49-1; EtSH, 75-08-1; $CH_3C(CH_2Br)_3$, 60111-68-4; $EtSCH_2CH_2SCH_2CH_2SEt$, 6052-45-5; $HSCH_2CH_2SCH_2CH_2SH$, 3570-55-6; EtI, 75-03-6; SMe_2, 75-18-3; SEt_2, 352-93-2; $\overline{S(CH_2)_3CH_2}$, 110-01-0; S-*n*-Bu_2, 544-40-1; S-*i*-Bu_2, 592-65-4; S-*t*-Bu_2, 107-47-1; $PhSCH_3$, 100-68-5; decyl methyl sulfide, 22438-39-7.

Supplementary Material Available: Tables of crystallographic details, atomic coordinates, bond lengths and bond angles, and anisotropic temperature factors for compound **16** (7 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (22 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Ruthenium(II)-Catalyzed Thioether Oxidation. 2. Syntheses and Crystal Structures of Two Ruthenium(II) Complexes with the New Linear Tridentate Ligand 3-(Ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane

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Syntheses of a new tridentate mixed sulfur-donor ligand, 3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane (EESP) (**3**), and two of its ruthenium(II) complexes, $RuX_2(Me_2SO)[EtS(CH_2)_3SO(CH_2)_3SEt]$ (X = Cl, (**4**), Br (**5**)), are described. Only one geometric isomer is produced when **3** reacts with either *cis*-$RuCl_2(Me_2SO)_4$ or *trans*-$RuBr_2(Me_2SO)_4$; X-ray structures show that the two products, **4** and **5**, contain the same geometric isomer. Complexes **4** and **5** possess a symmetrical structure, as deduced from ^{13}C and ^1H NMR spectra. Single-crystal structure determinations were carried out for **4** and **5**. Crystals of **5**: monoclinic, space group $P2_1$ (No. 4), with $a = 8.715$ (2) Å, $b = 13.342$ (3) Å, $c = 9.030$ (2) Å, $\beta = 105.47$ (2)°, and $Z = 2$. Crystals of **4**: $a = 8.718$ (2) Å, $b = 13.182$ (3) Å, $c = 8.912$ (2) Å, and $\beta = 105.87$ (2)°. The absolute configuration of **5** was determined by the Bijvoet method. Least-squares refinement of **5** resulted in $R = 0.030$ and $R_w = 0.029$ on the basis of 2264 reflections with $|F_o| > 5.0\sigma(|F_o|)$ including the Bijvoet pairs. Least-squares refinement of **4** gave $R = 0.023$ and $R_w = 0.029$ on the basis of 1777 unique reflections with $|F_o| > 2.5\sigma(|F_o|)$. The coordination geometry in both **4** and **5** is trans-thioether, cis-halo, and cis-sulfoxide. The tridentate, chelate ligand coordinates meridionally to the Ru(II) ion. In both structures, the two six-atom chelate rings have different conformations: one ring has a distorted chair conformation and the other ring has a twist-boat conformation. The major geometrical details for **5** are Ru–Br(1) = 2.601 (1) Å, Ru–Br(2) = 2.578 (1) Å, Ru–S(1) = 2.275 (2) Å, Ru–S(2) = 2.393 (2) Å, Ru–S(3) = 2.235 (2) Å, Ru–S(4) = 2.372 (2) Å, and Br(1)–Ru–Br(2) = 86.4 (1)°. The related details for the chloro complex, **4**, are Ru–Cl(1) = 2.467 (1) Å, Ru–Cl(2) = 2.444 (1) Å, Ru–S(1) = 2.269 (1) Å, Ru–S(2) = 2.386 (1) Å, Ru–S(3) = 2.218 (1) Å, Ru–S(4) = 2.365 (1) Å, and Cl(1)–Ru–Cl(2) = 86.4 (1)°.

Introduction

In the preceding paper in this series, we presented the evidence and arguments indicating that in the $RuX_2(Me_2SO)_4$-catalyzed oxygen oxidation of thioethers the most oxygen-active species leading to catalysis is generated in situ and is the *all-trans*-$RuX_2(R_2S)_2(R_2SO)_2$ complex. These results suggest that we could in principle (depending on the rates of ligand exchange) develop more active catalysts by the presynthesis of the all-trans complex rather than rely on an equilibrium process to generate some of the catalyst structure in solution. Additionally, in order to gain a complete understanding of the details of the electron-transfer mechanism involving ruthenium(II) and molecular oxygen, we need to be able to study discrete, stable complexes in solution. Model complexes containing multidentate ligands should be good candidates since they would be less susceptible to the loss of geometric integrity by dissociative processes. For these reasons, an effort has been made to synthesize examples of all-trans complexes with multidentate ligands.

In this report we describe the synthesis of the new symmetrical tridentate ligand **3** and the details of our attempts to make the all-trans complex with this new ligand. The results of our X-ray structure determinations reveal that complexes **4** and **5** correspond to the cis-X_2,cis-R_2SO, trans-R_2S geometry (isomer D of Figure 1 of the first article in this series). Surprisingly, this geometry forms when either *trans*-$RuBr_2(Me_2SO)_4$ or *cis*-$RuCl_2(Me_2SO)_4$ reacts with ligand **3** under a variety of conditions.

Experimental Section

General Considerations. The majority of the experimental procedures used in this work have been described in the first paper in this series. Mass spectra were obtained in the isobutane CI mode on a Hewlett-Packard Model 5985B mass spectrometer. All X-ray measurements were made at room temperature with a Syntex $P2_1$ autodiffractometer that was equipped with a Mo target X-ray tube and an incident-beam graphite monochromator.

Materials. 3-(Ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane. Ten grams (0.065 mol) of 3,3′-thiodipropanol (Aldrich) was converted to its corresponding ditosylate by standard procedures in 125 mL of dry pyridine at 0 °C by using 25 g (0.133 mol) of *p*-toluenesulfonyl chloride.[4] The solution was stirred at 0 °C for 16 h. The reaction workup proceeded by pouring the pyridine solution onto 400 g of crushed ice with vigorous stirring. The crude ditosylate compound precipitated and was collected by filtration. The crude product was redissolved in 100 mL of methylene chloride. This solution was washed with 150 mL of 0.1 N HCl, followed by two water washings. The methylene chloride layer was dried over Na_2CO_3, treated with activated charcoal, and filtered. The methylene chloride was removed on a rotary evaporator, and the clear, colorless oil was redissolved in diethyl ether. The ethereal solution was cooled to −78 °C, whereupon crystals formed that were collected and dried in vacuo to yield 20 g (66%) of the desired ditosylate, **1**.

1 was oxidized to yield the sulfoxide **2**. In a standard preparation 5 g (10.9 mmol) of ditosylate **1** was dissolved in 50 mL of methylene chloride at 10° C. To this stirred solution was added, in a dropwise

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0020-1669/86/1325-1821$01.50/0

fashion, 100 mL of a methylene chloride solution containing 1.88 g (11.1 mmol) of *m*-chloroperbenzoic acid (77% by weight; Aldrich). The perbenzoic acid solution was added until the reaction contained residual oxidant, as monitored by peroxide test paper. The solution was washed with 100 mL of aqueous sodium bisulfite saturated with NaCl. The methylene chloride layer was shaken with saturated aqueous NaCl and dried over Na_2SO_4 for several hours. The solution was filtered, and the methylene chloride was removed on a rotary evaporator. Addition of 30 mL of diethyl ether to the colorless oil gave a colorless solution, which crystallized when a few drops of methylene chloride were added with shaking. The yield of the ditosylate sulfoxide, **2**, was 4.3 g (83%).

2 was then converted to the desired tridentate thioether–sulfoxide–thioether ligand. To an ethanolic (dry) slurry containing 3.5 g (7.4 mmol) of **2** in 50 mL of ethanol was added 200 mL of a freshly prepared ethanolic solution of NaSEt (0.35 g (15.2 mmol) of Na plus 0.92 g (14.8 mmol) of EtSH (Aldrich)). The resultant solution was allowed to stand overnight under N_2. The solvent was removed on a rotary evaporator and the solid extracted with 50 mL of warm methylene chloride. The solution was dried over Na_2SO_4 and filtered. The methylene chloride was removed on a rotary evaporator. Addition of ~25 mL of diethyl ether with vigorous stirring at 0 °C to the clear, colorless oil gave 1.62 g of a white crystalline solid, corresponding to an 86% yield of the desired ligand, **3** (EESP). Anal. Calcd for $C_{10}H_{22}OS_3$: C, 47.20; H, 8.71; S, 37.80. Found: C, 47.38; H, 8.56; S, 37.60. Mass spectrum (parent ion): found, *m/e* 255; calcd, *m/e* 255.

Dibromo(dimethyl sulfoxide)(3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane)ruthenium(II) (4). To a toluene solution under N_2 containing 0.5 g (0.87 mmol) of *trans*-$RuBr_2(Me_2SO)_4$ was added 0.23 g (0.90 mmol) of tridentate ligand **3**. The solution was refluxed for $^1/_2$ h, during which time a yellow-orange crystalline material precipitated from solution. The solution was cooled and filtered to yield 0.35 g (68%) of complex **4**, $RuBr_2(EESP)(Me_2SO)$. When this complex was redissolved in methylene chloride, TLC on silica gel using a 98% methylene chloride/2% methanol solution as the eluent gave only one spot. Mixed TLC with the mother liquor also gave only one spot. Anal. Calcd for $C_{12}H_{28}Br_2O_2RuS_4$: C, 24.29; H, 4.76; Br, 26.93; S, 21.61. Found: C, 24.36; H, 4.38; Br, 26.76; S, 20.96.

Crystals suitable for the X-ray study were obtained by recrystallizing **4** from hot 90% ethanol/10% methylene chloride. After the solution was chilled to −40 °C and allowed to sit undisturbed for several days, yellow-orange crystals were obtained.

Dichloro(dimethyl sulfoxide)(3-(ethylthio)-1-((3-ethylthio)propyl)sulfinyl)propane)ruthenium(II) (5). This complex was synthesized in a manner analogous to that outlined above for the bromo analogue, **4**. In a typical preparation 0.95 g (2.0 mmol) of *cis*-$RuCl_2(Me_2SO)_4$ was reacted in 50 mL of chloroform under N_2 with 0.51 g (2.0 mmol) of ligand **3**. The reaction was refluxed for 75 min—by which time all of the starting material had been consumed, as shown by silica-gel thin-layer chromatography, to give one product. The $CHCl_3$ was removed via vacuum, and the resultant yellow solid was dissolved in a minimum volume of hot methanol (45 mL). This solution was allowed to cool slowly to room temperature, and after several hours large yellow crystals of complex **5**, $RuCl_2(EESP)(Me_2SO)$, formed. Additional cooling at −20 °C overnight followed by filtration gave 0.65 g of a yellow crystalline product. A yield of 64% of **5** was obtained. Additional crops of **5** were obtained by removal of some of the methanol solvent. Anal. Calcd for $C_{12}H_{28}Cl_2O_2RuS_4$: C, 28.6; H, 5.6; Cl, 14.1; O, 6.3; S, 25.4. Found: C, 28.81; H, 5.36; Cl, 14.21; O, 6.63; S, 25.41.

Table I. Summary of Crystal Data and Details of Data Collection for **5**

Crystal Data

formula	$C_{12}H_{28}O_2S_4Br_2Ru$	space group	$P2_1$ (No. 4)
fw	593.5	syst absences	0*k*0 for *k* odd
a, Å	8.715 (2)[a]	*d*(calcd), g cm^{-3}	1.95
b, Å	13.342 (3)	*F*(000)	588
c, Å	9.030 (2)	*T*, °C	21
β, deg	105.47 (2)	*Z*	2
vol, Å^3	1011.9		

Data Collection

cryst dimens, mm	0.08 × 0.08 × 0.12
λ(Mo K$\bar{\alpha}$), Å	0.71073
μ(Mo K$\bar{\alpha}$), cm^{-1}	50.7
limiting sphere, deg	2.5 < 2*θ* < 45.0
scan mode	*θ*–2*θ*
scan rate, deg/min	variable, 4–29.3
Miller indexes collcd	(±*h*,*k*,±*l*)
no. of reflcns measd	3064
no. of unique reflcns measd	1414
no. of reflcns used[b] ($F_o > 5\sigma(F_o)$)	2264
merging *R*	0.018
check reflcns[c]	(005, 020, 400, 111)
abs cor	empirical[d]
min/max transmissn factors	0.541/0.641

[a] Lattice constants were obtained from a least-squares refinement of the observed setting angles of 15 general reflections. [b] Including Bijvoet pairs. [c] Analysis of these intensities revealed only random variations (<2% relative). [d] Pseudoellipsoid approximation of the crystal was made from experimental *ψ* scans.

Table II. Atom Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3) for **5**

atom	*x*	*y*	*z*	*U*[a]
Ru	1202 (1)	0	2757 (1)	23 (1)
Br(1)	2075 (1)	1870 (1)	2978 (1)	45 (1)
Br(2)	265 (1)	302 (1)	5197 (1)	41 (1)
S(1)	1905 (2)	−199 (2)	523 (2)	30 (1)
S(2)	3942 (3)	−252 (2)	4087 (2)	37 (1)
S(3)	714 (3)	−1633 (2)	2937 (2)	30 (1)
S(4)	−1410 (2)	364 (2)	1242 (2)	32 (1)
O(1)	3452 (7)	−658 (5)	616 (7)	44 (2)
O(2)	1007 (7)	−2335 (4)	1770 (7)	44 (2)
C(1)	494 (11)	−875 (7)	−917 (9)	42 (4)
C(2)	1824 (13)	931 (7)	−512 (10)	46 (4)
C(3)	6151 (11)	−143 (11)	6909 (11)	77 (5)
C(4)	4402 (11)	19 (9)	6119 (9)	55 (4)
C(5)	4373 (11)	−1570 (7)	4069 (10)	46 (4)
C(6)	3552 (12)	−2285 (8)	4936 (12)	60 (4)
C(7)	1808 (11)	−2098 (7)	4782 (10)	47 (4)
C(8)	−1271 (10)	−1891 (7)	3091 (10)	40 (3)
C(9)	−2544 (10)	−1525 (7)	1738 (11)	47 (4)
C(10)	−2872 (10)	−420 (7)	1806 (12)	50 (4)
C(11)	−3627 (11)	1895 (8)	604 (13)	66 (5)
C(12)	−2070 (12)	1581 (7)	1677 (11)	52 (4)

[a] Equivalent isotropic *U* is defined as $^1/_3$(trace U_{ij}).

Crystallographic Studies of 4 and 5. The crystal data and details of data collection for **4** are given in Table I. Since the structure of complex **5** is isomorphous to that of complex **4**, the experimental details, final atomic coordinates, bond lengths, and bond angles for **5** have been deposited with the supplementary material. All structural calculations were made with the SHELXTL[5] software package on a Data General Eclipse computer. Scattering factors for all atoms and the real and the imaginary corrections for anomalous dispersion were taken from ref 6. The systematic absences in Table I are consistent with the space group choice of $P2_1$ or $P2_1/m$. The successful solution and refinement of the structure, including the determination of enantiomorph, confirm the choice of the space group as $P2_1$. The locations of the Ru and Br ions were obtained from a sharpened, three-dimensional Patterson map. The remaining non-hydrogen atoms of the structure were located in a subsequent difference electron density map. After convergence of the least-squares refinement of the structure with anisotropic thermal parameters, reasonable positions for most of the H atoms were revealed in a difference electron density map. The parameters refined in the final least-squares cycles were an overall scale factor and the positional and anisotropic thermal parameters of the non-hydrogen atoms. The H atoms were included at their fixed, idealized positions with *d*(C–H) = 0.96 Å and isotropic thermal parameters fixed at 1.2 times the equivalent isotropic thermal parameter of the parent atom. The weighting function used was computed as $w = (\sigma^2(|F_o|) + 0.0004|F_o|^2)^{-1}$, where $\sigma(|F_o|)$ is the standard deviation of the structure factor based solely on counting statistics. The final values of *R* and R_w are 0.030 and 0.029, respectively. A final difference electron density map revealed a featureless background below 0.6 e Å^{-3}, except for peaks with magnitudes ≤0.9 e Å^{-3} near the Ru, Br, and S atoms. The proper choice of enantiomorph was determined by the Bijvoet method. The structure was inverted, and a parallel least-squares refinement was performed, which gave *R* = 0.060 and R_w = 0.060. On the basis of the Hamilton *R*-factor ratio test,[7] the possibility that the

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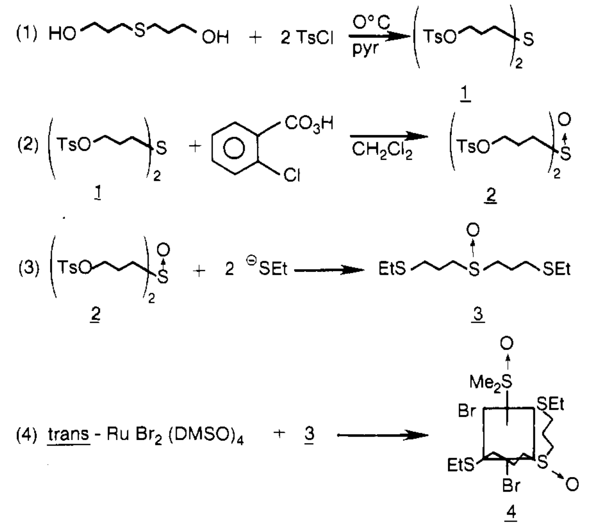
Scheme I. Synthesis of Ligand **3** and Its Ru Complex **4**



second enantiomer is correct can be rejected at the 0.5% probability level. The atomic coordinates given in Table II correspond to the model that gave the lower *R* factors.

Results

Syntheses and Characterizations. A summary of the synthesis of the new ligand **3** is shown in Scheme I. This ligand was synthesized in an overall yield of about 60%. Ligand **3** readily complexes with the Ru(II) starting complex, *trans*-RuBr$_2$(Me$_2$SO)$_4$, in a variety of solvents including toluene, methylene chloride, chloroform, methanol, and 2-methoxyethanol, at their reflux temperatures. Chromatography on silica gel of each reaction mixture indicates that only one product is formed. Isolation and chemical analysis confirm the formulation of this complex as the six-coordinate RuBr$_2$(Me$_2$SO)[EtS(CH$_2$)$_3$SO(CH$_2$)$_3$SEt] species.

In order to identify the structure of this complex, standard spectroscopic techniques were employed, including IR spectra, ^{1}H NMR, and ^{13}C NMR. The solid-state IR spectra of both **4** and **5** reveal two S → O sulfoxide stretching absorptions at 1074 and 1081 cm^{-1}. The sulfoxide stretch in the free ligand occurs at 1025 cm^{-1}. This frequency shift indicates that the sulfoxide ligands (**3** and Me$_2$SO) are S-bound in these complexes.[8] The electronic spectrum of **4** shows two bands in the UV/Vis region: λ^{max} (ϵ) = 27 000 (665) and 37 300 cm^{-1} (5800). Similarly, complex **5** also shows two bands: λ^{max} (ϵ) = 28 000 (610) and 38 600 (2970). The intensities of the "d–d" band at 27 000 cm^{-1} in **4** and 28 000 cm^{-1} in **5** suggest that these complexes possess a *cis*-dihalo structure with lower symmetry rather than a *trans*-dihalo structure,[9] but this interpretation is not conclusive.

Solution ^{1}H NMR studies of the symmetrical free ligand reveal three sets of multiplets: a sharp triplet of methyl resonances at δ 1.14, a broad quintet at δ 2.05 due to the central methylene H atoms of the trimethylene linkage, and a complex multiplet at about δ 2.7 corresponding to the two different types of methylene H atoms α to the S atom and α to the sulfoxide group.[8a,10] Complexation of this ligand to yield **4** or **5** gives simplified ^{1}H NMR spectrum. There is still a sharp triplet in each complex from a methyl group at about δ 1.15 that indicates the equivalency of the terminal SEt groups of ligand **3**. In addition, ^{1}H NMR spectra of **4** and **5** contain broad resonances at δ 2.5, a broad multiplet at δ 3.2, and two peaks in the ratio 3:2 at δ 3.4 and 3.5. These correspond to the coordinated S-bound sulfoxide groups[8a] of the Me$_2$SO ligand and ligand **3**, respectively. The ^{13}C NMR spectrum of ligand **3** reveals five resonances. These occur at δ 14.7 (methyl), 22.4 (CH$_2$), 25.6 (SCH$_2$), 30.3 (SCH$_2$), and 50.7 (OSCH$_2$).[11] The ^{13}C NMR spectrum of complex **4** shows a seven-line pattern with resonances at δ 13.3, 14.7, 19.4, 29.1, 31.7, 46.9, and 53.4. The far downfield shifts of the last two resonances are consistent with the assignment of these resonances to two different types of C atoms α to the sulfoxide groups from the Me$_2$SO ligand and ligand **3**.[11] The resonances at δ 29.1 and 31.7 result from two symmetry-equivalent pairs of C atoms α to thioether linkages. INEPT experiments indicate that the resonances at δ 13.3 and 19.4 are due to methylene resonances. The resonance at δ 14.7 is due to the equivalent methyl groups. The ^{13}C NMR of complex **5** is more symmetrical than that of **4**, showing a clean six-line spectrum consistent with a symmetrical

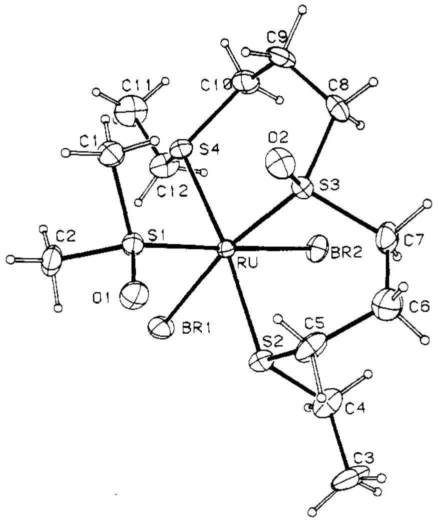


Figure 1. Perspective drawing of complex **5**, dibromo(dimethyl sulfoxide)(3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane)ruthenium(II), illustrating 50% probability ellipsoids. The H atoms are drawn artificially small.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for **5**

Ru–Br(1)	2.601 (1)	Ru–Br(2)	2.578 (1)
Ru–S(1)	2.275 (2)	Ru–S(2)	2.393 (2)
Ru–S(3)	2.235 (2)	Ru–S(4)	2.372 (2)
S(1)–O(1)	1.463 (6)	S(1)–C(1)	1.779 (8)
S(1)–C(2)	1.766 (10)	S(2)–C(4)	1.807 (8)
S(2)–C(5)	1.800 (9)	S(3)–O(2)	1.481 (6)
S(3)–C(7)	1.795 (8)	S(3)–C(8)	1.805 (9)
S(4)–C(10)	1.823 (10)	S(4)–C(12)	1.801 (10)
Br(1)–Ru–Br(2)	86.4 (1)	Br(1)–Ru–S(1)	92.2 (1)
Br(2)–Ru–S(1)	176.4 (1)	Br(1)–Ru–S(2)	82.2 (1)
Br(2)–Ru–S(2)	95.4 (1)	S(1)–Ru–S(2)	87.7 (1)
Br(1)–Ru–S(3)	170.9 (1)	Br(2)–Ru–S(3)	88.9 (1)
S(1)–Ru–S(3)	93.0 (1)	S(2)–Ru–S(3)	90.6 (1)
Br(1)–Ru–S(4)	93.7 (1)	Br(2)–Ru–S(4)	89.3 (1)
S(1)–Ru–S(4)	87.5 (1)	S(2)–Ru–S(4)	173.5 (1)
S(3)–Ru–S(4)	94.0 (1)	Ru–S(1)–O(1)	117.4 (3)
Ru–S(1)–C(1)	114.2 (3)	Ru–S(1)–C(2)	112.8 (4)
C(1)–S(1)–C(2)	97.1 (4)	Ru–S(2)–C(4)	113.8 (3)
Ru–S(2)–C(5)	108.4 (3)	C(4)–S(2)–C(5)	102.4 (5)
Ru–S(3)–O(2)	119.5 (3)	Ru–S(3)–C(7)	109.9 (3)
Ru–S(3)–C(8)	113.3 (3)	C(7)–S(3)–C(8)	98.3 (4)
Ru–S(4)–C(10)	110.9 (3)	Ru–S(4)–C(12)	111.8 (3)
C(10)–S(4)–C(12)	99.7 (5)		

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(11) To aid in these assignments, ^{13}C NMR spectra of the previously characterized *trans*-RuCl$_2$(SMe$_2$)$_4$ and *trans*-RuBr$_2$(SMe$_2$)$_3$(Me$_2$SO) complexes were compared. For *trans*-RuCl$_2$(SMe$_2$)$_4$, a single resonance at δ 19.5 was observed. For *trans*-RuCl$_2$(SMe$_2$)$_3$(Me$_2$SO) the methyl groups of the two nonequivalent types of SMe$_2$ ligands occur at δ 18.5 and 19.8, while the methyl resonances of the Me$_2$SO ligand occur far downfield at δ 43.3.[3]

structure with resonances at δ 12.7, 19.1, 29.2, 29.5, 45.3, and 53.0. The far downfield shifts of the last two resonances are again consistent with two different types of C atoms α to sulfoxide groups. The resonances at δ 29.2 and 29.5 result from C atoms α to thioether linkages. Unlike the case of complex **4**, there is only one resonance for the central methylene carbons. INEPT experiments indicate that the resonance at δ 19.1 is due to these methylenes, while the singlet at δ 12.7 is due to the equivalent methyl carbon atoms.

Attempts to isomerize complex **4** result only in recovery of starting material. Refluxing complex **4** in toluene or removal of the bromide ions in alcohol solvents with $AgBF_4$ followed by treatment with LiBr gives only original complex **4**. Additionally, in solution neither complex **4** nor **5** reacts with O_2 even at high pressures (250 psi) or elevated temperatures (105 °C).

A perspective drawing of complex **4** as determined by the crystal structure analysis is shown in Figure 1. Bond lengths and bond angles are given in Table III. The structure of each complex corresponds to the geometry of isomer D (Figure 1 in the first paper of this series) and consists of an octahedral Ru(II) complex with each sulfoxide ligand coordinated trans to a bromide ion. The tridentate ligand coordinates meridionally to the metal ion.

Discussion

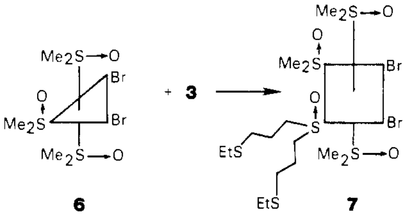
Crystal Structures of 4 and 5. The structures of **4** and **5** represent the first observations of a RuSCCCS six-membered chelate ring. A search of the Cambridge crystallographic database yielded examples of metalladithiacyclohexane chelate rings with other transition metals whose conformations can be compared with those of complexes **4** and **5**. A wide variety of conformations have been documented. Chair conformers occur most frequently and are observed in the structure of $[CH_2(CH_2S(CH_2)_2PPh_2)_2NiI]BPh_4$,[12] $[CH_2(CH_2S(CH_2)_2PPh_2)_2Ni](ClO_4)_2$,[13] and $(CH_2(CH_2S\text{-}t\text{-}Bu)_2)W(CO)_4$.[14] The chelate ring of *fac*-$Cr(CO)_3((EtS_2C)_2CS(CH_2)_3S)$[15] and one of the chelate rings of $MoO(S(CH_2)_3S)_2$[16] have boat conformations. Another chelate ring of $MoO(S(CH_2)_3S)_2$ and the three chelate rings of $Mo_2O_2(\mu\text{-}N_3)(S(CH_2)_3S)_3$[16] have twist-boat conformations. The six-atom chelate rings of **4** and **5** have distinctly different conformations that prevent the structures from crystallizing on the mirror plane in the higher symmetry space group $P2_1/m$. The chelate ring containing the atoms S(3) and S(4) has a distorted chair conformation. The other chelate ring has a twist-boat conformation in which the atoms Ru, S(2), S(3), and C(6) are approximately coplanar and the atoms C(5) and C(7) are equidistant from opposite sides of that plane. These conformations correspond to the two lowest energy conformers for a six-atom chelate ring.[17] As a consequence of the nonequivalence of the two chelate rings, atom S(3) is chiral and requires the complex to crystallize in the optically active space group. The stereochemical nonequivalence of the chelate rings also explains the magnetic nonequivalence of the two central C atoms of the trimethylene-containing chelate rings in complex **4**. Figure 1 shows that these two methylene C atoms are in much different environments in the solid state. The ^{13}C NMR results suggest that even in solution these chelate rings are nonequivalent. Although the chelate rings of chloro complex **5** have virtually the same geometries as those of **4** in the solid state, in solution the chelate rings of complex **5** are equivalent by ^{13}C NMR spectroscopy. Also, the Ru–S–C–C linkages involving the terminal ethyl moieties are oriented trans in order to minimize the steric interactions involving these groups.

The Ru–S bond lengths to the sulfoxide ligands (2.275 (2) and 2.235 (2) Å in **4** and 2.269 (1) and 2.218 (1) Å in **5**) are similar to those observed in other structures with halide ligands trans to S-bonded sulfoxide ligands (2.252 (2)–2.273 (5) Å in the $RuCl_3(Me_2SO)_3^-$ ion[18] and 2.277 (1) Å in $RuCl_2(Me_2SO)_4$[19]). Among a group of Ru(II)–S sulfoxide-containing complexes for which a ligand that is both a σ- and π-donor and non-π-acceptor is trans to the S-bound sulfoxide ligand, the Ru(II)–S bond lengths are shorter and range from 2.188 (3) Å for $Ru(NH_3)_5(Me_2SO)$[20] to 2.260 (3) Å for $Ru(Me_2SO\text{-}S)_3(Me_2SO\text{-}O)_3(BF_4)_2$.[21] These shorter Ru(II)–S bonds are expected when the π-accepting 3d π-orbital of the sulfoxide S atom is trans to a σ-donor ligand such as a halogen or O atom. These Ru–S bonds are thus expected to be stronger and less labile than the Ru–S bonds involving trans-related pairs of sulfoxide ligands, as seen in *trans*-$RuBr_2(Me_2SO)_4$ (2.360 (1) Å).[22] The Ru–S(thioether) bond lengths, 2.393 (2) and 2.372 (2) Å in **4** and 2.386 (1) and 2.365 (1) Å in **5**, are only slightly longer than the Ru–S bond length in *trans*-$RuBr_2(Me_2SO)_4$. The other bond lengths and bond angles show no unusual features.

Stereochemistry of Complexes 4 and 5. The rearrangement of the halogen ligands from trans to cis during the synthesis of complex **4** was unanticipated, since in solution under catalytic conditions only the trans disposition of halogen ligands is observed for the Ru(II) complexes with monodentate thioether and sulfoxide ligands. Since the structures of complexes **4** and **5** are retained under the reaction conditions, it is not surprising that these complexes exhibit no catalytic activity.

The observed structures of complexes **4** and **5** are apparently thermodynamically favored. The mechanism underlying the loss of the *trans*-dibromo configuration upon chelation of ligand **3** to the Ru(II) center of *trans*-$RuBr_2(Me_2SO)_4$ requires comment, especially since the same isomeric structure is obtained with the *cis*-$RuCl_2(Me_2SO)_4$ complex. The observed product stereochemistry of **4** can be rationalized assuming that chelation proceeds via a dissociative mechanism involving a five-coordinate intermediate.[23,24] Only one pathway, involving either trigonal-bipyramidal (tbp) or square-pyramidal (sp) geometries, ultimately leads to the observed geometry for complex **4**.

This pathway requires that the *cis*-dihalo geometry arises from the loss of a Me_2SO ligand followed by interconversion of the Berry type[24] to give **6** and that once the polydentate ligand is coordinated at one site, **7**, the interception of a vacated coordination site on the metal by the remaining donor functions of the polydentate ligand **3** occurs faster than the Berry type interconversions of the subsequent five-coordinate intermediates.



6 **7**

Formation of proposed intermediate **7** would be expected to be more energetically favorable since the sulfoxide-*S* ligand is a better π-acid than the thioether ligand. Since the trans-related Ru–S(sulfoxide) bonds in **7** are probably longer and thus probably more labile than the Ru–S bonds trans to the halide ions, we could anticipate that the trans-related sulfoxide ligands in intermediate **7** would be replaced by a thioether S atom of ligand **3** to yield

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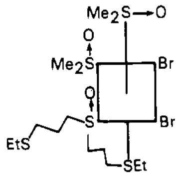
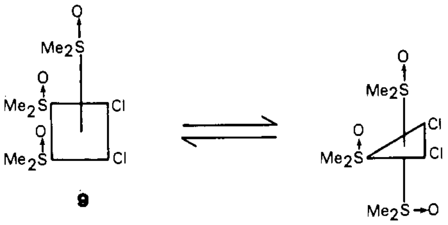
structure **8**. Loss of the dimethyl sulfoxide trans to the thioether



8

ligand of **8** followed by coordination of the remaining thioether atom of ligand **3** would produce the observed product.

For cis-chloro complex **5**, displacement of the more weakly bound axial O-bound sulfoxide of the *cis*-$RuCl_2(Me_2SO)_4$ complex should occur first[10] to form a square-pyramidal intermediate complex, **9**.



9 **10**

Such an intermediate is actually the initial intermediate along the reaction coordinate of the Berry interconversion that yields **6**. Interconversion of **9** would generate the five-coordinate complex **10**, which has the same geometry as complex **6**. The subsequent complexation of ligand **3** should occur via the same pathway as outlined above for the bromo complex. Thus, while the occurrence of the same structure for complexes **4** and **5** is surprising, it can be rationalized as a logical consequence of this substitution model. This observation provides additional support for such an interpretation of the mode of coordination of tridentate ligand **3** to ruthenium(II).

The surprising inertness of complexes **4** and **5** toward oxygen oxidation can be understood by examining the oxidation potential of each complex. In methylene chloride solution, both **4** and **5** exhibit one irreversible one-electron oxidation by cyclic voltammetry, at 1.45 and 1.42 V, respectively. Such high oxidation potentials reveal that these complexes are very difficult to oxidize. Thus, such structures would be poor candidates for the oxygen-active species formed in these catalytic systems. Further, the high oxidation potential of these complexes also points to enhanced stability of the highest occupied molecular orbital (HOMO) of this isomer relative to that of the other isomers of this stoichiometry.[3] It is also interesting to note that the geometry of these complexes is different from those previously observed with other ligands, and we find that complexes **4** and **5** each oxidize at a potential very different from those observed with other isomers.[3b]

The problem of synthesizing an all-trans complex is clearly more complex than one might imagine. It appears that controlling the stereochemistry of such isomeric complexes is difficult due to the interconversion of five-coordinate intermediates via a pseudorotation process.

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Registry No. **1**, 101810-60-0; **2**, 101810-61-1; **3**, 101810-62-2; **4**, 101834-82-6; **5**, 101834-83-7; NaSEt, 811-51-8; *trans*-$RuBr_3(Me_2SO)_4$, 72904-46-2; *cis*-$RuCl_2(Me_2SO)_4$, 59091-96-2; 3,3′-thiodipropanol, 10595-09-2.

Supplementary Material Available: Listings of crystal data, data collection details, and atomic coordinates for **4** and anisotropic thermal parameters, H atom coordinates, bond lengths, bond angles, and torsion angles for the chelate rings for both **4** and **5** (11 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (25 pages), are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Ruthenium(II)-Catalyzed Thioether Oxidation. 3. Syntheses and Structure of Model Complexes with the New Linear Tridentate Ligand Bis(3-(ethylsulfinyl)propyl) Sulfide

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Received November 1, 1984

A new tridentate mixed-sulfur-donor ligand, bis(3-(ethylsulfinyl)propyl) sulfide (BEPS) (**3**), has been synthesized, and its reaction with *trans*-$RuBr_2(\overline{S(CH_2)_3CH_2})_4$ has been carried out in an attempt to synthesize an *all-trans*-$RuBr_2$(thioether)$_2$(sulfoxide)$_2$ complex. Under a variety of conditions only the same two isomers are obtained: *mer*-(BEPS)-*cis*-Br_2(THT)Ru (**9**) and *fac*-(BEPS)-*cis*-Br_2(THT)Ru (**10**; the major isomer) (THT = tetrahydrothiophene). ^{13}C and ^1H NMR studies indicate **9** to be highly symmetrical by contrast with **10**. The ^{13}C NMR spectrum of the major isomer, **10**, exhibited 11 resonances, which is only consistent with an all-cis, folded structure. The ^{13}C NMR spectrum of the minor isomer, **9**, exhibited seven resonances, which is consistent with several other symmetrical isomers. A single-crystal structure determination of **9** reveals this complex to possess a six-coordinate pseudooctahedral structure consisting of trans-sulfoxide donors, cis-bromo donors, and cis-thioether donors. The complex has pseudomirror symmetry through the Ru(II) ion, the bromo donors, and the thioether donors. The tridentate ligand coordinates meridionally to the Ru(II) ion with six-atom chelate rings in distorted chair conformations. Selected geometrical details are Ru–Br(1) = 2.564 (1) Å, Ru–Br(2) = 2.574 (1) Å, Ru–S(1) = 2.321 (1) Å, Ru–S(2) = 2.340 (1) Å, Ru–S(3) = 2.355 (1) Å, Ru–S(4) = 2.351 (1) Å, and Br–Ru–Br = 93.3 (1)°. The crystals are monoclinic, $P2_1/n$ (nonstandard setting of No. 14), with $a = 10.742$ (1) Å, $b = 12.890$ (2) Å, $c = 15.771$ (2) Å, $\beta = 101.41$ (1)°, and $Z = 4$. Least-squares refinement of the structure on the basis of 2867 unique reflections with $|F| > 4\sigma(|F|)$ has produced $R = 0.034$ and $R_w = 0.038$.

Introduction

In the first paper of this series we reported that an all-trans Ru(II) complex with the stoichiometry $RuX_2(SR_2)_2(R_2SO)_2$ (**1**)[2] is the probable structure for the most oxygen-active species leading to catalysis in these thioether oxidation systems.[3,4]

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