

Photocrystallographic structure determination of a new geometric isomer of $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\eta^1\text{-OSO})][\text{MeC}_6\text{H}_4\text{SO}_3]_2$

Katharine F. Bowes,^a Jacqueline M. Cole,^{*a} Shamus L. G. Husheer,^a Paul R. Raithby,^{*bc} Teresa L. Savarese,^b Hazel A. Sparkes,^b Simon J. Teat^d and John E. Warren^c

Received (in Cambridge, UK) 20th March 2006, Accepted 21st April 2006

First published as an Advance Article on the web 4th May 2006

DOI: 10.1039/b604039j

The structure of a new metastable geometric isomer of $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_2)][\text{MeC}_6\text{H}_4\text{SO}_3]_2$ in which the SO_2 group is coordinated through a single oxygen in an $\eta^1\text{-OSO}$ bonding mode has been determined at 13 K; the new isomer was obtained as a 36% component of the structure within a single crystal upon irradiation using a tungsten lamp.

Photocrystallography is a new and developing technique for determining the structures of molecules in metastable or excited states that have been generated by illuminating a single crystal with high intensity light.^{1,2} In the area of “small molecule” crystallography the technique has been pioneered by Coppens and Ohashi who have determined the structures of both metastable species, and those with excited state lifetimes in the range 10–50 μs , at temperatures below 30 K.³ For example, the anion $[\text{Ru}(\text{NO}_2)_4(\text{OH})(\text{NO})]^{2-}$ exhibits a metastable state upon photoactivation where the nitrosyl changes coordination mode to adopt a $\eta^2\text{-N,O}$ arrangement.⁴ The diplatinum tetraanion $[\text{Pt}_2(\text{pop})_4]^{4-}$ (pop = pyrophosphate $(\text{H}_2\text{P}_2\text{O}_5)^{2-}$)³ and the dirhodium dication $[\text{Rh}_2(\text{diprop})_4]^{2+}$ (diprop = 1,3-diisocyanopropane)⁵ display short-lived excited state species, upon photoactivation, that show significant changes in metal–metal bond lengths compared with the ground state structures. In addition, Coppens has shown that the Cu(I) complex, $[\text{Cu}(\text{dmp})(\text{dppe})]^+$ (dmp = 2,10-dimethylphenanthroline; dppe = 1,2-bis(diphenylphosphino)ethane), shows a distinct geometry change towards a more flattened tetrahedral geometry upon excitation by 50 ns pulses of 355 nm laser radiation, at 16 K.⁶ In all these reported examples the conversion to the metastable or excited state is not complete, as this would result in crystal degradation caused by the generated changes in the crystal structure and, hitherto, the highest level of conversion is ca. 20%, the remaining 80% comprising the unchanged ground state structure.^{1,2}

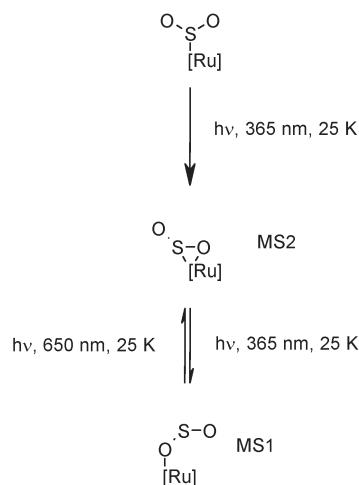
Among their studies, Coppens and co-workers have investigated the metastable linkage isomers of $[\text{Ru}(\text{NH}_3)_4\text{Cl}(\text{SO}_2)]^+$ and $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_2)]^{2+}$, and shown that when the complexes were irradiated with a 488 nm Ar⁺ CW laser at temperatures below 250 K the ground state planar $\eta^1\text{-SO}_2$ bonding mode of the sulfur dioxide is converted into the metastable $\eta^2\text{-side-S,O}$ -bound linkage

isomer.^{7,8} This isomer had previously been reported as metastable state 2, MS2, by Johnson and Dew⁹ from spectroscopic studies, in which a second metastable isomer, MS1, was also identified at a temperature of 25 K. For MS1 the bonding mode was not identified unambiguously but it was proposed that it might involve an $\eta^1\text{-OSO}$ coordination.⁹ The photochemically activated inter-conversion modes between the two metastable species, MS1 and MS2, proposed as a result of the spectroscopic studies, carried out at 25 K, are illustrated in Scheme 1. While Coppens *et al.* did not determine the structure of MS1 crystallographically, they concurred that it was an η^1 -oxygen bound linkage isomer from DFT calculations.⁷

In this paper we describe our successful photocrystallographic experiment to determine the structure of MS1, and show that it is indeed an $\eta^1\text{-OSO}$ linkage isomer of $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_2)]^{2+}$. The structure represents a bonding mode for SO_2 not previously structurally characterised in ruthenium coordination chemistry.

The experiment was performed at Station 9.8, at the SRS, CCLRC Daresbury Laboratory, using a Bruker APEX II CCD diffractometer, with monochromatic ($\lambda = 0.6896 \text{ \AA}$) radiation. The crystal was cooled to 13 K with helium gas from an Oxford Diffraction Helijet, and illuminated with a broad-band 200 W tungsten lamp.

A single crystal of $[\text{Ru}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{SO}_2)][\text{MeC}_6\text{H}_4\text{SO}_3]_2$ was prepared by literature methods,⁸ and the data collection strategy involved flash cooling the crystal to 13 K, in the dark, and collecting a full sphere of diffraction data to give a “clean” ground state structure devoid of any light pollution. The crystal was then



Scheme 1

^aDepartment of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: jmc61@cam.ac.uk

^bDepartment of Chemistry, University of Bath, Claverton Down, Bath, UK BA2 7AY. E-mail: p.r.raithby@bath.ac.uk

^cCCLRC Daresbury Laboratory, Daresbury, Warrington, UK WA4 4AD

^dDiamond Light Source, Rutherford Appleton Laboratories, Chilton, Didcot, Oxon, UK OX11 0QX

irradiated for 75 min with the tungsten lamp, at 13 K, to give the maximum conversion of the ground state to MS1 (the optimum time having been established from preliminary photocrystallographic experiments), the lamp switched off (to eliminate any heating effects), and after 5 min to allow the temperature within the crystal to equilibrate, a further sphere of diffraction data was recorded. This data set contained contributions from molecules in the MS1 state, the ground state, and some in the MS2 state, since it was not possible to obtain a crystal that did not have some of the previously characterised MS2 state present. The cell dimensions showed small, but significant changes between the unpolluted ground state data set and the data set that contained the excited state components.¹⁰ In order to account for this, the ground state coordinates were normalised relative to the changes associated with the cell dimensions of the photoactivated dataset. The resulting coordinates were then used to represent the ground state component of the model as a fixed rigid-body in the refinement of the photoactivated data. The excess electron density after rigid-body refinement of the ground state structure, showing the MS1 and MS2 contributions, was modelled as a disorder component. Fig. 1 shows a section of the electron density difference map, through the Ru(1)S(1)O(1)O(2) plane, for the photoactivated data set after the rigid-body refinement; having modelled the ground state structure already. The additional electron density is attributable to the atoms in the two disordered components in the MS1 metastable state. Both MS1 and MS2 are disordered over two positions, as would be expected given the C_{2v} symmetry of the ligand which allows two orientations of the η^1 -OSO ligand and two orientations of the η^2 -S-O bond, respectively. Considering the ground state as well, it was therefore necessary to model the SO₂ group over five positions in total. Once the positions of the MS1 and MS2 SO₂ atoms had been identified within the disorder model, the ground state coordinates for all the other atoms not involved in the photoexcitation process were released from their rigid-body constraints, and the atomic positions and displacement parameters were allowed to refine freely, all with occupancies set at unity. The proportion of the ground state SO₂ group and each

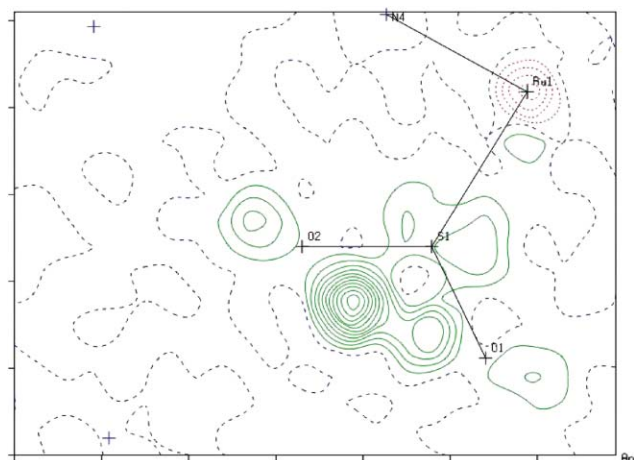


Fig. 1 The electron density difference map through the ground state Ru(1)S(1)O(1)O(2) plane computed using the rigid-body ground state structure and the photoactivated data set. The highest residual electron density in the map (green) corresponds to the positions of the two disordered components of the η^1 -OSO MS1 linkage isomer.

associated excited state present in the photoactivated data set was modelled, using PARTs within SHELXL,¹¹ by associating the site occupation factors for each of the sulfur atoms with different free variables, the sum of which was set to unity, using SUMP (SHELXL¹¹). Because of the five possible positions for the SO₂ group, equivalent bond lengths were constrained with SADI. All anisotropic displacement parameters for the SO₂ group were tied together using SIMU. Populations of each photoexcited sulfur atom refined to 24% (S(1a)) and 12% (S(1b)) for MS1, and 6% (S(1c)) and 2% (S(1d)) for MS2. This gives an overall level of excitation of *ca.* 44% and an excitation level of *ca.* 36% for the MS1 component. The various structural contributions to the overall model (except for the second orientation of the MS2 mode (S(1d)) which was only present at the 2% level) are shown in Fig. 2. The level of excitation obtained here, achieved without significant crystal degradation, is much higher than the maximum of *ca.* 20% achieved in any other photoreversible metastable or excited state system, with the exception of certain spin-crossover systems where the photoactivation through the crystal is cooperative and high levels of conversion are common.¹² This substantial photoexcited population was achieved using broad-band white light *via* a continuous wave tungsten lamp, rather than a single-wavelength of irradiation, *via* a pulsed monochromatic laser. The use of such

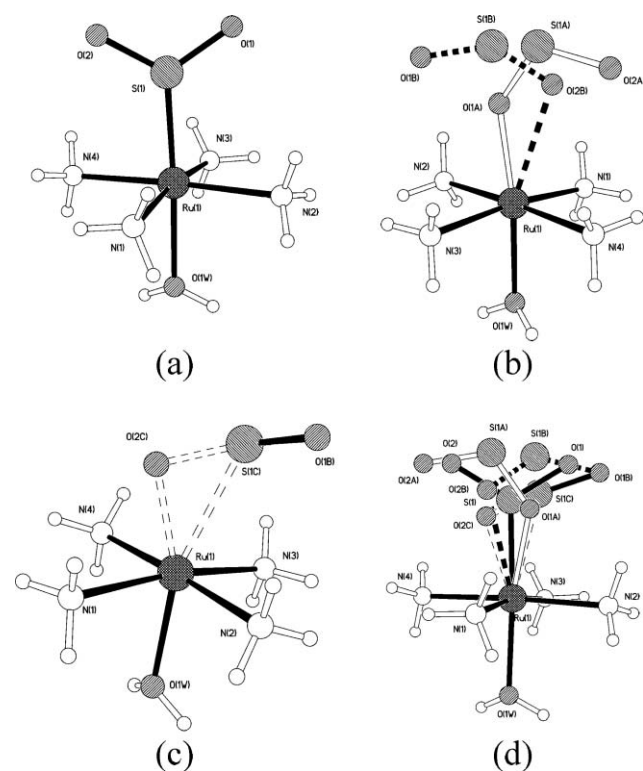


Fig. 2 The ground state and MS1 and MS2 contributions to the photoactivated structure of the cation in [Ru(NH₃)₄(H₂O)(SO₂)] [MeC₆H₄SO₃]₂. (a) The ground state [Ru(NH₃)₄(H₂O)(η^2 -SO₂)]²⁺ component with 56% occupancy of the η^2 -SO₂ group. (b) The two orientations of the MS1 metastable state [Ru(NH₃)₄(H₂O)(η^1 -OSO)]²⁺ component with a total occupancy of 36%. (c) The more significant component of the MS2 metastable state [Ru(NH₃)₄(H₂O)(η^2 -OSO)]²⁺ with the η^2 -OSO ligand with 6% occupancy. (d) The complete model showing the contributions from the ground state, the two orientations of the MS1 state, and the more significant component of the MS2 state.

white-light sources may point the way to achieving higher excitation levels in metastable species that have broad absorption bands, since a range of wavelengths will allow photons to penetrate deeper into the crystal thus exciting more molecules, as opposed to laser irradiation where all of the photons are absorbed within a few microns of the crystal surface if wavelength selection is not entirely appropriate to both ground and excited state absorption profiles. However, for time-resolved excited state experiments, that involve pump-probe techniques, a pulsed laser capable of pumping the sample at a time consistent with the lifetime of the excited state will still be necessary, simply due to the instantaneous flux required. As suggested by Johnson and Dew,⁹ and confirmed by our further photocrystallographic experiments at elevated temperatures, the MS1 state can be generated with lower efficiency at up to 120 K, and decomposes rapidly with almost complete conversion into the MS2 state above 160 K. The MS2 state, when cooled below 120 K and further irradiated, similarly converts into the MS1 state.

Unfortunately, the disorder of MS1 over two sites and the requirement to tie the parameters together precludes an accurate assessment of the bond parameters within the molecule. However, within the MS1 structure the *trans*-oxygen angles are 169.3(3)° (O(1a)–Ru(1)–O(1w)) and 161.7(4)° (O(2b)–Ru(1)–O(1w)) showing significant distortions from linearity. The angles at sulfur, O(1a)–S(1a)–O(2a) and O(1b)–S(1b)–O(2b), for the two disordered SO₂ groups are 116.2(8) and 118.1(11)°, respectively, which are similar to the O(1)–S(1)–O(2) angle of 116.2(3)°, in the ground state where the SO₂ group is η¹-SO₂ bound.

The experiments have clearly shown the generation of significant levels of an η¹-OSO metastable linkage isomer of [Ru(NH₃)₄(H₂O)(SO₂)] [MeC₆H₄SO₃]₂, and that the structure is in general agreement with those predicted in a DFT calculation.⁷ η¹-OSO coordinated ligands are relatively rare and a search of the Cambridge Structural Database (CSD)¹³ reveals only three examples, one coordinated to manganese,¹⁴ one coordinated to nickel,¹⁵ and one coordinated to titanium.¹⁶

We are grateful to the CCLRC for the award of beamtime. JMC thanks the Royal Society for a URF and St Catharine's College, Cambridge, for a Senior Research Fellowship. KFB wishes to thank the EPSRC and the Centre for Molecular Structure and Dynamics (CMSD) for financial support. SLGH is indebted to the Cambridge Commonwealth Trust, the New Zealand Bright Futures Trust and the CCLRC Daresbury Laboratory for support for a studentship. HAS is grateful to the EPSRC and the Cambridge Crystallographic Data Centre for financial support. TLS thanks the States of Jersey and the CCLRC

Daresbury Laboratory for a studentship. We are also grateful to Professor Philip Coppens, SUNY Buffalo, USA, for helpful discussions.

Notes and references

- P. Coppens, D. V. Fomitchev, M. D. Carducci and K. Culp, *J. Chem. Soc., Dalton Trans.*, 1998, 865; P. Coppens, I. I. Vorontsov, T. Graber, M. Gembicky and A. Yu. Kovalevsky, *Acta Crystallogr., Sect. A*, 2005, **61**, 162.
- J. M. Cole, *Chem. Soc. Rev.*, 2004, **33**, 501.
- C. D. Kim, S. Pillet, G. Wu, W. K. Fullagar and P. Coppens, *Acta Crystallogr., Sect. A*, 2002, **58**, 133; I. V. Novozhilova, A. V. Volkov and P. Coppens, *J. Am. Chem. Soc.*, 2003, **125**, 1079; Y. Ozawa, M. Terashima, M. Mitsumi, K. Toriumi, N. Yasuda, H. Uekusa and Y. Ohashi, *Chem. Lett.*, 2003, **32**, 62.
- D. V. Fomitchev and P. Coppens, *Inorg. Chem.*, 1996, **35**, 7021.
- P. Coppens, O. Gerlits, I. I. Vorontsov, A. Yu. Kovalevsky, Y.-S. Chen, T. Graber, M. Gembicky and I. V. Novozhilova, *Chem. Commun.*, 2004, 2144.
- P. Coppens, I. I. Vorontsov, T. Graber, A. Yu. Kovalevsky, Y.-S. Chen, G. Wu, M. Gembicky and I. V. Novozhilova, *J. Am. Chem. Soc.*, 2004, **126**, 5980.
- A. Yu. Kovalevsky, K. A. Bagley and P. Coppens, *J. Am. Chem. Soc.*, 2002, **124**, 9241.
- A. Yu. Kovalevsky, K. A. Bagley, J. M. Cole and P. Coppens, *Inorg. Chem.*, 2003, **42**, 140.
- D. A. Johnson and V. C. Dew, *Inorg. Chem.*, 1979, **18**, 3273.
- Crystal data for ground and metastable structures: C₁₄H₂₈N₄O₉S₃Ru, *M* = 593.65, triclinic, space group *P* $\bar{1}$ (No. 2), *T* = 13 K, ground state: *a* = 6.6945(33), *b* = 13.1054(5), *c* = 13.6251(6) Å, α = 94.457(2), β = 92.854(24), γ = 103.579(4)°, *V* = 1155.6(8) Å³, *Z* = 2, μ = 1.009 mm⁻¹, 8324 reflections (6.68 ≤ 2θ ≤ 59.29°), *R*1 = 0.0231, *wR*2(all) = 0.0628; metastable: *a* = 6.655(3), *b* = 13.109(6), *c* = 13.715(6) Å, α = 91.663(4), β = 96.450(4), γ = 104.721(4)°, *V* = 1147.8(9) Å³, *Z* = 2, μ = 1.008 mm⁻¹, 13556 reflections (5.831 ≤ 2θ ≤ 59.28°), *R*1 = 0.0428, *wR*2(all) = 0.0877. CCDC 602437 and 604229. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b604039j.
- G. M. Sheldrick, *SHELXL, a program for the refinement of crystal structures*, University of Göttingen, Germany, 1997.
- M. A. Leech, J. A. K. Howard, S. Dahaoui, N. K. Solanki and M. A. Halcrow, *Chem. Commun.*, 1999, 2245; V. A. Money, I. Radosavljevic Evans, M. A. Halcrow, A. E. Goeta and J. A. K. Howard, *Chem. Commun.*, 2003, 158; E. J. MacLean, C. M. McGrath, C. J. O'Connor, C. Sangregorio, J. M. W. Seddon, E. Sinn, F. E. Sowrey, S. L. Teat, A. E. Terry, G. B. M. Vaughan and N. A. Young, *Chem. Eur. J.*, 2003, **9**, 5314; A. L. Thompson, A. E. Goeta, J. A. Real, A. Galet and M. C. Munoz, *Chem. Commun.*, 2004, 1390.
- Cambridge Structural Database: F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380.
- G. A. Gott, J. Fawcett, C. A. McAuliffe and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1984, 1283.
- R. Maggini, Z. Mews, W.-D. Stohrer and M. Noltemeyer, *Chem. Ber.*, 1990, **123**, 29.
- E. Solari, C. Floriani and K. Schenk, *J. Chem. Soc., Chem. Commun.*, 1990, 963.