Table V. The Volume of the Cavity ($Å^3$) for the Cyanoethyl Group in the Related Crystals

complex[a]	A cn group	B cn group	ref
second class			
R-cn-py	8.89	11.34	5
R-cn-cnpy	7.97	10.37	6
R-cn-4mepy	11.05	12.61	7
third class			
R-cn-dpmp	17.08	18.01	2
present crystal			
R-cn-3mepy (293 K)	10.24	14.29	
R-cn-3mepy (343 K)	10.84	12.79	

[a] *R*-cn-py, *R*-cn-cnpy, *R*-cn-4mepy, and *R*-cn-dpmp contain pyridine, 4-pyridinecarbonitrile, 4-methylpyridine, and diphenylmethylphosphine as axial ligands instead of 3-methylpyridine.

whereas the volume of the A cavity is a little smaller than those of the other reactive groups. The reason why not only B but also A cn groups can be inverted at the initial stage can be explained by the fact that the crystalline-field to produce the inversion symmetry in the present crystal would be weaker than that in the crystals of the second class since the pseudoinversion center does not meet the crystal symmetry in the former crystal. However, either of the A and B cavities is too small to accommodate the disordered racemate and the molecules would be more favorably packed when the two cn groups have opposite configurations. This causes the reinversion of the A cn group, and finally all the B cn groups will be converted to the opposite configuration and all the A cn groups to the original configuration.

In a crystal of the second class, on the other hand, some portion of the A cn groups would be inverted at the intermediate stages. However, the reinversion of the A cn group may occur so fast that the intermediate state as shown in Figure 8c cannot be detected. For a crystal of the third class, both of the A and B cavities have enough volume to accommodate the disordered racemate and the contraction of the unit cell would be prohibited because of the bulky phosphine ligand. The disordered structure would gain in entropy.

In the present crystal, the interaction between the two cn groups is not so strong or not so weak that we were able to analyze directly the concerted change of the two groups at several intermediate stages. Such a stepwise structure analysis, which we call "dynamical structure analysis", would be a powerful tool in elucidating the reaction mechanism. Further quantitative study on the mechanism is in progress.

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Supplementary Material Available: Tables of atomic parameters for non-H and H atoms, anisotropic thermal parameters for non-H atoms, and the observed and calculated structure factors at the nine stages I to VI and I′ to III′ except the atomic parameters for non-H atoms at the stages I and VI (143 pages). Ordering information is given on any current masthead page.

Crown Thioether Chemistry. Synthetic, Structural, and Physical Studies of the Cu(II) and Cu(I) Complexes of Hexathia-18-crown-6

JudithAnn R. Hartman 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 June 4, 1985*

Abstract: The copper(II) and copper(I) complexes of hexathia-18-crown-6 have been synthesized and characterized by electron paramagnetic resonance, electrochemical, and X-ray diffraction methods. The copper(II) complex, [Cu·(hexathia-18-crown-6)](picrate)$_2$, crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 6.661$ (1) Å, $b = 9.669$ (2) Å, and $c = 13.594$ (3) Å, $\alpha = 84.84$ (2)°, $\beta = 75.52$ (2)°, and $\gamma = 76.80$ (2)°, and $Z = 1$. The copper(I) complex, [Cu·(hexathia-18-crown-6)](BF_4), crystallizes in the orthorhombic system, space group $Pna2_1$, with $a = 10.855$ (4) Å, $b = 18.592$ (7) Å, $c = 10.137$ (4) Å, and $Z = 4$. The centrosymmetric copper(II) complex adopts an axially elongated octahedral geometry, with Cu–S(eq) distances of 2.323 (1) and 2.402 (1) Å and a Cu–S(ax) distance of 2.635 (1) Å. Glasses at 77 K of [Cu·(hexathia-18-crown-6)](picrate)$_2$ in 1:1 nitromethane–toluene yield an EPR spectrum with $g_x = 2.028$, $g_y = 2.035$, and $g_z = 2.119$, $A_{\parallel} = 0.0153$ cm^{-1}, and $A_{\perp} \approx 0.0019$ cm^{-1}. The copper(I) complex assumes a distorted four-coordinate geometry that can be considered as derived from a linear two-coordinate complex by addition of two thioether groups; Cu–S distances are 2.253 (2) and 2.245 (2), and 2.358 (2) and 2.360 (2) Å, respectively, for these two types of ligands. Cyclic voltammetry shows that the Cu(II) and Cu(I) complexes are connected by an essentially reversible one-electron redox process at very high potential: +0.96 V vs. NHE.

Elucidation of the structure of the blue copper proteins plastocyanin[1,2] and azurin[3] has demonstrated thioether coordination to the copper ion but left unresolved the origin of the peculiar electronic structure of the metal-containing active site.[4,5] To clarify the relationship between electronic and molecular structure numerous studies have been directed toward synthesis of low molecular weight copper complexes with coordination spheres similar to those now known for the proteins.[6-19] Two fundamental issues have been stirred by the unusual redox, optical, and electron paramagnetic resonance characteristics of these proteins: First, to what extent, if any, are these properties attributable simply

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

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to the presence of a thioether group in the coordination sphere? Second, how are these properties affected by geometric deformations?[20,21]

Homoleptic thioether complexes provide the most promising case in which to answer questions that address the electronic consequences of thioether coordination. For this reason a considerable number of homoleptic thioether complexes of four- and five-coordinate copper have been studied by Rorabacher and co-workers.[22-30] In contrast to the substantial information now available on these four- and five-coordinate complexes, however, six-coordinate thioether complexes are not well studied; indeed, only one structurally characterized example exists.[31] Our earlier work on hexathia-18-crown-6 (1,4,7,10,13,16-hexathiacyclooctadecane),[32] and its complexes with Ni(II)[33] and Co(II),[34] encouraged us to attempt synthesis of the analogous copper(II) compound with a view toward preparing and thoroughly studying a six-coordinate homoleptic thioether complex of Cu(II).

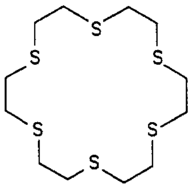

Table I. Crystallographic Data for $[\text{Cu(hexathia-18-crown-6)}](\text{picrate})_2$ and $[\text{Cu(hexathia-18-crown-6)}](\text{BF}_4)$

	$[\text{Cu}^{\text{II}}\cdot(\text{L})]^{2+}$	$[\text{Cu}^{\text{I}}\cdot(\text{L})]^{+}$
mol wt	880.43	511.08
space group	$P\bar{1}$	$Pna2_1$
a, Å	6.661 (1)	10.855 (4)
b, Å	9.669 (2)	18.592 (7)
c, Å	13.594 (3)	10.137 (4)
α, deg	84.84 (2)	90
β, deg	75.52 (2)	90
γ, deg	76.80 (2)	90
vol, Å^3	824.78	2047.27
d_{calcd}, g/cm^3	1.88	1.66
Z	1	4
λ	Mo Kα	Mo Kα
$F(000)$	450.92	1047.88
μ, cm^{-1}	11.02	16.86
cryst. size, mm	0.25 × 0.34 × 0.48	0.22 × 0.60 × 0.05
refl. coll.	$\pm h,\pm k,+l$	$+h,+k,+l$
no. of refl. coll.	5481	3492
unique data with $F^2 > 2\sigma(F^2)$	4598	2247
2θ range, deg	3–62	3–57
final R, %	3.01	5.15
final R_w, %	3.50	5.46
GOF[a]	1.173	1.169
no. of var.	232	213
temp	ambient	ambient
scan rate	2.00–5.00	2.00–6.00
mode	θ–2θ	θ–2θ
max. trans. factor	0.510	0.676
min. trans. factor	0.416	0.568
R_{merg}	0.0074	0.0259

[a] The goodness of fit is defined as $[w(|F_o| - |F_c|)^2(n_o - n_v)]$,[12] where n_o and n_v denote the number of data and variables, respectively.

This paper describes the results of our synthetic, spectroscopic, electrochemical, and structural investigation of both $[\text{Cu}^{\text{II}}\cdot(\text{hexathia-18-crown-6})]^{2+}$ as well as the corresponding Cu(I) complex and augments the small number of cases where both the copper(II) and -(I) complexes of the same ligand have been structurally characterized. In addition, comparison of $[\text{Cu}^{\text{II}}\cdot(\text{hexathia-18-crown-6})]^{2+}$ with the recently published $[\text{Cu}^{\text{II}}\cdot(\text{trithia-9-crown-3})_2]^{2+}$ [31] illuminates the effect of stereochemistry upon the redox potentials, optical spectra, and EPR parameters of these copper(II) complexes, which differ only in geometrical details.

Experimental Section

Physical Measurements. Electronic spectra were recorded with quartz cuvettes on a Perkin-Elmer 559A spectrophotometer; infrared spectra were obtained on KBr pellets or Nujol mulls with a Perkin-Elmer 683 spectrometer, which was calibrated with use of polystyrene. Cyclic voltammetric measurements were performed with a Princeton Applied Research (PAR) Model 175 programmer, 173 potentiostat, and 179 digital coulometer. 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 was prepared by a modification of the procedure of Ochrymowycz et al.[35] Cupric picrate was prepared from copper(II) carbonate and picric acid and carefully

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dried in vacuo over phosphorus pentoxide. **Caution.** Although this compound gave no evidence of unusual sensitivity to shock or heat, owing to the danger of detonation it should be prepared only in small quantities. Nitromethane was distilled from CaH_2 and stored over molecular sieves; acetonitrile and methylene chloride were freshly distilled from CaH_2. Copper(I) tetraacetonitrile tetrafluoroborate was prepared by the published method.[36] All other chemicals were used as received. Elemental analyses for C, H, S, and N were performed by Galbraith Laboratories, Inc., Knoxville, TN. Copper analysis was carried out by EDTA titration.[37] All other chemicals were used as received.

[Cu·(hexathia-18-crown-6)](picrate)$_2$ was prepared by addition of hexathia-18-crown-6 (0.038, g, 106 mmol) dissolved in 2 mL of nitromethane at 50 °C to a solution of copper(II) picrate (56 mg, 107 mmol) in 2 mL of nitromethane. The resulting very dark green solution was allowed to stand at 50 °C for 1 h and then at room temperature for 9 h. The black crystalline product was collected by filtration, washed with methylene chloride, and dried in vacuo overnight. Yield 70.4 mg (76.1%). Recrystallization from nitromethane gave black monoclinic prisms suitable for X-ray diffraction. Anal. Calcd for $C_{24}H_{28}N_6O_{14}S_6Cu$: C, 32.81; H, 2.99; N, 9.56; S, 21.90. Found: C, 32.87; H, 3.20; N, 9.65; S, 21.62. IR (cm^{-1}, KBr, Nujol): 1698 (vw), 1635 (s), 1608 (sh), 1556 (s), 1504 (vw), 1365 (s), 1348 (m), 1310 (m), 1295 (sh), 1260 (s), 1235 (m), 1188 (w), 1160 (w), 1150 (w), 1080 (m), 945 (m), 935 (m), 904 (w), 840 (w), 810 (w), 790 (m), 747 (m), 720 (m), 710 (m), 685 (w). Interference from the intense absorption bands of the picrate anions precluded meaningful optical measurements.

1,4,7-Trithiacyclononane was prepared by a modification of the procedure of Setzer et al.[31] A solution of 3-thiapentane-1,5-dithiol (5.50 g; 35.6 mmol) and 1,2-dichloroethane (3.529 g; 35.6 mmol) in 150 mL of DMF was added over 18 h to a suspension of Cs_2CO_3 (13.0 g; 39.9 mmol) in 250 mL of DMF at 50 °C. After addition was complete the solution was stirred for 7 h before the DMF was removed at reduced pressure and the resulting white solid purified by flash chromatography on silica gel with 5% (v/v) EtOAc in hexane as eluant. The second fraction yielded 1.33 g (20.7%) of the product (mp 79–80° C (lit. mp 84 °C)[31], NMR δ 3.12 (s); *m/e* 180).

[Cu·(hexathia-18-crown-6)](BF$_4$) was prepared by addition of a solution of $[Cu(CH_3CN)_4](BF_4)$ (290 mg, 0.92 mmol) in 5 mL of acetonitrile to a solution of hexathia-18-crown-6 (260 mg, 0.72 mmol) in 8 mL of acetonitrile at 50 °C. The resulting colorless solution was filtered to remove a small amount of brown solid (the corresponding Cu(II) complex) and then concentrated to 6 mL. The mixture was heated to 50 °C to redissolve product that had precipitated and then cooled slowly to 5 °C. The resulting white needles were collected by filtration, washed well with methylene chloride, and dried in vacuo overnight. Yield 190 mg (51.6%). Anal. Calcd for $C_{12}H_{24}S_6CuBF_4$: C, 28.20; H, 4.73; S, 37.64. Found: C, 28.06; H, 4.73; S, 37.06. IR (cm^{-1}, KBr): 3000 (w), 2960 (w), 2920 (ms), 1430 (sh), 1426 (s), 1415 (sh), 1404 (m), 1384 (w), 1300 (sh), 1290 (m), 1265 (m), 1258 (m), 1250 (sh), 1228 (m), 1214 (w), 1205 (m), 1199 (ms), 1189 (m), 1175 (w), 1159 (m), 1060 (br s), 938 (m), 913 (ms), 902 (m), 856 (m), 840 (w), 827 (s), 780 (w), 770 (w), 765 (w), 736 (w), 718 (w), 710 (w), 700 (w), 685 (m), 678 (w), 670 (w), 653 (w), 630 (m), 530 (w), 520 (m), 458 (m), 405 (w). A crystal suitable for X-ray analysis was obtained by recrystallization from a nitromethane–ether mixture.

Collection of X-ray Diffraction Data. A crystal of [Cu·(hexathia-18-crown-6)](picrate)$_2$ (0.25 mm × 0.34 mm × 0.48 mm) mounted in a glass capillary was centered on a Nicolet R3 diffractometer equipped with a graphite-crystal monochromator. Twenty reflections chosen from a rotation photograph gave a triclinic unit cell isomorphous to that of [Co(hexathia-18-crown-6)](picrate)$_2$.[34] The unit cell dimensions and orientation matrix were determined by least-squares refinement of the setting angles of twelve sets of Friedel pairs of reflections with $2\theta > 25°$. The corresponding primitive, Delaunay reduced cell has a = 14.370 Å, b = 15.230 Å, c = 9.668 Å, α = 113.62°, β = 98.18°, and γ = 138.94°. A summary of crystallographic details is presented in Table I. Three reflections (0,0,11, 070, 300) were checked every 123 reflections as orientation and intensity standards. The data were corrected for Lorentz and polarization effects and also empirically corrected for absorption, but not for decomposition (which was <2%). The structure as solved with use of 3773 unique reflections with $I > 2\sigma(I)$. For both structures calculations were performed on a Nova 3 minicomputer with the Nicolet SHELXTL crystallographic package and use of scattering factors from the usual source.[38]

Table II. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for [Cu(hexathia-18-crown-6)](picrate)$_2$

atom	x	y	z	U^a
Cu	0	0	0	23 (1)
S(1)	−1282 (1)	88 (1)	1753 (1)	27 (1)
S(4)	3431 (1)	−1198 (1)	241 (1)	27 (1)
S(7)	−715 (1)	−2563 (1)	−36 (1)	30 (1)
C(2)	−975 (3)	834 (2)	−2243 (1)	31 (1)
C(3)	3144 (3)	−837 (2)	1559 (1)	33 (1)
C(5)	3523 (3)	−3084 (2)	221 (1)	32 (1)
C(6)	−1430 (3)	3576 (2)	−486 (1)	33 (1)
C(8)	−138 (3)	2811 (2)	1391 (1)	40 (1)
C(9)	1699 (3)	−1952 (2)	−2019 (1)	39 (1)
O(1)	2872 (3)	1794 (2)	2891 (1)	56 (1)
O(21)	3361 (3)	−688 (2)	3932 (1)	55 (1)
O(22)	1964 (3)	−578 (2)	5539 (1)	61 (1)
O(61)	2507 (4)	6025 (2)	3078 (1)	72 (1)
O(62)	3703 (3)	4274 (2)	2085 (1)	64 (1)
O(41)	2382 (3)	3278 (2)	7331 (1)	64 (1)
O(42)	2437 (3)	5357 (2)	6574 (1)	71 (1)
N(2)	2655 (2)	−19 (2)	4715 (1)	39 (1)
N(4)	2459 (3)	4075 (2)	6564 (1)	47 (1)
N(6)	3041 (3)	4747 (2)	2939 (1)	42 (1)
C(11)	2832 (3)	2301 (2)	3699 (1)	35 (1)
C(12)	2666 (3)	1499 (2)	4673 (1)	33 (1)
C(13)	2550 (3)	2061 (2)	5580 (1)	34 (1)
C(14)	2582 (3)	3492 (2)	5605 (1)	36 (1)
C(15)	2723 (3)	4355 (2)	4733 (1)	36 (1)
C(16)	2867 (3)	3783 (2)	3821 (1)	34 (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 [Cu^{II}·(hexathia-18-crown-6)](picrate)$_2$

Cu–S(1)	2.323 (1)	Cu–S(4)	2.402 (1)
Cu–S(7)	2.635 (1)	C(8)–C(9)	1.525 (3)
S(1)–C(2)	1.812 (2)	S(1)–C(9a)	1.814 (2)
S(4)–C(3)	1.811 (2)	S(4)–C(5)	1.813 (2)
S(7)–C(6)	1.802 (2)	S(7)–C(8)	1.807 (2)
C(2)–C(3)	1.510 (2)	C(6)–C(5)	1.523 (2)
S(1)–Cu–S(4)	89.5 (1)	S(1)–Cu–S(7)	92.4 (1)
S(4)–Cu–S(7)	85.8 (1)	Cu–S(1)–C(2)	103.7 (1)
Cu–S(1)–C(9a)	104.4 (1)	C(2)–S(1)–C(9a)	106.6 (1)
Cu–S(4)–C(3)	100.7 (1)	Cu–S(4)–C(5)	106.2 (1)
C(3)–S(4)–C(5)	105.5 (1)	Cu–S(7)–C(6)	99.1 (1)
Cu–S(7)–C(8)	99.0 (1)	C(6)–S(7)–C(8)	105.6 (1)
S(1)–C(2)–C(3)	116.6 (1)	S(4)–C(3)–C(2)	115.3 (1)
S(4)–C(5)–C(6)	118.2 (1)	S(7)–C(6)–C(5)	118.2 (1)
S(7)–C(8)–C(9a)	118.0 (1)	S(1a)–C(9)–C(8)	118.4 (1)

Structure Solution and Refinement. The coordinates of Cu and the three unique sulfur atoms were determined from a sharpened Patterson map, and the remaining atoms were located by repeated cycles of difference Fourier synthesis and least-squares refinement. All hydrogen atoms were located in the difference map; each was included in the refinement with an isotropic thermal parameter 20% greater than that of the carbon atom to which it is bonded.

Block-cascade least-squares refinements with anisotropic temperature factors for all non-hydrogen atoms gave final agreement factors of R = 3.01% and R_w = 3.50% for 232 variables, where $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = \sum(w^{1/2}|F_o| - |F_c|)/\sum w^{1/2}F_o$. At convergence no parameter changed by more than 10% of its esd, and the highest peak in the difference Fourier map was near Cu and corresponded to 0.61 e$^-$/Å^3. Final positional parameters and selected bond lengths and angles appear in Tables II and III, respectively. Tables of positional parameters of the hydrogen atoms and thermal parameters for all atoms are available as supplementary material.

[Cu·(hexathia-18-crown-6)](BF$_4$). Data Collection. A needle-shaped crystal of [Cu·(hexathia-18-crown-6)](BF$_4$) was cut to the dimensions 0.60 mm × 0.22 mm × 0.05 mm and mounted in a quartz capillary. Fifteen reflections from a rotation photograph indicated an orthorhombic cell, and the systematic absences (h00, h = odd; 0k0, k = odd; 00l, l = odd; $h0l$, h = l = odd; and hk0; k = odd) were consistent with the space groups $P2_1nb$ (a nonstandard setting of $Pna2_1$) or $Pmnb$. Subsequent refinement indicated the former to be correct, and the data were transformed to the standard group $Pna2_1$ for final refinement. (A summary of crystallographic details is presented in Table I.) Three reflections

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Table IV. Atomic Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for [Cu·(hexathia-18-crown-6)](BF_4)

atom	*x*	*y*	*z*	U^a
Cu	8132 (1)	7690 (1)	2500	41 (1)
S(10)	8754 (2)	8792 (1)	3142 (2)	43 (1)
S(7)	7061 (2)	7426 (1)	4468 (2)	44 (1)
S(4)	9558 (2)	6761 (1)	2912 (2)	43 (1)
S(1)	7333 (2)	7162 (1)	702 (2)	45 (1)
S(16)	9901 (2)	8330 (1)	−1923 (3)	54 (1)
S(13)	8804 (2)	10131 (1)	685 (3)	55 (1)
C(9)	8526 (9)	8641 (5)	4883 (9)	57 (3)
C(8)	7358 (8)	8289 (5)	5287 (8)	50 (3)
C(6)	8226 (9)	6837 (5)	5189 (8)	52 (3)
C(5)	8682 (9)	6313 (4)	4189 (9)	48 (3)
C(3)	9280 (9)	6235 (4)	1466 (9)	56 (3)
C(2)	7983 (9)	6269 (4)	924 (10)	54 (3)
C(18)	8031 (7)	7499 (5)	−799 (7)	43 (3)
C(17)	9370 (7)	7690 (4)	−678 (8)	43 (3)
C(15)	9175 (8)	9152 (5)	−1352 (9)	50 (3)
C(14)	9687 (7)	9433 (4)	−41 (9)	48 (3)
C(12)	7501 (7)	9639 (4)	1346 (8)	43 (3)
C(11)	7558 (8)	9456 (4)	2780 (9)	50 (3)
B	5534 (6)	9289 (4)	7932 (7)	48 (6)
F(1)	6066 (8)	8841 (4)	8799 (9)	55 (3)
F(2)	4895 (10)	9792 (5)	8585 (10)	77 (4)
F(3)	4771 (10)	8916 (6)	7150 (11)	145 (7)
F(4)	6405 (9)	9605 (5)	7197 (9)	76 (3)
Ba	5292 (7)	9224 (4)	7910 (8)	54 (7)
F(1a)	5987 (9)	8664 (6)	8284 (12)	90 (5)
F(2a)	4109 (7)	9021 (6)	7852 (11)	81 (4)
F(3a)	5414 (12)	9758 (6)	8787 (12)	140 (8)
F(4a)	5658 (10)	9452 (6)	6719 (10)	94 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor for all anisotropic atoms (i.e., all except B and F).

Table V. Bond Lengths (Å) and Angles (deg) for [Cu·(hexathia-18-crown-6)](BF_4)

Cu–S(10)	2.253 (2)	Cu–S(7)	2.360 (2)
Cu–S(4)	2.358 (2)	Cu–S(1)	2.245 (2)
S(10)–C(9)	1.804 (9)	S(10)–C(11)	1.829 (9)
S(7)–C(8)	1.835 (9)	S(7)–C(6)	1.826 (9)
S(4)–C(5)	1.809 (9)	S(4)–C(3)	1.787 (9)
S(1)–C(2)	1.817 (9)	S(1)–C(18)	1.812 (8)
S(16)–C(17)	1.828 (8)	S(16)–C(15)	1.814 (9)
S(13)–C(14)	1.774 (9)	S(13)–C(12)	1.813 (8)
C(9)–C(8)	1.484 (13)	C(6)–C(5)	1.491 (12)
C(3)–C(2)	1.513 (13)	C(18)–C(17)	1.501 (11)
C(15)–C(14)	1.533 (13)	C(12)–C(11)	1.494 (12)
S(10)–Cu–S(7)	95.3 (1)	S(10)–Cu–S(4)	114.7 (1)
S(7)–Cu–S(4)	91.2 (1)	S(10)–Cu–S(1)	138.4 (1)
S(7)–Cu–S(1)	113.9 (1)	S(4)–Cu–S(1)	94.4 (1)
Cu–S(10)–C(9)	95.8 (3)	Cu–S(10)–C(11)	110.1 (3)
C(9)–S(10)–C(11)	101.8 (4)	Cu–S(7)–C(8)	96.6 (3)
Cu–S(7)–C(6)	97.0 (3)	C(8)–S(7)–C(6)	102.8 (4)
Cu–S(4)–C(5)	96.8 (3)	Cu–S(4)–C(3)	98.3 (3)
C(5)–S(4)–C(3)	104.3 (4)	Cu–S(1)–C(2)	98.6 (3)
Cu–S(1)–C(18)	111.6 (3)	C(2)–S(1)–C(18)	104.9 (4)
C(17)–S(16)–C(15)	101.0 (4)	C(14)–S(13)–C(12)	101.9 (4)
S(10)–C(9)–C(8)	117.1 (6)	S(7)–C(8)–C(9)	114.2 (6)
S(7)–C(6)–C(5)	110.5 (6)	S(4)–C(5)–C(6)	111.1 (6)
S(4)–C(3)–C(2)	115.6 (6)	S(1)–C(2)–C(3)	116.4 (6)
S(1)–C(18)–C(17)	114.7 (6)	S(16)–C(17)–C(18)	113.7 (6)
S(16)–C(15)–C(14)	113.9 (6)	S(13)–C(14)–C(15)	114.4 (6)
S(13)–C(12)–C(11)	116.2 (6)	S(10)–C(11)–C(12)	112.3 (6)

(008, 040, 400) were checked every 123 reflections as orientation and intensity standards but revealed no decomposition. The data were empirically corrected for absorption, as well as Lorentz and polarization effects. The structure was solved by use of 2247 unique reflections with $I > 2\sigma(I)$.

Structure Solution and Refinement. A sharpened Patterson map revealed the coordinates of the copper atom; the remaining atoms (including all hydrogen atoms) were located by repeated cycles of difference Fourier synthesis and least-squares refinement. Scattering factors were taken from the usual source.[38] 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.

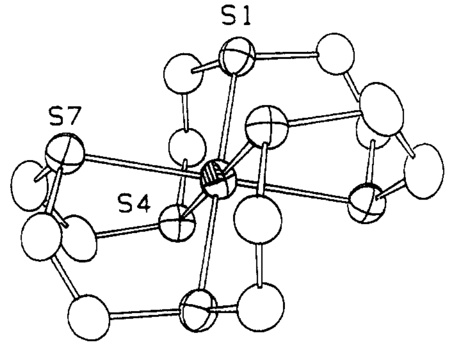

Figure 1. ORTEP drawing of the [Cu^{II}·(hexathia-18-crown-6)]$^{2+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity). Number of unique atoms follows IUPAC convention, i.e., atoms are numbered sequentially around the ring (S1, C2, etc.).

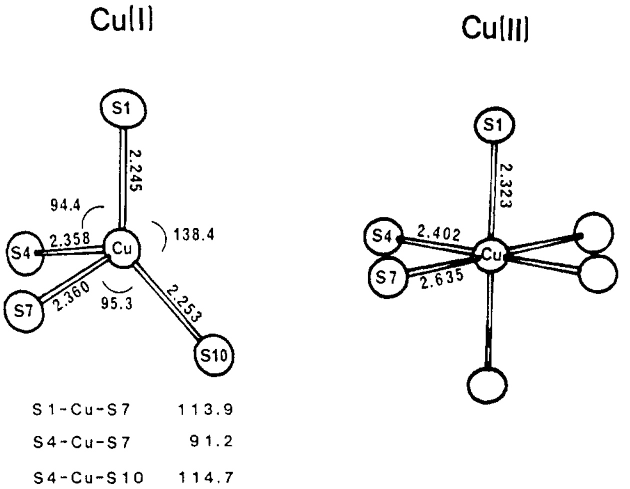

Figure 2. Coordination sphere of the copper ions in [Cu^{I}·(hexathia-18-crown-6)]$^+$ and [Cu^{II}·(hexathia-18-crown-6)]$^{2+}$

Block-cascade least-squares refinements with anisotropic temperature factors for all non-hydrogen atoms gave final agreement factors of $R = 5.16\%$ and $R_w = 5.47\%$ for 213 variables, where $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = \sum(w^{1/2}|F_o| - |F_c|)/\sum w^{1/2}F_o$.

The disordered tetrafluoroborate anion was fit with two molecules of equal occupancy, each of which was constrained to tetrahedral geometry, boron–fluorine bond lengths of 1.34 Å, and isotropic thermal parameters for all five atoms. The handedness of the crystal was not determined. The highest peak in the final difference Fourier map had an electron density of 0.97 $e^-/Å^3$ and was located near the disordered tetrafluoroborate group.

Final positional parameters and selected bond lengths and angles appear in Tables IV and V, respectively. Tables of positional parameters of the hydrogen atoms and thermal parameters for all atoms are available as supplementary material.

Results and Discussion

Descriptions of the Structures. In common with the related cobalt(II) and nickel(II) complexes of hexathia-18-crown-6,[33,34] [Cu^{II}·L]$^{2+}$ crystallizes as the centrosymmetric meso isomer, in which each triad of adjacent sulfur atoms coordinates to a trigonal face of the coordination octahedron (Figure 1). This arrangement maximizes the number of gauche placements at the C–S bonds, a marked tendency of macrocyclic thioethers generally that has been pointed out previously.[32] All six S atoms of the ligand coordinate to the metal ion to give a tetragonally-distorted octahedron with four short (2.323 (1) and 2.402 (1) Å) and two long (2.635 (1) Å) Cu–S bonds (Figure 2). This large axial elongation (>0.2 Å) of [Cu^{II}·L]$^{2+}$ derives not from the ligand—the corresponding Ni(II) complex, [Ni^{II}·L]$^{2+}$, is essentially perfectly octahedral[33]—but instead from a Jahn–Teller elongation of extraordinary magnitude. Nevertheless, the copper coordination sphere lacks obvious strain, since all of the S–Cu–S bond angles

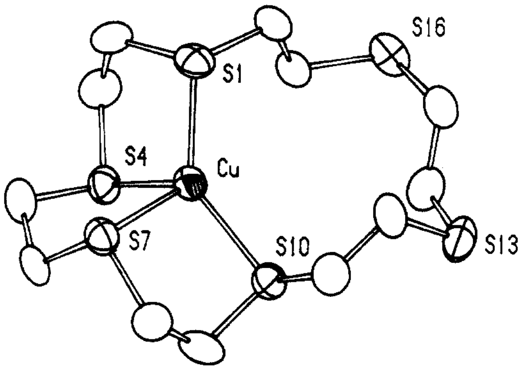

Figure 3. ORTEP drawing of the $[\mathrm{Cu^{I}\cdot(hexathia\text{-}18\text{-}crown\text{-}6)}]^{+}$ cation showing thermal ellipsoids at the 50% probability level (hydrogen atoms are omitted for clarity). Numbering of unique atoms follows IUPAC convention, i.e., atoms are numbered sequentially around the ring (S1, C2, etc.).

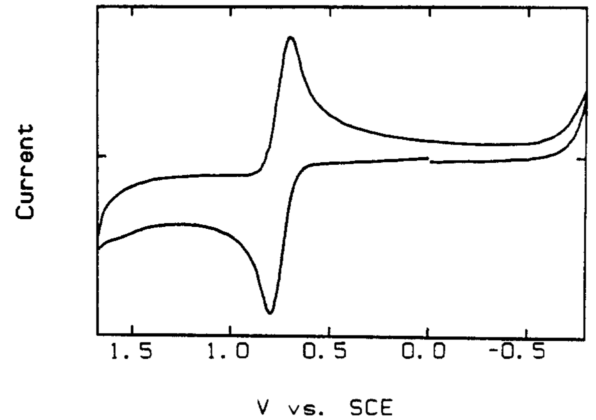

Figure 4. Cyclic voltammogram at a glassy carbon electrode of $[\mathrm{Cu^{II}\cdot(hexathia\text{-}18\text{-}crown\text{-}6)}](\mathrm{picrate})_2$ at 1 mM concentration in $\mathrm{CH_3NO_2}$ scan rate = 20 mV/s; supporting electrolyte 0.1 M $\mathrm{Et_4N\cdot PF_6}$.

are within 4° of those expected for octahedral coordination.

The equatorial copper–sulfur distances of $[\mathrm{Cu^{II}\cdot L}]^{2+}$ (2.323 (1) and 2.402 (1) Å (Table II, Figure 2)) compare well with those found in, e.g., $[\mathrm{Cu^{II}(2,5\text{-}dithiahexane)_2}]^{2+}$ (2.315 (2) and 2.319 (2) Å),[39] several mixed imidazole–thioether complexes (2.322 (2),[13] 2.434 (2), and 2.561 (2) Å,[14] $[\mathrm{Cu^{II}(3,6\text{-}dithiaoctane)Cl_2}]$[40] (2.311 (1) and 2.326 (1) Å), and $[\mathrm{Cu^{II}(trithia\text{-}9\text{-}crown\text{-}3)_2}]$[31] (2.419 (3), 2.426 (3), and 2.459 (3) Å)[41] but are rather longer than those very recently reported for $[\mathrm{Cu^{II}\cdot pentathia\text{-}15\text{-}crown\text{-}5}]^{2+}$ (which range from 2.289 (2) to 2.338 (2) Å).[27] (This difference is probably largely due to the difference in coordination number (Shannon radii for 5- and 6-coordinate Cu(II) are 0.65 and 0.73 Å, respectively).[52]) The axial Cu–S distance (2.635 (1) Å) found here is unusually long (particularly by comparison with $[\mathrm{Cu^{II}\cdot pentathia\text{-}15\text{-}crown\text{-}5}]^{2+}$, for which *d*(Cu–S(ax)) = 2.398 (2) Å[27]); longer $\mathrm{Cu^{II}}$–thioether distances have been reported in only a few cases.[42,43]

Carbon–sulfur bond lengths in the crown itself (range: 1.802 (2) to 1.814 (2) Å) are similar to those found in $[\mathrm{Ni^{II}\cdot L}]^{2+}$[33] and $[\mathrm{Co^{II}\cdot L}]^{2+}$[34] (1.805 (3) to 1.823 (5) Å). As in other crown structures,[44,45] the crown C–C distances (range: 1.510 (2) to 1.525 (3) Å) are somewhat shorter than would normally be expected for $\mathrm{C(sp^3)}$–$\mathrm{C(sp^3)}$ bonds (1.54 Å).[46] Bond distances and angles in the picrate groups are unexceptional, with *d*(C–O) = 1.235 (2) Å, and average N–O, C–C, and C–N distances of 1.23, 1.41, and 1.45 Å, respectively.[47]

Unlike the tetragonally-elongated six-coordinate copper(II) complex, the corresponding Cu(I) complex $[\mathrm{Cu^{I}\cdot L}]^{+}$ adopts a severely distorted tetrahedral geometry (Figures 2 and 3). Alternatively, the $\mathrm{CuS_4}$ coordination sphere can be described as derived from a linear two-coordinate complex (S(1)–Cu–S(10)) by addition of two thioether groups (S(4) and S(7)) (with concomitant diminution of the S(1)–Cu–S(10) angle to 138.4 (1)°).[48,49] (This should not be taken to imply anything about how the complex is actually formed, or indeed why it adopts this structure, but rather solely to provide a way of describing it.) Bond lengths to S(1) and S(10) (2.253 (2) and 2.245 (2) Å, respectively) are unusually short, while those to S(4) and S(7) (2.360 (2) and 2.358 (2) Å, respectively) are longer than any others reported except[50] for that in a mixed benzimidazoyl–thioether complex (2.469 (9) Å).[13] The $[\mathrm{Cu^{I}\cdot L}]^{+}$ structure is reminiscent of that found for the copper(I) complex of tetrathia-14-crown-4[25] and is particularly similar to the very recently published structure of $[\mathrm{Cu^{I}\cdot(pentathia\text{-}15\text{-}crown\text{-}5)}]^{+}$.[27] This latter structure also has two short (2.245 (5) and 2.243 (5) Å) Cu–S bonds at a S–Cu–S angle approaching linearity (135.6°) and long (2.317 (5) and 2.338 (5) Å) Cu–S bonds to the remaining two sulfur atoms. Previously reported $\mathrm{Cu^{I}}$–S(thioether) bond lengths include those of $[\mathrm{Cu^{I}(2,5\text{-}dithiahexane)_2}](\mathrm{ClO_4})$ (2.263 (6) Å),[51] $[\mathrm{Cu^{I}(3,6\text{-}dithiaoctane)_2}](\mathrm{BF_4})$ (range: 2.280 (4) to 2.318 (5) Å),[39] several $\mathrm{Cu^{I}}$–thioxane complexes (range: 2.261 to 2.342 Å),[53] $[\mathrm{Cu^{I}\cdot(2,5\text{-}dithiahexane)(Cl)}]$ (2.315 (1), 2.336 (1), and 2.342 (1) Å),[54] $[\mathrm{Cu^{I}\cdot(tetrathia\text{-}14\text{-}crown\text{-}4)(ClO_4)}]_x$ (range: 2.260 (4) to 2.342 (3) Å),[25] and $[\mathrm{Cu^{I}\cdot(3\text{-}methoxy\text{-}1,5\text{-}dithiacyclooctane)}](\mathrm{ClO_4})$ (range: 2.294 (3) to 2.335 (3) Å).[70]

Carbon–sulfur bond lengths in $[\mathrm{Cu^{I}\cdot L}]^{+}$ range from 1.774 (9) to 1.835 (9) Å while C–C bond distances (which range from 1.484 (13) to 1.533 (13) Å) are rather shorter than expected, although as mentioned above, unusually short C–C distances are a common feature of crown structures. No significant difference in either C–S or C–C bond lengths occurs between the bound and unbound portions of the ligand.

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(41) Curiously, $[\mathrm{Cu^{II}\cdot(trithia\text{-}9\text{-}crown\text{-}3)_2}]^{2+}$[31] lacks virtually any observable Jahn–Teller distortion (≈0.04 Å). This difference cannot derive from trithia-9-crown-3, which permits a substantial axial elongation (>0.12 Å) in $[\mathrm{Co^{II}\cdot(trithia\text{-}9\text{-}crown\text{-}3)_2}]^{2+}$[31] (which itself is low-spin (see following paper in this issue), as is the low-spin, Jahn–Teller distorted $[\mathrm{Co^{II}\cdot L}]^{2+}$ cation);[34] instead, it probably results either from a dynamic Jahn–Teller distortion (resulting in a time-averaged structure) or from a static one coupled with positional disorder of the cations (resulting in a space-averaged structure). It is also interesting to note that, despite the difference in the bond lengths themselves, the *sum* of the bond lengths in the two complexes agrees to within 0.02 Å; this observation suggests that the trithia-9-crown-3 complex is also Jahn–Teller distorted, even if the distortion is not obvious in the crystal structure. We are grateful to a referee for pointing this out.

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(46) *Spec. Publ.-Chem. Soc.* **1965**, No. 18.

(47) Maartmann-Moe, K. *Acta Crystallogr.* **1969**, *B25*, 1452–7.

(48) Considering these complexes as those of a linear, two-coordinate Cu(I) to which one or more additional ligands have added also provides insight into the unusually long $\mathrm{Cu^{I}}$–S distance and short $\mathrm{Cu^{I}}$–N distances reported for the T-shaped bis(benzimidazole) thioether complex;[13] moreover, it makes clear the relationship between all of these various copper(I) complexes.

(49) For a linearly-coordinated Cu(I) in which the thioether groups do not coordinate at all see ref 15.

(50) Note that reduction of Cu(II) to Cu(I) *decreases* the mean Cu–S bond distance by ≈0.15 Å (from ≈2.45 to 2.30 Å). Although this decrease is remarkably large (cf. those reported previously: 0.06 Å,[51] and 0.01 Å[39]) and might be taken as evidence for stronger Cu–S bonding in the cuprous complex, in fact it parallels the 0.17-Å decrease in Shannon ionic radius between six- and four-coordinate Cu(I).[52] Thus the difference in coordination numbers of the Cu(II) and Cu(I) ions in the two complexes alone can account for the observed difference in Cu–S bond lengths.

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(52) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–67.

(53) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Transition Met. Chem.* **1982**, *7*, 140–6.

(54) Baker, E. N.; Garrick, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 416–8.

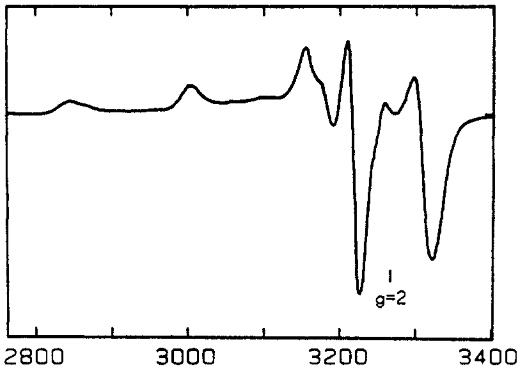

Figure 5. EPR spectrum of [Cu^{II}·(hexathia-18-crown-6)](picrate)$_2$ at 77 K in 1:1 CH_3NO_2/toluene glass, modulation amplitude 5 G, microwave power 12.5 mW.

Electrochemistry. Cyclic voltammetry of either [Cu^{II}·L]$^{2+}$ or [Cu^{I}·L]$^{+}$ at a glassy carbon electrode in CH_3NO_2 reveals an essentially reversible one-electron wave at +0.72 V vs. SCE, with ΔE_{pp} of 60 mV for scan rates <20 mV/s (Figure 4). Faster scan rates yield progressively less reversible waves (e.g., ΔE_{pp} = 110 mV at ν = 200 mV/s), although at all scan rates $i_p^c/i_p^a \approx 1$. No other waves appear within the potential limits of the solvent.

In light of the gross structural differences between the Cu(II) and Cu(I) complexes, observation of an electrochemically reversible redox process between them is surprising. (Indeed, the corresponding [Cu$^{II/I}$·hexaaza-18-crown-6]$^{2+,+}$ couple is completely irreversible.[55]) Redox reactions that involve changes in coordination number (e.g., VO(IV)/V(III))[56] are usually irreversible because bond formation/cleavage is typically slower than electron transfer, whereas reversible behavior requires that electron transfer determine the rate of the redox process.[57]

Two explanations can be advanced for the reversibility of the [Cu$^{II/I}$·L]$^{2+,+}$ couple. In principle it could be caused by dissociation in solution of two thioether groups from [Cu^{II}·L]$^{+}$ to give a four-coordinate complex that could undergo reduction to Cu(I) without change in coordination number. Electron paramagnetic resonance data (vide infra), however, militate against this suggestion by showing that the complex retains its integrity in solution: the compound yields similar g values as a microcrystalline powder (which was shown by X-ray powder patterns to be isomorphous with the single crystal used for the structural study) and in low-temperature glasses, and, furthermore, both average to the g value found in fluid solution. The other, and more likely, possibility is that reversibility results from ligand binding being faster than electron transfer as a consequence of the high effective concentration of free thioether groups in [Cu^{I}·L]$^{+}$, i.e., an inorganic "anchimeric effect."

In addition to its reversibility, the [Cu$^{II/I}$·L]$^{+}$ couple is also noteworthy for its high redox potential (+0.72 V vs. SCE). Typical Cu(II)/(I) couples with nitrogen- or oxygen-donor ligands exhibit redox potentials between 0 and −0.7 V vs. SCE,[58] in contrast to the much higher potentials found for complexes with thioethers. For example, a series of Cu^{II}–thioether complexes (of both linear and macrocyclic ligands) show formal reduction potentials (E_f)[57] that range from +0.43 to +0.65 V vs. SCE (in 80% aqueous methanol).[26] Such high potentials reflect thermodynamic stabilization of Cu(I) over Cu(II) by either electronic or stereochemical properties of the ligands and result, for example, when a ligand forces Cu(II) to assume a geometry (e.g., tetrahedral) more appropriate to Cu(I).[58] Stereochemical considerations, however, cannot account for the high E_f of the [Cu$^{II/I}$·L]$^{+}$ couple: comparison of [Cu^{II}·L]$^{2+}$ with [Cu^{I}·L]$^{+}$ suggests that hexathia-18-crown-6 geometrically *disfavors* the Cu(I) complex. Instead, the high potential must derive from the electronic properties of thioethers, which, like phosphines, have considerable π-acidity.[59,60] Indeed, molecular orbital calculations indicate that the characteristically high redox potentials of copper–thioether complexes are caused by this π-acidity.[61]

Electron Paramagnetic Resonance. Room temperature solutions of [Cu^{II}·L](picrate)$_2$ in nitromethane exhibit an EPR spectrum with g = 2.07 and $A(^{63,65}Cu)$ = 0.0064 cm^{-1}, while solutions at 77 K in 1:1 nitromethane–toluene glass yield a spectrum (Figure 5) that is essentially axial with a small rhombic component (g_x = 2.028, g_y = 2.035, and g_z = 2.119), $A_\parallel$ = 0.0153 cm^{-1}, $A_\perp \approx$ 0.0019 cm^{-1}.[62] (By comparison [Cu^{II}·(tetrathia-14-crown-4)]$^{2+}$ has $g_\parallel$ = 2.085 and $g_\perp$ = 2.037, with $A_\parallel$ = 0.0165 cm^{-1} and $A_\perp \approx$ 0.0036 cm^{-1}.[63]) The [Cu^{II}·L]$^{2+}$ cation exhibits smaller hyperfine anisotropy, $||A_\parallel| - |A_\perp||$ = 0.0087 cm^{-1}, than either [Cu^{II}·14S4]$^{2+}$, for which $||A_\parallel| - |A_\perp|| \approx$ 0.0124 cm^{-1}[63]), or four-coordinate planar complexes of oxygen-containing ligands (for which typically $||A_\parallel| - |A_\perp|| \approx$ 0.0155 cm^{-1}).[64,65]

These EPR data, like the electrochemical results, underscore the π-acidity of thioethers and provide further insight into the electronic consequences of their coordination to a metal ion. Apparently by accepting electron density from the metal ion, thioethers reduce the effective spin–orbit coupling constant— and hence the deviation from g_e—from the values found with oxygen- or nitrogen-based ligands.[58] For example, in [Cu^{II}(H_2O)$_6$]$^{2+}$ $g_\parallel$ = 2.46,[66] while in [Cu^{II}·(tetrathia-14-crown-4)]$^{2+}$ $g_\parallel$ = 2.08.

In fact, this diminution of deviations from g_e attendant upon thioether coordination vitiates a structural benchmark commonly used for copper(II) complexes. Observation of a g value <2.03 has previously been taken to indicate compressed tetragonal-octahedral or trigonal-bipyramidal stereochemistry at the Cu(II) ion (i.e., a d_{z^2} ground state).[67] As pointed out previously,[68] copper(II)–thioether complexes in general violate this generalization: for example, although [Cu^{II}·L]$^{2+}$ fulfills the above criterion for compressed O_h coordination (since one of the g values, g_x, is less than 2.03),[67] the complex is in fact *elongated*, as shown by both X-ray diffraction and EPR data ($g_\parallel > g_\perp$, which implies a $d_{x^2-y^2}$ ground state). Clearly, for complexes of π-acidic ligands inference of coordination geometry from such criteria must be undertaken with caution.[68]

Relation to [Cu^{II}(trithia-9-crown-3)$_2$]$^{2+}$. Our electrochemical and EPR results on [Cu^{II}·L]$^{2+}$ prompted us to examine [Cu^{II}·(trithia-9-crown-3)$_2$]$^{2+}$.[31] Comparison of these two complexes provides a unique opportunity to examine the effect of "clipping" the macrocyclic ring and thereby to examine the effect of geometry upon redox potential. Under conditions identical with those used for the hexathia-18-crown-6 complex, [Cu^{II}·(trithia-9-crown-3)$_2$]$^{2+}$ is reduced in a quasireversible fashion at +0.61 V vs. SCE (with ΔE_{pp} = 90 mV at ν = 20 mV/s)—hence these two hexakis(thioether) copper(II) complexes differ in redox potential by 120 mV. This difference indicates that trithia-9-crown-3 stabilizes Cu(I) over Cu(II) to a considerably lesser degree than does hexathia-18-crown-6.

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We have also examined the EPR spectrum of [Cu^{II}·(trithia-9-crown-3)$_2$]$^{2+}$. At room temperature nitromethane solutions of this complex exhibit $g = 2.059$, with $A(^{63,65}\mathrm{Cu}) = 62.5 \times 10^{-4}$ 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}·L]$^{2+}$ and [Cu^{II}·(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}·(trithia-9-crown-3)$_2$]$^{2+}$, 83650-39-9; [Cu(CH$_3$CN)$_4$](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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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·(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.

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