

The first example of a double bridged diruthenium(II) complex containing the rare bridging S,O bidentate dimethyl sulfoxide ligand which defines a stable Ru–Cl–Ru–S–O five-membered ring

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The diruthenium(II) complex $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-Me}_2\text{SO-S,O})\text{Cl}_3(\text{Me}_2\text{SO-S})_3(\text{CO})_2]$ has been synthesized from *cis, fac*- $[\text{RuCl}_2(\text{Me}_2\text{SO})_3(\text{CO})]$ in refluxing acetone and characterized by X-ray crystallography; unusual solution (^1H and ^{13}C NMR) and solid-state (IR) spectral features were found for the bridging sulfoxide, besides a remarkable inertness towards substitution reactions.

Following earlier studies on chloro(dimethyl sulfoxide)ruthenium species,¹ we recently described a series of carbonyl derivatives.² We found that co-ordination of CO *trans* to a $\text{Me}_2\text{SO-S}$ molecule always involved its isomerization from the S- to O-bonded ($\text{Me}_2\text{SO-O}$). The new carbonyl- Me_2SO complexes proved to be very useful precursors for the selective synthesis of substituted derivatives by replacement of the labile $\text{Me}_2\text{SO-O}$ ligand(s) *trans* to CO. In particular, the reactivity of *cis, fac*- $[\text{RuCl}_2(\text{Me}_2\text{SO})_3(\text{CO})]$ **1** with pyridylporphyrins allowed us to prepare several supramolecular adducts.³ The further investigation of the solution chemistry and reactivity of **1** led us to the synthesis and structural characterization of the novel double bridged dimer $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-Me}_2\text{SO-S,O})\text{Cl}_3(\text{Me}_2\text{SO-S})_3(\text{CO})_2]$ **2** (Fig. 1), which contains the rare $\mu\text{-Me}_2\text{SO-S,O}$ moiety that bridges the two ruthenium centers *via* the S- and O-atoms.† The dinuclear complex consists of a *cis*- $[\text{RuCl}_2(\text{Me}_2\text{SO-S})_2(\text{CO})]$ unit linked to *cis*- $[\text{Ru}(\text{Me}_2\text{SO-S})_2\text{Cl}(\text{CO})]$ by Cl and Me_2SO bridges, so that both metal atoms achieve a nearly octahedral environment $[\text{Ru}(1) \cdots \text{Ru}(2)$ 2.9794(9) Å]. The dimer thus defines the Ru-Cl-Ru-S-O five membered ring. It is interesting to observe that in the $\text{Me}_2\text{SO-S,O}$ bridge the oxygen atom is *trans* to CO, while the sulfur atom is *trans* to Cl. In fact, O-bonding in ruthenium complexes is favoured only in the presence of *trans* π acceptor ligands (*e.g.* $\text{Me}_2\text{SO-S}$, CO or NO).^{2,5}

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† Heating *cis, fac*- $[\text{RuCl}_2(\text{Me}_2\text{SO})_3(\text{CO})]$ (0.15 g, 0.34 mmol) in refluxing acetone (20 mL) for 4 h yielded a pale yellow solution whose volume was then reduced to *ca.* 10 mL. Crystals of **2** (50% yield) grew within 3 d from the solution stored at 4 °C (Found: C, 17.01; H, 3.36. $\text{C}_{10}\text{H}_{24}\text{Cl}_4\text{O}_6\text{Ru}_2\text{S}_4$ requires C, 16.85; H, 3.39%). IR (KBr): $\nu(\text{CO})$ 2008, 1997 cm^{-1} (vs); $\nu(\text{SO})$ 1141, 1107 cm^{-1} (vs, $\text{Me}_2\text{SO-S}$), 1010 cm^{-1} (vs, $\mu\text{-Me}_2\text{SO-S,O}$); $\nu(\text{Ru-O})$ 480 cm^{-1} (m); $\nu(\text{Ru-S})$ 425 cm^{-1} (s); $\nu(\text{Ru-Cl})$ 380 cm^{-1} (m). ^1H NMR (400 MHz, CD_3NO_2 , vs. CH_3NO_2 at δ 4.30) 3.26 (s, 3 H, Me^a), 3.42 (s, 3 H, Me^b), 3.43 (s, 3 H, Me^c), 3.44 (s, 3 H, Me^d), 3.45 (s, 3 H, Me^e), 3.50 (s, 3 H, Me^f), 3.89 (s, 3 H, Me^g), 3.92 (s, 3 H, Me^h). ^{13}C NMR (100 MHz, CD_3NO_2 , vs. CH_3NO_2 at δ 62.8): δ 43.9 (Me^a), 44.8 (Me^e), 45.2 (Me^e), 45.9 (Me^e), 48.3 (Me^d), 48.6 (Me^b), 49.2 (Me^f), 51.8 (Me^h), 193.3 (CO), 197.1 (CO). ^1H and ^{13}C resonances marked with ^{a-h} are correlated in the 2-D ^1H - ^{13}C HETCOR spectrum. Pairs of methyls marked $\text{Me}^{a,c}$, $\text{Me}^{b,d}$, $\text{Me}^{e,f}$ and $\text{Me}^{g,h}$ belong to the same Me_2SO according to the 2-D NOESY spectrum. The structure of **2** was determined by an X-ray crystallographic analysis. Crystal data: $\text{C}_{10}\text{H}_{24}\text{Cl}_4\text{O}_6\text{Ru}_2\text{S}_4$, $M = 712.47$, monoclinic, space group $P2_1/n$ (no. 14), $a = 9.506(1)$, $b = 13.447(1)$, $c = 19.208(3)$ Å, $\beta = 91.19(1)^\circ$, $V = 2458(5)$ Å³, $Z = 4$, $\mu = 2.03 \text{ mm}^{-1}$, $T = 293 \text{ K}$, $R1 = 0.047$ for 3183 unique reflections. CCDC reference number 186/1063. See <http://www.rsc.org/suppdata/dt/1998/2447/> for crystallographic files in .cif format.

Ruthenium dimers are not uncommon, but the two units are normally held together by a triple bridge, such as in $[\text{Ru}_2(\mu\text{-Cl})_3\text{Cl}(\text{Me}_2\text{SO-S})_5]$.⁶ To the best of our knowledge, $[\text{Ru}_2(\mu\text{-Br})_2\text{Br}_4(\text{Et}_2\text{SO-S})_2(\text{NO})_2]$ is the only example of a structurally characterized double bridged ruthenium dimer.⁷ Examples of structurally characterized sulfoxides bridging two metals are quite rare, and involve mainly electrostatic interactions between an alkali-metal ion and the oxygen atom of a sulfoxide S-bonded to a 'soft' transition-metal ion (*e.g.* $\text{Ru-S-O} \cdots \text{Li}$).^{8,9} The first example of $\mu\text{-Me}_2\text{SO-S,O}$ bridging two neutral Ru^{II} atoms was reported by Tanase *et al.* in 1996 for the triple bridged dimer $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-Me}_2\text{SO-S,O})\text{Cl}_2(\text{Me}_2\text{SO-S})_4]$ **3**, which also featured a Ru–Ru bond $[\text{Ru}(1)\text{-Ru}(2)$ 2.8435(7) Å].¹⁰

Several important structural and spectroscopic details of dimers **2** and **3** are significantly different from each other. In **2** the Ru(1)–S(2) distance of 2.275(2) Å is hardly shorter than those of the terminal Me_2SO ligands [2.282(2)–2.291(2) Å], but markedly longer than that found in **3** [2.188(2) Å]. This lengthening is likely due to the presence of the carbonyl groups. In fact, the Ru–S bond lengths range from 2.279(2) to 2.313(5) Å in similar complexes containing one CO per metal atom.^{2b} The Ru(2)–O(2) distance of 2.122(5) Å is shorter than that in **3**

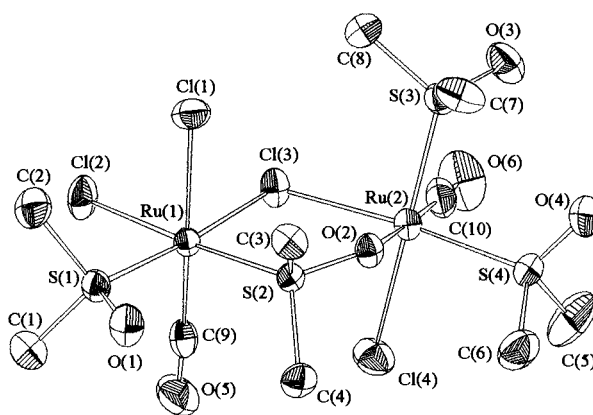


Fig. 1 An ORTEP⁴ plot of **2** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (°): Ru(1)–Cl(1) 2.430(2), Ru(1)–Cl(2) 2.384(2), Ru(1)–Cl(3) 2.440(2), Ru(1)–S(1) 2.282(2), Ru(1)–S(2) 2.275(2), Ru(1)–C(9) 1.870(8), Ru(2)–Cl(3) 2.414(2), Ru(2)–Cl(4) 2.411(2), Ru(2)–S(3) 2.291(2), Ru(2)–S(4) 2.283(2), Ru(2)–O(2) 2.122(5), Ru(2)–C(10) 1.840(9), S(1)–O(1) 1.480(5), S(2)–O(2) 1.508(5), S(3)–O(3) 1.472(6), S(4)–O(4) 1.455(7); Cl(1)–Ru(1)–Cl(2) 90.02(8), Cl(1)–Ru(1)–Cl(3) 86.37(4), Cl(1)–Ru(1)–S(1) 90.99(7), Cl(1)–Ru(1)–S(2) 87.63(7), Cl(2)–Ru(1)–Cl(3) 86.93(6), Cl(2)–Ru(1)–S(1) 87.63(7), Cl(2)–Ru(1)–C(9) 88.3(2), Cl(3)–Ru(1)–S(1) 174.75(7), Cl(3)–Ru(1)–S(2) 90.30(6), Cl(3)–Ru(1)–C(9) 90.8(2), S(1)–Ru(1)–S(2) 94.61(7), S(1)–Ru(1)–C(9) 90.7(2), S(2)–Ru(1)–C(9) 94.0(2), Cl(3)–Ru(2)–Cl(4) 87.24(8), Cl(3)–Ru(2)–S(3) 92.94(7), Cl(3)–Ru(2)–O(2) 87.2(1), Cl(3)–Ru(2)–C(10) 92.3(3), Cl(4)–Ru(2)–S(4) 88.54(8), Cl(4)–Ru(2)–O(2) 89.1(1), Cl(4)–Ru(2)–C(10) 92.8(3), S(3)–Ru(2)–S(4) 91.24(7), S(3)–Ru(2)–O(2) 90.4(1), S(3)–Ru(2)–C(10) 87.7(3), S(4)–Ru(2)–O(2) 88.8(1), S(4)–Ru(2)–C(10) 91.9(3)

[2.160(2) Å] and close, within experimental error, to the mean value of 2.137(5) Å found in **1**.^{2b} Interestingly, the S(2)–O(2) bond length of 1.508(5) Å is intermediate between the average values found for the S–O bond in S- [1.478(1) Å] and O-bonded [1.538(3) Å] Ru^{II}–sulfoxide complexes, not too far from that found in free sulfoxides [average 1.492(1) Å].⁵ The conformation of the five-membered ring is best described as a *twist* one. The bond angles involving the sulfoxide bridge [Ru–S–O 115.9(2), Ru–O–S 130.4(3)°] are significantly distorted from those found in η¹ complexes [Ru–S–O average 117.6(3), Ru–O–S average 122.4(9)°].¹⁰ Also the Ru(1)–Cl(3)–Ru(2) bond angle of 110.14(7)° appears to be rather larger than usually found in μ-Cl bridges [80–90°].^{6,10}

The SO stretching frequency in the solid state and ¹H and ¹³C NMR resonances in solution are diagnostic of the Me₂SO binding mode.[‡]^{5,11} However, the effect of the inclusion of S–O into a five-membered ring on the spectroscopic features is unknown. No IR attribution was reported in the case of the triple bridged dimer **3**.¹⁰ The solid-state IR spectrum of **2** (KBr) has two ν(SO) bands in the region of Me₂SO–S (1141 and 1107 cm⁻¹), but none in that of O-bonded sulfoxide. However, comparison with the spectrum of the precursor **1**, allowed us to attribute to the bridging Me₂SO–S,*O* a strong band at 1010 cm⁻¹, which partially overlaps with bands due to C–H rocking modes. Based on the S–O bond length of the bridging sulfoxide, an S–O stretching frequency slightly shifted to lower frequencies compared to free Me₂SO was expected.

The ¹H NMR spectrum of **2** in CD₃NO₂, consisting of eight equally intense well resolved singlets, suggests that the dimer maintains its integrity in this solvent.§ However, while six resonances lie in the region between δ 3.2 and 3.5, typical for S-bonded Me₂SO^{11a} (also in mononuclear carbonyl derivatives),^{2b} the remaining two signals have unprecedented downfield shifts (δ 3.89 and 3.92) and were attributed to the methyl groups of the bridging sulfoxide.¶ On the contrary, only typical resonances were reported for dimer **3**.¹⁰ The ¹³C NMR spectrum of **2**, beside the resonances of the two CO's, showed eight methyl resonances in the range δ 44.0–52.0 (compared to the range δ 42.0–48.0 found by us for S-bonded Me₂SO in mono-

meric ruthenium–sulfoxide–carbonyl complexes).^{2b} However, while the most downfield proton resonance at δ 3.92 was correlated to the most downfield carbon resonance (δ 51.8) in a 2-D hetero-correlated H–C COSY spectrum, the other downfield proton signal at δ 3.89 had a cross-peak with a carbon resonance in the 'normal' range (δ 44.8). Thus, both ¹H and ¹³C resonances of the bridging sulfoxide fall mostly outside the range of frequencies established for terminal Me₂SO.

The ¹H NMR CD₃NO₂ spectrum of **2** was found unaltered after several days, indicating that the dimer is stable in solution. To our surprise, the spectrum of **2** also remained unaltered for several hours after addition of pyridine (only very slowly did small signals for co-ordinated pyridine appear), indicating that, despite the apparent structural strain, the five-membered ring is remarkably stable toward reaction with nucleophiles that normally readily replace Me₂SO–*O trans* to CO.

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‡ The ν(SO) stretch is typically shifted to lower frequencies compared to free Me₂SO (1055 cm⁻¹) by co-ordination through oxygen (900–950 cm⁻¹), while it is shifted to higher frequencies (1080–1150 cm⁻¹) by co-ordination through sulfur.

§ A very similar spectrum, except for the overlap of the two most downfield resonances, was observed also in CDCl₃, where **2** is sparingly soluble: δ (vs. CHCl₃ at δ 7.26) 3.30 (s, 3 H, Me), 3.41 (s, 3 H, Me), 3.44 (s, 3 H, Me), 3.48 (s, 3 H, Me), 3.49 (s, 3 H, Me), 3.51 (s, 3 H, Me), 3.88 (s, 6 H, 2Me).

¶ The two resonances were clearly linked by a cross-peak in a 2-D NOESY spectrum, confirming that they belong to methyl groups on the same Me₂SO.