The present and previous[6] results indicate that the species $[(\text{ligand})_3CuF_2Cu(\text{ligand})_3]^{2+}$ seems to occur quite generally and that stabilization in the solid state by hydrogen-bonding interactions is significant. The copper dimers studied so far show a very weak magnetic exchange interaction, which is likely to be intramolecular. The weak coupling between the copper(II) ions can be understood on the basis of recent results of Kahn[19] and the fact that the square-pyramidal copper coordination geometry results in $d_{x^2-y^2}$ as the magnetic orbitals. With use of this model a co-square-planar geometry for the dimeric unit $[L_2CuF_2CuL_2]$ would result in a significant antiferromagnetic interaction. Such systems are being studied.

Acknowledgment. The authors are indebted to Dr. H. B. Broer-Braam, Prof. Dr. W. J. A. Maaskant, and Dr. G. C. Verschoor for helpful discussions. Thanks are also due to F. B. Hulsbergen and W. Vreugdenhil (all from the State University of Leiden) for their contributions in the early stages of this research. The investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. I, 87861-49-2; II, 87861-51-6; $[CuF_2(dmpz)_6](BF_4)_2$, 76171-85-2; $Cu(BF_4)_2$, 38465-60-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, least-squares planes, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

---

[19] Julve, M.; Verdaguer, M.; Kahn, O.; Gleizes, A.; Philoche-Levisalles, M. *Inorg. Chem.* **1983**, *22*, 368–370.

Contribution from The Procter & Gamble Company,
Miami Valley Laboratories, Cincinnati, Ohio 45247

Synthesis and Crystal Structure of Dibromotetrakis(dimethyl sulfoxide)ruthenium(II). Structural Implications for O_2 Oxidation Catalysis

JOEL D. OLIVER* and DENNIS P. RILEY

Received April 26, 1983

In an effort to elucidate the mechanism of the oxygen oxidations of sulfides to sulfoxides with the $RuX_2(Me_2SO)_4$ (X = Cl or Br) catalysts, we determined the crystal structure of the $RuBr_2(Me_2SO)_4$ catalyst. Unlike the chloro-based catalyst that possesses a cis geometry and O- and S-bonded Me_2SO ligands, $RuBr_2(Me_2SO)_4$ has a trans structure with all S-bonded Me_2SO ligands. The molecule has crystallographic $4/m$ (D_{4h}) symmetry with the Ru, S, and O atoms lying on the crystallographic mirror plane. The Ru–S bond lengths exhibit a trans influence. Principal metrical details are Ru–Br = 2.540 (1) Å, Ru–S = 2.360 (1) Å, S–O = 1.484 (3) Å, S–C = 1.789 (3) Å, Ru–S–O = 112.5 (1)°, Ru–S–C = 116.0 (1)°, C–S–O = 105.7 (1)°, and C–S–C′ = 99.6 (2)°. Crystals of the complex are tetragonal, of space group $I4/m$ (No. 87), with a = 9.181 (2) Å, c = 11.121 (2) Å, and Z = 2. Least-squares refinement of the structure has resulted in R = 0.018 and R_w = 0.025 based on 403 unique reflections with $|F| \geq 5\sigma(|F_o|)$.

Introduction

Our interest in Ru(II) complexes of the type $RuX_2(Me_2SO)_4$[1] stems from our observation that such complexes act as excellent, selective sulfide oxidation catalysts using molecular oxygen.[2] A puzzling aspect of our work with these catalysts is that the $RuBr_2(Me_2SO)_4$ complex is a much more active catalyst than the $RuCl_2(Me_2SO)_4$ complex.[3] The possible structural origin of such reactivity differences prompted us to determine the solid-state structure of the $RuBr_2(Me_2SO)_4$ catalyst.

The structure of the $RuCl_2(Me_2SO)_4$ complex (**1**) has been determined previously by X-ray diffraction techniques[4] and was shown to have a cis arrangement of the chloride ligands with three S-bonded Me_2SO ligands and one O-bonded Me_2SO mutually cis to each chloro ligand. Attempts to determine the structure of $RuBr_2(Me_2SO)_4$ unambiguously using IR, ^1H NMR, and UV–vis spectra did not provide a conclusive structural assignment. Thus, an X-ray structure analysis of the complex was initiated. The results of this X-ray study are presented herein.

Experimental Section

Materials. The $RuBr_2(Me_2SO)_4$ complex (**2**) was prepared by the method of James et al.[1] Crystals of **2** suitable for the X-ray diffraction study were obtained by dissolving under an Ar atmosphere 0.5 g of the pale yellow crude $RuBr_2(Me_2SO)_4$ in 100 mL of hot (110 °C) 70% toluene–30% Me_2SO solvent mixture. Filtration of this hot solution followed by slow cooling at 20 °C gave orange-red crystals after 2 days. These crystals were collected by filtration to give 0.21 g of **2**. Storage of the filtrate at −40 °C for an additional 2 weeks gave a second crystalline crop of 0.23 g of **2**. Both crops were shown to be structurally identical with the starting material by comparison of their IR and UV–vis spectra. Electronic spectrum ($CHCl_3$) [λ_{max}, cm^{-1} (ϵ)]: 21 380 (207), 32 050 (sh), 37 600 (2740). Selected absorptions in the infrared spectrum [cm^{-1} (assignment,[5] intensity)]: 1300 ($\delta(d)_{CH}$, s), 1289 ($\delta(d)_{CH}$, s), 1082 (ν_{SO}, s), 1028 (CH rock, s), 720 (ν_{CS}, s), 674 (ν_{CS}, s) 520 (broad and intense), 479 (ν_{RuS}, s), 431, 390 (δ_{CSO}, s).

Physical Measurements. ^1H NMR spectra were recorded in $CDCl_3$ solution at 270 MHz on a JEOL FX-270 spectrometer. Solid-state infrared spectra were recorded as Nujol mulls between CsBr windows on Perkin-Elmer Model 298 and 621 spectrophotometers. Electronic spectra were recorded in the UV–vis regions on a Beckman DU-7 spectrophotometer as chloroform solutions in stoppered quartz cells.

Crystallographic Study of 2. The crystals changed color from orange-red to yellow during storage prior to collecting the single-crystal diffraction data. The solution ($CHCl_3$) UV–vis spectrum and the solid-state IR spectrum of the yellow crystals were identical with those of the orange crystals. The source of this color change remains unclear (vide infra). A yellow, octahedral-shaped crystal was mounted on a glass fiber and transferred to a Syntex P2_1 diffractometer equipped with a graphite monochromator and a Mo-target X-ray tube. The crystal data and details of the data collection are presented in Table I.

The systematic absences listed in Table I are consistent with the space group choice of $I4$, $I\bar{4}$, or $I4/m$ for the crystals. The crystal structure was solved intuitively by placing the Ru atom at a $4/m$ site and placing the Br atom along the 4-fold axis 2.5 Å above the Ru atom in space group $I4/m$. A difference map revealed the locations

---

[1] James, B. R.; Ochiai, E.; Rempel, G. I. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 781.

[2] Riley, D. P. *Inorg. Chem.* **1983**, *22*, 1965.

[3] Ledlie, M. A.; Allum, K. G.; Howell, I. V.; Pitkethly, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1734–8.

[4] Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480–3.

[5] Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, *204*.

Table I. Summary of Crystal Data and Details of Data Collection

Crystal Data

formula	$C_8H_{24}O_4S_4Br_2Ru$	space group	$I4/m$ (No. 87)
fw	573.4	systematic absences	hkl, $h + k + l = 2n$; $hk0$, $h + k = 2n$; $00l$, $l = 2n$
a, Å	9.181 (2)[a]		
c, Å	11.121 (2)		
Z	2	d(calcd), g cm^{-3}	2.03
vol, Å^3	937.4	F(000)	564
		T, °C	22

Data Collection

cryst dimens, mm	0.25 × 0.25 × 0.25
λ(Mo K$\bar{\alpha}$)	0.71073
μ(Mo K$\bar{\alpha}$)	54.8
limiting sphere	$2 \leqslant 2\theta \leqslant 50$
scan mode	θ–2θ
scan rate (deg/min)	variable, 4–29.3
Miller index range	$h, \pm k, l$
reflcns measd	960
unique reflcns used	403
R(merge)	0.012
signif criterion	$\|F\| > 5\sigma(\|F\|)$
check reflcns[b]	002, 040, 400, 34$\bar{1}$
abs cor	empirical
max (min) trans factor	0.048 (0.029)

[a] Lattice constants were obtained from least-squares refinement of observed setting angles of 15 locally intense reflections.
[b] Analysis of these intensities revealed only random variations (<1% relative).

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (×10^3) for **2**

atom	x	y	z	U_{eq},[a] Å^2
Ru	0	0	5000	27 (1)
Br	0	0	2716 (1)	41 (1)
S	2543 (1)	374 (1)	5000	34 (1)
O	3373 (3)	−1012 (3)	5000	49 (1)
C	3252 (4)	1414 (4)	3772 (3)	57 (1)

[a] The equivalent isotropic thermal parameter is defined as one-third of the trace of the U_{ij} tensor.

Table III. Bond Lengths (Å) and Bond Angles (deg) for **2**

Ru–Br	2.540 (1)	S–O	1.484 (3)
Ru–S	2.360 (1)	S–C	1.789 (3)
Ru–S–O	112.5 (1)	C–S–O	105.7 (1)
Ru–S–C	116.0 (1)	C–S–C′	99.6 (2)

of the unique C, O, and S atoms of the structure. After convergence of the least-squares refinement of the model employing anisotropic thermal parameters, a difference density map was calculated and revealed the locations of the methyl H atoms. Least-squares refinement of the eight atoms of the structure with the non-hydrogen atoms treated anisotropically gave $R = \sum\Delta F/\sum|F_o| = 0.018$ and $R_w = (\sum w(\Delta F)^2/w|F_o|^2)^{1/2} = 0.025$, where $\Delta F = ||F_o| - |F_c||$ and $w = (\sigma_2(|F_o|) + 0.0005|F_o|^2)^{-1}$. The successful refinement of this model for the complex confirms the choice of space group as $I4/m$ for the crystals. A final difference density map revealed several peaks (0.3–0.5 e Å^{-3}) near the Ru and Br atoms and smaller peaks (<0.25 e Å^{-3}) at chemically unreasonable positions.

All crystallographic computations were performed on a Data General Eclipse computer using the SHELXTL software package.[6] The neutral-atom scattering factors and the real ($\Delta f'$) and imaginary components ($\Delta f''$) for all atoms were taken from ref 7. Final atomic coordinates are given in Table II. Bond lengths and bond angles are listed in Table III. Thermal parameters, hydrogen atom parameters, additional bond lengths and angles, a stereoscopic packing diagram, and structure factor amplitudes, as $10|F_o|$ and $10|F_c|$ in electrons, have been deposited as supplementary material.

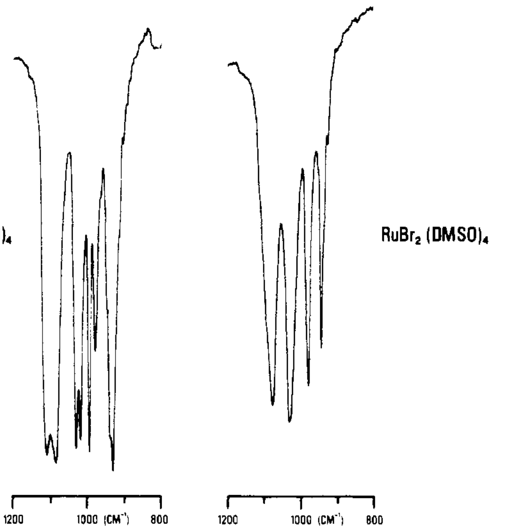

Figure 1. Solid-state infrared spectra of the $RuX_2(Me_2SO)_4$ complexes in the dimethyl sulfoxide S→O stretching region.

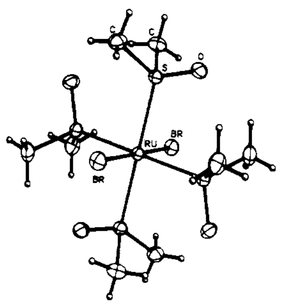

Figure 2. Perspective drawing of the $RuBr_2(Me_2SO)_4$ complex indicating the atom-labeling scheme.

Results

Spectroscopic Studies. From standard spectroscopic methods it was not possible to determine the structure of complex **2** unambiguously. The solid-state IR spectrum of the complex exhibits a much less complex spectrum than that of the $RuCl_2(Me_2SO)_4$ complex. For example, only a single S→O stretch is observed at 1082 cm^{-1} (see Figure 1). While this suggests the structural equivalence of the four Me_2SO ligands, our failure to observe or assign either a singlet or doublet for the Ru–Br stretch in the far-IR spectrum made it impossible to unambigously determine the structure of this complex on the basis of IR evidence alone. The IR spectrum also suggests that the complex possesses all S-bonded Me_2SO ligands, since the magnitude of the S→O stretching frequency is higher than in free Me_2SO.[8,9]

The ^{1}H NMR solution spectrum of **2** was complex at room temperature and as a result was not helpful in determining the structure. On the basis of IR studies, a single resonance due to the CH_3 groups of all the S-bonded Me_2SO ligands was expected. The observed spectra consisted of a complex pattern of at least four singlets from δ 3.4 to 3.5 and a singlet at δ 2.6 (free Me_2SO[10]). This ^{1}H NMR is very similar to that observed previously for $RuBr_2$ $(Me_2SO)_4$ and reported in ref 9. The results are consistent with dissociation of Me_2SO in $CDCl_3$ solution to give mixtures of five- and six-coordinate species. But such solution results do not aid in assigning the structure of **2**. Thus, the X-ray structure determination was necessary to assign the geometry of this complex.

---

(6) Sheldrick, G. M. "SHELXTL: A Minicomputer Package for Crystal Structure Determination"; Nicolet XRD Division: Cupertino, CA, 1981.

(7) Ibers, J. A.; Hamilton, W. C. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(8) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley: New York, 1970; 210–11.

(9) Ruiz-Ramirez, L.; Stephenson, T. A.; Switkes, E. S. *J. Chem. Soc. Dalton Trans.* **1973**, 1770.

Crystal Structure. A perspective drawing of complex **2** is shown in Figure 2. The complex has crystallographic $4/m$ (D_{4h}) symmetry, a trans arrangement of the bromide ligands, and the all-S-bonded disposition of the Me_2SO ligands. The Ru, S, and O atoms of the complex lie on a crystallographic mirror plane.

The Ru–S bond length, 2.360 (1) Å, for **2** reveals a strong trans influence[10] of the S-bonded Me_2SO ligands. This bond length is significantly longer than the Ru–S bonded lengths observed in **1** (2.277 (1) Å),[4] $[RuCl_3(Me_2SO)_3]^-$ (2.261 (8) Å),[11] and $[Ru(NH_3)_5(Me_2SO)]^{2+}$ (2.188 (3) Å).[12] The Ru–S–O bond angle (112.5 (1)°) is slightly smaller and the Ru–S–C bond angle (116.0 (1)°) is slightly larger than the values observed in other Ru(II) complexes with Me_2SO ligands.[4,11,12] These slight distortions may be the result of steric crowding due to the four S-O bonds lying in the same principal coordination plane of the Ru(II) ion. In other octahedral complexes the Me_2SO ligands tend to be arranged in a propellar fashion with the S–O bonds each lying in a different principal coordination plane where possible. The geometry of the Me_2SO ligands in complex **2** is similar to the geometries observed in other Ru(II) complexes with Me_2SO ligands[4,11,12] and in free Me_2SO.[13]

In an effort to rationalize the observation that the crystals changed color from orange-red to pale yellow during storage prior to collecting the single-crystal diffraction data, we isolated a fresh, red-orange crystal of the complex and redetermined the structure. The crystal structure was identical with that of the yellow crystal form. The possibility that the complex originally crystallizes in a lower symmetry form (space group $I4$ or $I\bar{4}$) can thus be ruled out. We have been unable to determine the cause of the color change for the crystals.

Discussion

The principal purpose of this investigation was to aid our understanding of the superior catalytic activity of complex **2** compared to complex **1** in catalytic oxidations. The crystal structure reveals that **2** is the *trans*-$RuBr_2(Me_2SO)_4$ complex, which is indeed structurally different from that of the cis complex **1**. Not only are the bromo ligands trans but also there are no O-bonded Me_2SO ligands. These results confirm that there are fundamental differences between the halide ligands in complexes of the type $RuX_2(Me_2SO)_4$. Nonetheless, some questions still remain. For example, what is responsible for the structural differences and do these structural differences account for the reactivity differences of these two oxidation catalysts?

Since it is known that sulfoxide ligands are very sensitive to steric effects,[14] solely on the basis of steric considerations, one would predict that the $RuBr_2(Me_2SO)_4$ complex would prefer cis coordination of the bromo ligands in order to have three Me_2SO ligands cis and one Me_2SO ligand trans to each bromo ligand. This logic adequately rationalizes the structures of $[RuCl_3(Me_2SO)_3]^-$[11] and $RuCl_2(Me_2SO)_4$[4] but clearly is not the dominant factor in determining the structure of **2**.

Some of the factors governing the mode of coordination of the Me_2SO ligand in complexes **1** and **2** can be identified by comparison to the crystal structures of other low-spin d^6 metal complexes: $(CH_3)_2NH_2[RuCl_3(Me_2SO)_3]$ (**3**),[11] $Na[RhCl_4(Me_2SO)_2]$ (**4**),[15] and $RhCl_3(Me_2SO)_3$ (**5**).[16] The structures of **1**, **3**, and **5** reveal that each Me_2SO ligand coordinates to the metal atom through the S atom when the Me_2SO ligand is trans to a chloro ligand. The structures of **1** and **5** also show trans-related pairs of Me_2SO ligands coordinated to the metal atoms with one O-bonded and one S-bonded Me_2SO ligand. The structures of **2** and **4** reveal trans-related pairs of Me_2SO ligands coordinated to the metal atoms exclusively through the S atoms. These variations in the mode of bonding of Me_2SO ligands suggest that the mode of coordination of the Me_2SO ligands to Ru(II) and Rh(III) centers is sensitive to both steric and electronic effects. It is clear that the Ru(II) center of the *trans*-$RuBr(Me_2SO)_4$ complex prefers to coordinate through the softer, π-acceptor S atoms of the Me_2SO ligands in preference to the harder, σ-donating O atoms.

The origin of the structural differences between *trans*-$RuBr_2(Me_2SO)_4$ and *cis*-$RuCl_2(Me_2SO)_4$ may lie in the thermodynamic stabilities of the crystalline products, but several experimental results discount this being a major factor. For example, prolonged heating of either the chloro or the bromo complex in Me_2SO followed by cooling gives only the original complex in both cases. Similarly, other attempts to isomerize the *cis*-$RuCl_2(Me_2SO)_4$ complex to the trans complex were unsuccessful. Heating the *cis*-$RuCl_2(Me_2SO)_4$ complex in methanol or Me_2SO with excess LiCl or treatment of *cis*-$RuCl_2(Me_2SO)_4$ with 1 equiv of $AgBF_4$ in methanol followed by the addition of LiCl yielded only the *cis*-$RuCl_2(Me_2SO)_4$ complex. Consequently, there appears to be inherent stability differences associated with the $RuX_2(Me_2SO)_4$ complexes such that the cis geometry of the chloro ligands and the trans geometry of the bromo ligands are favored. Whether the structural preferences arise from electronic factors, steric factors, or both is not understood.

The effects of the structure on the catalytic chemistry could be significant. The relative Ru–S bond lengthening observed in the *trans*-$RuBr_2(Me_2SO)_4$ complex may make the Me_2SO ligands more labile than those of the *cis*-$RuCl_2(Me_2SO)_4$ complex especially when the metal is in a higher oxidation state.[2] Increased lability may contribute to the enhanced catalytic activity of the bromo complex. The question that arises with these homogeneous catalysts is whether or not the catalysts retain their structure during the catalytic sequence. We are currently investigating the interelation of structure and redox activity, but it is clear that this is a very complex issue. The *trans*-dihalo structure is definitely more reactive than the cis structure in this catalytic system, but the subtle interplay of steric, structural, and electronic factors upon the redox chemistry has not yet been integrated into a coherent picture.

Registry No. **2**, 72904-46-2.

Supplementary Material Available: A stereoscopic packing diagram and listings of bond lengths and angles, anisotropic thermal parameters, H atom coordinates, and structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

---

(10) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(11) McMillan, R. S.; Mercer, A.; James, B. R.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 1006.

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

(13) (a) Thomas, R.; Shoemaker, C. B.; Eriks, K. *Acta Crystallogr.* **1966**, *21*, 12. (b) Viswamitra, M. A.; Kannan, K. K. *Nature (London)* **1966**, *209*, 1016. (c) Feder, W.; Dreizler, H.; Rudolph, H. D.; Typke, V. *Z. Naturforsch., A* **1969**, *24A*, 266.

(14) Canovece, L.; Catalini, L.; Marangoni, G.; Michelon, G.; Nicolini, M.; Tobe, M. L. *J. Coord. Chem.* **1982**, *12*, 63.

(15) Sokol, V. I.; Rubtsova, N. D.; Gribenyuk, A. Y. *Zh. Strukt. Khim.* **1974**, *15*, 318.

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