A Diruthenium–dilithium Complex containing Four Different Bonding Types of Tetramethylenesulfoxide Ligands

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The tetranuclear complex $[Br_6(\text{tm}\mathit{s}\text{o})_2Ru_2(\mu_2\text{-tm}\mathit{so})_2(\mu_3\text{-tm}\mathit{so})_2Li_2(\text{tms}\mathit{o})_2]$ (tmso = tetramethylenesulfoxide; *s* and *o* imply sulfur- and oxygen-bonded sulfoxide, respectively) has been synthesized; four types of coordinated tmso are present, including a unique μ_3-type.

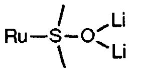
The antitumour activity, and mutagenic and radiosensitizing properties, as well as catalytic properties of Ru sulfoxide complexes, with or without ancillary nitrogen-donor ligands, are of current interest.[1–4] Following earlier studies on chloro(dimethyl sulfoxide) species, we decided to extend the range of available complexes by varying the halide and sulfoxide.[1] This has led to the synthesis and characterization of the remarkable compound $[Br_6(\text{tm}\mathit{s}\text{o})_2Ru_2(\mu_2\text{-tm}\mathit{so})_2(\mu_3\text{-tm}\mathit{so})_2Li_2(\text{tms}\mathit{o})_2]$, **1**, which contains four different types of the same sulfoxide, including a new μ_3-type that bridges three metal atoms *via* the S-atom (attached to Ru) and the O-atom (attached to two Li atoms), as well as a related but rare type that bridges two metals (here, Ru and Li) *via* the S- and O-atoms.

A mixture of $RuCl_3{\cdot}3H_2O$ (0.25 g, 1.0 mmol) and LiBr (1.0 g, 11.5 mmol) was refluxed in dry MeOH (20 ml) for 30 min in air and filtered hot; tmso (1.5 ml, 16.7 mmol) was added and refluxing continued for 2 h. Concentration of the solution volume to *ca.* 5 ml and subsequent cooling at 0 °C precipitated a yellow solid that was purified by washing with CCl_4 and drying *in vacuo* (45% yield). A crystal of **1** was grown from a 2 : 1 EtOH–acetone solution of the complex, and the structure determined by X-ray analysis (Fig. 1).†

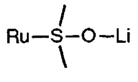
The centrosymmetric dimeric molecule consists of two octahedral Ru^{II} moieties, each having *fac*-bromo and -tm*s*o ligand sets, with two of the latter bridging *via* the O-atom to either one or two Li atoms. Each Li is bonded to: two oxygens of *fac*-tm*s*o ligands at one Ru, one oxygen of a tm*s*o ligands at the other Ru and the oxygen of an otherwise uncoordinated tmso ligand. The dimer thus contains a central, planar, four-membered Li_2O_2 ring fused to two six-membered rings.

To our knowledge, complex **1** is the first to demonstrate the existence of a sulfoxide using the O- and S-atoms to bridge three metals **I**; the structure also shows tmso bridging two metals **II** and we know of only one other example of this bonding mode of sulfoxide, within a Pt–S–O–K derivative incorporating dmso (dimethyl sulfoxide).[5] The type **III** bridging sulfoxide, the only type of sulfoxide binding not found in **1**, is more common,[6,7] and indeed is found in a dimeric (tetramethylenediamine)lithium-benzyl(phenyl)-sulfoxide structure containing an Li_2O_2 ring, similar to that found in **1**.[7] A distorted tetrahedral O_4-donor ligand set as found in **1** is common.[8]

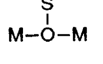
The ν(SO) bands in the IR are generally useful for distinguishing between S- and O-bonded sulfoxides including tmso;[1a,9–11] frequencies 50–100 cm^{-1} above and below the



I



II



III

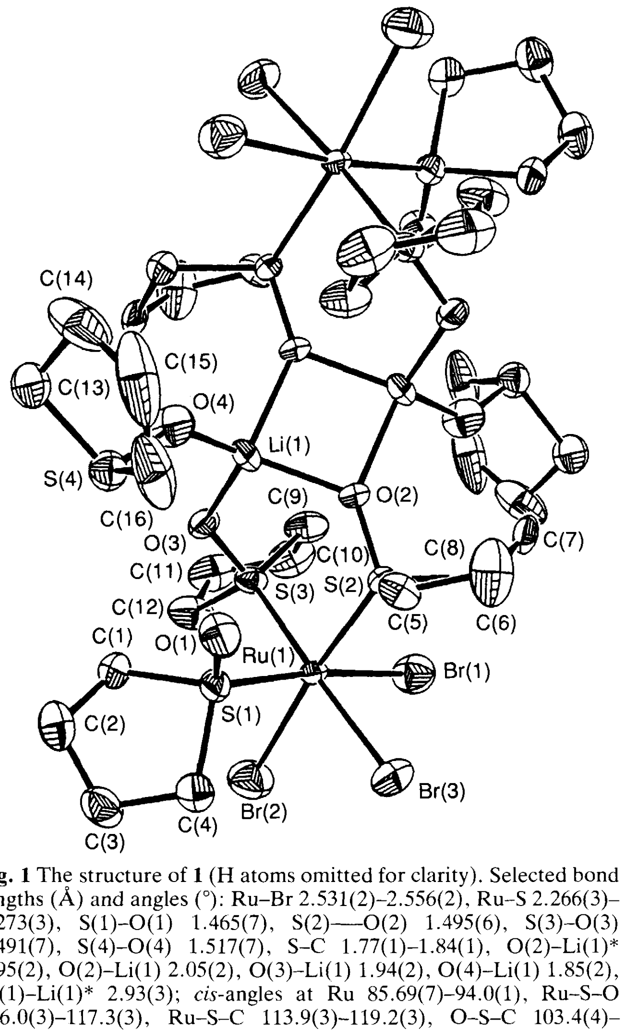


Fig. 1 The structure of **1** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Ru–Br 2.531(2)–2.556(2), Ru–S 2.266(3)–2.273(3), S(1)–O(1) 1.465(7), S(2)—O(2) 1.495(6), S(3)–O(3) 1.491(7), S(4)–O(4) 1.517(7), S–C 1.77(1)–1.84(1), O(2)–Li(1)* 1.95(2), O(2)–Li(1) 2.05(2), O(3)–Li(1) 1.94(2), O(4)–Li(1) 1.85(2), Li(1)–Li(1)* 2.93(3); *cis*-angles at Ru 85.69(7)–94.0(1), Ru–S–O 116.0(3)–117.3(3), Ru–S–C 113.9(3)–119.2(3), O–S–C 103.4(4)–107.1(5), C–S–C 90.7(7)–93.6(5), S(2)–O(2)–Li(1) 127.7(6), S(2)–O(2)–Li(1)* 137.6(6), Li(1)–O(2)–L(1)* 94.2(7), S(3)–O(3)–Li(1) 123.2(6), S(4)–O(4)–Li(1) 137.1(7), O(2)–Li(1)–O(2)* 85.8(7), O(2)–Li(1)–O(3) 99.9(8), O(2)–Li(1)–O(4) 131(1), O(2)*–Li(1)–O(3) 119(1), O(2)*–Li(1)–O(4) 104.2(8), O(3)–Li(1)–O(4) 114.8(8).

* Denotes symmetry operation: $1 - x, 1 - y, 1 - z$.

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† *Crystal data*: $C_{32}H_{64}Br_6Li_2O_8Ru_2S_8$, $M = 1528.78$, monoclinic, space group $P2_1/n$, $a = 9.489(3)$, $b = 15.828(3)$, $c = 16.984(3)$ Å, $\beta = 101.45(2)°$, $V = 2500.3(9)$ Å^3, $Z = 2$, $D_c = 2.03$ g cm^{-3}. Data were collected on a Rigaku AFC6S diffractometer at 294 K. The final unit-cell parameters were obtained by least-squares analysis on the setting angles for 25 reflections with $2\theta = 38.2–44.0$. The intensities of three standard reflections, measured every 200 reflections, throughout the data collection, decayed uniformly by 6.1%. The structure was solved by conventional heavy atom methods, the coordinates of the Ru and Br atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent Fourier synthesis. Calculations were performed using a TEXSAN/TEXRAY structure analysis package (Molecular Structure Corporation, 1985). The final R and R_w values were 0.053 and 0.062, respectively, for 3087 reflections with $I \geqslant 3.0\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

free ligand value (1022 cm^{-1}) have been assigned to S- and O-bonded ligands, respectively, although the lower region also contains ν(ring) bands.[11] Of seven bands shown by **1** in the 950–1130 cm^{-1} region (solid state) only those at 1111 and 1130 cm^{-1} are assigned with any confidence (to the terminal Ru-tm*s*o). The ready solubility of **1** in $CHCl_3$, coupled with the fact that no free tmso is seen in the ^1H NMR spectrum in $CDCl_3$, suggest that the dimer maintains its integrity in this solvent; the room temepprature ^1H NMR spectrum shows five complex multiplets between δ 4.10–2.15, the region expected for the α- and β-protons of bonded tmso,[1a,9–11] but assignments cannot be made at this stage.

Of interest, a synthesis of Li(*fac*-$RuBr_3$(dm*s*o)$_3$] has recently been described, the basic procedure being essentially that given here but using dmso and a final recrystallization from a MeOH–LiBr solution.[12] We find that a recrystallization from EtOH–acetone (as used in the tmso system) gives *trans*-$RuBr_2$(dm*s*o)$_4$,[2d,3,10] the LiBr having been washed out. The tmso ligand seems dominant in directing the assembly of the more novel complex of type **1**. The CCl_4 washings from the synthesis of **1** slowly deposit in about a 10% yield pure *cis*-$RuBr_2$(tm*s*o)$_4$,[9] the LiBr washed out product.

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