

Linear-Chain Ordering in a Spin- $3/2$ System: Magnetic Susceptibilities of $[\text{Cr}(\text{py})_3\text{Cl}_3]$

K. E. Merabet and Richard L. Carlin*

Received April 20, 1989

The magnetic susceptibilities at zero-applied field of single crystals of $[\text{Cr}(\text{py})_3\text{Cl}_3]$ have been measured from below 1 to 4.2 K. No evidence of long-range magnetic ordering is observed. This spin $S = 3/2$ material appears to behave as an antiferromagnetic linear chain; the parameters resulting from the data analysis are $J/k_B = -0.04$ K, $2D/k_B = -0.14$ K, and $\langle g \rangle = 1.96$. A small rhombic term ($E/k_B = 0.04$ K) is also present.

Introduction

As part of our program in chromium(III) magnetochemistry,¹ we have recently reported on several chromium linear chains.² They include $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, what appears to be $[\text{Cr}(\text{N}_2\text{H}_5)_3\text{Br}]\text{Br}_2$, and an unstable compound, $[\text{Cr}(\text{NH}_3)_5\text{F}](\text{NO}_3)_2$. These materials are of intrinsic interest because so few linear-chain magnets of spin $3/2$ have been prepared, but the subject has also become one of intense interest because of recent developments concerning what is called the Haldane conjecture.³⁻¹¹ None of the above materials are available as yet as large single crystals for the neutron studies that are required in order to characterize the spin wave spectrum and to test the implications of the Haldane conjecture.

According to Haldane, integer-spin Heisenberg-like antiferromagnetic chains differ radically in their $T = 0$ behavior from half-integer-spin quantum chains. In particular, integer-spin chains are expected to show an excitation gap whose magnitude is related to the value of the spin. A number of experimental investigations⁶⁻¹¹ have already considered this remarkable prediction. Our contribution to this field, as described further below, concerns the synthesis and characterization of new one-dimensional systems.

Chromium is the ion of choice for control experiments concerning the Haldane conjecture. Spin- $1/2$ and spin- $3/2$ systems should show no gap, while spin-1 systems should. The first experiments reported concerning the anticipated gap were carried out, by neutron diffraction, on the nearly isotropic (Heisenberg) quasi-one-dimensional antiferromagnet CsNiCl_3 .⁶ The work supports the conjecture of Haldane, in that there appears to be a gap in the excitation spectrum. The anisotropy is small, and further experiments on CsNiCl_3 support the above result.⁷ Experiments on CsVCl_3 , which is even more isotropic, with $S = 3/2$, gave no unexpected spin wave behavior.¹¹

Chromium has the advantage of having very small anisotropy; this is shown by the small values of the zero-field splitting found in our studies. The requisite linear-chain materials are still lacking. An important recent discovery of ours is that exchange interaction is unexpectedly weak in many chromium(III) compounds. This

effect has been documented in several of our publications.¹

We report here susceptibility studies on small single crystals of $[\text{Cr}(\text{py})_3\text{Cl}_3]$, where py is pyridine, which suggest that it may be the candidate system we have been looking for. The crystal structure of $[\text{Cr}(\text{py})_3\text{Cl}_3]$ has been reported.¹² The molecular material has the (1,2,6)-mer configuration and is available to us in single-crystal form. There are at the moment no other single-crystal examples of spin $S = 3/2$, chromium(III) magnetic linear-chain systems.

Chemical Preparation and Crystal Structure Description

Trichlorotris(pyridine)chromium(III) was prepared by the reaction of pyridine and anhydrous chromium(III) chloride as described in the literature.^{13,14} A round-bottom flask fitted with a water condenser and Vigreux column, mounted on a heating mantle, and containing a magnetic stirrer was used as the reaction vessel. Anhydrous chromium chloride (26.4 g), pyridine (79 g) and a stirring magnet were placed into the flask. This was then heated slowly and stirred until the pyridine boiled. In an hour, the violet color of CrCl_3 vanished and the solution turned a deep green. The solution was then heated and occasionally stirred for 24 h. The large dark green, well-formed crystals, which formed on cooling, were collected and washed with cold water. Very good chemical analysis resulted. Anal. Calcd: Cr, 13.15; C, 45.53; H, 3.79; N, 10.62; Cl, 26.90. Found: Cr, 13.03; C, 45.47; H, 3.83; N, 10.54; Cl, 26.08.

The crystal structure of $[\text{Cr}(\text{py})_3\text{Cl}_3]$ has been reported.¹² The system is monoclinic with space group $P2_1/n$. The unit cell contains four molecules; $a = 9.088$ (1) Å, $b = 12.442$ (1) Å, $c = 15.557$ (1) Å, and $\beta = 91.33^\circ$. The geometry around the central chromium atom agrees with the expected octahedral configuration. Brenic¹⁵ assigned the (1,2,6)-mer stereometric configuration for the compound. The average value for the Cr-Cl bond lengths is 2.32 Å, and the Cr-N bond length is 2.11 Å. All four chromium atoms of the unit cell lie on the same plane parallel to the c axis and at an angle of 5° with the b axis. There is no metal atom between these planes in the a direction; therefore, the metal atoms are separated by a distance of 9.088 Å along that direction. Since there is not a good superexchange path between these metals, one anticipates a very weak exchange interaction along the a axis. Consequently we should expect a low-dimensional magnetic behavior. A projection of the unit cell on the b - c plane is shown in Figure 1. We clearly see chains of octahedra lying along the b axis. The Cr-Cr distance along this axis is only 6.22 Å. A likely superexchange path along this direction is Cr-Cl...Cl-Cr, with the shortest Cl-Cl distance of only 2.35 Å. In the c direction each chromium is additionally surrounded by two others at 8.8 and 8.1 Å. But along this direction, as along the a axis, the Cr atoms are only connected via complicated pathways involving the larger pyridine groups. Therefore, magnetic interactions can be assumed to be very much smaller along these two directions, and we should have a system of well-isolated linear chains.

Magnetic susceptibility measurements were performed by an ac mutual inductance technique.¹⁶ An ac field of a few millioersted and a frequency of 16 Hz were used. A ^3He - ^4He dilution refrigerator was used to obtain temperatures as low as 100 mK. The x , y , z directions along which we measured the susceptibilities were defined as follows. The x

- (1) Carlin, R. L.; Burriel, R. *Phys. Rev. B* **1983**, *27*, 3012. Carlin, R. L.; Burriel, R.; Pons, J.; Casabo, J. *Inorg. Chem.* **1983**, *22*, 2832. Burriel, R.; Casabo, J.; Pons, J.; Carnegie, D. W., Jr.; Carlin, R. L. *Physica* **1985**, *132B*, 185.
- (2) Merabet, K. E.; Burriel, R.; Carlin, R. L. *Phys. Rev. B* **1988**, *38*, 11589.
- (3) Steiner, M. Private communication.
- (4) Haldane, F. D. M. *Phys. Rev. Lett.* **1983**, *50*, 1153.
- (5) See, for example: Bonner, J. C. *J. Appl. Phys.* **1987**, *61*, 3941.
- (6) Buyers, W. J. L.; Morra, R. M.; Armstrong, R. L.; Hogan, M. J.; Gerlach, P.; Hirakawa, K. *Phys. Rev. Lett.* **1986**, *56*, 371. Morra, R. M.; Buyers, W. J. L.; Armstrong, R. L.; Hirakawa, K. *Phys. Rev. B* **1988**, *38*, 543.
- (7) Steiner, M.; Kakurai, K.; Kjems, J. K.; Petitgrand, D.; Pynn, R. *J. Appl. Phys.* **1987**, *61*, 3953.
- (8) Renard, J. P.; Verdager, M.; Regnault, L. P.; Erkelens, W. A. C.; Rossat-Mignod, J.; Stirling, W. G. *Europhys. Lett.* **1987**, *3*, 945.
- (9) Steiner, M. In *Organic and Inorganic Low Dimensional Crystalline Materials*; NATO ASI Series; Plenum: New York, 1987; p 63.
- (10) Kopinga, K.; de Jonge, W. J. M. In *Organic and Inorganic Low Dimensional Crystalline Materials*; NATO ASI Series; Plenum: New York, 1987; p 141.
- (11) Kadowaki, H.; Hirakawa, K.; Ubokashi, K. *J. Phys. Soc. Jpn.* **1987**, *52*, 1799.

- (12) Howard, S. A.; Hardcastle, K. I. *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 643.
- (13) Pfeiffer, P. Z. *Anorg. Chem.* **1900**, *24*, 283.
- (14) Taft, J. C.; Jones, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 4196.
- (15) Brenic, J. V. Z. *Anorg. Allg. Chem.* **1974**, *403*, 218.
- (16) van der Bilt, A.; Jong, K. O.; Carlin, R. L.; de Jongh, L. J. *Phys. Rev B* **1980**, *22*, 1259.

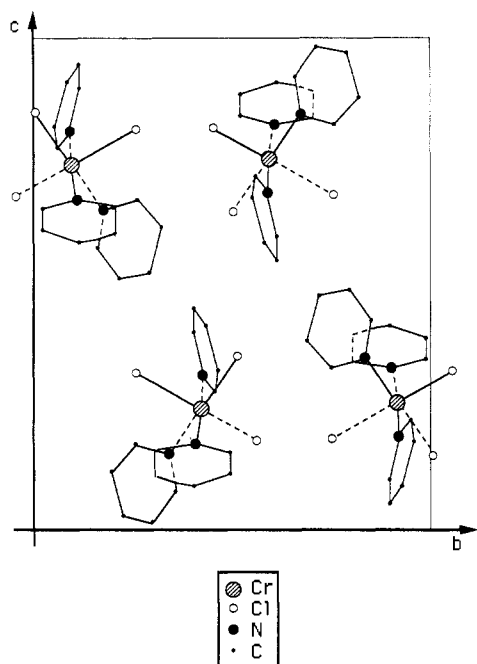


Figure 1. Projection of the unit cell of $[\text{Cr}(\text{py})_3\text{Cl}_3]$ on the b - c plane.

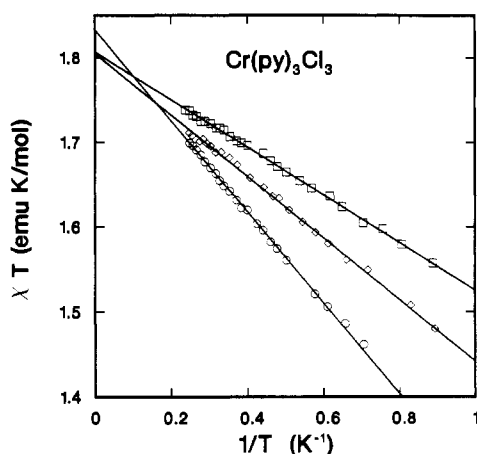


Figure 2. Experimental susceptibility of $[\text{Cr}(\text{py})_3\text{Cl}_3]$ above 0.7 K plotted as χT vs $1/T$. The linear least-squares fits to eq 4-6 in the three principal directions provide the constants g_x , g_y , and g_z (from the ordinate intercepts), and D , E , and J (from the slopes): z axis (circles); x axis (squares); y axis (diamonds).

direction is associated with the b axis, which is by symmetry a principal axis of the susceptibility tensor. The y and z directions lie on the a^*c plane, which is perpendicular to the b axis, and are determined by measuring the zero-field susceptibility as a function of angle in the plane. We then used the equation¹⁷

$$\chi = \chi_z \cos^2 \phi + \chi_x \sin^2 \phi \quad (1)$$

to fit the data. We found that the z axis, which corresponds to the maximum susceptibility, is located at $18 \pm 2^\circ$ from the a^* axis toward the c axis. The y axis is perpendicular to both the x and z axes.

Results and Discussion

The data in the temperature range above 1 K are presented in Figure 2 in the form χT vs $1/T$. This procedure provides a Curie-Weiss law fit to the high-temperature data as explained below. When a small axial crystalline field and a rhombic distortion are considered, the paramagnetic Hamiltonian describing a spin $3/2$ system is¹⁸

$$\mathbf{H} = g\mu_B \vec{H} \cdot \vec{S} + D[S_z^2 - 1/3 S(S+1)] + E(S_x^2 - S_y^2)$$

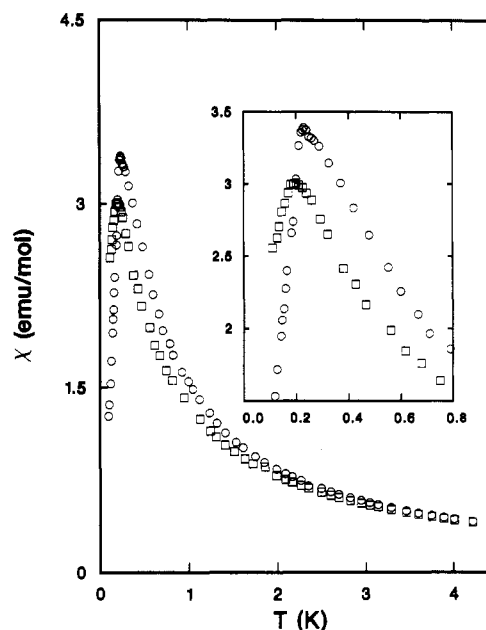


Figure 3. Experimental susceptibilities: χ_z (circles) and χ_x (squares).

Exchange interactions can be accounted for by adopting a molecular field approximation. Therefore, the term $2zJ\vec{S} \cdot (\vec{S})$ is added to the Hamiltonian.

In the linear approximation, when $|D|$, $z|J|$, and $|E|$ are much smaller than $k_B T$, the paramagnetic susceptibilities of this system are given by¹⁹

$$\chi_i = \frac{\chi'_i}{1 - A\chi'_i} \quad (i = x, y, z) \quad (2)$$

where

$$A = 2zJ/Ng_i^2\mu_B^2 \quad (3)$$

and

$$\chi'_x = (Ng_x^2\mu_B^2/3k_B T)[1/4 + \{7/8 zJ/k_B + 3/2(D - 3E)/k_B\}(1/T)] \quad (4)$$

$$\chi'_y = (Ng_y^2\mu_B^2/3k_B T)[1/4 + \{7/8 zJ/k_B + 3/2(D + 3E)/k_B\}(1/T)] \quad (5)$$

$$\chi'_z = (Ng_z^2\mu_B^2/3k_B T)[1/4 + \{7/8 zJ/k_B - 3D/k_B\}(1/T)] \quad (6)$$

We can see that if we know the empirical slope and intercept of each plot of χT vs $1/T$ in Figure 2, eq 4-6 can be solved simultaneously to yield all the parameters. The results are

$$D/k = -0.076 \pm 0.003 \text{ K}$$

$$E/k = +0.038 \pm 0.003 \text{ K}$$

$$zJ/k = -0.087 \pm 0.003 \text{ K}$$

$$g_x = 1.97 \pm 0.01$$

$$g_y = 1.96 \pm 0.01$$

$$g_z = 1.96 \pm 0.01$$

Within the experimental uncertainty, the g factor is isotropic and equal to $g = 1.96 \pm 0.01$. This value is typical of those found for chromium by EPR measurements.¹⁸ The value of $|D|$ is of the same order of magnitude as that observed in other chromium compounds.²⁰ The negative sign of D indicates that the lower

(17) Bhatia, S. N.; Carlin, R. L.; Filho, A. P. *Physica* **1977**, *92B*, 330.

(18) Mc Garvey, B. R. In *Transition Metal Chemistry*, Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 3.

(19) Carlin, R. L.; Burriel, R. *Phys. Rev. B* **1983**, *27*, 3012.

(20) Merabet, K. E.; Burriel, R.; Carlin, R. L.; Zora, J. A.; Seddon, K. R. To be submitted for publication.

Table I. Critical Parameters

	χ_z	χ_x	χ_y	1-D Heisenberg ^a	quadratic Heisenberg ^a
$k_B T(\chi_{\text{max}})/ J $	5.4	4.5	4.30	4.75	2.1
$\chi_{\text{max}} J /N_0 g^2 \mu_B^2$	0.099	0.090	0.095	0.091	0.0547
$\chi_{\text{max}} T(\chi_{\text{max}})/g^2$	0.20	0.152	0.153	0.16	

^aReference 21.Kramers' doublet is the $|\pm 3/2\rangle$ state.

The experimental data over the entire temperature range are illustrated in Figures 3 and 4. All three susceptibilities rise rapidly as the temperature is lowered. The relatively small anisotropy becomes more noticeable at low temperatures as shown in Figure 3. In the z direction χ_z reaches a maximum at 245 ± 5 mK and then falls as T goes toward zero. In the other directions χ_x and χ_y also pass through maxima at $T = 200 \pm 5$ mK and $T = 189 \pm 5$ mK, respectively. They decrease slightly at lower temperatures but do not extrapolate to zero and approach a constant value. The axial anisotropy causes the susceptibility maximum along the z direction to appear at a higher temperature than that of the two other susceptibilities. For the isotropic case, all three maxima should appear at the same temperature. There is no evidence suggestive of a transition to long-range order down to $T = 100$ mK. The ordering temperature is usually obtained from the point of maximum slope but there is not clear change of slope maximum in any of the three directions measured. This indicates that we may indeed have a low-dimensional antiferromagnetic system as already suggested by the crystal structure.

The results found for the critical parameters are summarized in Table I in reduced units. We also include the theoretical predictions for the 1-D Heisenberg and quadratic Heisenberg models for $S = 3/2$ calculated by using extrapolation techniques of the high-temperature series based on the Pade approximants.²¹ We see that the calculated parameters for the Heisenberg linear-chain model are right between our experimental parameters. The small differences are due to the anisotropies.

To analyze these data further, we need to apply the high-temperature series expansions for quantum-mechanical spin $S = 3/2$ on chains. Since the crystal field anisotropy factors are of the same order of magnitude as the exchange constant, these terms should be introduced together in the exchange Hamiltonian and treated equally. Unfortunately we are not aware of any such calculation on the magnetic susceptibility for spin $3/2$. So we turned to Fisher's classical model²² for a linear chain with small axial anisotropy.²³ The familiar equations are

$$\chi_0 = \frac{Ng^2 S(S+1)\mu_B^2}{3k_B T} \left(\frac{1+u}{1-u} \right) \quad (7)$$

where

$$u = (T/T_0) - \coth(T_0/T)$$

with

$$T_0 = 2JS(S+1)/k_B$$

$$\chi_{\parallel} = \chi_0 - \frac{4}{15}\chi_c [DS(S+1)/k_B T] F \quad (8)$$

$$\chi_{\perp} = \chi_0 + \frac{2}{15}\chi_c [DS(S+1)/k_B T] F \quad (9)$$

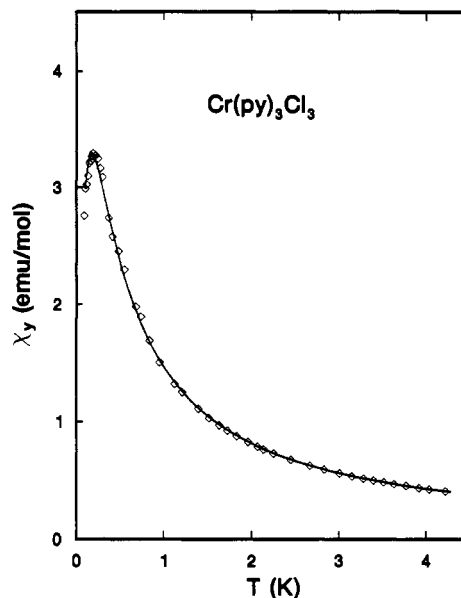
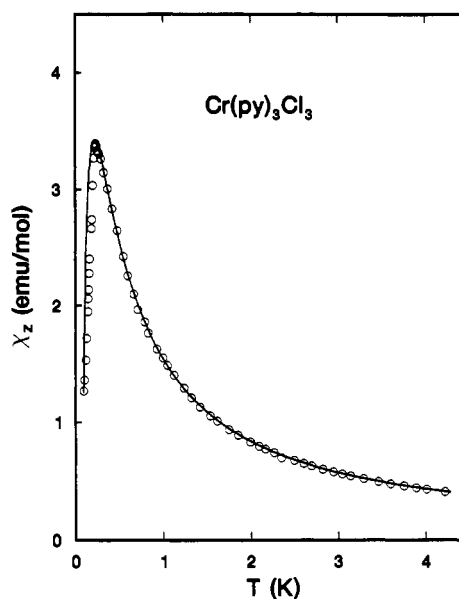
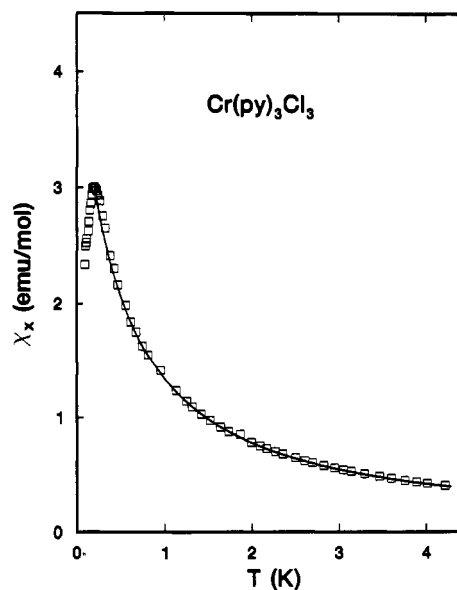
where

$$F = \frac{(1+u)(1+v)}{(1-u)(1-v)} + \frac{2u}{1-u}$$

$$v = 1 - [3uk_B T / 2JS(S+1)]$$

$$\chi_c = Ng^2 \mu_B^2 S(S+1) / 3k_B$$

Finally, as explained in a previous investigation of $\text{Cs}_2\text{CrCl}_5 \cdot 4\text{H}_2\text{O}$,¹⁹ to take into account the rhombic term E , we replace

(21) de Jongh, L. J.; Miedema, A. R. *Adv. Phys.* **1974**, *23*, 1.(22) Fisher, M. E. *Am. J. Phys.* **1964**, *32*, 343.(23) Smith, T.; Friedberg, S. A. *Phys. Rev.* **1968**, *176*, 660.Figure 4. Susceptibility χ_y , along with the fit.Figure 5. Susceptibility χ_z , along with the fit.Figure 6. Susceptibility χ_x , along with the fit.

D by an effective parameter $D_x = D - 3E$ for χ_x and $D_y = D + 3E$ for χ_y . χ_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.

Acknowledgment. This research was supported by Grants DMR-8515224 and DMR-8815798 of the Solid State Chemistry Program of the Division of Materials Research of the National Science Foundation.

Registry No. Cr(py)₃Cl₃, 14284-76-5.

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 Thioethers¹

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

Received December 19, 1988

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, C₁₀H₁₄MoO₃S₃; 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) Å³, $Z = 2$, $R = 0.020$.

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 surprisingly large ligand field strengths.⁴ Thioethers function as good π -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 π -acidity of thioethers has been described as intermediate between those of phosphines and amines, and the relative π -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 π -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

- (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.
- (2) American Chemical Society, Petroleum Research Fund Undergraduate Scholar, 1988.
- (3) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365-414.
- (4) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141-146.
- (5) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266-271.
- (6) Cooper, S. R.; Rawle, S. C.; Hartman, J. R.; Hints, E. J.; Admans, G. A. *Inorg. Chem.* **1988**, *27*, 1209-1214.
- (7) Wiegardt, K.; Kuppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067-3071.
- (8) Wilson, G. S.; Swanson, D. D.; Glass, R. S. *Inorg. Chem.* **1986**, *25*, 3827-3829.
- (9) Sellman, D.; Zapf, L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 807-808.
- (10) Ashby, M. T.; Lichtenberger, D. L. *Inorg. Chem.* **1985**, *24*, 636-638.
- (11) Ashby, M. T.; Lichtenberger, D. L.; Enemark, J. H.; Ortega, R. B. *Inorg. Chem.* **1986**, *25*, 3154-3157.
- (12) For an excellent review of the coordination chemistry of this ligand, see: Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141-146 and references cited therein.
- (13) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1970; pp 116-121.

[†] The University of Tennessee at Chattanooga.

[‡] The University of Alabama in Huntsville.

[§] Georgia Institute of Technology.