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Structural Changes Accompanying Electron Transfer in Copper(II)/Copper(I) Complexes Involving Related Open-Chain and Cyclic Tetrathia Ether Ligands

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Crystal structures have been resolved at room temperature for the Cu(I) and Cu(II) complexes formed with an open-chain quadridentate ligand, 3,6,10,13-tetrathiapentadecane (Et₂-2,3,2-S₄), the crystals studied having the empirical formulas [Cu^IL](ClO₄) and [Cu^{II}L(OH₂)(OCIO₃)](ClO₄) where L represents the tetrathia ether ligand. In addition, complete data are provided for a crystal structure previously communicated involving the Cu(I) complex formed with the closely related cyclic tetrathia ether, 1,4,8,11-tetrathiacyclotetradecane ([14]aneS₄), for which the empirical formula is also [Cu^IL](ClO₄). The respective space groups, lattice constants, and final *R* factors for these three compounds are as follows: for monoclinic [Cu^I(Et₂-2,3,2-S₄)](ClO₄), space group *P2*₁/*c*, *a* = 9.283 (2) Å, *b* = 12.392 (5) Å, *c* = 27.536 (7) Å, β = 143.15 (3)°, *Z* = 4, *R* = 0.033, *R*_w = 0.053; for monoclinic [Cu^{II}(Et₂-2,3,2-S₄)(OH₂)(OCIO₃)](ClO₄), space group *P2*₁/*c*, *a* = 16.141 (3) Å, *b* = 9.244 (2) Å, *c* = 15.131 (3) Å, β = 103.84 (1)°, *Z* = 4, *R* = 0.051, *R*_w = 0.073; for orthorhombic [Cu^I([14]aneS₄)](ClO₄), space group *Fdd2*, *a* = 25.514 (4) Å, *b* = 32.356 (7) Å, *c* = 8.067 (1) Å, *Z* = 16, *R* = 0.042, *R*_w = 0.053. These three structures are compared with that previously reported for [Cu^{II}([14]aneS₄)(OCIO₃)₂] to examine the structural changes that occur upon reduction of the copper center when it is complexed to similar open-chain and cyclic quadridentate ligands. Both Cu(II) complexes are six-coordinate, with the copper atom and all four sulfur donor atoms coplanar in the [14]aneS₄ complex while the copper atom and three sulfurs are coplanar in the corresponding Et₂-2,3,2-S₄ complex with the fourth sulfur 0.78 Å out of this plane, apparently being forced out by the steric interference of the two terminal ethyl groups in this ligand. In the Cu(II)-cyclic ligand crystal, the inner coordination sphere is completed by two axial perchlorate ions, while in the corresponding Cu(II)-open-chain ligand crystal the axial ligands consist of one perchlorate ion and one water molecule, the former being located on the same side of the copper-sulfur plane as the displaced sulfur atom. In the crystals studied, both Cu(I) complexes were found to exist as tetrahedrally coordinated polymers, the Et₂-2,3,2-S₄ complex having two sulfur donor atoms from each of two ligand molecules coordinated to each copper atom while the [14]aneS₄ complex has three sulfurs from one ligand and one sulfur from a second ligand coordinated to each copper. On the basis of molecular models, however, it is postulated that, in dilute aqueous solutions, the Cu^I(Et₂-2,3,2-S₄) complex exists as a 1:1 species with all four sulfurs coordinated to a single copper in a tetrahedral arrangement while the Cu^I([14]aneS₄) complex is inferred to have three sulfur donor atoms from a single ligand and one water molecule coordinated to the copper in a tetrahedral arrangement with the fourth sulfur noncoordinated. It is speculated that the 0.2–0.3-V difference in the Cu^{II}L/Cu^IL potentials observed for these two complexes in solution is largely attributable to this presumed difference in the number of sulfur donor atoms coordinated to Cu(I).

Introduction

Among the redox-active metal ions prevalent in biological systems, considerable emphasis has recently been placed on the influence of structure upon copper systems.² The relatively large difference in the coordination geometry normally preferred by Cu(II) (tetragonal) and by Cu(I) (tetrahedral) suggests that steric constraints imposed by the coordinated ligand could particularly affect the electrochemical potentials of copper redox couples.³



Ligands that constrain the coordination sphere toward a tetrahedral geometry are generally assumed to stabilize Cu(I), resulting in a relatively high formal potential value for the Cu^{II}L/Cu^IL redox couple. Conversely, ligands that are predisposed toward square-planar coordination (with one or two axially coordinated species present to complete a square-pyramidal or tetragonal coordination sphere) are assumed to stabilize Cu(II) and result in a relatively low formal potential value.

Interest in the possible influence of structure on the electrochemical properties of copper has markedly increased with the discovery that the type 1 copper sites in blue copper proteins have a distorted tetrahedral coordination sphere (with the copper atom displaced toward one face).⁴ Since these proteins are characterized by relatively high potential values, many workers have concluded that the potentials of these systems are directly related to the copper coordination geometry.^{4,5}

Several electrochemical studies have been reported on low molecular weight copper complexes that purport to show the influence of coordination geometry on the formal potential values.^{3,6,7} Unfortunately, these studies have frequently involved the use of ligands with varying donor atoms, and definitive structural information has been unavailable to substantiate the inferred variations in the inner-sphere geometry of the complexes studied.

In order to examine the effect of structure upon the electron-transfer properties of copper in a systematic manner, it is necessary to determine the structures of the corresponding Cu^{II}L and Cu^IL complexes formed with a single multidentate ligand and then compare a series of such redox couples in which the coordination geometry is varied while maintaining a constant set of donor atoms. Until a few years ago, however, no structural studies had been reported for Cu^{II}L and Cu^IL complexes in which both oxidation states of copper were coordinated to the same or even similar ligands.

Baker and Norris⁸ were the first investigators to report the structures of Cu(II) and Cu(I) complexes with similar coordinated ligands. Shortly thereafter, we reported^{9,10} the first example of Cu^{II}L and Cu^IL structures in which both oxidation states of copper were coordinated to *exactly* the same ligand: 1,4,8,11-tetrathi-

- (1) (a) Wayne State University. (b) University of Wisconsin—Eau Claire.
- (2) Karlin, K. D.; Zubieta, J., Eds. "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Adenine Press: Guilderland, NY, 1983.
- (3) Dorfman, J. R.; Bereman, R. D.; Whangbo, M. H. Reference 2, pp 75–96.
- (4) Freeman, H. C. *Coord. Chem.* **1980**, *21*, 29–51 and references therein.
- (5) Lundeen, M. J. *Coord. Chem.* **1982**, *12*, 1–17; *Inorg. Chim. Acta* **1981**, *56*, 149–156.

- (6) Patterson, G. S.; Holm, R. H. *Bioinorg. Chem.* **1975**, *4*, 257–275.
- (7) Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341–1349. Addison, A. W. Reference 2, pp 109–128.
- (8) Baker, E. N.; Norris, G. E. *J. Chem. Soc., Dalton Trans.* **1977**, 877–882.
- (9) Glick, M. D.; Gavel, D. P.; Diaddario, L. L.; Rorabacher, D. B. *Inorg. Chem.* **1976**, *15*, 1190–1193. In preparing the current publication, we have discovered that the bond angles labeled Cu–S1–C1, Cu–S2–C2, Cu–S2–C3, S1–C1–C2, and S2–C2–C1 in Table II were mislabeled and should read Cu–S2'–C1, Cu–S2–C2, Cu–S2–C5, S2'–C1–C2, and S1–C2–C1, respectively; these errors have been corrected in Table III of the current publication.
- (10) Dockal, E. R.; Diaddario, L. L.; Glick, M. D.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1977**, *99*, 4530–4532.

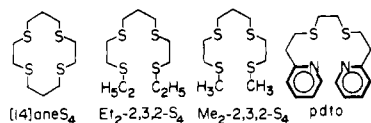


Figure 1. Ligands discussed in this work.

Table I. Formal Potential Values for Representative Blue Copper Proteins and Low Molecular Weight Copper Complexes at 25 °C^a

system	$E^f(\text{CV})$		$E^f(\text{kinetic})$ (aqueous), V
	(80% CH ₃ OH), V	(aqueous), V	
Cu(aq) ^{2+/+}		0.15 ^b	
azurin ^c		0.29–0.33 ^d	
plastocyanin ^c		0.35–0.37 ^d	
Cu(pdto) ^{2+/+}		0.60 ^e	0.62
Cu([12]aneS ₄) ^{2+/+}	0.72	0.64	0.87
Cu([13]aneS ₄) ^{2+/+}	0.67	0.60	0.82
Cu([14]aneS ₄) ^{2+/+}	0.69	0.60	0.72
Cu([15]aneS ₄) ^{2+/+}	0.79	0.73	0.73
Cu([16]aneS ₄) ^{2+/+}	0.80	0.77	0.81
Cu(Me ₂ -2,3,2-S ₄) ^{2+/+}	0.89	0.82	1.04
Cu(Et ₂ -2,3,2-S ₄) ^{2+/+}	0.89		1.04

^a Unless otherwise specified, all values are from ref 17.

^b Huheey, J. E. "Inorganic Chemistry", 2nd ed.; Harper & Row: New York, 1978. ^c Azurin and plastocyanin are representative blue copper proteins containing a single (type 1) copper atom.

^d Holwerda, R. A.; Wherland, S.; Gray, H. B. *Annu. Rev. Biophys. Bioeng.* 1976, 5, 363–396. ^e Brubaker et al. report $E^f = 0.58$ V for this system.¹¹

acyclotetradecane ([14]aneS₄, see Figure 1). Despite the pre-disposition of this quadridentate ligand to accommodate square-planar coordination, we found that, in the crystalline state, the Cu^IL species acquired a tetrahedral geometry by rupturing one of the Cu–S bonds at the expense of considerable distortion within the ligand backbone. As a result, both copper oxidation states maintained their preferred geometric environments. Nonetheless, the potential of the Cu([14]aneS₄)^{2+/+} system is very positive, suggesting that the presence of π -donor atoms is more essential to the high potentials of the blue copper proteins than is the tetrahedral geometry imposed by the protein superstructure.

This latter conclusion appears to be corroborated by the report of Brubaker and co-workers¹¹ on the structures of the Cu(II) and Cu(I) complexes of 1,8-di-2-pyridyl-3,6-dithiaoctane (pdto). Favorable geometries were found for both oxidation states of copper (i.e., square pyramidal for Cu(II) and tetrahedral for Cu(I)), yet the potential of this system exceeds that found for most of the blue copper proteins (Table I) even though the donor atom set (two heterocyclic nitrogens and two sulfurs) is nearly identical with that found at the type 1 copper center.

Although several additional structural reports have recently appeared in which both oxidation states of copper are complexed to the same or very similar ligands,^{12–15} no reliable electrochemical data exist for most of these systems. Thus, no definitive conclusions can be drawn about the effects of varying the geometric constraints imposed upon the copper center to the electron-transfer properties.

In an attempt to rectify this situation, we have made extensive potential measurements on a series of copper tetrathiaether complexes ostensibly involving the same donor set.^{16,17} As il-

lustrated in Table I, the apparent potential values of these copper systems fall within the range of 0.60–1.04 V in aqueous solution (with some variability in the values depending on the experimental approach) and similar values have been obtained in 80% methanol. Under all circumstances, the [14]aneS₄ complex exhibits the lowest potential value within this series while the highest values are found for the complexes formed with the closely related open-chain tetrathia ethers: 2,5,9,12-tetrathiatridecane (Me₂-2,3,2-S₄) and 3,6,10,13-tetrathiapentadecane (Et₂-2,3,2-S₄) (see Figure 1). Therefore, it seemed particularly pertinent to compare the structures for the Cu(II) and Cu(I) complexes formed with these specific ligands to determine the extent to which structure factors might account for the significant differences in their potential values.

Using single-crystal X-ray diffractometry, we have now successfully determined the structures of compounds having the formulas [Cu^{II}(Et₂-2,3,2-S₄)(OH₂)(OCIO₃)](ClO₄) and [Cu^I(Et₂-2,3,2-S₄)](ClO₄). Complete structural information for the compound [Cu^I([14]aneS₄)](ClO₄) (which was previously communicated in part¹⁰) is also now available. The structural parameters of these three compounds, along with those previously reported for [Cu^{II}([14]aneS₄)(OCIO₃)₂],⁹ are compared and interpreted in terms of the differing physical properties for the two redox couples represented.

Experimental Section

The Et₂-2,3,2-S₄ and [14]aneS₄ ligands were synthesized and purified by methods that have been previously described.¹⁸ A crystal of [Cu^{II}(Et₂-2,3,2-S₄)(OH₂)(OCIO₃)](ClO₄) was prepared by evaporation from 80% (w/w) methanol to which stoichiometric quantities of hydrated Cu(ClO₄)₂ and Et₂-2,3,2-S₄ had been added. A suitable crystal was selected and mounted on a glass fiber with epoxy cement.

Solutions of the two Cu(I) complexes were prepared by exhaustive controlled-potential electrolysis of the corresponding Cu(II)–ligand solutions in 80% methanol. Since the Cu(I) complexes are somewhat sensitive to reoxidation by oxygen, the solutions to be electrolyzed were deaerated with nitrogen that had been bubbled through two successive towers containing concentrated chromium(II) perchlorate solution. After completion of the electrolysis, the electrodes were removed from the cell and the Cu(I) complexes were allowed to crystallize slowly as scrubbed nitrogen was swept over the solutions. Suitable crystals were selected and sealed in glass capillaries with a portion of the mother liquor.

All diffraction data were collected at ambient temperature on a Syntex P2, automated diffractometer with Mo K α radiation ($\lambda = 0.71069$ Å) diffracted from a highly oriented graphite monochromator in the parallel mode with a takeoff angle of 4°. Initial examination by rotation and axial photographs and by preliminary data sets yielded approximate lattice constants and established the symmetry. The final crystal parameters resulted from least-squares analysis of 15 reflections, with 2 θ between 15 and 30°. These parameters are listed in Table II.

In collection of the diffraction data, three standard reflections were measured every 97 reflections and were statistically constant. Backgrounds were measured at the end of each scan. Scan ranges and scan rates are included in Table II.

Standard computer programs modified for local use were employed.¹⁹ Correction was made for Lorentz–polarization effects but not for absorption. The atomic positions and thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares techniques. The

- (11) Brubaker, G. R.; Brown, J. N.; Yoo, M. K.; Kinsey, R. A.; Kutchan, T. M.; Mottel, E. A. *Inorg. Chem.* 1979, 18, 299–302.
 (12) Karlin, K. D.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *J. Chem. Soc. Chem. Commun.* 1980, 906–908. Zubieta, J.; Karlin, K. D.; Hayes, J. C. Reference 2, pp 97–108.
 (13) Casella, L.; Ibers, J. A. *Inorg. Chem.* 1981, 20, 2438–2448.
 (14) Dagdigian, J. V.; McKee, V.; Reed, C. A. *Inorg. Chem.* 1982, 21, 1332–1342.
 (15) Olmstead, M. M.; Musker, W. K.; Kessler, R. M. *Inorg. Chem.* 1981, 20, 151–157.
 (16) Dockal, E. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* 1976, 98, 4322–4324.

- (17) Rorabacher, D. B.; Martin, M. J.; Koenigbauer, M. J.; Malik, M.; Schroeder, R. R.; Endicott, J. F.; Ochrymowycz, L. A. Reference 2, pp 167–202.
 (18) Ochrymowycz, L. A.; Mok, C. P.; Michna, J. D. *J. Org. Chem.* 1974, 39, 2079–2084.
 (19) Local versions of the following computer programs were used: (a) SYNCOR, W. Schmonsees' program for data production; (b) FASTES, W. Schmonsees' program for generation of normalized structure factors; (c) REL, R. E. Long's program for phase determination by Sayre's method; (d) FORDAP, A. Zalkin's Fourier program; (e) ORFLS and ORFFE, W. Busing, K. Martin, and H. Levy's full-matrix least-squares program and function-and-error program; (f) ORTEP, C. K. Johnson's program for drawing crystal models; (g) MULTAN78, P. Main's system for solutions of crystal structures using the tangent formula of Karle and Hauptman; (h) HFINDR, A. Zalkin's program to calculate hydrogen atom positions; (i) PLANES, D. L. Smith's program to calculate least-squares planes; (j) INFO, A. Zalkin's program to calculate density, molecular weight, and reciprocal dimensions; (k) TRACER, Lawton and Jacobson's program for cell reduction; (l) EQUIV, local program for averaging equivalent reflections.

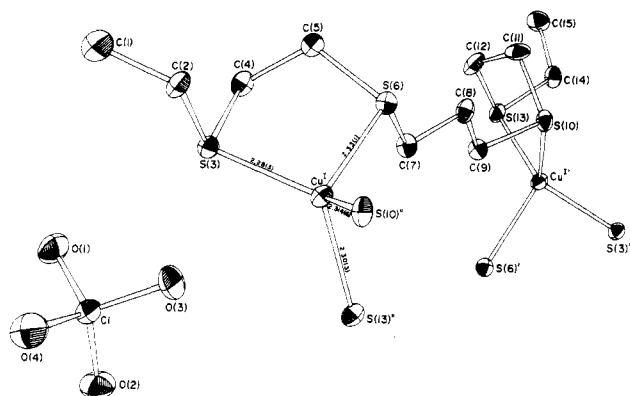


Figure 2. Atom-labeling scheme for $[\text{Cu}^{\text{I}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)](\text{ClO}_4)_x$ showing the two copper atoms bonded to a single open-chain ligand molecule. The S(3') and S(6') atoms are from a second ligand molecule while the S(10'') and S(13'') atoms are from a third ligand molecule, thereby extending the polymer chain in both directions.

quantity minimized was $\sum w_i(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors, respectively. Correction for anomalous dispersion of the copper atom was applied. Discrepancy factors were defined as follows: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w_i(|F_o| - |F_c|)^2 / \sum w_i|F_o|^2]^{1/2}$.

Results

Structure Determinations. $[\text{Cu}^{\text{I}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)](\text{ClO}_4)$. The crystal was found to be monoclinic with systematic absences of $l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, uniquely consistent with space group $P2_1/c$. The position of the copper atom was found by direct methods. Successive difference maps yielded the positions of the remaining non-hydrogen atoms. The positions of the hydrogen atoms were calculated with a C-H bond distance of 1.08 Å. Full-matrix least-squares refinement of all non-hydrogen position coordinates and anisotropic thermal parameters, with isotropic hydrogen atoms included as fixed contributions, yielded $R = 0.033$ and $R_w = 0.053$.

The resultant structure of the $\text{Cu}^{\text{I}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)$ complex with the atom-labeling scheme is shown in Figure 2. The interatomic bond distances and bond angles are listed in Table III based on the atomic coordinates for all non-hydrogen atoms as listed in Table IV.

In the crystal analyzed, the $\text{Cu}^{\text{I}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)$ complex exists as a linear polymer in which two sulfur atoms from a ligand molecule are bonded to one copper atom while the other two sulfurs are bonded to a second copper atom. Each of these copper atoms, in turn, is bonded to two sulfurs from other ligand molecules, yielding a distorted tetrahedral coordination sphere for each copper. The resulting 2:2 coordination polymer is shown more clearly in Figure 3 in which two ligand molecules are shown to be bridged by one copper atom while two other copper atoms, coordinated to the other ends of these ligands, continue the polymer chain to additional ligand molecules that are not shown. The perchlorate ion is noncoordinating.

$[\text{Cu}^{\text{II}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)(\text{OH}_2)(\text{OCIO}_3)](\text{ClO}_4)$. The data for this crystal showed the same systematic absences observed for the preceding Cu(I) compound, uniquely consistent with the space group $P2_1/c$. The position of the copper atom was found by direct methods while the positions of the remaining non-hydrogen atoms as well as the water hydrogens were obtained from successive difference maps. The positions of the alkyl hydrogen atoms were calculated with a fixed C-H bond length of 1.08 Å. Full-matrix least-squares refinement of all non-hydrogen position coordinates and anisotropic thermal parameters, with isotropic hydrogen atoms included as fixed contributions, yielded the discrepancy factors $R = 0.051$ and $R_w = 0.073$.

The resultant structure of the $[\text{Cu}^{\text{II}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)(\text{OH}_2)(\text{OCIO}_3)](\text{ClO}_4)$ complex with the atom-labeling scheme is shown in Figure 4. The coordinates for all non-hydrogen atoms are listed in Table V while the interatomic bond distances and angles are included in Table III.

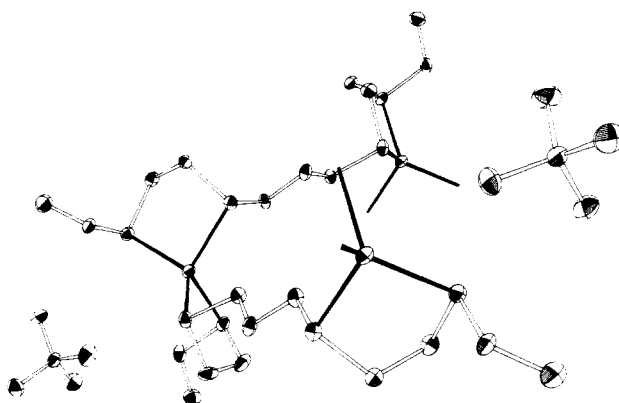


Figure 3. An extended view of the polymeric structure found in the $[\text{Cu}^{\text{I}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)](\text{ClO}_4)_x$ crystal showing two complete ligand molecules with the Cu-S coordinate bonds indicated as solid lines. The copper atom at left is coordinated to both of the ligand molecules shown while two other copper atoms (at right) are each coordinated to the two remaining sulfur donor atoms on one of these ligands with two additional coordinate bonds to sulfur atoms belonging to ligand molecules which are not shown here.

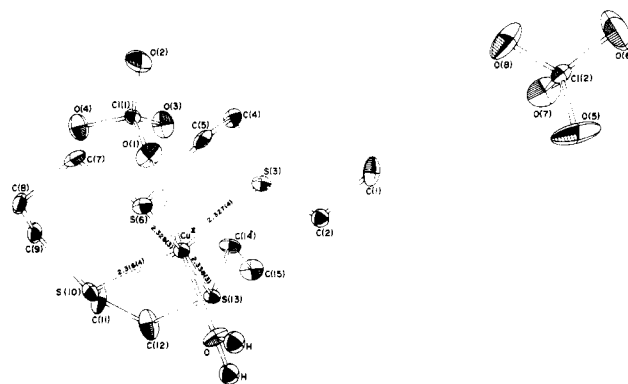


Figure 4. Atom-labeling scheme for $[\text{Cu}^{\text{II}}(\text{Et}_2\text{-}2,3,2\text{-S}_4)(\text{OH}_2)(\text{OCIO}_3)](\text{ClO}_4)$. The S(3) atom is displaced 0.78 Å above the equatorial plane defined by atoms Cu, S(6), S(10), and S(13).

The copper atom and three of the sulfur atoms are coplanar within ± 0.05 Å while the fourth sulfur atom, S(3), is displaced from this equatorial plane by 0.78 Å, although all four Cu-S distances are similar. The axial coordination sites are occupied by a water oxygen and a loosely bonding perchlorate ion, the latter being on the same side of the CuS_3 plane as the displaced sulfur. The second perchlorate ion per formula unit is noncoordinating.

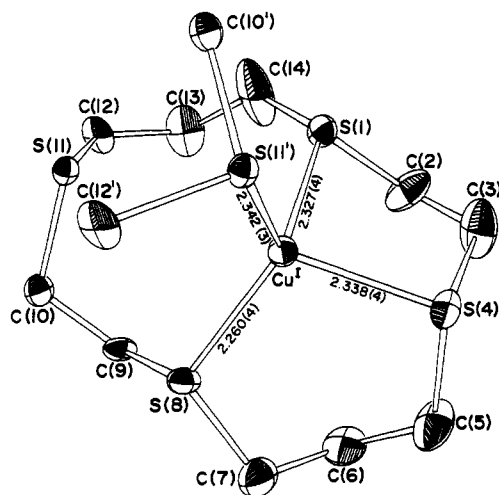
$[\text{Cu}^{\text{I}}(\text{[14]aneS}_4)](\text{ClO}_4)$. Axial-rotation photographs and a preliminary data set showed the crystal system to be orthorhombic with systematic absences of $h + k$, $h + l$, $k + l = 2n + 1$ for hkl ; $k + l = 4n + 1$ for $0kl$; and $h + l = 4n + 1$ for $h0l$, uniquely consistent with space group $Fdd2$. The position of the copper atom was found by direct methods. Successive difference maps yielded the positions of the remaining non-hydrogen atoms. The positions of the hydrogen atoms were calculated with a C-H bond length of 1.08 Å. Full-matrix least-squares refinement of all non-hydrogen position coordinates and anisotropic thermal parameters, with isotropic hydrogen atoms included as fixed contributions, yielded the discrepancy factors $R = 0.042$ and $R_w = 0.053$.

The resultant structure of the $[\text{Cu}^{\text{I}}(\text{[14]aneS}_4)](\text{ClO}_4)$ complex with the atom-labeling scheme is shown in Figure 5. The coordinates for all non-hydrogen atoms are listed in Table VI while the interatomic bond distances and angles are given in Table III.

As reported in a preliminary communication,¹⁰ the Cu(I) atom is coordinated to three sulfur atoms from a single ligand, with the fourth sulfur rotated away and coordinated, instead, to an adjacent copper. Thus, each Cu(I) forms four Cu-S bonds, three from one ligand and the fourth involving the available sulfur on an adjacent ligand. The resulting 3:1 coordination polymer is illustrated more vividly in Figure 6 where three copper-ligand subunits are shown. The perchlorate ion is noncoordinating.

Table II. Crystal Parameters and Experimental Details for X-ray Diffraction Studies on the Copper(I) and Copper(II) Complexes Formed with Et₂-2,3,2-S₄ and [14]aneS₄

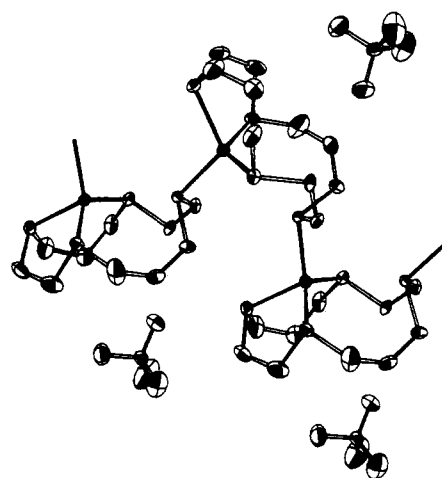
	[Cu ^I (Et ₂ -2,3,2-S ₄)]-(ClO ₄)	[Cu ^{II} (Et ₂ -2,3,2-S ₄)-(OH ₂)(OCIO ₃)](ClO ₄)	[Cu ^I ([14]aneS ₄)]-(ClO ₄)	[Cu ^{II} ([14]aneS ₄)-(OCIO ₃) ₂]
(A) Crystal Data				
color	colorless	very dark red	colorless	very dark red
lattice type	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>Fdd2</i>	<i>P2₁/c</i>
cell dimens: <i>a</i> , Å	9.283 (2)	16.141 (3)	25.514 (4)	7.904 (3)
<i>b</i> , Å	12.392 (5)	9.244 (2)	32.356 (7)	8.830 (4)
<i>c</i> , Å	27.536 (7)	15.131 (3)	8.067 (1)	16.840 (6)
<i>β</i> , deg	143.15 (3)	103.84 (1)	90	126.33 (2)
<i>V</i> , Å ³	1899 (1)	2192.2 (8)	6660 (2)	946.8 (6)
empirical formula	CuC ₁₁ H ₂₄ S ₄ ClO ₄	CuC ₁₁ H ₂₆ S ₄ Cl ₂ O ₈	CuC ₁₀ H ₂₀ S ₄ ClO ₄	CuC ₁₀ H ₂₀ S ₄ Cl ₂ O ₈
fw	447.55	565.01	431.50	530.96
no. of waters/formula unit	0	1	0	0
<i>Z</i>	4	4	16	2
<i>F</i> (0,0,0) electrons	928	1164	3552	542
<i>d</i> (obsd), g/mL	1.61	1.70	1.76	1.90
<i>d</i> (calcd), g/mL	1.56	1.66	1.71	1.87
(B) X-ray Intensity Measurements				
scan method	<i>θ</i> -2 <i>θ</i>	<i>θ</i> -2 <i>θ</i>	<i>θ</i> -2 <i>θ</i>	<i>θ</i> -2 <i>θ</i>
scan range for data collcn ± spectral disp cor, deg	1.0	1.0	1.0	1.0
max 2 <i>θ</i> range, deg	45	45	45	50
scan rate, deg/min	2.0	2.0	2.0	4.0
no. of data between std reflcns	97	97	97	97
decomp indicated	none	none	none	none
linear abs coeff (μ), cm ⁻¹	17.3	18.5	19.66	19.35
no. of indep reflcns	1492	1439	1252	1378
no. of obsd reflcns	1166	1114	985	968
criteria for obsd reflcns	>3σ	>3σ	>3σ	>3σ
(C) Final Model Refinement				
<i>R</i> , <i>R</i> _w	0.033, 0.053	0.051, 0.073	0.042, 0.053	0.032, 0.038
highest peak on final diff Fourier, e/Å ³	0.40	0.47	0.13	0.58
anisotropic	yes	yes	yes	yes
fixed Me H atoms	yes	yes	yes	yes

**Figure 5.** Atom-labeling scheme for [Cu^I([14]aneS₄)_x(ClO₄)_x] showing one complete cyclic ligand molecule and a small segment (C(10')-S(11')-C(12')) of the next adjacent ligand molecule. The copper atom shown is tetrahedrally coordinated to three sulfurs of the main ligand and one sulfur (S(11')) of the adjacent ligand while the S(11) atom is coordinated to an adjacent copper atom (not shown).

Structure of [Cu^{II}([14]aneS₄)(OCIO₃)₂]. As reported in an earlier publication,⁹ the structure of [Cu^{II}([14]aneS₄)(OCIO₃)₂] is illustrated in Figure 7 for comparative purposes. In this compound, the copper atom and all four sulfur atoms are coplanar, with the two perchlorate ions coordinated axially on either side of the CuS₄ plane to complete a tetragonal coordination sphere.

Discussion

General Structural Features. Copper(II) Complexes. As has been pointed out in our previous report on the structures of the

**Figure 6.** Extended view of the polymeric structure found in the [Cu^I([14]aneS₄)_x(ClO₄)_x] crystal showing three copper-ligand subunits. The copper atoms are represented as solid circles and the copper-sulfur coordinate bonds as solid lines.

Cu(II) complexes formed with a series of cyclic tetrathia ethers ([12]aneS₄ through [16]aneS₄),²⁰ the sum of the Cu(II)-donor atom bonds in these complexes is remarkably constant as long as the same set of donor atoms (e.g., S₄O₂) is involved in the inner coordination sphere. In that publication, we noted that the [Cu^{II}(Et₂-2,3,2,-S₄)(OH₂)(OCIO₃)₂]⁺ cation also fits into this pattern despite the displacement of one sulfur atom by 0.78 Å

(20) Pett, V. B.; Diaddario, L. L., Jr.; Dockal, E. R.; Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661-3670.

Table III. Interatomic Bond Distances (Å) and Bond Angles (deg) in the Cu(I) and Cu(II) Compounds Formed with Et₂-2,3,2-S₄ and [14]aneS₄ with Estimated Standard Deviations^a

atoms	Et ₂ -2,3,2-S ₄		[14]aneS ₄		
	[Cu ^I L] _x (ClO ₄) _x	[Cu ^{II} L(OCIO ₃)- (OH ₂)](ClO ₄)	[Cu ^I L] _x (ClO ₄) _x	[Cu ^{II} L- (OCIO ₃) ₂] ^b	atoms ^b
Bond Distances					
Cu-S(3)	2.28 (3)	2.327 (4)	2.327 (4)	2.308 (1)	Cu-S(1)
Cu-S(6)	2.33 (1)	2.329 (3)	2.338 (4)	2.297 (1)	Cu-S(4)
Cu-S(10)	2.314 (6) ^c	2.316 (4)	2.260 (4)	2.308 (1)	Cu-S(8)
Cu-S(13)	2.30 (3) ^c	2.338 (3)	2.342 (3) ^d	2.297 (1)	Cu-S(11)
Cu-O		2.296 (7)		2.652 (4)	Cu-O(1)
Cu-O(1)		2.812 (8)		2.652 (4)	Cu-O(1')
S(3)-C(2)	1.84 (1)	1.83 (1)	1.79 (2)	1.828 (5)	S(1)-C(14)
S(3)-C(4)	1.80 (2)	1.82 (1)	1.81 (2)	1.831 (5)	S(1)-C(2)
S(6)-C(5)	1.81 (2)	1.87 (1)	1.84 (2)	1.825 (5)	S(4)-C(3)
S(6)-C(7)	1.842 (8)	1.82 (1)	1.83 (2)	1.829 (5)	S(4)-C(5)
S(10)-C(9)	1.831 (9)	1.82 (1)	1.81 (2)	1.828 (5)	S(8)-C(7)
S(10)-C(11)	1.82 (3)	1.83 (1)	1.83 (1)	1.831 (5)	S(8)-C(9)
S(13)-C(12)	1.79 (1)	1.79 (2)	1.82 (1)	1.825 (5)	S(11)-C(10)
S(13)-C(14)	1.799 (9)	1.80 (1)	1.82 (1)	1.829 (5)	S(11)-C(12)
C(1)-C(2)	1.50 (2)	1.49 (2)	1.38 (3)	1.551 (6)	C(13)-C(14)
C(4)-C(5)	1.53 (1)	1.51 (1)	1.40 (3)	1.528 (5)	C(2)-C(3)
C(7)-C(8)	1.53 (1)	1.59 (2)	1.49 (2)	1.550 (6)	C(5)-C(6)
C(8)-C(9)	1.54 (1)	1.53 (2)	1.51 (2)	1.551 (6)	C(6)-C(7)
C(11)-C(12)	1.51 (1)	1.40 (2)	1.48 (2)	1.528 (5)	C(9)-C(10)
C(14)-C(15)	1.53 (3)	1.49 (2)	1.41 (2)	1.550 (6)	C(12)-C(13)
Cl(1)-O(1)	1.42 (2)	1.401 (7)	1.31 (1)	1.441 (4)	Cl(1)-O(1)
Cl(1)-O(2)	1.42 (1)	1.41 (1)	1.40 (1)	1.421 (4)	Cl(1)-O(2)
Cl(1)-O(3)	1.424 (7)	1.41 (1)	1.41 (1)	1.443 (4)	Cl(1)-O(3)
Cl(1)-O(4)	1.423 (6)	1.40 (1)	1.40 (1)	1.428 (4)	Cl(1)-O(4)
Cl(2)-O(5)		1.380 (9)		1.441 (4)	Cl(1')-O(1')
Cl(2)-O(6)		1.32 (1)		1.421 (4)	Cl(1')-O(2')
Cl(2)-O(7)		1.426 (9)		1.443 (4)	Cl(1')-O(3')
Cl(2)-O(8)		1.39 (1)		1.428 (4)	Cl(1')-O(4')
Bond Angles					
S(3)-Cu-S(6)	95 (1)	89.7 (1)	88.8 (4)	89.91 (4)	S(1)-Cu-S(4)
S(6)-Cu-S(10)	110.1 (3) ^c	88.6 (1)	106.7 (1)	90.09 (4)	S(4)-Cu-S(8)
S(10)-Cu-S(13)	94.7 (8) ^c	87.9 (1)	110.3 (1) ^d	89.91 (4)	S(8)-Cu-S(11)
S(13)-Cu-S(3)	121.5 (7) ^c	94.7 (1)	106.7 (1) ^d	90.09 (4)	S(11)-Cu-S(1)
S(3)-Cu-S(10)	121.1 (3) ^c	162.8 (1)	129.7 (2)	180.00	S(1)-Cu-S(8)
S(6)-Cu-S(13)	116.0 (7) ^c	175.0 (1)	113.0 (2) ^d	180.00	S(4)-Cu-S(11)
Cu-S(3)-C(2)	103.1 (5)	104.7 (4)	127.9 (7)	104.2 (2)	Cu-S(1)-C(14)
Cu-S(3)-C(4)	98.2 (9)	100.9 (4)	98.3 (6)	99.1 (2)	Cu-S(1)-C(2)
Cu-S(6)-C(5)	98 (1)	101.8 (4)	99.9 (7)	100.8 (2)	Cu-S(4)-C(3)
Cu-S(6)-C(7)	103.2 (5)	106.8 (4)	107.2 (7)	104.7 (2)	Cu-S(4)-C(5)
Cu-S(10)-C(9)	100.9 (3) ^c	108.9 (4)	109.5 (6)	104.2 (2)	Cu-S(8)-C(7)
Cu-S(10)-C(11)	97.6 (7) ^c	100.3 (5)	109.3 (4)	99.1 (2)	Cu-S(8)-C(9)
Cu-S(13)-C(12)	104.8 (4) ^c	100.8 (6)	<i>d</i>	100.8 (2)	Cu-S(11)-C(10)
Cu-S(13)-C(14)	98.9 (9) ^c	110.5 (5)	<i>d</i>	104.7 (2)	Cu-S(11)-C(12)
C(2)-S(3)-C(4)	103.2 (8)	103.0 (5)	102 (1)	104.6 (2)	C(14)-S(1)-C(2)
C(5)-S(6)-C(7)	104.3 (4)	100.7 (6)	106 (1)	105.0 (2)	C(3)-S(4)-C(5)
C(9)-S(10)-C(11)	104.1 (4)	100.9 (7)	102.7 (8)	104.6 (2)	C(7)-S(8)-C(9)
C(12)-S(13)-C(14)	103.7 (6)	104.8 (6)	100.1 (7)	105.0 (2)	C(10)-S(11)-C(12)
S(3)-C(2)-C(1)	113.6 (7)	112.0 (8)	127 (2)	109.3 (5)	S(1)-C(14)-C(13)
S(3)-C(4)-C(5)	116.5 (6)	110.8 (8)	112 (2)	107.7 (3)	S(1)-C(2)-C(3)
S(6)-C(5)-C(4)	115.0 (8)	114.2 (8)	118 (2)	107.9 (3)	S(4)-C(3)-C(2)
S(6)-C(7)-C(8)	110.9 (6)	110.9 (8)	119 (1)	112.0 (4)	S(4)-C(5)-C(6)
S(10)-C(9)-C(8)	112.4 (6)	114.4 (7)	116 (1)	109.3 (5)	S(8)-C(7)-C(6)
S(10)-C(11)-C(12)	114.4 (6)	110 (1)	111 (1)	107.7 (3)	S(8)-C(9)-C(10)
S(13)-C(12)-C(11)	115.4 (8)	119 (1)	115.6 (9)	107.9 (3)	S(11)-C(10)-C(9)
S(13)-C(14)-C(15)	114.5 (7)	114.1 (9)	120 (1)	112.0 (4)	S(11)-C(12)-C(13)
C(7)-C(8)-C(9)	107.4 (7)	112 (1)	118 (2)	114.9 (5)	C(5)-C(6)-C(7)
			129 (2)	114.9 (5)	C(12)-C(13)-C(14)
O(1)-Cl(1)-O(2)	110 (1)	105.5 (7)	111 (1)	109.8 (3)	O(1)-Cl-O(2)
O(1)-Cl(1)-O(3)	109.7 (5)	110.6 (6)	113 (1)	108.2 (2)	O(1)-Cl-O(3)
O(1)-Cl(1)-O(4)	109.3 (4)	107.8 (6)	107 (1)	109.1 (3)	O(1)-Cl-O(4)
O(2)-Cl(1)-O(3)	109.4 (5)	112.6 (7)	108 (1)	109.5 (3)	O(2)-Cl-O(3)
O(2)-Cl(1)-O(4)	109.1 (5)	111.1 (7)	107 (1)	110.9 (3)	O(2)-Cl-O(4)
O(3)-Cl(1)-O(4)	109.9 (5)	109.0 (7)	111 (1)	109.3 (2)	O(3)-Cl-O(4)
O(5)-Cl(2)-O(6)		111.1 (9)		109.8 (3)	O(1')-Cl-O(2')
O(5)-Cl(2)-O(7)		107.6 (6)		108.2 (2)	O(1')-Cl-O(3')
O(5)-Cl(2)-O(8)		110.7 (8)		109.1 (3)	O(1')-Cl-O(4')
O(6)-Cl(2)-O(7)		108.8 (8)		109.5 (3)	O(2')-Cl-O(3')
O(6)-Cl(2)-O(8)		109.1 (8)		110.9 (3)	O(2')-Cl-O(4')
O(7)-Cl(2)-O(8)		109.4 (6)		109.3 (2)	O(3')-Cl-O(4')

^a The estimated standard deviations given in parentheses correspond to the least significant digits in the adjacent values. This convention is also used in the supplementary data. ^b Note that the atom-labeling scheme utilized here for [Cu^{II}([14]aneS₄)(OCIO₃)₂] is in accordance with the IUPAC nomenclature for the ligand as illustrated in Figure 7. The correspondence to the original atom-labeling scheme used in ref 9

Footnotes to Table III (Continued)

is as follows (current atom label \rightarrow ref 9 atom label): S(1) \rightarrow S(1'), C(2) \rightarrow C(2'), C(3) \rightarrow C(1'), S(4) \rightarrow S(2), C(5) \rightarrow C(5), C(6) \rightarrow C(4), C(7) \rightarrow C(3), S(8) \rightarrow S(1), C(9) \rightarrow C(2), C(10) \rightarrow C(1), S(11) \rightarrow S(2'), C(12) \rightarrow C(5'), C(13) \rightarrow C(4'), C(14) \rightarrow C(3'). (Note also that errors in the identification of five bond angles in ref 9, Table II, have been corrected here.) ^c For $[\text{Cu}^{\text{I}}(\text{Et}_2\text{-2,3,2-S}_4)]_x(\text{ClO}_4)_x$, the atoms labeled S(10) and S(13) actually represent atoms S(10'') and S(13'') from the second coordinated ligand in the case of the listed Cu-S bond distances and the S-Cu-S bond angles. ^d For $[\text{Cu}^{\text{I}}(\text{[14]aneS}_4)]_x(\text{ClO}_4)_x$, the atom labeled S(11) actually represents atom S(11') from the second coordinated ligand in the case of the listed Cu-S bond distance and the S-Cu-S bond angles.

Table IV. Atomic Positional Parameters for $[\text{Cu}^{\text{I}}(\text{Et}_2\text{-2,3,2-S}_4)](\text{ClO}_4)$ with Estimated Standard Deviations

atom	x	y	z
Cu	0.1677 (2)	0.6675 (1)	0.6885 (1)
Cl	0.2602 (4)	0.7814 (2)	0.5493 (1)
S(3)	0.5245 (4)	0.6247 (2)	0.7487 (1)
S(6)	0.3039 (4)	0.6339 (2)	0.8040 (1)
S(10)	-0.0106 (4)	0.3400 (2)	0.8589 (1)
S(13)	0.1836 (4)	0.0832 (2)	0.9279 (1)
O(1)	0.4879 (11)	0.7326 (6)	0.6175 (4)
O(2)	0.0957 (11)	0.7036 (5)	0.4871 (4)
O(3)	0.1751 (12)	0.8229 (5)	0.5714 (4)
O(4)	0.2814 (11)	0.8665 (5)	0.5206 (4)
C(1)	0.9168 (17)	0.7499 (8)	0.8252 (6)
C(2)	0.6786 (15)	0.7555 (7)	0.7862 (5)
C(4)	0.6663 (14)	0.5613 (6)	0.8382 (5)
C(5)	0.6175 (14)	0.6114 (6)	0.8747 (5)
C(7)	0.1854 (14)	0.4983 (6)	0.7852 (5)
C(8)	0.1677 (14)	0.4796 (6)	0.8351 (5)
C(9)	0.0493 (14)	0.3683 (6)	0.8109 (5)
C(11)	0.2820 (17)	0.3036 (8)	0.9624 (5)
C(12)	0.3776 (16)	0.1962 (9)	0.9707 (5)
C(14)	0.1687 (16)	0.0718 (7)	0.9890 (5)
C(15)	0.4116 (17)	0.0546 (8)	1.0793 (6)

Table V. Atomic Positional Parameters for $[\text{Cu}^{\text{II}}(\text{Et}_2\text{-2,3,2-S}_4)(\text{OH}_2)(\text{OClO}_3)](\text{ClO}_4)$ with Estimated Standard Deviations

atom	x	y	z
Cu	0.2276 (1)	0.1748 (1)	0.4314 (1)
Cl(1)	0.4517 (2)	0.3230 (4)	0.6116 (3)
Cl(2)	-0.1105 (2)	0.2448 (4)	0.8185 (3)
S(3)	0.1888 (2)	0.2067 (3)	0.5687 (2)
S(6)	0.1759 (2)	0.4050 (3)	0.3857 (2)
S(10)	0.3021 (2)	0.1797 (3)	0.3183 (2)
S(13)	0.2769 (2)	-0.0617 (3)	0.4638 (2)
O(1)	0.3734 (5)	0.2840 (10)	0.5538 (6)
O(2)	0.4351 (8)	0.4486 (14)	0.6570 (9)
O(3)	0.4843 (5)	0.2091 (12)	0.6716 (7)
O(4)	0.5087 (7)	0.3517 (11)	0.5574 (7)
O(5)	-0.1673 (7)	0.1828 (11)	0.7456 (8)
O(6)	-0.1489 (9)	0.2827 (14)	0.8829 (11)
O(7)	-0.0468 (6)	0.1396 (11)	0.8544 (7)
O(8)	-0.0721 (7)	0.3662 (13)	0.7910 (9)
O ^a	0.1082 (2)	0.0771 (8)	0.3363 (5)
C(1)	0.0340 (8)	0.2141 (15)	0.6149 (10)
C(2)	0.0754 (7)	0.1609 (13)	0.5434 (8)
C(4)	0.1884 (6)	0.4030 (12)	0.5763 (8)
C(5)	0.1401 (6)	0.4689 (12)	0.4875 (9)
C(7)	0.2682 (7)	0.5202 (13)	0.3917 (9)
C(8)	0.3135 (8)	0.4835 (15)	0.3122 (9)
C(9)	0.3657 (7)	0.3443 (15)	0.3300 (8)
C(11)	0.3845 (9)	0.0455 (17)	0.3624 (11)
C(12)	0.3478 (10)	-0.0789 (20)	0.3894 (11)
C(14)	0.3450 (7)	-0.0723 (15)	0.5769 (8)
C(15)	0.3716 (8)	-0.2225 (15)	0.6073 (9)

^a O represents the oxygen atom of the coordinated water molecule.

out of the equatorial plane containing the copper atom and the other three sulfur atoms.

This displacement of the S(3) atom, which appears to result from the steric repulsion of the two terminal ethyl groups, might be expected to result in a weaker coordinate bond to the copper atom. However, as seen in Table III, the Cu-S(3) bond is not elongated relative to the other three Cu-S bonds in this complex. Within this context, it is also worth noting that, in aqueous solution

Table VI. Atomic Positional Parameters for $[\text{Cu}^{\text{I}}(\text{[14]aneS}_4)](\text{ClO}_4)$ with Estimated Standard Deviations

atom	x	y	z
Cu	0.5595 (1)	0.7175 (0)	0.6200 (0)
Cl	0.7332 (1)	0.6583 (1)	0.1796 (6)
S(1)	0.6165 (1)	0.7717 (1)	0.5603 (5)
S(4)	0.6201 (1)	0.6933 (1)	0.8148 (5)
S(8)	0.5367 (1)	0.6624 (1)	0.4637 (5)
S(11)	0.5149 (1)	0.7529 (1)	0.2416 (5)
O(1)	0.6820 (5)	0.6568 (5)	0.1709 (23)
O(2)	0.7552 (8)	0.6199 (5)	0.1409 (26)
O(3)	0.7555 (7)	0.6879 (4)	0.0719 (21)
O(4)	0.7464 (5)	0.6667 (5)	0.3443 (19)
C(2)	0.6773 (6)	0.7463 (6)	0.6137 (35)
C(3)	0.6754 (7)	0.7278 (8)	0.7701 (31)
C(5)	0.6403 (9)	0.6417 (7)	0.7486 (29)
C(6)	0.6326 (8)	0.6291 (5)	0.5727 (25)
C(7)	0.5778 (8)	0.6188 (5)	0.5166 (24)
C(9)	0.5544 (5)	0.6724 (4)	0.2472 (17)
C(10)	0.5154 (5)	0.6998 (4)	0.1685 (17)
C(12)	0.5712 (5)	0.7733 (4)	0.1284 (24)
C(13)	0.6202 (7)	0.7768 (7)	0.2087 (28)
C(14)	0.6312 (9)	0.7936 (8)	0.3624 (33)

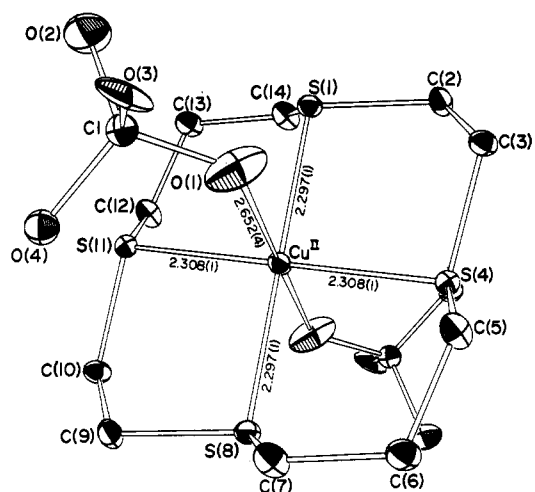


Figure 7. ORTEP view of $[\text{Cu}^{\text{II}}(\text{[14]aneS}_4)(\text{OClO}_3)_2]$ showing the labeling scheme used in referring to this compound in this paper. The copper and all four sulfur atoms are coplanar. (See footnote in Table III for the correspondence of the atom-labeling scheme used here relative to that used in ref 9 and 20.)

at 25 °C (0.1 M ClO_4^-), the $\text{Cu}^{\text{II}}(\text{Et}_2\text{-2,3,2-S}_4)$ complex has a slightly higher stability constant than does $\text{Cu}^{\text{II}}(\text{Me}_2\text{-2,3,2-S}_4)$ ²¹ despite the fact that all four sulfur atoms should be coplanar in the latter species (since the terminal methyl groups should not exhibit steric hindrance). Although the latter ligand, when uncomplexed, may be slightly better solvated than $\text{Et}_2\text{-2,3,2-S}_4$ in aqueous solution, thereby affecting the comparative stability constants to a slight extent, we infer that the displacement of the S(3) atom in the diethyl derivative has not significantly affected either the strength of the Cu-S(3) bond itself or the total strength of the four Cu-S bonds. This conclusion is in qualitative agreement with earlier observations that π -bonding donor atoms endow Cu(II) with the ability to distort its coordination sphere

toward a tetrahedral geometry even in the absence of steric forces.³

From both structural²⁰ and equilibrium²¹ considerations, [14]aneS₄ provides an optimal fit for planar coordination. In comparison to Cu^{II}(Et₂-2,3,2-S₄), the average Cu-S bond length in Cu^{II}([14]aneS₄) is 0.02 Å shorter²⁰ and the 25 °C stability constant in aqueous solution is 100-fold larger. However, from a thermodynamic standpoint, the enthalpies of formation of Cu^{II}([14]aneS₄) and Cu^{II}(Et₂-2,3,2-S₄) are very similar (-4.2 and -3.7 kcal mol⁻¹, respectively, in 0.1 M ClO₄⁻).²¹ The difference in the two stability constants is primarily due to the difference in the entropies of formation (+5.6 and -2.5 eu, respectively),²¹ which is attributed to the greater loss in entropy experienced by the flexible open-chain ligand upon becoming coordinated to the metal ion. Since this same difference in entropy contributions should prevail in the formation of the two Cu(I) complexes, we conclude that there is *no significant difference in the properties of the two Cu(II) complexes that can account for the potential difference* observed in these two systems.

Perhaps some comment should also be made regarding the nature of the axial ligands in the two Cu(II) crystals. Both axial sites are occupied by perchlorate ions in the Cu^{II}([14]aneS₄) complex while the Cu^{II}(Et₂-2,3,2-S₄) crystal contains one tightly bound axial water and one loosely bound axial perchlorate ion. This behavior is consistent with our earlier observation²⁰ that, for crystals grown under identical conditions, water molecules preferentially occupy the axial sites of these CuS₄ complexes when short axial Cu-O bonds are involved while perchlorate ions (which are crystallographically present for charge neutrality) appear in these sites when longer axial bonds are necessitated.

In the case of Cu^{II}(Et₂-2,3,2-S₄), the displaced S(3) atom sterically blocks one axial site, thereby elongating the axial Cu-O bond on that side of the CuS₃ equatorial plane. Compensatorily, the other axial Cu-O bond shortens and is preferentially occupied by water.

In aqueous solution, equilibrium measurements provide evidence for very weak association by one perchlorate ion in both of these complexes.^{21,22} However, by varying the concentration of the perchlorate ion, it has been demonstrated that this association has no discernible effect upon the electrochemical behavior of these complexes.¹⁷ This is consistent with the molecular mechanical calculations of Brubaker and Johnson²³ who, in substituting water molecules in the axial sites in place of the crystallographic perchlorate ions, generated bond lengths and angles from their calculations that are virtually identical with those obtained experimentally from the X-ray diffraction data. In fact, the exceptional agreement between the crystallographic structural parameters found in this study and those generated in the molecular mechanical calculations, lends credence to the hypothesis that the solution structures of the Cu^{II}L complexes parallel those revealed in the single-crystal measurements reported here.

Cu(I) Complexes. When the two copper polythia ether complexes are reduced to the Cu(I) state, the copper coordination number reduces from 6 to 4, adopting a tetrahedral coordination geometry. The fact that both Cu(I) complexes crystallized as coordination polymers, however, obfuscates the probable structures of these complexes as they exist in solution.

Electron-transfer kinetic studies carried out in our laboratory¹⁷ reveal that both Cu^IL complexes reported here exist as monomers in dilute aqueous solution. To date, we have been unable to obtain independent structural information on the monomeric species. However, their probable structures can be inferred from the polymeric structures determined in this work.

We note at the outset that the average Cu-S bond length in these complexes is nearly identical with that found in the corresponding Cu(II) complexes. Since the structure of the [14]aneS₄ ligand is nearly ideal for achieving planar coordination, the generation of a tetrahedral Cu^I([14]aneS₄) complex must result

Table VII. Comparative Stability Constant Values for the Cu(II) and Cu(I) Complexes Formed with [14]aneS₄ and Et₂-2,3,2-S₄ at 25 °C (0.1 M ClO₄⁻)

	[14]aneS ₄	Et ₂ -2,3,2-S ₄
$K_{\text{Cu}^{\text{II}}\text{L}}/K_{\text{Cu}^{\text{I}}\text{L}}^a$	4.3×10^9	1.1×10^{15}
$K_{\text{Cu}^{\text{II}}\text{L}}(\text{exptl})^b$	$2.1_8 \times 10^4$	$1.5_1 \times 10^2$
$K_{\text{Cu}^{\text{I}}\text{L}}(\text{calcd})$	9×10^{13}	2×10^{17}

^a Reference 17. ^b Reference 21.

from the strong tendency of the Cu(I) atom to achieve tetrahedral coordination rather than from any intrinsic tendency for the ligand to distort.

As revealed by the data in Table III, the S-Cu^I-S bond angles involving ethylene-bridged chelate rings (i.e., S(3)-Cu-S(6) and S(10'')-Cu-S(13'') in Cu^I(Et₂-2,3,2-S₄) and S(1)-Cu-S(4) in Cu^I([14]aneS₄)) remain close to 90°, presumably reflecting the restricted bridging ability of a two-carbon chain between proximal sulfur donor atoms. With a propylene-bridged chelate ring (as exemplified by the S(4)-Cu-S(8) bond angle in Cu^I([14]aneS₄)), however, the S-Cu^I-S bond angle approaches an ideal tetrahedral value. In view of the fact that the existing S(6)-Cu-S(10'') bond angle in Cu^I(Et₂-2,3,2-S₄) is only very slightly larger than this, we infer that a monomeric species of the latter compound could be formed with minimal alteration of the remaining bond distances and bond angles. Thus, we postulate that such a monomer, with all four sulfur donor atoms coordinated to a single Cu(I) atom, predominates in dilute aqueous solution.

In the case of the Cu^I([14]aneS₄) complex, the alternating ethylene and propylene chains in the cyclic ligand do not allow sufficient flexibility to achieve a regular tetrahedral coordination sphere while retaining all four Cu-S coordinate bonds to a single ligand. As confirmed by molecular models, a flattened tetrahedron is the best that can be achieved for a monomeric species with an S₄ donor set. However, by rupturing one Cu-S bond and inverting one of the remaining coordinated sulfur donor atoms, the other three sulfur atoms can move to positions roughly approximating three corners of a regular tetrahedron, leaving the fourth site available for occupation by a fourth donor species. In the "high-concentration" environment of the crystal, this fourth site is occupied by the uncoordinated sulfur from an adjoining ligand. In dilute aqueous solution we postulate that this fourth site would be occupied by a water molecule to yield an S₃O donor set. It should be noted that the bending away of the S(11) atom is achieved at the expense of some internal ligand strain in the vicinity of the C(13), C(14), and S(1) atoms as revealed by the anomalously large bond angles for C(12)-C(13)-C(14), S(1)-C(14)-C(13), and Cu-S(1)-C(14) in Table III.

Clearly, both of the foregoing conformations for Cu^I([14]aneS₄) are feasible in solution. The formal potential for the Cu([14]aneS₄) system must reflect the more stable of these two Cu(I) species and, thus, places an upper limit on the stability constant for either species.

Correlation of Structures to Reduction Potentials. From a thermodynamic standpoint, the formal potential value for a specific copper complex redox couple in aqueous solution, E_{CuL}^f , should be related to the potential for the aquocopper(II/I) redox couple, $E_{\text{Cu(aq)}}^f$, by the logarithmic ratio of the complexes formed with Cu(I) and Cu(II) (i.e., $K_{\text{Cu}^{\text{I}}\text{L}}$ and $K_{\text{Cu}^{\text{II}}\text{L}}$, respectively,²⁴ viz.

$$E_{\text{CuL}}^f = E_{\text{Cu(aq)}}^f + (RT/nF) \ln (K_{\text{Cu}^{\text{I}}\text{L}}/K_{\text{Cu}^{\text{II}}\text{L}}) \quad (2)$$

The values of $K_{\text{Cu}^{\text{II}}\text{L}}$ for the complexes formed with [14]aneS₄ and Et₂-2,3,2-S₄ have been previously determined²¹ and are listed in Table VII. Inserting these equilibrium constant values and the potential values from Table I into eq 2 yields the apparent $K_{\text{Cu}^{\text{I}}\text{L}}$ values for these two systems as listed in Table VII.

Within the limits of accuracy of the data used, the $K_{\text{Cu}^{\text{I}}\text{L}}$ value for Cu^I(Et₂-2,3,2-S₄) appears to be more than 3 orders of magnitude larger than the corresponding value for Cu^I([14]aneS₄).

(22) Young, I. R.; Ochrymowycz, L. A.; Rorabacher, D. B., submitted for publication.

(23) Brubaker, G. R.; Johnson, D. W. *Inorg. Chem.* **1984**, *23*, 1591-1595; *Coord. Chem. Rev.* **1984**, *53*, 1-36.

(24) Laitinen, H. A.; Harris, W. E. "Chemical Analysis", 2nd ed.; McGraw-Hill: New York, 1975; p 227 ff.

This difference may reflect the replacement of one Cu-S bond by a weaker Cu-OH₂ bond in the latter complex if the monomer involves an S₃O donor set with a structural arrangement similar to that observed in the crystalline polymer. Alternatively, the lower K_{CuL} may largely be ascribable to increased internal ligand strain if a flattened tetrahedral complex is formed with an S₄ donor set. In fact, however, both monomeric conformations clearly result in a significantly lowered K_{CuL} value since, as noted above, the experimental value must reflect the more stable Cu(I) species. We favor the former species. Future physical measurements and molecular mechanical calculations will be aimed at differentiating between these two possibilities.

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Registry No. [Cu^I(Et₂-2,3,2-S₄)](ClO₄), 93778-95-1; [Cu^{II}(Et₂-2,3,2-S₄)(OH₂)(OCIO₃)](ClO₄), 93645-97-7; [Cu^I([14]aneS₄)](ClO₄), 93645-99-9.

Supplementary Material Available: Listings of all atomic positional parameters (including calculated hydrogen positional parameters), thermal parameters, and the final observed and calculated structure factors for all three compounds (31 pages). Ordering information is given on any current masthead page.

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Structure of Tantalum Cresoxide

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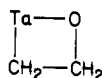
The synthesis of tantalum cresoxide (II) from TaCl₅ and NaO-*p*-C₆H₄CH₃ is reported. The crystal structure of II was determined for C₇₀H₇₀O₁₀Ta₂. Cell dimensions: $a = 12.17$ (1) Å, $b = 18.02$ (1) Å, $c = 14.71$ (1) Å, $\beta = 91.17$ (6)°. The crystals are monoclinic of space group $P2_1/n$ with $Z = 4$. The structure of II is a dimer with two bridging cresoxides. The structure is discussed in terms of multiple bonding between Ta and O. The solid-state structure of II is compared to the solution structure of II (¹³C NMR and ¹H NMR) and to the solution structure of Ta₂(OPh)₁₀ (I).

Introduction

The structure of metal alkoxides has been widely studied by a number of groups in recent years.¹ Far less work has focused on the structure of metal phenoxide complexes.²

During an investigation of tantalum phenoxide, it was found that little accurate structural information was available for this compound. In fact, since the first report³ of its synthesis very few references to the compound exist at all.⁴ The structure as derived from NMR data for tantalum methoxide has been reported,⁵ and it is a dimer with two bridging methoxides. Titanium phenoxide is the closest analogue of tantalum phenoxide for which a crystal structure determination has been made.⁶

Recently, it was reported that tantalum ethoxide "Ta₂(OEt)₁₀" catalyzed the deuteration (on the methyl group only) of ethanol with D₂.⁷ It was proposed that a four-membered ring intermediate was in part responsible for this reaction.



This would require that a monomeric tantalum ethoxide be present to some extent, and some evidence for this was given.⁷ Recently, a dimeric structure was proposed for tantalum phenoxide on the basis of infrared analysis.⁸

Bradley and co-workers measured the nuclearity of a number of tantalum alkoxides.⁹ As the steric requirement increased (from ethyl to isopropyl to *tert*-butyl), the complexes were found to be

Table I. Crystal Data and Summary of Intensity Data for II

formula	C ₇₀ H ₇₀ O ₁₀ Ta ₂
mol wt	1433.21
lattice const	$a = 12.17$ (1) Å $b = 18.02$ (1) Å $c = 14.71$ (1) Å $\beta = 91.17$ (6)°
λ	0.710 69 Å
temp	ambient
radiation	Mo K α monochromatized
space group	$P2_1/n$ (no space group ambiguities)
Z	2
μ	36.4 cm ⁻¹ (no abs cor applied)
diffractometer	Nicolet P3F automated diffractometer
geometry	ω -2 θ scan
conditions	$4 \leq 2\theta \leq 50^\circ$ $0 \leq h \leq 13$ $0 \leq k \leq 22$ $-18 \leq l \leq 18$
no. of reflns	5063 collcd; 2700 unique obsd reflns with $F > 4\sigma(F)$
struct determ	direct methods; SHELXTL program package
R	0.0600
R_w	0.0558
w^{-1}	$\sigma^2(F) + 0.00032F^2$; $\Sigma w(F_o - F_c)^2$

monomeric. In the present work, the structure of tantalum phenoxide was investigated in order to firmly determine the molecularity of the molecule. In addition, NMR results (vide infra) suggested that there may be some ring carbon-metal interactions not unlike those found in a number of ortho-metallated complexes.¹⁰ Thus, it was of interest to learn what interaction (if any) existed between the phenoxide rings with each other or of the phenoxide rings with the metal.

Experimental Section

All operations were carried out in a Vacuum Atmospheres drybox filled with Argon. TaCl₅ was sublimed before use. ¹H NMR were recorded on a Varian EM 390 NMR spectrometer. ¹³C{¹H} NMR were recorded on a Varian FT 80 NMR spectrometer (20 MHz).

(10) Lewis, L. N., unpublished results.

- (1) Bradley, D. C.; Mehrottra, R. C.; Gaur, D. P. "Metal Alkoxides"; Academic Press: London, 1978.
- (2) Malhotra, K. C.; Martin, R. L. *J. Organomet. Chem.* **1982**, *159*.
- (3) Funk, H.; Niederlander, K. *Chem. Ber.* **1929**, *62*, 1688.
- (4) Mehrottra, R. C.; Rai, A. K.; Kapoor, P. N.; Bohra, R. *Inorg. Chim. Acta* **1976**, *16*, 237.
- (5) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259.
- (6) Svetich, G. W.; Voge, A. A. *Acta Crystallogr.* **1972**, *B28*, 1760.
- (7) Nugent, W. A.; Ovenall, D. W.; Holmes, S. J. *Organometallics* **1983**, *2*, 161.
- (8) Malhotra, K. C.; Banerjee, U. K.; Chaudhry, S. C. *J. Ind. Chem.* **1980**, *57*, 868.
- (9) Bradley, D. C.; Chakravarti, B. N.; Chatterjee, A. K.; Wardlaw, W.; Whitley, A. *J. Chem. Soc.* **1958**, 99.