isomerization. Upon careful examination of the crystals during irradiation, the crystal not only demonstrates dramatic changes in color (Figure 2, Figure S2; consistent with solution observations), but fracture lines along  $(\bar{1}01)$  are also evident. The emergence of fracture planes in the crystal indicate strain in the lattice presumably caused by the stress associated

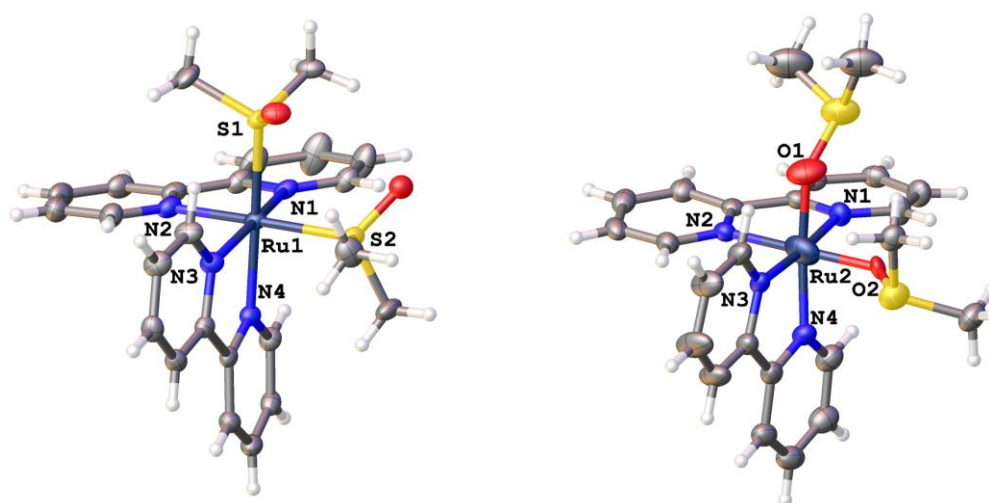


Figure 1. Ground state structure of  $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$  (left). Isolated molecular structure of bis-[O,O]- $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$  after irradiation with 405 nm light (right). Ruthenium, navy; nitrogen, blue; oxygen, red; sulfur, yellow; carbon, grey; hydrogen, white.

with the proposed sulfoxide isomerization (deep coloration) in the crystal. This is supported by the fact that the dmsO ligands align along  $(\bar{1}01)$  (see Figure S3). If the crystal is irradiated with 405 nm light for a prolonged time (>30 minutes), delamination occurs at the surface seemingly parallel to (100) (Figure S4).

Single-crystal X-ray diffraction data of  $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2][\text{B}(\text{Ph})_4]_2$  study corroborates that the dmsO ligands isomerize within the lattice. Photodifference maps are a useful tool for the visualization of light-induced electron density distribution changes in photocrystallography experiments.<sup>45</sup> A photodifference map calculated using the experimental intensities from the initial and final data collections (details in supporting information) reveals regions of positive and negative density changes near the dmsO ligands consistent with  $\text{S} \rightarrow \text{O}$  isomerization (Figure 3). Red surfaces, corresponding to negative changes in electron density, are observed near the initial ground state positions of the sulfur, oxygen and carbon atoms of both dmsO ligands indicating a reduction of electron density at these positions. As expected, the approximate volume of these surfaces tracks with atom size ( $\text{S} > \text{O} > \text{C}$ ). The green surfaces near the dmsO ligands, corresponding to positive changes, are observed in close proximity to the ground-state Ru-S and S-C bonds. These regions are consistent with the approximate new positions of the sulphur and oxygen atoms following light-induced S-O isomerization and served as the basis for the subsequent refinement of the position and orientation of the dmsO groups.

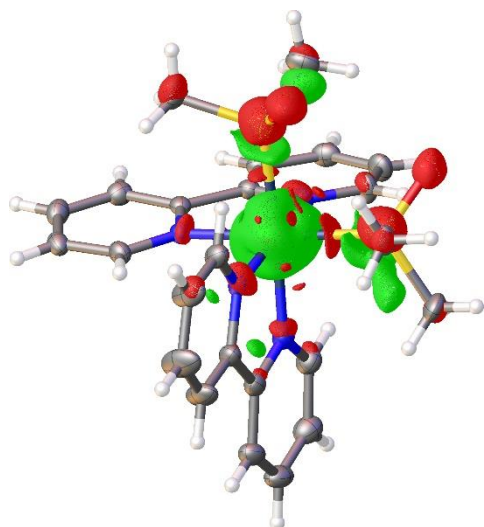


Figure 3. Photodifference map (surface:  $e/\text{\AA}^3=0.766$ ) showing the ground state geometry of the Ru dmsO complex. The positive and negative electron density isosurfaces are represented in green and red respectively.

Shown in Figure 1 is the ground state structure of  $[\text{S,S}]\text{[Ru}(\text{bpy})_2(\text{dmsO})_2][\text{B}(\text{Ph})_4]_2$  (tetraphenylborate anion not shown) prior to laser irradiation. After *ex situ* irradiation with 405 nm light, the crystal structure revealed a mixture of *bis* S-bonded and *bis* O-bonded isomers. When modelling the disorder for partly isomerized structure (O,O-isomer), the dmsO groups and the Ru were each refined independently. The dmsO *trans* to N4 contains 10.0% in the O bonded conformation whereas the dmsO *cis* to N4 contains 6.0%. The observation of

disorder in both dmsO ligands clearly indicates that both ligands isomerize, though given the differences in isomerization for both sulfoxides both S,O and O,O products are likely formed in the crystal lattice. The structure of the *bis* O,O bonded complex is displayed in Figure 1, right. This structure clearly features two O-bonded dmsO ligands with a tetrahedral geometry about the sulfur, indicating that the sulfur has not changed oxidation state. We note that the unit cell volume of the crystal is essentially unchanged between the two structures ( $\Delta V \sim 0.13\%$ ;  $V_{\text{S,S}} = 6139.9(4) \text{\AA}^3$ ;  $V_{\text{O,O}} = 6148.3(4) \text{\AA}^3$ ; Table S1). In addition to the new coordination mode of dmsO, there are other changes in the new O,O-bonded structure relative to the initial S,S-bonded complex.

Table 1. Crystallographically determined bond lengths and angles for the ground state and metastable state isomers.

S,S-bonded isomer		O,O-bonded isomer	
Bond	distance ( $\text{\AA}$ )	Bond	distance ( $\text{\AA}$ )
Ru1-S1	2.291	Ru2-O1	1.813
Ru1-S2	2.285	Ru2-O2	1.803
Ru1-N1	2.073	Ru2-N1	2.028
Ru1-N2	2.099	Ru2-N2	1.983
Ru1-N3	2.080	Ru2-N3	2.099
Ru1-N4	2.083	Ru2-N4	1.883
S1-O1	1.481	S1-O1	1.561
S2-O2	1.482	S2-O2	1.533
Bond angle	angle ( $^\circ$ )	Bond angle	angle ( $^\circ$ )
N2-Ru1-N4	86.763 $^\circ$	N2-Ru2-N4	96.23 $^\circ$
S1-Ru1-N2	91.186 $^\circ$	O1-Ru2-N2	90.569 $^\circ$
S2-R1-N4	94.207 $^\circ$	O2-Ru2-N4	81.314 $^\circ$
S1-Ru1-S2	88.067 $^\circ$	O1-Ru2-O2	92.514 $^\circ$
Ru1-S1-O1	116.518 $^\circ$	Ru2-O1-S1	136.729 $^\circ$
Ru1-S2-O2	115.338 $^\circ$	Ru2-O2-S2	126.280 $^\circ$

Table 1 summarizes the structural parameters of each isomer. Notably, there is a distinctive shortening of the bond between the Ru and the dmsO from  $\sim 2.3 \text{\AA}$  to  $\sim 1.8 \text{\AA}$ , which is consistent with isomerization from Ru-S to Ru-O coordination modes. We find Ru-S bond distances of 2.291 and 2.285  $\text{\AA}$ , which are consistent with that found in other salts of  $[\text{Ru}(\text{bpy})_2(\text{dmsO})_2]^{2+}$  as well as related bis(sulfoxides).<sup>46-48</sup> Moreover, Calligaris has categorized geometric and infrared data for a wide variety of metal sulfoxide complexes in both S- and O-bonded coordination modes. He reports that the average Ru(II)-S bond distance is 2.260(2)  $\text{\AA}$  from 474 independent ruthenium sulfoxide structures, which is in accord with our present findings.<sup>43</sup> Whereas an average Ru(II)-O bond distance of 2.10(1)  $\text{\AA}$  is obtained from statistical analysis of 291 independent structures. The bond distances of the Ru(II)-O bond reported here differ slightly from literature, which is likely a consequence of modelling low occupancy disorder. For example, the Ru-O bond distances in *cis*- $[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$  are

2.147(4) and 2.152(4) Å.<sup>49</sup> In  $[\text{Ru}(\text{bpy})_2(\text{ox})]^{2+}$  (ox is oxalate), the Ru–O bond distances are 2.087(7) and 2.093(6) Å.<sup>50</sup> Lastly, Ru–O bond distances of 2.050(8) and 2.030(8) Å were found in  $[\text{Ru}(\text{bpy})_2(\text{DBSQ})]^{2+}$ , where DBSQ is 3,5-di-*tert*-butyl-1,2-semiquinato.<sup>51</sup>

The S–O bond distances for the ground state S,S structure (1.481 Å and 1.482 Å) are in accord with many existing structures (1.489(1) Å) and the S–O bond distances for the O,O structure are similar (1.561 Å and 1.533 Å) to what is typically observed (1.545(3) Å).<sup>43, 44</sup> The S–C bond distances for a Ru(II) S-bonded and O-bonded sulfoxide are 1.784(1) and 1.783(5) Å, respectively. The ground state structure reveals commensurate distances (1.768–1.786 Å) while the S–C bond distances for the O-bonded metastable state are close to the expected value (ranging from 1.659 to 1.804 Å). Likewise, the Ru–S–O angle (116.5° and 115.3°) is in good agreement with the literature data (Ru–S–O: 117.6°), while the Ru–O–S angles (136.7° and 126.2°) in the metastable state are just slightly wider than that outlined by Calligaris (122.0°).

There is also a distortion of the geometry about Ru between the ground state and metastable state structures. Specifically, the N2–Ru1–N4 angle is 86.763° for the S,S-isomer, while this angle is 96.23° for the O,O isomer (Figure 1). Similarly, the S1–Ru1–S2 angle for the S,S-isomer is 88.067°, whereas the corresponding angle in the O,O-isomer (O1–Ru2–O2) is 92.514°. We are in the process of preparing new complexes to define these distances and angles more precisely of the metastable state. Nevertheless, the diffraction data unequivocally show changes in the coordination mode of dmsol following irradiation of the crystal.

We performed an *in-situ* SC-XRD data collection study to determine if the extent of dmsol isomerization was related to the total exposure to visible light (405 nm). Five complete data sets were collected sequentially on the same crystal during continuous irradiation (405 nm), and then the crystal structure was solved after each run to determine the percent of the O-bonded isomer as a function of total time irradiated. It was difficult to reproducibly observe the isomerization at cryogenic temperatures, so these data sets were collected at room temperature unlike the *ex situ* studies described above. This led to lower quality data sets; however, relevant conclusions may be drawn from this experiment. Chiefly, we confirmed that the concentration of the bis O-bonded isomer increased as a function of total light exposure (Figure S5). From the first data set to the final data set, the percent of the O-bonded dmsol gradually increased from ~10.1% to ~12.2% and ~7.7% to ~10.4% for dmsol1 and dmsol2, respectively. Although XRD is unable to determine the precise distribution of S and O bonded isomers in the lattice (*e.g.*, whether it is a mix of S,S and O,O or a mix of S,O/O,S), the dmsol ligands refined independently and only differ in occupancies of the S and O bonded isomer by ~3% throughout the entire data collection. This suggests that the isomerization of the dmsol ligands is correlated with light exposure. The plateau observed is consistent with achieving a photostationary state within the crystalline environment.

Consistent with solution measurements, the isomerization is thermally reversible. When a dark red crystal containing a

mixture of isomers (~10% and 6%) was isolated in the dark for a week, the crystal reverted to a pale orange color, characteristic of the S-bonded isomer (Figure S6). SC-XRD measurements on this crystal (in Supporting information) revealed conversion back to the ground state structure. Subsequent refinement showed only 2.6% of dmsol 1 remained O-bonded, whereas dmsol 2 displayed no evidence of the O-bonded isomer.

## Conclusions

In aggregate, the data presented here establish that the metastable product from irradiation of photochromic  $[\text{Ru}(\text{bpy})_2(\text{dmsol})_2][\text{BPh}_4]_2$  is an O-bonded sulfoxide. This result is consistent with the proposal first outlined by Taube in 1982. This study is enabled by the incorporation of large, flexible, weakly coordinating anion within the salt. Future studies will focus on revealing the mechanistic details of the isomerization by photocrystallography and transient absorption spectroscopy in this and related complexes.

## Data Availability

Crystallographic data for the structures reported herein have been deposited as CCDC 2226309–2226311. Additional experimental details and data are provided in the ESI, including a full description of synthetic procedures, crystallographic modelling techniques, UV-visible spectra of single crystals, and images showing changes to a single crystal upon irradiation

## Author Contributions

Z. Y. M., R. T. M., J. B. B., and J. J. Rack were responsible for conceptualization. Z. Y. M., R. T. M., and B. F. were responsible for the investigation. Z. Y. M and B. F. for formal analysis. J. B. B. and J. J. Rack for funding acquisition. All authors participated in writing – review and editing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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