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Synthesis and characterization of new halogen–tetramethylene sulfoxide–ruthenium(II) and ruthenium(III) complexes; crystal structure of *cis*-dichlorotetrakis(tetramethylene sulfoxide)ruthenium(II) and hydrogen *trans*-bis(tetramethylene sulfoxide)tetrachlororuthenate(III)

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Abstract

In this paper we report the synthesis and characterization of the following ruthenium(II) and ruthenium(III) complexes with tetramethylene sulfoxide (TMSO): *cis*-$RuCl_2(TMSO)_4$ (**1**), *trans*-$RuCl_2(TMSO)_4$ (**2**), the corresponding dibromo derivatives *cis*- and *trans*-$RuBr_2(TMSO)_4$ (**3** and **4**, respectively), (TMSO)H[*trans*-$Ru(TMSO)_2Cl_4$] (**5**) and *mer*-$RuCl_3(TMSO)_3$ (**6**). Most of the reported complexes are described here for the first time, together with a new, easy synthetic path for the previously known complexes **1** and **3**. The chemical behavior of **1** and **2** in solution of aprotic, non-coordinating solvents is described. Among the Ru(II) derivatives, the *cis* isomers are thermodynamically more stable and a photochemically driven *cis* to *trans* isomerization reaction is observed in tetramethylene sulfoxide solution. We also report the crystal structures of *cis*-$RuCl_2(TMSO)_4$ (**1**) and (TMSO)H[*trans*-$Ru(TMSO)_2Cl_4$] (**5**), as determined by three dimensional X-ray analyses. Crystal data: **1**, $a = 9.104(2)$, $b = 11.317(2)$, $c = 21.867(6)$ Å, $\beta = 90.62(2)°$, monoclinic, space group $P2_1/c$, $Z = 4$; **5**, $a = 14.642(4)$, $b = 14.999(4)$, $c = 9.667(4)$ Å, $\beta = 103.57(1)°$, monoclinic, space group $P2_1/c$, $Z = 4$. Least-squares refinement based on 3813 (**1**) and 4706 (**5**) reflections converged to $R = 0.032$ and 0.033 for **1** and **5**, respectively. In **1**, all the TMSO ligands are S-bonded to Ru, with average Ru–S bond distances of 2.355(6) (*trans* to S) and 2.273(1) (*trans* to Cl) Å. The TMSO ligands in **5** are both S-bonded to Ru (av. 2.33(1) Å). The protonated TMSO molecule is hydrogen bonded to one of the two crystallographically independent anions.

Introduction

In recent years we have thoroughly investigated the chemistry of ruthenium–dimethyl sulfoxide (DMSO) complexes. We have reported the synthesis and characterization of some new halogen–DMSO–ruthenium(II) isomers, such as *trans*-$RuCl_2(DMSO)_4$ and *cis*-$RuBr_2(DMSO)_4$ [1]. More recently, we described the structure and chemical behavior of the first well characterized halogen–DMSO–ruthenium(III) derivatives: $(DMSO)_2$-H[*trans*-$Ru(DMSO)_2Cl_4$] and *mer*-$RuCl_3(DMSO)_3$ [2, 3].

Ruthenium–DMSO complexes are currently studied in the field of medicinal chemistry for their antitumor properties [4] and as precursors for radiosensitizing agents [5]. Investigations about their interactions with DNA and related molecules have been stimulated by their biological properties [5, 6]. Moreover, these complexes find applications as versatile precursors in inorganic synthesis [7, 8] as well as in the field of homogeneous catalysis [9].

However, although the synthetic [1–3, 7, 10–12] and structural [13–17] aspects of ruthenium–DMSO complexes have been widely investigated since the early studies by James *et al.* [18], only a few reports appeared on the corresponding tetramethylene sulfoxide (TMSO) derivatives. The synthesis of $RuX_2(TMSO)_4$ complexes ($X = Cl$, Br, I) was first described by Bora and Singh in 1978 [19]. On the basis of infrared data, they found that all the sulfoxide ligand were S-bonded to ruthenium, but did not advance any hypothesis on the structure of the complexes. The same authors stated that no Ru(III) complex could be synthesized with TMSO. A recent,

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more detailed, paper by James and co-workers [20] reported an alternative synthetic method for $RuCl_2(TMSO)_4$. The authors tentatively attributed a *trans* configuration to the complex. In this paper we present the synthesis and characterization of a series of Ru(II) and Ru(III)–halogen–TMSO complexes, namely *cis*-$RuCl_2(TMSO)_4$ (**1**), *trans*-$RuCl_2(TMSO)_4$ (**2**), the corresponding dibromo derivatives *cis*- and *trans*-$RuBr_2(TMSO)_4$ (**3** and **4**, respectively), (TMSO)H[*trans*-$Ru(TMSO)_2Cl_4$] (**5**) and *mer*-$RuCl_3(TMSO)_3$ (**6**). The crystal structures of **1** and **5** are also described and compared to those of the corresponding DMSO derivatives. Particularly easy and rapid synthetic routes, based on DMSO/TMSO ligand exchange reactions, are reported for the Ru(II) derivatives.

Experimental

Materials

Commercial $RuCl_3 \cdot 3H_2O$ and $RuBr_3 \cdot 3H_2O$ were purchased from Metalli Preziosi SpA and Strem Chemicals, respectively, and used as received. Tetramethylene sulfoxide (Aldrich) was vacuum distilled prior to use. Analytical grade solvents (Baker) were used without further purification for synthetic and spectroscopic purposes.

Physical measurements

Electronic absorption spectra were obtained in stoppered quartz cells with a Perkin-Elmer Lambda 5 UV–Vis spectrophotometer equipped with a Haake F3 thermo-cryostat. Infrared spectra (Nujol mull) were recorded between CsI windows on a Perkin-Elmer 983G spectrometer. Solution spectra were obtained between BaF_2 windows in the range 1200–800 cm^{-1} (0.025 mm spacer) or between KBr windows in the range 1200–900 cm^{-1} (1.0 mm spacer). Solvent absorption was subtracted from the solution spectrum by means of a Perkin-Elmer 983 data-station. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 80 and 20.1 MHz, respectively, on a Bruker WP-80 spectrometer operating in the Fourier Transform mode. All spectra were recorded at room temperature with tetramethylsilane (Me_4Si) as an internal standard for $CDCl_3$ solutions. Photochemical reactions were carried out at room temperature in a water-cooled photoreactor equipped with a medium pressure lamp (main emission at 365 nm).

Synthesis of the complexes

cis- and *trans*-$RuX_2(DMSO)_4$ (X = Cl, Br) were synthesized and recrystallized according to the reported procedures [1].

cis-Dichlorotetrakis(tetramethylene sulfoxide)-ruthenium(II) (cis-$RuCl_2(TMSO)_4$ (1))

The complex was prepared either by the method reported by Bora and Singh [19], or by the following alternative procedure, which involves a DMSO/TMSO ligand exchange reaction. One gram of recrystallized *cis*-$RuCl_2(DMSO)_4$ was partially dissolved in 10 ml of methanol by gentle heating under stirring. Upon addition of 2.5 ml of TMSO, the starting complex dissolved immediately. The yellow solution was refluxed under stirring for 1 h. After a few minutes the product began to precipitate as a yellow solid. After cooling the reaction mixture to room temperature, the product was filtered, washed with ethanol and vacuum-dried (yield 80%). The complex can be recrystallized from methanol.

Anal. Calc. for $RuCl_2(TMSO)_4$ (M_r 588.64): C, 32.64; H, 5.48; Cl, 12.05; S, 21.78. Found: C, 31.9; H, 5.35; Cl, 11.90; S, 21.92%.

trans-Dichlorotetrakis(tetramethylene sulfoxide)-ruthenium(II) (trans-$RuCl_2(TMSO)_4$ (2))

The complex was synthesized by two different procedures, one (a) involving a DMSO/TMSO ligand exchange reaction and the other (b) involving a photochemical isomerization of the *cis* isomer.

(a) 1 g of of recrystallized *trans*-$RuCl_2(DMSO)_4$ was partially dissolved in 10 ml of methanol and 2 ml of TMSO at room temperature under stirring. After 2 h the yellow product was filtered, washed with methanol and vacuum-dried (yield 85%).

(b) 1 g of *cis*-$RuCl_2(TMSO)_4$ was dissolved in 20 ml of tetramethylene sulfoxide by gentle heating. The solution was transferred into the photoreactor and irradiated for 6 h. The reaction product, which gradually separated from the solution as a deep yellow solid, was filtered, washed with methanol and vacuum dried (yield 65%).

Anal. Calc. for $RuCl_2(TMSO)_4$ (M_r 588.64): C, 32.64; H, 5.48; Cl, 12.05; S, 21.78. Found: C, 32.6; H, 5.56; Cl, 11.92; S, 21.87%.

cis-Dibromotetrakis(tetramethylene sulfoxide)-ruthenium(II) (cis-$RuBr_2(TMSO)_4$ (3))

The synthesis procedure was the same as that reported for the analogous chloro derivative, starting from *cis*-$RuBr_2(DMSO)_4$ (yield 86%).

Anal. Calc. for $RuBr_2(TMSO)_4$ (M_r 677.54): C, 28.36; H, 4.76; S, 18.93. Found: C, 27.94; H, 4.60; S, 18.78%.

trans-Dibromotetrakis(tetramethylene sulfoxide)ruthenium(II) (trans-$RuBr_2(TMSO)_4$ (4))

The complex could be synthesized using either of the procedures reported for the analogous chloro derivative, that is DMSO/TMSO ligand exchange from *trans*-$RuBr_2(DMSO)_4$ or photochemical isomerization of *cis*-$RuBr_2(TMSO)_4$ (yield 85%).

Anal. Calc. for $RuBr_2(TMSO)_4$ (M_r 677.54): C, 28.36; H, 4.76; S, 18.39. Found: C, 28.68; H, 4.56; S, 17.96%.

Hydrogen trans-bis(tetramethylene sulfoxide)tetrachlororuthenate(III) ((TMSO)H[trans-$Ru(TMSO)_2Cl_4$] (5))

One gram of commercial hydrated $RuCl_3$ was refluxed for 3 h in 30 ml of ethanol. The deep green solution was then filtered and vacuum evaporated to 3 ml. The concentrated solution was heated to 80 °C, 1 ml of 37% aqueous HCl and 2 ml of TMSO added under stirring. Within 10 min its colour turned to red–orange. To the cooled transparent solution 10 ml of acetone were added. On standing at room temperature red crystals of the product formed, which were filtered off, washed with cold acetone and diethyl ether and vacuum-dried. Crystal formation could be hastened and increased by the addition of small amounts of diethyl ether (yield 80%). The complex can be recrystallized from TMSO/acetone/diethyl ether (yield 80%). Melting point: 124 °C.

Anal. Calc. for (TMSO)H[$Ru(TMSO)_2Cl_4$] (M_r 556.39): C, 25.9; H, 4.53; Cl, 25.48; S, 17.28. Found: C, 25.7; H, 4.35; Cl, 25.82; S, 16.93%.

mer-Trichlorotris(tetramethylene sulfoxide)ruthenium(III) (mer-[$RuCl_3(TMSO)_3$] (6))

A total of 1.12 g of finely ground (TMSO)H[*trans*-$Ru(TMSO)_2Cl_4$] (2 mmol) was partially dissolved in 80 ml of acetone. TMSO (0.5 ml) was added and the mixture heated under vigorous stirring. To the refluxing mixture 400 mg of anhydrous $AgBF_4$ (2 mmol) dissolved in 20 ml of acetone were added dropwise. After filtering off the AgCl precipitate, the cool solution was evaporated to 10 ml and 1 ml of diethyl ether added. On standing 24 h at 4 °C, red crystals of the product formed, which were filtered off, washed with cold acetone and diethyl ether and vacuum-dried (yield 70%). The complex can be recrystallized from dichloromethane/diethyl ether (yield 80%). Melting point: 145 °C.

Anal. for $RuCl_3(TMSO)_3$ (M_r 519.93): C, 27.7; H, 4.65; Cl, 20.45; S, 18.49. Found: C, 28.1; H, 4.87; Cl, 20.18; S, 18.70%.

Crystal data

Crystals of **1** were grown by dissolving the crude product in refluxing methanol followed by slow cooling. Crystals of **5** were obtained directly from the reaction mixture.

TABLE 1. Crystallographic data for **1** and **5**

	1	5
Formula	$C_{16}H_{32}Cl_2O_4S_4Ru$	$C_{12}H_{25}Cl_4O_3S_3Ru$
Molecular weight	588.7	556.4
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.104(2)	14.642(4)
b (Å)	11.317(2)	14.999(4)
b (Å)	21.867(6)	9.667(4)
β (°)	90.62(2)	103.57(1)
V (Å^3)	2252.8(9)	2064(1)
Z	4	4
D_{calc} (g cm^{-3})	1.736	1.790
λ (Å)	0.71069 (graphite-monochromated Mo Kα)	
μ (Mo Kα) (cm^{-1})	13.0	15.7
Scan type	$\omega/2\theta$	$\omega/2\theta$
θ range (°)	3.0–28.0	2.5–30.0
Intensity monitors[a]	3	3
Unique data with $I > 3\sigma(I)$	3813	4706
R[b]	0.032	0.033
R$_w$[c]	0.033	0.032
w	1	1
GOF[d]	1.6	1.3

[a] Measured after each 4000 s. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [d] $GOF = [\Sigma w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$; m = no. of observations, n = no. of variables.

TABLE 2. Fractional atomic coordinates and B_{eq} of **1**

Atom	x	y	z	B (Å^2)
Ru	0.23540(3)	0.21137(3)	0.12446(1)	2.085(4)
Cl1	0.0838(1)	0.37810(9)	0.15315(5)	3.58(2)
Cl2	0.3785(1)	0.2356(1)	0.21803(4)	3.56(2)
S1	0.3780(1)	0.05222(8)	0.10272(4)	2.40(2)
S2	0.1012(1)	0.20095(9)	0.03644(4)	2.49(2)
S3	0.4092(1)	0.34039(9)	0.08213(5)	3.19(2)
S4	0.0618(1)	0.09597(9)	0.17702(4)	2.78(2)
O1	0.5158(3)	0.0772(3)	0.0700(2)	4.24(7)
O2	−0.0347(3)	0.1300(3)	0.0387(1)	3.93(6)
O3	0.3991(4)	0.3597(4)	0.0155(2)	6.02(9)
O4	0.0799(4)	−0.0333(3)	0.1727(2)	5.15(8)
C1	0.2940(5)	−0.0701(4)	0.0626(2)	3.03(8)
C2	0.3559(7)	−0.1820(4)	0.0915(3)	5.4(1)
C3	0.4577(8)	−0.1572(5)	0.1421(3)	6.6(1)
C4	0.4291(5)	−0.0377(4)	0.1681(2)	4.02(9)
C5	0.0478(5)	0.3425(4)	0.0047(2)	4.02(9)
C6	0.0305(7)	0.3193(5)	−0.0625(2)	5.4(1)
C7	0.1458(7)	0.2387(5)	−0.0833(2)	5.4(1)
C8	0.1945(5)	0.1556(4)	−0.0324(2)	3.30(8)
C9	0.4086(6)	0.4840(4)	0.1199(3)	6.0(1)
C10	0.5615(7)	0.5145(5)	0.1352(3)	7.3(2)
C11	0.6661(7)	0.4344(6)	0.1122(5)	10.5(2)
C12	0.6027(5)	0.3158(4)	0.1000(2)	4.1(1)
C13	0.0553(5)	0.1340(6)	0.2578(2)	4.8(1)
C14	−0.1005(6)	0.1672(5)	0.2723(2)	4.4(1)
C15	−0.2008(5)	0.1085(5)	0.2266(2)	4.3(1)
C16	−0.1305(4)	0.1283(5)	0.1646(2)	3.65(9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\ \gamma)B(1,2)+ac(\cos\ \beta)B(1,3)+bc(\cos\ \alpha)B(2,3)]$.

Unit cell parameters of both compounds were obtained by least-squares methods from the setting angles of 25 accurately centered reflections on an Enraf-Nonius CAD4 diffractometer. A summary of the crystal data, data collection and refinement are given in Table 1. Intensities were corrected for Lorentz–polarization factors and an empirical absorption correction was also applied, by using ψ scan data. No correction for extinction was applied.

Structure determination and refinement

The structures of **1** and **5** were solved by the heavy atom method through Patterson and Fourier syntheses. All hydrogen atoms were included at calculated positions, except the H atom between O1 and O3 in **5**, H25, which was located in a final difference Fourier map (O3–H25, 0.98 Å; O1...H25, 1.74 Å; O1–H25–O3, 143°). Hydrogen atom parameters were held fixed during refinement with isotropic thermal factors $B=1.3B_{eq}$ of the atom to which they are bonded. The final full-matrix least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms, converged to $R=0.032$ for **1** and 0.033 for **5**.

Neutral atom scattering factors and anomalous dispersion terms were taken from the literature [21]. All calculations were done by using the Enraf-Nonius SDP programs [22] on a MicroVAX 2000 computer.

The final positional parameters for non-hydrogen atoms of **1** and **5** are listed in Tables 2 and 3, respectively.

Since in **5** the Ru atoms lie on centres of symmetry (Wyckoff sites, *a* and *d*), the crystallographically independent unit consists of two 'half' molecules. The numbering scheme in Fig. 3 refers to the crystallographically independent 'half' anion at site *a* (the primed atoms are related to the not primed ones by the inversion centre). The other atoms in Table 3 refer to the second independent 'half' anion, at site *d*, and to the protonated TMSO cation (see Table 5).

Bond lengths and angles are given in Tables 4. and 5. See also 'Supplementary material'.

Results and discussion

Ru(II)–TMSO complexes

Complex **1** was synthesized either according to the reported procedure [19] or, more easily, from *cis*-$RuCl_2(DMSO)_4$ by means of a DMSO/TMSO

TABLE 3. Fractional atomic coordinates and B_{eq} of **5**

Atom	x	y	z	B (Å^2)
Ru1	0.000	0.000	0.000	2.114(5)
Ru2	0.500	0.000	0.500	2.302(5)
Cl1	0.12306(5)	0.10295(5)	0.06175(9)	3.29(1)
Cl2	0.03771(6)	−0.05821(6)	0.23265(8)	3.34(1)
Cl3	0.34560(6)	−0.05500(9)	0.4307(1)	5.66(2)
Cl4	0.45964(8)	0.08573(7)	0.67870(9)	5.37(2)
S1	−0.09631(5)	0.10954(5)	0.05902(8)	2.49(1)
S2	0.45261(6)	0.11290(6)	0.33146(8)	3.13(1)
S3	0.15847(6)	0.09662(6)	0.43330(9)	3.60(2)
O1	−0.0910(2)	0.1214(2)	0.2135(2)	3.69(5)
O2	0.3995(3)	0.1875(2)	0.3713(3)	7.01(8)
O3	0.0578(2)	0.1404(2)	0.4177(3)	6.19(7)
C1	−0.2185(2)	0.0976(3)	−0.0279(4)	3.75(7)
C2	−0.2564(3)	0.1897(3)	−0.0517(7)	7.6(2)
C3	−0.1843(4)	0.2496(4)	−0.0725(8)	11.7(2)
C4	−0.0866(3)	0.2189(2)	−0.0131(5)	4.54(8)
C5	0.3884(3)	0.0733(3)	0.1614(4)	4.17(8)
C6	0.4201(4)	0.1286(4)	0.0537(4)	5.9(1)
C7	0.5211(4)	0.1423(5)	0.1029(5)	8.0(2)
C8	0.5454(3)	0.1578(3)	0.2595(5)	6.4(1)
C9	0.2281(3)	0.1819(2)	0.5347(4)	3.87(7)
C10	0.2123(3)	0.1740(3)	0.6829(4)	4.57(9)
C11	0.2120(3)	0.0757(3)	0.7160(4)	4.75(9)
C12	0.1639(3)	0.0269(3)	0.5841(4)	4.66(9)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter refined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\ \gamma)B(1,2)+ac(\cos\ \beta)B(1,3)+bc(\cos\ \alpha)B(2,3)]$.

TABLE 4. Bond distances (Å) and angles (°) for 1

Distances			
Ru–Cl1	2.424(1)	S4–O4	1.475(3)
Ru–Cl2	2.430(2)	S4–C13	1.819(4)
Ru–S1	2.273(1)	S4–C16	1.806(4)
Ru–S2	2.272(1)	C1–C2	1.520(6)
Ru–S3	2.350(2)	C2–C3	1.464(9)
Ru–S4	2.359(2)	C3–C4	1.492(7)
S1–O1	1.478(3)	C5–C6	1.500(7)
S1–C1	1.805(5)	C6–C7	1.467(8)
S1–C4	1.812(5)	C7–C8	1.519(7)
S2–O2	1.476(3)	C9–C10	1.469(8)
S2–C5	1.810(5)	C10–C11	1.411(9)
S2–C8	1.810(5)	C11–C12	1.484(8)
S3–O3	1.475(4)	C13–C14	1.505(7)
S3–C9	1.823(6)	C14–C15	1.502(7)
S3–C12	1.821(4)	C15–C16	1.521(6)
Angles			
Cl1–Ru–Cl2	89.75(4)	Ru–S3–C9	111.7(3)
Cl1–Ru–S1	177.04(4)	Ru–S3–C12	118.3(2)
Cl1–Ru–S2	87.55(4)	O3–S3–C9	108.4(3)
Cl1–Ru–S3	90.35(4)	O3–S3–C12	106.6(2)
Cl1–Ru–S4	85.32(4)	C9–S3–C12	92.7(2)
Cl2–Ru–S1	87.91(4)	Ru–S4–O4	116.2(2)
Cl2–Ru–S2	176.50(4)	Ru–S4–C13	111.8(2)
Cl2–Ru–S3	84.53(4)	Ru–S4–C16	117.9(2)
Cl2–Ru–S4	90.46(4)	O4–S4–C13	107.5(3)
S1–Ru–S2	94.86(3)	O4–S4–C16	107.5(2)
S1–Ru–S3	91.24(4)	C13–S4–C16	93.2(2)
S1–Ru–S4	92.89(4)	S1–C1–C2	106.5(4)
S2–Ru–S3	93.25(4)	C1–C2–C3	112.5(4)
S2–Ru–S4	91.56(3)	C2–C3–C4	110.6(5)
S3–Ru–S4	173.34(4)	S1–C4–C3	104.6(3)
Ru–S1–O1	116.0(1)	S2–C5–C6	104.2(3)
Ru–S1–C1	118.1(1)	C5–C6–C7	110.1(4)
Ru–S1–C4	115.0(2)	C6–C7–C8	111.3(5)
O1–S1–C1	105.6(2)	S2–C8–C7	107.3(3)
O1–S1–C4	106.1(2)	S3–C9–C10	107.8(4)
C1–S1–C4	93.3(3)	C9–C10–C11	114.1(6)
Ru–S2–O2	116.3(1)	C10–C11–C12	112.4(6)
Ru–S2–C5	114.8(2)	S3–C12–C11	105.9(3)
Ru–S2–C8	117.8(1)	S4–C13–C14	107.7(4)
O2–S2–C5	105.8(3)	C13–C14–C15	108.5(5)
O2–S2–C8	105.9(2)	C14–C15–C16	105.6(4)
C5–S2–C8	93.4(3)	S4–C16–C15	104.6(3)
Ru–S3–O3	116.5(2)		

TABLE 5. Bond distances (Å) and angles (°) for 5

Distances			
(a) $[\mathrm{Ru(TMSO)_2Cl_4}]^-$			
Anion *a*		Anion *d*	
Ru1–Cl1	2.3415(8)	Ru2–Cl3	2.352(1)
Ru1–Cl2	2.3548(8)	Ru2–Cl4	2.338(1)
Ru1–S1	2.3219(8)	Ru2–S2	2.3397(8)
S1–O1	1.488(2)	S2–O2	1.465(4)
S1–C1	1.798(3)	S2–C5	1.793(4)
S1–C4	1.801(4)	S2–C8	1.796(5)
C1–C2	1.488(6)	C5–C6	1.488(7)
C2–C3	1.437(8)	C6–C7	1.459(7)
C3–C4	1.484(6)	C7–C8	1.490(7)
(b) $[\mathrm{(TMSO)H}]^+$			
S3–O3	1.589(3)		
S3–C9	1.780(4)		
S3–C12	1.781(4)		
C9–C10	1.509(6)		
C10–C11	1.509(6)		
C11–C12	1.496(6)		
O3–H25	0.98		
Angles			
(a) $[\mathrm{Ru(TMSO)_2Cl_4}]^-$			
Anion *a*		Anion *d*	
Cl1–Ru1–Cl2	90.40(3)	Cl3–Ru2–Cl4	90.62(4)
Cl1–Ru1–S1	86.91(3)	Cl3–Ru2–S2	86.97(4)
Cl2–Ru1–S1	92.72(3)	Cl4–Ru2–S2	91.81(3)
Ru1–S1–O1	116.1(1)	Ru2–S2–O2	117.3(1)
Ru1–S1–C1	114.2(1)	Ru2–S2–C5	113.9(1)
Ru1–S1–C4	116.2(2)	Ru2–S2–C8	114.4(2)
O1–S1–C1	107.1(2)	O2–S2–C5	107.3(2)
O1–S1–C4	106.8(2)	O2–S2–C8	108.2(2)
C1–S1–C4	94.0(2)	C5–S2–C8	92.9(2)
S1–C1–C2	105.9(3)	S2–C5–C6	105.9(3)
C1–C2–C3	110.0(4)	C5–C6–C7	108.0(4)
C2–C3–C4	115.1(5)	C6–C7–C8	109.6(4)
S1–C4–C3	106.1(3)	S2–C8–C7	108.3(3)
(b) $[\mathrm{(TMSO)H}]^+$			
O3–S3–C9	98.9(2)		
O3–S3–C12	100.5(2)		
C9–S3–C12	93.5(2)		
S3–C9–C10	105.7(3)		
C9–C10–C11	106.6(3)		
C10–C11–C12	108.8(3)		
S3–C12–C11	109.4(3)		
S3–O3–H25	106		

[a] *a* and *d* refer to the Wyckoff letter of the Ru1 and Ru2 crystal sites.

ligand exchange reaction. It had already been shown that, in the presence of deuterated dimethyl sulfoxide, the DMSO ligands in *cis*-$\mathrm{RuCl_2(DMSO)_4}$ undergo a complete exchange reaction [7]. We adopted the same reaction as a general procedure for the synthesis of Ru(II)–TMSO derivatives, starting from the corresponding more soluble and easily available Ru–DMSO complexes.

As already pointed out [19, 20], *cis*-$\mathrm{RuCl_2(TMSO)_4}$ contains only S-bonded TMSOs. This is clearly shown by the solid state infrared spectrum (nujol mull), which has only one S=O stretching band at 1122 $\mathrm{cm^{-1}}$ (shoulder at 1110 $\mathrm{cm^{-1}}$). The band is considerably shifted to higher frequencies relative to that of free TMSO (1023 $\mathrm{cm^{-1}}$ in $\mathrm{CH_2Cl_2}$ solution; see also refs. 19, 23, 24) and is indicative of coordination of the ligand through the sulfur atom. A strong band at 1061 $\mathrm{cm^{-1}}$ may be attributed to ν_{ring} [24]. Two partially overlapping bands of medium intensities at 382 and 371 $\mathrm{cm^{-1}}$ might be ascribed to Ru–S stretching modes, in agreement with similar

TABLE 6. Infrared and visible absorption data for Ru(II)–DMSO and Ru(II)–TMSO complexes

Complex	ν(SO) (cm^{-1})	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))[a]	Reference
cis-$RuCl_2(DMSO)_4$	1122[b], 1109[b], 933[c,d]	358 (484); 308 (322)	
cis-$RuCl_2(TMSO)_4$	1118[b,d]	360 (500); 301 (297)	
trans-$RuCl_2(DMSO)_4$	1089[b,d]	441 (212)	1
trans-$RuCl_2(TMSO)_4$	1129, 1109[b,d]	441 (202)	
cis-$RuBr_2(DMSO)_4$	1111[b], 1084[b], 924[c,e]	373 (484)	1
cis-$RuBr_2(TMSO)_4$	1125, 1107[b,e]	374 (480)	
trans-$RuBr_2(DMSO)_4$	1082[b,e]	468 (207)	26
trans-$RuBr_2(TMSO)_4$	1104, 1080[b,e]	461 (198)	

Electronic absorption bands of Ru(II)–sulfoxide complexes have been previously assigned to d–d electronic transitions: $^1A_{1g} \rightarrow {}^1T_{1g}$ (band at lower frequency) and $^1A_{1g} \rightarrow {}^1T_{2g}$ [19]. [a] $CHCl_3$ solution. [b] S-bonded. [c] O-bonded. [d] CH_2Cl_2 solution. [e] Nujol mull.

attributions in Pd–TMSO complexes [23]. Two bands of low intensities at 320 and 302 cm^{-1} might be assigned to the Ru–Cl stretching modes.

The presence of only S-bonded TMSOs induced some authors to attribute to complex 1 a *trans* structure [20], in analogy to *trans*-$RuCl_2(DMSO)_4$ which has only S-bonded DMSOs. On the contrary the absence of any strong band in the Ru–Cl stretching region attributable to two *trans* chlorine atoms, and the close similarity between the UV–Vis spectra of 1 and *cis*-$RuCl_2(DMSO)_4$ (Table 6), suggested a *cis* structure for the complex. This was fully confirmed by single-crystal X-ray analysis*.

As shown in Fig. 1, the molecular structure of *cis*-$RuCl_2(TMSO)_4$ (1) differs from that of *cis*-$RuCl_2(DMSO)_4$ in the bonding mode of one of the two *trans* sulfoxide ligands. In fact, in the latter, one of the *trans* DMSO molecules is bonded via the S atom and the other via the O atom, while in 1, both the *trans* TMSO molecules are S-bonded to Ru.

The Ru–Cl (av. 2.427(4) Å) as well as the Ru–S (*trans* to Cl) (av. 2.272(1) Å) bond distances are very close to the values found in related Ru(II)–DMSO complexes: Ru–Cl, 2.428(11) Å; Ru–S, 2.278(14) Å [1, 13, 14, 16]. On the other hand, the two *trans* Ru–S bond distances of 2.350(2) and 2.359(2) Å compare well with the average value of 2.358(7) Å found in *trans* Ru(II)–DMSO complexes [1, 26]. These distances are longer than those *trans* to Cl, as expected from the greater *trans* influence of S ligands with respect to Cl and from a decrease in the metal to ligand π back-donation.

The average S–O bond length of 1.476(1) Å compares well with that of 1.48(1) Å found in S-bonded

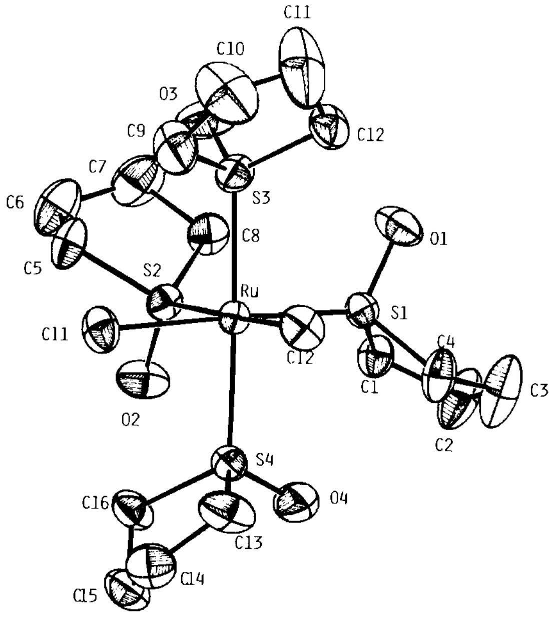

Fig. 1. ORTEP drawing of *cis*-$RuCl_2(TMSO)_4$ (1) showing the atom numbering scheme (thermal ellipsoids at 50% probability level).

DMSO molecules and is consistent with a considerable double bond character [2]. The C–S–C bond angles of the coordinated TMSO ligands average 93.3(5)°, a value which is practically identical to those of 93.5(8) and 93.5(2)° found in the $RuCl_4(TMSO)_2$ anions and H(TMSO) cation of 5, respectively (see below). On the contrary, while the O–S–C bond angles compare well with those of the anions of 5, averaging 107(1)°, they appear to be significantly larger than those of the H(TMSO) cation (av. 100(1)°). The narrowing of the O–S–C angle in the O-protonated TMSO moiety is easily explained considering the compression exerted by the lone-pair of pyramidal sulfur atoms on the less bulky bonding pairs.

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*We have learned from B. R. James (private communication) that complex 1 has been recently structurally characterized also by his group and the *cis* structure confirmed [25].

It is interesting to observe that the average C–S–C bond angle (93.3(4)°) is significantly narrower than that found for the S-bonded DMSO ligand (99.0(15)°), while the O–S–C bond angles are quite similar (107(1)° in TMSO versus 106(1)° in DMSO) [2]. This implies that TMSO has a lower 'cone angle' and hence is less bulky than DMSO. Therefore, the Ru–TM*S*O bonding is sterically less hindered than the Ru–DM*S*O bonding (TM*S*O = S-bonded TMSO; TMS*O* = O-bonded TMSO).

The bonding properties of sulfoxides, because of their ambidentate nature, are still a matter of question. Available data seem indicate that in ruthenium complexes S-bonding is preferred, as expected from the 'soft' character of both kinds of atoms. However, S-bonding is controlled by intramolecular steric interactions, as well as by electronic effects, such as the competition between *trans* S-bonded ligands for the Ru π orbital electrons. Thus, the bonding mode of sulfoxides is the result of a balance between steric and electronic effects, the latter being related to the electron density on the metal atom determined by the nature of the coordinated ligands and by the net charge of the complex. On this basis, it is possible to rationalize the different geometries of *cis*-RuCl$_2$(TM*S*O)$_4$ and *cis*-RuCl$_2$(DM*S*O)$_3$(DMS*O*).

A total of four resonances would be expected for the ^{1}H NMR spectrum of a *cis* complex (two couples of equivalent TMSO ligands, with two resonances per TMSO). On the contrary, the spectrum of **1** in CDCl$_3$ solution consists of three sets of multiplets centered at 2.27, 3.40 and 4.01 ppm, respectively, with an integration ratio of 2:1:1. The spectrum of the free ligand in the same solvent consists of two multiplets of equal intensities, centered at 2.22 and 2.88 ppm, respectively (see also ref. 27). A downfield shift of about 0.7 to 1.1 ppm relative to the signals of the free ligand is expected for the S–CH$_2$ protons of the TM*S*O ligands. On the contrary the S–C–CH$_2$ protons, which are further removed form the positively charged sulfur atom, are almost unshifted by coordination [20, 24, 27]. In agreement with such considerations and with the different Ru–S bond lengths of the two sets of TMSOs (see above), the multiplet at 4.01 ppm is attributed to the S–CH$_2$ protons of the two TMSOs *trans* to the chlorine atom, while the signal at 3.40 ppm is assigned to the S–CH$_2$ protons of the two TMSOs *trans* to each other. An overlap of the resonances of the two sets of S–C–CH$_2$ protons should account for the multiplet of double intensity at higher field.

No free TMSO could be detected in solution. In this respect, *cis*-RuCl$_2$(TMSO)$_4$ differs from its DMSO analog, which in chloroform solution slowly dissociates the O-bonded DMSO [7]. This feature is confirmed by the infrared spectrum of the complex in CH$_2$Cl$_2$ solution which, in the region of the S=O stretching modes, shows only one sharp band for S-bonded TMSOs at 1118 cm^{-1} and no absorption at 1023 cm^{-1} (free TMSO).

trans-RuCl$_2$(TMSO)$_4$ (**2**) was synthesized either from *trans*-RuCl$_2$(DMSO)$_4$ by means of a DMSO/TMSO ligand exchange reaction, or through a photochemical isomerization of the *cis* isomer (**1**) in tetramethylene sulfoxide solution.

As shown by the solid state infrared spectrum, also in **2** all the TMSO ligands are S-bonded to ruthenium. In fact, the spectrum (nujol mull) presents two partially overlapping S=O stretching bands due to S-bonded TMSOs at 1130 and 1106 cm^{-1}. The far-IR spectrum contains a band at 390 cm^{-1}, attributed to the metal–sulfur stretching modes [23], and a strong Ru–Cl stretching band at 342 cm^{-1}. This latter feature is strongly indicative of a *trans* geometry of the two chlorine atoms. The *trans* structure of the complex is further confirmed by the UV–Vis spectral pattern of **2** in chloroform solution, which is closely similar to that of the corresponding DMSO derivative, *trans*-RuCl$_2$(DMSO)$_4$ (Table 6).

The ^{1}H NMR spectrum of **2** in CDCl$_3$ solution is rather complex and shows four multiplets centered at 2.26, 2.88, 3.38 and 3.88 ppm, respectively, with an integration ratio of 8:2:3:3. The multiplet at 2.88 ppm corresponds to one of the two multiplets of free TMSO, the other one being overlapped by the signals centered at 2.26 ppm. This spectral pattern is consistent with the complete dissociation of one sulfoxide ligand, as already observed with the DMSO analog. In fact, if the multiplet at 2.88 ppm represents four protons of free TMSO (probably the more deshielded S–CH$_2$ protons), the two multiplets at 3.38 and 3.88 ppm account for the 6+6 S–CH$_2$ protons of the three S-bonded TMSOs, while the last multiplet accounts for the remaining 12 S–C–CH$_2$ protons of the coordinated TMSOs plus the four S–C–CH$_2$ protons of the free ligand. According to these attributions, the relative intensity of the S-bonded resonances to free tetramethylene sulfoxide is 3:1.

Even though the nature of the resulting species could not be easily deduced from the ^{1}H spectrum, further insight was given by the ^{13}C{^{1}H} NMR spectrum of the complex in the same medium. The spectrum consists mainly of a set of two signals of equal intensity for free TMSO (24.36 and 54.42 ppm) and of a similar set for coordinated TMSOs (25.19 and 56.89 ppm). In agreement with the attributions of the ^{1}H spectrum, the downfield signals are attributed to the S-bound carbon atoms of free (54.42 ppm) and S-bonded (56.89 ppm) TMSO. The intensity ratio between the corresponding signals of the two sets is approximately 3:1, accounting for the complete dissociation of one TMSO. Therefore, the ^{13}C spectrum unambiguously shows that the main species in solution is a trigonal bipyramid with three equivalent TMSO molecules in the equatorial plane, as was the case for the DMSO analog [1]. Signals of minor intensity fall close to the main resonances, suggesting the existence in solution of low amounts of other species of unknown structure. According to the results of the ^{13}C spectrum, the presence of the two multiplets of equal intensity in the ^{1}H spectrum (see above) might be attributed to the magnetic unequivalency of the two protons of each $S\text{–}CH_2$ group of coordinated TMSOs [20].

The dissociation of one ligand in non-coordinating solvents is confirmed by the IR spectrum of the complex in CH_2Cl_2 solution which, besides two $\nu(SO)$ at 1130 and 1108 cm^{-1} for the S-bonded TMSOs, shows the characteristic S=O stretching band of the free ligand at 1023 cm^{-1}.

As already observed with the DMSO analog, *trans*-$RuCl_2(TMSO)_4$ is thermodynamically unstable with respect to *cis*-$RuCl_2(TMSO)_4$. In fact, even if TMSO is sterically less demanding than DMSO, four in-plane S-bonded sulfoxide ligands increase the molecular energy, destabilizing the *trans* isomer.

In tetramethylene sulfoxide solution, **2** slowly isomerizes with first-order kinetics, as indicated spectrophotometrically in Fig. 2. The reversal *cis*-to-*trans* isomerization is observed when a tetramethylene sulfoxide solution of **1** is irradiated with UV light. On such bases, the following reaction scheme can be drawn for the two isomers:

$$\textit{cis}\text{-}RuCl_2(TMSO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \textit{trans}\text{-}RuCl_2(TMSO)_4$$

The dibromo derivatives, *cis*-$RuBr_2(TMSO)_4$ (**3**) and *trans*-$RuBr_2(TMSO)_4$ (**4**), show UV-Vis spectral patterns very similar to those of their dimethyl sulfoxide analogs (Table 6), suggesting the same ligand disposition. As shown by the IR spectra (Table 6), in both complexes all the TMSO ligands are S-bonded to ruthenium. As already observed [1], the Ru–Br stretching bands fall at wavenumber values out of the examined range. The two complexes are also related, in tetramethylene sulfoxide solution, by thermal and photochemical isomerization processes completely similar to those reported for the dichloro derivatives.

Ru(III)–TMSO complexes

Ru(III)–TMSO complexes were investigated mainly by means of IR and UV–Vis spectra, since the paramagnetism of the metal nucleus prevented a detailed NMR study.

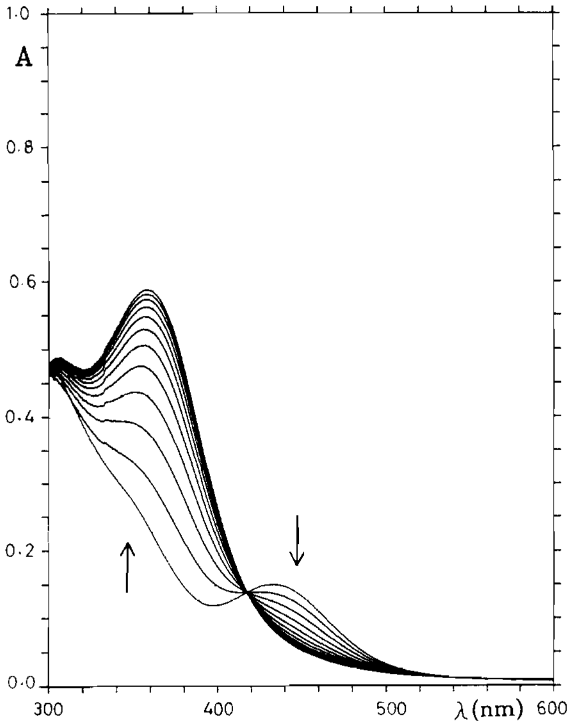

Fig. 2. Spectral changes observed during the thermal isomerization of *trans*-$RuCl_2(TMSO)_4$ to *cis*-$RuCl_2(TMSO)_4$ in tetramethylene sulfoxide solution at 55 °C; scan time interval = 1.5 h.

The solid.state IR spectrum of complex **5** (nujol mull) shows only S-bonded TMSOs ($\nu(SO) = 1120$ cm^{-1}) and is characterized by a strong Ru–Cl stretching band at 337 cm^{-1}. A rather weak band, assigned to the Ru–S stretching mode, falls at 385 cm^{-1}.

The crystal structure of **5** consists of $[H(TMSO)]^+$ cations and *trans*-$[Ru(TMSO)_2Cl_4]^-$ anions. The two crystallographically independent ruthenium atoms lie on the centers of symmetry at sites *a* (Ru1) and *d* (Ru2) of the space group $P2_1/c$, so that for each of the two anions in the asymmetric unit, only two Cl atoms and one TMSO molecule are crystallographically independent. The cation is hydrogen bonded only to the Ru1 anion (O1...O3, 2.590(3) Å), as shown in Fig. 3. The Ru2 anion has normal van der Waals contacts with the Ru1 anion and the cation TMSO moiety. If we exclude the hydrogen bonding effects, the geometries of the two anions are quite similar.

The average Ru–Cl and Ru–S bond distances of 2.347(8) and 2.33(1) Å, respectively, are very close to those of 2.34(2) and 2.34(1) Å found for *trans* Ru–Cl and *trans* Ru–S distances in related Ru(III) complexes [2, 17]. It is worth noting that both these distances are shorter than those of 2.402(2) [1] and 2.358(7) [1, 14] Å found in Ru(II) complexes. Such

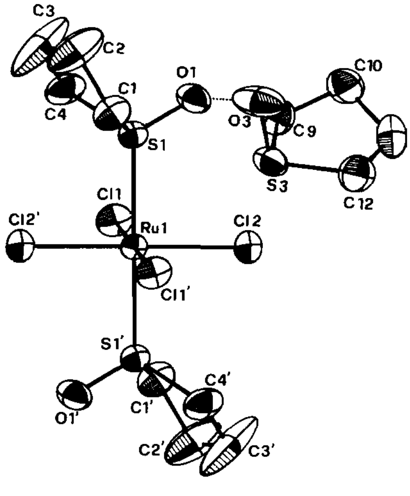

Fig. 3. ORTEP drawing (thermal ellipsoids at 50% probability) of one of the two anions of *trans*-$[RuCl_4(TMSO)_2]^-$ (5), showing the H-bonding to the cation $[(TMSO)H]^+$. Primed atoms are referred to the not primed ones by a centre of symmetry located on the Ru atom. The cation bonded to O1′ is not shown.

a shortening may be explained in terms of the increase of the Ru oxidation state. In fact, a shortening of 0.04 Å has been found in metal–ligand bond distances on passing from Ru(II) to Ru(III) compounds [28]. However, it may be observed that the decrease is much less marked for the Ru–S bond lengths than for the Ru–Cl distances. This has already been observed in DMSO complexes and has been attributed to the lower π back-donation ability of Ru(III) with respect to Ru(II) [2]. Therefore, the decrease of the atomic radius, passing from Ru(II) to Ru(III), is in part counterbalanced by the decrease of the Ru–S bond order.

It is interesting to observe that the S–O bond distance of 1.589(3) Å in $[H(TMSO)]^+$ is markedly longer than those found in coordinated TMSO molecules of both **1** (see above) and **5**. This is clearly due to the protonation of O3 (O3–H25, 0.98 Å) and the consequent change of its hybridization state towards sp^3 (S3–O3–H25, 106°), which yields a S3–O3 single bond. Moreover the S1–O1 bond distance of 1.488(2) Å is significantly longer than S2–O2 (1.465(4) Å), as a consequence of the hydrogen bonding between O1 and O3, which provokes a decrease of charge density in the S1–O1 bond.

The UV–Vis spectral pattern of **5** is closely similar to that of the DMSO analog (Table 7). Like the latter, complex **5** rapidly dissociates a Cl^- anion in methanol solution. The process was conveniently followed by time-drive spectrophotometric experiments (Fig. 4). The existence of only two species in solution during the process is suggested by the five isosbestic points maintained in the examined wavelength range. The final spectrum is closely similar to that of complex **6** (Table 7) in the same solvent, in agreement with the chloride dissociation process.

When an acetone/tetramethylene sulfoxide (1%) solution of **5** is treated with an equivalent of $AgBF_4$, the neutral complex $RuCl_3(TMSO)_3$ (**6**) can be isolated after removal of AgCl. The solid state IR spectrum of **6** (nujol mull) shows three bands of almost equal intensity in the S=O stretching region: two partially overlapping bands at 1124 and 1115 cm^{-1}, attributed to S-bonded TMSOs, and one band at 914 cm^{-1}, attributed to an O-bonded TMSO [23, 24]. This is the first reported example of a tetramethylene sulfoxide moiety bound to ruthenium through the oxygen atom. The far-IR spectrum contains a strong Ru–Cl stretching band at 340 cm^{-1}, partially overlapping the weaker Ru–S vibrational mode at 365 cm^{-1}, and is characterized by the new feature of a band of medium intensity at 442 cm^{-1}. This latter, in agreement with previous attributions [23], is assigned to a complex vibrational mode with a strong contribution of the Ru–O vibration. In CH_2Cl_2 solution the two S-bonded TMSOs give a single sharp S=O stretching band at 1128 cm^{-1}. The S=O stretching frequency of the O-bonded TMSO remains unchanged with respect to the solid state spectrum (913 cm^{-1}). No free TMSO is observed.

Both the IR and the UV–Vis spectral pattern of this complex are closely similar to those of *mer*-$RuCl_3(DMSO)_3$ (Table 7), whose structure has been

TABLE 7. Infrared and visible absorption data for Ru(III)–DMSO and Ru(III)–TMSO complexes

Complex	ν(SO)^a (cm^{-1})	λ_{max} (nm) (ϵ(M^{-1} cm^{-1}))	Reference
$(DMSO)_2H$[*trans*-$Ru(DMSO)_2Cl_4$]	1115^b	463 (515), 396 (4340)^c	2
$(TMSO)H$[*trans*-$Ru(TMSO)_2Cl_4$]	1120^b	464 (510), 396 (4085)^c	
mer-$RuCl_3(DMSO)_3$	1126^b, 1107^b, 911^d	438 (1110), 372 (3230)^e	2
mer-$RuCl_3(TMSO)_3$	1124^b, 115^b, 914^d	437 (947), 373 (3150)^e	

Electronic absorption bands of Ru(III)–sulfoxide complexes, due to their relatively high ε values, have been usually attributed to ligand-to-metal charge transfer transitions [29] (see also ref. 30). ^{a}Nujol mull. ^{b}S-bonded. ^{c}H_2O solution. ^{d}O-bonded. ^{e}CH_3OH solution.

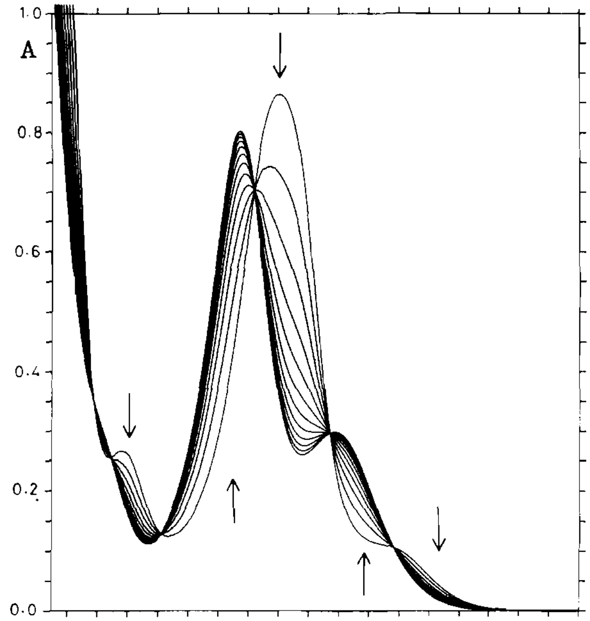

Fig. 4. Spectral changes observed in methanol solution during the chloride dissociation from **5** ($T = 24.0$ °C, scan time interval = 4 min).

previously solved by our group [2]. On the basis of such strong analogies, we feel confident in assigning to **6** the same structure as that determined for the DMSO analog, that is with the three chlorine atoms in meridional configuration and the two S-bonded TMSOs *trans* to each other. The complex can be therefore formulated as *mer,trans*-[$RuCl_3$-$(TMSO)_2$(TMSO)].

One of the two *trans* S-bonded TMSOs can be easily replaced by a stronger ligand L (e.g. nitrogen donor ligands), to give complexes of general formula *mer*-$RuCl_3$(TMSO)(TMSO)(L). The synthesis and characterization of this class of complexes will be the subject of a forthcoming paper.

Supplementary material

Anisotropic thermal parameters, hydrogen atom coordinates and tables of observed and calculated structure factors are available from the authors on request.

Acknowledgements

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