We have also examined the EPR spectrum of $[Cu^{II}\cdot(\text{trithia-9-crown-3})_2]^{2+}$. At room temperature nitromethane solutions of this complex exhibit $g = 2.059$, with $A(^{63,65}Cu) = 62.5 \times 10^{-4}$ cm^{-1}, while frozen solutions at 77 K have $g_{\parallel} = 2.120$ and $g_{\perp} = 2.029$ and $A_{\parallel} = 154 \times 10^{-4}$ cm^{-1}. Thus despite the large difference in axial elongation between $[Cu^{II}\cdot L]^{2+}$ and $[Cu^{II}\cdot(\text{trithia-9-crown-3})_2]^{2+}$ (vide supra), the spin Hamiltonian parameters for the two complexes agree remarkably closely with each other.

Conclusions

Hexathia-18-crown-6 binds copper to form an electrochemically reversible couple that cycles between six- and four-coordinate complexes. It apparently facilitates the transformation between these rather disparate species by (1) constraining the Cu(I) complex to the geometry of a fragment of a distorted octahedron and (2) maintaining the unbound donor atoms close to the Cu(I) ion. The high potential of this couple evidently results less from geometric factors than from the electronic properties of the thioether ligands, in particular their ability to act as π-acids, an ability also indicated by EPR data. Differences in redox potential and EPR spectra of the hexathia-18-crown-6 and bis(trithia-9-crown-3) complexes apparently derive largely from the geometric constraints imposed by the small-ring ligand.

The present work supports the conclusions of Rorabacher[28] and Brubaker[69] and their co-workers that high reduction potentials for Cu(II) can be induced in the absence of tetrahedral distortion by thioether donor atoms. In the present case, the ligand distinctly favors Cu(II) over Cu(I) geometrically, but nevertheless this system has a redox potential among the highest known for the Cu(II)/(I) couple.

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Registry No. [Cu·(hexathia-18-crown-6)](picrate)$_2$, 99783-15-0; [Cu·(hexathia-18-crown-6)](BF$_4$), 99783-17-2; $[Cu^{II}\cdot(\text{trithia-9-crown-3})_2]^{2+}$, 83650-39-9; $[Cu(CH_3CN)_4](BF_4)$, 15418-29-8; 3-thiapentane-1,5-dithiol, 3570-55-6; 1,2-dichloroethane, 107-06-2; 3,6,9-trithiacyclononane, 6573-11-1.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (48 pages). Ordering information is given on any current masthead page.

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(69) Brubaker, G. R.; Brown, J. N.; Yoo, M. K.; Kinsey, R. A.; Kutchan, T. M.; Mottel, E. A. *Inorg. Chem.* **1979**, *18*, 299-302.

Crown Thioether Chemistry. The Co(II) Complexes of Hexathia-18-crown-6 and Bis(trithianonane)

JudithAnn R. Hartman, Eric J. Hintsa, and Stephen R. Cooper*

Contribution from the Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, England, and the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received August 6, 1985*

Abstract: The cobalt(II) complexes of hexathia-18-crown-6 (18S6) and 2,5,8-trithianonane (ttn) have been synthesized and characterized by electron paramagnetic resonance, electrochemical, magnetic, and X-ray diffraction methods. [Co·(hexathia-18-crown-6)](picrate)$_2$ crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 6.659$ (2) Å, $b = 9.565$ (3) Å, and $c = 13.591$ (4) Å, $\alpha = 85.15$ (2)°, $\beta = 76.05$ (2)°, and $\gamma = 76.08$ (2)°, and $Z = 1$. $[Co\cdot(\text{trithianonane})_2](BF_4)_2$ crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 10.321$ (5) Å, $b = 12.181$ (5) Å, $c = 21.522$ (14) Å, and $Z = 4$. In both complexes the cobalt ion is coordinated solely by thioether groups to give bona fide low-spin six-coordinate Co(II) complexes both in the solid state and solution. Consistent with the low-spin formulation, the complexes exhibit $S = {}^1/_2$ magnetic moments, and EPR spectra with $g_{\parallel} \approx 2$, $g_{\perp} > 2$, and their CoS$_6$ coordination spheres display marked Jahn-Teller elongation. In addition, cyclic voltammetric measurements show that the complexes exhibit extraordinarily high potentials for the Co(III/II) couple (>+840 mV vs. NHE). These results emphasize the ability of thioether ligands to stabilize low-spin and oxidation states by virtue of their π acidity.

Recent development of the coordination chemistry of thioethers[1] has been spurred by the discovery of thioether coordination to copper in the blue copper proteins.[2-4] Metal ligation through thioethers has been considered to contribute not only to the anomalously high redox potentials of these proteins but also to their exceptionally rapid electron-transfer reactions.[5,6] Another source of interest in thioether coordination chemistry is its potential similarity to that of phosphines. Twenty-five years ago phosphines were considered to have a meager chemistry, but subsequent investigation established not only the inherent richness but also the practical utility of phosphine complexes in industrial processes. In some respects the chemistry of thioethers is now at a state comparable to that of phosphines before its extensive development.

Our approach to investigation of thioether coordination chemistry centers on a new environment for transition-metal ions, hexakis(thioether) coordination. This environment is offered by the crown thioether hexathia-18-crown-6 (18S6)[7-11] which forms

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* Address correspondence to this author at the University of Oxford.

(1) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365-414.

(2) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature* (*London*) **1978**, *272*, 319-324.

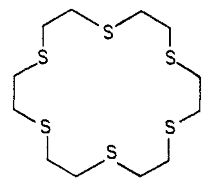
(3) Guss, J. M.; Freeman, H. C. *J. Mol. Biol.* **1983**, *169*, 521-563.

(4) Adman, E. T.; Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1978**, *123*, 35-47.

(5) Beinert, H. *Coord. Chem. Rev.* **1980**, *33*, 55-85.

(6) Karlin, K. D.; Zubieta, J., Eds. "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Adenine Press: Guilderland, NY, 1983.

0002-7863/86/1508-1208$01.50/0



complexes with Ni(II),[10] Cu(II)[11], and Cu(I).[11] The present paper addresses the effects of this environment on Co(II), the only common d^7 ion.[12] It describes synthetic, structural, and physicochemical studies of $[\mathrm{Co^{II}}\cdot(18\mathrm{S6})]^{2+}$[13] and also $[\mathrm{Co^{II}}\cdot(\text{trithianonane})_2]^{2+}$ and shows both to be bona fide examples of low-spin $\mathrm{Co^{II}L_6}$ complexes. It also includes further characterization of $[\mathrm{Co^{II}}\cdot(\text{trithia-9-crown-3})_2]^{2+}$, the structure of which has recently been reported,[14] and establishes that this complex, too, is low-spin. The work reported here therefore permits comprehensive comparison of these three hexakis(thioether) complexes and thereby allows dissection of the electronic effects of thioether coordination and geometric deformation. Furthermore, this paper augments the work of Sargeson and co-workers[15-17] on cobalt (sepulchrate) complexes with N_6 and S_3N_3 coordination by providing several examples of the terminal member of the series, S_6 coordination. Lastly, since the complexes it describes remain low-spin and six-coordinate in solution, the present work provides ideal cases for study of Co(III/II) electron transfer without spin state change.

Experimental Section

Physical Measurements. Electronic spectra were recorded with quartz cuvettes on a Perkin-Elmer 559A spectrophotometer; infrared spectra were obtained on Nujol mulls with NaCl plates with a Perkin-Elmer 683 spectrometer, which was calibrated with use of polystyrene. Electron paramagnetic resonance (EPR) spectra were recorded with a Varian E-9 spectrometer with diphenylpicrylhydrazyl radical as g marker (g = 2.0037); quartz flat cells were used for fluid solutions and cylindrical quartz tubes were employed for powders and frozen solutions.

Preparation of Compounds. Hexathia-18-crown-6 (18S6) and 2,5,8-trithianonane (ttn) were prepared as described previously.[18,19] Cobalt(II) picrate was prepared from cobalt(II) carbonate and picric acid and then carefully dried in vacuo over phosphorus pentoxide. **Caution**: although this compound does not appear to be particularly sensitive to shock or heat, it, like all picrates, should be prepared only in small quantities and handled carefully. Nitromethane was distilled from calcium hydride and stored over molecular sieves; acetonitrile and methylene chloride were freshly distilled from barium oxide. All other chemicals were used as received. C, H, S, and N analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Cobalt analysis was carried out with use of the Kitson procedure.[20] Electrochemical measurements were performed with a Princeton Applied Research Model 175 programmer, 173 potentiostat, 179 digital coulometer, and Houston xy recorder on nitromethane solutions that were 0.1 M in $\mathrm{Et_4N\cdot PF_6}$. A standard three-electrode cell was employed with a glassy carbon working electrode and a platinum gauze auxiliary electrode; all potentials are relative to the saturated calomel electrode (SCE). For controlled potential coulometry a platinum basket working electrode and a platinum flag auxiliary electrode were used.

Table I. Crystallographic Data for $[\mathrm{Co}\cdot(\text{hexathia-18-crown-6})](\text{picrate})_2$ and $[\mathrm{Co}\cdot(\text{trithianonane})_2](\mathrm{BF_4})_2\cdot\mathrm{CH_3NO_2}$

	Co(18S6)	$\mathrm{Co(ttn)_2}$
mol wt	875.82	658.33
space group	$P\bar{1}$	$P2_12_12_1$
a, Å	6.659 (2)	10.321 (5)
b, Å	9.565 (3)	12.181 (5)
c, Å	13.591 (4)	21.522 (14)
α, deg	85.15 (2)	90
β, deg	76.05 (2)	90
γ, deg	76.08 (2)	90
vol, $Å^3$	815.13	2705.71
d_{calcd}, g/cm^3	1.78	1.62
Z	1	4
λ	Mo Kα	Mo Kα
$F(000)$	448.93	1347.84
μ, cm^{-1}	9.69	11.44
cryst. size, mm	0.30 × 0.30 × 0.20	0.35 × 0.42 × 0.40
refl. coll.	$+h,\pm k,\pm l$	$+h,+k,+l$
no. of refl. coll.	3892	4518
unique data with $F^2 > 2\sigma(F^2)$	2742	2894
2θ range, deg	3-54	3-57
final R, %	3.86	7.16
final R_w, %	4.05	7.66
GOF[a]	1.151	1.445
no. of var.	232	307
temp	ambient	ambient
scan rate, deg/min	2.00-29.3	2.00-29.3
mode	θ-2θ	θ-2θ
max. trans factor	0.744	0.616
min. trans. factor	0.687	0.518
R_{merg}	0.0161	0.0572

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

Magnetic susceptibility measurements on solid samples were performed with a Faraday balance with use of a Bruker Research B-E15 B8 Magnet, a Cahn RG Electrobalance, and a Hewlett-Packard 3465A Digital Multimeter; measurements in solution were obtained on a Bruker WM300 NMR spectrometer with use of concentric NMR tubes.[21-24]

$[\mathrm{Co}\cdot(18\mathrm{S6})](\text{picrate})_2$. Hexathia-18-crown-6 (20 mg, 0.055 mmol) dissolved in 15 mL of acetone at 50 °C was added to a hot solution of cobalt(II) picrate (28.5 mg, 0.055 mmol) in 3 mL of acetone to give a brown solution. After addition of 5 mL of acetonitrile and refluxing for 15 min, the solution was allowed to cool slowly to room temperature. The resulting dark brown needles were collected by filtration, washed with methylene chloride, and dried in vacuo overnight. Yield 31 mg (64%). Anal. Calcd for $\mathrm{C_{24}H_{28}S_6N_6O_{14}Co}$: C, 32.91; H, 3.22; N, 9.60; S, 21.97. Found: C, 32.89; H, 3.16; N, 9.53; S, 21.75. IR (NaCl, Nujol, cm^{-1}): 1640 (sh), 1632 (m), 1608 (m), 1558 (w), 1552 (sh), 1548 (m), 1538 (sh), 1512 (w), 1428 (m), 1368 (m), 1338 (m), 1310 (m), 1290 (m), 1220 (m), 1185 (w), 1160 (m), 1080 (w), 950 (m), 920 (w), 910 (w), 811 (m), 790 (m), 752 (m), 725 (m), 711 (m), 635 (w), 610 (w), 545 (w), 520 (w). The electronic spectrum of $[\mathrm{Co^{II}}\cdot(18\mathrm{S6})](\text{picrate})_2$ is dominated by the intense picrate band at ≈410 nm but also shows shoulders at 560 and 720 nm.

$[\mathrm{Co}\cdot(2,5,8\text{-trithianonane})_2](\mathrm{BF_4})_2$. To a suspension of cobalt(II) tetrafluoroborate hexahydrate (300 mg, 0.882 mmol) in 10 mL of nitromethane was added trithianonane (0.85 g, 4.7 mmol) to yield a deep magenta solution, which was concentrated to 3 mL and allowed to stand. After 30 min the resulting deep red crystals were collected by filtration, washed with methylene chloride, and dried in vacuo overnight. Yield 280 mg (53%). Anal. Calcd for $\mathrm{C_{12}H_{28}S_6B_2F_8Co}$: C, 24.13; H, 4.73, S, 32.21, Co, 9.86. Found: C, 23.86; H, 4.59; S, 31.89; Co, 9.81%. IR (NaCl, Nujol, cm^{-1}): 1442 (s), 1418 (m), 1333 (w), 1290 (w), 1268 (w), 1170 (sh), 1142 (sh), 1122 (sh), 1045 (s, br), 985 (sh), 968 (m), 945 (w), 922 (m), 850 (m), 832 (w), 768 (vw), 735 (sh), 723 (w), 668 (vw), 655

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(7) The coordination chemistry of this ligand was first examined by Black and McLean: Black, D. St. C.; McLean, I. A. *Tetrahedron Lett.* **1969**, 3961-4.

(8) Black, D. St. C.; McLean, I. A. *Aust. J. Chem.* **1971**, *24*, 1401-11.

(9) Hartman, J. R.; Rawle, S. C.; Hintsa, E. J.; Cooper, S. R., in preparation.

(10) Hintsa, E. J.; Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 3738-9.

(11) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* preceding paper in this issue.

(12) Greenwood, N. N.; Earnshaw, A. "Chemistry of the Elements"; Pergamon: Oxford, 1984; p 1313.

(13) Hartman, J. R.; Hintsa, E. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1984**, 386-7.

(14) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266-71.

(15) Creaser, I. I.; Geve, R. J.; Harrowfield, J. MacB.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016-25.

(16) Gahan, L. R.; Hambley, T. W.; Sargeson, A. M.; Snow, M. R. *Inorg. Chem.* **1982**, *21*, 2699-06.

(17) Hammershoi, A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 3554-61.

(18) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079-84.

(19) Hartman, J. R.; Ochrymowycz, L. A.; Cooper, S. R., submitted for publication.

(20) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664-7.

(21) Reilly, C. A.; McConnell, H. M.; Meisenheimer, R. G. *Phys. Rev.* **1955**, *98*, 264.

(22) Klein, M. P.; Holder, B. E. *Phys. Rev.* **1955**, *98*, 265.

(23) Evans, D. F. *J. Chem. Soc.* **1959**, 2003-5.

(24) Bartle, K. D.; Jones, D. W.; Maricic, S. *Croat. Chem. Acta* **1968**, *40*, 227-40.

Table II. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^{-4}) for [Co·(hexathia-18-crown-6)](picrate)$_2$

atom	x	y	z	U^a
Co	0	0	0	18 (1)
S(1)	−721 (1)	−2414 (1)	−52 (1)	27 (1)
S(4)	3310 (1)	−1142 (1)	223 (1)	24 (1)
S(7)	−1259 (1)	54 (1)	1693 (1)	24 (1)
C(2)	1371 (5)	−3529 (3)	486 (2)	30 (1)
C(3)	3489 (5)	−3069 (3)	218 (3)	30 (1)
C(5)	3132 (5)	−816 (4)	1542 (2)	31 (1)
C(6)	995 (5)	−835 (3)	2223 (2)	29 (1)
C(8)	−1729 (6)	1926 (3)	2006 (2)	36 (1)
C(9)	−159 (7)	2767 (4)	1397 (3)	37 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å) and Angles (deg) for [Co·(hexathia-18-crown-6)](picrate)$_2$

Co–S(7)	2.251 (1)	Co–S(4)	2.292 (1)
Co–S(1)	2.479 (1)	C(8)–C(9)	1.517 (5)
S(7)–C(6)	1.816 (3)	S(7)–C(8)	1.812 (3)
S(4)–C(5)	1.816 (3)	S(4)–C(3)	1.818 (3)
S(1)–C(2)	1.805 (3)	S(1)–C(9a)	1.813 (3)
C(6)–C(5)	1.502 (4)	C(3)–C(2)	1.530 (5)

S(7)–Co–S(4)	90.1 (1)	S(1)–Co–S(7)	91.3 (1)
S(4)–Co–S(1)	87.8 (1)	Co–S(7)–C(6)	105.2 (1)
Co–S(7)–C(8)	105.1 (1)	C(6)–S(7)–C(8)	104.0 (2)
Co–S(4)–C(5)	102.8 (1)	Co–S(4)–C(3)	107.1 (1)
C(5)–S(4)–C(3)	103.5 (2)	Co–S(1)–C(2)	100.9 (1)
Co–S(1)–C(2)	105.2 (1)	C(2)–S(1)–C(9a)	104.0 (2)
S(7)–C(6)–C(5)	114.9 (2)	S(4)–C(5)–C(6)	113.7 (3)
S(4)–C(3)–C(2)	115.8 (2)	S(1)–C(2)–C(3)	115.7 (2)
S(1a)–C(9)–C(8)	116.0 (3)	C(9)–C(8)–S(7)	116.4 (2)

(vw), 622 (vw), 519 (m). The electronic spectrum shows bands at 950 nm (ϵ = 33 M^{-1} cm^{-1}) and 504 nm (ϵ = 304 M^{-1} cm^{-1}). Recrystallization from ether/nitromethane afforded diffraction quality crystals as the nitromethane solvate.

X-ray Diffraction Data Collection. The same general procedure was used in both structure determinations, the crystallographic details of which are summarized in Table I. In both cases a crystal was mounted in a glass capillary and centered on a Syntex R3 diffractometer, and cell dimensions and orientation matrix were determined by least-squares refinement on 12 sets of Friedel pairs with $20 < 2\theta < 30°$. During the data collection three reflections were checked every 123 reflections as orientation and intensity standards, but no decomposition was noted in either case. Data were corrected for Lorentz and polarization effects, and empirical absorption corrections were performed for both structures. The SHELXTL suite of crystallographic programs was used for all calculations. Atomic scattering factors, including anomalous dispersion, were taken from the usual source.[25]

[Co·(18S6)](picrate)$_2$. Twenty reflections chosen from a rotation photograph were indexed to give a triclinic unit cell, which subsequent solution of the structure showed to be $P\bar{1}$. The structure was solved with use of 2742 unique reflections with $I > 2\sigma(I)$.

[Co(trithianonane)](BF$_4$)$_2$·CH$_3$NO$_2$. Indexing of 16 reflections taken from a rotation photograph yielded an orthorhombic primitive unit cell that was uniquely determined to be space group $P2_12_12_1$ by observation of the systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; and $00l$, $l = 2n + 1$. The structure was solved with use of 2894 unique reflections with $I > 2\sigma(I)$.

Structure Solution and Refinement. For both structures a sharpened Patterson map revealed the coordinates of the cobalt and two sulfur atoms; the remaining atoms (including all hydrogen atoms in the 18S6 structure) were located by repeated cycles of difference Fourier synthesis and least-squares refinement. Hydrogen atoms were allowed to ride on the carbon atoms to which they are bonded and their isotropic thermal parameters were constrained to be 20% greater than that of the bound carbon atom.

Table IV. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for [Co(trithianonane)$_2$](BF$_4$)$_2$

atom	x	y	z	U^a
Co	5074 (1)	4619 (1)	1385 (1)	33 (1)
S(2a)	4879 (3)	3746 (2)	2501 (1)	50 (1)
S(5a)	3540 (2)	5810 (2)	1701 (1)	45 (1)
S(8a)	3513 (3)	3552 (2)	972 (1)	51 (1)
S(2b)	5273 (3)	5531 (2)	307 (1)	53 (1)
S(5b)	6602 (2)	5814 (2)	1703 (1)	44 (1)
S(8b)	6641 (3)	3368 (2)	1197 (1)	44 (1)
C(1a)	6224 (13)	4161 (12)	2976 (6)	82 (5)
C(3a)	3549 (11)	4568 (10)	2803 (5)	63 (4)
C(4a)	3501 (11)	5738 (9)	2534 (5)	58 (4)
C(6a)	2013 (9)	5235 (10)	1457 (5)	65 (4)
C(7a)	2064 (11)	4044 (11)	1298 (9)	113 (7)
C(9a)	3475 (14)	2208 (8)	1298 (8)	98 (6)
C(1b)	3935 (14)	6413 (13)	136 (7)	99 (6)
C(3b)	6550 (11)	6524 (10)	443 (6)	75 (5)
C(4b)	6566 (13)	6902 (8)	1140 (5)	64 (4)
C(6b)	8116 (11)	5112 (10)	1580 (7)	79 (5)
C(7b)	8090 (11)	4143 (12)	1197 (8)	104 (7)
C(9b)	6657 (14)	2881 (11)	424 (5)	77 (5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor

Table V. Bond Lengths (Å) and Angles (deg) for [Co·(trithianonane)$_2$](BF$_4$)$_2$·CH$_3$NO$_2$

Co–S(2a)	2.635 (3)	Co–S(5a)	2.254 (3)
Co–S(8a)	2.253 (3)	Co–S(2b)	2.580 (3)
Co–S(5b)	2.253 (3)	Co–S(8b)	2.258 (3)
S(2a)–C(1b)	1.797 (14)	S(2a)–C(3a)	1.820 (12)
S(5a)–C(4a)	1.795 (10)	S(5a)–C(6a)	1.803 (11)
S(8a)–C(7a)	1.757 (14)	S(8a)–C(9a)	1.781 (12)
S(2b)–C(1b)	1.788 (15)	S(2b)–C(3b)	1.812 (12)
S(5b)–C(4b)	1.796 (11)	S(5b)–C(6b)	1.801 (12)
S(8b)–C(7b)	1.768 (13)	S(8b)–C(9b)	1.766 (12)
C(3a)–C(4a)	1.540 (16)	C(6a)–C(7a)	1.492 (19)
C(3b)–C(4b)	1.571 (17)	C(6b)–C(7b)	1.440 (20)

S(2a)–Co–S(5a)	86.0 (1)	S(2a)–Co–S(8a)	94.1 (1)
S(5a)–Co–S(8a)	89.3 (1)	S(2a)–Co–S(2b)	178.3 (1)
S(5a)–Co–S(2b)	92.9 (1)	S(8a)–Co–S(2b)	87.2 (1)
S(2a)–Co–S(5b)	92.1 (1)	S(5a)–Co–S(5b)	89.1 (1)
S(8a)–Co–S(5b)	173.4 (1)	S(2b)–Co–S(2b)	86.5 (1)
S(2a)–Co–S(8b)	86.9 (1)	S(5a)–Co–S(8b)	172.7 (1)
S(8a)–Co–S(8b)	93.0 (1)	S(2b)–Co–S(8b)	94.2 (1)
S(5b)–Co–S(8b)	89.4 (1)	Co–S(2a)–C(1a)	110.3 (5)
Co–S(2a)–C(3a)	99.3 (4)	C(1a)–S(2a)–C(3a)	102.9 (6)
Co–S(5a)–C(4a)	106.6 (4)	Co–S(5a)–C(6a)	106.0 (4)
C(4a)–S(5a)–C(6a)	104.6 (5)	Co–S(8a)–C(7a)	104.7 (5)
Co–S(8a)–C(9a)	113.0 (5)	C(7a)–S(8a)–C(9a)	98.0 (7)
Co–S(2b)–C(1b)	112.5 (5)	Co–S(2b)–C(3b)	101.5 (4)
C(1b)–S(2b)–C(3b)	101.2 (6)	Co–S(5b)–C(4b)	104.9 (4)
Co–S(5b)–C(6b)	104.9 (4)	C(4b)–S(5b)–C(6b)	105.6 (6)
Co–S(8b)–C(7b)	104.2 (5)	Co–S(8b)–C(9b)	113.7 (5)
C(7b)–S(8b)–C(9b)	99.9 (7)	S(2a)–C(3a)–C(4a)	113.5 (8)
S(5a)–C(4a)–C(3a)	114.9 (7)	S(5a)–C(6a)–C(7a)	114.4 (8)
S(8a)–C(7a)–C(6a)	117.0 (9)	S(2b)–C(3b)–C(4b)	111.0 (8)
S(5b)–C(4b)–C(3b)	115.3 (7)	S(5b)–C(6b)–C(7b)	117.2 (9)
S(8b)–C(7b)–C(6b)	117.0 (9)		

Both structures were refined by use of block-cascade least-squares methods, with anisotropic temperature factors for all non-hydrogen atoms except as noted below. For [Co^{II}·(18S6)](picrate)$_2$ refinement converged at R = 3.86 and R_w = 4.05 for 232 variables, where $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, and $w = 1/(\sigma^2(F) + G^*F^2)$ (where G is the factor used to reduce the weight of intense reflections). The highest peak in the final difference Fourier map had an electron density of 0.41 e/Å^{-3}. Final positional parameters for this structure are given in Table II, and selected bond lengths and angles appear in Table III.

In [Co(ttn)$_2$] (BF$_4$)$_2$·CH$_3$NO$_2$ one tetrafluoroborate anion was severely disordered and was modeled with two molecules, each with a site occupancy of 0.5 and isotropic thermal parameters. In addition, the other tetrafluoroborate anion and the nitromethane of solvation were slightly disordered as evidenced by large anisotropic thermal parameters. Refinement as above gave final agreement factors R = 7.16 and R_w = 7.66 for 307 variables. Refinement of Rogers polarity factor[26] converged to

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(25) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(26) Rogers, D. *Acta Crystallogr.* **1981**, *A37*, 734–41. See also Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881.

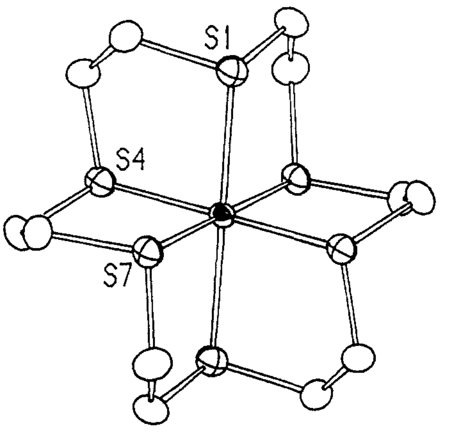


Figure 1. ORTEP drawing of the $[Co^{II}\cdot(hexathia\text{-}18\text{-}crown\text{-}6)]^{2+}$ cation showing thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity). Numbering of unique atoms follows IUPAC convention, i.e., atoms are numbered sequentially around the ring (S1, C2, etc.)

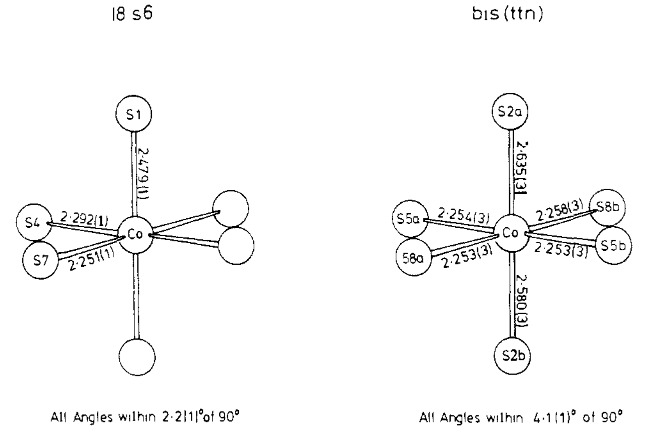


Figure 2. Coordination spheres of the cobalt ions in $[Co^{II}\cdot(hexathia\text{-}18\text{-}crown\text{-}6)]^{2+}$ (left) and $[Co^{II}\cdot(trithianonane)_2]^{2+}$ (right).

zero with small standard deviation; thus the handedness of this formally chiral complex could not be determined, possibly because the crystal was a racemic twin.[16] The highest peak in the final difference Fourier map had an electron density of 1.11 e/Å^{-3} and was located near the less severely disordered tetrafluoroborate; the next largest peak had an electron density of 0.40 e/Å^{-3}. Final positional parameters for this structure are given in Table IV, and selected bond lengths and angles appear in Table V.

Results and Discussion

Description of the Structures. Hexathia-18-crown-6 (18S6) binds Co(II) to give $[Co\cdot(18S6)]^{2+}$, in which the cobalt ion interacts with six thioether groups arranged in a tetragonally-elongated octahedral array (Figures 1 and 2, Table III). In this rigorously centrosymmetric complex the cobalt ion forms four short bonds (d(Co–S) = 2.251 (1) and 2.292 (1) Å) to the thioether groups in the equatorial plane and two extraordinarily long ones (d(Co–S) = 2.479 (1) Å) to those in the axial positions (Figure 2). This large axial elongation supports the low-spin formulation: low-spin Co(II), like Cu(II), is expected to be Jahn–Teller distorted by virtue of having a ^2E_g ground state (in O_h symmetry).[27] Furthermore, this distortion does not derive from the ligand, as $[Ni\cdot(18S6)]^{2+}$ exhibits regular octahedral coordination.[10] Despite this elongation, the cobalt coordination sphere appears unstrained, as judged by the minimal deviation of S–Co–S angles from those of octahedral coordination.

The Co–S bond lengths found here agree with those found for the few known low-spin Co^{II}–thioether complexes. Previously Co–S bond lengths of 2.29 (1) Å were reported for $[Co^{II}\cdot(di\text{-}thiahexane)_2](ClO_4)_2$,[28] which is quasi-square planar, with four equatorially-coordinated thioether groups and two semi-coordinated perchlorate anions. Recently Co–S distances of 2.240 (7), 2.356 (6), and 2.367 (5) Å were reported for $[Co(trithia\text{-}9\text{-}crown\text{-}3)_2]^{2+}$.[14] This latter comparison is particularly appropriate since work reported in this paper (vide infra) substantiates our earlier suggestion[13] (based on Co–S bond lengths) that $[Co(trithia\text{-}9\text{-}crown\text{-}3)_2]^{2+}$ is low-spin.

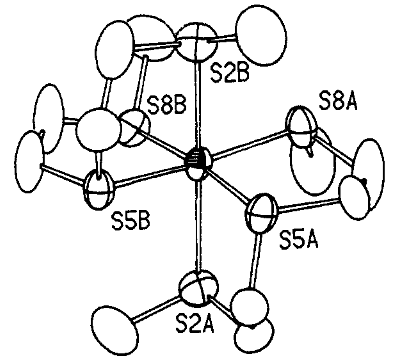
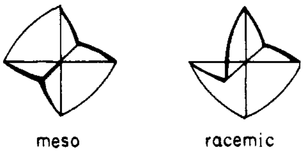


Figure 3. ORTEP drawing of the $[Co^{II}\cdot(trithianonane)_2]^{2+}$ cation showing thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity). Numbering of atoms following IUPAC convention, i.e., atoms are numbered sequentially (C1, S2, etc.)

In principle a ligand such as hexathia-18-crown-6 can wrap around an octahedral metal ion in either of two fashions, to yield meso and racemic isomers.[7] Like the nickel(II)[10] and copper(II)[11] complexes of hexathia-18-crown-6, $[Co^{II}\cdot(18S6)]^{2+}$ crystallizes as the centrosymmetric meso isomer,[13] in which each triad of adjacent sulfur atoms coordinates facially. Facial coordination results in gauche placements at all C–S bonds, a pronounced tendency of both free[9] and complexed[10,11] crown thioethers. In the crown itself C–S and C–C distances (Table II) range from 1.805 (3) to 1.818 (3) Å and from 1.502 (4) to 1.530 (5) Å, respectively, and agree with those observed previously for the corresponding Ni(II) and Cu(II) complexes.[10,11] Bond distances and angles in the picrate counterions are unexceptional.[29]



Comparison of the Co(II) complex of trithianonane (ttn) (Figure 3) with that of 18S6 reveals the influence of the macrocyclic ring upon the coordination sphere of cobalt(II). In $[Co^{II}\cdot(ttn)_2]^{2+}$ (Figure 2) the cobalt also assumes an axially elongated octahedral geometry, with axial Co–S bond lengths of 2.635 (3) and 2.580 (3) Å and equatorial bond lengths of 2.253 (3), 2.253 (3), 2.254 (3), and 2.258 (3) Å (Figure 2, Table V). Sulfur–cobalt–sulfur angles between cis coordination sites closely approach right angles, while angles between trans sites deviate from linearity by less than 8°. In view of the exceptionally long Co–S(ax) distances (which differ by 0.05 Å: 2.635 (3) vs. 2.580 (3) Å) the complex could be considered as essentially square-planar, with the two axial thioether groups tethered nearby rather than strongly coordinated.

The trithianonane ligands coordinate facially but are not centrosymmetrically related to each other, since each central thioether group is trans to a terminal thioether group of the other ligand (Figures 2 and 3). This arrangement minimizes repulsions between the terminal methyl groups (shortest Me–Me distance: 3.87 (2) Å). All of the C–C–S–C bonds adopt gauche placement except those at the sterically encumbered terminal positions. Carbon–sulfur distances range from 1.757 (14) to 1.820 (12) Å, while the minimum and maximum C–C distances are 1.440 (20) and 1.571

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[27] Indeed, the complexes $[M\cdot(18S6)]^{2+}$ (M = Co, Cu^{II}) are isostructural.

[28] Cotton, F. A.; Weaver, D. L. *J. Am. Chem. Soc.* **1965**, *87*, 4189–90.

[29] Maartmann-Moe, K. *Acta Crystallogr.* **1969**, *B25*, 1452–7.

(17) Å (Table V); however, disorder in the BF_4^- positions (see Experimental Section) precludes meaningful discussion of these distances.

Magnetic Behavior. Magnetic susceptibility measurements on $[Co\cdot(18S6)](picrate)_2$ and $[Co\cdot(ttn)_2](BF_4)_2$ establish both complexes to be low-spin ($S = ^1/_2$) systems.[30] At room temperature in the solid state these two complexes exhibit molar magnetic susceptibilities of 1.84 × 10^{-3} cm^3 mol^{-1} (μ = 1.81 μ_B) and 1.00 × 10^{-3} cm^3 mol^{-1} (1.78 μ_B), respectively. Parallel studies in nitromethane solution by the NMR method yield molar susceptibilities and moments of 1.10 × 10^{-3} cm^3 mol^{-1} (1.73 μ_B) and 1.62 × 10^{-3} cm^3 mol^{-1} (1.66 μ_B), respectively, and thereby demonstrate conclusively that these complexes remain low-spin in solution.

In view of the weak ligand field strength of thioethers,[31] the high-spin nature of several Co^{II}–tetrathioether complexes,[32,33] and in particular the observation that even $[Co(2,6\text{-dithiahexane})_3]^{2+}$ is only in a spin-equilibrium,[34] one might suspect that in $[Co^{II}\cdot(18S6)]^{2+}$ the crown causes low-spin behavior by compressing the metal ion.[13] To clarify the role of the crown we synthesized the analogous bis(trithianonane) complex. Since it, too, is low-spin, six thioethers apparently suffice to cause spin-pairing; no compression need be invoked. At the same time, however, the crown *does* in fact cause appreciable compression of the metal ion: Co–S(ax) bond lengths are over *0.1* Å shorter in the crown complex. Furthermore, in the corresponding Ni(II) complexes 18S6 exerts ≈10% greater ligand field strength than does trithianonane.[35]

Relatively few other low-spin six-coordinate Co(II) complexes have been proven to exist.[36] Cobalt(II) complexes of strong field ligands generally form four- or five-coordinate complexes (whose number is legion)[37] but rarely six-coordinate ones. For example, the existence of $[Co(CN)_6]^{4-}$ has yet to be demonstrated, as the complex is unstable with respect to loss of a cyanide anion. Only at very high concentrations of phenyl isocyanide does $[Co(NCPh)_5]^{2+}$ add a sixth ligand to form $[Co(NCPh)_6]^{2+}$, which was identified by its EPR spectrum but not isolated from solution.[38] Similarly, while the hexanitrito(cobaltate(II)) anion, $[Co(NO_2)_6]^{4-}$, is low-spin and six-coordinate in the solid state,[39-42] it too loses ligands in solution. More recently, $[Co(terpy)_2]^{2+}$ has been clearly shown to exist in a spin-state equilibrium at room temperature,[43] as have a number of diimine complexes.[44]

In addition, in the past a number of Co(II) complexes have been reported[45-49] that on the basis of magnetic moment could be members of this group, if they are assumed to be in fact six-coordinate. Low-spin six- and four-coordinate complexes can often be distinguished by magnetic behavior, as the latter generally exhibit moments of 2.1–2.9 μ_B, as opposed to the 1.79–2.0 μ_B expected for the former.[50] It should be noted, however, that rigorous distinction between five- and six-coordinate complexes cannot be made by this magnetic criterion; for example, the square-pyramidal[51] $[Co(CN)_5]^{3-}$ ion has μ(298 K) = 1.77 μ_B,[52,53] just as expected for a six-coordinate complex.

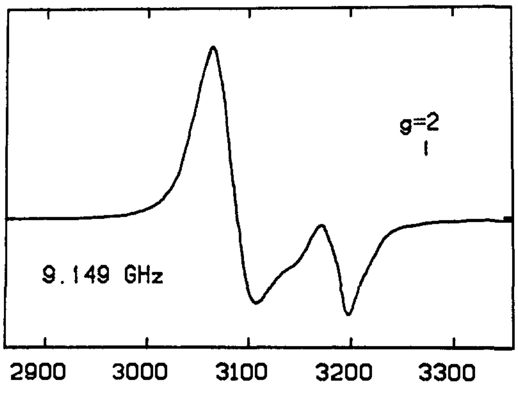

Figure 4. EPR spectrum of neat $[Co^{II}\cdot(\text{hexathia-18-crown-6})](picrate)_2$ at room temperature; modulation amplitude 5 G, microwave power 12.5 mW.

Electron Paramagnetic Resonance. Electron paramagnetic resonance data confirm the low-spin formulation of these complexes and further establish that the ground state is d_{z^2} (rather than $d_{x^2-y^2}$). Undiluted microcrystalline $[Co^{II}\cdot(18S6)]$ $(picrate)_2$ shows an essentially axial g tensor with a slight rhombic distortion: $g_x = 2.044$, $g_y = 2.121$, and $g_z = 2.135$ (Figure 4). (Intermolecular exchange interactions wash out the ^{59}Co hyperfine splitting but do not affect g values as there is only one magnetic site per unit cell.[54]) Moreover, double integration of the spectrum (relative to a fluid solution of $VO(acac)_2$ in CH_2Cl_2) establishes that it accounts for 95 ± 10% of the spins in the sample (which proves that the spectrum is characteristic of the bulk material and does not arise from an impurity). In 1:1 nitromethane:toluene glasses at 77 K $[Co^{II}\cdot(18S6)]^{2+}$ has $g_\perp = 2.14$ ($A_\perp = 0.070$ cm^{-1}) and $g_\parallel = 2.05$ (with $A_\parallel$ unresolved) (Figure 5), while for $[Co^{II}\cdot(ttn)_2]^{2+}$ $g_\perp = 2.17$ ($A = 0.051$ cm^{-1}) and $g_\parallel = 2.03$ ($A = 0.046$ cm^{-1}). In fluid solution the average g values of both complexes agree with the values found in the solid state (g_{av} = 2.11 and 2.12, respectively).

These g values ($g_\parallel \approx 2$, $g_\perp > 2$) unambiguously indicate a d_{z^2} ground state for both complexes, consistent with the axial elongation observed in their molecular structures. Deviations of g from the free electron value arise from orbital contributions to the angular momentum that for a d_{z^2} ground state are proportional to $\langle d_{z^2}|L|d\rangle$; hence $g_\parallel$ ($= g_e + c_1\langle d_{z^2}|L_z|d\rangle$) $\approx g_e$, while $g_\perp$ ($= g_e + c_2\langle d_{z^2}|L_x,L_y|d\rangle$) $> g_e$ since $\langle d_{z^2}|L_z|d\rangle$ vanishes for all d orbitals, whereas, e.g., $\langle d_{z^2}|L|d_{xz}\rangle$ does not. On the other hand, for a $d_{x^2-y^2}$ ground state both $g_\parallel$ and $g_\perp > 2$; for a high-spin ground state no spectrum at all would be seen (at room temperature).

Electrochemistry. Cyclic voltammetry of $[Co^{II}\cdot(18S6)]^{2+}$ and $[Co^{II}\cdot(ttn)_2]^{2+}$ in CH_3NO_2 shows one-electron waves at +844 and

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(30) Black and McLean[7,8] reported a Co complex of this ligand that was a monohydrate and had a much higher magnetic moment (μ(298 K) = 3.05 μ_B); hence this is apparently a different complex.

(31) Carlin, R. L.; Weissberger, E. *Inorg. Chem.* **1964**, *3*, 611–2.

(32) Levason, W.; McAuliffe, C. A.; Murray, S. G. *Inorg. Chim. Acta* **1976**, *17*, 247–52.

(33) Levason, W.; McAuliffe, C. A.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1566–70.

(34) Flint, C. D.; Goodgame, M. *J. Chem. Soc.* (*A*) **1968**, 2178–82.

(35) Hartman, J. R.; Cooper, S. R., manuscript in preparation.

(36) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 772.

(37) See, for example: Daul, C.; Shläpfer, von Zelewsky, A. *Struct. Bonding* **1979**, *36*, 129–171.

(38) Kataoka, N.; Kon, H. *J. Am. Chem. Soc.* **1968**, *90*, 2978–79.

(39) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55–132.

(40) Reinen, D.; Friebel, C. *Struct. Bonding* **1979**, *37*, 1–60.

(41) Bertrand, J. A.; Carpenter, D. A.; Kalyanaraman, A. R. *Inorg. Chim. Acta* **1971**, *5*, 113–4.

(42) Elliott, H.; Hathaway, B. J.; Slade, R. C. *Inorg. Chem.* **1966**, *5*, 669–677.

(43) Kremer, S.; Henke, W.; Reinen, D. *Inorg. Chem.* **1982**, *21*, 3013–22.

(44) Nishida, Y.; Ida, K.; Kida, S. *Inorg. Chim. Acta* **1980**, *38*, 113–6.

(45) Black, D. St. C.; McLean, I. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1004.

(46) Tasker, P. A.; Fleischer, E. B. *J. Am. Chem. Soc.* **1970**, *92*, 7072–7.

(47) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1960**, *82*, 5013–23.

(48) Dwyer, F. P.; Gill, N. S.; Gyarfas, E. C.; Lions, F. *J. Am. Chem. Soc.* **1957**, *79*, 1269–73.

(49) Lindoy, L. F.; Livingstone, S. E.; Lockyer, T. N.; Stephenson, N. C. *Aust. J. Chem.* **1966**, *19*, 1165–78.

(50) Figgis, B. N.; Nyholm, R. S. *J. Chem. Soc.* **1954**, 12–5.

(51) Brown, L. D.; Raymond, K. N. *Inorg. Chem.* **1975**, 2590–4.

(52) White, D. A.; Solodar, A. J.; Baizer, M. M. *Inorg. Chem.* **1972**, *11*, 2160–7.

(53) In aqueous solution pentacyanocobaltate anion is predominantly $[Co(CN)_5OH_2]^{3-}$, but under nonaqueous conditions (such as those used in the magnetic measurement)[52] it exists as $[Co(CN)_5]^{3-}$. Pratt, J. M.; Williams, R. J. P. *J. Chem. Soc.* (*A*) **1967**, 1291–8. See also ref 51.

(54) Bertini, I.; Gatteschi, D.; Scozzafava, A. *Coord. Chem. Rev.* **1979**, *29*, 67–84.

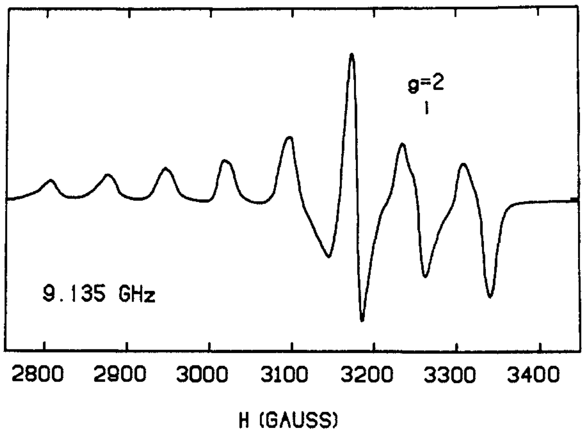

Figure 5. EPR spectrum of [Co^{II}·(hexathia-18-crown-6)](picrate)$_2$ at 77 K in 1:1 CH_3NO_2/toluene glass, modulation amplitude 5 G, microwave power 12.5 mW.

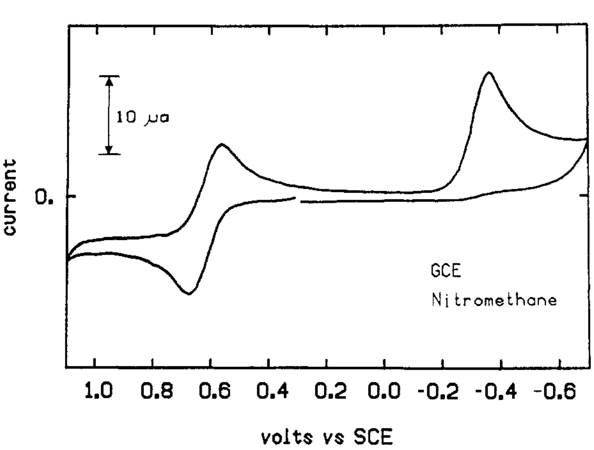

Figure 6. Cyclic voltammogram at a glassy carbon electrode of [Co^{II}·(trithianonane)$_2$]$^{2+}$ at 1 mM concentration in CH_3NO_2 scan rate = 20 mV/s; supporting electrolyte 0.1 M Et_4·NPF_6.

+864 mV vs. NHE, respectively, with ΔE_p $(=E_{p_a} - E_{p_c})$ = 77 and 108 mV (at a scan rate of 100 mV/s) (Figure 6).[55] Controlled potential coulometry establishes that oxidation to the Co(III) complexes is a one-electron process. In addition, the complexes also exhibit irreversible reduction waves at −160 and −116 mV vs. NHE, respectively.

Couples such as $[Co(NH_3)_6]^{3,2+}$ are generally irreversible electrochemically owing to unfavorable Franck–Condon factors arising from the changes in spin state and Co–L bond length.[56] Since they are already low-spin, the present Co(II) complexes do not suffer a spin state change upon oxidation. They therefore offer an unusual opportunity to study the electron-transfer kinetics of the Co(III)/II) couple in the absence of spin state restrictions. These hexakis(thioether) complexes are also remarkable for their unusually high redox potentials ($\approx$ +850 mV vs. NHE); typical Co(III/II) ammine couples have much lower potentials (all vs. NHE in water): −148 mV for [Co·(18N6)] (unpublished work), −300 mV for [Co·(sepulchrate)],[15] −410 mV for [Co(triaza-9-crown-3)$_2$],[57] and −204 mV for Co(dien)$_2$.[58] Indeed, in contrast to the air-sensitivity of most cobalt(II) complexes, including various N_6 and N_3S_3 Co(II) sepulchrate-type complexes prepared by Sargeson and coworkers[15-17] as well as [Co^{II}·(triaza-9-crown-3)$_2$]$^{2+}$,[57] [Co^{II}·(18S6)]$^{2+}$, and [Co^{II}·(ttn)$_2$]$^{2+}$ are only oxidized by such powerful oxidants as Br_2 and are completely stable with respect to oxidation by air.

The similarity in E_f between the complexes of trithianonane and hexathia-18-crown-6 suggests that the stabilization of cobalt(II) derives from the hexakis(thioether) coordination. By accepting electron density from the metal the thioether ligands not only stabilize cobalt(II) over -(III) but also stabilize the low-spin state of the former by reducing electron–electron repulsion.

Comparison of [Co^{II}·(18S6)]$^{2+}$ with [Co^{II}·(trithia-9-crown-3)$_2$]$^{2+}$, the structure of which has recently been reported,[14] provides insight into the effect of geometric constraints imposed by the ligands, and accordingly we have extended our magnetic, EPR, and electrochemical studies to this complex. Magnetic measurements on [Co^{II}·(trithia-9-crown-3)$_2$]$^{2+}$ show it too is low-spin, as suggested earlier on the basis of the Co–S bond lengths.[13] In fluid solution this complex yields an EPR spectrum with g_{av} = 2.091, with $A(^{59}Co)$ = 0.390 × 10^{-4} cm^{-1}; in frozen solution it has $g_\parallel$ = 2.136, and $g_\perp \approx 2.07$ with $A_\parallel$- and $A_\perp(^{59}Co)$ of 0.698 and 0.241 × 10^{-4} cm^{-1}, respectively. Cyclic voltammetry reveals an essentially reversible wave for the Co(III/II) couple at +680 mV vs. NHE[55] (ΔE_p = 97 mV at 50 mV/s), and, also, surprisingly, for the *Co(II/I)* couple at −214 mV (ΔE_p = 103 mV). Since the redox potential of a complex is related to the ratio of the stability constants of the reduced and oxidized forms,[59] the cathodic shift in the Co(III/II) potential between 18S6 and the bis(trithia-9-crown-3) complexes indicates that the Co(III) complex is relatively more stable for the latter ligand. Perhaps this difference arises from the trigonally "pinched" geometry of the ligand, which would tend to favor the smaller Co(III) ion over the larger Co(II). In summary, a change in ligand from hexathia-18-crown-6 to trithia-9-crown-3 decreases the stabilization of Co(II) over Co(III) and, remarkably, at the same time, permits facile formation of the corresponding Co(I) complex. Possibly hexathia-18-crown-6 precludes formation of a Co(I) complex because the cavity cannot expand, whereas in the bis(trithia-9-crown-3) complex the two tridentate ligands can move apart.

Comparison of the cobalt(III/II) bis(trithia-9-crown-3) and cobalt(III/II) bis(triaza-9-crown-3) couples[60] gives another interesting contrast in electrochemical behavior. The complex of the cyclic amine shows a reversible wave (in water) at −410 mV vs. NHE[57] (−654 mV vs. SCE), and hence it differs in redox potential from the cyclic sulfur complex by over 800 mV—a stark testimony to the ability of thioethers to stabilize lower spin and oxidation states by virtue of their π-acidity.

Conclusions

Hexakis(thioether) coordination to cobalt(II) results in production of low-spin octahedral complexes, wherein the nephelauxetic effect of the π-acidic ligands strongly stabilizes the complexes with respect to oxidation. These results, in conjunction with those previously reported for the corresponding Cu(II) complexes, show that thioethers parallel phosphines in their effect on electronic structures of metal ions. Indeed, the similar electronic structures found for thiacrown and phosphacrown complexes[61-63] of Co(II) suggest that complexes of thioethers may in some cases exhibit reactivity similar to those of phosphines, an exciting possibility in view of the extensive coordination chemistry of phosphines and its importance to homogeneous catalysis. Work direct toward examination of this hypothesis is currently in progress.

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[55] All potentials were measured relative to the saturated calomel electrode but have been referred to the normal hydrogen electrode (NHE) by addition of 244 mV.

[56] Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; pp 511-5.

[57] Wieghardt, K.; Schmidt, W.; Herrmann, W.; Kuppers, H. J. *Inorg. Chem.* **1983**, *22*, 2953-6.

[58] Ohsaka, T.; Oyama, N.; Yamaguchi, S.; Matsuda, H. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2475-81.

[59] Meites, L. "Polarographic Techniques"; Wiley: New York, 1965; p 279.

[60] Cobalt(II) bis(triaza-9-crown-3) is high spin.[57]

[61] Ciampolini, M.; Dapporto, P.; Dei, A.; Nardi, N.; Zanobini, F. *J. Chem. Soc., Chem. Commun.* **1980**, 177-8.

[62] Ciampolini, M.; Dapporto, P.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1983**, *22*, 13-17.

[63] Ciampolini, M.; Dapporto, P.; Dei, A.; Nardi, N.; Zanobini, F. *Inorg. Chem.* **1982**, *21*, 489-95.

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Registry No. [Co(18S6)](picrate)$_2$, 33270-89-2; [Co(2,5,8-trithianonane)$_2$](BF$_4$)$_2$, 99797-09-8.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

Chiroptical Properties of Compounds Containing Metal–Metal Bonds. Syntheses, Structures, and the Measurement and Interpretation of Electronic and Circular Dichroism Spectra of $Rh_2[(S)\text{-mandelate}]_4(EtOH)_2$ and $Rh_2[(R)\text{-}\alpha\text{-methoxy-}\alpha\text{-phenylacetate}]_4(THF)_2$

Pradyot A. Agaskar, F. Albert Cotton,* Larry R. Falvello,* and Scott Han

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843. *Received July 29, 1985*

Abstract: The preparation, the electronic and circular dichroism spectra in solution, and the crystal and molecular structures of two chiral dirhodium tetracarboxylato complexes are reported. $Rh_2[(S)\text{-mandelate}]_4(EtOH)_2$ (**1**) was prepared by reaction of $RhCl_3\cdot 3H_2O$ and (*S*)-mandelic acid (α-hydroxy-α-phenylacetic acid) in aqueous solution in the presence of dimethylformamide, followed by recrystallization from ethanol. Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 9.027$ (2) Å, $b = 27.110$ (5) Å, $c = 32.656$ (5) Å, $V = 7991$ (4) Å^3, and $Z = 8$. The structure was refined to least-squares residuals of $R = 0.0455$, $R_w = 0.0551$, and quality-of-fit = 1.026. $Rh_2[(R)\text{-}\alpha\text{-methoxy-}\alpha\text{-phenylacetate}]_4(THF)_2$ (**2**), prepared by reaction of $RhCl_3\cdot 3H_2O$ with (*R*)-α-methoxy-α-phenylacetic acid in water/ethanol, followed by extraction with THF, crystallizes in the triclinic space group $P1$ with $a = 11.263$ (2) Å, $b = 20.544$ (3) Å, $c = 10.325$ (2) Å, $\alpha = 91.83$ (1)°, $\beta = 110.21$ (1)°, $\gamma = 89.11$ (1)°, $V = 2234.5$ (6) Å^3, and $Z = 2$. The structure was refined to least-squares residuals of $R = 0.0460$, $R_w = 0.0543$, and quality-of-fit = 1.004. Absolute configurations were determined for both structures. The electronic spectra of **1** and **2** have bands near 600 and 450 nm in the visible region. The circular dichroism spectrum of each compound has three prominent bands, two bands with the same sign near 600 and 450 nm and a third band at 500 nm, opposite in sign to the first two. The circular dichroism effects are interpreted in terms of a static-coupling mechanism. The bands at 600 and 400 nm are assigned as electronically allowed components of the transitions $\pi^*(Rh–Rh) \rightarrow \sigma^*(Rh–O)$ and $\pi(Rh–Rh, Rh–O) \rightarrow \sigma^*(Rh–O)$, respectively. The band at 500 nm is assigned as an overlap of magnetically allowed components of the same transitions.

Over the past two decades a substantial body of literature has described the preparation and structures of the metal–metal singly bonded dirhodium complexes, the most common of which are the tetracarboxylato compounds of the type $Rh_2(O_2CR)_4L_2$, in which L represents a Lewis base and R an organic group.[1] Following an early report of a preparation[2] and the first accurate structure determination,[3] some three score compounds have been prepared and structurally characterized.[4]

In marked contrast to the large body of accurate structural characterization, the description of the electronic structures of these compounds has presented a more difficult problem. The electronic spectra show two predominant peaks in the visible region. The higher energy transition, which typically appears at ~450 nm and is often a shoulder on a charge-transfer band, is relatively insensitive to the nature of the axial ligand, while the lower energy band varies in the range 500–600 nm, depending on the identity of the axial donor atom. For complexes with oxygen donor atoms in the axial positions, the lower energy band appears at or near 600 nm.

Single-crystal electronic spectra were first reported by Martin and co-workers,[5] who measured the spectrum of a monoclinic crystal of $Rh_2(O_2CCH_3)_4(H_2O)_2$ at both 300 and 15 K. The low-energy band was found to be polarized perpendicular to the metal–metal bond, while the higher energy band was found to consist of two transitions, one polarized parallel to and one perpendicular to the crystallographic *b*-axis. All of the evidence at this point appeared consistent with an earlier assignment, based on Xα calculations,[6] which attributed the lower energy band to the transition $\pi^*(Rh–Rh) \rightarrow \sigma^*(Rh–Rh)$ ($^1A_{1g} \rightarrow {}^1E_u$ in D_{4h} symmetry). The (*xy*) component of the higher energy band (450 nm) was assigned to the transition $\pi^*(Rh–Rh) \rightarrow \sigma^*(Rh–O)$ (also $^1A_{1g} \rightarrow {}^1E_u$).

While these assignments were fully in line with the energies of the observed electronic transitions, a question remained about the Rh–Rh vibrational stretching frequency. Martin et al. observed a vibrational progression, with an average splitting of 297 cm^{-1}, on the 600-nm band at 15 K, implying a metal–metal stretching frequency of 297 cm^{-1} for the excited state. While ν(Rh–Rh) values in the range of 288–351 cm^{-1} have been suggested,[7,8] these values are quite high for a stretch involving singly

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[1] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

[2] Chernyaev, I. I.; Shenderetskaya, E. V.; Koryagina, A. A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1960**, *5*, 559.

[3] Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *J. Am. Chem. Soc.* **1970**, *92*, 2926. Cotton, F. A.; DeBoer, B. G.; LaPrade, M. D.; Pipal, J. R.; Ucko, D. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 1664.

[4] Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73.

[5] Martin, D. S.; Webb, T. R.; Robbins, G. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 475.

[6] Norman, J. G.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.

[7] Ketteringham, A. P.; Oldham, C. *J. Chem. Soc., Dalton Trans.* **1973**, 1067.

[8] Moller, M. R.; Bruck, M. A.; O'Connor, T.; Armatis, F. J.; Knolinski, E. A.; Kottmair, N.; Tobias, R. S. *J. Am. Chem. Soc.* **1980**, *102*, 4589.

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