Inorg. Chem. **1991**, *30*, 609–618

Contribution from the Dipartimento di Scienze Chimiche,
Università di Trieste, 34100 Trieste, Italy

Synthesis, Molecular Structure, and Chemical Behavior of Hydrogen *trans*-Bis(dimethyl sulfoxide)tetrachlororuthenate(III) and *mer*-Trichlorotris(dimethyl sulfoxide)ruthenium(III): The First Fully Characterized Chloride–Dimethyl Sulfoxide–Ruthenium(III) Complexes

Enzo Alessio,* Gabriele Balducci, Mario Calligaris, Giacomo Costa, Wahib M. Attia,† and Giovanni Mestroni

Received February 15, 1990

The synthesis, molecular structure and chemical behavior of two chloride–dimethyl sulfoxide–ruthenium(III) derivatives, namely $[(DMSO)_2H][$*trans*-$Ru(DMSO)_2Cl_4]$ (**1**) and *mer*-$Ru(DMSO)_3Cl_3$ (**2**), are reported. They represent the first examples of fully characterized halogen–dimethyl sulfoxide–ruthenium(III) complexes. Further relevance in their synthesis comes from the known antitumor properties of isostructural Ru(III) complexes with heterocyclic nitrogen ligands and of halogen–dimethyl sulfoxide–ruthenium(II) complexes as well. The crystal structures of **1** and **2** have been determined by three-dimensional X-ray analyses. Crystal data are as follows: $[(DMSO)_2H][$*trans*-$Ru(DMSO)_2Cl_4]$, monoclinic, space group $P2/n$, $a = 9.273$ (1) Å, $b = 16.509$ (3) Å, $c = 14.023$ (3) Å, $\beta = 100.79$ (2)°, $Z = 4$, $R = 0.041$; for *mer*-$Ru(DMSO)_3Cl_3$, monoclinic, space group $P2_1/c$, $a = 10.105$ (2) Å, $b = 13.832$ (3) Å, $c = 11.115$ (2) Å, $\beta = 94.39$ (2)°, $Z = 4$, $R = 0.028$. In **1** there are two crystallographically independent $[Ru(DMSO)_2Cl_4]^-$ anions lying on crystallographic 2-fold axes, passing through Ru and two trans Cl atoms, so that the other two Cl atoms and the two S-bonded DMSO molecules are also trans to each other. Cations are provided by protonated DMSO molecules, $[Me_2SO\cdots H\cdots OSMe_2]^+$. In **2** the three chlorine atoms are in the *mer* configuration, and the two trans DMSO molecules are S-bonded to Ru, while the third one is O-bonded. Both complexes are intermediates in the synthesis of *cis*-$RuCl_2(DMSO)_4$ from hydrated $RuCl_3$. Cyclic voltammetric evidence shows that, in dimethyl sulfoxide and dichloromethane solution, **2** is in equilibrium with an isomer that very likely differs in the coordination mode of one DMSO (S- to O-bonded isomerization). The chemical behavior of **1** and **2** in aqueous solution has been studied at low pH (<3), where the formation of polymeric species is prevented. When dissolved in water, both complexes rapidly release one of the two trans S-bonded DMSO's and, in about 24 h at room temperature, produce the same neutral species: *mer,cis*-$[RuCl_3(H_2O)_2(DMSO)]$. A completely similar behavior is found in methanol.

Introduction

The chemistry of halogen–dimethyl sulfoxide–ruthenium(II) complexes has been extensively studied in recent years,[1-13] and several derivatives have been structurally characterized.[14-17] In particular, *cis*-$RuCl_2(DMSO)_4$ is a well-known and versatile starting material for the synthesis of ruthenium(II) derivatives.[18]

We recently reported a detailed study of *cis*- and *trans*-$RuX_2(DMSO)_4$ complexes (X = Cl, Br), describing the synthesis and crystal structure of new isomers, the relative stability of cis and trans derivatives, and their chemical behavior in both protic and nonprotic solvents.[19] Our interest in the chemistry of these complexes arise from their antitumor and, in particular, antimetastatic activity against murine metastasizing tumors.[20-22] DNA was proved to be one of the cellular targets of *trans*-$RuCl_2(DMSO)_4$ in "in vivo" experiments.[22,23] Due to the high stability of the +2 oxidation state, these complexes proved also to be good models for the study of "in vitro" interactions of octahedral complexes with DNA and related molecules.[24]

Despite the remarkable number of publications about ruthenium(II)–DMSO derivatives, only a few, rather misleading, reports are known about ruthenium(III)–DMSO complexes.[3,4,25-28]

The synthesis of a complex formulated as $RuCl_3(DMSO)_3$ was first reported in the early studies of ruthenium–DMSO complexes by Wilkinson's group,[25] but the same authors were later unable to reproduce the synthesis by the published method.[2] A complex of the same formula, with only O-bonded DMSO's, was subsequently reported by Antonov et al.[27] More recently, a paper by Sarma et al. reported the synthesis of the *fac* and *mer* isomers of $RuCl_3(DMSO)_3$[28a] and of $RuBr_3(DMSO)_3$ (of unspecified configuration),[28b] their characterization being based mainly on elemental analysis and solid-state infrared spectroscopy. Almost on the same bases, Bora and Singh claimed the synthesis of pentakis- and hexakis-(dimethyl sulfoxide) chloro complexes, with both sulfur- and oxygen-bonded DMSO's, formulated as $[Ru(DMSO)_5Cl]Cl_2$ and $[Ru(DMSO)_6]Cl_3$, respectively.[3,26] The same authors also briefly reported the essentially uncharacterized anion $[RuCl_4(DMSO)_2]^-$.[3]

---

† On leave from the Physics Department, Suez Canal University, Ismailia, Egypt.

(1) James, B. R.; Ochiai, E.; Rempel, G. L. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 781.
(2) Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.
(3) Bora, M.; Singh, M. M. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1815.
(4) Bora, T.; Singh, M. M. *Transition Met. Chem.* (*Weinheim, Ger.*) **1978**, *3*, 27.
(5) Antonov, P. G.; Kukushkin, Yu. N.; Konnov, V. I.; Kostikov, Yu. P. *Koord. Khim.* **1980**, *6*, 1585.
(6) Hudaly, H. A.; Kingston, J. V.; Tayim, H. A. *Inorg. Chem.* **1979**, *18*, 1391.
(7) Heath, G. A.; Lindsay, A. J.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1982**, 2429.
(8) Farrell, N.; De Oliveira, N. G. *Inorg. Chim. Acta* **1980**, *44*, L225.
(9) Barnes, J. R.; Goodfellow, R. J. *J. Chem. Res., Miniprint* **1979**, 4301.
(10) Fotheringham, J. D.; Heath, G. A.; Lindsay, A. J.; Stephenson, T. A. *J. Chem. Res., Miniprint* **1986**, 801.
(11) Riley, D. P. *Inorg. Chem.* **1983**, *22*, 1965.
(12) Riley, D. P.; Shumate, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 3179.
(13) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1986**, *25*, 1814.
(14) Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480.
(15) McMillan, R. S.; Mercer, A.; James, B. R.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1006.
(16) Oliver, J. D.; Riley, D. P. *Inorg. Chem.* **1984**, *23*, 156.
(17) Attia, W. M.; Calligaris, M. *Acta Crystallogr. Sect. C* **1987**, *C43*, 1426.
(18) (a) Marks, D. N.; Siegl, W. O.; Gaugê, R. G. *Inorg. Chem.* **1982**, *21*, 3140. (b) Ritchie, G. L. D.; Cooper, M. K.; Calvert, R. L.; Dennis, G. R.; Phillips, L.; Vrbancich, J. *J. Am. Chem. Soc.* **1983**, *22*, 1965. (c) Ravindar, V.; Lindaiah, P.; Veera Reddy, K. *Inorg. Chim. Acta* **1984**, *87*, 35. (d) Marzin, C.; Tarrago, G.; Gal, M.; Zidane, I.; Hours, T.; Lerner, D.; Andrieux, C.; Gampp, H.; Saveant, J. M. *Inorg. Chem.* **1986**, *25*, 1775.
(19) Alessio, E.; Mestroni, G.; Nardin, G.; Attia, W. M.; Calligaris, M.; Sava, G.; Zorzet, S. *Inorg. Chem.* **1988**, *27*, 4099.
(20) Sava, G.; Zorzet, S.; Giraldi, T.; Mestroni, G.; Zassinovich, G. *Eur. J. Cancer Clin. Oncol.* **1984**, *20*, 841.
(21) Alessio, E.; Attia, W. M.; Calligaris, M.; Cauci, S.; Dolzani, L.; Mestroni, G.; Monti-Bragadin, C.; Nardin, G.; Quadrifoglio, F.; Sava, G.; Tamaro, M.; Zorzet, S. In *Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*; Nicolini, M., Ed.; Martinus Nijhoff: Boston, MA, 1988; p 617.
(22) Mestroni, G.; Alessio, E.; Calligaris, M.; Attia, W. M.; Quadrifoglio, F.; Cauci, S.; Sava, G.; Zorzet, S.; Pacor, S.; Monti-Bragadin, C.; Tamaro, M.; Dolzani, L. In *Progress in Clinical Biochemistry and Medicine*; Springer-Verlag: Berlin, Heidelberg, 1989; Vol. 10, p 71.
(23) Cauci, S. Ph.D. Dissertation, University of Udine, Udine, Italy, 1990.

0020-1669/91/1330-0609$02.50/0

None of the Ru(III) complexes mentioned has ever been structurally characterized. In this paper we describe the synthesis and structural characterization of two new ruthenium(III) chloride dimethyl sulfoxide complexes, namely [(DMSO)$_2$H][*trans*-Ru(DM*S*O)$_2$Cl$_4$] (**1**) and *mer*-RuCl$_3$(DM*S*O)$_2$(DMS*O*) (**2**),[29] and their role as intermediates in the synthesis of *cis*-RuCl$_2$(DMSO)$_4$ from hydrated RuCl$_3$. The chemical behavior of **1** and **2** in protic (H_2O, CH_3OH) and nonprotic (CH_2Cl_2, DMSO) solvents, studied by means of cyclic voltammetry and infrared and electronic spectroscopy, is also described. Paramagnetism of the Ru(III) nucleus prevented a detailed NMR study of the complexes in solution. The detailed electrochemical behavior of **1** and **2** in dimethyl sulfoxide and water solution will be reported elsewhere.[30]

Despite earlier claims,[4] similar anionic and neutral complexes could be synthesized with tetramethylene sulfoxide (TMSO), their formula being (TMSO)H[*trans*-Ru(TM*S*O)$_2$Cl$_4$] and *mer*-RuCl$_3$(TM*S*O)$_2$(TMS*O*), respectively.[31]

Experimental Section

Materials. Analytical grade dimethyl sulfoxide (C. Erba) and solvents (Baker) were used without further purification for synthetic purposes. Distilled dimethyl sulfoxide was used in spectrophotometric experiments. In the kinetic experiments in methanol, no difference was found between the commercial solvent and a dehydrated sample. Commercial $RuCl_3 \cdot 3H_2O$ was purchased from Metalli Preziosi SpA. Anhydrous silver tetrafluoroborate, dimethyl-d_6 sulfoxide, and methanol-d_1 were purchased from Fluka Chemie. The Burdick & Jackson "distilled in glass" dimethyl sulfoxide used for the electrochemical measurements was stored under inert atmosphere. Tetraethylammonium perchlorate (TEAP) was recrystallized from hot water. Triply distilled water and analytical grade $NaClO_4 \cdot 2H_2O$ and 70% $HClO_4$ (C. Erba) were employed for the electrochemical experiments in aqueous solution.

Physical Measurements. Electronic absorption spectra were recorded in stoppered quartz cells with a Perkin-Elmer Lambda 5 UV/vis spectrophotometer equipped with a Haake F3 thermocryostat. Conductivity measurement were carried out at 25.0 °C on a Beckman RC-18A conductivity bridge equipped with a fill-type cell and thermostated with a Julabo F40 thermostatic bath. Infrared spectra were obtained on a Perkin-Elmer 983G spectrometer. Solid-state spectra were recorded in KBr pellets or in Nujol mulls between CsI windows. Solution spectra were obtained between BaF_2 windows in the range 1200–800 cm^{-1} (0.01-mm spacer in H_2O, 0.025-mm spacer in CH_2Cl_2) or between KBr windows in the range 600–350 cm^{-1} (1.0-mm spacer). Solvent absorption was subtracted from the solution spectrum by means of a Perkin-Elmer 983 data station. ^1H NMR spectra were recorded at 80 MHz on a Bruker WP-80 spectrometer operating in the Fourier transform mode. All spectra were run at room temperature with tetramethylsilane (Me_4Si) as an internal standard for CD_2Cl_2 and CD_3OD solutions and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for D_2O solutions. The magnetic susceptibility was measured at 10 °C with a DSM 5 magnetometer equipped with a Bruker BE-15 electromagnet operating at 1.4 T and an Oxford Instrument CF12005 continuous-flow cryostat. All electrochemical measurements were performed under inert-gas atmosphere (Ar) in a three-electrode cell thermostated at 25.0 °C (unless otherwise stated). A gold working electrode was used in DMSO solution, while a platinum electrode was adopted in H_2O solution. A NaCl saturated calomel electrode (SCE) was used as reference. It was fitted into a Luggin probe filled with the same solution used for the measurements. The potentiostat was an Amel Model 553 connected to an Amel 568 function generator for the cyclic voltammetric measurements. CV traces were stored in a Nicolet 2090 IIIa digital oscilloscope, from which they could be transferred to an Apple IIe personal computer for data handling. Owing to the low scan rates employed (0.1–1.0 V/s), no attempt was made to compensate for *iR* drop. The half-wave potentials for the cyclic voltammetric reversible signals were estimated by the average of the anodic and cathodic peak potentials ($E_{1/2} \approx (E_{pa} + E_{pc})/2$) and are referred to the SCE. Cyclic voltammetric simulations were performed on a CDC Cyber 170–173 machine, by using the standard explicit finite differences algorithm.[32]

Synthesis of the Complexes. Hydrogen *trans*-Bis(dimethyl sulfoxide)tetrachlororuthenate(III) ([(DMSO)$_2$H][*trans*-Ru(DMSO)$_2$Cl$_4$]). The complex could be synthesized by two different procedures:

(a) A 1.5-g amount of commercial hydrated $RuCl_3$ was partially dissolved in 7 mL of DMSO, and 1 mL of 37% aqueous HCl added. The vigorously stirred mixture was heated to 80 °C and kept at this temperature for 20 min, until $RuCl_3$ was completely dissolved. The dense, deep red solution was then heated to 100 °C for 10 min. It gradually became more fluid, and its color turned to bright orange. To the cool transparent solution, 30 mL of acetone was added. Big red-orange crystals of the product formed after some hours at room temperature and were filtered off, washed with cold acetone and diethyl ether, and vacuum-dried. Crystal formation could be hastened and increased by addition of small amounts of diethyl ether (yield 80%).

(b) A 1-g amount 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. A 1-mL volume of 37% aqueous HCl and 2 mL of DMSO were added, and the solution was heated to 80 °C under stirring. Within 10 min its color turned to red-orange. To the cooled transparent solution was added 10 mL of acetone. Red crystals of the product formed after some hours at room temperature and were filtered off, washed with cold acetone and diethyl ether, and vacuum-dried. Crystal formation could be hastened and increased by addition of small amounts of diethyl ether (yield 80%). This second procedure has been particularly useful in the synthesis of the deuterated derivative.

The complex can be recrystallized from DMSO/acetone/diethyl ether (yield 85%). Mp: 120 °C. Anal. Calcd for [(DMSO)$_2$H][Ru(DMSO)$_2$Cl$_4$] (M_r 556.40): C, 17.3; H, 4.53; Cl, 25.48; S, 23.04. Found: C, 17.5; H, 4.55; Cl, 25.30; S, 23.25. $\mu_{eff} = 1.89\ \mu_B$. Electronic spectra (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): in dimethyl sulfoxide solution, 496 (540), 420 (5010); in H_2O solution, 463 (515), 396 (4340), 294 (1440); in methanol solution, 478 (400), 402 (3880), 298 (1145). Λ_M at 25.0 °C (Ω^{-1} cm^2 mol^{-1}): 26 in DMSO; 361 in H_2O; 148 in methanol.

Sodium *trans*-Bis(dimethyl sulfoxide)tetrachlororuthenate(III) (Na[*trans*-Ru(DMSO)$_2$Cl$_4$]). A 1.12-g sample of finely ground [(DMSO)$_2$H][*trans*-[Ru(DMSO)$_2$Cl$_4$] (2 mmol) was dissolved in a mixture of 50 mL of ethanol and 0.7 mL of water. To the clear solution was added 175 mg of NaCl (3 mmol) dissolved in 0.5 mL of water. The product rapidly precipitated from the solution as light orange microcrystals, which were filtered off, washed with cold ethanol and diethyl ether, and vacuum-dried (yield 90%). Mp: 235 °C. Anal. Calcd for Na[Ru(DMSO)$_2$Cl$_4$] (M_r 422.13): C, 11.4; H, 2.86; Cl, 33.59; S, 15.18. Found: C, 11.3; H, 2.93; Cl, 33.20; S, 15.56. Λ_M at 25.0 °C (Ω^{-1} cm^2 mol^{-1}): 36 in DMSO; 114 in H_2O; 104 in methanol.

The complex can be recrystallized from DMSO/acetone/diethyl ether (yield 75%). The recrystallized complex contains two DMSO molecules of crystallization and can be better formulated as Na[*trans*-Ru(DMSO)$_2$Cl$_4$]·2DMSO. Anal. Calcd for Na[Ru(DMSO)$_2$Cl$_4$]·2DMSO (M_r 578.38): C, 16.6; H, 4.18; Cl, 24.51; S, 22.17. Found: C, 16.4; H, 4.22; Cl, 24.35; S, 21.95.

***mer*-Trichlorotris(dimethyl sulfoxide)ruthenium(III) (*mer*-RuCl$_3$(DM*S*O)$_2$(DMS*O*)).** A 1.12-g amount of finely ground [(DMSO)$_2$H][*trans*-Ru(DMSO)$_2$Cl$_4$] (2 mmol) was partially dissolved in 80 mL of acetone. A 0.5-mL volume of DMSO was added and the mixture heated under vigorous stirring. To the refluxing mixture was added dropwise 400 mg of anhydrous $AgBF_4$ (2 mmol) dissolved in 20 mL of acetone. After filtration of the AgCl precipitate, the cool solution was evaporated to 10 mL and 1 mL of diethyl ether added. Red crystals of the product formed within 24 h at 4 °C and 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 85%). Mp: 155 °C. Anal. Calcd for RuCl$_3$(DMSO)$_3$ (M_r 441.81): C, 16.3; H, 4.10; Cl, 24.07; S, 21.76. Found: C, 16.5; H, 4.17; Cl, 24.10; S, 21.48. $\mu_{eff} = 1.87\ \mu_B$. Electronic spectra (λ_{max}, nm (ϵ, M^{-1} cm^{-1})): in dichloromethane solution, 446 (1280), 380 (3565), 265 (sh) (6340); in dimethyl sulfoxide solution, 440 (1445), 380 (3665); in H_2O solution, 426 (1060), 364 (3260); in methanol solution, 438 (1110), 371.5 (3230). Λ_M at 25.0 °C (Ω^{-1} cm^2 mol^{-1}): 1.2 in DMSO; 3.6 in methanol.

***mer*-Trichlorobis(dimethyl sulfoxide)(methanol)ruthenium(III) (*mer*-RuCl$_3$(DM*S*O)(DMS*O*)(CH$_3$OH)).** A 0.5-g amount of finely ground

---

(24) Alessio, E. Xu, Y.; Cauci, S.; Mestroni, G.; Quadrifoglio, F.; Viglino, P.; Marzilli, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 7066.

(25) Gilbert, J. D.; Rose, D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 2765.

(26) Bora, T.; Singh, M. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1975**, *20*, 231.

(27) Antonov, P. G.; Kukushkin, Yu. N.; Konnov, V. I.; Ionin, B. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 245.

(28) (a) Sarma, U. C.; Sarma, K. P.; Poddar, R. K. *Polyhedron* **1988**, *7*, 1727. (b) Sarma, U. C.; Poddar, R. K. *Ibid.* **1988**, *7*, 1737.

(29) DM*S*O = S-bonded dimethyl sulfoxide. DMS*O* = O-bonded dimethyl sulfoxide.

(30) Costa, G.; Balducci, G.; Tavagnacco, C.; Alessio, E.; Mestroni, G. *J. Electroanal. Chem. Interfacial Electrochem.*, in press.

(31) Alessio, E.; Milani, B.; Mestroni, G.; Calligaris, M.; Faleschini, P.; Attia, W. M. *Inorg. Chim. Acta* **1990**, *177*, 255.

(32) Britz, D. *Digital Simulation in Electrochemistry* (Lecture Notes in Chemistry, Vol. 23); Springer-Verlag: Berlin, Heidelberg, 1981.

Table I. Crystallographic Data for **1** and **2**

	1	**2**
Formula	$C_8H_{25}Cl_4O_4S_4Ru$	$C_6H_{18}Cl_3O_3S_3Ru$
M_r	556.4	441.8
cryst syst	monoclinic	monoclinic
space group	$P2/n$	$P2_1/c$
a, Å	9.273 (1)	10.105 (2)
b, Å	16.509 (3)	13.832 (3)
c, Å	14.023 (3)	11.115 (2)
β, deg	100.79 (2)	94.39 (2)
V, Å^3	2108.8 (6)	1549.0 (5)
Z	4	4
D_{calc}, g cm^{-3}	1.75	1.90
λ, Å	0.71069 (graphite-monochromated Mo Kα)	
μ(Mo Kα), cm^{-1}	14.3	19.0
scan type	$\omega-2\theta$	$\omega-2\theta$
θ range, deg	2.5–30	2.5–30
intens monitors[a]	3	3
no. unique data with $I > 3\sigma(I)$	4052	3919
data/param ratio	21.0	27.0
R[b]	4.1	2.8
R_w[c]	4.0	4.1
GOF[d]	1.94	1.74

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

mer-$RuCl_3(DMSO)_3$ was dissolved in 12 mL of methanol by vigorously stirring the mixture for 10 min at room temperature. After this period the product rapidly precipitated from the solution as a yellow solid, which was filtered off, washed with diethyl ether, and vacuum-dried (yield 67%). Mp: 150 °C. Anal. Calcd for $RuCl_3(DMSO)_2(CH_3OH)$ (M_r 395.73): C, 15.2; H, 4.07; Cl, 26.87; S, 16.20. Found: C, 15.3; H, 3.92; Cl, 26.30; S, 16.38.

Tetraethylammonium *fac*-Trichlorotris(dimethyl sulfoxide)ruthenate(II) ($[NEt_4][$*fac*-$RuCl_3(DMSO)_3]$). A 0.5-g amount of *cis*-$RuCl_2(DMSO)_4$ (≈1 mmol) was dissolved in 20 mL of a 1:1 mixture of CH_2Cl_2 and CH_3OH and 400 mg of Et_4NCl (2 mmol) added. The pale yellow solution was refluxed for 15 min and then vacuum-evaporated to 10 mL. Bright yellow crystals of the product separated from the solution after some hours at room temperature and were filtered off, washed with acetone, and vacuum-dried (yield 70%). Anal. Calcd for $[NEt_4][RuCl_3(DMSO)_3]$ (M_r 572.07): C, 29.4; H, 6.69; N, 2.44; Cl, 18.59; S, 16.81. Found: C, 29.2; H, 6.73; N, 2.40; Cl, 18.48; S, 16.90.

Crystallographic Study. Crystals of **1** were grown directly from the reaction mixture (procedure a). Crystals of **2** were obtained upon recrystallization of the crude product from dichloromethane/diethyl ether mixtures. Unit cell parameters of both compounds were obtained by least-squares methods from the setting angles of 25 accurately centered reflections on a Enraf-Nonius CAD4 diffractometer. A summary of the crystal data and data collection and refinement is given in Table I. Intensities were corrected for Lorentz–polarization factors, and an empirical absorption correction was also applied, by using the ψ-scan data of three close-to-axial reflections.

The structures of **1** and **2** were solved by the heavy-atom method through Patterson and Fourier syntheses. All hydrogen atoms were included at calculated positions, except the H atom bridging O3 and O4 in **1**, which was located on a final difference Fourier map (O3–H25 = 0.87 Å; O3⋯O4 = 2.423 Å; O3–H25–O4 = 164°). Hydrogen atoms were held fixed during refinement with isotropic B factors = $1.3B_{eq}$ of the carbon atoms to which they are bonded. The final full-matrix least-squares refinement, with anisotropic temperature factors for all non-hydrogen atoms, converged to $R = 0.041$ for **1** (based on 4052 reflections) and to 0.028 for **2** (based on 3919 reflections).

Neutral atomic scattering factors and anomalous dispersion terms were taken from the literature.[33] All calculations were performed by using the Enraf-Nonius SDP programs[34] on a PDP 11/44 computer. The final coordinates of non-hydrogen atoms are listed in Tables II and III for **1** and **2**, respectively. Bond lengths and angles are given in Tables IV and V (**1**) and in Table VI (**2**). The labeling schemes are shown in Figures 1 and 2. For **1** the labeling of the second molecule is obtained from that of Figure 1 by increasing the identification number by 1 for Ru, S, and O labels, 2 for C, and 3 for the Cl labels.

Table II. Positional Parameters for Non-Hydrogen Atoms and Their Estimated Standard Deviations for **1**

atom	x	y	z	B,[a] Å^2
Ru1	0.250	0.58283 (3)	0.250	1.997 (8)
Ru2	0.750	−0.00617 (3)	0.250	1.897 (8)
Cl1	0.250	0.7253 (1)	0.250	5.15 (5)
Cl2	0.250	0.4413 (1)	0.250	3.83 (4)
Cl3	0.2185 (1)	0.5838 (1)	0.07950 (9)	4.03 (3)
Cl4	0.750	0.1356 (1)	0.250	8.4 (1)
Cl5	0.750	−0.1458 (1)	0.250	11.4 (1)
Cl6	0.7110 (2)	−0.0031 (2)	0.0820 (1)	9.00 (7)
S1	0.5066 (1)	0.58087 (8)	0.26683 (8)	2.62 (2)
S2	0.4940 (1)	−0.00614 (7)	0.23859 (8)	2.30 (2)
S3	0.5352 (2)	0.31169 (9)	0.0979 (1)	3.78 (3)
S4	0.0815 (2)	0.19722 (9)	0.0972 (1)	3.64 (3)
O1	0.5660 (4)	0.5723 (3)	0.1779 (3)	4.67 (9)
O2	0.4380 (4)	−0.0011 (3)	0.3299 (3)	3.97 (8)
O3	0.4269 (4)	0.2731 (2)	0.1541 (3)	4.19 (9)
O4	0.1876 (5)	0.2511 (3)	0.0536 (3)	6.1 (1)
C1	0.5879 (6)	0.5041 (4)	0.3472 (5)	5.6 (1)
C2	0.5917 (6)	0.6666 (4)	0.3290 (5)	5.1 (1)
C3	0.4096 (5)	0.0725 (3)	0.1621 (4)	3.3 (1)
C4	0.4099 (6)	−0.0904 (3)	0.1713 (5)	4.0 (1)
C5	0.5323 (7)	0.2500 (4)	−0.0054 (5)	5.6 (2)
C6	0.4462 (7)	0.3989 (4)	0.0428 (4)	4.7 (1)
C7	−0.0575 (8)	0.2657 (6)	0.1097 (6)	7.7 (2)
C8	−0.003 (1)	0.1389 (5)	−0.0018 (6)	6.7 (2)

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

Table III. Positional Parameters for Non-Hydrogen Atoms and Their Estimated Standard Deviations for **2**

atom	x	y	z	B,[a] Å^2
Ru	0.77705 (3)	0.00819 (2)	0.72375 (3)	1.743 (4)
Cl1	1.00699 (9)	0.01294 (8)	0.7290 (1)	2.89 (2)
Cl2	0.7757 (1)	0.09489 (8)	0.9051 (1)	3.06 (2)
Cl3	0.7491 (1)	−0.07838 (8)	0.54212 (9)	2.96 (2)
S1	0.4954 (1)	0.00581 (9)	0.83301 (9)	2.65 (2)
S2	0.7892 (1)	−0.13593 (7)	0.8326 (1)	2.39 (2)
S3	0.7683 (1)	0.15300 (8)	0.6127 (1)	2.50 (2)
O1	0.5711 (3)	0.0105 (2)	0.7175 (3)	2.55 (5)
O2	0.6602 (3)	−0.1737 (3)	0.8675 (4)	3.87 (7)
O3	0.8021 (4)	0.2435 (2)	0.6782 (4)	4.12 (8)
C1	0.3573 (5)	−0.0677 (5)	0.7872 (6)	5.2 (1)
C2	0.4163 (7)	0.1200 (5)	0.8337 (6)	5.6 (1)
C3	0.9026 (5)	−0.1279 (4)	0.9637 (5)	4.0 (1)
C4	0.8699 (5)	−0.2290 (4)	0.7552 (5)	3.8 (1)
C5	0.6083 (5)	0.1671 (4)	0.5330 (5)	4.0 (1)
C6	0.8718 (5)	0.1452 (4)	0.4902 (4)	3.33 (9)

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

Table IV. Bond Distances (Å) for **1**

(a) Ru Anions			
Ru1–Cl1	2.352 (1)	Ru2–Cl4	2.341 (2)
Ru1–Cl2	2.337 (1)	Ru2–Cl5	2.306 (2)
Ru1–Cl3	2.3539 (9)	Ru2–Cl6	2.316 (1)
Ru1–S1	2.3474 (8)	Ru2–S2	2.3492 (7)
S1–O1	1.461 (3)	S2–O2	1.472 (3)
S1–C1	1.769 (5)	S2–C3	1.770 (4)
S1–C2	1.768 (5)	S2–C4	1.777 (4)
(b) $[(DMSO)_2H]$ Cation			
S3–O3	1.528 (4)	S4–C7	1.748 (5)
S3–C5	1.766 (6)	S4–C8	1.749 (6)
S3–C6	1.764 (5)	O3⋯O4	2.423 (5)
S4–O4	1.536 (3)		

Results

Synthesis and Molecular Structure of 1. $[(DMSO)_2H][$*trans*-$Ru(DMSO)_2Cl_4]$ (**1**) (d^5 low spin, $\mu_{eff} = 1.89\ \mu_B$) was first isolated from the mother liquors in the synthesis of *cis*-$RuCl_2$-

---

(33) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(34) *Enraf-Nonius SDP Package*; B. A. Frenz & Associates, Inc., College Station, TX 77840; Enraf-Nonius, Delft, Holland.

Table V. Bond Angles (deg) for **1**[a]

(a) Ru Anions			
Cl1-Ru1-Cl2	180	Cl6-Ru2-S2	88.13 (3)
Cl1-Ru1-Cl3	89.60 (3)	Cl6-Ru2-S2′	91.87 (3)
Cl1-Ru1-S1	90.79 (3)	S2-Ru2-S2′	180.01 (3)
Cl2-Ru1-Cl3	90.41 (3)	Ru1-S1-O1	116.9 (1)
Cl2-Ru1-S1	89.21 (3)	Ru1-S1-C1	112.1 (2)
Cl3-Ru1-Cl3′	179.18 (6)	Ru1-S1-C2	112.9 (2)
Cl3-Ru1-S1	91.89 (3)	O1-S1-C1	106.9 (2)
Cl3-Ru1-S1′	88.12 (3)	O1-S1-C2	107.1 (2)
S1-Ru1-S1′	178.43 (6)	C1-S1-C2	99.3 (3)
Cl4-Ru2-Cl5	180	Ru2-S2-O2	117.3 (2)
Cl4-Ru2-Cl6	88.73 (6)	Ru2-S2-C3	111.6 (1)
Cl4-Ru2-S2	89.99 (2)	Ru2-S2-C4	111.9 (1)
Cl5-Ru2-Cl6	91.27 (6)	O2-S2-C3	107.4 (2)
Cl5-Ru2-S2	90.01 (2)	O2-S2-C4	108.4 (2)
Cl6-Ru2-Cl6′	177.5 (1)	C3-S2-C4	98.8 (2)
(b) [(DMSO)$_2$H] Cation			
O3-S3-C5	105.8 (3)	O4-S4-C8	103.2 (3)
O3-S3-C6	105.5 (2)	C7-S4-C8	101.9 (3)
C5-S3-C6	100.2 (3)	O3-H···O4	164
O4-S4-C7	101.8 (3)		

[a] Primed atoms are referred to the nonprimed ones by crystallographic 2-fold axes.

Table VI. Bond Distances (Å) and Angles (deg) for **2**

(a) Distances			
Ru-Cl1	2.321 (1)	S1-C2	1.771 (7)
Ru-Cl2	2.347 (1)	S2-O2	1.484 (4)
Ru-Cl3	2.346 (2)	S2-C3	1.788 (5)
Ru-S2	2.330 (2)	S2-C4	1.780 (5)
Ru-S3	2.351 (1)	S3-O3	1.474 (4)
Ru-O1	2.077 (3)	S3-C5	1.793 (5)
S1-O1	1.545 (4)	S3-C6	1.782 (5)
S1-C1	1.770 (6)		
(b) Angles			
Cl1-Ru-Cl2	92.02 (5)	O1-S1-C2	102.7 (3)
Cl1-Ru-Cl3	95.20 (4)	C1-S1-C2	99.6 (4)
Cl1-Ru-S2	89.89 (4)	Ru-S2-O2	115.2 (1)
Cl1-Ru-S3	89.23 (4)	Ru-S2-C3	112.0 (2)
Cl1-Ru-O1	177.5 (1)	Ru-S2-C4	112.1 (2)
Cl2-Ru-Cl3	172.78 (4)	O2-S2-C3	109.3 (2)
Cl2-Ru-S2	89.71 (4)	O2-S2-C4	108.4 (2)
Cl2-Ru-S3	90.75 (4)	C3-S2-C4	98.7 (3)
Cl2-Ru-O1	87.10 (9)	Ru-S3-O3	117.8 (2)
Cl3-Ru-S2	90.47 (4)	Ru-S3-C5	110.4 (2)
Cl3-Ru-S3	89.20 (4)	Ru-S3-C6	110.4 (2)
Cl3-Ru-O1	85.68 (9)	O3-S3-C5	108.6 (2)
S2-Ru-S3	179.02 (4)	O3-S3-C6	107.5 (2)
S2-Ru-O1	92.48 (9)	C5-S3-C6	100.9 (2)
S3-Ru-O1	88.41 (9)	Ru-O1-S1	122.0 (2)
O1-S1-C1	102.4 (2)		

(DMSO)$_4$.[19] The yield of the complex could be greatly improved by running the reaction at 100 °C in the presence of small amounts of concentrated HCl. On the contrary, attempts to isolate the corresponding bromo derivative failed due to the easier reducibility of RuBr$_3$ relative to RuCl$_3$; for example, overnight stirring of a solution of hydrated RuBr$_3$ in dimethyl sulfoxide (room temperature, under air) yields almost quantitatively *trans*-RuBr$_2$(DMSO)$_4$.[35]

The main features of the solid-state infrared spectrum of **1** are reported in Table VII. Only one S=O stretching band is observed at 1115 cm^{-1} (S-bonded DMSO).[36,37] The existence of a single ν(S=O) suggests a trans configuration. A very broad band centered at 725 cm^{-1} can be attributed to the hydrogen-bridged cation [(DMSO)$_2$H]$^+$, as previously reported for a rhodium(III) chloride dimethyl sulfoxide complex.[38,39] The band assignment is confirmed by the infrared spectrum of the deuterated complex (Table VII). The structure was definitively determined by a single-crystal X-ray analysis.

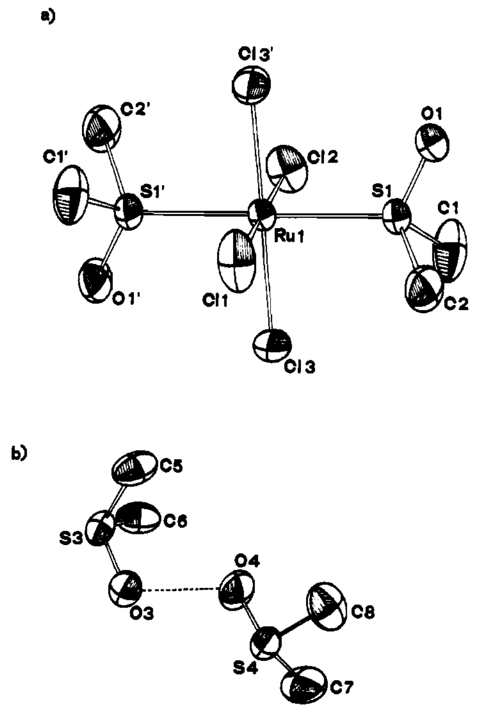


Figure 1. ORTEP drawing of the [*trans*-Ru(DM*S*O)$_2$Cl$_4$]$^-$ anion (a) and of the [(DMSO)$_2$H]$^+$ cation (b) with the atom-labeling scheme.

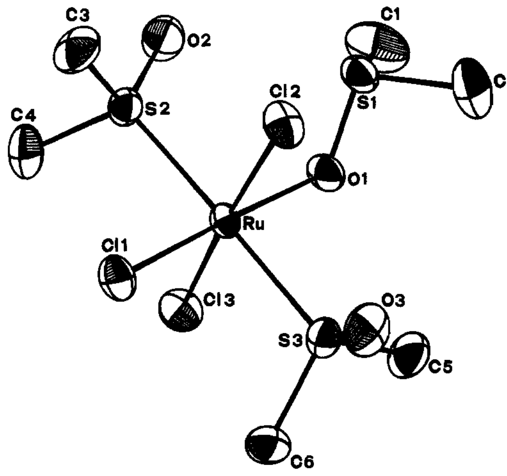


Figure 2. ORTEP drawing of *mer*-[RuCl$_3$(DM*S*O)$_2$(DMS*O*)]^0 with the atom-labeling scheme.

The crystal structure of complex **1**[40] consists of [(DMSO)$_2$H]$^+$ cations and *trans*-[Ru(DMSO)$_2$Cl$_4$]$^-$ anions, held together by van der Waals forces. Two crystallographically independent anions lie on crystallographic 2-fold axes passing through the metal atoms and two trans chlorine atoms, so that for each Ru there are three Cl and one DMSO independent ligands. The molecular structures of one of the two anions and of the cation are shown in Figure 1. Complex **1** is essentially isostructural with the Rh analogue,[38] in which, however, the chlorine atoms of one of the two independent anions were too disordered to be located. In fact, also in **1**, the four chlorine atoms around Ru2 have rather large thermal

---

[35] Alessio, E. Ph.D. Dissertation, University of Trieste, Trieste, Italy, 1989.
[36] Reynolds, W. L. *Prog. Inorg. Chem.* **1970**, *12*, 1.
[37] Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 115.
[38] James, B. R.; Morris, R. H.; Einstein, F. W. B.; Willis, A. *J. Chem. Soc., Chem. Commun.* **1980**, 31.
[39] James, B. R.; Morris, R. H. *Can. J. Chem.* **1980**, *58*, 399.
[40] Note: After submission of our manuscript, we became aware of an independent paper, submitted by J. Jaswal, S. J. Retting, and B. R. James, to *Can. J. Chem.*, describing the synthesis and crystal structure of **1**. The cell parameters are in excellent agreement with those reported in Table I. The complex was isolated while the authors were trying to reproduce the synthesis of *fac*-RuCl$_3$(DMSO)$_3$ as reported by Poddar's group in ref 28a.

Table VII. Vibrational Frequencies (cm^{-1}) for the Main Absorption Bands of $[(DMSO)_2H]$[*trans*-$Ru(DMSO)_2Cl_4$] (**1**), *mer*-$[RuCl_3(DMSO)_3]$ (**2**), and Their Hexadeuterated Analogues **1**(DMSO-d_6) and **2**(DMSO-d_6) between 1500 and 200 cm^{-1}

freq, cm^{-1}					
1	**1**(DMSO-d_6)	**2**	**2**[a]	**2**(DMSO-d_6)	assgnt
1397 m[b]	1021 m	1405 s		1030 sh	$\delta(CH_3)$[c]
1296 m	1008 m	1308 s		1007 s	
1289 m		1287 s		944 m	
1115 s	1112 s	1127 s	1129 s	1126 s	ν(S=O) (DM*S*O)
		1107 s	1119 sh	1107 s	
1018 s	838 s	1017 s	1018 s	821 s	$\rho(CH_3)$
970 m	822 s	978 m	980 m	764 s	
916 w	772 m	962 m	970 w		
		912 s	918 s, br	910 s	ν(S=O) (DMS*O*)
peaks hidden by cation abs		725 m		702 w (1.03)[d]	ν(C–S)
		677 m		623 w (1.08)	
		496 m	494 s, br	472 m (1.05)	ν(Ru–O)
			432 m		ν(Ru–S)
415 w	384 w (1.08)	411 m	409 s	376 m (1.09)	
381 w	*e*	371 w		348 w (1.06)	δ(C–S–O)
345 sh	340 sh	342 s, br		330 s, br	ν(Ru–Cl)
329 s	326 s				

[a] In CH_2Cl_2 solution. [b] sh, shoulder; w, weak; m, medium; s, strong; br, broad. [c] ν, stretching; δ, deformation; ρ, rocking. [d] Numbers in parentheses refer to the isotopic ratios. [e] Peak hidden by Ru–Cl stretching.

factors (see Table II). This explains the shortening of the Ru2–Cl5 and Ru2–Cl6 bond distances (Table IV) with respect to the other Ru–Cl bond distances, which average 2.346 (8) Å. This value is practically equal to the values found for trans Ru(III)–Cl bond distances in **2** (see below). The structure of the protonated dimethyl sulfoxide, $[(DMSO)_2H]^+$, is equal, within experimental error, to that of the Rh analogue.[38] Of interest, in both compounds the structural parameters of the two DMSO molecules are not perfectly equivalent.

The corresponding sodium and potassium salts of **1** could be easily isolated from H_2O/ethanol solutions of the complex treated with a slight excess of the corresponding chloride salt.

Synthesis and Molecular Structure of 2. When an acetone/dimethyl sulfoxide (1%) solution of **1** is treated with 1 equiv of $AgBF_4$, the neutral complex $RuCl_3(DMSO)_3$ (**2**) (d^5 low spin, μ_{eff} = 1.87 μ_B) can be isolated after removal of AgCl (eq 1).

$$\textit{trans}\text{-}[Ru(DMSO)_2Cl_4]^- + Ag^+ \xrightarrow{DMSO} RuCl_3(DMSO)_3 + AgCl \quad (1)$$

The treatment of **1** with 2 or more equiv of $AgBF_4$ yielded only the Ru(II) complex *trans*-$RuCl_2(DMSO)_4$. No evidence for the claimed pentakis- and hexakis(dimethyl sulfoxide)ruthenium(III) derivatives, $[Ru(DMSO)_5Cl]Cl_2$ and $[Ru(DMSO)_6]Cl_3$,[3,26] could be obtained.

The solid-state infrared spectrum of **2** (Table VII) shows the presence of two S-bonded and one O-bonded DMSO's. Irrespective of the facial or meridional ligand disposition, the complex should have one Ru–O, two Ru–S, and three Ru–Cl infrared-active stretching modes.[41] The presence of a single ν(Ru–S) might suggest a trans disposition of the two DM*S*O's. The three Ru–Cl stretching bands expected might be enclosed in the relatively broad band at 341 cm^{-1}. Band assignment[2,41–43] is confirmed by replacement of DMSO with DMSO-d_6. As expected, the S=O stretching frequencies do not shift upon deuteration, while the isotopic shifts of ν(Ru–O) and ν(Ru–S) are close to the expected value of 1.05.[41]

The spectrum of **2** is considerably different from that reported by Sarma et al. for the complex formulated as *mer*-$RuCl_3$(DM*S*O)(DMS*O*)$_2$.[28a] In that report, however, the absence of the deuterated analogue makes the band assignments not unequivocal. Indeed, a recent work by the group of James[40] describes the structural characterization of a dimethyl sulfide (DMS) complex, *mer*-$RuCl_3(DMS)_3$, obtained while they were trying to reproduce the synthesis of *mer*-$RuCl_3$(DM*S*O)(DMS*O*)$_2$ claimed in ref 28a. The close similarity between the spectra of the two complexes suggests that also the product isolated by Poddar's group[28a] might have been actually a DMS complex.[40]

Table VIII. Average Structural Parameters (Å and deg) for Ru(II) S- and O-Bonded DMSO Complexes, $[RuX_a(DMSO)_b]^c$ (X = Cl, Br)

	x^a	σ^b	μ^c	n^d	ref
Ru–S[e]	2.358	0.007	0.003	2	*g*
Ru–S[f]	2.278	0.014	0.002	14	*h*
Ru–Cl[e]	2.428	0.011	0.002	12	*h*
		S-Bonded DMSO			
S–C	1.785	0.018	0.002	50	*i*
S–O	1.479	0.012	0.002	26	*i*
O–S–C	105.9	1.2	0.1	46	*i*
C–S–C	99.0	1.5	0.3	23	*i*
		O-Bonded DMSO			
S–C	1.773	0.013	0.003	20	*l*
S–O	1.539	0.013	0.004	10	*l*
O–S–C	103.1	1.4	0.3	14	*l*
C–S–C	98.6	0.9	0.4	7	*l*

[a] Weighted mean, $x = \sum_i w_i x_i / \sum_i w_i$; $w_i = 1/\sigma_i^2$. [b] Standard deviation, $\sigma = [\sum_i (x_i - x)^2/(n-1)]^{1/2}$. [c] Standard deviation of the mean, $\mu = [(\sum_i w_i (x_i - x)^2 / \sum_i w_i)/(n-1)]^{1/2}$. [d] Number of observations. [e] Trans to S. [f] Trans to Cl. [g] References 15 and 19. [h] References 14, 15, 17, and 19. [i] References 14–17, 19, and 45. [l] References 14, 17, 19, and 45.

The molecular structure of **2** is shown in Figure 2. Ruthenium has a distorted octahedral coordination with three chlorine atoms in a *mer* configuration. Two DMSO molecules are S-bonded to Ru in trans position, while the third one is O-bonded, constituting a isomer different from the Rh(III) analogue, where the O-bonded DMSO is trans to one S-bonded DMSO ligand.[44] The Ru–S distances (Table VI) are not equivalent, but the average value is close to that of 2.348 (1) Å found in **1**. The S–O bond distance of the O-bonded DMSO is markedly longer than those of the S-bonded DMSO ligands, just as found in the Ru(II) derivatives (Table VIII), showing a considerable decrease of the double-bond character of the sulfur–oxygen bond upon coordination to the metal atom via oxygen. The different electronic situation of the sulfur atom is reflected in the significant narrowing (ca. 5.9°) of the O–S–C bond angles, passing from the S- to the O-bonded DMSO ligands. This can be attributed to the compression effect

---

(41) Fadeev, Yu. V.; Kukushkin, Yu. N.; Khokhryakov, K. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1975**, *20*, 1519.

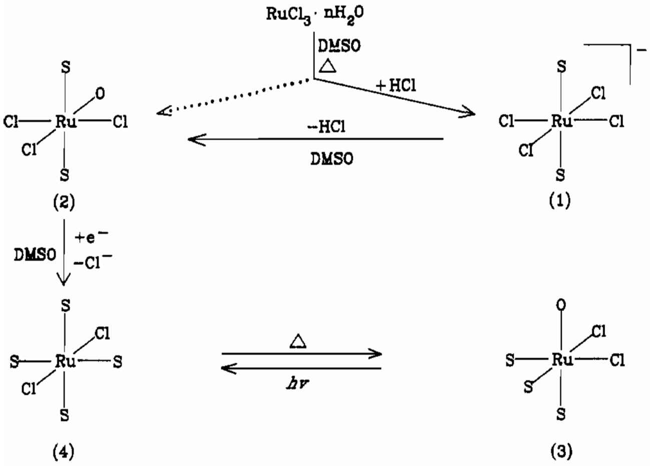
(42) Price, J. H.; Williamson, A. N.; Schramm, R. F.; Wayland, B. B. *Inorg. Chem.* **1972**, *11*, 1280.

(43) Barnes, J. R.; Goggin, P. L.; Goodfellow, R. J. *J. Chem. Res., Miniprint* **1979**, 1610.

(44) Sokol, V. I.; Porai-Koshits, M. A. *Koord. Khim.* **1975**, *1*, 577.

(45) Davies, A. R.; Einstein, F. W. B.; Farrell, N. P.; James, B. R.; McMillan, R. S. *Inorg. Chem.* **1978**, *17*, 1965.

Scheme I. Synthetic Connections between Ruthenium(III) and Ruthenium(II) Chloride Dimethyl Sulfoxide Complexes[a]



[a] Dotted line means not experimentally verified. Throughout all the schemes, S = S-bonded DMSO and O = O-bonded DMSO.

of the bulkier lone pair of the pyramidal sulfur atom on the bonding pairs.

Chemical Behavior in Dimethyl Sulfoxide Solution. When either $[(DMSO)_2H][$*trans*-$Ru(DMSO)_2Cl_4]$ or *mer*-$RuCl_3(DMSO)_3$ is refluxed in dimethyl sulfoxide solution, *cis*-$RuCl_2(DMSO)_4$ (**3**) is obtained in high yield. This suggests that both complexes are intermediates in the synthesis of **3** from hydrated $RuCl_3$. A scheme for the reaction mechanism can be proposed (Scheme I) and each step conveniently followed by time-drive electronic spectroscopy, the spectral pattern of each isolated intermediate being known. Complex **1** is the first intermediate isolated from $RuCl_3$. In dimethyl sulfoxide solution, one chloride of **1** is slowly replaced by a third DMSO molecule to give the neutral derivative **2**, the process being almost complete within 24 h at 60 °C. Complex **2** undergoes a slow spontaneous one-electron reduction, accompanied by an almost 10-fold decrease of the molar extinction coefficients in the visible region. The process is complete in 3 days at 70 °C. As clearly shown by the final spectrum, the product of the homogeneous reduction is **3**. According to the *mer* geometry of the Ru(III) precursor (**2**) and to the greater trans effect of DMS*O* with respect to Cl,[39] *trans*-$RuCl_2(DMSO)_4$ (**4**) should be the first neutral Ru(II) complex formed in the reduction process. However, its spectral pattern cannot be observed, since at high temperature **4** is known to isomerize readily to the thermodynamically more stable cis isomer **3**.[19]

The nature of the reducing agent in the reduction of Ru(III) in dimethyl sulfoxide is still uncertain and deserves comment. The problem is further affected by the presence of Ru(IV) species in the commercial hydrated $RuCl_3$.[46] In the bulk reduction of $RuCl_3$ to **3**, the DMSO/Ru molar ratio is lower than 20.[35] Therefore, the hypothesis that the reducing agent might be an impurity of DMSO, such as dimethyl sulfide,[40] can scarcely account for the high yield of the reaction (>70%). Ledlie et al. suggested that DMSO may be the reductant, itself being oxidized to dimethyl sulfone according to eq 2.[47]

$$2Ru(III) + Me_2SO + H_2O \rightarrow 2Ru(II) + Me_2SO_2 + 2H^+ \quad (2)$$

Indeed, we have gas chromatographical evidence that, in the bulk reduction of **2** to **3** in hot dimethyl sulfoxide (under Ar), dimethyl sulfone is formed in approximately the stoichiometric amount required by eq 2. Moreover, also paraformaldehyde, together with other unidentified products, is formed during the reduction process. This might suggest the presence of radical side reactions leading to the decomposition of dimethyl sulfoxide. No such products are formed when **3** is heated in dimethyl sulfoxide, excluding the possibility that they derive from side reactions catalyzed by Ru(II). The experimental observation that ruthenium(III) chloride complexes bearing at least two DMSO's undergo slow reduction also in water and methanol (see below) might suggest that electron transfer from the coordinated ligand should spontaneously occur when the Ru(III) redox potential has been sufficiently increased by an appropriate number of coordinated DMSO's.[13] This would also explain the formation of **4** when **1** is treated with more than 1 equiv of silver salt in acetone/DMSO solution (see above).

Table IX. Redox Potentials (mV vs SCE) for All the Proposed Species in DMSO and H_2O Solutions

complex	DMSO[a]	H_2O[b]	complex	DMSO[a]	H_2O[b]
1	−182	*c*	**2**	70[d]	
1a		107	**2i**	−127[d]	
1b		225	**2a**		186
			2b ≡ **1b**		225

[a] Determined at 25.0 °C with 0.1 M TEAP on the Au electrode. [b] Determined at 25.0 °C with 0.1 M $NaClO_4/HClO_4$ (pH = 1) on the Pt electrode. [c] For further details, see ref 30. [d] Estimated from simulation.

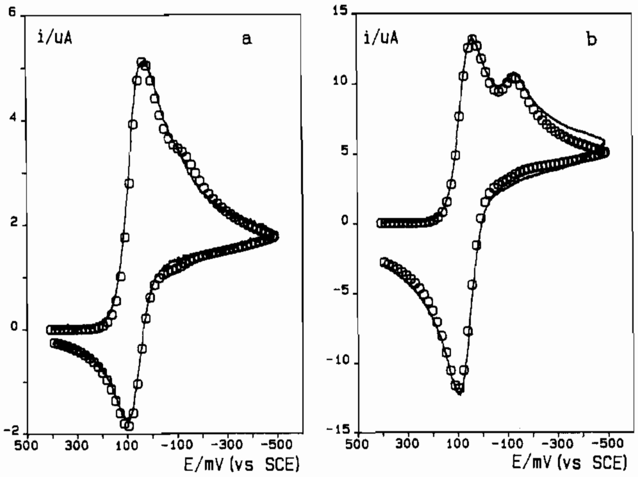


Figure 3. Cyclic voltammetry patterns of *mer*-$[RuCl_3(DMSO)_3]^0$ in dimethyl sulfoxide solution at 0.1 V/s (a) and 1.0 V/s (b). Full lines are the experimental signals, while the points represent the simulated curves.

The steps proposed in Scheme I are also supported by the following electrochemical evidence (the sodium salt of **1**, **1Na**, was used to avoid the presence of the peak due to proton discharge): (i) The redox potentials of **1** and **2** (Table IX) show that, as expected, the neutral derivative is more easily reduced than the anionic precursor. This is consistent with the hypothesis that **2**, and not **1**, is the species that undergoes the homogeneous one-electron reduction process. (ii) The hypothesis that **4** is the kinetic product of the thermal reduction process is supported by controlled-potential reduction at room temperature of **2**, which results in the consumption of approximately 1 Faraday/mol of complex and gives **4** with good yield. This process represents also a new route to the synthesis of **4**, alternative to the photochemical isomerization of **3**.[19]

Cyclic voltammetric experiments provide another interesting aspect of the chemical behavior of **2** in dimethyl sulfoxide solution. At a scan rate of 0.1 V/s only a single Ru(III)/Ru(II) electron transfer can be detected at 31 mV, showing only partial chemical reversibility (i_{pa}/i_{pc} = 0.62) (Figure 3a). When the scan rate is gradually increased up to 1.0 V/s, the chemical process that follows the electron transfer is almost completely inhibited (i_{pa}/i_{pc} = 1.17) and a second irreversible cathodic peak appears at more negative potentials (E_{pc} = −130 mV) (Figure 3b). According to the dependence of the cyclic voltammograms on the scan rate,[48]

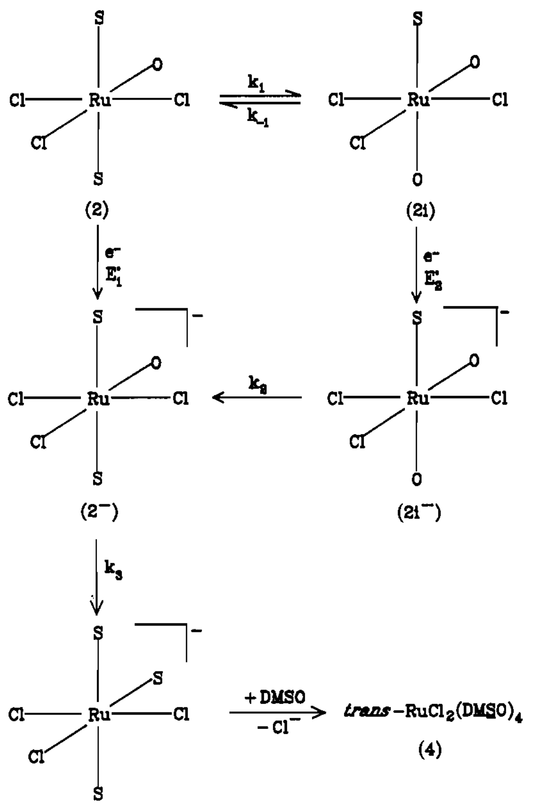
---

(46) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium* (Topics in Inorganic and General Chemistry, Vol. 19); Elsevier: Amsterdam, 1984; p 159.

(47) Ledlie, M. A.; Allum, K. G.; Howell, I. V.; Pitkethly, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1734.

(48) Faure, D.; Lexa, D.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *140*, 269.

Scheme II. Proposed Reaction Scheme to Account for the Cyclic Voltammetric Patterns of *mer*-$[RuCl_3(DMSO)_3]^0$ in Dimethyl Sulfoxide Solution



the new peak can be attributed to an isomer of **2**, **2i**, in equilibrium with the parent compound. The two species can be separately observed at the highest scan rate ("frozen equilibrium"), while, at the lowest scan rate, the reduction process proceeds exclusively through the more easily reducible species **2**, the conversion of **2i** into **2** being faster than diffusion. The two isomers can be reasonably thought to differ only in the binding mode of one coordinated DMSO, and a sulfur to oxygen isomerization (S/O) of one of the two trans DM*S*O's is tentatively proposed (Scheme II). The second DMS*O* should increase the complex solubility.[19] Accordingly, **2i** could not be isolated by precipitation from its solutions, being in equilibrium with the less soluble isomer **2**.

The reverse O/S isomerization should immediately occur in the reduced form of **2i**, $\mathbf{2i}^-$, to give the same reduced species, $\mathbf{2}^-$, as from **2** (Scheme II). This hypothesis is in agreement with the greater affinity of Ru(II) for S-bonded DMSO's and would explain the irreversibility of the reduction of **2i** as well as why the i_{pa}/i_{pc} ratio is significantly greater than unity.

In order to confirm the proposed mechanism, CV simulation of the electrochemical system depicted in Scheme II was carried out to fit the experimental data recorded at both 0.1 and 1.0 V/s. Fairly good agreement was obtained by using the following values for the parameters involved: $k_1 = 0.84\ s^{-1}$; $k_{-1} = 2.5\ s^{-1}$; $k_2 = 84\ s^{-1}$; $k_3 = 0.16\ s^{-1}$; $E°_1 = 70$ mV; $E°_2 = -127$ mV (Figure 3a,b). Also the rather fast chemical reaction governed by k_3, which converts $\mathbf{2}^-$ into a nonelectroactive species, might be assumed as a further O/S isomerization (Scheme II), leading to the *mer* isomer of the long-known complex *fac*-$[RuCl_3(DMSO)_3]^-$ (**5**).[15] The third DMS*O* could stabilize the Ru(II) anion to such an extent as to shift its oxidation potential to inaccessible values (for comparison, **5** shows an irreversible oxidation peak at 1210 mV). Substitution of the more labile chloride (the one trans to DM*S*O) will give the final product **4**, which is completely electroinactive in the available potential range. Even though the electrochemical data do not preclude the reversal of the last two steps (i.e. chloride dissociation followed by O/S isomerization), this hypothesis is disfavored by the experimental observation that chloride dissociation from **5** is a rather slow step (about 3 h at 30 °C from spectrophotometric evidence). According to this result, a fast chloride dissociation from $\mathbf{2}^-$ seems rather improbable.

Similar equilibria between isomers differing in the binding mode of one DMSO have been found for some chloro(dimethyl sulfoxide)rhodium(III) complexes in aprotic solvents.[43] Interestingly enough, an S/O isomerization was observed with the cationic complex $[RhCl(DMSO)_5]^{2+}$,[43] while an opposite O/S isomerization was proposed in the case of the neutral complex *mer*-$RhCl_3(DMSO)_3$,[39,43] confirming a definite trend to decrease the number of S-bonded DMSO's as the formal positive charge of the metal atom increases. The differences between rhodium and ruthenium neutral isomers can be attributed mainly to the different electronic structures of the two metal centers, Rh(III) being a better π donor than Ru(III) and therefore favoring DMSO coordination through sulfur.

Chemical Behavior in Dichloromethane Solution. The equilibrium between **2** and **2i** occurs also in aprotic, noncoordinating solvents such as dichloromethane. The cyclic voltammetric pattern of the frozen equilibrium is observed even at a scan rate of 0.1 V/s (5 °C). ^1H NMR and IR spectroscopy show that no free dimethyl sulfoxide is present in solution, ruling out the possibility that **2i** is a pentacoordinated species resulting from **2** upon dissociation of one DMSO.

The region of the ruthenium–ligand stretching frequencies in the solution infrared spectrum (Table VII) further supports the hypothesis on the nature of **2i**. The band at 432 cm^{-1} does not appear in the solid-state spectrum and can therefore be assigned to the single Ru–S stretching mode of isomer **2i**. The observed shift of ν(Ru–S) to higher frequencies relative to **2** is in agreement with the expected strengthening of the Ru–S bond (see Discussion). Overlap of the S=O and M—O stretching frequencies due to O-bonded DMSO's in **2** and **2i** could account for the enlarged band shapes in CH_2Cl_2 solution.

A mechanism, involving DM*S*O dissociation followed by recoordination of the same ligand through the oxygen atom before it leaves the complex solvation sphere, can be envisaged for the isomerization process.

Chemical Behavior in Aqueous Solution. In view of their potential biological interest, the chemical behavior of **1** and **2** in aqueous solutions was studied in detail.

Dilute solutions (2×10^{-4} M) of both **1Na** and **2** turn greenish gray in a few hours at 25 °C. The changes in their electronic spectral patterns with time are accompanied by a steady increase of diffuse background absorption in the visible region. This latter effect may be attributed to the formation of polymeric species of Ru(III),[49] probably with hydroxo or μ-oxo bridges, as suggested by the simultaneous pH drop. In further agreement with the hypothesis of polymeric species, the phenomenon was found to be concentration dependent. Attempts to perform CV experiments similarly failed, owing to the precipitation of insoluble products on the electrode surface.

Chloride concentrations up to 0.3 M did not significantly influence the processes in solution. On the contrary, a strong pH dependence was observed. On gradual lowering of the pH with $HClO_4$, the changes with time of the electronic spectral patterns of both complexes were slowed. At the same time the background absorption increase was considerably reduced, until completely inhibited at pH < 3.

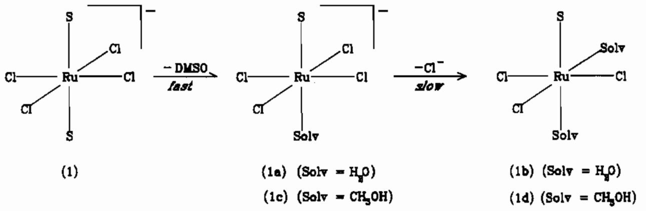
Therefore, to prevent aggregate formation, all the following experiments were performed at pH = 1.0 ($HClO_4$). Under such conditions no increase in background absorption was observed in the visible spectra, and reproducible cyclic voltammograms could be obtained.

The chemical behavior of **1**, introduced into solution as its sodium salt **1Na**, is summarized in Scheme III. Upon dissolution in water, one DM*S*O is quickly displaced to give the monoaquo species **1a**. Evidence for this rapid and complete DMSO dissociation comes from IR spectra of fresh concentrated aqueous solutions of **1Na**. Two bands of almost equal intensity are found

---

(49) Taqui Khan, M. M.; Ramachandraiah, G.; Prakash Rao, A. *Inorg. Chem.* **1986**, *25*, 665.

Scheme III. Chemical Behavior of *trans*-[Ru(DMSO)$_2$Cl$_4$]$^-$ in Aqueous and Methanolic Solution



in the S═O stretching region at 1090 and 1014 cm^{-1}, respectively. The band at 1014 cm^{-1}, even though partially overlapping with a CH$_3$ rocking frequency at 1025 cm^{-1}, can be easily assigned to free DMSO. The band at 1090 cm^{-1} is instead attributed to the remaining DM*S*O. The two bands do not shift significantly upon deuteration (1100 and 1026 cm^{-1}, respectively), while the overlapping between CH$_3$ rocking and free DMSO S═O stretching frequencies is avoided. When [(DMSO)$_2$H][Ru(DMSO)$_2$Cl$_4$] is used, the intensity ratio of free to S-bonded DMSO is approximately 3/1, confirming almost complete dissociation of one DMSO also in the presence of the free ligand. The fast displacement of one DMSO is confirmed also by the ^{1}H NMR spectra of fresh solutions of **1Na**, which, besides a very broad peak at −16.7 ppm attributable to the remaining DM*S*O, show a relatively sharp peak for free DMSO at 2.72 ppm.

The fast DMSO dissociation from **1Na** is in agreement with the relatively large trans effect of S-bonded DMSO.[37] Similar behavior was found also for the Rh(III) analogue, *trans*-[Rh(DM*S*O)$_2$Cl$_4$]$^-$, the dissociation of one DMSO being complete in a few seconds at 35 °C.[39]

Cyclic voltammetry of **1a** could be easily performed in freshly prepared solutions. At a scan rate of 1.0 V/s, a single Ru(III)/Ru(II) electron transfer, showing almost complete chemical reversibility, is observed (Table IX). A detailed CV investigation of **1a** is reported elsewhere.[30]

The rapid DMSO dissociation step is followed by slow and complete dissociation of one chloride to give complex **1b** (Scheme III). The electronic spectral pattern of **1b** is closely similar to that of complex **2** but for a small shift (3 nm) in the absorption band positions, attributable to the presence of coordinated water instead of DMS*O* in the equatorial plane. The first-order chloride dissociation process can be conveniently followed by time-drive electronic spectroscopy. The six isosbestic points maintained in the scanned wavelength range (Figure 4) suggest the presence of only two species in solution, **1a** and **1b**, even though a rapid preequilibrium between **1** and **1a** cannot be excluded. The rate constants have been determined at five temperatures in the range 30–45 °C, and the activation parameters were calculated: $k_{25\,°\mathrm{C}} = 1.1 \times 10^{-5}$ s^{-1}; $\Delta H^{*} = 115 \pm 3$ kJ/mol; $\Delta S^{*} = 46 \pm 6$ J/(mol·K). No dependence of the rate constant on the pH of the solution was found in the pH range 0–2.

The slow chloride dissociation can be followed also be time-drive cyclic voltammetry: the signal of **1b** (Table IX) appears at more positive potentials and grows at the expense of the original signal of **1a**, until this latter signal has completely disappeared.

No evidence for further chloride dissociation was found. Addition of more than 1 equiv of silver nitrate to a solution of **1Na** resulted in slow precipitation of silver chloride, but no new spectral pattern, attributable to a monocationic Ru(III) complex, appeared. AgCl precipitation was instead accompanied by a constant decrease of the absorption band intensities, ascribable to the formation of Ru(II) species. A similar behavior was observed in acetone/DMSO solution (see above).

The chemical behavior of **2** in acidic aqueous solution is summarized in Scheme IV. Also in this case, as shown by infrared and NMR spectroscopy, the first step is the rapid dissociation of one DM*S*O to give complex **2a**. In fact, IR spectra of fresh concentrated solutions of **2** reveal an S═O stretching band for free DMSO (1013 cm^{-1}) of approximately the same intensity as that of S-bonded DMSO (1097 cm^{-1}). Strong solvent absorption prevents the observation of the S═O stretching frequency for O-bonded DMSO. However, ^{1}H NMR spectra present the sharp peak of free DMSO at 2.72 ppm, together with two very broad peaks of coordinated DMSO's centered at −15 and 9 ppm, respectively. Comparison of the ^{1}H NMR spectra of **1Na** and **2** allows one to assign the broad peak at negative fields to DM*S*O and the peak at about 8–9 ppm to DMS*O*. This latter peak, in fact, is absent in the spectra of **1Na** and is sharper than the other one in the spectra of **2**, in agreement with the methyl protons being further removed from the paramagnetic nucleus in O-bonded DMSO.

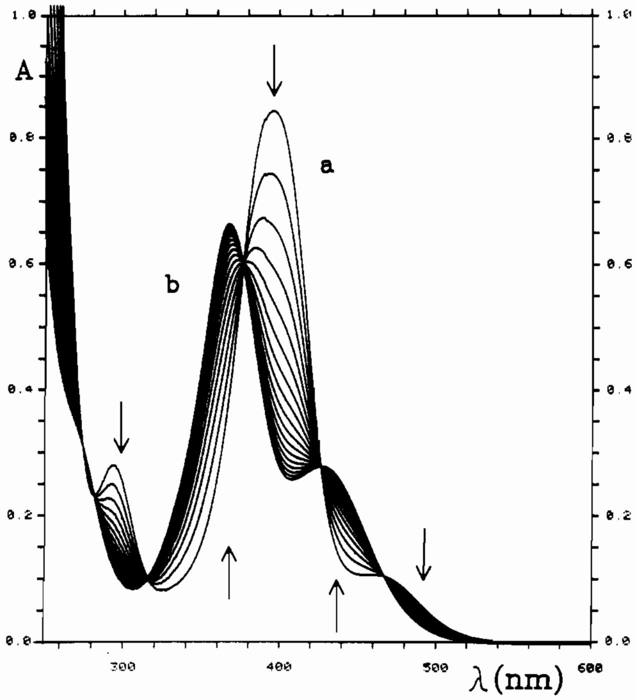
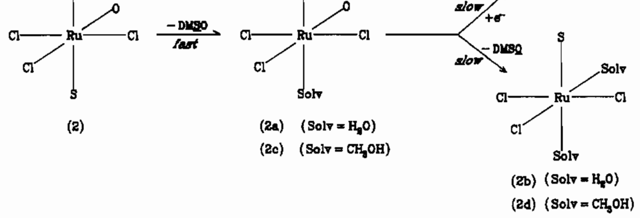


Figure 4. Spectral changes observed in aqueous solution (pH = 1) during the chloride dissociation from **1a** ([**1a**] = 2 × 10^{-4} M, *T* = 35 °C, scan-time interval 1 h): (a) *trans*-[Ru(DMSO)(H$_2$O)Cl$_4$]$^-$ (**1a**), initial spectrum; (b) *mer,cis*-[RuCl$_3$(H$_2$O)$_2$(DMSO)]^0 (**1b**), final spectrum.

Scheme IV. Chemical Behavior of *mer*-[RuCl$_3$(DMSO)$_3$]^0 in Aqueous and Methanolic Solution



Cyclic voltammetry of freshly prepared solutions of **2** shows only one uncomplicated quasi-reversible Ru(III)/Ru(II) electron transfer (Table IX) at all scan rates in the range 0.1–1.0 V/s.

Both the absorption spectrum and the cyclic voltammetric pattern of **2a** slowly evolve to those characteristic of **1b**, accounting for DMS*O* dissociation. The reaction is complete in about 24 h at 25 °C. It can therefore be concluded that both **1** and **2** produce the same final species in acidic aqueous solution (**2b** ≡ **1b** = *mer,cis*-RuCl$_3$(H$_2$O)$_2$(DMS*O*)). However, the DMS*O* dissociation from **2a** is accompanied by a parallel reaction that causes a general decrease of the absorption spectrum intensity and of the cathodic peak current in CV experiments. As can be evidenced by both these methods, the concentration of **1b** in a solution of **2** aged 24 h is approximately 60% of that in an equimolar aged solution of **1**. Since no new absorption peak or cyclic voltammetric pattern appears, the products of the side reaction must have much smaller absorption coefficients and be nonelectroactive in the scanned range as well. Another direct piece of evidence for the parallel formation of nonelectroactive species arises from the

Table X. Vibrational Frequencies (cm^{-1}) for the Main Absorption Bands of $RuCl_3(DMSO)_2(CH_3OH)$ (**2c**), $RuCl_3(DMSO\text{-}d_6)_2(CH_3OH)$ (**2c**($DMSO\text{-}d_6$)), and $RuCl_3(DMSO)_2(CH_3OD)$ (**2c**(CH_3OD)) between 4000 and 200 cm^{-1}

freq, cm^{-1}			
2c	**2c**($DMSO\text{-}d_6$)	**2c**(CH_3OD)	assgnt
3255 m[a]	3260 m	2434 m (1.33)[c]	ν(O–H)[b]
1401 s	1044 s	1400 s	$\delta(CH_3)$
1320 m	1013 s	1320 m	
1302 m	942 m	1302 m	
1080 s	1082 s	1090 s	ν(S=O) (DM*S*O)
1038 m	830 s	1038 m	$\rho(CH_3)$
1026 m	794 w	1026 m	
987 s	777 w	990 s	
911 s	912 s	911 s	ν(S=O) (DMS*O*)
736 m	724 w (1.02)	729 m	ν(C–S)
696 m	640 w (1.08)	695 m	
561 w	559 w	558 w	$\nu(Ru\text{–}OCH_3)$
497 s	471 s (1.05)	496 s	ν(Ru–O)
442 s	408 s (1.08)	440 s	ν(Ru–S)
346 s	343 s	345 s	ν(Ru–Cl)
332 s	326 s	331 s	

[a] sh, shoulder; w, weak; m, medium; s, strong. [b] ν, stretching; δ, deformation; ρ, rocking. [c] Numbers in parentheses refer to the isotopic ratios.

measured charge consumption in bulk reduction experiments. In fact, while 0.94 Faraday/mol of complex is consumed by a fresh solution of **2**, only 0.53 Faraday is consumed when the experiment is run on an equimolar solution aged 24 h. Consequently, we suggest that the parallel reaction is a monoelectronic reduction of **2a** to nonelectroactive Ru(II) species. This hypothesis is also supported by the growth with time of a sharp peak at 3.33 ppm in the ^1H NMR spectrum of a solution of **2**, attributable to S-bonded DMSO in a Ru(II) species. The final neutral species with only one DM*S*O (**1b**), even though it has a reduction potential slightly more positive than **2a**, seems unable to undergo a spontaneous homogeneous reduction under these conditions, its spectral and CV pattern being stable with time.[30]

No evidence for chloride dissociation was found. In the presence of very high concentration of free chloride ($[Cl^-]/[Ru] = 10^4$), the spectral pattern of **2** slowly evolves to that of **1**, accounting for the slow replacement of the O-bonded DMSO for Cl^- in the equatorial plane.

Chemical Behavior in Methanol Solution. As evidenced by ^1H NMR and IR spectroscopy, the chemical behavior of both **1** and **2** in methanol solution is very similar to that in water (Scheme III and IV, respectively).

It is interesting to observe that the process of chloride dissociation from **1c** to give complex **1d** (Scheme III) is about 2 orders of magnitude faster than in water ($t_{1/2} = 7.3 \times 10^2$ s vs 6.3×10^4 s, at 25 °C; activation parameters: $k_{25\,°C} = 9.5 \times 10^{-4}\ s^{-1}$; $\Delta H^{\ddagger} = 107 \pm 2$ kJ/mol; $\Delta S^{\ddagger} = 57 \pm 6$ J/(mol·K)). No difference in the measured dissociation rates was found when either **1** or **1Na** was used as a precursor.

In the case of **2**, the first intermediate in the solvolytic process (**2c**) could be isolated as a yellow solid from fresh concentrated solutions of the parent compound. The complex was characterized by means of infrared spectroscopy. The analogous derivatives with either DMSO-d_6 or CH_3OD allowed unambiguous band assignment (Table X).

Discussion

The existence of relatively few examples of complexes of "soft" or "borderline" metal atoms with trans DM*S*O's has usually been attributed to the moderately high trans influence of such a ligand,[50,51] to steric effects, and to π-back-bonding competition.[19] Comparison of the structures and vibrational spectra of Ru(III) and Ru(II)–DMSO derivatives allows one to get a better understanding of the Ru–DMSO bond.

The average trans Ru–Cl bond distances in **1** and **2** are significantly shorter than the corresponding value of 2.402 (2) Å, found in **4**,[19] as expected from the reduction of the metal covalent radius (0.04 Å) passing from Ru(II) to Ru(III).[52] It is worth noting that the difference between the Ru–S average distance in **1** and **2** and the average value of 2.358 (2) Å found in Ru(II) complexes (see Table VIII) is less than that found for the Ru–Cl bond distances. This suggests that the decrease of the atomic radius is in part counterbalanced by a decrease of the Ru–S bond order, attributable to a reduced π-back-bonding contribution.

Accordingly, the π-back-bonding competition between trans DM*S*O's should be much less important in Ru(III) than in Ru(II) compounds. In fact, although partial S/O isomerization can occur in solution (see above), the trans DM*S*O's disposition appears more favorable than in Ru(II)–DMSO complexes, which thermally isomerize to the corresponding more stable cis derivatives.[19]

A valuable tool in roughly estimating the relative importance of σ and π contributions in Ru–DMSO bonds may be represented by the S=O stretching frequency.[36,37] From a general point of view, DMSO–metal bonds of prevailing σ character should induce a fractional positive charge on the sulfur atom and thereby increase the p_π–d_π overlap between oxygen and sulfur orbitals, with consequent increase of the S=O bond order and stretching frequency as well.[37] On the other hand, a substantial contribution of metal to sulfur π back-donation should diminish the sulfur positive charge and also the oxygen–sulfur orbital overlap. Accordingly, a smaller ν(S=O) increase, relative to the free ligand, should be expected.

In agreement with the above considerations and the reduced π-back-bonding contribution in Ru(III)–DM*S*O bonds, ν(S=O) falls at a considerably higher frequency in **2** than in **4** (1129 vs 1089 cm^{-1}, both measured in CH_2Cl_2 solution). Comparison of the solid-state infrared spectra of **2** and **2c** (Table VII and X) provides further insight into this problem. Replacement of one DM*S*O for a methanol molecule promotes both a decrease of ν(S=O) and an increase of ν(Ru–S) for the remaining DM*S*O ligand. The strengthening of the Ru–S bond can be explained in terms of increased π back-donation of electron density from the metal to the sulfur atom, owing to the reduced competition between the two trans ligands. Alternatively, it might be attributed to an increased σ contribution of the sulfur atom, arising from the lower trans influence of methanol with respect to DM*S*O. In this case, however, a shift of ν(S=O) to higher wavenumbers should be expected.

The strong involvement of the metal to ligand π contribution in Ru(II)–DM*S*O bonds is confirmed by the structural[53] and spectroscopic[54] data available for the complex $[Ru(NH_3)_5DMSO]^{2+}$. In this case the Ru–S bond distance of 2.188 (3) Å is markedly shorter than the average of 2.358 (2) Å found in Ru(II) complexes with trans DM*S*O's.[16,19] The S=O bond order is correspondingly very low, and the S=O stretching frequency follows the predicted trend to such an extent that it is even lower than that of free DMSO.[54] This clearly shows that the absence of competing groups for the available ruthenium π-donor orbitals increases to a large extent the metal to ligand π interaction, which is further enhanced by the σ-donor power of the five NH_3 molecules.

It might be concluded that large positive $\Delta(\nu_{SO})$ values (defined as ν_{SO} of S-bonded DMSO − ν_{SO} of free DMSO) are to be expected when DM*S*O acts mainly as a σ-donor. On the contrary, low positive (or even negative) $\Delta(\nu_{SO})$ values can be attributed either to a weak DM*S*O–metal σ bond or to a strong metal–DM*S*O bond with a substantial metal to sulfur π-back-bonding contribution.

Conclusions

The synthesis of $[(DMSO)_2H]$[*trans*-$Ru(DMSO)_2Cl_4$] and *mer*-$RuCl_3(DMSO)_3$ and the characterization of their structures and chemical behavior in solution establish a foundation for the

---

(50) Kukushkin, Yu. N. *Inorg. Chim. Acta* **1974**, *9*, 117.

(51) Elding, L. I.; Gröning, O. *Inorg. Chem.* **1978**, *17*, 1872.

(52) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.

(53) March, F. C.; Ferguson, G. *Can. J. Chem.* **1971**, *49*, 3590.

(54) Senoff, C. V.; Maslowsky, E., Jr.; Goel, R. G. *Can. J. Chem.* **1971**, *49*, 3585.

chemistry of Ru(III)–DMSO derivatives. The mechanism of the synthesis of *cis*-$RuCl_2(DMSO)_4$ from hydrated $RuCl_3$ has been partially elucidated, and a detailed picture of the relationships between the redox state of the ruthenium atom and the composition and stability of its coordination sphere has been obtained. Comparison of the structures and vibrational spectra of Ru(III)– and Ru(II)–DMSO derivatives has allowed one to draw an analysis of the relative importance of σ-donor and π-acceptor properties of the DMSO ligand.

In view of our results and of those reported in ref 40, all the previous literature on this subject should be reconsidered. In our opinion, most of the complexes described as Ru(III)–DMSO derivatives are actually either Ru(II)–DMSO or Ru(III)–DMS species. In the absence of magnetic moment measurements, a careful examination of the complexes' NMR or visible spectra (extinction coefficients of Ru(III)–DMSO complexes are about 1 order of magnitude greater than those of Ru(II) derivatives) should allow an easy determination of the metal oxidation state. On the other hand, the systematic synthesis of the corresponding hexadeuterated derivatives should allow unambiguous IR assignments, avoiding confusion between DMSO and DMS complexes. Finally, in agreement with the trend of the complex reduction potentials versus the number of coordinated DMSO's, we believe that the existence of stable Ru(III) complexes with more than three DMSO ligands, such as $[Ru(DMSO)_5Cl]Cl_2$ and $[Ru(DMSO)_6]Cl_3$, is rather improbable.

New perspectives in the chemistry of the reported complexes can be easily envisaged. For example, due to the rather unfavorable situation of the two trans S-bonded DMSO's in both **1** and **2**, substitution of at least one of them with a stronger σ-donor ligand should be a relatively easy task.

As to their potential biological properties, the activities of **1** and **2** will be compared to that of the halogen–DMSO–Ru(II) derivatives against metastasizing tumor models. It is worthy of note that complex **1** is isoelectronic and isostructural with the imidazole (Im) derivative [(Im)H][*trans*-$Ru(Im)_2Cl_4$], which shows very good activity toward the chemically induced colorectal murine tumor (a model against which cisplatin is completely inactive)[55–58] and is presently entering phase-one clinical trials.[56] Comparison between the biological and chemical properties (in particular kinetic and redox) of these complexes will help to understand the influence of the axial ligands on their antitumor properties. Interestingly enough, in view of the "activation by reduction mechanism" proposed for Ru(III) complexes as antitumor agents,[59–61] both **1** and **2** have biologically accessible reduction potentials.[61]

Acknowledgment. We thank Dr. Andrea Caneschi (Solid State Inorganic Chemistry Laboratory, University of Firenze, Firenze, Italy) for the magnetic susceptibility measurements and the ICTP (Trieste, Italy) for a research fellowship to W.M.A. Financial support by Boehringer Mannheim Italia SpA and by the MURST (Rome, 40% Grant) is gratefully acknowledged.

Supplementary Material Available: For **1** and **2**, tables of anisotropic temperature factors for non-hydrogen atoms and positional and thermal parameters for hydrogen atoms (4 pages); tables of calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

---

(55) Keppler, B. K.; Rupp, W. *J. Cancer Res. Clin. Oncol.* **1986**, *111*, 166.

(56) Garzon, F. T.; Berger, M. R.; Keppler, B. K.; Schmähl, D. *Cancer Chemother. Pharmacol.* **1987**, *19*, 347.

(57) Keppler, B. K.; Rupp, W.; Juhl, U. M.; Endres, H.; Niebl, R.; Balzer, W. *Inorg. Chem.* **1987**, *26*, 4366.

(58) Keppler, B. K. In *Progress in Clinical Biochemistry and Medicine*; Springer-Verlag: Berlin, Heidelberg, 1989; Vol. 10, p 41.

(59) Clarke, M. J. *Metal Ions in Biological Systems* Marcel Dekker Inc.,: Basel, New York, 1980; Vol. 11, p 231.

(60) Clarke, M. J.; Galang, R. D.; Rodriguez, V. M.; Kumar, R.; Pell, S.; Bryan, D. M. In *Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*; Nicolini, M., Ed.; Martinus Nijhoff: Boston, MA, 1988; p 582.

(61) Clarke, M. J. In *Progress in Clinical Biochemistry and Medicine*; Springer-Verlag: Berlin, Heidelberg, 1989; Vol. 10, p 25.

Contribution from the Department of Chemistry and Biochemistry,
University of Notre Dame, Notre Dame, Indiana 46556

Inner-Sphere Electron-Transfer Stereoselectivities in the Oxidation of Bis(1,2-diaminoethane)cobalt(II) Derivatives by $[Co(ox)_3]^{3-}$

Rosemary A. Marusak, Marie A. Ivanca, Kenneth J. Haller, and A. Graham Lappin*

Received July 31, 1990

$[Co(N,N\text{-}Me_2en)_2(ox)]^+$ ($N,N\text{-}Me_2en$ = *N*,*N*-dimethyl-1,2-diaminoethane, ox^{2-} = oxalate(2−)) is the sole product in the inner-sphere reduction of $[Co(ox)_3]^{3-}$ by cobalt(II) in solutions of $N,N\text{-}Me_2en$ and is formed stereoselectively with an enantiomeric excess of 4.3% ΔΛ. The structure of this product has been determined by X-ray crystallography. [Δ-$Co(N,N\text{-}Me_2en)_2(ox)$]I crystallizes in the orthorhombic space group *Pbca* (No. 61) with $Z = 8$, $a = 15.206$ (2) Å, $b = 12.523$ (2) Å, $c = 16.999$ (2) Å, and $R = 0.039$ for 2681 reflections. Four inner-sphere products are isolated in the corresponding reaction with $N,N'\text{-}Me_2en$ ($N,N'\text{-}Me_2en$ = *N*,*N*′-dimethyl-1,2-diaminoethane). The structure of the major product [Λ(*RS*,*RS*)/Δ(*SR*,*SR*)-$Co(N,N'\text{-}Me_2en)_2(ox)]^+$ (40%) has been determined by X-ray crystallography. [Δ(*SR*,*SR*)-$Co(N,N'\text{-}Me_2en)_2(ox)]I\cdot 2H_2O$ crystallizes in the monoclinic space group $P2_1$ (No. 4) with $Z = 2$, $a = 8.260$ (2) Å, $b = 7.735$ (1) Å, $c = 13.697$ (3) Å, $\beta = 101.96$ (1)°, and $R = 0.088$ for 2434 reflections. Two isomers Λ(*RR*,*SS*)/Δ(*RR*,*SS*) (24%) and Λ(*SS*,*RS*)/Δ(*RR*,*SR*) (22%) are also formed as products. Stereoselectivities are 7.8% ΔΔ, 8.1% ΔΔ, and 7.7% ΔΔ, respectively. The fourth, minor product is also formed stereoselectively but is not unambiguously characterized. Stereoselectivities reflect hydrogen bonding in outer-sphere intermediates in the formation of the inner-sphere precursor complexes.

Introduction

Reduction of $[Co(ox)_3]^{3-}$ (ox^{2-} = oxalate(2−)) by the labile $[Co(en)_3]^{2+}$ (en = 1,2-diaminoethane) occurs[1] by two parallel pathways, an outer-sphere pathway leading to $[Co(en)_3]^{3+}$ and an inner-sphere pathway leading to $[Co(en)_2(ox)]^+$. When [Δ-$Co(ox)_3]^{3-}$ is used, both products show chiral induction, and in particular, that for the inner-sphere pathway shows an enantiomeric excess of 1.5% of the Δ isomer, a 1.5% ΔΔ process. There are few other reports of stereoselectivity in inner-sphere reactions,[2,3] and further study of this system is warranted. The small chiral induction in the formation of $[Co(en)_2(ox)]^+$ is proposed to be a consequence of the bidentate oxalate bridge, which prevents intimate contact of the discriminating, nonbridging ligands. In

---

(1) Marusak, R. A.; Osvath, P.; Kemper, M.; Lappin, A. G. *Inorg. Chem.* **1989**, *28*, 1542–1548.

(2) Wong, Y.; Petersen, J. D.; Geldard, J. I. *Inorg. Chem.* **1985**, *24*, 3352–3357.

(3) Bernauer, K.; Pousaz, P.; Porret, J.; Jeanguenat, A. *Helv. Chim Acta* **1988**, *71*, 1339–1348.

0020-1669/91/1330-0618$02.50/0