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Synthesis and structural characterization of *cis*-dichlorotetrakis(tetramethylenesulfoxide-*S*)ruthenium(II) and *mer*-trichlorotris(tetrahydrothiophene)ruthenium(III)

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Abstract

The complexes *cis*-$RuCl_2(TMSO)_4$ (**1**) and *mer*-$RuX_3(TMS)_3$, X = Cl (**2**) and Br (**3**) have been synthesized and characterized, including X-ray crystallographic analyses of complexes **1** (which exists as two different crystallographic forms, **1a** and **1b**) and **2**; TMSO = tetramethylenesulfoxide. Crystal data are as follows: **1a**, monoclinic, $C2/c$, $a = 17.676(2)$, $b = 14.132(2)$, $c = 9.101(2)$ Å, $\beta = 94.51(2)°$, $Z = 4$, $R = 0.030$ and $R_w = 0.038$ for 1831 reflections with $I \geqslant 3\sigma(I)$; **1b**, monoclinic, $P2_1/c$, $a = 9.108(3)$, $b = 11.336(4)$, $c = 21.898(3)$ Å, $\beta = 90.64(2)°$, $Z = 4$, $R = 0.034$ and $R_w = 0.038$ for 4242 reflections ($I \geqslant 3\sigma(I)$); **2**, orthorhombic, $Pna2_1$, $a = 12.170(4)$, $b = 10.743(4)$, $c = 14.114(3)$ Å, $Z = 4$, $R = 0.025$ and $R_w = 0.030$ for 3104 reflections ($I \geqslant 3\sigma(I)$). The structures were solved by heavy atom methods and were refined by full matrix least-squares procedures. Complexes **1**–**3** are readily prepared from reactions of TMSO with commercially available $RuCl_3 \cdot 3H_2O$.

Introduction

Earlier studies from this laboratory on sulfoxide ligands focussed on the potential of complexes of ruthenium(II) as catalysts for homogeneous hydrogenations, in particular with the use of chiral sulfoxides [1]. In more recent years, the potential of such sulfoxide complexes as antitumor agents has been developed following initial reports that *cis*- and *trans*-$RuCl_2(DMSO)_4$** possess mutagenic properties, exhibit antitumor activity and interact with nucleobases of DNA [2]. Related bioinorganic studies have evolved from our laboratories, where several Ru(II)–sulfoxide–nitroimidazole complexes have been evaluated as radiosensitizers *in vitro* [3, 4]. The starting material used for the synthesis of these nitroimidazoles was initially *cis*-$RuCl_2(DMSO)_4$ [2c, 5], while later work was extended to the use of $RuCl_2(TMSO)_4$ which we prepared and tentatively proposed for it a *trans* configuration, based on spectroscopic data [3].

Our goals are to synthesize Ru–sulfoxide–nitroimidazole complexes and to study the effects on the complex's radiosensitizing ability by varying the sulfoxide, nitro-substituted organic bases, and the required associated anions within both Ru(II) and Ru(III) complexes. Nitroimidazoles themselves are used as dioxygen mimicers in radiotherapy as hypoxic (low oxygen content) cell radiosensitizers, and are thought to act mechanistically as electron acceptors, via reduction of the nitro group and 'fixing' DNA damage induced by ionizing radiation [6]. Unfortunately, nitroimidazoles often exhibit a level of toxicity that outweighs their therapeutic benefits [7].

We have been able to improve the radiosensitizing ability of some 2- and 4-nitroimidazoles by their coordination to Ru(II) via *cis*-$RuCl_2(DMSO)_4$ [8] and $RuCl_2(TMSO)_4$ [3]. The lipophilicity of the sulfoxide/nitroimidazole complexes is increased by using TMSO versus DMSO, and this and the reduction potentials of the nitroimidazole moiety are two factors of importance in radiation treatment [3].

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**Abbreviations used: DMSO = dimethylsulfoxide, TMSO = tetramethylenesulfoxide, DMS = dimethylsulfide, TMS = tetramethylene sulfide (or tetrahydrothiophene).

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A correlation between the radiosensitizing ability of a series of nitroimidazoles and their reduction potentials has been suggested, where the higher the reduction potential, the more effective the radiosensitizer [6]. It has been demonstrated that the reduction potential of a nitroimidazole is increased when coordinated to Ru(II) [3] and Pt(II) [9].

One priority was to synthesize some corresponding Ru(III) complexes, where certainly an increase in reduction potential of a nitroimidazole upon coordination should be quite marked. During our attempts to use $RuX_2(DMSO)_4$ (X = Cl, Br) as precursors with chemical oxidants [10], reports appeared by Poddar and coworkers describing apparently simple routes to Ru(III)–sulfoxide compounds using as starting material, $RuCl_3 \cdot 3H_2O$ [11, 12]. The four synthetic procedures reported for *fac-* and *mer-*$RuCl_3(DMSO)_3$, $RuBr_3(DMSO)_3$ and a chloro-bridged dimer $Ru_2Cl_6(DMSO)_4$ [11, 12] were repeated but instead *trans*-$[(DMSO)_2H^+[RuCl_4(DMSO)_2]^-$, *mer*-$RuCl_3(DMS)_3$, *mer*-$RuBr_3(DMS)_3$ and *trans*-$RuCl_2(DMSO)_4$ were isolated, respectively [13]. Similar synthetic routes were then tried in an attempt to make Ru(III) complexes of TMSO but the corresponding TMS complexes, $RuCl_3(TMS)_3$ (**2**) and $RuBr_3(TMS)_3$ (**3**), were obtained, and this present paper reports on the synthesis and characterization of these complexes, as well as further details on the $RuCl_2(TMSO)_4$ complex (**1**) [3]. Crystallographic analyses of **1**, of which there are two forms (both *cis*) and **2** are reported.

Experimental

Instrumentation and methods

Electronic spectra were recorded on a Perkin-Elmer 552A spectrometer, IR spectra (Nujol or CsI) on a Nicolet 5DXFT spectrometer and room temperature ^1H NMR spectra were recorded in $CDCl_3$ on a Varian XL-300 (FT mode) instrument with shifts in ppm relative to TMS. Magnetic susceptibilities measurements were done by the Evan's method [14], using solutions of the complexes in $CDCl_3$/t-butanol and the same solvent mixture as a reference in a sealed capillary tube in the NMR tube. Equivalent conductivities were measured at 25 °C at 10^{-3} M concentration using a Thomas Serfass conductivity bridge and a cell from Yellow Springs Instrument Co. Elemental analyses were performed by P. Borda of this department.

All synthetic procedures were done in air except where noted, inert atmosphere techniques not being required generally. Complexes **1**–**3** are not air-sensitive either in the solid state or solution, and all physical measurements were carried out in air.

Reagents

All solvents used were of analytical grade; diethylether and MeOH were refluxed for 2 h over Na/benzophenone and Mg powder, respectively, prior to distillation. TMSO (Aldrich), LiBr and HBr(48%) (Fisher Scientific), and conc. HCl (BDH) were used as received. Ruthenium was obtained as $RuCl_3 \cdot 3H_2O$ (43.96% Ru) on loan from Johnson Matthey Ltd.

cis-$RuCl_2(TMSO)_4$ (1)

$RuCl_3 \cdot 3H_2O$ (2.00 g, 7.65 mmol) was refluxed in MeOH (40 ml) under an H_2 atmosphere for about 7 h when the colour of the solution turned from deep brown to deep blue. TMSO (8 ml, 89.1 mmol) was added and refluxing continued under H_2 for a further 4 h to give a yellow–green precipitate. The solution was filtered hot and a fine powder (**1**) collected, washed with cold acetone (10 ml), and dried *in vacuo*. Yield 95%. Yellow crystals (**1b**) suitable for X-ray analysis were obtained by dissolving the powder in hot MeOH followed by slow cooling. *Anal.* Calc. for $C_{16}H_{32}Cl_2O_4S_4Ru$:C, 32.60; H, 5.44. Found: C, 32.65; H, 5.58%. λ_{max} (log ϵ), $CHCl_3$: 355 (3.03); 300 (2.76) nm. δH ($CDCl_3$) 2.26 (4H, m, C–CH_2–CH_2–C); 3.44 and 4.13 (each 2H, m, –CH_2–S(O)–CH_2–). ν(S=O) 1121 and 1064 cm^{-1}.

Crystals of **1a** were obtained following an attempted reaction of the $RuCl_2(TMSO)_4$ powder (0.286 g, 0.49 mmol) with a 2-nitroimidazole derivative called etanidazole [3] (0.141 g, 0.66 mmol), using a 6 h reflux procedure in MeOH (30 ml) under N_2. The resulting blue solution was filtered hot, concentrated to 10 ml and cooled at 0 °C; crystals of **1a** (together with some of **1b**) formed overnight.

mer-$RuCl_3(TMS)_3$(2)

$RuCl_3 \cdot 3H_2O$ (0.25 g, 0.95 mmol) was dissolved in TMSO (1.5 ml, 16.7 mmol). Conc. HCl (5 ml) was added to the syrup obtained and the mixture refluxed at 130 °C for 10 min, during which time a red complex formed and separated. The mixture was then cooled and filtered. The red precipitate was washed with CCl_4 (2 ml) and dried *in vacuo*. Yield 83%. Crystals suitable for X-ray diffraction were obtained by dissolving 100 mg of **2** in acetone (5 ml) and adding n-hexane (3 ml). Red crystals formed after 3 days at room temperature. *Anal.* Calc. for $C_{12}H_{24}Cl_3S_3Ru$: C, 30.54; H, 5.09. Found: C, 30.41; H, 5.07. λ_{max} (log ϵ), $CHCl_3$: 440 (3.32), 380 (3.43) nm. ν(Ru–Cl) 355, 325, 302 cm^{-1}. μ_{eff} = 1.65 BM.

mer-$RuBr_3(TMS)_3$ (3)

Hydrobromic acid (5 ml) was added to a mixture of $RuCl_3 \cdot 3H_2O$ (0.25 g, 0.95 mmol) and LiBr (1 g, 11.50 mmol). The resulting cloudy solution was warmed for about 10 min to give a clear solution. TMSO (1.5 ml, 16.7 mmol) was added, and the mixture heated at 80 °C for 10 min and then stirred at room temperature for 1 h. The precipitated black solid obtained was filtered off, washed with water (3 ml) and diethyl ether (3 ml) and dried *in vacuo*. Yield 83%. *Anal.* Calc. for $C_{12}H_{24}Br_3RuS_3$: C, 23.80; H, 3.95. Found: C, 23.53; H, 3.90. λ_{max} (log ϵ), $CHCl_3$: 510 (3.17), 280 (3.96) nm. ν(Ru–Br) 271, 247, 226 cm^{-1}. $\mu_{eff}=1.87$ BM.

X-ray crystallographic analyses

Crystallographic data for the three compounds appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta=21.0$–31.3° for **1a**, 25.4–37.5° for **1b**, and 40.6–47.7° for **2**. The intensities of the three standard reflections, measured every 200 reflections throughout the data collections, remained essentially constant in each case. The data were processed [15] and corrected for Lorentz and polarization effects, and absorption (empirical, based on azimuthal scans for four reflections).

The structure analyses of **1a** and **2** were all initiated in the space groups *C*2/*c* and *Pna*2$_1$, respectively, on the basis of the Patterson functions. These choices were confirmed by the subsequent successful solutions and refinements of the structures. The structures were solved by conventional heavy atom methods, the coordinates of Ru, Cl and S atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent Fourier syntheses. Complex **1a** has crystallographically imposed twofold symmetry. All non-hydrogen

TABLE 1. Crystallographic data[a]

Compound	*cis*-$RuCl_2(tmso)_4$ (**1a**)	*cis*-$RuCl_2(tmso)_4$ (**1b**)	*mer*-$RuCl_3(tms)_3$ (**2**)
Formula	$C_{16}H_{32}Cl_2O_4RuS_4$	$C_{16}H_{32}Cl_2O_4RuS_4$	$C_{12}H_{24}Cl_3RuS_3$
Formula weight	588.64	588.64	471.93
Color, habit	yellow–green, prism	yellow, prism	red–orange, prism
Crystal size (mm)	0.15×0.20×0.25	0.25×0.25×0.40	0.30×0.35×0.35
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*C*2/*c*	*P*2$_1$/*c*	*Pna*2$_1$
a (Å)	17.676(2)	9.108(3)	12.170(4)
b (Å)	14.132(2)	11.336(4)	10.743(4)
c (Å)	9.101(2)	21.898(3)	14.114(3)
β (°)	94.51(2)	90.64(2)	90
V ($Å^3$)	2266.5(6)	2261(1)	1845(2)
Z	4	4	4
ρ_{calc} (g/cm^3)	1.72	1.73	1.70
F(000)	1208	1208	956
μ(Mo Kα) (cm^{-1})	12.90	12.94	15.86
Transmission factors	0.942–1.00	0.945–1.00	0.848–1.00
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan range, ω (°)	$1.42+0.35\tan\theta$	$1.21+0.35\tan\theta$	$1.42+0.35\tan\theta$
Scan speed (°/min)	32	16	32
Data collected	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, -l$
$2\theta_{max}$ (°)	55	65	70
Crystal decay	negligible	negligible	negligible
Total no. reflections	2799	8972	4546
No. unique reflections	2714	8519	4546
R_{merge}	0.036	0.040	
Reflections with $I>3\sigma(I)$	1831	4242	31.04
No. variables	132	253	189
R	0.030	0.034	0.025
R_w	0.038	0.038	0.030
GOF	1.51	1.25	1.19
Max. Δ/σ (final cycle)	0.06	0.04	0.02
Residual density (e/Å^3)	−0.48 to +0.89	−0.38 to +0.45	−0.51 to +0.51

[a] Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation ($\lambda=0.71069$ Å), 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), $\sigma^2(F^2)=[S^2(C+4B)+(0.03F^2)^2]/Lp^2$ (S = scan speed, 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 $GOF=[\Sigma(|F_o|-|F_c|)^2/(m-n)]^{1/2}$. Values given for R, R_w and GOF are based on those reflections with $I\geqslant 3\sigma(I)$.

atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (d(C–H) = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). In all three structures, twofold conformational disordering of one thiacyclopentane ring was noted. Split-atom disordered models involving one ring carbon atom for **1a** and **1b** and the ring carbon atoms for **2** were refined, site occupancy factors being estimated from relative Fourier peak heights and subsequently adjusted to give approximately equal equivalent isotropic thermal parameters for both partially occupied sites. Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref. 16. A parallel refinement of the structure of **2** having the opposite polarity gave $R = 0.029$ and $R_w = 0.033$. Final atomic coordinates and equivalent isotropic thermal parameters $[B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}(\bar{a}_i\bar{a}_j)]$, bond lengths and bond angles appear in Tables 2–4, respectively. See also 'Supplementary material'.

Results and discussion

cis-RuCl₂(TMSO)₄ (1)

The synthesis of $RuCl_2(TMSO)_4$ (**1**) was carried out in these laboratories for use as a precursor to Ru(II)–sulfoxide–nitroimidazole complexes; X-ray photoelectron spectroscopy, IR and ^1H NMR data revealed that the sulfoxides were all sulfur-bonded [3]. The ν(S=O) stretch of TMSO is seen to shift from 1020 to 1121 cm^{-1} upon coordination of the free ligand to the metal in **1**, which is consistent with S-bonded sulfoxides [3, 17, 18]. Bora and Singh first reported the syntheses of $RuX_2(TMSO)_4$ complexes (X = Cl, Br, I), which were made by refluxing ethanol solutions of the appropriate RuX_3 salt with TMSO [19]; our IR and electronic spectral data are in good agreement with their reported data, except that our molar extinction coefficients for the electronic absorption maxima at 355 and 300 nm are about twice the published values [19]. The ^1H NMR spectrum of free TMSO in $CDCl_3$ shows three sets of multiplets centred at δ 2.58 (β-protons), 2.00 and 1.63 ppm (α-protons) with an integration of 2:1:1, respectively. Upon TMSO coordination to Ru(II) within **1**, the β-protons shift slightly upfield to δ 2.26 ppm while the two sets of α-protons shift slightly to δ 4.13 and 3.44 ppm, respectively; no dissociation of TMSO ligand is observed in $CDCl_3$. The shifts are consistent with S-bonded TMSO [3, 17].

The crystal structures of both **1a** and **1b** (Fig. 1) confirm the S-bonded TMSO but reveals *cis* rather than the originally assigned *trans* geometry; the major evidence for the *trans* assignment was the relatively simple ^1H NMR data which tend to indicate equivalent TMSO ligands [3]. In a *cis* geometry, there will be two types of TMSO ligands (2 *trans* to Cl^-, and 2 mutually *trans*), and more complex ^1H NMR data would be anticipated; clearly shift differences in the sets of CH_2-protons within the two types of S-bonded TMSO ligands are too small to be delineated within the observed multiplet patterns. Indeed, the width of the multiplets are 5–10 times larger than, for example, differences in the methyl resonances of the various DMSO ligands in *cis*-$RuCl_2(DMSO)_4$ which in the solid state contains 2 S-bonded sulfoxides *trans* to the chlorides, and mutually *trans* O- and S-bonded sulfoxides, with the O-bonded DMSO dissociating completely in solutions of the complex [2c, 5a, 20]*.

The yellow–green crystals of **1a** resulted from the work-up of an unsuccessful reaction of $RuCl_2(TMSO)_4$ with a 2-nitroimidazole; some yellow crystals of **1b** were also obtained during this work-up (see 'Experimental'), but were more readily formed from the synthesis of **1** from $RuCl_3 \cdot 3H_2O$. We believe the blue tinge results from the presence of trace 2-nitroimidazole in **1a** (perhaps within a charge-transfer complex), because a trace amount of nitrogen was found in elemental analyses of **1a**. The two crystal forms have different monoclinic space groups: $C2/c$ for **1a**, and $P2_1/c$ for **1b**.

Structures **1a** and **1b** reveal close to octahedral geometry at the Ru atom. The Ru–Cl bond lengths in **1a** (average 2.425 Å) and **1b** (average 2.430 Å) are essentially the same, and correspond closely to those found in *cis*- and *trans*-$RuCl_2(DMSO)_4$ (2.435 and 2.432 Å, respectively) [2c, 5b]. The two Ru–S bonds within **1a** and **1b** (*trans* to S or Cl) are different (2.341 versus 2.274 Å, and 2.357 versus 2.275 Å, respectively); the relative lengthening when *trans* to S is attributed to the *trans* influence of S (competitive π-bonding within *trans* TMSO ligands) [22], analogous to the effects found in related DMSO systems [1e, 2c, 5a, 23]. The average S–O bonds in **1a** (1.476 Å) and **1b** (1.479 Å) are shorter than in crystalline TMSO (1.527 Å [24]), because of an increase in (S–O)π-bonding which results from electron density transfer from S to the metal [18]; the IR data reflect the same phenomenon. As noted above, *cis*-$RuCl_2(DMSO)_4$ contains one O-bonded sulfoxide,

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*A private communication from E. Alessio informs us that researchers at Trieste have also structurally characterized complex **1** in the form of **1b** [21]; the *trans*-$RuCl_2(TMSO)_4$ species, with all S-bonded sulfoxides, has also been made, and more complex ^1H NMR data result because of complete dissociation of one sulfoxide ligand [21].

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

Atom	x	y	z	B_{eq}
cis-RuCl$_2$(TMSO)$_4$ (**1a**)				
Ru(1)	0	0.24306(3)	1/4	2.12(2)
Cl(1)	0.06447(6)	0.12201(7)	0.4015(1)	3.40(4)
S(1)	0.06514(5)	0.35230(6)	0.3932(1)	2.57(4)
S(2)	−0.09537(5)	0.23197(6)	0.4136(1)	2.81(4)
O(1)	0.0294(2)	0.3832(2)	0.5263(3)	4.1(1)
O(2)	−0.1579(2)	0.3012(3)	0.3935(4)	5.1(2)
C(1)	0.0947(2)	0.4595(3)	0.3049(4)	3.4(2)
C(2)	0.1761(3)	0.4778(4)	0.3632(6)	6.0(3)
C(3)	0.2021(3)	0.4100(4)	0.4732(8)	7.0(3)
C(4)	0.1613(2)	0.3189(3)	0.4536(5)	3.9(2)
C(5)	−0.0669(2)	0.2275(3)	0.6085(4)	3.8(2)
C(6)	−0.1004(6)	0.1361(6)	0.670(1)	4.0(4)
C(6A)	−0.1377(7)	0.1820(8)	0.672(1)	4.3(5)
C(7)	−0.1659(2)	0.1062(3)	0.5664(5)	4.0(2)
C(8)	−0.1361(2)	0.1151(3)	0.4166(5)	4.0(2)
cis-RuCl$_2$(TMSO)$_4$ (**1b**)				
Ru(1)	0.23550(3)	0.21129(2)	0.12445(1)	2.04(1)
Cl(1)	0.0836(1)	0.37808(9)	0.15314(5)	3.59(4)
Cl(2)	0.3786(1)	0.2353(1)	0.21802(4)	3.51(4)
S(1)	0.3780(1)	0.05206(8)	0.10275(4)	2.39(3)
S(2)	0.1013(1)	0.20089(8)	0.03643(4)	2.48(3)
S(3)	0.4091(1)	0.34040(9)	0.08217(5)	3.17(4)
S(4)	0.0616(1)	0.09599(9)	0.17695(4)	2.81(4)
O(1)	0.5157(3)	0.0774(3)	0.0701(1)	4.2(1)
O(2)	−0.0348(3)	0.1301(3)	0.0391(1)	4.1(1)
O(3)	0.3984(4)	0.3600(3)	0.0154(1)	6.0(2)
O(4)	0.0795(4)	−0.0335(3)	0.1726(2)	5.2(2)
C(1)	0.2941(4)	−0.0703(3)	0.0626(2)	2.9(2)
C(2)	0.3570(6)	−0.1813(4)	0.0915(2)	5.2(3)
C(3)	0.4562(8)	−0.1571(4)	0.1416(2)	6.6(3)
C(4)	0.4283(5)	−0.0377(4)	0.1682(2)	3.7(2)
C(5)	0.1948(5)	0.1560(4)	−0.0327(2)	3.3(2)
C(6)	0.1450(6)	0.2391(5)	−0.0829(2)	5.2(3)
C(7)	0.0302(6)	0.3196(4)	−0.0621(2)	5.5(3)
C(8)	0.0483(5)	0.3429(4)	0.0043(2)	4.0(2)
C(9)	0.4091(6)	0.4833(4)	0.1195(3)	5.8(3)
C(10)	0.5614(7)	0.5146(5)	0.1346(3)	7.1(3)
C(11)	0.6700(8)	0.4371(8)	0.1021(4)	4.5(4)
C(11A)	0.651(2)	0.428(2)	0.1405(8)	4.5(8)
C(12)	0.6020(4)	0.3159(4)	0.0999(2)	4.1(2)
C(13)	0.0542(5)	0.1343(5)	0.2582(2)	4.7(2)
C(14)	−0.1016(5)	0.1665(4)	0.2719(2)	4.3(2)
C(15)	−0.2004(5)	0.1084(4)	0.2270(2)	4.3(2)
C(16)	−0.1314(4)	0.1284(4)	0.1644(2)	3.6(2)
mer-RuCl$_3$(TMS)$_3$ (**2**)				
Ru(1)	0.27827(2)	0.47381(2)	0.25000	2.277(7)
Cl(1)	0.44890(7)	0.51681(8)	0.17893(6)	3.18(3)
Cl(2)	0.11726(7)	0.4401(1)	0.33786(7)	3.86(3)
Cl(3)	0.20367(7)	0.39479(9)	0.10886(7)	3.52(3)
S(1)	0.35023(7)	0.55602(8)	0.39481(6)	3.11(3)
S(2)	0.34904(7)	0.27298(7)	0.28857(7)	3.15(3)
S(3)	0.20692(7)	0.67429(8)	0.21267(7)	3.11(3)
C(1)	0.3869(4)	0.7204(4)	0.3840(3)	4.4(2)
C(2)	0.4924(4)	0.7316(5)	0.4390(4)	5.2(2)
C(3)	0.5620(3)	0.6234(5)	0.4125(3)	4.9(2)
C(4)	0.4923(3)	0.5065(4)	0.4169(3)	3.9(1)
C(5)	0.4064(3)	0.2005(4)	0.1823(3)	4.0(2)

(*continued*)

TABLE 2. (*continued*)

Atom	x	y	z	B_{eq}
C(6)	0.335(2)	0.100(1)	0.155(2)	5.9(6)
C(6A)	0.342(3)	0.069(2)	0.174(3)	6(1)
C(7)	0.2827(8)	0.0449(6)	0.245(1)	5.5(4)
C(7A)	0.239(1)	0.084(2)	0.215(1)	6.0(8)
C(8)	0.2384(4)	0.1602(4)	0.2997(5)	5.3(2)
C(9)	0.2730(3)	0.7356(4)	0.1062(3)	4.1(2)
C(10)	0.1812(4)	0.7912(4)	0.0494(3)	4.7(2)
C(11)	0.0888(4)	0.6981(4)	0.0518(3)	4.7(2)
C(12)	0.0729(3)	0.6601(4)	0.1553(3)	4.3(2)

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

Atom	Atom	Distance	Atom	Atom	Distance
cis-RuCl$_2$(TMSO)$_4$ (**1a**)					
Ru(1)	S(1)	2.274(1)	C(1)	C(2)	1.516(6)
Ru(1)	S(2)	2.341(1)	C(2)	C(3)	1.436(8)
Ru(1)	Cl(1)	2.425(1)	C(3)	C(4)	1.479(6)
S(1)	O(1)	1.475(3)	C(5)	C(6)	1.54(1)
S(1)	C(4)	1.807(4)	C(5)	C(6A)	1.56(1)
S(1)	C(1)	1.811(4)	C(6)	C(7)	1.49(1)
S(2)	O(2)	1.477(3)	C(6A)	C(7)	1.50(1)
S(2)	C(8)	1.802(4)	C(7)	C(8)	1.505(6)
S(2)	C(5)	1.806(4)			
cis-RuCl$_2$(TMSO)$_4$ (**1b**)					
Ru(1)	Cl(1)	2.430(1)	S(4)	C(13)	1.832(4)
Ru(1)	Cl(2)	2.431(1)	S(4)	C(16)	1.814(4)
Ru(1)	S(1)	2.276(1)	C(1)	C(2)	1.518(5)
Ru(1)	S(2)	2.274(1)	C(2)	C(3)	1.438(7)
Ru(1)	S(3)	2.352(1)	C(3)	C(4)	1.498(6)
Ru(1)	S(4)	2.362(1)	C(5)	C(6)	1.514(6)
S(1)	O(1)	1.479(3)	C(6)	C(7)	1.464(7)
S(1)	C(1)	1.807(4)	C(7)	C(8)	1.486(6)
S(1)	C(4)	1.812(4)	C(9)	C(10)	1.466(7)
S(2)	O(2)	1.478(3)	C(10)	C(11)	1.51(1)
S(2)	C(5)	1.818(4)	C(10)	C(11A)	1.28(2)
S(2)	C(8)	1.819(4)	C(11)	C(12)	1.51(1)
S(3)	O(3)	1.480(3)	C(11A)	C(12)	1.61(1)
S(3)	C(9)	1.815(5)	C(13)	C(14)	1.499(6)
S(3)	C(12)	1.817(4)	C(14)	C(15)	1.481(6)
S(4)	O(4)	1.480(3)	C(15)	C(16)	1.531(6)
mer-RuCl$_3$(TMS)$_3$ (**2**)					
Ru(1)	Cl(1)	2.352(1)	C(1)	C(2)	1.507(6)
Ru(1)	Cl(2)	2.347(1)	C(2)	C(3)	1.486(7)
Ru(1)	Cl(3)	2.3481(9)	C(3)	C(4)	1.517(7)
Ru(1)	S(1)	2.393(1)	C(5)	C(6)	1.44(2)
Ru(1)	S(2)	2.386(1)	C(5)	C(6A)	1.62(3)
Ru(1)	S(3)	2.381(1)	C(6)	C(7)	1.54(2)
S(1)	C(1)	1.827(4)	C(6A)	C(7A)	1.40(4)
S(1)	C(4)	1.836(4)	C(7)	C(8)	1.56(1)
S(2)	C(5)	1.828(4)	C(7A)	C(8)	1.44(2)
S(2)	C(8)	1.818(5)	C(9)	C(10)	1.499(6)
S(3)	C(9)	1.827(4)	C(10)	C(11)	1.506(7)
S(3)	C(12)	1.827(4)	C(11)	C(12)	1.530(7)

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

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
cis-$RuCl_2(TMSO)_4$ (**1a**)							
S(1)	Ru(1)	S(1)*	94.50(5)	O(2)	S(2)	C(5)	107.1(2)
S(1)	Ru(1)	S(2)	92.19(3)	O(2)	S(2)	Ru(1)	116.5(1)
S(1)	Ru(1)	S(2)*	93.02(3)	C(8)	S(2)	C(5)	92.0(2)
S(1)	Ru(1)	Cl(1)	87.64(3)	C(8)	S(2)	Ru(1)	112.3(1)
S(1)	Ru(1)	Cl(1)*	177.42(5)	C(5)	S(2)	Ru(1)	117.9(1)
S(2)	Ru(1)	S(2)*	172.32(5)	C(2)	C(1)	S(1)	106.6(3)
S(2)	Ru(1)	Cl(1)	85.45(3)	C(3)	C(2)	C(1)	111.9(4)
S(2)	Ru(1)	Cl(1)*	89.13(3)	C(2)	C(3)	C(4)	111.7(4)
Cl(1)	Ru(1)	Cl(1)*	90.26(5)	C(3)	C(4)	S(1)	104.3(3)
O(1)	S(1)	C(4)	106.3(2)	C(6)	C(5)	S(2)	107.4(4)
O(1)	S(1)	C(1)	105.9(2)	C(6A)	C(5)	S(2)	102.0(5)
O(1)	S(1)	Ru(1)	116.2(1)	C(7)	C(6)	C(5)	108.1(6)
C(4)	S(1)	C(1)	93.2(2)	C(7)	C(6A)	C(5)	107.1(7)
C(4)	S(1)	Ru(1)	114.7(1)	C(6)	C(7)	C(8)	103.7(5)
C(1)	S(1)	Ru(1)	117.7(1)	C(6A)	C(7)	C(8)	113.5(5)
O(2)	S(2)	C(8)	108.2(2)	C(7)	C(8)	S(2)	105.0(3)
cis-$RuCl_2(TMSO)_4$ (**1b**)							
Cl(1)	Ru(1)	Cl(2)	89.78(4)	C(5)	S(2)	C(8)	92.9(2)
Cl(1)	Ru(1)	S(1)	177.02(4)	Ru(1)	S(3)	O(3)	116.4(1)
Cl(1)	Ru(1)	S(2)	87.55(4)	Ru(1)	S(3)	C(9)	112.0(2)
Cl(1)	Ru(1)	S(3)	90.27(5)	Ru(1)	S(3)	C(12)	118.3(1)
Cl(1)	Ru(1)	S(4)	85.30(4)	O(3)	S(3)	C(9)	108.1(3)
Cl(2)	Ru(1)	S(1)	87.90(4)	O(3)	S(3)	C(12)	106.7(2)
Cl(2)	Ru(1)	S(2)	176.53(4)	C(9)	S(3)	C(12)	92.6(2)
Cl(2)	Ru(1)	S(3)	84.58(4)	Ru(1)	S(4)	O(4)	116.3(1)
Cl(2)	Ru(1)	S(4)	90.45(4)	Ru(1)	S(4)	C(13)	111.9(2)
S(1)	Ru(1)	S(2)	94.83(4)	Ru(1)	S(4)	C(16)	117.9(1)
S(1)	Ru(1)	S(3)	91.37(4)	O(4)	S(4)	C(13)	107.6(2)
S(1)	Ru(1)	S(4)	92.85(4)	O(4)	S(4)	C(16)	107.4(2)
S(2)	Ru(1)	S(3)	93.21(4)	C(13)	S(4)	C(16)	93.1(2)
S(2)	Ru(1)	S(4)	91.54(4)	S(1)	C(1)	C(2)	106.1(3)
S(3)	Ru(1)	S(4)	173.36(4)	C(1)	C(2)	C(3)	113.0(4)
Ru(1)	S(1)	O(1)	115.8(1)	C(2)	C(3)	C(4)	111.1(4)
Ru(1)	S(1)	C(1)	118.1(1)	S(1)	C(4)	C(3)	104.0(3)
Ru(1)	S(1)	C(4)	114.8(1)	S(2)	C(5)	C(6)	106.9(3)
O(1)	S(1)	C(1)	105.7(2)	C(5)	C(6)	C(7)	111.8(4)
O(1)	S(1)	C(4)	106.5(2)	C(6)	C(7)	C(8)	110.1(4)
C(1)	S(1)	C(4)	93.2(2)	S(2)	C(8)	C(7)	104.3(3)
Ru(1)	S(2)	O(2)	116.0(1)	S(3)	C(9)	C(10)	108.2(4)
Ru(1)	S(2)	C(5)	117.9(1)	C(9)	C(10)	C(11)	112.1(5)
Ru(1)	S(2)	C(8)	114.8(1)	C(9)	C(10)	C(11A)	115.9(8)
O(2)	S(2)	C(5)	106.4(2)	C(10)	C(11)	C(12)	106.0(5)
O(2)	S(2)	C(8)	106.0(2)	C(10)	C(11A)	C(12)	112(1)
S(3)	C(12)	C(11)	105.3(4)	C(13)	C(14)	C(15)	109.1(4)
S(3)	C(12)	C(11A)	104.8(7)	C(14)	C(15)	C(16)	106.0(4)
S(4)	C(13)	C(14)	107.3(3)	S(4)	C(16)	C(15)	104.0(3)
mer-$RuCl_3(TMS)_3$ (**2**)							
Cl(1)	Ru(1)	Cl(2)	173.11(3)	C(5)	S(2)	C(8)	94.0(2)
Cl(1)	Ru(1)	Cl(3)	92.90(4)	Ru(1)	S(3)	C(9)	110.3(1)
Cl(1)	Ru(1)	S(1)	88.20(3)	Ru(1)	S(3)	C(12)	110.4(1)
Cl(1)	Ru(1)	S(2)	87.49(3)	C(9)	S(3)	C(12)	93.4(2)
Cl(1)	Ru(1)	S(3)	92.86(4)	S(1)	C(1)	C(2)	104.0(3)
Cl(2)	Ru(1)	Cl(3)	93.99(4)	C(1)	C(2)	C(3)	107.0(4)
Cl(2)	Ru(1)	S(1)	84.91(4)	C(2)	C(3)	C(4)	108.6(3)
Cl(2)	Ru(1)	S(2)	92.36(4)	S(1)	C(4)	C(3)	106.2(3)
Cl(2)	Ru(1)	S(3)	87.25(4)	S(2)	C(5)	C(6)	108(1)
Cl(3)	Ru(1)	S(1)	178.70(2)	S(2)	C(5)	C(6A)	104(2)

(continued)

TABLE 4. (*continued*)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
Cl(3)	Ru(1)	S(2)	90.36(4)	C(5)	C(6)	C(7)	108(1)
Cl(3)	Ru(1)	S(3)	89.90(4)	C(5)	C(6A)	C(7A)	108(2)
S(1)	Ru(1)	S(2)	90.39(4)	C(6)	C(7)	C(8)	104.2(7)
S(1)	Ru(1)	S(3)	89.35(4)	C(6A)	C(7A)	C(8)	114(2)
S(2)	Ru(1)	S(3)	179.6(1)	S(2)	C(8)	C(7)	103.3(4)
Ru(1)	S(1)	C(1)	112.0(1)	S(2)	C(8)	C(7A)	107.6(7)
Ru(1)	S(1)	C(4)	112.5(1)	S(3)	C(9)	C(10)	104.8(3)
C(1)	S(1)	C(4)	93.7(2)	C(9)	C(10)	C(11)	106.3(3)
Ru(1)	S(2)	C(5)	109.6(1)	C(10)	C(11)	C(12)	107.0(4)
Ru(1)	S(2)	C(8)	110.8(2)	S(3)	C(12)	C(11)	106.8(3)

[a] Starred item: symmetry operation $-x$, y, $\frac{1}{2}-z$.

in contrast to the *cis*-$RuCl_2(TMSO)_4$ complex which contains all S-bonded sulfoxides. This implies that S-bonded TMSO is sterically less demanding than S-bonded DMSO, and this is evident in the relative average C–S–C bond angles within the two complexes: 98.3° for the DMSO complex [2c, 5b] and 92.8° for **1a** and **1b**, while the averaged O–S–C bond angles are more similar, being 105.5 and 106.1°, respectively. Our structural data for **1b** are in excellent agreement with those of Alessio *et al.* [21].

mer-$RuCl_3(TMS)_3$ (2) and $RuBr_3(TMS)_3$ (3)

As mentioned in the 'Introduction', our attempts to synthesize complexes such as $RuX_3(DMSO)_3$ (X = halide) by using literature procedures [11, 12] led instead to the thioether analogues, $RuX_3(DMS)_3$ [13]. The corresponding TMS thioether complexes **2** and **3** are obtained by analogous procedures using TMSO instead of DMSO; the method involves refluxing concentrated HX solutions of $RuCl_3 \cdot 3H_2O$ in the presence of TMSO. It seems that the relatively high temperature (130 °C) in the strongly acidic conditions leads to the generation of the thioether; this new route to thioether complexes via the sulfoxide reagents is convenient in that it avoids the use of the obnoxious thioether reagents and, although not well understood mechanistically, the process likely involves the equilibrium shown below [13, 25].

$$2Ru^{III} + R_2S + H_2O \rightleftharpoons 2Ru^{II} + R_2SO + 2H^+$$

The structure of **2** (Fig. 1) reveals the *mer* configuration with close to octahedral geometry, within an orthorhombic crystal system, analogous to the corresponding DMS complex [13]. Three strong IR bands at 335, 325 and 302 cm^{-1}, tentatively assigned to ν(Ru–Cl), are consistent with such a formulation. Infrared stretches for **3**, the bromide analogue, at 271, 247 and 226 cm^{-1}, are tentatively assigned to ν(Ru–Br) with again a *mer* configuration. The solution magnetic moments of **2** and **3** (1.65 and 1.87 BM, respectively) are consistent with the expected low spin d^5 configuration, as are the solution ^1H NMR spectra which show weak, broad resonances.

The Ru–Cl bond lengths in **2** (2.384 Å, *trans* to S; and 2.350 Å, *trans* to Cl) are significantly shorter (by 0.08 Å) than in **1**, and this seems reasonable for the low spin d^5 (Ru(III) complex compared to the low-spin d^6 Ru(II) complex and has been noted by others [20, 21, 26]. A similar shortening of the Ru–Cl bond lengths is seen on comparing structural data for *mer*-$RuCl_3(DMS)_3$ with those for *cis*- and *trans*-$RuCl_2(DMSO)_4$ [2c, 13]. All three Ru–S bond lengths in **2** are essentially the same: 2.383 and 2.385 Å for the mutually *trans* TMS ligands, and 2,393 Å for the S *trans* to Cl. The findings are very similar to the data for the analogous *mer*-$RuCl_3(DMS)_3$ complex [13], and indicate the absence of any significant *trans* influence of the thioether ligand. The available data for the averaged Ru–S bond lengths in Ru(III)-sulfoxide complexes are all in the range 2.32–2.35 Å, within complexes such as *trans*-$[(TMSO)H]^+[RuCl_4(TMSO)_2]^-$ [21], *mer*-$RuCl_3(DMSO)_3$ [27] and *trans*-$[(DMSO)_2H]^+[RuCl_4(DMSO)_2]^-$ [13, 27]; the shorter bonds in the sulfoxides can be rationalized on considering a resonance contribution from $M \leftarrow S^- = O^+$.

Supplementary material

Tables of hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes for structures **1a**, **1b** and **2** are available from the authors on request.

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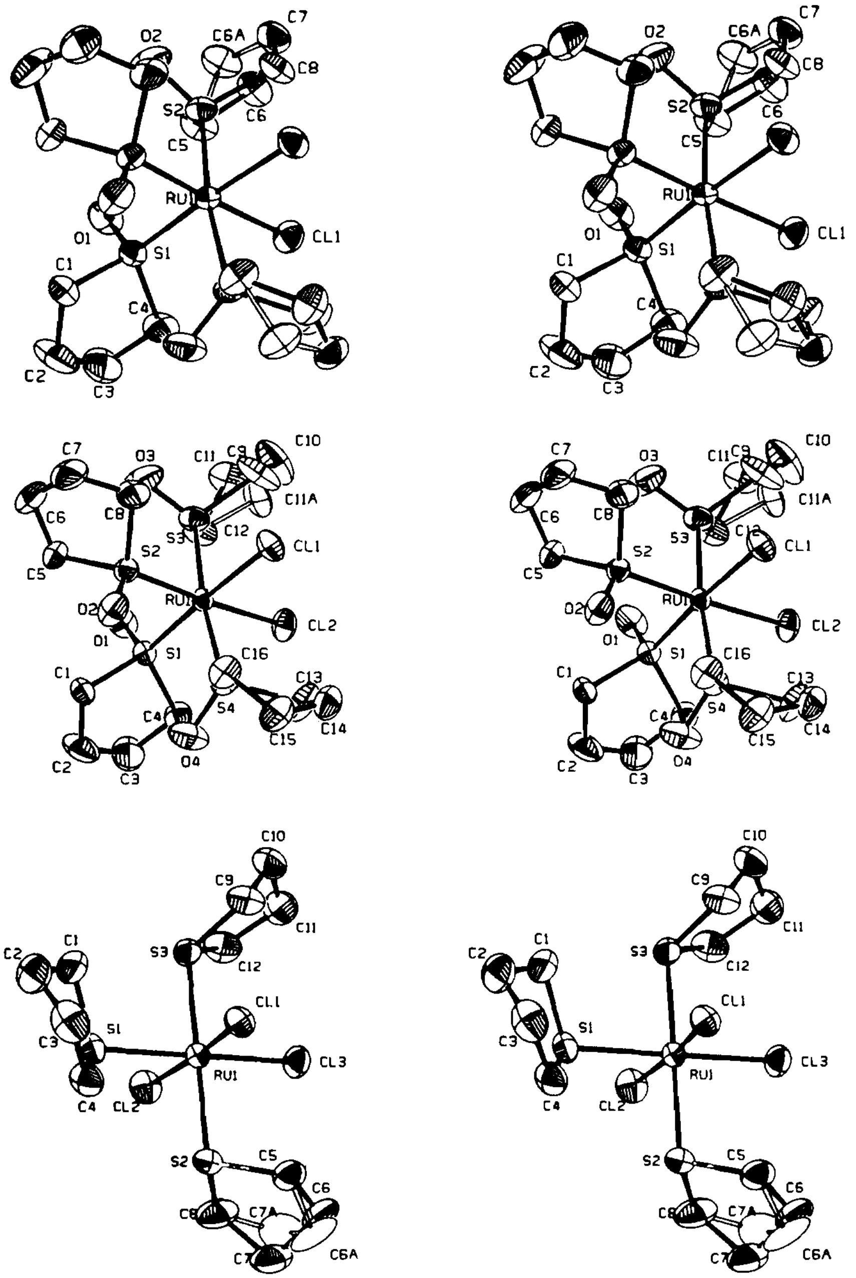

Fig. 1. Stereoviews of the *cis*-dichlorotetrakis(tetramethylenesulfoxide-*S*)ruthenium(II) (**1a**, top; **1b**; middle) and *mer*-trichlorotris(tetramethylenesulfide)ruthenium(III) (**2**, bottom) molecules; 50% probability thermal ellipsoids are shown for the non-hydrogen atoms. Labelled non-hydrogen atoms comprise the asymmetric unit for **1b**.

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