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Spectroscopy and Electrochemistry of *mer*-[RuCl$_3$(dmso)(tmen)]. Dimethylsulfoxide Is Sulfur-Bonded to Ru(II), Ru(III), and Ru(IV)

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The discovery that halo−ruthenium(sulfoxide) complexes exhibit anticancer activity[1−4] has stimulated interest in the nature of bonding of metal ions to dimethylsulfoxide (dmso).[5−8] Both M−S and M−O bonds are observed in metal complexes containing dmso, with the former mode prevalent with "soft" metal centers. The importance of dπ-S back-bonding in S-bonded complexes has been addressed by several investigators.[9,10] Especially revealing was the finding by Taube and co-workers that S to O linkage isomerism can be induced by oxidation of pentaammineruthenium(II) to ruthenium(III),[11−13] thereby suggesting that dπ-S bonding is a stabilizing factor only in the lower oxidation state. However, the observation that other Ru(III)(chloro)(dmso) complexes are S-bonded led Alessio and Calligaris to propose a role for dπ-S bonding in Ru(III) as well.[9,14] In the course of our work on a related complex, *mer*-[RuCl$_3$(dmso)(tmen)] (dmso is dimethylsulfoxide; tmen is *N,N,N′,N′*-tetramethylethylenediamine), we have found that dmso also can be S-bonded to Ru(IV). Our findings suggest that S(dmso) σ-donation to Ru is extensive in the Ru(III) and Ru(IV) states.

The structure of *mer*-[RuCl$_3$(dmso)(tmen)] features an S-bonded dmso ligand trans to one N-atom donor from tmen (Figure 1).[15] There are two distinct molecules in the unit cell, one of which exhibits disorder in the placement of the methylene carbons within the ethylene bridge of tmen. The Ru−S bond distances for the two molecules are 2.2912(8) and 2.2912(9) Å, and the S−O bond lengths are 1.476(2) and 1.474(2) Å. The S−O bond lengths are much shorter than that of free dmso (1.492(1) Å),[9] indicating greater S−O double bond character for the S-bonded molecule. The Ru−S and S−O bond lengths of S-bonded [Ru(NH$_3$)$_5$(dmso)]$^{2+}$ are significantly shorter (2.188(3) Å) and longer (1.527(7) Å), respectively,[16] than those of *mer*-[RuCl$_3$(dmso)(tmen)]. However, in *trans*-Na[Ru^{III}Cl$_4$(dmso)(NH$_3$)] and *mer,cis*-[Ru^{III}Cl$_3$(dmso)(1Me-im)$_2$] (1Me-im is 1-methylimidazole) complexes, where the dmso is trans to an N-atom donor, the Ru−S and S−O bond lengths are 2.2797(7), 1.479(3) Å and 2.299(2), 1.464(6) Å, respectively.[17,18]

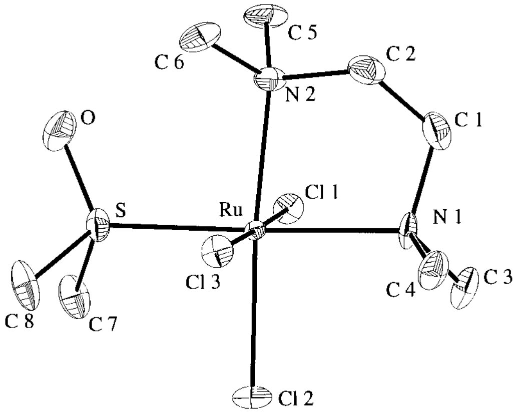

Figure 1. Structure of *mer*-[RuCl$_3$(dmso)(tmen)]. Selected distances (Å) and bond angles (deg) for the non-disordered molecule: Ru−S, 2.2912(8); S−O, 1.476(2); Ru−N(2), 2.194(2); Ru−N(1), 2.204(2); Ru−Cl(3), 2.3340(9); Ru−Cl(1), 2.3497(9); Ru−Cl(2), 2.3503(8); N(2)−Ru−N(1), 82.72(9); N(2)−Ru−S, 96.02(6); N(1)−Ru−S, 176.77(6); N(2)−Ru−Cl(3), 88.17(6); N(1)−Ru−Cl(3), 91.74(6); S−Ru−Cl(3), 91.20(3); N(2)−Ru−Cl(1), 91.87(6); N(1)−Ru−Cl(1), 89.95(6); S−Ru−Cl(1), 87.11(3); Cl(3)−Ru−Cl(1), 178.31(2); N(2)−Ru−Cl(2), 173.38(6); N(1)−Ru−Cl(2), 91.62(7); S−Ru−Cl(2), 89.81(3); Cl(3)−Ru−Cl(2), 88.57(2); Cl(1)−Ru−Cl(2), 91.55(2).

The infrared spectrum of *mer*-[RuCl$_3$(dmso)(tmen)] displays a single ν(SO) peak at 1115 cm^{-1} (Nujol mull, KBr disk). This value is much greater than that of free dmso (1055 cm^{-1}),[10] as well as those of [Ru(NH$_3$)$_5$(dmso)]$^{2+}$ (1045),[19] *trans*-Na[RuCl$_4$(dmso)(NH$_3$)] (1088), and *trans*-Na[RuCl$_4$(dmso)(im)] (1088),[17] and is identical with ν_{asym}(SO) for [RuCl$_4$(dmso)$_2$]$^-$.[8] The infrared spectrum of *mer,cis*-[Ru^{III}Cl$_3$(dmso)(1Me-im)$_2$] was not reported.[18] In the IR spectrum of *mer*-[Ru^{II}Cl$_3$(dmso)(tmen)]$^-$ in acetonitrile solution (prepared by reaction of the Ru(III) compound with Zn/Hg amalgam), ν(SO) = 1080 cm^{-1}. Both structural and IR data show that the S−O bond in III and II oxidation states of *mer*-[RuCl$_3$(dmso)(tmen)] is stronger than that found in unbound dmso.

The electronic spectrum (Figure 2A) of *mer*-[RuCl$_3$(dmso)(tmen)] in acetonitrile features two low-energy bands with absorption maxima at 396 (ϵ = 3420) and 456 nm (ϵ = 1075 M^{-1} cm^{-1}). These bands, which red-shift slightly in dichlo-

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(15) Red-orange crystals of *mer*-RuCl$_3$(dmso)(tmen) were isolated from the reaction of *cis*-RuCl$_2$(dmso)$_4$ with 1 equiv of the diamine ligand in ethanol at room temperature, followed by addition of 0.1 M HCl. X-ray data were collected at 85 K on a CAD-4 diffractometer. The structure was solved by direct methods. In the final least squares refinement cycle on F^2, R = 3.62%, R_w = 6.63%, and GOF = 1.727 on 8665 reflections with 450 parameters. The crystal data are a = 14.086(4) Å, b = 8.716(2) Å, c = 24.444(4) Å, β = 97.13(2)°, V = 2977.9(12) Å^3, space group $P2_1/n$, Z = 8, MW = 401.8, and ρ(calc) = 1.792 g/cm.

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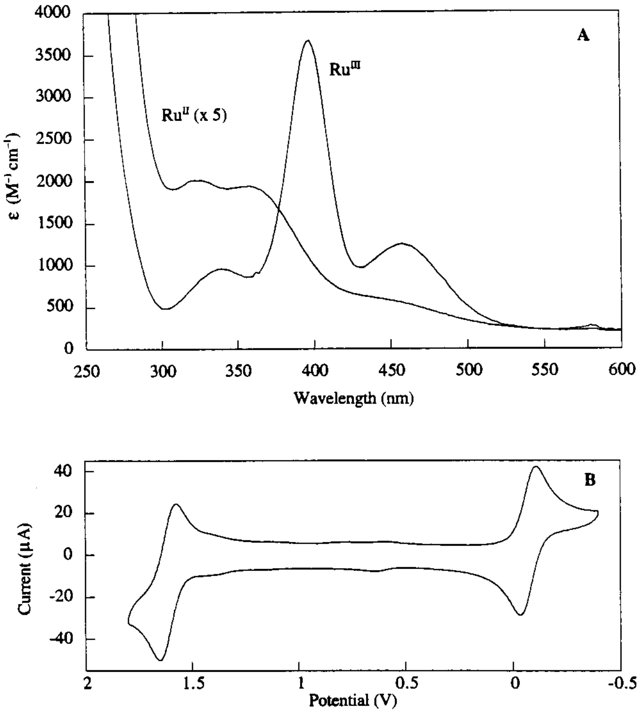

Figure 2. (A) Electronic spectra of *mer*-[RuCl$_3$(dmso)(tmen)]$^{0/-}$ in CH$_3$CN. (B) Cyclic voltammogram of *mer*-[RuCl$_3$(dmso)(tmen)] in CH$_3$CN (glassy carbon working electrode, Ag/AgCl reference electrode, 100 mV/s, m = 0.1 M).

romethane solution to 400 (ϵ = 3540) and 460 nm (ϵ = 1020 M^{-1} cm^{-1}), are attributed to Cl pπ → Ru dπ LMCT transitions. The band at 346 nm (ϵ = 830 M^{-1} cm^{-1}) could represent a ligand-field transition that is coupled to the charge-transfer transition at 396 nm. The spectrum of the corresponding Ru(II) complex (prepared by reaction of the Ru(III) compound with Zn/Hg amalgam) in acetonitrile exhibits bands at 322 (ϵ = 402), 358 (ϵ = 388), and 435 nm (ϵ = 126 M^{-1} cm^{-1}). All three bands are attributable to ligand-field transitions.

In acetonitrile solution *mer*-[RuCl$_3$(dmso)(tmen)] exhibits two *reversible* one-electron waves (0.11 V (ΔE_{pk} = 95 mV) and 1.78 V (ΔE_{pk} = 100 mV) vs NHE),[20] corresponding to the Ru(III/II) and the Ru(IV/III) couples, respectively (Figure 2B). The reversible nature of the second peak is remarkable; it shows not only that the Ru(IV) complex is robust but also that it does not isomerize to an O-bonded dmso species. In [Ru(NH$_3$)$_5$(dmso)]$^{2+}$ and related complexes,[11−13,21] $E_{1/2}$ for Ru(III/II) of the S-bonded species is ca. 1.0 V (vs NHE), whereas E$_{1/2}$ for the Ru(III/II) of the O-bonded species is ca. 0.01 V (vs NHE). While E$_{1/2}$ for the O-bonded species is reasonable (E$_{1/2}$ = 0.07 V vs NHE for [Ru(NH$_3$)$_5$(H$_2$O)]$^{3+/2+}$),[22] E$_{1/2}$ for the S-bonded species is very high (cf. E$_{1/2}$ = 0.3 V vs NHE for [Ru(NH$_3$)$_5$(py)]$^{3+/2+}$).[23] The Ru(II) must π-back-bond to dmso in [Ru(NH$_3$)$_5$(dmso)]$^{2+}$ because E$^{1/2}$ is comparable to that found for [Ru(NH$_3$)$_5$(N$_2$)]$^{3+/2+}$ (1.1 V vs NHE).[24] Furthermore, the short (strong) Ru−S bond and the long (weak) S−O bond are in accord with this model. On the basis of these comparisons, we conclude that dmso in *mer*-[RuCl$_3$(dmso)(tmen)] is primarily a σ-donor (ν(SO) = 1115 cm^{-1}).

Since there is no indication of π-back-bonding between Ru(III) or Ru(II) and dmso in *mer*-[RuCl$_3$(dmso)(tmen)], it is surprising that S→O isomerization is not observed on the CV time scale (0.005−50 V/s) upon oxidation to the IV state. One possibility is that synergistic donor interactions involving dmso strengthen both the Ru−S and S═O bonds: in this electronic structural formulation, stronger σ(S) donation to Ru(IV) would enhance π(O) to S bonding, thereby stabilizing the S-bonded complex. Further work, especially electronic structure calculations, will test this bonding hypothesis; in particular, it will be of interest to learn the role ancillary halo ligands play in stabilizing S-bonded structures.

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Supporting Information Available: Complete tables of crystal data, atomic coordinates, bond distances and angles, and figures for *mer*-[RuCl$_3$(dmso)(tmen)] (13 pages). Ordering information is given on any current masthead page.

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(20) Cyclic voltammograms were collected in a traditional two-compartment cell using a polished and sonicated 3-mm-diameter glassy carbon working electrode (BAS), Pt wire auxiliary electrode, and Ag/AgCl reference electrode. Measurements were conducted at room temperature with a CH instruments 660 electrochemical workstation. Solutions for electrochemical measurements were performed in acetonitrile (Burdick and Jackson) containing 0.1 M *n*-tetrabutylammonium hexafluorophosphate (SACHEM) and were fully deaerated with argon. Current was linearly dependent upon $\nu^{1/2}$ for the scan rates studied (0.005−50 V/s).

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