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Ruthenium(II) Chloride Complexes of the Mesocyclic Ligand 1,5-Dithiacyclooctane 1-Oxide. Preparation and Structure of the "All-Trans" Complex

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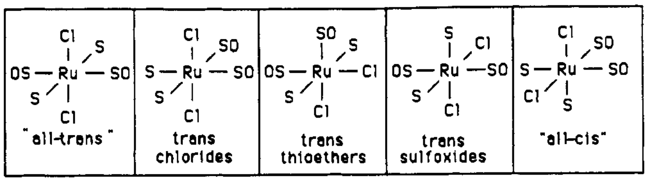
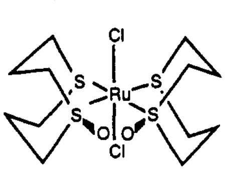
Syntheses and crystal structures of *trans*-RuCl$_2$(1,5-DTCO)$_2$ (**1**) (1,5-DTCO = 1,5-dithiacyclooctane), *cis*-RuCl$_2$(1,5-DTCO-O)$_2$ (**2**) (1,5-DTCO-O = 1,5-dithiacyclooctane 1-oxide), *trans*-RuCl$_2$(1,5-DTCO-O)$_2$ (**3**), a complex having four different ligands attached to ruthenium, [RuCl(1,5-DTCO-O)(1,5-DTCO)(THT)]BPh$_4$ (**4**) (THT = tetrahydrothiophene), and a complex in which one 1,5-DTCO-O ligand has been replaced by two DMSO ligands, RuCl$_2$(1,5-DTCO-O)$_2$(DMSO)$_2$ (**5**), are described. Complex **2** is the first example of a complex having a cis arrangement of mesocyclic bidentate ligands. Complex **3** is the first isolated example of a RuX$_2$(R$_2$S)$_2$(R$_2$SO)$_2$ complex in which all the functional groups are trans. The trans complex **3**, relative to the cis complex **2**, has a longer Ru-S(O) bond distance of 2.298 (4) Å (compared to 2.239 (3) Å), a shorter Ru-Cl bond distance of 2.413 (4) Å (compared to 2.467 (3) Å), and a shorter S-O bond distance of 1.459 (12) Å (compared to 1.485 (8) Å). The ^{13}C NMR spectrum of **1** in CHCl$_3$ reveals partial dissociation, while **2** and **3** give a more complicated pattern. In DMSO-d_6, **2** predominantly retains its structure but **3** undergoes further dissociation to give a pentacovalent complex and **5**. Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K are as follows. **1**: a = 12.183 (6) Å, b = 12.960 (8) Å, c = 10.479 (3) Å, Z = 4; space group *Pbca*; R = 0.037 (R_w = 0.039). **2**: a = 27.054 (9) Å, b = 16.274 (5) Å, c = 7.860 (3) Å, Z = 8; space group *Fdd*2; R = 0.045 (R_w = 0.043). **3**: a = 11.555 (4) Å, b = 12.789 (6) Å, c = 12.089 (4) Å, Z = 4; space group *Pcab*; R = 0.054 (R_w = 0.056). **4**: a = 10.548 (3) Å, b = 23.210 (5) Å, c = 15.427 (4) Å, β = 93.85 (2)°, Z = 4; space group $P2_1/n$; R = 0.066 (R_w = 0.055).

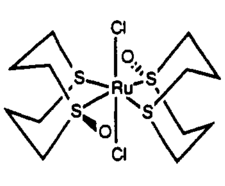
Introduction

An "all-trans" relationship of thioether, sulfoxide, and halide groups in an octahedral ruthenium(II) complex is reported to describe the active species in the catalytic oxidation of thioethers to sulfoxides with oxygen.[1] In a series of articles by Riley and Oliver,[1-3] several approaches to the synthesis of a ruthenium(II) complex having this arrangement of donor atoms were reported, but each approach was unsuccessful and no molecule having this special geometry could be prepared. In our previous studies of complexes of eight-membered-ring bidentate ligands, we had observed that substituents on the heteroatoms are always constrained to lie in the plane of the metal and the two donor atoms.[4-6] Because of this relationship, we thought that in ruthenium complexes in which the chlorides were in trans positions, the sulfoxide groups could not occupy cis positions because the oxygen atoms would sterically interact with one another in the equatorial plane. Therefore, the all-trans complex would be sterically favored.





Cis sulfoxides in equatorial plane



Trans sulfoxides in equatorial plane

We wish to report the synthesis and X-ray crystal structure of the all-trans complex by treatment of *trans*-RuCl$_2$(1,5-DTCO)$_2$ (1,5-DTCO = 1,5-dithiacyclooctane) with 1,5-dithiacyclooctane 1-oxide (1,5-DTCO-O). In addition to the all-trans complex, a complex with trans thioethers (the first example of a cis arrangement of mesocyclic bidentate ligands) and a complex of 1,5-DTCO itself with trans chlorides have been prepared. An unusual complex having four different ligands (Cl, tetrahydrothiophene (THT), 1,5-DTCO, and 1,5-DTCO-O) attached to ruthenium and a complex with one 1,5-DTCO-O and two DMSO ligands have also been prepared and characterized.

Experimental Section

All reactions were carried out under dry nitrogen with dry degassed solvents. Infrared spectra were recorded as KBr pellets on an IBM IR32 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 FT NMR spectrometer operating at 300 MHz.

Cyclic voltammograms were recorded on a BAS CV-27 potentiostat at sweep rates of 100-500 mV/s. All samples were measured in 0.01 M tetra-*n*-butylammonium tetrafluoroborate in chloroform and methylene chloride. The supporting electrolyte was recrystallized from an ethyl acetate-hexane solution. The methylene chloride was distilled from CaH$_2$ while under nitrogen. The chloroform was shaken with concentrated H$_2$SO$_4$, washed twice with water, dried over CaCl$_2$, distilled under nitrogen, and stored over molecular sieves. Both the methylene chloride and chloroform were degassed by the freeze-thaw method prior to use. All experiments were done in a three-compartment, three-electrode cell composed of a platinum working electrode, a platinum-wire auxiliary electrode, and a Ag/AgCl reference electrode.

Structure Determination and Refinement. The main details of the crystal data, data collection methods, and refinement procedures for **1**-**4** are given in Table I. Full listings of bond lengths and angles, hydrogen atom coordinates, and calculated and observed structure factors for the above complexes and **5** are provided as supplementary material.

Crystals of the title complexes were coated with a hydrocarbon oil to retard decomposition, attached to a glass fiber with silicone grease, and mounted in a cold stream of a Syntax P2$_1$ graphite monochromator-diffractometer (Mo Kα, λ = 0.71069 Å), equipped with a locally modified LT-1 low-temperature device (T = 130 K). No decay in the intensity of standard reflectons was observed during data collection. Solution of the structure was accomplished by the Patterson technique. All computing was carried out with the SHELXTL version 5 program installed on a Data General Eclipse computer. Atomic scattering factors and anomalous dispersion corrections were from common sources.[7] An absorption correction[8] was applied, and structural refinement proceeded smoothly in the case of all compounds. All non-hydrogen atoms were assigned anisotropic thermal parameters except those of compound (**2**) for which only the non-hydrogen and non-carbon atoms were assigned anisotropic thermal parameters. Hydrogen atoms were refined by using a riding model in which an idealized C-H vector 0.96 Å in length was recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal pa-

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(1) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1986**, *25*, 1814.
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(6) Love, L. M.S. Dissertation, University of California, Davis, 1983.
(7) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1976; Vol. IV.
(8) Program XABS was written by H. Hope and B. Moezzi. The program obtains an absorption tensor from $F_o - F_c$ difference: Moezzi, B. Ph.D. Dissertation, University of California, Davis, 1987.

0020-1669/91/1330-0440$02.50/0

Table I. Summary of Crystal Data, Data Collected, and Structure Refinement Parameters for Compounds **1–4**[a]

	1	**2**	**3**	**4**
formula	$RuCl_2(C_6H_{12}S_2)_2$	$RuCl_2(C_6H_{12}S_2O)_2$	$RuCl_2(C_6H_{12}S_2O)_2$	$[RuCl(C_4H_8S)(C_6H_{12}S_2)(C_6H_{12}S_2O)]BPh_4$
fw	468.54	500.54	500.54	845.78
cryst system	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group (No.)	*Pcba* (61)	*Fdd*2 (43)	*Pcab* (61)	$P2_1/n$ (14)
a, Å	10.470 (3)	27.054 (9)	11.555 (4)	10.541 (3)
b, Å	12.960 (8)	16.274 (5)	12.789 (6)	23.199 (5)
c, Å	12.183 (6)	7.860 (3)	12.089 (4)	15.414 (4)
β, deg				93.85 (2)
V, Å^3	1653 (2)	3460 (2)	1786 (1)	3760 (1)
Z	4	8	4	4
cryst dimens, mm	0.2 × 0.14 × 0.13	0.13 × 0.14 × 0.24	0.25 × 0.23 × 0.13	0.26 × 0.23 × 0.15
ρ_{calcd}, g cm$^{-}_{3}$	1.88	1.92	1.86	1.49
μ(Mo Kα), cm^{-1}	17.29	16.66	19.20	7.48
range of transm fctrs	0.50–0.68	0.49–0.69	0.34–0.66	0.65–0.83
R_b	0.037	0.045	0.054	0.066
R_w[b]	0.039	0.043	0.056	0.055

[a] $F > 4\sigma(R)$ for **1–4**. [b] $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||/w^{1/2}$, where $w = 1/\sigma^2(F_o)$ for **1–4**.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for *trans*-$RuCl_2$(1,5-DTCO)$_2$ (**1**)

	x	*y*	*z*	*U*[a]
Ru	0	0	5000	13 (1)
C(1)	324 (1)	−1010 (1)	6672 (1)	21 (1)
S(1)	159 (1)	1529 (1)	6020 (1)	16 (1)
S(2)	2224 (1)	163 (1)	4789 (1)	17 (1)
C(1)	1255 (5)	1373 (4)	7157 (4)	22 (2)
C(2)	2666 (5)	1096 (4)	6929 (4)	24 (2)
C(3)	2987 (5)	226 (4)	6133 (4)	22 (2)
C(4)	2609 (5)	1397 (4)	4174 (4)	20 (2)
C(5)	2259 (5)	2390 (4)	4781 (4)	21 (2)
C(6)	898 (5)	2541 (4)	5207 (4)	19 (1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for *trans*-$RuCl_2$(1,5-DTCO)$_2$ (**1**)

Ru–Cl	2.445 (1)	S(2)–C(3)	1.824 (5)
Ru–S(2)	2.352 (1)	S(1)–C(6)	1.817 (5)
Ru–S(1A)[a]	2.345 (1)	S(2)–C(4)	1.811 (5)
S(1)–C(1)	1.810 (5)		
Cl–Ru–S(1)	90.1 (1)	Ru–S(2)–C(3)	109.9 (2)
S(1)–Ru–S(2)	84.9 (1)	C(3)–S(2)–C(4)	103.5 (2)
S(1)–Ru–Cl(A)[a]	89.9 (1)	Cl–Ru–S(2)	90.1 (1)
Cl–Ru–S(1A)[a]	89.9 (1)	S(1)–Ru–S(2A)[a]	95.1 (1)
S(2)–Ru–S(2A)[a]	180.0 (1)	Ru–S(1)–C(1)	110.9 (2)
Ru–S(1)–C(6)	110.6 (2)	Ru–S(2)–C(4)	110.2 (2)

[a] A = −*x*, −*y*, 1 − *z*.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for *cis*-$RuCl_2$(1,5-DTCO-O)$_2$ (**2**)

	x	*y*	*z*	*U*
Ru	2500	2500	5000	10 (1)[a]
Cl	2228 (1)	3397 (2)	7350 (5)	19 (1)[a]
S(1)	2369 (1)	3562 (2)	3246 (4)	14 (1)[a]
S(2)	3329 (1)	2954 (2)	5057 (5)	16 (1)[a]
O	1862 (3)	3745 (4)	2632 (12)	16 (2)
C(1)	2549 (4)	4510 (7)	4254 (16)	22 (3)
C(2)	3092 (4)	4627 (7)	4707 (16)	21 (3)
C(3)	3342 (4)	4002 (7)	5818 (18)	24 (3)
C(4)	3583 (4)	3102 (7)	2916 (15)	19 (3)
C(5)	3242 (4)	3073 (7)	1444 (18)	26 (3)
C(6)	2783 (4)	3596 (8)	1441 (18)	25 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

rameter of the bonded atom. Further details are given in Table I. Atom coordinates for **1–4** are given in Tables II, IV, VI, and VIII respectively. Computer-generated thermal ellipsoidal plots of **1–4** are given in Figures 1–4, respectively. A computer-generated thermal ellipsoidal plot of **5** is also given as supplementary material.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for *cis*-$RuCl_2$(1,5-DTCO-O)$_2$ (**2**)

Ru–Cl	2.467 (3)	S(1)–C(6)	1.807 (13)
Ru–S(1)	2.239 (3)	S(2)–C(3)	1.808 (12)
Ru–S(2)	2.363 (2)	S(2)–C(4)	1.834 (12)
S(1)–C(1)	1.802 (11)	S(1)–O	1.485 (8)
Cl–Ru–S(1)	87.5 (1)	Ru–S(2)–C(4)	112.3 (4)
S(1)–Ru–S(2)	85.4 (1)	Cl–Ru–S(2)	94.8 (1)
S(1)–Ru–Cl(A)[a]	164.8 (1)	S(1)–Ru–S(1A)[a]	104.0 (2)
S(2)–Ru–S(1A)[a]	95.9 (1)	Ru–S(2)–C(3)	108.6 (4)
Cl–Ru–S(2A)[a]	83.5 (1)	Ru–S(1)–O	120.1 (3)
S(2)–Ru–S(2A)[a]	177.8 (2)	O–S(1)–C(1)	102.7 (5)
Ru–S(1)–C(6)	114.2 (4)	O–S(1)–C(6)	108.1 (6)
C(1)–S(1)–C(6)	98.7 (6)	S(1)–Ru–S(1A)[a]	104.0 (2)
S(1)–Ru–Cl(A)[a]	83.0 (1)		

[a] A = 0.5 − *x*, 0.5 − *y*, *z*.

Table VI. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^3) for *trans*-$RuCl_2$(1,5-DTCO-O)$_2$ (**3**)

	x	*y*	*z*	*U*[a]
Ru	10000	0	0	14 (1)
Cl	8425 (4)	−1137 (3)	−520 (3)	20 (1)
S(1)	8832 (4)	1428 (3)	−292 (3)	20 (1)
S(2)	9278 (5)	85 (3)	1823 (3)	26 (1)
O	8778 (13)	1907 (9)	−1386 (10)	42 (5)
C(1)	9175 (18)	2491 (12)	645 (14)	30 (5)
C(2)	9072 (18)	2335 (13)	1874 (14)	36 (6)
C(3)	9563 (15)	1365 (12)	2421 (13)	28 (5)
C(4)	7663 (14)	−25 (13)	1817 (12)	28 (5)
C(5)	7014 (14)	829 (13)	1211 (13)	26 (5)
C(6)	7329 (15)	1135 (11)	54 (14)	27 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VII. Selected Bond Lengths (Å) and Bond Angles (deg) for *trans*-$RuCl_2$(1,5-DTCO-O)$_2$ (**3**)

Ru–Cl	2.413 (4)	S(1)–C(6)	1.826 (18)
Ru–S(1)	2.298 (4)	S(2)–C(3)	1.820 (17)
Ru–S(2)	2.359 (4)	S(2)–C(4)	1.871 (17)
S(1)–C(1)	1.814 (17)	S(1)–O	1.459 (12)
Cl–Ru–S(1)	89.8 (1)	Cl–Ru–S(2)	90.2 (2)
S(1)–Ru–S(2)	84.2 (1)	S(1)–Ru–S(1A)[a]	180.0 (1)
Ru–S(1)–C(1)	111.8 (6)	S(1)–Ru–S(2A)[a]	95.8 (1)
Ru–S(1)–C(6)	111.1 (5)	Ru–S(1)–O	119.9 (6)
C(1)–S(1)–C(6)	102.6 (8)	Ru–S(2)–C(3)	110.4 (6)
Ru–S(2)–C(4)	110.2 (5)	O–S(1)–C(1)	105.1 (7)
C(3)–S(2)–C(4)	104.4 (8)	O–S(1)–C(6)	104.7 (8)

[a] A = 2 − *x*, −*y*, −*z*.

Materials. The ligands 1,5-dithiacyclooctane (1,5-DTCO)[9] and 1,5-dithiacyclooctane 1-oxide[10] (1,5-DTCO-O) were synthesized as previously

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$) for [RuCl(THT)(1,5-DTCO)(1,5-DTCO-O)]BPh_4 (**4**)

	x	*y*	*z*	*U*
Ru	2699 (1)	5748 (1)	6120 (1)	17 (1)1*a*
Cl	2376 (2)	5210 (1)	4750 (1)	22 (1)[a]
S(1)	2820 (2)	6093 (1)	7501 (2)	25 (1)[a]
S(2)	2856 (2)	4834 (1)	6782 (1)	22 (1)[a]
S(3)	4902 (2)	5802 (1)	5941 (1)	22 (1)[a]
S(4)	2583 (2)	6624 (1)	5354 (2)	24 (1)[a]
S(5)	420 (2)	5770 (1)	6074 (2)	26 (1)[a]
O	2859 (18)	6710 (7)	7628 (11)	73 (8)[a]
C(1)	1608 (8)	5770 (4)	8140 (6)	28 (3)[a]
C(2)	1497 (8)	5120 (4)	8280 (5)	23 (3)[a]
C(3)	1568 (8)	4727 (4)	7494 (6)	26 (3)[a]
C(4)	4289 (8)	4811 (4)	7507 (6)	30 (3)
C(5)	4493 (9)	5222 (4)	8267 (6)	37 (4)[a]
C(6)	4256 (9)	5858 (4)	8103 (5)	32 (4)[a]
C(7)	5104 (8)	5816 (4)	4783 (5)	25 (3)[a]
C(8)	4632 (8)	6343 (4)	4292 (6)	32 (4)[a]
C(9)	3255 (9)	6520 (4)	4325 (5)	29 (3)[a]
C(10)	3655 (9)	7179 (4)	5840 (6)	28 (3)[a]
C(11A)	4638 (14)	6992 (6)	6458 (10)	26 (5)
C(11B)	5109 (28)	7063 (12)	5968 (21)	26 (10)
C(12)	5594 (9)	6505 (4)	6264 (6)	30 (3)[a]
C(13)	−241 (8)	5866 (4)	4963 (5)	29 (3)[a]
C(14)	−1345 (9)	6280 (4)	5060 (7)	41 (4)[a]
C(15)	−857 (9)	6759 (4)	5650 (6)	34 (4)[a]
C(16)	−150 (9)	6476 (4)	6434 (6)	32 (4)[a]
B	2478 (9)	1388 (4)	3674 (7)	19 (3)[a]
C(17)	3041 (8)	1785 (3)	2892 (5)	21 (3)[a]
C(18)	2582 (9)	2337 (4)	2659 (6)	25 (3)[a]
C(19)	3104 (10)	2676 (4)	2033 (6)	35 (4)[a]
C(20)	4156 (10)	2498 (4)	1636 (6)	42 (4)[a]
C(21)	4689 (9)	1968 (4)	1872 (6)	35 (4)[a]
C(22)	4131 (8)	1623 (4)	2480 (6)	26 (3)[a]
C(23)	3202 (8)	1636 (3)	4559 (5)	21 (3)[a]
C(24)	2643 (10)	1991 (4)	5151 (5)	30 (3)[a]
C(25)	3325 (10)	2213 (4)	5899 (6)	34 (4)[a]
C(26)	4598 (10)	2093 (4)	6037 (6)	39 (4)[a]
C(27)	5181 (9)	1747 (4)	5468 (5)	29 (3)[a]
C(28)	4502 (8)	1525 (4)	4757 (5)	25 (3)[a]
C(29)	909 (8)	1437 (4)	3709 (5)	21 (3)[a]
C(30)	383 (9)	1156 (4)	4405 (5)	27 (3)[a]
C(31)	−934 (9)	1160 (4)	4508 (6)	43 (4)[a]
C(32)	−1768 (9)	1431 (4)	3930 (7)	38 (4)[a]
C(33)	−1260 (9)	1708 (4)	3224 (6)	34 (4)[a]
C(34)	32 (8)	1700 (4)	3118 (6)	24 (3)[a]
C(35)	2772 (7)	701 (4)	3537 (5)	22 (3)[a]
C(36)	3103 (8)	333 (4)	4219 (5)	21 (3)[a]
C(37)	3271 (8)	−262 (4)	4115 (6)	26 (3)[a]
C(38)	3095 (8)	−500 (4)	3305 (6)	25 (3)[a]
C(39)	2758 (8)	−152 (4)	2587 (6)	25 (3)[a]
C(40)	2617 (8)	431 (4)	2711 (5)	22 (3)[a]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

described. The syntheses of *cis*-$RuCl_2(DMSO)_4$[11] and $RuCl_2(THT)_4$[1] are reported elsewhere. Tetrahydrothiophene was purchased from Aldrich Chemical Co. and distilled prior to use.

***trans*-Dichlorobis(1,5-dithiacyclooctane)ruthenium(II) (1).** In 5 mL of chloroform, 1.10 g (7.42 mmol) of 1,5-DTCO was added dropwise to 50 mL of a refluxing solution of chloroform containing 0.179 g (0.342 mmol) of $RuCl_2(THT)_4$. After refluxing for 2 h, the solution was cooled and stored at −10 °C overnight. An orange solid was collected by suction filtration, washed with diethyl ether, and dried under reduced pressure. TLC analysis showed three spots in 5% methanol in methylene chloride: $R_f = 0.90$, $RuCl_2(THT)_4$; $R_f = 0.35$, compound **1**; $R_f = 0.24$. Additional solid was precipitated from the filtrate by the addition of diethyl ether. TLC analyses showed both solids to be identical. The total yield was 0.113 g (70%). The same product was obtained when the reaction was run in either methylene chloride or ethanol. Orange/yellow crystals suitable for structural determination were grown by slow diffusion of diethyl ether into a methylene chloride solution of **1**. UV: $\lambda_1 = 264$ nm, $\epsilon_1 = 1820\ m^{-1}\ cm^{-1}$, $\lambda_2 = 420$ nm, $\epsilon_2 = 220\ M^{-1}\ cm^{-1}$. CV: $E_{1/2} = 0.77$

Table IX. Selected Bond Lengths (Å) and Bond Angles (deg) for [RuCl(THT)(1,5-DTCO)(1,5-DTCO-O)]BPh_4 (**4**)

Ru-Cl	2.455 (2)	Ru-S(1)	2.269 (2)
Ru-S(2)	2.353 (2)	Ru-S(3)	2.361 (2)
Ru-S(4)	2.349 (2)	Ru-S(5)	2.398 (2)
S(1)-O	1.447 (17)	S(1)-C(1)	1.827 (9)
S(1)-C(6)	1.804 (9)	S(2)-C(3)	1.821 (9)
S(2)-C(4)	1.817 (9)	S(3)-C(7)	1.814 (8)
S(3)-C(12)	1.841 (9)	S(4)-C(9)	1.797 (9)
S(4)-C(10)	1.838 (9)	S(5)-C(13)	1.818 (8)
S(5)-C(16)	1.844 (10)		
Cl-Ru-S(1)	168.9 (1)	Cl-Ru-S(2)	85.3 (1)
S(1)-Ru-S(2)	85.0 (1)	Cl-Ru-S(3)	90.3 (1)
S(1)-Ru-S(3)	95.6 (6)	S(2)-Ru-S(3)	93.3 (1)
Cl-Ru-S(4)	90.4 (1)	S(1)-Ru-S(4)	99.4 (1)
S(2)-Ru-S(4)	175.4 (1)	S(3)-Ru-S(4)	85.0 (1)
Cl-Ru-S(5)	84.6 (1)	S(1)-Ru-S(5)	90.7 (1)
S(2)-Ru-S(5)	94.2 (1)	S(3)-Ru-S(5)	170.6 (1)
S(4)-Ru-S(5)	87.1 (1)	Ru-S(1)-O	118.4 (7)

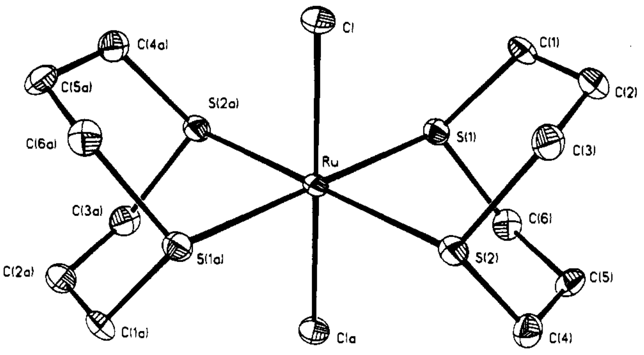

Figure 1. Molecular structure of *trans*-$RuCl_2(1,5\text{-}DTCO)_2$ (**1**), showing 50% probability ellipsoids.

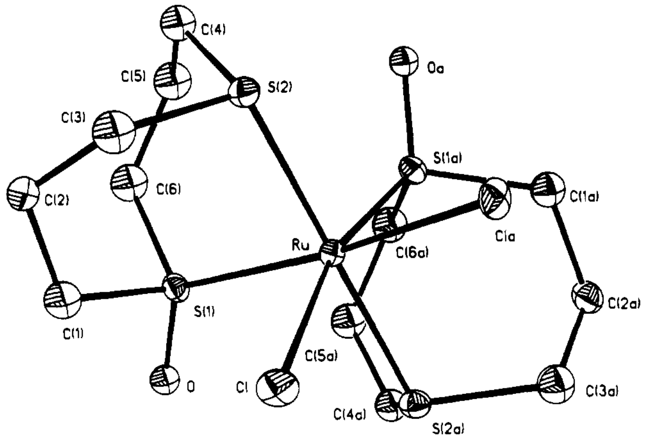

Figure 2. Molecular structure of *cis*-$RuCl_2(1,5\text{-}DTCO\text{-}O)_2$ (**2**), showing 50% probability ellipsoids.

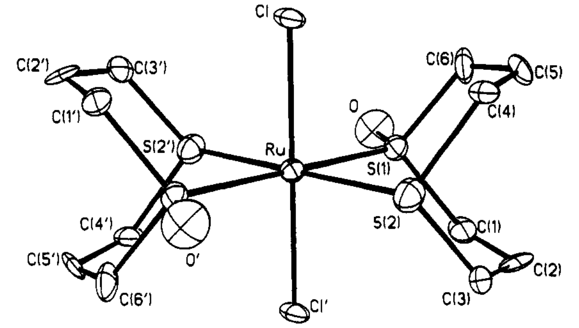

Figure 3. Molecular structure of *trans*-$RuCl_2(1,5\text{-}DTCO\text{-}O)_2$ (**3**), showing 50% probability ellipsoids.

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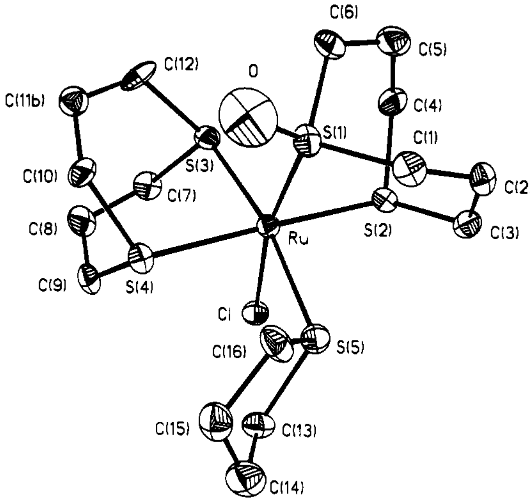

Figure 4. Molecular structure of [RuCl(THT)(1,5-DTCO)(1,5-DTCO-O)]BPh$_4$ (**4**), showing 50% probability ellipsoids.

V. IR: 352 cm^{-1} (Ru–Cl); 1035 (s) cm^{-1} (–CH$_2$– rocking). ^{1}H NMR (DMSO-d_6): δ 2.7 (m, 1 H), 2.5 (t, 2 H). ^{13}C NMR (CDCl$_3$): δ 31.28, 30.91, 30.08, 29.73, 29.31, 27.62, 26.93, 25.97, 23.97.

***cis*-Dichlorobis(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (2).** To a refluxing solution of chloroform (25 mL) containing 0.134 g (0.255 mmol) of RuCl$_2$(THT)$_4$ was added 0.27 g (1.64 mmol) of 1,5-DTCO-O. After refluxing for a few minutes, the solution turned orange and then yellow. The solution was refluxed for an additional 2 h and then cooled to −10 °C for 12 h. A yellow precipitate was collected by filtration, washed with cold chloroform, and dried under reduced pressure. Additional product was recovered by the addition of diethyl ether to the filtrate. The total yield was 0.106 g (83%). The same product was obtained when the reaction was run in either methylene chloride or ethanol. TLC in 5% methanol in methylene chloride showed only one spot at the origin. Yellow crystals suitable for structural determination were obtained by dissolving **2** in warm ethanol and a minimum amount of DMSO (approximately a 10% DMSO–ethanol mixture), cooling the mixture to −10 °C, and allowing it to stand undisturbed for several days. UV: λ_1 = 264 nm, ϵ_1 = 2465 M^{-1} λ_2 = 336 nm, ϵ_2 = 266 m^{-1} cm^{-1}. CV: $E_{1/2}$ = 0.99 V. IR: 353, 382 cm^{-1} (Ru–Cl); 1035 (s) cm^{-1} (–CH$_2$– rocking); 1070 cm^{-1} (S–O). ^{1}H NMR (DMSO-d_6): δ 3.0, 2.5, 2.1. ^{13}C NMR (DMSO-d_6): δ 52.56, 49.85, 29.64, 24.56, 24.34, 23.96.

***trans*-Dichlorobis(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (3). Method A.** To a refluxing solution of chloroform (50 mL) containing 0.037 g (7.90 × 10^{-2} mmol) of RuCl$_2$(1,5-DTCO)$_2$ was added 0.026 g (0.159 mmol) of 1,5-DTCO-O. After refluxing for 3 h, the solution was cooled to −10 °C, and the product was collected by suction filtration and dried under reduced pressure. The total yield was 0.026 g (66%). TLC showed only one product in 6% methanol in methylene chloride: R_f = 0.15. The same product was obtained when the reaction was run in chloroform or ethanol. Orange crystals suitable for structural determination were grown by slow diffusion of diethyl ether into a methylene chloride solution of *trans*-RuCl$_2$(1,5-DTCO-O)$_2$ (**3**).

Method B. In a solution of 50 mL of absolute ethanol was dissolved 1 equiv of RuCl$_2$(THT)$_4$ (0.025 g, 4.76 × 10^{-2} mmol). Two equivalents of 1,5-DTCO (0.014 g, 9.53 × 10^{-2} mmol) in 5 mL of absolute ethanol was added dropwise. One equivalent of NaIO$_4$/equiv of 1,5-DTCO ligand was added to the solution. The solution was stirred at reflux for 6 h. After the volume of the solution was reduced by half, it was cooled to −10 °C overnight. An orange precipitate was collected by vacuum filtration and dried under reduced pressure. The total yield was 0.010 g (60% yield). TLC analysis showed only one spot in 5% methanol in methylene chloride: R_f = 0.15. The same product was obtained when H$_2$O$_2$ was used as an oxidant or when O$_2$(g) was bubbled through the solution while being refluxed for 24 h. Crystals were grown as described in method A. UV: λ_1 = 245 nm, ϵ_1 = 5160 M^{-1} cm^{-1}, λ_2 = 332 nm, ϵ_2 = 194 M^{-1} cm^{-1}. CV: $E_{1/2}$ = 0.80 ; IR: 345 cm^{-1} (Ru–Cl); 1040 (s) cm^{-1} (–CH$_2$– rocking); 1080 cm^{-1} (S–O). ^{1}H NMR (CDCl$_3$): δ 3.0, 2.5, 2.0. ^{13}C NMR (DMSO-d_6): δ 52.56, 49.84, 30.51, 29.64, 29.28, 24.56, 24.33, 23.94.

Chloro(1,5-dithiacyclooctane)(1,5-dithiacyclooctane 1-oxide)(tetrahydrothiophene)ruthenium(II) Tetraphenylborate (4). A suspension of 0.255 g (0.479 mmol) of RuCl$_2$(THT)$_4$ in absolute ethanol was refluxed for 20 min. A solution of 0.143 g (0.965 mmol) of 1,5-DTCO in 5 mL of chloroform was added dropwise. After the mixture was allowed to reflux for another 20 min, 0.100 g (0.468 mmol) of 30% hydrogen peroxide dissolved in 10 mL of absolute ethanol was added dropwise to oxidize the 1,5-DTCO or 1,5-DTCO-O. The solution immediately turned dark green. Aliquots were removed and allowed to slowly diffuse into an ethanolic NaBPh$_4$ solution, and yellow crystals suitable for X-ray analysis were obtained. Addition to NaBPh$_4$ to the mother solution yielded a green precipitate. Numerous attempts to recrystallize this material proved unsuccessful. IR: 1038 cm^{-1} (–CH$_2$– rocking); 1075 cm^{-1} (S–O).

***trans*-Dichlorobis(dimethyl sulfoxide)(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (5).** *trans*-RuCl$_2$(1,5-DTCO-O)$_2$ (0.2 g, 0.4 mmol) was dissolved in warm 10% DMSO–ethanol, and the mixture was placed in the freezer (T = −10 °C). After 48 h, yellow and orange crystals formed. From the cell dimensions, the yellow crystals were found to be *cis*-RuCl$_2$(DMSO)$_4$; 90% yield. The orange crystals were RuCl$_2$(1,5-DTCO)(DMSO)$_2$ (**5**); 0.01 g (5% yield). The crystals were mechanically separated, and the X-ray crystal structure determination of **5** was carried out to confirm its identity. Since no particularly significant features were present in the structure of **5**, no additional details are provided here.

Results

***trans*-Dichlorobis(1,5-dithiacyclooctane)ruthenium(II) (1).** Reaction of *trans*-RuCl$_2$(THT)$_4$ with 1,5-DTCO in chloroform gives *trans*-dichlorobis(1,5-dithiacyclooctane)ruthenium(II) (**1**). If *cis*-RuCl$_2$(DMSO)$_4$ is used instead of *trans*-RuCl$_2$(THT)$_4$, **1** is still the major product but the yield is lower and a number of other uncharacterized byproducts are obtained. The solid-state infrared spectrum of 1 reveals only one weak Ru–Cl stretching vibration at 352 cm^{-1}, indicating a trans arrangement of halides.[1] The solid-state IR spectrum also shows a strong peak at 1035 cm^{-1} in the region where a sulfur-coordinated sulfoxide S–O stretch would be expected. However, this peak has to be a –CH$_2$– rocking vibration, since no S–O bond is present. There are two absorption bands in the UV/visible region at 264 nm (ϵ = 1820 M^{-1} cm^{-1}) and 420 nm (ϵ = 220 M^{-1} cm^{-1}).

The crystal structure of **1** (Figure 1) shows a centrosymmetric molecule with the Ru(II) ion at the inversion center of the molecule; the mesocycles are coordinated to the Ru(II) center to give an overall octahedral geometry. The crystal data and details of data collected are given in Table I, the final atomic coordinates are given in Table II, and the bond lengths and bond angles are given in Table III. The 1,5-DTCO ligand adopts a boat–boat conformation, probably the result of the trans arrangement of chlorides. In other complexes of 1,5-DTCO, such as [Ni(1,5-DTCO)$_2$]Cl$_2$, the eight-membered-ring mesocycle adopts either a chair–chair or boat–chair conformation.[4-6] The Ru–S bond distances (2.352 (1) and 2.345 (1) Å) are slightly longer than those found for other Ru(II) thioether complexes such as [Ru(1,4,7-trithiacyclononane)$_2$](BPh$_4$)$_2$·2DMSO, which has an average Ru–S bond length of 2.332 Å.[12] Examination of bond angles reveals that the S(1)–Ru–S(2) angle of the 1,5-DTCO ligand is 84.9 (1)°, approximately the same size bite angle that has been seen for other complexes of 1,5-DTCO.[5,6]

***cis*-Dichlorobis(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (2).** Reaction of *trans*-RuCl$_2$(THT)$_4$ with 1,5-DTCO-O in chloroform results in a yellow precipitate of *cis*-dichlorobis(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (**2**). If *cis*-RuCl$_2$(DMSO)$_4$ is used instead of *trans*-RuCl$_2$(THT)$_4$, **2** is still the major product but the yield is lower and number of other uncharacterized byproducts are present. The solid-state infrared spectrum shows three medium absorptions at 313, 253, and 382 cm^{-1}, consistent with a cis arrangement of chlorides.[1] There is a strong band at 1035 cm^{-1}, which can be assigned to –CH$_2$– rocking, and one at 1072 cm^{-1}, due to the S–O stretch of a coordinated sulfur of the sulfoxide group. The observation that the band at 1072 cm^{-1} was more intense than the band at 1035 cm^{-1} was used as a criterion to distinguish **2** from **3**. There are two absorption bands in the UV/visible region at 264 nm (ϵ = 2465 M^{-1} cm^{-1}) and 336 nm (ϵ = 266 m^{-1} cm^{-1}).

The solid-state X-ray structure shows that the coordination geometry around the ruthenium atom is distorted octahedral with the 1,5-DTCO-O ligands cis to each other. This is the first

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example of a molecule with a cis arrangement of mesocyclic ligands (Figure 2). The crystal data and details of data collected are given in Table I, and the final atomic coordinates are listed in Table IV. Bond lengths and bond angles are given in Table V. The thioether groups are trans to each other, while the chlorides are cis to each other and trans to the sulfoxide groups. This geometry exemplifies the desire of an S-bonded sulfoxide group (a weak π acceptor) to be trans to a chloride ligand (a strong σ donor with little competition for the electrons of ruthenium).[1,13]

The sum of the covalent radii of ruthenium(II) (1.33 Å) and sulfur (1.04 Å) is 2.37 Å. This is significantly longer than the Ru–S(O) bond distance (2.239 (3) Å) of **2**. This suggests that there must be some π back-donation of electron density from the ruthenium to the sulfoxide. The Ru–S(O) bond length in the S-bonded $[\mathrm{Ru(NH_3)_5(Me_2SO)}](\mathrm{PF_6})_2$ complex is 2.188 (3) Å.[15] In this molecule, where there are no ligands to compete with the sulfur for metal π-electron density, the Ru–S(O) bond is probably as short as possible. The Ru–Cl bond length in **2**, 2.467 (3) Å, is significantly longer than typical values (2.424 (1) Å) for a Ru–Cl bond where the chloride is *trans* to a sulfur-bound sulfoxide group.[13]

The S–O bond distance (1.485 (8) Å) of **2** is rather long for a sulfur-coordinated sulfoxide group. Typical values range from 1.450 to 1.470 Å, but a few are as long as 1.512 Å.[2,3,13,14,16] The trend is that the S–O bond in a sulfur-coordinated sulfoxide group is lengthened and the M–S(O) bond is shortened when electron density is transferred from the sulfur to the metal.

The Ru–S bond (2.363 (2) Å) is considerably longer than the Ru–S(*O) bond. The mean Ru–S bond distance reported for $[\mathrm{Ru(1,4,7\text{-}trithiacyclononane)_2}](\mathrm{BPh_4})_2\cdot 2\mathrm{DMSO}$, which has its thioethers trans to each other, is 2.332 Å,[12] which is ~0.03 Å shorter than the Ru–S bond length in **2**.

***trans*-dichlorobis(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (3).** Regardless of whether the starting material had a cis or trans arrangement of chlorides, *trans*-$\mathrm{RuCl_2(THT)_4}$ or *cis*-$\mathrm{RuCl_2(DMSO)_4}$, when either complex was treated with 1,5-DTCO-O, the product had a cis arrangement of chlorides. On the other hand, the product of the reaction of either *trans*-$\mathrm{RuCl_2(THT)_4}$ or cis-$\mathrm{RuCl_2(DMSO)_4}$ with 1,5-DTCO had a trans arrangement of chlorides. In light of these results, it seemed reasonable that if a 1,5-DTCO ligand on *trans*-$\mathrm{RuCl_2(1,5\text{-}DTCO)_2}$ (**1**) could be either oxidized to 1,5-DTCO-O while coordinated to the metal or exchanged with a 1,5-DTCO-O molecule in solution, the resulting complex might retain its arrangement of trans chlorides. As predicted, when *trans*-$\mathrm{RuCl_2(1,5\text{-}DTCO)_2}$ is treated with 1,5-DTCO-O, *trans*-dichlorobis(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (**3**) is obtained. Alternatively, when *trans*-$\mathrm{RuCl_2(THT)_4}$ is treated with 1,5-DTCO and an oxidizing agent is added, **3** is also formed. In this reaction, 1,5-DTCO probably reacts with *trans*-$\mathrm{RuCl_2(THT)_4}$ to give **1**, and then free 1,5-DTCO is oxidized to 1,5-DTCO-O. The 1,5-DTCO-O then exchanges with the 1,5-DTCO ligands on the ruthenium to give **3**.

The infrared spectrum of **3** shows one weak absorption at 345 cm^{-1}, consistent with a trans arrangement of chlorides.[1] There is one strong band at 1040 cm^{-1}, which can be assigned to $-\mathrm{CH_2}-$ rocking, and another one at 1080 cm^{-1}, due to the S–O stretch of a coordinated sulfur of the sulfoxide group. The band at 1080 cm^{-1} is less intense than the band at 1040 cm^{-1} and could be used as a criterion to distinguish **3** from **2**. There are two absorption bands in the UV/visible region at 245 nm (ϵ - 5160 M^{-1} cm^{-1}) and 332 nm (ϵ = 194 M^{-1} cm^{-1}).

The geometry around the ruthenium atom in **3** is closely related to that of **1** (Figure 3). The crystal data and details of data collected are given in Table I, and the final atomic coordinates are listed in Table VI. Bond lengths and bond angles are given in Table VII. The functional groups are in an all-trans relationship, and the S–O bonds on both ligands lie in the same plane as the ruthenium atom. The Ru–Cl bond, 2.413 (4) Å, is considerably shorter in **3** than in **2**, 2.467 (3) Å, but still longer than typical values found in ruthenium complexes with trans chlorides such as $\mathrm{RuCl_3(}p\mathrm{\text{-}N_2C_6H_4Me)(PPh_3)_2\cdot Me_2CO}$,[17] Ru–Cl = 2.390 Å, and $\mathrm{RuCl_3(NO)(PMePh_2)_2}$,[18] Ru–Cl = 2.398 (7) Å.

The Ru–S bond length in **3** is 2.359 (4) Å. This value is larger than the Ru–S bond length of **1** but virtually identical in both **3** and **2**, 2.359 (4) Å vs 2.363 (2) Å, respectively. However, there is a lengthening of the Ru–S(O) bond in **3** (2.298 (4) Å) relative to **2** (2.239 (3) Å). The S–O bond in **3** (1.459 (12) Å) is shorter than that in **2** (1.485 (8) Å). Overall, when **3** is compared to **2**, we see a shortening of the Ru–Cl bond, a lengthening of the Ru–S(O) bond, and a shortening of the S–O bond. The lengthening of the Ru–S(O) bond and the shortening of the S–O bond are a direct result of the mutual trans influence of the sulfoxide groups. Since the empty orbitals on sulfur having π symmetry are not interacting as effectively with the orbitals on ruthenium, they appear to be interacting more effectively with the appropriate orbitals on oxygen, resulting in a shortening of the S–O bond. The shortening of the Ru–Cl bond is not as easily understood.

Chloro(1,5-dithiacyclooctane)(1,5-dithiacyclooctane 1-oxide)(tetrahydrothiophene)ruthenium(II) Tetraphenylborate (4). If *trans*-$\mathrm{RuCl_2(THT)_4}$ is treated with 1,5-DTCO in the same manner as described for the synthesis of **1**, except that an oxidant ($\mathrm{O_2}$, $\mathrm{H_2O_2}$, or $\mathrm{NaIO_4}$) is added and aliquots are removed and allowed to slowly diffuse into an ethanolic $\mathrm{NaBPh_4}$ solution, chloro(1,5-dithiacyclooctane)(1,5-dithiacyclooctane 1-oxide)(tetrahydrothiophene)ruthenium(II) tetraphenylborate (**4**) is obtained.

Compound **4** has a S–O stretch in the solid-state IR spectrum at 1075 cm^{-1} and $-\mathrm{CH_2}-$ rocking at 1038 cm^{-1}. Crystal data and details of data collected for **4** are given in Table I. Final atomic coordinates, bond lengths, and bond angles for **4** are given in Tables VIII and IX, respectively. The structure reveals a distorted octahedral geometry around the ruthenium atom (Figure 4). It should be noted that complete oxidation of one of the thioether groups has not been achieved. This can be seen in the structure because the electron density of the oxygen atom attached to the sulfur is only 40% of the expected value. As expected, the Ru–S(O) bond length in **4** has been decreased relative to the Ru–S bond length.

***trans*-Dichlorobis(dimethyl sulfoxide)(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (5).** As started previously, *cis*-$\mathrm{RuCl_2(1,5\text{-}DTCO\text{-}O)_2}$ (**2**) can be recrystallized from a 10% DMSO–ethanol solution without decomposition. If the highly polar solvent DMSO helps to induce $\mathrm{RuCl_2(1,5\text{-}DTCO\text{-}O)_2}$ to crystallize in the cis arrangement, it seemed reasonable that if *trans*-$\mathrm{RuCl_2(1,5\text{-}DTCO\text{-}O)_2}$ (**3**) was recrystallized from a solution containing 10% DMSO–ethanol, it might isomerize to *cis*-$\mathrm{RuCl_2(1,5\text{-}DTCO\text{-}O)_2}$ (**2**). However, when **3** was recrystallized from 10% DMSO–ethanol under the same conditions as **2**, yellow and orange crystals were recovered. The yellow crystals were *cis*-$\mathrm{RuCl_2(DMSO)_4}$, and the orange crystals were *trans*-dichlorobis(dimethyl sulfoxide)(1,5-dithiacyclooctane 1-oxide)ruthenium(II) (**5**). The crystal structure determination, of **5** was simply carried out to confirm its identity, but there were so few important structural details in this molecule that we decided not to include a full description of its structure. Thus the 1,5-DTCO-O ligands in **3** are much more labile than the 1,5-DTCO-O ligands in **2**, since DMSO is able to displace them from the complex to give *cis*-$\mathrm{RuCl_2(DMSO)_4}$ and *trans*-$\mathrm{RuCl_2(DMSO)_2(1,5\text{-}DTCO\text{-}O)}$ (**5**).

The only aspect of the structure of **5** worthy of note is that the S–O bonds of the DMSO ligands lie in the plane formed by the four sulfur and ruthenium atoms. The S–O bond in the 1,5-DTCO-O ligand also lies in the same plane. Although there are

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no constraints on the S–O bonds in the DMSO ligands to lie in the plane, they still orientate themselves in that manner. Having all the S–O bonds lie in the equatorial plane products the proper symmetry for maximum electron delocalization due to the overlap of a p orbital on oxygen, a d orbital on sulfur, and a d orbital on ruthenium.

Dicussion

The structures of ruthenium chloride complexes of 1,5-DTCO-O show that mesocyclic ligands can induce a metal to achieve a distribution of functional groups that may be inaccessible to either monodentate or polydentate acyclic ligands. The crystal structures confirm the identity of the all-trans complex and the cis isomer with trans arrangement of thioether groups.

Because of the relationship of **3** to the catalytic all-trans complex proposed by Riley,[1] cyclic voltammograms of each of the complexes were generated in chloroform and methylene chloride, and pseudo/reversible half-wave potentials were obtained. Only one reduction potential is observed for each compound: $E_{1/2} = 0.77$ V (**1**), 0.99 (**2**), 0.80 V (**3**). However, the compounds are very insoluble in these nonpolar solvents and the solutions had to be stirred for a long period of time to effect dissolution. Subsequently, the ^{13}C NMR spectra of these complexes in $CHCl_3$ indicated that the monomeric species that were found by an X-ray diffraction study of the solids are not retained in solution. Therefore, the cyclic voltammetric results do not correspond to the original solid complexes and the $E_{1/2}$ value for **3** does not represent the reduction potential of the all-trans complex. However, when the $CHCl_3$ solutions were evaporated to dryness and the recovered product was examined, the original complex was recovered. Thus, it appears that dissolution in $CHCl_3$ causes an opening of the chelated mesocyclic ligand to give either a pentacoordinated complex or a chloride-bridged dimer. Unfortunately, the resolution of the peaks in the ^{13}C NMR spectra of **2** and **3** in $CHCl_3$ was so poor that we were unable to interpret the data.

Complex **1** is sufficiently soluble in $CHCl_3$ that a ^{13}C NMR spectrum consisting of nine peaks could be obtained. The ^{13}C NMR spectrum of uncoordinated 1,5-DTCO exhibits only two peaks, and complex **1** should also exhibit two peaks. However, the 1,5-DTCO ligand does not dissociate completely, since none of the peaks grew in intensity when free 1,5-DTCO was added to the solution. However, if one end of the 1,5-DTCO ligand dissociates from the ruthenium in $CHCl_3$, the spectrum could correspond to an equilibrium mixture between the original octahedral complex and either a pentacoordinated species or a chloride-bridged dimer. This equilibrium mixture would exhibit signals from nine different types of carbons and could account for all nine peaks in the spectrum if the chelated 1,5-DTCO exhibits a boat–chair conformation.

Complex **2** is virtually insoluble in most solvents except DMSO. The ^{13}C spectrum of **2** in DMSO-d_6 has six peaks. The peaks at 52.56, 29.64, and 23.96 ppm belong to the free ligand because they are enhanced when 1,5-DTCO-O is added to the NMR solution. This leaves the peaks at 49.85, 24.56, and 24.34 ppm as belonging to the complex. The ^{13}C spectrum of **3** in DMSO-d_6 exhibits eight peaks. As with **2**, the peaks at 52.56, 29.64, and 23.96 ppm were identified as belonging to the free ligand and the peaks at 49.84, 24.56, and 24.33 ppm are identical with those observed in the cis complex **2**. After elimination of all the peaks common to both complexes, **3** has two additional peaks.

Since there are three peaks in both **2** and **3** that appear at 49.85, 24.56, and 24.34 ppm, some coordinated 1,5-DTCO-O is present in both complexes. Thus, the predominant ruthenium complex present when **2** is dissolved in DMSO-d_6 is presumably the original bis complex **2**, since **2** can be recrystallized from 10% ethanol–DMSO.

Any prediction of the structure of **3** in DMSO-d_6 is more complicated because only eight peaks are observed. However, every 1,5-DTCO-O molecule should exhibit three peaks in the ^{13}C NMR spectrum regardless of whether it is free or bonded to ruthenium as either a monodentate or a bidentate ligand. The three peaks due to free 1,5-DTCO-O are seen, and the three peaks in common with **2** reveal at least one coordinated 1,5-DTCO-O, but since only two additional peaks are observed, we believe that one end of a 1,5-DTCO-O ligand may still be attached to the ruthenium and that the missing peak due the carbon α to the sulfoxide is masked by the peak at 52.56 or 49.84 ppm. The observation that free 1,5-DTCO-O is present shows that some of the ligand is completely detached from the ruthenium and could be replaced by two DMSO ligands to give **5**, but we do not see any ^{13}C signals due to coordinated DMSO. However, they could be buried under the strong peaks of the solvent.

Conclusion

Compound **2** is the first reported complex having a cis arrangement of mesocyclic ligands. Compound **3** is the first reported example of a complex of ruthenium having an all–trans arrangement of a halide, thioether, and sulfoxide ligands, the species that has been reported to be the active catalyst in the oxidation of thioethers to their sulfoxides.[1] Compound **2** is synthesized by reaction of $RuCl_2(THT)_4$ with 1,5-DTCO-O, and compound **3** is normally synthesized from the reaction of $RuCl_2(1,5\text{-DTCO})_2$ with 1,5-DTCO-O.

The chemistries of both compounds are different. Compound **2** can be recrystallized from a 10% DMSO–ethanol solution; compound **3** dissociates under the same conditions. All the complexes dissociate in nonpolar solvents, so the electrochemical data do not correspond to the solid-state structures. The ^{13}C NMR spectrum of **2** in DMSO-d_6 suggests that the complex partially dissociates to give free 1,5-DTCO-O but most of it retains its identity. The ^{13}C NMR spectrum of complex **3** appears to show a monocoordinated 1,5-DTCO-O as well as complete loss of one 1,5-DTCO-O to give **5**.

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Supplementary Material Available: Tables of distances, angles, anisotropic thermal parameters, and H atom coordinates associated with **1**–**5** and a figure of the molecular structure of $[RuCl_2(1,5\text{-DTCO})(DMSO)_2]$ (**5**), showing 50% probability ellipsoids (13 pages); listings of structure factors (46 pages). Ordering information is given on any current masthead page.