

(Na3-O distances 2.216 (10)-2.862 (8) Å). (Cl3)O₄⁻ is not disordered.

Finally, we have also solved the structure of a mixed crystal of [FeL₂][FeLL¹](ClO₄)₄.³⁸ There are two formula units in the triclinic space group *P* $\bar{1}$; the iron(II) centers are located on two crystallographic centers of symmetry at (0, 0, 0) and (0, 1/2, 1/2), with a occupancy factors of 0.5. Thus, the [FeL₂]²⁺ and [FeLL¹]²⁺ cations are again statistically disordered. When the occupancy factors of the two independent sulfoxyl oxygen atoms were treated as variables in the last refinement cycles, these values converged at 0.20 and 0.33 (mean 0.265), indicating that the distribution of the two cations in the unit cell may not be completely at random, but the structure determination does confirm within experimental error the ratio of [FeL₂]²⁺/[FeLL¹]²⁺ to be 1:1 as was determined from ¹H NMR measurements. The gross overall structure of the cations is identical with the one shown in Figure 9 with the exception of the apparent Fe-S(O) bond distance of the iron-sulfoxide bond, which is longer (average 2.224 (1) Å) than the one observed in [FeLL¹](ClO₄)₂·2NaClO₄·H₂O due to the superimposed thioether Fe-S bonds of [FeL₂]²⁺ and of [FeLL¹]²⁺. If this is taken into account, a true Fe-S(O) bond distance of 2.16 Å may be calculated, in excellent agreement with the previous estimate (see above). The ClO₄⁻ anions were not found to be disordered; their oxygen atoms were readily refined with reasonable

anisotropic thermal parameters.

Conclusion. We have shown in this study that the crown thioether 1,4,7-trithiacyclononane forms stable complexes of iron(II/III). Oxidation of [FeL₂]²⁺ with PbO₂ leads to the homoleptic low-spin [Fe^{III}L₂]³⁺ cation, which is a very strong one-electron oxidant. Magnetic susceptibility and Mössbauer measurements unambiguously show that the oxidation is metal-centered and that the low-spin [FeS₆]³⁺ core is Jahn-Teller-distorted even at room temperature. This shows that saturated crown thioether ligands coordinate also to metal centers in high oxidation states, although the lower oxidation states are clearly stabilized by the thioether π -acceptor properties, contrasting in this respect with the case for the pure σ -donor 1,4,7-triazacyclononane.³⁹

Depending on the nature of the oxidant used, it is also possible to oxidize the coordinated thioether ligand in [FeL₂]²⁺ without concomitant oxidation of the metal center. Thus, sodium peroxodisulfate was found to yield [FeLL¹]²⁺ cations, which contain one coordinated 1,4,7-trithiacyclononane 1-oxide in addition to one 1,4,7-trithiacyclononane ligand.

Acknowledgment. We thank Professor P. Gülich (Universität Mainz, FRG) for measuring the Mössbauer spectrum of [Fe-([9]aneN₃)₂]Cl·5H₂O. We are grateful to the Fonds der Chemischen Industrie for financial support of this work.

Supplementary Material Available: Tables S1, S2, S2A, and S2B for [FeLL¹](ClO₄)₂·2NaClO₄·H₂O, listing calculated positional parameters of hydrogen atoms, thermal parameters, bond distances, and bond angles, Tables S4-10 for [FeL₂][FeLL¹](ClO₄)₄, listing experimental details of the structure determination, atomic coordinates, bond lengths and bond angles, thermal parameters, and calculated coordinates of hydrogen atoms, and perspective views of the iron coordination environments in [FeL₂][FeLL¹](ClO₄)₂ (12 pages); Tables S3 and S10, listing calculated and observed structure factors for both compounds (55 pages). Ordering information is given on any current masthead page.

(38) Crystal data for [FeL₂][FeLL¹](ClO₄)₄: C₂₄H₄₈Cl₄Fe₂O₁₇S₁₂; mol wt 1249.2; triclinic; space group *P* $\bar{1}$; *a* = 8.848 (8), *b* = 11.499 (6), *c* = 11.679 (7) Å; α = 86.04 (5), β = 84.48 (8), γ = 72.40 (5)°; *V* = 1126.2 (7) Å³, *Z* = 2; *d*_{calcd} = 1.84 g cm⁻³; μ = 14.9 cm⁻¹; crystal dimensions 0.26 × 0.26 × 0.35 mm³; 6620 measured reflections (3.0 < 2 θ < 60°) and 3023 unique reflections (*I* ≥ 2 σ (*I*)); radiation Mo K α ; empirical absorption correction; 275 least-squares parameters; anisotropic thermal parameters for all non-hydrogen atoms; H atoms in calculated positions (*d*(C-H) = 0.96 Å sp³-hybridized carbon atoms) with common isotropic *U* = 0.058 Å²; *R* = 0.033; *R*_w = 0.032; GOF = 2.0; shift/esd in last cycle 0.01 (mean), 0.06 (maximum). Tables of atom coordinates, anisotropic temperature factors, bond distances and angles, and observed and calculated structure amplitudes are available as supplementary material.

(39) Reinen, D.; Ozarowski, A.; Jakob, B.; Pebler, J.; Stratemeier, H.; Wieghardt, K.; Tolksdorf, I. *Inorg. Chem.*, in press.

Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England

Crown Thioether Chemistry. Ruthenium(II) Complexes of 1,4,7-Trithiacyclononane and 1,5,9-Trithiacyclododecane

Simon C. Rawle, Timothy J. Sewell, and Stephen R. Cooper*

Received March 20, 1987

Reaction of [Ru(Me₂SO)₆](BF₄)₂ with tridentate thioether ligands in methanol yields the oxidatively and hydrolytically robust complexes [RuL₂]²⁺ (L = 2,5,8-trithianonane, 1,4,7-trithiacyclononane (9S3), and 1,5,9-trithiacyclododecane (12S3)), in which the central Ru(II) ion coordinates to an octahedral array of six thioether S atoms. Optical, NMR, electrochemical, and single-crystal X-ray diffraction studies of the latter two complexes provide a benchmark for the development of the coordination chemistry of thioethers with heavy transition elements in moderate and low oxidation states. Crystal data for [Ru(9S3)₂](CF₃SO₃)₂: *a* = 7.677 (5) Å, *b* = 9.465 (3) Å, *c* = 18.423 (3) Å, α = 83.61 (2)°, β = 88.48 (4)°, γ = 83.05 (4)°; triclinic, space group *P* $\bar{1}$; final *R* = 4.03%, *R*_w = 4.82%. Crystal data for [Ru(12S3)₂](BF₄)₂·2MeNO₂: *a* = 20.355 (3) Å, *b* = 8.006 (3) Å, *c* = 22.540 (2) Å, β = 114.844 (9)°; monoclinic, space group *I*2/*a*; final *R* = 2.85%, *R*_w = 3.32%.

Introduction

Complexes of simple mono- and bidentate thioethers with heavy transition-metal ions have long attracted interest because of their potential analogy to catalytically active phosphine complexes.¹⁻³ In a broader context this possible parallel raises the issue of the

electronic consequences of thioether coordination, a question that has also risen recently with regard to the blue copper proteins.⁴ This question is most simply and rigorously addressed in complexes that only have thioether ligands. Unfortunately, however, to date few such homoleptic thioether complexes have proven synthetically tractable owing to the low stability of ML₆ (L = Me₂S) and M(L-L)₃ (L-L = MeSCH₂CH₂SMe) complexes.⁵

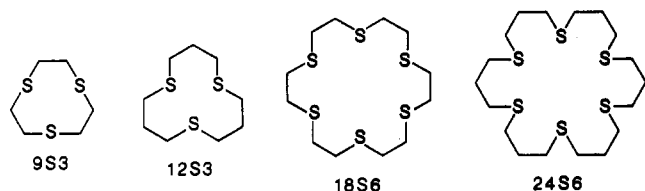
(1) Lemke, W.; Travis, K.; Takvoryan, N.; Busch, D. H. *Adv. Chem. Soc.* 1976, No. 150, 358.

(2) Walton, R. A. *J. Chem. Soc. A* 1967, 1852.

(3) Chatt, J.; Leigh, G. J.; Storace, A. P. *J. Chem. Soc. A* 1971, 1380.

(4) Jones, T. E.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* 1975, 97, 7485.

Recently, however, a solution to this problem has become apparent. Crown thioethers such as 1,4,7-trithiacyclononane (9S3),⁶⁻⁸ 1,5,9-trithiacyclododecane (12S3),⁹ 1,4,7,10,13,16-hexathiacyclooctadecane (18S6),^{10,11} and 1,5,9,13,17,21-hexathiacyclotetradecane (24S6)¹² form complexes typified by much



greater robustness and stability.¹³ Consequently, these ligands have proved especially useful in preparation of homoleptic thioether complexes of first-row transition-metal ions. Furthermore, very recent synthetic advances^{9,14-17} have made these once precious ligands readily available.

Crown thioethers not only bind first-row transition-metal ions strongly but also induce in them unusual optical, redox, magnetic, and kinetic behavior.^{4,12,18-20} For example, hexakis(thioether) coordination provides rare examples of low-spin octahedral Co(II) complexes,^{21,22} and it results in the highest potentials known for the Cu(II/I) couple.^{19,23} Very recent results show that it also gives one of the few known monomeric complexes of Rh(II).²⁴ These results stimulate further interest in related complexes of other second- and third-row metal ions since the peculiar electronic effects of thioether complexation, if reproduced in the heavier metals, may engender exceptional reactivity.^{1,25-30} Particular

- (5) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.
- (6) Abbreviations used: 9S3, 1,4,7-trithiacyclononane (trithia-9-crown-3); 10S3, 1,4,7-trithiacyclododecane (trithia-10-crown-3); 12S4, 1,4,7,10-tetrathiacyclododecane (tetraathia-12-crown-4); 18S6, 1,4,7,10,13,16-hexathiacyclooctadecane (hexathia-18-crown-6); 20S6, 1,4,7,11,14,17-hexathiacycloicosane (hexathia-20-crown-6); 14S4, 1,4,8,11-tetrathiacyclotetradecane; 24S6, 1,5,9,13,17,21-hexathiacyclotetradecane (hexathia-24-crown-6).
- (7) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.
- (8) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.
- (9) Rawle, S. C.; Admans, G. A.; Cooper, S. R. *J. Chem. Soc., Dalton Trans.*, in press.
- (10) Hartman, J. R.; Wolf, R. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 131.
- (11) Hints, E. J.; Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 3738.
- (12) Rawle, S. C.; Hartman, J. R.; Watkin, D. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1986**, 1083.
- (13) Not all macrocyclic thioethers show stronger binding than linear ones, however (i.e., display the macrocyclic effect). See: Margerum, D. W.; Smith, G. F. *J. Chem. Soc., Chem. Commun.* **1975**, 807.
- (14) Sellman, D.; Zapf, L. *J. Organomet. Chem.* **1985**, *289*, 57.
- (15) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, *46*, 4481.
- (16) Wolf, R. E., Jr.; Hartman, J. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1987**, *109*, 4328.
- (17) Blower, P. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 2009.
- (18) Küppers, H.-J.; Neves, A.; Pomp, C.; Ventur, D.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 2400.
- (19) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202.
- (20) Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Moy, I.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1985**, *107*, 2399.
- (21) Hartman, J. R.; Hints, E. J.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1208.
- (22) Thorne, C. M.; Rawle, S. C.; Admans, G. A.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 306.
- (23) Ochrymowycz, L. A.; Rorabacher, D. B.; Dockal, E. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4322.
- (24) Rawle, S. C.; Yagbasan, R.; Prout, K.; Cooper, S. R. *J. Am. Chem. Soc.*, in press.
- (25) Ashby, M. T.; Enemark, J. H.; Lichtenberger, D. L.; Ortega, R. B. *Inorg. Chem.* **1986**, *25*, 3154.
- (26) Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636.

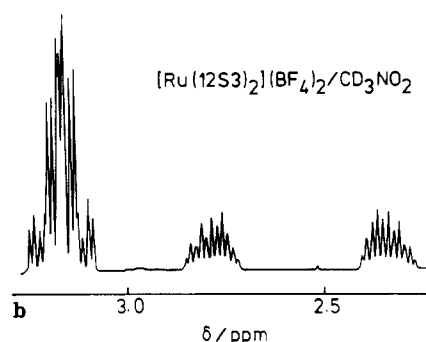
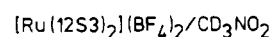
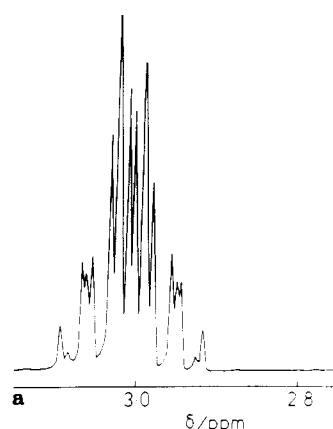
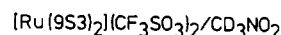


Figure 1. ¹H NMR spectrum (300 MHz, CD₃NO₂) of (a) [Ru(9S3)₂](CF₃SO₃)₂ and (b) [Ru(12S3)₂](BF₄)₂·2MeNO₂.

interest centers on Ru(II) because its homoleptic thioether complexes may have novel photophysical properties (cf. [Ru(bpy)₃]²⁺).³¹

Which crown thioethers are ideal for binding Ru? Previous results have demonstrated the exceptional ligating properties of 9S3,^{7,32,33} a ligand in which the S atoms are endodentate⁸ (i.e., pointing into the macrocyclic cavity).³⁴ In 9S3 the enthalpic price of arranging the donor atoms for coordination to a trigonal face has been paid during synthesis of the ligand. Indeed, because of the avidity with which it chelates metal ions, 9S3 is rapidly becoming part of the repertoire of both coordination and organometallic chemists. The small cavity of this ligand, however, results in compression even of first-row ions, as evidenced by short M-S bond lengths and unusually high ligand field strengths.^{7,21} These results suggest that 9S3 should have difficulty accommodating a second-row metal ion such as Ru(II) and that the corresponding propyl-linked analogue, 12S3,³⁵ should be more suitable. This latter ligand, however, adopts an exodentate conformation⁹ (i.e., the S atoms point out of the ring)³⁴ that is inappropriate for chelation. Thus while 9S3 is conformationally well suited to act as a ligand, it provides a cavity size that may be too small to bind

- (27) Clarkson, J. A.; Yagbasan, R.; Blower, P. J.; Rawle, S. C.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1987**, 950.
- (28) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Lavery, A. J.; Odulate, M. O.; Schroeder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 118.
- (29) Yoshida, T.; Ueda, T.; Adachi, T.; Yamamoto, K.; Higuchi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1137.
- (30) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1982**, *22*, 3361.
- (31) Kuehn, C. G.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 689. Root, M. J.; Sullivan, B. P.; Meyer, T. J.; Deutsch, E. *Inorg. Chem.* **1986**, *24*, 2731.
- (32) Wilson, G. S.; Swanson, D. D.; Glass, R. S. *Inorg. Chem.* **1986**, *25*, 3827.
- (33) Wieghardt, K.; Küppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067.
- (34) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 762.
- (35) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 942; *J. Coord. Chem.* **1975**, *5*, 181.
- (36) Rosen, W.; Busch, D. H. *Inorg. Chem.* **1970**, *9*, 262.

Ru(II) optimally; 12S3, on the other hand, is conformationally ill-suited for chelation, but in principle it offers a more appropriate cavity size.³⁶ To address the question of which ligand, 9S3 or 12S3, is more appropriate for Ru (and second-row metal ions generally) and to assess the utility of 12S3 as a ligand, we have synthesized and characterized the complexes $[\text{Ru}(9\text{S}3)_2]^{2+}$ ³⁷ and $[\text{Ru}(12\text{S}3)_2]^{2+}$, the first examples of homoleptic thioether complexes of ruthenium.

Experimental Section

Methanol, nitromethane, diethyl ether, and dichloromethane were freshly distilled under nitrogen from magnesium methoxide, calcium chloride, sodium benzophenone ketyl, and phosphorus pentoxide, respectively. Water was filtered through activated charcoal, passed through an ion-exchange resin, and then distilled. Ruthenium trichloride trihydrate (Johnson Matthey Chemicals Ltd.) and acetone (AnalaR, BDH) were used as supplied. Hexakis(dimethyl sulfoxide)ruthenium(II) tetrafluoroborate, $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$, and silver triflate (hemibenzene solvate), $\text{AgCF}_3\text{SO}_3 \cdot \frac{1}{2}\text{C}_6\text{H}_6$, were prepared by the literature methods.^{38,39} The ligands 1,4,7-trithiacyclononane (9S3), 2,5,8-trithianonane (ttn), and 1,5,9-trithiacyclododecane (12S3) were all synthesized by the published procedures.^{9,14,17,21} Standard Schlenk techniques were used for preparation of all the Ru complexes.

Electronic spectra were recorded in 1-cm quartz cuvettes on a Perkin-Elmer 552 spectrophotometer. ¹H NMR spectra were recorded on CD_3NO_2 solutions with a WH300 Fourier transform NMR spectrometer calibrated against residual solvent protons. Electrochemical experiments were performed under a nitrogen atmosphere on 1 mM solutions of the complexes in dry acetonitrile that contained 0.1 M Et_4NBF_4 . Platinum working electrodes were used with a saturated calomel electrode (SCE) as reference. A Princeton Applied Research Model 175 programmer, Model 179 digital coulometer, and Model 173 potentiostat were used. Analyses were performed by M. Gascoyne, J. Kench, and A. Douglas of the Analytical Service of the Inorganic Chemistry Laboratory, Oxford, England.

Synthesis of Complexes. $[\text{Ru}(9\text{S}3)_2](\text{CF}_3\text{SO}_3)_2$. A solution of ruthenium(III) trifluoromethanesulfonate (triflate, trif) in MeOH was prepared by refluxing " $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ " (2.09 g, 8 mmol) with $\text{AgCF}_3\text{SO}_3 \cdot \frac{1}{2}\text{C}_6\text{H}_6$ (7.15 g, 24 mmol) in 100 mL of MeOH under N_2 overnight. After removal of the precipitated silver chloride by filtration, a 2-mL portion (0.16 mmol) of the solution was refluxed for 24 h with 9S3 (100 mg, 0.55 mmol, 3.5 equiv), during which time the color changed from brown to pale yellow. The solution was cooled and filtered, and methanol was removed under vacuum. The residue was washed with a small portion (2 mL) of acetone and then recrystallized from acetone to yield $[\text{Ru}(9\text{S}3)_2](\text{trif})_2$ as colorless needles (75 mg, 62%). Anal. Calcd for $\text{RuC}_{14}\text{H}_{24}\text{S}_8\text{O}_6\text{F}_6$: C, 22.13; H, 3.19. Found: C, 22.18; H, 3.38. Electronic spectrum (H_2O ; λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 338 (172), 292 (195). ¹H NMR (300 MHz, CD_3NO_2) shows a symmetric multiplet (16 peaks) centered at 3.009 ppm (Figure 1a).

$[\text{Ru}(9\text{S}3)_2](\text{BF}_4)_2$. To a suspension of $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ (148 mg, 0.2 mmol) in 5 mL of MeOH was added 9S3 (90 mg, 0.5 mmol). The resulting mixture was refluxed overnight under N_2 and filtered to yield a clear, colorless solution. Cooling to -10°C yielded the product as colorless needles (80 mg, 63%). Anal. Calcd for $\text{RuC}_{12}\text{H}_{24}\text{S}_6\text{B}_2\text{F}_8$: C, 22.68; H, 3.81. Found: C, 22.65; H, 3.70.

$[\text{Ru}(\text{ttn})_2](\text{BF}_4)_2$. A 10-mL portion (0.80 mmol) of the ruthenium(III) triflate solution was added to 2,5,8-trithianonane (ttn) (584 mg, 3.20 mmol, 4 equiv) and refluxed for 24 h under N_2 . During this time the color changed from brown to yellow. To the cooled solution was then added an excess of Et_4NBF_4 , which precipitated $[\text{Ru}(\text{ttn})_2](\text{BF}_4)_2$ as yellow prisms (300 mg, 60%).

$[\text{Ru}(\text{ttn})_2](\text{BF}_4)_2$ could also be made from $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ by a modification of the procedure for $[\text{Ru}(9\text{S}3)_2](\text{BF}_4)_2$. To a suspension of $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ (296 mg, 0.4 mmol) in 10 mL of MeOH under nitrogen was added ttN (182 mg, 1 mmol), and the resulting mixture was refluxed overnight under N_2 to yield a clear yellow solution. The compound was obtained as yellow crystals (180 mg, 70%) when the solution was allowed to stand at -20°C for 24 h. Anal. Calcd for

$\text{RuC}_{12}\text{H}_{28}\text{S}_6\text{B}_2\text{F}_8$: C, 22.52; H, 4.38. Found: C, 22.94; H, 4.52. Electronic spectrum (H_2O ; λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$): 352 (445), 308 (437). ¹H NMR (300 MHz, CD_3NO_2) shows a broad feature at $\delta = 3.5\text{--}2.8$ (8 H, $-\text{CH}_2-$), and singlets at $\delta = 2.697$ (3 H, CH_3) and $\delta = 2.376$ (3 H, CH_3). The observation of two distinct methyl environments implies that this complex adopts the racemic configuration (observed previously in $[\text{Co}(\text{ttn})_2]^{2+}$),²¹ in which two of the terminal SCH_3 groups are trans to each other but the other two are trans to interior CH_2SCH_2 groups.

$[\text{Ru}(12\text{S}3)_2](\text{BF}_4)_2$. 12S3 (100 mg, 0.45 mmol), dissolved in 10 mL of warm MeOH, was added with stirring to a suspension of $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ (150 mg, 0.20 mmol) in MeOH. This mixture was refluxed under N_2 for 30 min to give a clear yellow solution. Partial removal of the solvent and cooling to -10°C precipitated yellow crystals that were collected, washed with dichloromethane, and vacuum dried at room temperature (70 mg, 49%). Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{S}_8\text{B}_2\text{F}_8\text{Ru}$: C, 30.02; H, 5.00. Found: C, 29.55; H, 5.01. The electronic spectrum is dominated by a band at 312 nm ($\epsilon = 289\text{ M}^{-1}\text{cm}^{-1}$) and a shoulder at 348 nm ($\epsilon = 211\text{ M}^{-1}\text{cm}^{-1}$). Vapor diffusion of dry ether into a saturated nitromethane solution afforded diffraction-quality crystals as the nitromethane solvate. The ¹H NMR spectrum (Figure 1b) (300 MHz, CD_3NO_2) shows multiplets centered at $\delta = 2.33$ (11 peaks, 6 H), $\delta = 2.79$ (11 peaks, 6 H), and $\delta = 3.16$ (16 peaks, 24 H).

$[\text{Ru}(10\text{S}3)_2](\text{BF}_4)_2$. By a method identical with that used for $[\text{Ru}(12\text{S}3)_2](\text{BF}_4)_2$, reaction of 10S3 (60 mg, 0.31 mmol) and $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ (100 mg, 0.134 mmol) yielded pale brown crystals (21 mg, 22%) of $[\text{Ru}(10\text{S}3)_2](\text{BF}_4)_2$. Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{S}_6\text{B}_2\text{F}_8\text{Ru}$: C, 25.32; H, 4.22. Found: C, 25.57; H, 4.15.

$[\text{Ru}(20\text{S}6)](\text{BF}_4)_2$. A mixture of 1,4,7,11,14,17-hexathiacycloicosane (20S6) (60 mg, 0.15 mmol) and $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ (100 mg, 0.134 mmol) was suspended in 15 mL of MeOH and refluxed for 4 days under N_2 . After this time, unreacted $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$ was removed by filtration and the resulting yellow solution was cooled to -10°C for several days, whereupon crystals of both the free ligand (colorless) and $[\text{Ru}(20\text{S}6)](\text{BF}_4)_2$ (yellow) were deposited. The mixture of crystals was washed with dichloromethane, and the product was collected and vacuum dried at room temperature (14.8 mg, 16.6%). Anal. Calcd for $\text{C}_{14}\text{H}_{28}\text{S}_6\text{B}_2\text{F}_8\text{Ru}$: C, 25.32; H, 4.22. Found: C, 25.05; H, 4.44.

Riley and Oliver⁴⁰ have recently reported that $\text{Ru}(\text{Me}_2\text{SO})_2\text{Cl}_2$ catalyzes the aerial oxidation of thioethers to sulfoxides, in which mixed sulfoxide/thioether complexes of Ru(II) are the O_2 -sensitive species. The hexakis(thioether) complexes reported here were prepared under nitrogen, and once isolated, they do not appear to react with either air or water. This robustness may be either kinetic or thermodynamic in origin.

X-ray Crystallography. $[\text{Ru}(9\text{S}3)_2](\text{CF}_3\text{SO}_3)_2$. A crystal of dimensions $0.7 \times 0.25 \times 0.4$ mm was sealed in an X-ray capillary and centered on an Enraf-Nonius CAD4 automatic diffractometer that generated $\text{Mo K}\alpha$ (0.71069 Å) radiation (graphite monochromator). Least-squares fitting of the setting angles of 25 reflections collected by an automatic search routine yielded a triclinic unit cell with $a = 7.677$ (5) Å, $b = 9.465$ (3) Å, $c = 18.423$ (3) Å, $\alpha = 83.61$ (2)°, $\beta = 88.48$ (4)°, $\gamma = 83.05$ (4)°, and $V = 1320.46$ Å³. 10031 unique data with $2\theta < 64^\circ$ were collected in ω - 2θ mode. Three standard reflections that were measured every hour showed no decay. An empirical absorption correction was applied. Data reduction yielded 6917 data with $I > 3\sigma(I)$ that were used for subsequent structure solution and refinement. The merging R value was 1.17%. Calculations were performed on a VAX 11/750 computer with the CRYSTALS⁴¹ suite of crystallographic programs. A three-dimensional Patterson map was consistent with the presence of two crystallographically independent Ru atoms at the inversion centers 0, 0, 0 and $0, \frac{1}{2}, \frac{1}{2}$ in $P\bar{1}$ (No. 2). A Fourier map phased by the Ru atoms showed the remaining non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged to $R = 4.03\%$ and $R_w = 4.82\%$ for 321 variables. Most of the H atoms were located by Fourier difference syntheses, though all were included in calculated positions and a group isotropic thermal parameter was refined. The highest peak in the final difference map was near the S atom (S2) of one of the triflate anions, which is slightly disordered.

$[\text{Ru}(12\text{S}3)_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$. The data were collected from a crystal of dimensions $0.4 \times 0.5 \times 0.6$ mm by a procedure analogous to that above. The relevant data are collected in Table I. The disordered BF_4^- anion was modeled by two orientations of the remaining three F atoms (occupancies 0.6 and 0.4) around a common B-F unit. Difference maps revealed most of the H atoms, although those of the nitromethane solvate could not be located and were not included in the model. The remaining H atoms were placed in calculated positions, and a group isotropic thermal parameter was refined.

(36) No structural data have yet been published for facially coordinated 12S3, but the $\text{Mo}(\text{CO})_3$ complex of the phosphine analogue, 1,5,9-triphosphinocyclododecane, has been structurally characterized: Diel, B. N.; Haltiwanger, R. C.; Norman, A. D. *J. Am. Chem. Soc.* **1982**, *104*, 4700.
 (37) A preliminary report of this work has been published: Rawle, S. C.; Cooper, S. R. *J. Organomet. Chem. Commun.* **1987**, 308.
 (38) Dines, M. B. *J. Organomet. Chem.* **1974**, *67*, C55.
 (39) Davies, A. R.; Einstein, F.; Farrell, N.; James, B. R.; McMillan, R. S. *Inorg. Chem.* **1978**, *17*, 1965.

(40) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1986**, *25*, 1814.

(41) Carruthers, J. R. *CRYSTALS User Guide*; Oxford University Computing Laboratory: Oxford, England, 1975.

Table I. Crystallographic Data for $[\text{Ru}(\text{9S3})_2](\text{CF}_3\text{SO}_3)_2$ and $[\text{Ru}(\text{12S3})_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$

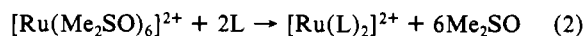
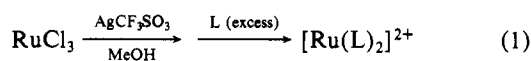
mol wt	759.9	841.5
space group	$P\bar{1}$	$I2/a$
<i>a</i> , Å	7.677 (5)	20.355 (3)
<i>b</i> , Å	9.465 (3)	8.006 (3)
<i>c</i> , Å	18.423 (3)	22.540 (2)
α , deg	83.61 (2)	90
β , deg	88.48 (4)	114.844 (9)
γ , deg	83.05 (4)	90
vol, Å ³	1320.5	3333.3
d_{calcd} , g/cm ³	1.91	1.68
<i>Z</i>	2	4
λ	Mo K α	Mo K α
<i>F</i> (000)	764	1720
μ , cm ⁻¹	12.61	8.96
cryst size, mm	0.7 × 0.25 × 0.4	0.4 × 0.5 × 0.6
reflens colld	$\pm h, \pm k, +l$	$\pm h, +k, +l$
no. of reflens colld	10031	8253
no. of unique data with $F^2 > 3\sigma(F^2)$	6917	3384
2θ range, deg	2–64	2–56
final <i>R</i> , %	4.03	2.85
final <i>R</i> _w , %	4.82	3.32
GOF ^a	1.05	1.02
no. of variables	321	225
temp	ambient	ambient
scan rate, deg/min	0.5–1.5	1.2–3.6
mode	ω - 2θ	ω - 2θ
max abs cor	1.08	1.15
<i>R</i> _{merge} , %	1.17	1.27

^aThe goodness of fit is defined as $[\sum w(|F_o| - |F_c|)^2 / (n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and number of variables, respectively.

Atomic coordinates of non-hydrogen atoms for both structures are given in Tables II and IV; important distances and angles appear in Tables III and V. The major structural features are summarized in Table VIII. A complete list of atomic coordinates, hydrogen atom coordinates, anisotropic temperature factors, and interatomic distances and angles for both structures is available as supplementary material.

Results

Synthesis. Thioethers usually fail to displace halides or other strongly bound species from transition-metal ions. Consequently, synthesis of homoleptic thioether complexes requires either removal of halides prior to addition of ligand or use of a transition-metal source that lacks strongly coordinated ligands. Both of these approaches proved fruitful for synthesis of $[\text{Ru}(\text{L})_2]^{2+}$, with high yields obtained by either (1) reaction of RuCl_3 with silver triflate,⁴² followed by addition of L, or (2) direct reaction of L with $[\text{Ru}(\text{Me}_2\text{SO})_6]^{2+}$.



Several factors favor the second route. Reaction 2, unlike reaction 1, does not waste some of the precious ligand as a reductant for Ru(III). (No attempt was made to isolate the products of ligand oxidation.) Moreover, it proceeds both more rapidly and more cleanly than reaction 1. In addition, the method is more general, since alternatively $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ru}(\text{DMF})_6]^{2+}$ can be used as starting materials.⁴³ Together these advantages make reaction 2 the method of choice.

In both $[\text{Ru}(\text{9S3})_2]^{2+}$ and $[\text{Ru}(\text{12S3})_2]^{2+}$ cations two crown thioether ligands sandwich the metal ion to produce a homoleptic thioether complex with idealized octahedral symmetry (Tables III, VI, and VIII; Figures 2–4). In each of these two complexes, which are the first reported homoleptic thioether complexes of

Table II. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\text{\AA}^2 \times 10^4$) for $[\text{Ru}(\text{9S3})_2](\text{CF}_3\text{SO}_3)_2$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
Ru1	0	0	0	238
Ru2	0	5000	5000	253
S1	2922 (1)	4416.4 (7)	8326.1 (4)	373
S2	3837 (1)	384 (1)	2955.5 (7)	560
S11	-831.2 (8)	2478.9 (6)	-109.1 (3)	312
S14	-2588.1 (8)	-258.7 (7)	679.7 (4)	345
S17	1353.6 (8)	239.4 (6)	1094.7 (3)	306
S21	1637.5 (8)	2840.7 (7)	5437.8 (4)	361
S24	-1707.3 (7)	4786.2 (7)	6062.7 (4)	332
S27	1882.3 (8)	6171.6 (8)	5636.3 (4)	366
C1	5315 (5)	4206 (5)	8256 (2)	524
C2	4849 (7)	953 (5)	3726 (3)	570
C12	-2932 (4)	2728 (3)	394 (2)	387
C13	-3925 (4)	1432 (4)	427 (2)	432
C15	-2041 (4)	-89 (4)	1625 (2)	411
C16	-107 (5)	-551 (3)	1771 (2)	404
C18	898 (4)	2139 (3)	1233 (1)	327
C19	657 (4)	3078 (3)	518 (1)	335
C22	684 (4)	2302 (3)	6333 (2)	412
C23	-1255 (4)	2890 (4)	6388 (2)	439
C25	-600 (4)	5632 (4)	6742 (2)	425
C26	497 (5)	6758 (4)	6386 (2)	505
C28	3399 (4)	4746 (4)	6112 (2)	419
C29	3685 (3)	3442 (4)	5717 (2)	405
F11	5988 (5)	2883 (4)	8503 (2)	803
F12	5970 (4)	5117 (5)	8637 (2)	796
F13	5861 (4)	4443 (5)	7566 (2)	759
F21	4618 (17)	119 (10)	4282 (4)	1571
F22	4321 (6)	2314 (4)	3832 (3)	917
F23	6631 (6)	895 (7)	3564 (5)	1100
O11	2424 (4)	5873 (3)	8034 (2)	517
O12	2394 (4)	3380 (3)	7887 (2)	556
O13	2624 (6)	4135 (4)	9095 (2)	604
O21	4311 (9)	1386 (7)	2333 (3)	1048
O22	4647 (5)	-1028 (4)	2927 (2)	673
O23	2041 (6)	559 (7)	3131 (4)	930

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

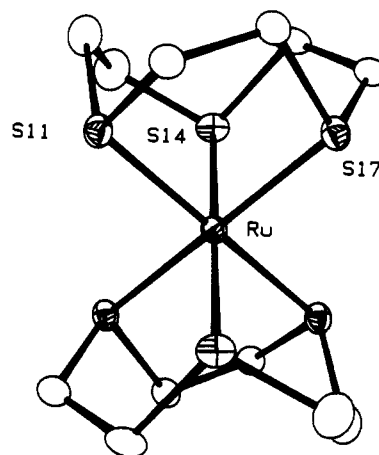


Figure 2. ORTEP drawing of the $[\text{Ru}(\text{9S3})_2]^{2+}$ cation (molecule 1) showing thermal ellipsoids at the 30% probability level (hydrogen atoms are omitted for clarity). Ligand atoms from molecule 1 are numbered sequentially around the ring (S11, C12, C13, etc.), so that the units place follows IUPAC numbering.

Ru, the metal ion occupies a crystallographic inversion center. As a consequence, the complexes of both ligands have trigonal twist angles of 60° .

As expected from the difference in ring sizes, 9S3 and 12S3 yield Ru(II) complexes that differ substantially in metal–sulfur bond lengths. (The unit cell of $[\text{Ru}(\text{9S3})_2](\text{trif})_2$ contains two crystallographically independent cations; since they are essentially identical, they will be discussed together.) Ruthenium–sulfur distances in $[\text{Ru}(\text{9S3})_2]^{2+}$ range from 2.331 (1) to 2.344 (1) Å (average 2.339 Å), while those in $[\text{Ru}(\text{12S3})_2]^{2+}$ range from 2.368

(42) Dixon, N. E.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Inorg. Synth.* **1986**, *24*, 243.

(43) Bernhard, P.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1985**, *1985*, 1516.

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Ru}(\text{9S3})_2](\text{CF}_3\text{SO}_3)_2$

Ru1-S11	2.3436 (5)	Ru2-S21	2.3394 (6)
Ru1-S14	2.3437 (6)	Ru2-S24	2.3306 (6)
Ru1-S17	2.3385 (6)	Ru2-S27	2.3364 (7)
S11-C12	1.842 (3)	S21-C22	1.832 (3)
S11-C19	1.825 (2)	S21-C29	1.840 (3)
S14-C13	1.815 (4)	S24-C23	1.823 (3)
S14-C15	1.831 (3)	S24-C25	1.837 (3)
S17-C16	1.814 (3)	S27-C26	1.816 (4)
S17-C18	1.834 (3)	S27-C28	1.832 (3)
C12-C13	1.515 (4)	C22-C23	1.530 (4)
C15-C16	1.519 (5)	C25-C26	1.520 (5)
C18-C19	1.509 (4)	C28-C29	1.492 (6)
S14-Ru1-S11	87.72 (2)	S24-Ru2-S21	87.77 (2)
S14-Ru1-S11'	92.28 (2)	S24-Ru2-S21'	92.23 (2)
S17-Ru1-S11	87.67 (2)	S27-Ru2-S21	87.80 (3)
S17-Ru1-S11'	92.33 (2)	S27-Ru2-S21'	92.20 (3)
S17-Ru1-S14	87.65 (2)	S27-Ru2-S24	87.74 (2)
S17-Ru1-S14'	92.35 (2)	S27-Ru2-S24'	92.26 (2)
C12-S11-Ru1	105.4 (1)	C22-S21-Ru2	105.9 (1)
C19-S11-Ru1	102.33 (9)	C29-S21-Ru2	102.2 (1)
C19-S11-C12	101.1 (1)	C29-S21-C22	100.4 (2)
C13-S14-Ru1	102.7 (1)	C23-S24-Ru2	102.9 (1)
C15-S14-Ru1	105.6 (1)	C25-S24-Ru2	105.9 (1)
C15-S14-C13	101.7 (2)	C25-S24-C23	102.3 (2)
C16-S17-Ru1	102.1 (1)	C26-S27-Ru2	102.5 (1)
C18-S17-Ru1	105.87 (9)	C28-S27-Ru2	105.4 (1)
C18-S17-C16	101.1 (1)	C28-S27-C26	101.5 (2)
C13-C12-S11	112.5 (2)	C23-C22-S21	111.9 (2)
C12-C13-S14	114.1 (2)	C22-C23-S24	113.6 (2)
C16-C15-S14	111.5 (2)	C26-C25-S24	111.9 (2)
C15-C16-S17	114.0 (2)	C25-C26-S27	113.9 (2)
C19-C18-S17	111.7 (2)	C29-C28-S27	112.5 (2)
C18-C19-S11	114.3 (2)	C28-C29-S21	113.5 (2)

Table IV. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($\text{Å}^2 \times 10^4$) for $[\text{Ru}(\text{12S3})_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$

atom	x	y	z	U^a
Ru1	2500	2500	2500	233
S1	3485.8 (2)	2149.1 (6)	3540.3 (2)	316
S5	1829.9 (2)	3948.6 (6)	2982.8 (2)	322
S9	1961.6 (2)	-111.3 (5)	2514.6 (2)	322
C1	9435 (2)	2390 (4)	575 (2)	689
C2	3503 (1)	3872 (3)	4071 (1)	403
C3	2889 (1)	4021 (3)	4282 (1)	465
C4	2153 (1)	3321 (3)	3837 (1)	420
C6	907 (1)	3142 (3)	2688 (1)	414
C7	824 (1)	1290 (3)	2792 (1)	453
C8	1014 (1)	88 (3)	2367 (1)	418
C10	2321 (1)	-1184 (3)	3294 (1)	435
C11	3148 (1)	-1195 (3)	3614 (1)	463
C12	3484 (1)	335 (3)	4028 (1)	437
N1	8947 (1)	2277 (4)	907 (1)	661
O1	9205 (2)	2248 (5)	1492 (2)	988
O2	8315 (2)	2154 (6)	581 (2)	1183
B1	4795 (2)	2724 (4)	874 (2)	574
F1	5230 (1)	3574 (3)	1422 (1)	829
F2	4087 (2)	3648 (7)	619 (2)	945
F3	4567 (3)	1354 (6)	1086 (3)	889
F4	4972 (4)	2691 (12)	396 (3)	983
F12	5328 (4)	1520 (9)	795 (4)	945
F13	4701 (7)	3632 (11)	362 (4)	1105
F14	4258 (6)	1855 (21)	844 (6)	1076

^aEquivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(1) to 2.377 (1) Å (average 2.373 Å) (Table VIII). Thus, on average, the Ru-S distances in the 12S3 complex exceed those in the analogous 9S3 complex by 0.03 Å. Previously reported ruthenium(II)-thioether bond lengths range from 2.26 to 2.40 Å,^{44,45} with values strongly dependent on the nature of the other ligands in the coordination sphere and especially on the identity

Table V. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Ru}(\text{12S3})_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$

Ru1-S1	2.3772 (4)	Ru1-S5	2.3736 (4)
Ru1-S9	2.3676 (4)		
S1-C2	1.815 (2)	S1-C12	1.824 (2)
S5-C4	1.824 (2)	S5-C6	1.827 (2)
S9-C8	1.822 (2)	S9-C10	1.812 (2)
C2-C3	1.517 (3)	C3-C4	1.517 (3)
C6-C7	1.522 (4)	C7-C8	1.516 (3)
C10-C11	1.528 (4)	C11-C12	1.518 (3)
S5-Ru1-S1	90.86 (2)	S5-Ru1-S1'	89.14 (2)
S9-Ru1-S1	94.92 (2)	S9-Ru1-S1'	85.08 (2)
S9-Ru1-S5	93.80 (2)	S9-Ru1-S5'	86.20 (2)
C2-S1-Ru1	109.53 (7)	C12-S1-Ru1	118.32 (7)
C12-S1-C2	102.2 (1)	C4-S5-Ru1	109.09 (7)
C6-S5-Ru1	111.20 (7)	C6-S5-C4	98.4 (1)
C8-S9-Ru1	112.41 (8)	C10-S9-Ru1	115.59 (7)
C10-S9-C8	100.6 (1)		
C3-C2-S1	118.4 (2)	C4-C3-C2	118.6 (2)
C3-C4-S5	114.5 (2)	C7-C6-S5	116.9 (2)
C8-C7-C6	116.6 (2)	C7-C8-S9	118.0 (1)
C11-C10-S9	112.1 (2)	C12-C11-C10	114.1 (2)
C11-C12-S1	112.7 (2)		

Table VI. Torsional Angles (deg) for $[\text{Ru}(\text{9S3})_2](\text{CF}_3\text{SO}_3)_2$

S11-C12-C13-S14	46.9 (1)	C16-S17-C18-C19	-134.3 (1)
C12-C13-S14-C15	66.4 (1)	S17-C18-C19-S11	48.2 (1)
C13-S14-C15-C16	-134.4 (1)	C18-C19-S11-C12	66.1 (1)
S14-C15-C16-S17	49.0 (1)	C19-S11-C12-C13	-132.4 (1)
C15-C16-S17-C18	64.8 (1)		
S21-C22-C23-S24	-47.3 (1)	C26-S27-C28-C29	135.5 (1)
C22-C23-S24-C25	-67.1 (1)	S27-C28-C29-S21	-48.8 (1)
C23-S24-C25-C26	133.3 (1)	C28-C29-S21-C22	-66.3 (1)
S24-C25-C26-S27	-47.1 (1)	C29-S21-C22-C23	133.2 (1)
C25-C26-S27-C28	-65.3 (1)		

Table VII. Torsional Angles (deg) for $[\text{Ru}(\text{12S3})_2](\text{BF}_4)_2 \cdot 2\text{MeNO}_2$

S1-C2-C3-C4	-27.7 (1)	C7-C8-S9-C10	70.4 (1)
C2-C3-C4-S5	-48.7 (1)	C8-S9-C10-C11	-167.7 (1)
C3-C4-S5-C6	-170.9 (1)	S9-C10-C11-C12	86.9 (1)
C4-S5-C6-C7	-56.8 (1)	C10-C11-C12-S1	-78.7 (1)
S5-C6-C7-C8	-72.2 (1)	C11-C12-S1-C2	154.7 (1)
C6-C7-C8-S9	69.6 (1)	C12-S1-C2-C3	-59.3 (1)

Table VIII. Comparison of the Major Structural Features of $[\text{Ru}(\text{9S3})_2]^{2+}$ and $[\text{Ru}(\text{12S3})_2]^{2+}$

param	$[\text{Ru}(\text{9S3})_2]^{2+}$	$[\text{Ru}(\text{12S3})_2]^{2+}$
M-S _{av} , Å	2.339	2.373
chelating S-M-S, deg	87.72	93.19
nonchelating S-M-S, deg	92.28	86.81
S-C _{av} , Å	1.823	1.821
C-C _{av} , Å	1.514	1.520
M-S-C _{av} , deg	104.1	116.0
C-S-C _{av} , deg	101.4	100.4
S-C-C _{av} , deg	113.0	115.5
C-C-C _{av} , deg		116.4

of the trans ligand. Ruthenium-sulfur distances of the 9S3 complex lie roughly in the middle of this range, while those of the 12S3 complex lie toward the longer end.

In $[\text{Ru}(\text{9S3})_2]^{2+}$, chelating S-Ru-S angles (average 87.7°) are approximately 5° smaller than nonchelating ones (average 92.3°) (Table VIII; Figure 4). In contrast, the 12S3 complex shows the opposite pattern; here chelating S-Ru-S angles exceed nonchelating ones by approximately 7° (average values 93.2° and 86.8°, respectively). Consequently the average S...S nonchelate distance in the 9S3 complexes (3.37 Å) exceeds that in the 12S3 complex (3.26 Å), even though the former has shorter Ru-S distances. The resulting trigonal flattening in $[\text{Ru}(\text{12S3})_2]^{2+}$, combined with the overall dilation of the RuS₆ coordination sphere, reflects the larger effective cavity size of 12S3 relative to that of 9S3. In a word,

(45) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 5379.

(44) Lai, T.-F.; Poon, C. K. *J. Chem. Soc., Dalton Trans.* **1982**, 1465.

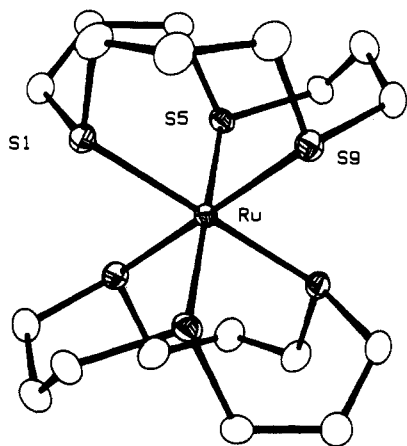


Figure 3. ORTEP drawing of the $[\text{Ru}(\text{12S3})_2]^{2+}$ cation showing thermal ellipsoids at 30% probability level (hydrogen atoms are omitted for clarity). Ligand atoms are numbered sequentially around the ring (S1, C2, C3, etc.) following IUPAC nomenclature.

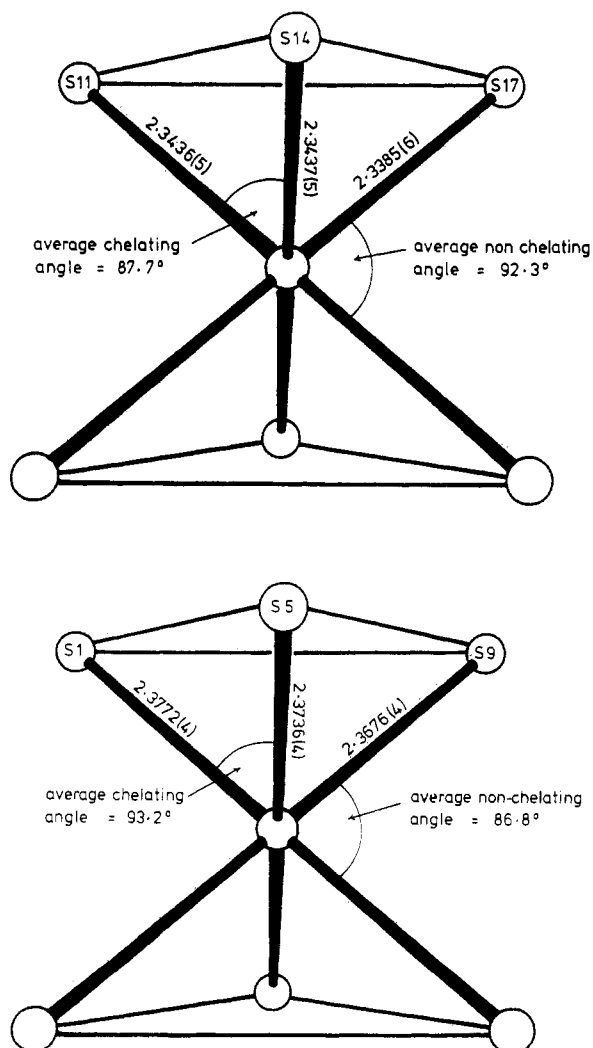


Figure 4. Coordination spheres of the $[\text{Ru}(\text{9S3})_2]^{2+}$ (molecule 1) (top) and $[\text{Ru}(\text{12S3})_2]^{2+}$ (bottom) cations.

9S3 "perches", whereas 12S3 "engulfs".

As well as causing this difference in coordination mode, the additional methylene group in each $-\text{S}-\text{C}-\text{C}-\text{S}$ linkage of 12S3 has two other consequences. First, it forces $\text{Ru}-\text{S}-\text{C}$ angles to increase by 12° (from 104.1° in $[\text{Ru}(\text{9S3})_2]^{2+}$ to 116.0° in $[\text{Ru}(\text{12S3})_2]^{2+}$) (Table VIII). Second, it disrupts the conformational regularity of the ligand. Each of the $\text{C}-\text{C}-\text{C}$ linkages adopts a different conformation (Figure 3); as a consequence, the

Table IX. Electronic Spectra of $[\text{RuL}_2]^{2+}$ ($\text{L} = \text{9S3}, \text{12S3}$) and Derived Values of the Ligand Field Strength, $10Dq$, and the Racah Parameter, B

	9S3	12S3	ttn
$\nu_1, 10^3 \text{ cm}^{-1} (\epsilon)$	29.59 (172)	28.74 (210)	28.41 (445)
$\nu_2, 10^3 \text{ cm}^{-1} (\epsilon)$	34.25 (195)	32.05 (290)	32.47 (437)
$10Dq, 10^3 \text{ cm}^{-1}$	30.76	29.57	29.43
$B, \text{ cm}^{-1}$	291	207	254

six-membered rings formed by the Ru and consecutive chelating $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$ units adopt chair, flattened-chair, and twist-boat forms (Figure 3).⁴⁶ This conformational heterogeneity, which in this case may partially result from repulsions between H atoms of adjacent propyl linkages,^{36,47} indicates that 12S3 is poorly adapted for facial coordination to a metal ion.

Electrochemistry. In contrast to the facile electrochemistry exhibited by most ruthenium complexes, the hexakis(thioether) complexes prepared here resist oxidation to a remarkable degree. Cyclic voltammetric measurements reveal quasi-reversible waves at $+1.99$ and $+1.66$ V vs NHE for the 9S3 and 12S3 complexes, respectively. These potentials considerably exceed those for oxidation of the free ligands. These high $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ potentials contrast with those typically found for $\text{Ru}(\text{II})$ -hexamine complexes ($E_f \approx 0$ V vs NHE), which exhibit ligand field splittings roughly comparable to those reported here. This comparison highlights the stabilization of $\text{Ru}(\text{II})$ over $\text{Ru}(\text{III})$ by the hexakis(thioether) environment, and it exemplifies the π acidity of thioether ligands.

Electronic Spectra. $[\text{Ru}(\text{9S3})_2]^{2+}$ is essentially colorless both in solution and in the solid state, whereas the 12S3, ttn, 10S3 and 20S6 analogues are yellow. In aqueous solution all the complexes display d-d bands (at approximately 350 and 300 nm) attributable to the $^1A_{1g} \rightarrow ^1T_{1g}$ (ν_1) and $^1A_{1g} \rightarrow ^1T_{2g}$ (ν_2) transitions of octahedral $\text{Ru}(\text{II})$, respectively (Table IX).

The optical spectra show that these thioether ligands exert greater ligand field strengths ($10Dq = 30760 \text{ cm}^{-1}$ for $[\text{Ru}(\text{9S3})_2]^{2+}$)⁴⁸ than either water ($10Dq = 19800 \text{ cm}^{-1}$ for $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$)⁴⁹ or ethylenediamine ($10Dq = 28100 \text{ cm}^{-1}$ for $[\text{Ru}(\text{en})_3]^{2+}$).⁵⁰ In addition, the Racah electron-electron repulsion parameter diminishes considerably on replacement of water or en ($B = 490$ and 420 cm^{-1} , respectively) with thioethers ($B = 290 \text{ cm}^{-1}$). This decrease indicates that the thioethers exert considerable π -acidity, consistent with the strong stabilization of $\text{Ru}(\text{II})$ over $\text{Ru}(\text{III})$ inferred from electrochemical measurements (vide supra). Curiously, B decreases by 30% from $[\text{Ru}(\text{9S3})_2]^{2+}$ to $[\text{Ru}(\text{12S3})_2]^{2+}$, whereas $10Dq$ decreases by only 4%.⁵¹ In summary, the optical properties of hexakis(thioether) complexes of $\text{Ru}(\text{II})$ demonstrate that the electronic consequences of thioether coordination to first-row transition-metal ions are reproduced in the second row.

NMR. Proton NMR spectroscopy of $[\text{Ru}(\text{12S3})_2]^{2+}$ (Figure 1a) distinguishes two classes of protons, $-\text{SCH}_2-$ and $-\text{CH}_2-\text{CH}_2-$. The $-\text{SCH}_2-$ protons can be further subdivided into two sets of 12 each: those that point toward the metal ion and those that point away from it. As a consequence of coupling between these sets of protons and the small difference of chemical shift, the $-\text{SCH}_2$ protons yield a complicated second-order spectrum similar both to that of $[\text{Ru}(\text{9S3})_2]^{2+}$ (Figure 1b) and

(46) Each of these three conformations of trimethylene chelates has been observed frequently in other molecules; their occurrence together in this one molecule reinforces the suggestion that they are all of approximately the same energy. This is the origin of the flexibility usually associated with $-\text{CH}_2\text{CH}_2\text{CH}_2-$ linkages.

(47) Other workers have also noted the importance of steric interactions when two trimethylene chelates share a trigonal face: Kyba, E. P.; Davis, R. E.; Liu, S. T.; Hassett, K. A.; Larson, S. B. *Inorg. Chem.* **1985**, *24*, 4629. Davis, R. E.; Kyba, E. P.; John, A. M.; Yep, J. M. *Inorg. Chem.* **1980**, *19*, 2540.

(48) Ligand field strengths and Racah parameters were calculated from $\nu_1 = 10Dq - C$ and $\nu_2 = 10Dq - C + 16B$ with the approximation $C = 4B$.

(49) Mercer, E.; Buckley, R. R. *Inorg. Chem.* **1965**, *4*, 1692.

(50) Schmidtke, H.; Garthoff, D. *Helv. Chim. Acta* **1966**, *49*, 2039.

(51) In the analogous nickel and iron systems B remains constant but $10Dq$ decreases by 10%. The origin of this contrast is not yet clear.

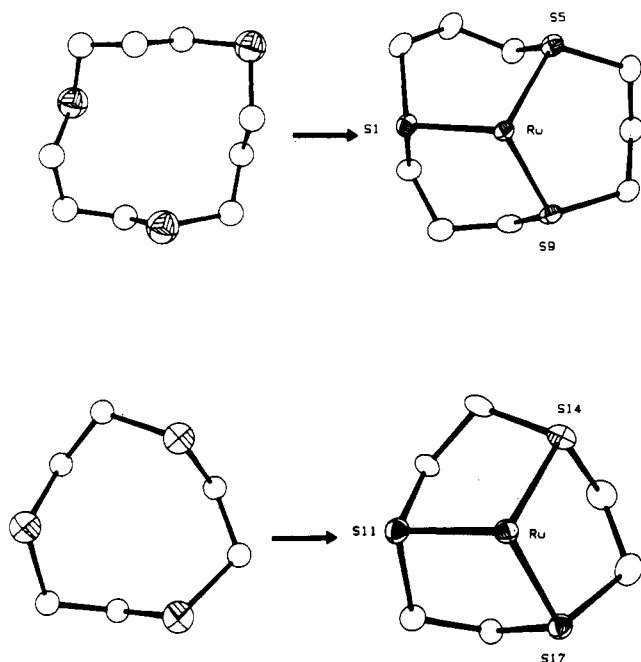


Figure 5. ORTEP views showing conformational changes of L on formation of $[\text{RuL}_2]^{2+}$: top, L = 12S3⁹; bottom, L = 9S3.⁸ Only one ligand of each complex is shown; the second is generated by the crystallographic inversion center at Ru. Thermal ellipsoids are at 30% probability level; hydrogen atoms are omitted for clarity.

to those reported recently for $[\text{M}(9\text{S}3)_2]^{n+}$ (M = Fe ($n = 2$),³³ Co ($n = 3$),¹⁸ Rh ($n = 3$)²⁴). In addition, protons on the central CH_2 units of $[\text{Ru}(12\text{S}3)_2]^{2+}$ appear as two widely separate multiplets centered at 2.79 and 2.33 ppm.

Discussion

Ligand Conformations. The influence of conformation on the binding affinity (and indeed binding mode) of ligands is becoming increasingly apparent. Crown thioether complexes add further evidence supporting the importance of conformational considerations. For example, the conformation of free 9S3⁸ closely resembles that in its complexes,^{7,18,26,27,33,37} all of which are noteworthy for their exceptional stability compared to those of other tridentate thioethers.³²

As pointed out previously,²⁶ the S-C-C-S torsional angles of 9S3 provide a sensitive measure of the "pinching in" of the S atoms. Upon coordination of the free ligand to Ru(II) this tor-

sional angle (Table IV; Figure 5) diminishes from 58.6 to 48.3°, while the average intraligand S...S distance decreases from 3.45 to 3.24 Å. Structural studies of other 9S3 complexes have revealed a modest correlation of the S-C-C-S torsion angle with the ligand-metal distance.⁵²

Conformationally 12S3 behaves rather differently from 9S3. Like 9S3, part of the coordinated 12S3 ring (C6-C7-C8-S9-C10-C11-C12) retains the conformation of the free ligand (Table VII; Figure 5).⁹ In contrast, however, the remainder of the ring suffers considerable conformational change, which must diminish the stability of 12S3 complexes with respect to those of 9S3. Qualitative observations support this inference. For example, $[\text{Fe}(12\text{S}3)_2]^{2+}$ decomposes instantly on contact with water, but $[\text{Fe}(9\text{S}3)_2]^{2+}$ resists attack by this solvent.⁵³ These observations underscore how profoundly the conformational preferences of ligands can influence their coordination chemistry.

Conclusions

Hexakis(thioether) coordination to Ru(II) gives octahedral complexes that are greatly stabilized with respect to oxidation. Crystallographic studies provide a structural benchmark for the design of thioether complexes of ruthenium and related heavy transition metals. Electronically thioethers resemble phosphines as ligands, which encourages attempts to mimic the commercially important catalytic reactivity of phosphine complexes with thioether analogues. The apparently high affinity of Ru(II) for thioether coordination, coupled with the increasing availability of 9S3, 12S3, and other crown thioethers suggests that they may prove useful as auxiliary ligands in catalysts based upon Ru and other second- and third-row transition metals.

Acknowledgment. This work has been supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $[\text{Ru}(9\text{S}3)_2](\text{CF}_3\text{SO}_3)_2$, 108187-29-7; $[\text{Ru}(9\text{S}3)_2](\text{BF}_4)_2$, 110486-18-5; $[\text{Ru}(10\text{S}3)_2](\text{BF}_4)_2$, 110509-39-2; $[\text{Ru}(12\text{S}3)_2](\text{BF}_4)_2$, 110486-22-1; $[\text{Ru}(12\text{S}3)_2](\text{BF}_4)_2 \cdot 2\text{CH}_3\text{NO}_2$, 110486-25-4; $[\text{Ru}(20\text{S}6)](\text{BF}_4)_2$, 110486-24-3; $[\text{Ru}(\text{ttn})_2](\text{BF}_4)_2$, 110486-20-9; $[\text{Ru}(\text{Me}_2\text{SO})_6](\text{BF}_4)_2$, 66373-94-2.

Supplementary Material Available: Tables containing bond distances and angles, anisotropic thermal parameters, hydrogen atomic coordinates, and torsional angles (6 pages); tables of structure factors (47 pages). Ordering information is given on any current masthead page.

(52) In the case of $[\text{Ag}(9\text{S}3)_2]^+$ which displays extremely long M-S bonds (average 2.73 Å), the S-C-C-S torsion angles (average 59.2°) actually slightly exceed those in the free ligand.²⁷

(53) Rawle, S. C.; Sewell, T. J.; Cooper, S. R., unpublished observations.