

# Ru–OSO Coordination Photogenerated at 100 K in Tetraammineaqua(sulfur dioxide)ruthenium(II) ( $\pm$ )-Camphorsulfonate

Anthony E. Phillips,<sup>†,‡</sup> Jacqueline M. Cole,<sup>\*,†,§</sup> Thierry d'Almeida,<sup>†,⊥</sup> and Kian Sing Low<sup>†</sup>

<sup>†</sup>Cavendish Laboratory, University of Cambridge, J. J. Thomson Ave, Cambridge CB3 0HE, U.K.

<sup>§</sup>Department of Chemistry, University of New Brunswick, P.O. Box 4400, Fredericton, New Brunswick E3B 5A3, Canada

## Supporting Information

**ABSTRACT:** The photoinduced O-bound coordination mode in RuSO<sub>2</sub> complexes, previously observed only at 13 K, has been generated at 100 K in tetraammineaqua(sulfur dioxide)ruthenium(II) ( $\pm$ )-camphorsulfonate. This coordination state, often denoted MS1, decays to the  $\eta^2$ -bound MS2 state, with an estimated half-life of 3.4(8) h and a long-lived population of 2.9(4)% at 120 K.

The phenomenon of photoinduced linkage isomerism, known since the time of Werner, has been observed in an increasing number of materials over the past decade, including those based upon the active ligands NO,<sup>1</sup> NO<sub>2</sub>,<sup>2</sup> N<sub>2</sub>,<sup>3</sup> dimethyl sulfoxide,<sup>4</sup> and other organic sulfoxides.<sup>5</sup> In particular, several ruthenium–sulfur dioxide complexes are known to exhibit this behavior.<sup>6–9</sup> In these materials, the  $\eta^1$ -S-bound SO<sub>2</sub> ligand rotates upon irradiation with light to bind either in an  $\eta^2$  fashion through the S–O bond or through the O atom in an  $\eta^1$ -O-bound “OSO” configuration. If these materials are cooled to sufficiently low temperatures, these coordination modes become metastable, allowing their structures to be determined using photocrystallographic techniques;<sup>10</sup> above these temperatures, they decay rapidly to the original S-bound coordination. Initial observations revealed that the  $\eta^2$ -bound metastable state (conventionally denoted as MS2) can be induced by irradiation at 90–100 K. Density functional theory (DFT) calculations predicted the existence of the second, O-bound metastable state (MS1),<sup>7</sup> which was subsequently observed at 13 K.<sup>8</sup> This state, however, has hitherto not been observed at higher temperatures. From a materials chemistry perspective, the phenomenon of photolinkage isomerism is of particular interest for its potential use in optical data storage applications, for which metastability under ambient conditions would be ideal.<sup>11</sup> To reach this goal, it is important to understand the temperature ranges under which presently known materials exhibit metastability. To this end, we report in this Communication the first example of a metastable O-bound (MS1) state at 100 K. Photocrystallographic experiments on single crystals of tetraammineaqua(sulfur dioxide)ruthenium(II) ( $\pm$ )-camphorsulfonate (**1**) revealed a significant population of the MS1 (O-bound) coordination mode when irradiated at 100 K, in addition to the expected MS2 ( $\eta^2$ , reported elsewhere<sup>9</sup>) and original S-bound geometries.

The same experimental method as that in previous reports was used;<sup>9</sup> for convenience, it is briefly summarized here. Single crystals of **1** were mounted onto a laboratory diffractometer and cooled to 100 K in the dark; a full crystal structure determination was then performed. Next, the crystal was irradiated in situ for 2 h with broad-band, unpolarized light from a tungsten source, while continuously rotating the crystal to ensure uniform exposure to the light. The light source was then removed, and the same set of data as that for the previous “dark” collection was acquired.

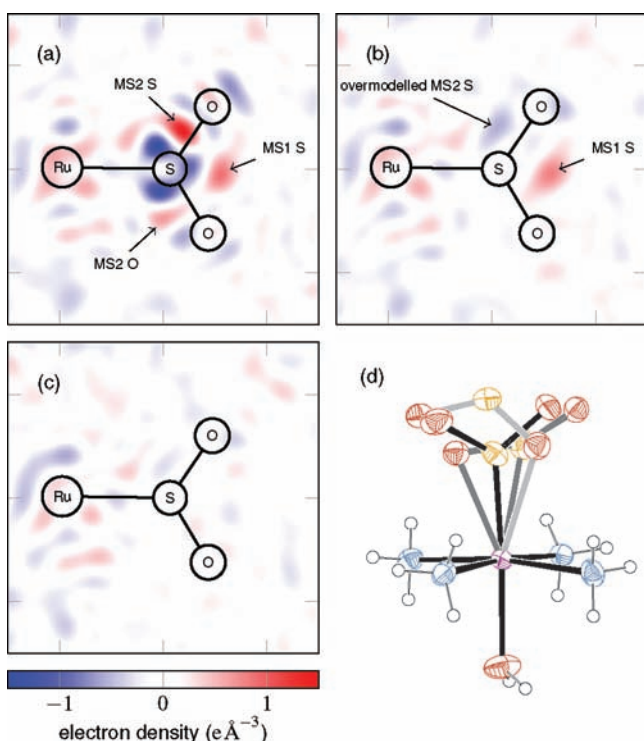
The post-irradiation data set was initially refined against a structural model containing only the ground state. The Fourier difference map between the ground-state model and the observed data, which reveals residual electron density that the ground-state model does not account for, was then calculated (Figure 1a).<sup>12</sup> The highest residual peak corresponds to the MS2 S atom, with the Ru-bound O atom also clearly visible. The ground-state S atom, however, is at the center of a trough of negative electron density, indicating that this site is overmodelled; smaller troughs are also visible around the ground-state O atoms.

The atoms of the MS2 metastable state were subsequently introduced into the model, with initial positions identified from the peaks in the Fourier difference map. The atomic parameters and occupancy of this state were then refined against the observed data before a new Fourier difference map was calculated (Figure 1b). As expected, there are fewer distinct features in this map. However, the largest peak of residual electron density remains clearly above the background; we attribute this to the S atom of a significant MS1 (O-bound) population. In addition, there is an electron density trough of similar depth surrounding the MS2 S atom, suggesting that this site is overmodelled to compensate for the unmodelled MS1 population.

Accordingly, the same procedure was followed to give a model also incorporating MS1. The resulting difference map displays only small fluctuations, with no discernible features other than slight Fourier transform ripples arising from the finite data set used (Figure 1c). We can thus be confident both that these data are sufficient to sustain this three-state model and that our final model accounts for the full observed electron density. A Bayesian comparison of the possible models

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**Figure 1.** Sections of Fourier difference maps in the plane of the ground-state  $\text{RuSO}_2$  group, shown for reference. These show the electron density not accounted for by (a) the ground-state model, (b) a model including ground and  $\eta^2$ -bound (MS2) states, and (c) a model including ground,  $\eta^2$ -bound (MS2), and O-bound (MS1) states. (d) Fully refined model for the photoexcited structure. The Ru atom is shown in purple, S in yellow, O in red, N in blue, and H in white. Ground-state bonds are shown in black, MS1 in light gray, and MS2 in dark gray.

corroborates the three-state model with overwhelming probability; the full details of this approach will be published elsewhere.<sup>13</sup>

The final refined structure of the irradiated ruthenium complex (Figure 1d) has metastable state populations of 12.2(11)% (MS2) and 13.2(8)% (MS1). The  $R$  value calculated on  $F$  for observations with  $I > 2\sigma$  was 0.1033; the highest peak and lowest trough in the residual electron density were respectively 0.777 and  $-0.826 \text{ e}\text{\AA}^{-3}$ . We believe that this value is slightly higher than comparable results from related systems because of the disorder between enantiomers at one of the camphorsulfonate sites (see the Supporting Information for this paper and ref 9); certainly, the Fourier difference maps (Figure 1a–c) indicate an excellent fit in the crucial region surrounding the  $\text{RuSO}_2$  moiety.

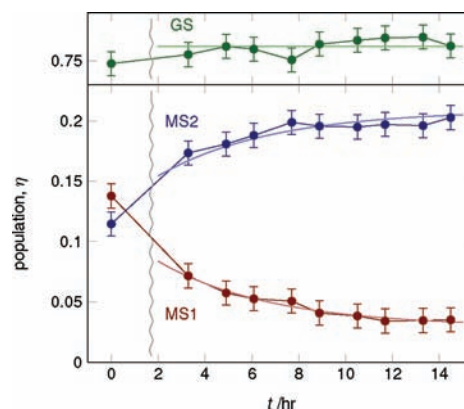
The model, containing 561 parameters, was refined against 4376 unique data and 522 restraints. A large number of restraints were necessary to overcome the strong negative correlations between the atomic displacement parameters of overlapping atoms (the various  $\text{SO}_2$  geometries and the disorder at one camphorsulfonate site). These correlations arise naturally because these parameters represent electron density in the same periodic region of space in the partial-occupancy model invariably used with disordered systems. However, in order not to bias the refined model, no restraints were placed on atomic positions based on prior information about the geometry of the metastable states. Externally derived restraints would yield better refinement statistics in the case

where the populations are very low, but it would be unconvincing to introduce restraints based on previous observations of MS1 before demonstrating that it is definitely present in the data obtained here. In fact, even without such restraints, the refined geometric parameters displayed excellent agreement with previous observations of this state in tetraammineaqua(sulfur dioxide)ruthenium(II) tosylate at 13 K. Full details of the crystallographic refinement are given as Supporting Information.

Variation of the metastable state populations with increasing temperature was then investigated. Once the 100 K data collection was complete, the temperature was raised at  $360 \text{ K}\cdot\text{h}^{-1}$  to 120 K, where the same data collection strategy was repeated continuously a further five times. Each ion in the 100 K model was imported into the 120 K model as a rigid body, allowing for a small change in the unit cell parameters but disregarding any small changes in the bond length due to the rise in temperature. The position and orientation of these ions were allowed to refine against each 120 K data set, along with all atomic displacement parameters and the occupancies of the metastable states. This is a reasonable model because we expect the increase of the temperature to have a far greater effect on the relative occupancies of the metastable states than their geometries. Not refining individual atomic positions allows small populations of MS1 to be measured via the electron density peak due to the S atom, even when the peaks due to the O atoms have disappeared below the level of background noise. Conversely, allowing atomic positions to refine precludes this possibility, giving unstable refinements after the first 120 K data collection.

Refining the three-state model against the first data set collected after the temperature increase gave different metastable state populations of 18.7(14)% (MS2) and 7.1(7)% (MS1). The *total* metastable state populations before and after the temperature change are in striking agreement [25.4(14)% at 100 K and 25.8(16)% at 120 K], suggesting that MS1 decays thermally to form MS2. At this temperature, MS2 persists for at least several days with no observable decline in population.<sup>7</sup>

Repeated data collections at 120 K revealed that the MS1 population has a finite lifetime at this temperature. Figure 2



**Figure 2.** Population of the metastable and ground states as a function of time. The temperature was raised from 100 to 120 K after the first ( $t = 0$ ) data collection. The time attributed to each population is the midpoint of the relevant data collection. The smooth lines are fits to first-order kinetics, assuming that the total metastable state population is constant.

shows the populations obtained by refinement of the same model against successive data collections. MS2 is known to decay via first-order kinetics at sufficiently high temperatures;<sup>7</sup> accordingly, a first-order kinetic model was fitted to these population values. The best-fit parameters indicated that MS1 decays with a half-life of 3.4(8) h to a long-lived occupancy of 2.9(4)%. Similar equilibrium mixtures between linkage isomers have previously been observed in  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2$ .<sup>14</sup> We note, however, that the uncertainties in these population values preclude any definite conclusion about the precise kinetic nature of this population decay: other possible models could also reproduce these data to within experimental uncertainty.

The similarities between the total metastable state populations immediately before and after raising the temperature from 100 to 120 K suggest that MS1 decays principally to MS2, so that the total metastable state population is constant. A kinetic model was therefore constructed in which MS1 is assumed to decay exclusively to MS2 over the course of this experiment: because the decay kinetics of MS1 were known from the discussion above, the only parameter in this model is the total MS population. Refining this value against the observed population data gave a reasonable fit with a total MS population of 23.8(4)%; encouragingly, this agrees within experimental error with the sum of the MS1 and MS2 values, 25.4(14)%, observed at 100 K.

As a result of these observations, the previously reported synchrotron data on **1** and on the related material tetraammineisonicotinamide(sulfur dioxide)ruthenium(II) tosylate (**2**) were revisited to check for any evidence for MS1.<sup>9</sup> This indeed revealed the presence of small MS1 populations (3–4%) in **1** and at one ruthenium site in **2**. This suggests that MS1 may be present in a number of  $[\text{Ru}(\text{SO}_2)(\text{NH}_3)_4\text{X}]\text{Y}$  complexes at much higher temperatures than previously anticipated, albeit in low populations, which may be difficult to detect. Indeed, because the temperatures required to stabilize MS2 are similar in most members of this family, one might analogously expect MS1 to persist at nitrogen temperatures in many members of this family rather than just the compounds studied here, although, of course, the exact energetics will vary from system to system, just as they do with MS2.<sup>7,9</sup>

These results represent the highest temperature at which Ru–OSO coordination has, to date, been recorded. An immediate practical implication is that this coordination mode is accessible using nitrogen cooling rather than requiring the more costly helium. We further anticipate that analysis of the lifetimes of metastable states in known compounds will aid in the rational design of novel materials with metastable states at ambient temperatures. Other experimental methods such as IR spectroscopy would allow the decay kinetics to be more accurately determined. However, previous DFT calculations suggest that the vibrational frequencies of MS2 and MS1 are very similar (symmetric stretches of 934 and 945  $\text{cm}^{-1}$  and antisymmetric stretches of 1208 and 1206  $\text{cm}^{-1}$  respectively),<sup>7</sup> so that high-resolution measurements would be needed to distinguish them. Further work on the thermal decay of metastable states will depend heavily on our ability to accurately determine low populations. In particular, Fourier difference maps become more difficult to interpret convincingly as the residual peaks approach the background noise level. Statistical approaches such as Bayesian analysis will help to confirm the degree to which observed crystallographic data support the presence of states with very low populations; we explore such approaches more fully elsewhere.<sup>13</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

X-ray crystallography data in CIF format, full experimental procedures, and the final refined crystallographic models. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jmc61@cam.ac.uk](mailto:jmc61@cam.ac.uk).

### Present Addresses

<sup>‡</sup>Centre for Condensed Matter and Materials Physics, Queen Mary University of London, Mile End Road, London E1 4NS, <sup>†</sup>U.K.

<sup>‡</sup>CEA DAM, Gramat, F 465000 Gramat, France.

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