A diruthenium(II) complex containing an unprecedented bridging S,O-bidentate dimethyl sulfoxide ligand

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The diruthenium(II) complex [$Ru_2(\mu$-Cl)(μ-H)(μ-Me_2SO)$Cl_2(Me_2SO)_4]\cdot 2CH_2Cl_2$ is prepared from [$RuCl_2(Me_2SO)_4$] in methanol in the presence of Na_2(xdk) [H_2xdk = *m*-xylenediamine bis(Kemp's triacid imide)] and characterized by X-ray crystallography which reveals an unprecedented S,O-bidentate bridging Me_2SO ligand.

A variety of transition-metal complexes with dimethyl sulfoxide are useful starting materials for many inorganic and organometallic compounds.[1] Me_2SO can coordinate through both S and O donor atoms in a monodentate fashion, and can also (rarely) bridge two metal atoms *via* O.[2] Although the S,O-bidentate bridging mode of Me_2SO has been considered as viable,[3] structurally characterized examples have not, as yet, been reported. Here we report the synthesis and characterization of a diruthenium(II) complex, [$Ru_2(\mu$-Cl)(μ-H)(μ-Me_2SO)$Cl_2(Me_2SO)_4]\cdot 2CH_2Cl_2$ **2**, which contains an unprecedented η^1,η^1-S,O bridging Me_2SO ligand.

Reaction of [$RuCl_2(Me_2SO)_4$] **1**[4,5] with $Na_2(xdk)\cdot 4H_2O$ [H_2xdk = *m*-xylenediamine bis(Kemp's triacid imide)][6] in refluxing methanol for 2 h gave a solution which was evaporated to dryness. The residue was recrystallized from CH_2Cl_2–Et_2O to give orange crystals of [$Ru_2(\mu$-Cl)(μ-H)(μ-Me_2SO)$Cl_2(Me_2SO)_4]\cdot 2CH_2Cl_2$ (**2**$\cdot 2CH_2Cl_2$) in 11% yield.‡ Complex **2** is air-stable both in the solid state and in solution. Although the resultant product does not contain the dinucleating ligand xdk, use of $Na_2(xdk)\cdot 4H_2O$ was indispensable in the formation of **2**; presumably it mediates in a dinucleating process. A similar reaction of **1** with NaO_2CMe failed to produce complex **2**.

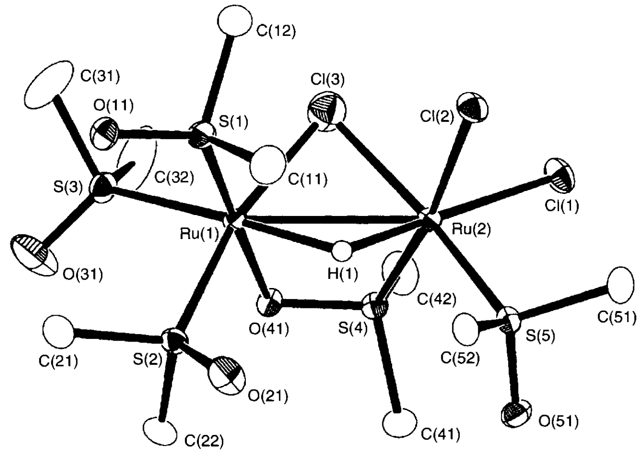

Fig. 1 ORTEP diagram of complex **2** with thermal ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (°); Ru(1)–Ru(2) 2.8435(7), Ru(1)–Cl(3) 2.406(2), Ru(1)–S(1) 2.232(2), Ru(1)–S(2) 2.263(2), Ru(1)–S(3) 2.313(2), Ru(1)–O(41) 2.160(4), Ru(2)–Cl(1) 2.425(1), Ru(2)–Cl(2) 2.431(2), Ru(2)–Cl(3) 2.412(2), Ru(2)–S(4) 2.188(2), Ru(2)–S(5) 2.223(2), S(1)–O(11) 1.485(4), S(2)–O(21) 1.481(4), S(3)–O(31) 1.442(5), S(4)–O(41) 1.532(4), S(5)–O(51) 1.486(4), Cl(3)–Ru(1)–S(1) 96.50(6), Cl(3)–Ru(1)–S(2) 167.71(6), Cl(3)–Ru(1)–S(3) 94.38(6), Cl(3)–Ru(1)–O(41) 83.4(1), S(1)–Ru(1)–S(2) 90.96(6), S(1)–Ru(1)–S(3) 96.03(6), S(1)–Ru(1)–O(41) 178.5(1), S(2)–Ru(1)–S(3) 94.54(6), S(2)–Ru(1)–O(41) 88.9(1), S(3)–Ru(1)–O(41) 85.5(1), Cl(1)–Ru(2)–Cl(2) 88.67(5), Cl(1)–Ru(2)–Cl(3) 94.69(6), Cl(1)–Ru(2)–S(4) 93.16(5), Cl(1)–Ru(2)–S(5) 92.79(6), Cl(2)–Ru(2)–Cl(3) 88.22(6), Cl(2)–Ru(2)–S(4) 171.53(6), Cl(2)–Ru(2)–S(5) 89.32(5), Cl(3)–Ru(2)–S(4) 83.39(6), Cl(3)–Ru(2)–S(5) 172.07(6), S(4)–Ru(2)–S(5) 98.84(5).

A perspective drawing of complex **2** is illustrated in Fig. 1.§ The complex consists of two octahedral ruthenium atoms bridged by hydride, chloride and Me_2SO. The triply bridged diruthenium structure is similar to that found in [$Ru_2(\mu$-Cl)(μ-H)(μ-NH_2NMe_2)(H)Cl(cod)$_2$] **3** (cod = cycloocta-1,5-diene).[9] The Ru–Ru distance is 2.8435(7) Å indicating the presence of a metal–metal single bond as observed in the hydride-bridged diruthenium(II) complexes, **3** [2.91(1) Å], [$Ru_2(\mu$-Cl)(μ-H)(μ-$NHCOCF_3)_2(PPh_3)_4$] [2.811(4) Å],[10] [$Ru_2(\mu$-Cl)(μ-H)(μ-$C_4H_4NO_2)_2(PPh_3)_4$] [2.827(4) Å][11] and [{(η-C_5H_5)Fe[η-C_5H_3(CHMeNMe$_2$)PPr$^i_2$-1,2]}(η^2-H_2)Ru(μ-Cl)$_2$(μ-H)Ru(H)-(PPh$_3$)$_2$] [2.811(2) Å].[12] The hydride ligand position was determined by difference Fourier synthesis and found to almost symmetrically bridge the two ruthenium atoms [Ru(1)–H(1) 1.85(1), Ru(2)–H(1) 1.78(1) Å, Ru(1)–H(1)–Ru(2) 103(1)°]. The other terminal coordination sites of the $Ru_2(\mu$-H)(μ-Cl)(μ-Me_2SO) core are ligated by four S-bound Me_2SO molecules and two Cl.

The most conspicuous feature is the S,O-bridging Me_2SO ligand coordinating to one ruthenium *via* S [Ru(2)–S(4) 2.188(2) Å] and to the other *via* O [Ru(1)–O(41) 2.160(2) Å], resulting in a four-membered ring [Ru(1)Ru(2)S(4)O(41)] [Ru(1)–Ru(2)–S(4) 71.35(4), Ru(2)–Ru(1)–O(41) 83.4(1)°]. The Ru(2)–S(4) bond length is significantly shorter than those of other terminal Me_2SO ligands (Ru–S 2.223–2.313 Å), resulting in an elongation of the S(4)–O(41) distance to 1.532(4) Å. It should be noted that the S–O bond length of the Me_2SO ligands in **2** is linearly correlated to the Ru–S bond length as shown in Fig. 2. Complex **2** is the first example containing a *syn*-type η^1,η^1-S,O-bridge of Me_2SO over a dinuclear transi-

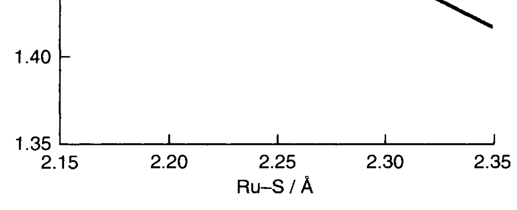

Fig. 2 Plot of S–O bond length (Å) of Me_2SO *vs.* Ru–S distance (Å). A linear correlation with r = 0.95 is observed.

tion-metal centre (on the basis of Cambridge Structure Database analysis). The present structural data significantly extend the coordination chemistry of Me_2SO.

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Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/223.

Footnotes

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‡ Complex **2** was obtained as orange needles with a small amount of Na_2(xdk) as impurity. Optimization of the synthetic procedure is being attempted which will be reported in due course. IR (Nujol): 1717, 1308, 1093, 1017, 966, 721, 677, 422 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.37 (s, 6 H, Me), 3.43 (s, 6 H, Me), 3.46 (s, 6 H, Me), 3.47 (s, 6 H, Me), 3.49 (s, 3 H, Me), 3.50 (s, 3 H, Me), −9.42 (s, μ-H).

§ The structure of **2**·$2CH_2Cl_2$ was determined by an X-ray crystallographic analysis. *Crystal data*: $C_{12}H_{35}Cl_7O_5Ru_2S_5$, triclinic, space group $P\bar{1}$ (no. 2), a = 12.108(3), b = 14.467(5), c = 9.885(3) Å, α = 110.01(3), β = 94.49(2), γ = 69.23(2)°, U = 1519.4(9) Å^3, Z = 2, D_c = 1.902 g cm^{-3}, T = −100 °C, R = 0.031, R_w = 0.035 [$w = 1/\sigma^2(F_o)$] for 4483 independent reflections [$I > 3\sigma(I)$] with 421 variables. The structure was solved by direct methods using SIR92[7] and refined by full-matrix least-squares techniques using the teXsan program package.[8]

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