$D$ by an effective parameter $D_x = D - 3E$ for $\chi_x$ and $D_y = D + 3E$ for $\chi_y$. $\chi_z$ is not affected by a rhombic distortion. The theoretical fits using eq 8 and 9 are shown in Figures 4–6. It may be seen that the model prediction fits the data very well down to the temperature of the maximum susceptibility. The derived parameters are $D/k = -0.075 \pm 0.005$ K, $J/k = -0.044 \pm 0.003$ K, and $E/k = 0.040 \pm 0.005$ K. They are in excellent agreement with the parameters obtained above. The $g$ values were not fitted and were taken as $g_x = 1.97$ and $g_y = g_z = 1.96$.

The susceptibility curve of Fisher's $S = \infty$ model scaled to $S = {}^3/_2$ usually lies above the curve obtained from the Pade approximant analysis of high-temperature series expansions for $S = {}^3/_2$, which are better approximations. So the actual $J/k_B$ value should be slightly different from the one given above.

At temperatures below $T(\chi_{max})$, the experimental points deviate sensibly from the theoretical curves. The axial anisotropy as well as the rhombic distortion makes it difficult to analyze the data in that temperature region. A purely isotropic one-dimensional antiferromagnetic system should not undergo a transition to long-range order at any finite temperature. However, a small amount of interchain interaction is inevitable in all physical realizations, and a cooperative transition occurs as the temperature goes down. The fact that this transition does not appear to occur down to the lowest temperatures measured makes this compound a good example of a magnetic chain. In order to compare this compound to other Heisenberg chains and to verify our experimental parameters, further experiments on the specific heat and neutron diffraction are necessary.

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Contribution from the Department of Chemistry, The University of Tennessee at Chattanooga, Chattanooga, Tennessee 37403,
Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899,
and School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

# Zerovalent Molybdenum Complexes of Mesocyclic and Macrocyclic Crown Thioethers[1]

Gregory J. Grant,[*,†] Joseph P. Carpenter,[†,2] William N. Setzer,[‡] and Donald G. VanDerveer[§]

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The tricarbonylmolybdenum(0) complex of 1,4,7-trithiacyclodecane (10S3) has been synthesized and characterized by single-crystal X-ray diffraction and by Fourier transform infrared spectroscopy. The complex shows structural and spectral properties similar to those of the previously prepared tricarbonylmolybdenum(0) complex of the thioethers 1,4,7-trithiacyclononane (9S3) and 2,5,8-trithianonane (ttn). Also, a zerovalent molybdenum complex of the potentially hexadentate ligand 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) has been prepared and gives a binuclear complex. Crystal data for (10S3)Mo(CO)$_3$, C$_{10}$H$_{14}$MoO$_3$S$_3$: monoclinic, space group $P2_1$, $a = 7.425$ (2) Å, $b = 12.308$ (2) Å, $c = 7.901(2)$ Å, $\beta = 108.22$ (2)°, $V = 685.85$ (20) Å$^3$, $Z = 2$, $R = 0.020$.

## Introduction

There has been a recent upsurge in the study of the coordination chemistry of thioether ligands. Two recent reviews on the coordination chemistry of thioether ligands has appeared, the latter dealing exclusively with crown thioether ligands.[3,4] Complexes that contain thioether ligands exhibit many unusual properties including suprisingly large ligand field strengths.[4] Thioethers function as good $\pi$-acceptors, as evidenced by their ability to complex metals in low oxidation states and by their tendency to generate low-spin configurations in metal ions such as Co(II) and Fe(II) through reduction of pairing energies.[5-8] The $\pi$-acidity of thioethers has been described as intermediate between those of phosphines and amines, and the relative $\pi$-acidity of a thioether can be measured via the infrared carbonyl absorption for the tricarbonyl complexes.[3,4] We are interested in examining whether or not this trend in relative $\pi$-acidity for thioethers parallels the trend in their ligand field strengths. The recent publication of a template synthesis of 1,4,7-trithiacyclononane (9S3) involving a carbonyl–Mo(0) moiety is another important consideration in examining thioether–Mo(0) complexation behavior.[9]

Two publications describing the synthesis and structure of tricarbonylmolybdenum(0) complexes with the tridentate thioethers 9S3 and 2,5,8-trithianonane (ttn) have recently appeared in the literature.[10,11] Both of these complexes have the general formula LM(CO)$_3$. We wish to extend this series of complexes with the report of the synthesis and structure of (10S3)Mo(CO)$_3$, the first complex containing an unsymmetrical crown thioether to be structurally characterized. In addition, we wish to examine the complexation of 1,4,7,10,13,16,-hexathiacyclooctadecane (18S6), a potentially hexadentate ligand, with zerovalent metals. Although the coordination chemistry of this ligand has recently received much attention, little work has been done with its complexation behavior toward metals in zerovalent oxidation states.[12] The structures for the two thioethers ligands 10S3 and 18S6 are shown in Figure 1.

## Experimental Section

**Materials.** The solvents dimethylformamide and acetonitrile were dried by common methods.[13] All other solvents were used as received. The compounds bis(2-mercaptoethyl) sulfide (Aldrich) and 1,3-dichloropropane (Aldrich) were distilled under vacuum before use. Molybdenum hexacarbonyl (Aldrich), cesium carbonate (Aldrich), and the

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[†] The University of Tennessee at Chattanooga.

[‡] The University of Alabama in Huntsville.

[§] Georgia Institute of Technology.

(1) Synthesis and Complexation Studies of Mesocyclic and Macrocyclic Polythioethers. 2. For part 1, see: Setzer, W. N.; Cacioppo, E. L.; Grant, G. J.; Glass, R. S. *Phosphorus, Sulfur, and Silicon*, in press. This work was presented in part at the 38th Southeastern Regional Meeting of the American Chemical Society, Louisville, KY, Nov 3–5, 1986, and the 40th Southeastern Regional Meeting of the American Chemical Society, Atlanta, GA, Nov 9–11, 1988.

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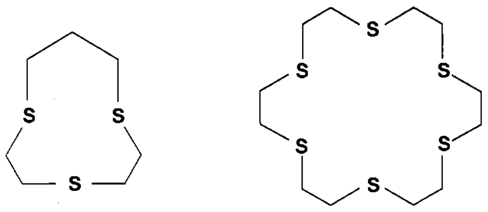

**Figure 1.** Crown thioethers 10S3 and 18S6.

thioether 1,4,7,10,13,16-hexathiacyclooctadecane (Aldrich) were used as received without additional purification.

**Measurements.** Analyses were performed by Atlantic Microlab, Inc., Atlanta, GA, or by Galbraith Laboratories, Inc., Knoxville, TN. Fourier transform infrared spectra were obtained by using a Beckman FT 1100 infrared spectrophotometer, and a thallium bromide cell (path length 0.0050 mm) was used for solution spectra. All 60-MHz proton NMR spectra were obtained on a JEOL JNM-PMX60 NMR spectrometer using TMS as an internal standard. Reported melting points are uncorrected.

**Preparation of 1,4,7-Trithiacyclodecane.**[14] The method used was based upon the Cooper synthesis of 1,4,7-trithiacyclononane.[15] A 1000-mL three-necked round-bottom flask equipped with a 125-mL pressure equalizing dropping funnel, a magnetic stir bar, a thermometer, and a nitrogen inlet–outlet, was charged with a slurry of 250 mL of dimethylformamide and cesium carbonate (13.03 g, 40.00 mmol). In the funnel was prepared a solution of bis(2-mercaptoethyl) sulfide (7.40 mL, 5.56 g, 36.0 mmol), 1,3-dichloropropane (3.42 mL, 4.07 g, 36.0 mmol), and 150 mL of DMF. The solution was added to the rapidly stirred, heated (100 °C) DMF/$Cs_2CO_3$ slurry at the rate of about 3 mL/h. After completion of the addition (48 h), the mixture was cooled to room temperature and stirred for an additional 24 h. A yellow supernatant solution and a white precipitate of CsCl had formed. CsCl was filtered out, and the solvent was removed in vacuo, leaving a brown sticky solid. The brown solid was taken up in 100 mL of $CH_2Cl_2$, and the mixture was filtered. The $CH_2Cl_2$ solution was washed with 100 mL of water, 2 × 100 mL of 0.1 M NaOH, and 2 × 100 mL of water again and dried over anhydrous $MgSO_4$. The drying agent was filtered, and $CH_2Cl_2$ was removed in vacuo. The brown sticky residue was chromatographed on a silica gel gravity column (3-cm diameter × 50-cm length), eluting with 10% ethyl acetate/hexane to give 1.24 g (17.7% yield) of 1,4,7-trithiacyclodecane as a colorless, viscous oil: IR (KBr, $cm^{-1}$) 2926.1, 1419.4, 1337.1, 1252.2, 1193.1, 1139.1, 1083.8, 833.1, 694.3, 681.4, 642.8; $^1H$ NMR ($CDCl_3$) $\delta$ 2.77 singlet, 8 H, $-SCH_2CH_2-$), 2.67 (triplet, 4 H, $-SCH_2CH_2CH_2-$), 1.93 (quintet, 2 H, $-SCH_2CH_2CH_2-$). Anal. Calcd for $C_7H_{14}S_3$: C, 43.27; H, 7.25; S, 49.49. Found: C, 43.33; H, 7.11; S, 49.56.

**Preparation of Tricarbonyl(1,4,7-trithiacyclodecane)molybdenum(0).**[16] The method used was based upon synthesis of tricarbonyl(1,4,7-trithiacyclononane)molybdenum(0) by Ashby and Lichtenberger.[10] Under nitrogen, $Mo(CO)_6$ (181 mg, 0.685 mmol) was dissolved in 5 mL of acetonitrile, and the mixture was refluxed for 1.5 h to give a yellow solution of $Mo(CO)_3(CH_3CN)_3$. The reaction solution was cooled to room temperature, and a solution of 1,4,7-trithiacyclodecane (100 mg, 0.514 mmol) in 7 mL of acetonitrile was added dropwise with stirring. The mixture immediately turned brown, and after several minutes the product precipitated as a light yellow-green solid. The product was filtered out, washed with 7 mL of hexane, and stored under nitrogen in the dark. A yield of 118 mg (61.5%) of product was obtained. The product was further purified by recrystallization from dimethylformamide using ether diffusion. A single crystal of $(10S3)Mo(CO)_3$ suitable for X-ray diffraction was grown by ether diffusion into a dimethylformamide solution: IR (KBr, $cm^{-1}$) 2931.3, 1913.0, 1789.6, 1404.0, 1275.4, 1121.1, 910.2, 833.1; IR (nitromethane, $cm^{-1}$) $\nu_{CO}$ 1933.6, 1815.3. Anal. Calcd for $C_{10}H_{14}MoO_3S_3$: C, 32.09; H, 3.77; S, 25.69. Found: C, 32.11; H, 3.69; S, 25.61.

**Table I.** Crystallographic Data and Details of Refinement for $(10S3)Mo(CO)_3$

| | | | |
|---|---|---|---|
| formula | $C_{10}H_{14}MoO_3S_3$ | Z | 2 |
| fw | 374.21 amu | $\mu$, $cm^{-1}$ | 0.137 |
| cryst syst | monoclinic | no. of rflns measd | 2511 |
| space group | $P2_1$ | no. of unique flns measd | 2418 |
| $a$, Å | 7.425 (2) | no. of indep rflns with $I \geq 2.5\sigma(I)$ | 2339 |
| $b$, Å | 12.308 (2) | | |
| $c$, Å | 7.901 (2) | $F(000)$ | 376 |
| $\beta$, deg | 108.22 (2) | no. of params defined | 168 |
| $V$, $Å^3$ | 685.85 (20) | $R$ | 0.020 |
| $D$(calcd), g $cm^{-3}$ | 1.813 | $R_w$ | 0.023 |

**Table II.** Atomic Positional Parameters for Non-Hydrogen Atoms in $(10S3)Mo(CO)_3$ with Esd's in Parentheses

| atom | $x$ | $y$ | $z$ | $B$,[a] $Å^2$ |
|---|---|---|---|---|
| Mo | 0.14047 (3) | 0.00000 | 0.96962 (3) | 2.317 (10) |
| S1 | −0.03117 (15) | 0.13539 (9) | 1.10858 (3) | 2.88 (4) |
| S2 | 0.35603 (13) | −0.05419 (10) | 1.27701 (13) | 3.53 (4) |
| S3 | −0.08059 (15) | −0.13138 (9) | 1.04855 (14) | 2.92 (4) |
| CCO1 | 0.2552 (6) | −0.1073 (3) | 0.8541 (5) | 3.06 (18) |
| OCO1 | 0.3208 (5) | −0.1685 (3) | 0.7760 (5) | 4.79 (17) |
| CCO2 | 0.3048 (6) | 0.1080 (4) | 0.9094 (6) | 3.14 (17) |
| OCO2 | 0.3989 (5) | 0.1692 (3) | 0.8632 (5) | 4.96 (17) |
| CCO3 | −0.0455 (5) | 0.0252 (3) | 0.7403 (5) | 3.38 (20) |
| OCO3 | −0.1605 (5) | 0.0386 (3) | 0.6028 (4) | 6.30 (20) |
| C1 | 0.1129 (7) | 0.1945 (4) | 1.3204 (5) | 4.05 (22) |
| C2 | 0.3145 (7) | 0.1524 (4) | 1.3974 (6) | 4.60 (22) |
| C3 | 0.3302 (6) | 0.0357 (4) | 1.4529 (5) | 4.39 (22) |
| C4 | 0.2489 (7) | −0.1801 (4) | 1.3200 (6) | 4.04 (20) |
| C5 | 0.0338 (7) | −0.1751 (4) | 1.2759 (6) | 3.79 (20) |
| C6 | −0.2668 (5) | −0.0426 (4) | 1.0723 (6) | 3.75 (20) |
| C7 | −0.1986 (6) | 0.0557 (4) | 1.1860 (6) | 3.79 (20) |

[a] $B$ is the mean of the principal axes of the thermal ellipsoid.

**Preparation of Hexacarbonyl(1,4,7,10,13,16-hexathiacyclooctadecane)dimolybdenum(0).**[16] Under nitrogen, $Mo(CO)_6$ (366 mg, 1.39 mmol) was dissolved in 5 mL of acetonitrile, and refluxed the mixture was for 1.5 h to give a yellow solution of $Mo(CO)_3(CH_3CN)_3$. The reaction solution was cooled to room temperature, and a solution of 1,4,7,10,13,16-hexathiacyclooctadecane (250 mg, 0.693 mmol) in 6 mL of chloroform was added dropwise with stirring. The mixture immediately turned brown, and after several minutes the product precipitated as a light yellow-green solid. The product was filtered out, washed with 7 mL of hexane, and stored under nitrogen in the dark. A yield of 202 mg (40.5%) of product was obtained. The insolubility of the complex in common solvents made solution IR work and recrystallization for single-crystal X-ray diffraction impractical: IR (KBr, $cm^{-1}$) 2921.0, 1918.2, 1794.8, 1414.2, 1258.5, 1206.4, 1176.0, 1146.3, 1121.5, 1019.4, 938.0, 915.4, 836.6, 750.8, 640.9, 612.7, 517.9. Anal. Calcd for $C_{18}H_{24}Mo_2O_6S_6$: C, 30.00; H, 3.36; S, 26.70. Found: C, 30.03; H, 3.47; S, 26.52.

**X-ray Crystal Structure of $(10S3)Mo(CO)_3$.** A clear yellow crystal suitable for X-ray diffraction and having approximate dimensions 0.30 × 0.25 × 0.25 mm was mounted on a Syntex $P2_1$ autodiffractometer equipped with a scintillation counter, Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å), and a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 15 independent reflections in the range of 18.5° < 2$\theta$ < 27.3° to obtain the unit cell dimensions, which are given in Table I. The $\omega$-scan technique over the range 4° ≤ 2$\theta$ ≤ 50° was used to collect the data of which those with $I \geq 2.5\sigma(I)$ were considered observed. No correction was made for absorption.

The structure was solved by the heavy-atom method. The position of the molybdenum atom was located from a three-dimensional Patterson map, and the remaining atoms were located by subsequent structure factor calculations and difference electron density maps.[17] The structure was refined by full-matrix least-squares techniques. The hydrogen atoms were located by difference maps and were isotropically refined (positional parameters were not refined). All non-hydrogen atoms were refined anisotropically converging at

$$R = \sum || F_o| - |F_c|| / \sum |F_o| = 0.020$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.023$$

and

$$\text{GoF} = [\sum w(|F_o| - |F_c|)^2(\text{no. of rflns} - \text{no. of params})]^{1/2} = 1.698$$

The final atomic parameters for $(10S3)Mo(CO)_3$ with their standard

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(17) The programs used for the solution and refinement of this structure were those in NRCVAX from the National Resource Council, Ottawa, Canada.

**Table III.** Selected Bond Lengths (Å) and Bond Angles (deg) for (10S3)Mo(CO)$_3$

Selected Bond Distances

| | | | | | |
|---|---|---|---|---|---|
| Mo–S1 | 2.5458 (11) | S1–C1 | 1.832 (4) | CCO1–OCO1 | 1.171 (5) |
| Mo–S2 | 2.5444 (12) | S1–C7 | 1.832 (4) | CCO2–OCO2 | 1.161 (6) |
| Mo–S3 | 2.5175 (11) | S2–C3 | 1.833 (5) | CCO3–OCO3 | 1.165 (5) |
| Mo–CCO1 | 1.947 (4) | S2–C4 | 1.822 (5) | C1–C2 | 1.520 (7) |
| Mo–CCO2 | 1.961 (5) | S3–C5 | 1.812 (5) | C2–C3 | 1.495 (7) |
| Mo–CCO3 | 1.929 (4) | S3–C6 | 1.818 (4) | C4–C5 | 1.526 (7) |
| | | | | C6–C7 | 1.497 (6) |

Selected Bond Angles

| | | | |
|---|---|---|---|
| S1–Mo–S2 | 90.59 (4) | S2–C3–C2 | 112.0 (3) |
| S1–Mo–S3 | 81.99 (4) | S3—Mo–CCO1 | 95.45 (12) |
| S1–Mo–CCO1 | 176.17 (12) | S3–Mo–CCO2 | 177.29 (13) |
| S1–Mo–CCO2 | 95.43 (13) | S3–Mo–CCO3 | 90.30 (11) |
| S1–Mo–CCO3 | 89.54 (11) | CCO1–Mo–CCO2 | 87.09 (17) |
| S2–Mo–S3 | 81.92 (4) | S2–Mo–CCO1 | 91.87 (13) |
| S2–Mo–CCO2 | 98.97 (13) | S2–Mo–CCO3 | 172.12 (11) |

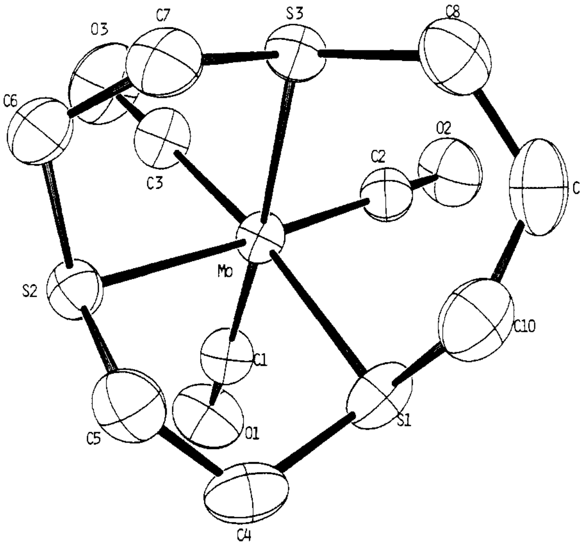

**Figure 2.** ORTEP perspective of (10S3)Mo(CO)$_3$ down the pseudo-3-fold axis of the molecule.

deviations are given in Table II. Selected bond distances and bond angles are given in Table III.

## Results and Discussion

**Structural Studies.** A view of the (10S3)Mo(CO)$_3$ molecule down the pseudo-3-fold axis of the complex is shown in Figure 2, and a side view of the molecule is shown in Figure 3. As expected, the thioether ligand coordinates facially in tridentate fashion. The environment around the Mo atom is pseudooctahedral, with the angles between the carbonyl groups close to 90°. All three carbonyl groups are nearly linear. The bond distances and bonds angles for the complex are similar to those obtained for the Mo(0) complex of 9S3.[10] The ligand adopts an unsymmetrical ($C_1$ symmetry) conformation.

**Spectral Studies.** The carbonyl region of the FT-IR spectrum of the Mo(0) complex of 18S6 shows that three facially coordinated carbonyl groups are indeed present. The FT-IR spectrum and the elemental analysis of the complex demonstrate the formation of a binuclear complex with which two Mo atoms are bridged by one 18S6 ligand. Molecular models show that a trans positioning of the tricarbonyl–Mo(0) fragments would be preferred, and the two molybdenum atoms would be bound in exo fashion to the 18S6 ligand. We suggest a structure in which the two adjacent three-sulfur segments are facially coordinated to one molybdenum atom, and this proposed structure is illustrated in Figure 4. Similar bridging of two metal ions by 18S6 has been found recently in several complexes containing transition metals including Rh(III), Ru(II), Os(II), and Cu(I).[18,19] We found no evidence for the formation of a mononuclear complex, even under reaction conditions of a 1:1 stoichiometric ratio of Mo(0) to 18S6.

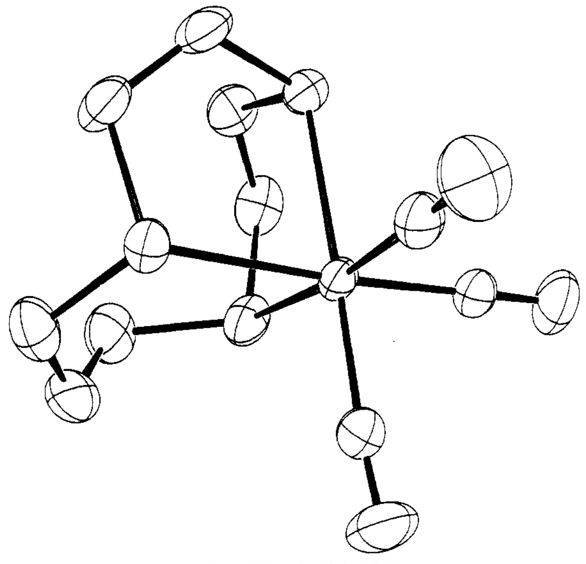

**Figure 3.** ORTEP perspective of (10S3)Mo(CO)$_3$.

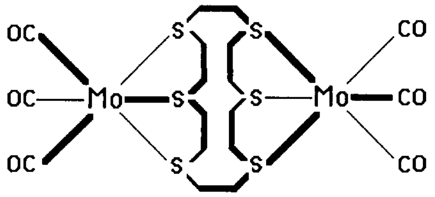

**Figure 4.** Suggested structure of (18S6)Mo$_2$(CO)$_6$.

**Table IV.** Carbonyl Stretching Frequencies for Selected Facial Tricarbonyl–Mo(0) Complexes

| complex[a] | freq, cm$^{-1}$ | wtd av | medium | ref |
|---|---|---|---|---|
| (py)$_3$Mo(CO)$_3$ | 1888, 1746 | 1793 | Nujol mull | 22 |
| (dien)Mo(CO)$_3$ | 1883, 1723 | 1805 | Nujol mull | 21, 22 |
| (9N3)Mo(CO)$_3$ | 1850, 1720 | 1763 | KBr disk | 23 |
| (9S3)Mo(CO)$_3$ | 1913.0, 1784.5 | 1827 | KBr disk | this work |
| (10S3)Mo(CO)$_3$ | 1913.0, 1789.6 | 1831 | KBr disk | this work |
| (18S6)Mo$_2$(CO)$_6$ | 1918.2, 1794.8 | 1836 | KBr disk | this work |
| (ttn)Mo(CO)$_3$ | 1918.2, 177..3 | 1826 | KBr disk | this work |
| (9S3)Mo(CO)$_3$ | 1933.6, 1820.5 | 1858 | CH$_3$NO$_2$ sol | this work |
| (10S3)Mo(CO)$_3$ | 1933.6, 1815.3 | 1855 | CH$_3$NO$_2$ sol | this work |
| (ttn)Mo(CO)$_3$ | 1928.5, 1815.3 | 1853 | CH$_3$NO$_2$ sol | this work |
| (ttu)Mo(CO)$_3$ | 1932, 1812 | 1856 | CH$_2$Cl$_2$ sol | *b* |
| (Et$_2$S)$_3$Mo(CO)$_3$ | 1930, 1826 | 1861 | CH$_2$Cl$_2$ sol | 22 |
| (PPh$_3$)Mo(CO)$_3$ | 1949, 1835 | 1873 | Nujol mull | 21 |

[a] Key: py = pyridine; dien = diethylenetriamine; 9N3 = 1,4,7-triazacyclononane; ttu = 3,6,9-trithiaundecane; Et$_2$S = diethyl sulfide; PPh$_3$ = triphenylphosphine. [b] Mannerskantz, H. C. E.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4454–4458.

Any complex that contains facially coordinated carbonyl groups is expected to exhibit two carbonyl bands of approximate relative intensities 1:2 (high-energy band to low-energy band), corresponding to vibrations of A$_1$ and E symmetries.[20,21] A simple comparison of the relative degree of metal electron density can be then made by using a calculated-weighted average of the carbonyl stretching frequencies. Table IV shows these calculated-weighted averages for several thioether, amine, and phosphine ligands. These calculated values are 1831 and 1836 cm$^{-1}$ for the solid-state spectra of the 10S3 and 18S6 complexes, respectively. The tricarbonyl complexes of 9S3 and ttn were prepared for

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**Table V.** *Dq* values for Octahedral Nickel(II) Complexes ($cm^{-1}$)

| complex | *Dq* | ref | complex | *Dq* | ref |
|---|---|---|---|---|---|
| $[Ni(9S3)_2]^{2+}$ | 1270 | 6 | $[Ni(ttn)_2]^{2+}$ | 1130 | 6, 14 |
| $[Ni(10S3)_2]^{2+}$ | 1240 | 14 | $[Ni(dien)_2]^{2+}$ | 1170 | *a* |
| $[Ni(18S6)]^{2+}$ | 1230 | 6 | $[Ni(9N3)_2]^{2+}$ | 1250 | *b* |

[a] Direct measurement in aqueous solution. [b] Zompa, L. J.; Margulis, T. N. *Inorg. Chim. Acta* **1980**, *45*, L263.

comparative purposes, and the published syntheses were used.[10,11] In agreement with earlier assessments, the π-acidity of the thioether ligands falls intermediate between those of the amine and the phosphine ligands.[3,4] For example, the weighted average for the amine ligand diethylenetriamine in the complex (dien)-$Mo(CO)_3$ is 1776 $cm^{-1}$, and the weighted average for the phosphine ligand triphenylphosphine in the complex $(PPh_3)_3Mo(CO)_3$ is 1873 $cm^{-1}$.[21,22] It is particularly interesting to note that the thioether 2,5,8-trithianonane, which has approximately the same *Dq* value for its bis nickel(II) complex (see Table V) as does the bis nickel(II) complex of diethylenetriamine, exhibits a much higher carbonyl stretching frequency in its tricarbonyl complex than does the amine.[11] This increase in the carbonyl stretching is indicative of enhanced π-bonding for the thioether. The observation is in agreement with Cooper, who notes a decrease in the nephelauxetic ratio ($\beta = B(\text{complex})/B(\text{free ion})$) from about 0.9 in the case of amine complexes to approximately 0.7 in the case of thioether complexes.[6] The tridentate crown amine ligand 1,4,7-triazacyclononane exhibits very similar behavior with a weighted average of 1763 $cm^{-1}$ in the complex tricarbonyl-(1,4,7-triazacyclononane)molybdenum(0),[23] and the enhanced π-acidity of mesocyclic thioethers such as 9S3 and 10S3 over mesocyclic amines such as 9N3 is supported by this value.

Table V presents the ligand field strengths for octahedral Ni(II) complexes containing some of the previously mentioned ligands. The ability of a ligand to function as a π-acid is an important factor in determining its relative position in the spectrochemical series.[24] Since the π-acidity of thioethers is an important aspect of their general coordination behavior, we were interested in seeing if there is a relationship between the *Dq* values of the thioether ligands and their relative π-acidity. However, there seems to be little correlation between the two, and the four thioethers discussed in this work all seem to be quite similar in their π-acceptor behavior, despite the differences in their ligand field strengths. Hence, there is little difference among the thioethers in their ability to function as π-acceptors. This observation suggests that the variation in the field strengths of the thioether ligands is largely due to steric constraints imposed upon the metal ions rather than electronic factors.

Although all four of the tridentate thioether tricarbonyl–Mo(0) complexes (9S3, ttn, 10S3, 18S6) are moderately stable toward air oxidation, the 10S3 complex is the least susceptible to decomposition.[25] A similar reaction between 9S3 and tris(acetonitrile)tricarbonyltungsten(0) was attempted to examine what effects, if any, a change in the metal atom would have on the spectroscopic properties of the complex, but no complex could be isolated. Also, a Mo(0) complex with the tridentate thioether ligand 1,5,8-trithiacyclodecane (12S3) could not be prepared using the tris(acetonitrile)tricarbonylmolybdenum(0) synthesis.

In summary, the thioethers discussed in this work function as moderate π-acceptors, intermediate between amine and phosphine ligands. Although the π-acceptor characteristics of thioethers are very important in their general behavior as ligands, differences in field strengths among the thioethers cannot be accounted for by the differences in their ability to function as π-acceptors. Rather, differences in complexation characteristics among the various thioether ligands arise from the geometrical constrictions that they impose on metal ions upon complexation and the preferred conformations of the thioethers.

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**Supplementary Material Available:** Listings of complete bond lengths and bond angles, complete atom positional parameters, anisotropic thermal parameters, and torsional angles (8 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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