Routes to ruthenium(II) bromo(sulfoxide) complexes, including the synthesis and structural characterization of a neutral dilithium/diruthenium(II) complex containing terminal and bridging tetramethylene sulfoxide ligands

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Abstract

The dimeric Ru(II) complex $[Br_6(TMSO)_2Ru_2(\mu_2\text{-}TMSO)_2(\mu_3\text{-}TMSO)_2Li_2(TMSO)_2]$ (**1**) has been isolated from solutions containing $RuCl_3 \cdot 3H_3O$, LiBr and TMSO (TMSO = tetramethylene sulfoxide, *O* and *S* indicating oxygen- and sulfur-bonding, respectively). Crystals of **1** are monoclinic, $a = 9.489(3)$, $b = 15.828(3)$, $c = 16.984(3)$ Å, $\beta = 101.45(2)°$, $Z = 2$, space group $P2_1/n$. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to $R = 0.053$ and $R_w = 0.062$ for 3087 reflections with $I \geqslant 3\sigma(I)$. **1** is remarkable in containing four different types of coordinated TMSO ligands: terminal TMS*O* at Li, terminal TM*S*O at Ru, a μ_2-type (Ru–S–O–Li) and a previously unreported μ_3-type (Ru–S–O(Li)$_2$); the complex contains a central, planar, four-membered Li_2O_2 ring fused to two six-membered Li–O–S–Ru–S–O rings. A co-product is *cis*-$RuBr_2(TMSO)_4$. A corresponding synthesis using dimethyl sulfoxide gives *trans*-$RuBr_2(DMSO)_4$ in high yield. More definitive assignments are presented for the ^1H NMR spectra of the *cis*-$RuX_2(TMSO)_4$ complexes (X = Cl, Br); these reveal the expected inequivalence of the $-SCH_2$ protons, but in free TMSO an inequivalence of the β-protons is more evident.

Introduction

The antitumor activity, and mutagenic and radiosensitizing properties of ruthenium sulfoxide complexes with or without ancillary nitrogen-donor ligands, remain of interest [1–5]. Synthetic and particularly structural studies by our group and by the Trieste group have now established a good data base for Ru(II) and Ru(III) complexes containing dimethyl sulfoxide (DMSO) ligands [2, 3, 6], following some incorrect formulations that appeared in the 1988 literature [7].

As a natural sequence to the DMSO systems, we and the Trieste group, simultaneously but independently, initiated studies on corresponding systems with tetramethylene sulfoxide (TMSO); the ruthenium(II) species, *cis*- and *trans*-$RuX_2(TMSO)_4$ (X = Cl, Br), and the ruthenium(III) species *mer*-$RuCl_3(TMSO)_3$ and (TMSO)H[*trans*-$RuCl_4(TMSO)_2$] have been characterized, including structural determinations of *cis*-$RuCl_2(TMSO)_4$ [1, 8] and the ionic complex containing the hydrogen-bonded cation $[(TMSO)H]^+$ [8]. The synthesis of $RuX_2(TMSO)_4$ complexes (X = Cl, Br, I) was first described by Bora and Singh in 1977, but the work lacked any structural or NMR studies [9].

Interesting aspects of coordination chemistry that have emerged from the structural studies on the DMSO and TMSO systems are: (i) the question of oxygen- versus sulfur-bonded sulfoxide ligands [1–4]; (ii) the existence of the H-bonded sulfoxide cations $[(DMSO)_2H]^+$ [2], $[(TMSO)H]^+$ [8] and $[(^nPr_2SO)_2H]^+$ [10a] associated with the ruthenium(III) anions *trans*-$[RuCl_4(sulfoxide)_2]^-$; (iii) the possibility of redox chemistry within sulfoxide ligand systems generating thioether complexes under certain synthetic reaction conditions, e.g. *mer*-$RuX_3(dimethylsulfide)_3$ (X = Cl, Br) from DMSO systems [2] and the corresponding tetrahydrothiophene complexes from TMSO systems [1].

This present paper principally reports on the isolation and structural characterization of an unusual lithium-containing complex of overall stoichiometry

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$Li_2Ru_2Br_6(TMSO)_8$, which is best written as $[Br_6(TMSO)_2Ru_2(\mu_2\text{-}TMSO)_2(\mu_3\text{-}TMSO)_2Li_2(TMSO)_2]$, (**1**), where *O* and *S* refer to oxygen- and sulfur-bonded TMSO, respectively; this species was the major product during our efforts to synthesize bromoruthenium–TMSO complexes using $RuCl_3 \cdot 3H_2O$ as precursor in the presence of LiBr. Complex **1** has been described briefly elsewhere [10b].

Experimental

The instrumentation used, synthetic procedures, and reagents used, have all been described in our earlier papers [1, 2, 11].

$Li_2Ru_2Br_6(TMSO)_8$ (1)

$RuCl_3 \cdot 3H_2O$ (0.25 g, 1 mmol) and LiBr (1.0, 11.5 mmol) were dissolved in dry MeOH (20 ml), and the mixture was refluxed for 30 min in air and filtered while hot; TMSO (1.5 ml, 16.7 mmol) was then added and refluxing continued for 2 h. The resulting orange solution was concentrated to ~5 ml and then stored overnight at 0 °C; the precipitated yellow–green material was collected in air, washed with CCl_4 (4×10 ml) and dried *in vacuo* at room temperature. Yield 45%. Orange crystals of **1** suitable for X-ray analysis were grown by dissolving ~100 mg of the material in EtOH (10 ml), adding acetone (5 ml), and leaving the mixture at room temperature for ~2 days. δ_H ($CDCl_3$, 20 °C) complex, broad multiplets centred at 2.15, 2.32, 2.90, 3.53, 4.10; ν 1130, 1111, 1091, 1059, 1030, 1005, 983, 895, 875 cm^{-1}.

cis-$RuBr_2(TMSO)_4$ (2)

The CCl_4 washings from the above synthesis for **1**, on standing for one day, deposited yellow crystals of *cis*-$RuBr_2(TMSO)_4$ (**2**). Yield 10%. *Anal.* Calc. for $C_{16}H_{32}Br_2O_4RuS_4$: C, 28.36; H, 4.76. Found: C, 28.53; H, 4.81%. λ_{max} (log ϵ), $CHCl_3$: 369 (2.76). δ_H ($CDCl_3$, 20 °C) complex multiplets in each of the ranges 2.00–2.50, 2.70–3.00, 3.30–4.30. ν 1125, 1109 cm^{-1}.

trans-$RuBr_2(DMSO)_4$ (3)

Following exactly the procedure described for the synthesis of **1**, but using dry EtOH instead of MeOH, and DMSO (1.5 ml, 18.8 mmol) instead of TMSO, precipitated a yellow complex; recrystallization from EtOH/acetone (2:1) yielded **3**. Yield 80%. *Anal.* Calc. for $C_8H_{24}Br_2O_4S_4Ru$: C, 16.76; H, 4.22. Found: C, 16.51; H, 4.19%. The spectroscopic data (IR, UV–Vis, NMR) are identical to those given in the literature [11–13] for the structurally characterized **3** [12].

X-ray crystallographic analysis of complex 1

Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least-squares 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 data were processed [14] and corrected for Lorentz and polarization effects, decay, and absorption (empirical, based on azimuthal scans for four reflections). A total of 7916 reflections was collected on a Rigaku AFC6S diffractometer; of these, 7506 were uniquc ($R_{int} = 0.063$) and those 3087

TABLE 1. Crystallographic data[a]

Compound	$[Br_6(TMSO)_2Ru_2(\mu_2\text{-}TMSO)_2\text{-}(\mu_3\text{-}TMSO)_2Li_2(TMSO)_2]$
Formula	$C_{32}H_{64}Br_6Li_2O_8Ru_2S_8$
Formula weight	1528.78
Color, habit	orange prism
Crystal size (mm)	0.15×0.25×0.30
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.489(3)
b (Å)	15.828(3)
c (Å)	16.984(3)
β (°)	101.45(2)
V (Å^3)	2500.3(9)
Z	2
ρ_c (g/cm^3)	2.030
F(000)	1504
Radiation	Mo
Wavelength (Å)	0.71069
μ (cm^{-1})	57.06
Transmission factors (relative)	0.73–1.00
Scan type	ω–2θ
Scan range (°) in ω	1.40+0.35 tan θ
Scan speed (°/min)	16
Data collected	$+h$, $+k$, $\pm l$
$2\theta_{max}$ (°)	60
Crystal decay (%)	6.1
Total no. reflections	7916
No. unique reflections	7506
R_{int}	0.063
No. reflections with $I \geq 3\sigma(I)$	3087
No. variables	262
R	0.053
R_w	0.062
GOF	2.03
Max Δ/σ (final cycle)	0.01
Residual density (e/Å^3)	−1.4 to +1.5 (both near Ru)

[a]Temperature 294 K, Rigaku AFC6S diffractometer, graphite monochromator, takeoff angle 6.0°, aperture 6.0×6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C+4B) + (0.04F^2)^2]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, and $GOF = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$. Values given for *R*, R_w and *GOF* are based on those reflections with $I \geq 3\sigma(I)$.

having $I \geqslant 3\sigma(I)$ were employed in the solution and refinement of the structure.

The structure was solved by conventional heavy-atom methods, the coordinates of the Ru and Br atoms being determined from the Patterson functions, and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). The thermal parameters of atoms C(14–16) of the terminal Li-bound TMSO ligand suggest a possible minor disordering in this region, but no attempt was made to model this disorder. Neutral atom-scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref. 15. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths and bond angles appear in Tables 2–4, respectively. See also 'Supplementary material'.

Results and discussion

The first effective radiosensitizers made by our group were of formulation $RuCl_2(DMSO)_2L_2$, where L is a nitroimidazole [11]. An extension to the more lipophilic

TABLE 2. Final atomic coordinates (fractional) and B_{eq}

Atom	x	y	z	B_{eq}
Ru(1)	0.53700(8)	0.25064(5)	0.60427(4)	1.79(3)
Br(1)	0.4112(1)	0.28267(9)	0.72075(7)	4.27(6)
Br(2)	0.6889(2)	0.14372(9)	0.69435(8)	4.83(6)
Br(3)	0.3518(1)	0.13574(8)	0.55780(8)	4.18(6)
S(1)	0.6507(3)	0.2084(2)	0.5054(1)	2.3(1)
S(2)	0.3835(2)	0.3377(1)	0.5229(1)	1.74(9)
S(3)	0.6942(3)	0.3583(2)	0.6424(1)	2.3(1)
S(4)	0.7603(3)	0.3840(2)	0.3433(2)	3.1(1)
O(1)	0.5988(8)	0.2437(5)	0.4252(4)	3.9(3)
O(2)	0.4376(6)	0.4237(4)	0.5075(4)	2.3(3)
O(3)	0.7496(6)	0.4014(4)	0.5767(4)	2.6(3)
O(4)	0.6947(8)	0.4495(5)	0.3904(4)	3.9(4)
C(1)	0.844(1)	0.2204(7)	0.5265(7)	3.4(5)
C(2)	0.898(1)	0.1488(8)	0.4802(7)	3.9(6)
C(3)	0.820(1)	0.0709(7)	0.5000(7)	4.0(5)
C(4)	0.659(1)	0.0930(7)	0.4941(6)	2.9(5)
C(5)	0.298(1)	0.3011(7)	0.4232(6)	2.9(5)
C(6)	0.142(1)	0.324(1)	0.4122(7)	5.5(7)
C(7)	0.116(1)	0.3838(7)	0.4740(7)	3.0(5)
C(8)	0.213(1)	0.3565(6)	0.5522(6)	2.6(4)
C(9)	0.634(1)	0.4403(7)	0.7015(6)	3.7(5)
C(10)	0.710(2)	0.4257(8)	0.7872(7)	4.9(6)
C(11)	0.861(1)	0.4003(8)	0.7836(7)	4.9(6)
C(12)	0.852(1)	0.3347(7)	0.7192(7)	4.1(5)
C(13)	0.854(1)	0.4469(8)	0.2809(7)	3.8(5)
C(14)	0.742(2)	0.491(1)	0.2234(8)	6.0(8)
C(15)	0.620(2)	0.430(2)	0.1973(8)	8(1)
C(16)	0.624(1)	0.360(1)	0.259(1)	6.5(8)
Li(1)	0.625(2)	0.453(1)	0.485(1)	2.6(7)

TABLE 3. Bond lengths (Å) with e.s.d.s in parentheses

Ru(1)–Br(1)	2.556(2)	O(2)–Li(1)	1.95(2)
Ru(1)–Br(2)	2.531(2)	O(2)–Li(1)[a]	2.05(2)
Ru(1)–Br(3)	2.543(2)	O(3)–Li(1)	1.94(2)
Ru(1)–S(1)	2.269(3)	O(4)–Li(1)	1.85(2)
Ru(1)–S(2)	2.266(3)	C(1)–C(2)	1.52(2)
Ru(1)–S(3)	2.273(3)	C(2)–C(3)	1.51(2)
S(1)–O(1)	1.465(7)	C(3)–C(4)	1.55(1)
S(1)–C(1)	1.81(1)	C(5)–C(6)	1.50(2)
S(1)–C(4)	1.84(1)	C(6)–C(7)	1.47(2)
S(2)–O(2)	1.495(6)	C(7)–C(8)	1.52(1)
S(2)–C(5)	1.82(1)	C(9)–C(10)	1.51(2)
S(2)–C(8)	1.81(1)	C(10)–C(11)	1.50(2)
S(3)–O(3)	1.491(7)	C(11)–C(12)	1.50(2)
S(3)–C(9)	1.80(1)	C(13)–C(14)	1.47(2)
S(3)–C(12)	1.82(1)	C(14)–C(15)	1.51(2)
S(4)–O(4)	1.517(7)	C(15)–C(16)	1.52(2)
S(4)–C(13)	1.81(1)	Li(1)–Li(1)[a]	2.93(3)
S(4)–C(16)	1.77(1)		

[a]Symmetry operation: $1-x$, $1-y$, $1-z$.

TABLE 4. Bond angles (°) with e.s.d.s in parentheses

Br(1)–Ru(1)–Br(2)	87.84(5)	C(5)–S(2)–C(8)	92.9(5)
Br(1)–Ru(1)–Br(3)	88.96(5)	Ru(1)–S(3)–O(3)	116.0(3)
Br(1)–Ru(1)–S(1)	174.16(8)	Ru(1)–S(3)–C(9)	115.9(4)
Br(1)–Ru(1)–S(2)	90.52(7)	Ru(1)–S(3)–C(12)	116.8(4)
Br(1)–Ru(1)–S(3)	90.66(8)	O(3)–S(3)–C(9)	106.6(5)
Br(2)–Ru(1)–Br(3)	89.14(5)	O(3)–S(3)–C(12)	105.5(5)
Br(2)–Ru(1)–S(1)	87.29(8)	C(9)–S(3)–C(12)	93.2(5)
Br(2)–Ru(1)–S(2)	174.60(7)	O(4)–S(4)–C(13)	103.6(5)
Br(2)–Ru(1)–S(3)	93.81(8)	O(4)–S(4)–C(16)	105.2(5)
Br(3)–Ru(1)–S(1)	87.72(8)	C(13)–S(4)–C(16)	90.7(7)
Br(3)–Ru(1)–S(2)	85.69(7)	S(2)–O(2)–Li(1)	127.7(6)
Br(3)–Ru(1)–S(3)	177.01(8)	S(2)–O(2)–Li(1)*	137.6(6)
S(1)–Ru(1)–S(2)	94.0(1)	Li(1)–O(2)–Li(1)*	94.2(7)
S(1)–Ru(1)–S(3)	92.9(1)	S(3)–O(3)–Li(1)	123.2(6)
S(2)–Ru(1)–S(3)	91.35(9)	S(4)–O(4)–Li(1)	137.1(7)
Ru(1)–S(1)–O(1)	117.1(3)	S(1)–C(1)–C(2)	104.5(8)
Ru(1)–S(1)–C(1)	115.8(4)	C(1)–C(2)–C(3)	105.1(9)
Ru(1)–S(1)–C(4)	113.9(3)	C(2)–C(3)–C(4)	109(1)
O(1)–S(1)–C(1)	106.5(5)	S(1)–C(4)–C(3)	106.1(7)
O(1)–S(1)–C(4)	107.1(5)	S(2)–C(5)–C(6)	106.5(8)
C(1)–S(1)–C(4)	93.6(5)	C(5)–C(6)–C(7)	112(1)
Ru(1)–S(2)–O(2)	117.3(3)	C(6)–C(7)–C(8)	106(1)
Ru(1)–S(2)–C(5)	119.2(3)	S(2)–C(8)–C(7)	103.0(7)
Ru(1)–S(2)–C(8)	115.7(3)	S(3)–C(9)–C(10)	106.5(9)
O(2)–S(2)–C(5)	103.4(4)	C(9)–C(10)–C(11)	106(1)
O(2)–S(2)–C(8)	104.8(4)	C(10)–C(11)–C(12)	107(1)
S(3)–C(12)–C(11)	107.4(9)		
S(4)–C(13)–C(14)	106(1)		
C(13)–C(14)–C(15)	108(1)		
C(14)–C(15)–C(16)	111(1)		
S(4)–C(16)–C(15)	108(1)		
O(2)–Li(1)–O(2)[a]	85.8(7)		
O(2)–Li(1)–O(3)	99.9(8)		
O(2)–Li(1)–O(4)	131(1)		
O(2)[a]–Li(1)–O(3)	119(1)		
O(2)[a]–Li(1)–O(4)	104.2(8)		
O(3)–Li(1)–O(4)	114.8(8)		

[a]Symmetry operation: $1-x$, $1-y$, $1-z$.

TMSO analogues [11] was effected using *cis*-$RuCl_2(TMSO)_4$ as precursor, which we synthesized by reaction of TMSO with the blue Ru solutions made by refluxing $RuCl_3 \cdot 3H_2O$ in MeOH under H_2 [1]. Alessio *et al.* [8] synthesized the same *cis* complex via either a sulfoxide exchange reaction with *cis*-$RuCl_2(DMSO)_3(DMSO)$, or refluxing ethanol solutions of $RuCl_3 \cdot 3H_2O$ with TMSO as originally described by Bora and Singh [9]. The bromo analogues *cis*- and *trans*-$RuBr_2(TMSO)_4$ have been made by TMSO ligand exchange with *cis*- and *trans*-$RuBr_2(DMSO)_4$, respectively [8], while the *trans* isomer was also made by photochemical isomerization of the *cis* form [8]. In attempts to utilize $RuCl_3 \cdot 3H_2O$ as a direct precursor to bromo derivatives, we simply carried out refluxing procedures in the presence of excess LiBr. As described in 'Experimental', refluxing the commercially available chloride trihydrate, LiBr and TMSO in MeOH does yield a bromo derivative, but it is of a much more interesting type than expected. The major product **1**, isolated in 45% yield, is structurally characterized as $[Br_6(TMSO)_2Ru_2(\mu_2\text{-}TMSO)_2(\mu_3\text{-}TMSO)_2Li_2(TMSO)_2]$.

The centrosymmetric dimeric molecule (Fig. 1) has exact crystallographic inversion (C_i) symmetry. The dimeric species consists of two octahedral Ru(II) moieties, each having *fac*-bromo and -TMSO ligand sets, with two of the latter bridging via the O atom to either one or two Li atoms. Each Li is bonded to (i) two oxygens of *fac*-TMSO ligands at one Ru, (ii) one oxygen of a TMSO ligand at the other Ru, and (iii) the oxygen of an otherwise uncoordinated TMSO ligand. An alternative description could be given in terms of bridging TMSO ligands, a μ_2-type from each Ru bridging to a single Li, and a μ_3-type from each Ru bridging two Li atoms. The dimer thus contains a central four-membered Li_2O_2 ring fused to two six-membered rings.

The geometry at each Ru is close to octahedral, all *cis* angles being in the range 85–94°. The Ru–Br lengths in **1** are very similar to those in *cis*- and *trans*-$RuBr_2(DMSO)_4$ [12, 13]. The Ru–S distances (av. 2.269 Å) are close to those *trans* to halide in *cis*-$RuCl_2(TMSO)_4$ [1, 8], and are about 0.12 Å shorter than those in *mer*-$RuCl_3(TMS)_3$ (TMS = tetramethylene sulfide ≡ tetrahydrothiophene) [1]. Ruthenium(II)–S bond lengths within thioether complexes are in the range 2.26–2.40 Å, most commonly 2.32–2.37 Å, and in the higher range 2.37–2.40 Å when the thioether links are mutually *trans* [2]; shorter metal–S bonds in sulfoxides than in corresponding thioether complexes could result from more π-backbonding from Ru(II) to S in the sulfoxides. In *trans*-$[RuCl_4(TMSO)_2]^-$ the Ru(III)–S distances (av. 2.33 Å [8]) are longer than in **1**; this could result from the *trans* disposition of the sulfoxides in the anion, or again some contribution of π-backbonding from the strongly π-basic Ru(II) in **1**.

The S–O bond length of the monodentate, non-bridging TMSO is 1.465 Å, shorter than in crystalline

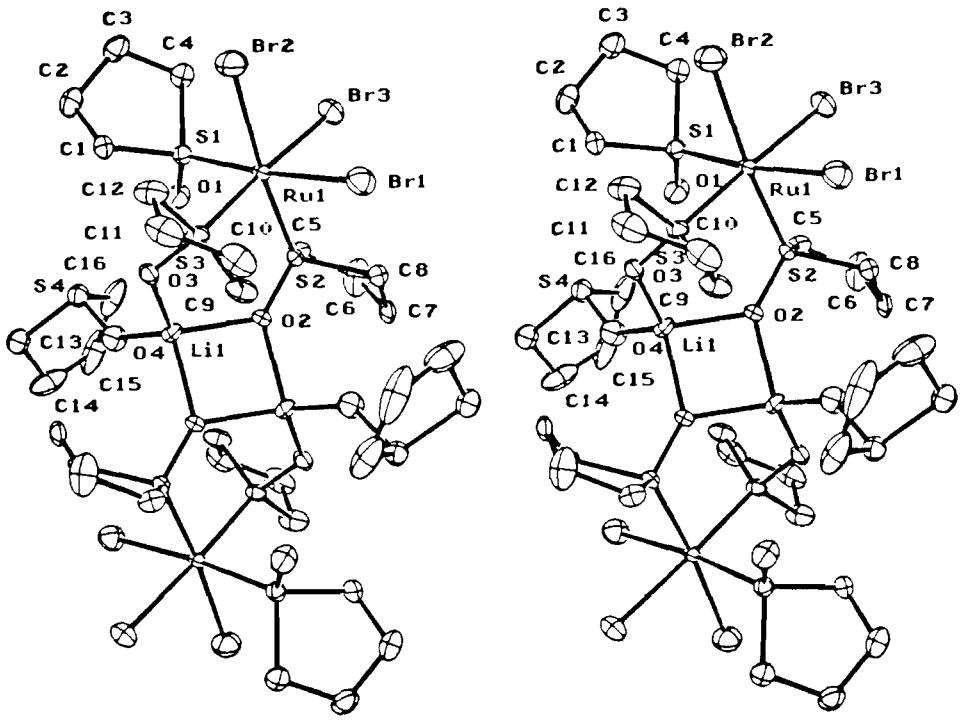


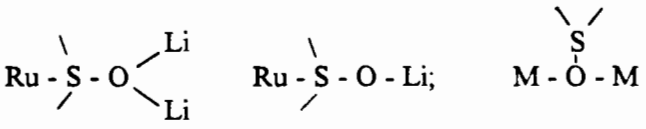
Fig. 1. ORTEP stereoview of complex **1**; 33% probability thermal ellipsoids are shown.

TMSO (1.527 Å) [16]; such shortening for S-bonded sulfoxides is consistent with considerable double-bond character and is well precedented [1, 8]. The S–O bond lengths of the μ_2- and μ_3-TMSO ligands are 1.491 and 1.495 Å, respectively; these lengths probably represent a compromise between the shortening expected via S-bonding and a perhaps expected lengthening via O-bonding, although the latter effect is typically hardly significant, at least as exemplified by DMSO systems [13, 17]. (O-bonded, as opposed to S-bonded sulfoxide, similarly gives generally smaller coordination shifts in ν(SO), and in δ_H within NMR resonances of the associated alkyl groups [1, 8, 11–13]). In this regard, it is noted that the S–O bond length within the Li–TMS*O* moiety is 1.517 Å, essentially that of crystalline TMSO.

The bond lengths and angles within the Ru–TM*S*O moieties generally, whether with the monodentate, μ_2- or μ_3-sulfoxides, are quite close and also are similar to those found in *cis*-$RuCl_2(TMSO)_4$ and *trans*-$[RuCl_4(TMSO)_2]^-$ [1, 8]. All corresponding bond lengths and angles are within about 0.1 Å and 5°, respectively. Within **1**, the C–S–C angles are $93.2 \pm 0.4°$, while the O–S–C bond angles are in the range $105.3 \pm 1.9°$; nevertheless, on going from the monodentate to μ_2- to μ_3-TM*S*O, there is a small but significant decrease in the C–S–C angle ($93.6 \rightarrow 93.2 \rightarrow 92.8°$) as well as in the average of the two O–S–C angles ($106.8 \rightarrow 106.0 \rightarrow 104.1°$). These angles conform to the conclusion that TM*S*O has a lower cone angle than DM*S*O [8]. Within the Li–TMS*O* moiety, the C–S–C angle is 90.7°, while the O–S–C angles are 103.6 and 105.2°.

The bond angles about the Li atom vary from 85.8 to 131°. The significant distortion from ideal tetrahedral geometry probably results from a combination of steric factors arising from ring-fusion effects and non-bonded contacts between the TMSO ligands. A distorted tetrahedral O_4-donor ligand set at Li is common [18–20]. The angles in the four-membered, planar Li_2O_2 ring are 85.8 and 94.2°, and the Li–Li separation is 2.93 Å; a somewhat more rectangular but slightly folded Li_2O_2 ring (with Li–Li = 2.65 Å) has been described within a structure where each O atom is that of a bridging (benzyl)phenyl sulfoxide (see below, type **III**), the coordination of each Li being completed by tetramethylethylene diamine [21].

To our knowledge, complex **1** is the first to demonstrate the existence of a sulfoxide using the O and S atoms to bridge three metal ions (**I**); the remarkable structure also demonstrates TMSO bridging two metal centres (**II**). We believe there is only one other structure of type **II**, a Pt–S–O–K derivative incorporating DMSO [22]. Exclusively O-bridged sulfoxides (**III**) are more well established [21, 23, 24]



I **II** **III**

The possibility of bonding modes such as **I** and **II** (involving alkali metal ions) playing a role in the biological properties of Ru–sulfoxide species [13, 25] is worthy of consideration.

That the complexes $[NMe_2H_2][fac\text{-}RuCl_3(DMSO)_3]$ [26] and $[NEt_4][fac\text{-}RuBr_3(DMSO)_3]\cdot 0.5MeOH$ [6] have both been characterized structurally, and that the synthesis of $Li[fac\text{-}RuBr_3(DMSO)_3]$ has also been described [3], suggest that the TMSO ligand is dominant in directing the assembly of the more novel complex **1**. In line with this, the chloro analogue of **1** does not appear to be formed on substituting LiCl for LiBr in the synthetic procedure. Within the ionic complexes just mentioned, there are H-bonding interactions between the cation hydrogens and oxygens and chlorines of the dimethylammonium complex [26], and possibly between the MeOH oxygen and bromine in the tetraethylammonium complex [6], but these structures are relatively simple compared to that of **1**. The reported $Li[fac\text{-}RuBr_3(DMSO)_3]$ complex, which certainly analyzes correctly [6], ruling out a formulation such as **1**, was synthesized by (i) refluxing a *cis*-$RuBr_2(DMSO)_4$/LiBr mixture in MeOH or (ii) refluxing a $RuCl_3\cdot 3H_2O$/LiBr/DMSO mixture in EtOH, followed by a recrystallization from a MeOH/LiBr solution [6]. Procedure (ii) without a recrystallization was in fact that used by Sarma *et al.* [7] for a reported synthesis of $RuBr_2(DMSO)_3$, but recent studies [6] have shown that the product is a mixture of $Li[fac\text{-}RuCl_nBr_{3-n}(DMSO)_3]$ ($n = 0$–3) species, although the recrystallization procedure does give solely $Li[fac\text{-}RuBr_3(DMSO)_3]$. We have also repeated the procedure of Sarma *et al.*, but with a subsequent recrystallization from EtOH/acetone, and obtained *trans*-$RuBr_2(DMSO)_4$ (**3**) in good yield (see 'Experimental'). This offers an alternative synthesis of **3** to those given in the literature using $RuBr_3\cdot 3H_2O$ [9, 12, 13, 27] or *cis*-$RuCl_2(DMSO)_4$ [11].

Of interest, before the crystallographic analysis of **1** was completed, we thought the complex might be $RuBr_2(TMSO)_3$; the calculated C and H elemental analyses of such a species are identical to those of **1**, and the corresponding DMSO complex had been reported [7], although this is now known to be erroneous [6].

The solid-state IR ν(SO) band for free TMSO occurs at 1022 cm^{-1}; the corresponding band(s) for TM*S*O and TMS*O* will appear at higher and lower frequencies, respectively [1, 8, 11, 25], while bridging (μ_2, μ_3) TMS*O*

ligands will presumably show bands within the same general range. For TM*S*O ligands at Ru, ν(SO) bands have been reported between 1133–1064 cm^{-1} [1, 8, 11]; ν(SO) values for TMS*O* generally are typically in the 970–925 cm^{-1} region [28–30], although ν(ring) bands have been noted in the 1095–880 cm^{-1} region for some Rh complexes [28]. Complex **1** contains the four types of TMSO ligand and shows a plethora of bands in the 1130–875 cm^{-1} region, but is seems safe to assign the 1130 and 1111 cm^{-1} bands to ν(SO).

The ^1H NMR spectrum of free TMSO in $CDCl_3$ shows three sets of multiplets centred at δ 2.58, 2.00 and 1.63, with relative integrations of 2:1:1, respectively. We had originally [1] assigned the δ 2.58 peak to the β-protons and the δ 2.00 and 1.63 peaks to the α-protons (despite the relative chemical shift values, whereby one would expect the α-protons to be the more deshielded), because we thought that the α-protons would be more inequivalent [28, 30, 31]. However, a HETCOR experiment reveals that the δ 2.58 ^1H NMR peak correlates with a $^{13}C\{^1H\}$ peak at δ 55 ppm, while the δ 2.00 and 1.63 ^1H peaks correlate with a $^{13}C\{^1H\}$ peak at δ 25 ppm; for the ^{13}C data, the α-carbon peak, because of proximity to the SO moiety, will be further downfield than that of the β-carbons (and indeed $-(CH_2)_n$ carbons typically give resonances in the 25 ppm range [32]). Thus, in free TMSO the δ 2.58 centred multiplet results from the α-protons, and the δ 2.00 and 1.63 multiplets to the β-protons. The Trieste group [8] and Rochon *et al.* [33], using 80 or 60 MHz instruments, respectively, had observed just two broad multiplets for free TMSO, and had correctly assigned the lower and higher field resonances to the α- and β-protons, respectively. It is not immediately clear why, in free TMSO, the β-protons appear more inequivalent than the α-protons; this is not the case when the TMSO is S-bonded within Ru(II) complexes, when the α-protons become more inequivalent (see below).

Based on the HETCOR data for TMSO, our initial description of the ^1H NMR spectrum of *cis*-$RuCl_2(TMSO)_4$ [1] needs some correction; the multiplets at δ 4.13 and 3.44 correspond to two sets of α-protons (which are shifted downfield from the δ 2.58 α-proton multiplet of the free ligand), and the broader multiplet centred at δ 2.26 corresponds to the β-protons (which are again shifted downfield from their δ 2.00 and 1.63 positions in the free ligand). The multiplets at δ 4.13 and 3.44 could arise from the two different types of TMSO ligands present in *cis*-$RuCl_2(TMSO)_4$ (*trans* to Cl, and the mutually *trans* ones), as suggested by Alessio *et al.* [8], which would mean that the inequivalence of the S–CH_2 protons within any one TMSO ligand [1, 28, 30, 31] is not well resolved within each of the multiplets, although there is very considerable 'fine structure' visible within each multiplet. However, a HETCOR experiment on a solution of the complex shows just the reverse situation: the different types of TMSO ligands are not well distinguished by ^1H NMR, while the S–$CH_a(H_b)$ protons are resolved. The $^{13}C\{^1H\}$ resonance at 25 ppm for the β-carbons of free TMSO remains essentially unchanged in the complex, and correlates as expected with a single, very broad ^1H multiplet in the δ 2.0–3.0 region. Of more significance, the ^{13}C resonance of the α-carbon of the free ligand now splits in the complex into two resonances at about δ 57 and 60, which we assign to the two types of TMSO ligands; and *each* of these resonances correlates with two proton resonances, one in *each* of the two lower field multiplets in the δ 3.4–4.4 region. Thus, in a solution of the complex, it is the sets of the S–$CH_a(H_b)$ protons that give rise to the two lower field multiplets.

The ^1H NMR spectrum of **1** in $CDCl_3$ is complex (see 'Experimental'). The intensities of the multiplets centred at δ 4.10 and 3.53 are similar and each is about half the combined intensity of the δ 2.90, 2.32 and 2.15 patterns; these three higher field resonances could result from the β-protons of S-bonded TMSO and protons of O-bonded TMSO, and the two lower field ones from sets of α-protons (see above) but, because of the different types of TMSO probably present, no definite assignments can be made. No free TMSO is seen and this, together with the ready solubility of **1** in $CDCl_3$, suggests the dimer maintains its integrity in this solvent; **1** shows an absorption maximum in $CHCl_3$ in the UV–Vis spectrum at 370 nm.

The CCl_4 washings from the synthesis of **1** slowly deposited crystalline samples of *cis*-$RuBr_2(TMSO)_4$ (**2**), the stoichiometry of which is that of complex **1** minus LiBr. The overall yield of this minor product **2** from $RuCl_3 \cdot 3H_2O$ is only 10%, but the synthesis offers an alternative procedure to those using $RuBr_3 \cdot 3H_2O$ [9] or *cis*-$RuBr_2(DMSO)_4$ [8] as precursors. The presence of TM*S*O ligands in **2** is suggested by the ν(SO) values, as proposed previously [8, 9]; the *cis* geometry has been assumed by analogy of the UV–Vis spectrum to that of the *cis*-dichloro analogue, which has been characterized crystallographically [1, 8]. The ^1H NMR spectrum of **2** has not been reported previously; the spectrum resembles generally that of the *cis*-dichloro complex (see above). We cannot understand in detail the ^1H NMR spectrum of **2**, but signals for the α-protons of the two types of TMSO ligands are again not obviously resolved.

Supplementary material

Tables of hydrogen-atom parameters, anisotropic thermal parameters, bond lengths and angles involving

H atoms, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure-factor amplitudes are available from the authors on request.

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