*J. Am. Chem. Soc.* **1985**, *107*, 2399-2404

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# Structures of a Labile Copper Redox Couple: Sterically Constrained Copper(II) and Copper(I) Complexes Formed with a Simple Cyclic Pentathia Ether, 1,4,7,10,13-Pentathiacyclopentadecane

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**Abstract:** Crystal structures have been resolved at room temperature for the perchlorate salts of the Cu(II) and Cu(I) complexes formed with the quinquedentate macrocycle 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS$_5$). The space groups, lattice constants, and final $R$ factors for these two compounds are as follows. For Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$: space group $P2_1/c$, $a$ = 17.966 (5) Å, $b$ = 9.908 (5) Å, $c$ = 11.230 (6) Å, $\beta$ = 90.66 (2)°, $Z$ = 4, $R$ = 0.039, and $R_w$ = 0.051. For Cu$^{I}$([15]aneS$_5$)(ClO$_4$): space group $P2_1/n$, $a$ = 11.354 (7) Å, $b$ = 14.759 (9) Å, $c$ = 11.749 (6) Å, $\beta$ = 113.16 (4)°, $Z$ = 4, $R$ = 0.083, and $R_w$ = 0.092. Both of the complexes exist as 1:1 monomers in the crystalline state. The Cu(II) complex has a square-pyramidal geometry with the copper atom situated 0.41 Å above the mean basal plane formed by four of the sulfur donor atoms while the fifth sulfur atom is coordinated apically but bent back by 12.8° from the perpendicular due to the steric constraints imposed by the ethylene bridges. The five Cu–S bond lengths are 2.331 (2), 2.315 (2), 2.289 (2), 2.338 (2), and 2.398 (2) Å, with the longest bond being to the apical sulfur. The Cu(I) complex has a distorted tetrahedral geometry which closely approximates the Cu(II) geometry except that one of the Cu–S bonds in the basal plane is broken. The four Cu–S bond lengths in this complex are 2.338 (5), 2.243 (5), 2.245 (5), and 2.317 (5) Å, with the nonbonded sulfur having two alternative orientations at distances of 3.442 (12) and 3.560 (11) Å from the copper atom. For both complexes the perchlorates are noncoordinating. The relatively minor change in structure which occurs on reducing Cu$^{II}$([15]aneS$_5$) to Cu$^{I}$([15]aneS$_5$) implies a relatively small Franck–Condon barrier for this redox couple. This is consistent with the results of kinetic studies on this system which indicate that this couple is more labile in its electron-transfer properties than any other copper–polythia ether or copper–poly(amino)thia ether complexes yet investigated.

As a result of the considerable plasticity of the inner-coordination sphere of copper(II)[2] and the marked difference in the coordination preferences exhibited by copper(II) and copper(I),[3] much emphasis has been placed upon the influence of coordination geometry on the electrochemical properties of Cu(II)/(I) redox couples.[4-7] This emphasis has been stimulated by the high level of interest in copper enzymes involved in electron-transfer processes. In particular, the type I copper sites in blue copper proteins are noted for exhibiting high redox potentials and rapid electron-transfer kinetics.[6-11] Both of these properties have been largely attributed to the distorted tetrahedral geometry of the inner-coordination sphere imposed upon the copper center by the protein superstructure.[11-15]

Direct evidence for the correlation of electrochemical properties to coordination geometry must rely on comparative studies on low molecular weight copper complexes. Such evidence is still extremely limited. Since the initial structural studies on corresponding Cu(II) and Cu(I) complexes by Baker and Norris[16] and by ourselves,[17] several other structures of copper redox pairs have been reported.[18-23] Many of these latter systems involve some coordinative distortion in the Cu(II) and/or Cu(I) species. However, almost no electrochemical information is available to demonstrate the influence of such distortions upon the properties of these redox couples. Conversely, very few structures have been resolved for both the Cu(II) and Cu(I) species of redox couples having unusual electrochemical parameters.

In extensive investigations on a series of copper–polythiaether complexes involving variable ligand structures, we have sought to determine the influence of structure upon their thermodynamic[24]

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and kinetic[25] properties, including their electrochemical behavior.[26,27] Primarily as a result of the stabilization of the Cu(I) oxidation state by the sulfur donor atoms, these complexes exhibit redox potentials ranging from 0.6 to 1.0 V (vs. SHE), the higher values representing the maximum potentials ever observed for Cu(II)/Cu(I).[27]

Recently, we reported the results of a structural study in which we compared the structures of the Cu(II) and Cu(I) complexes formed with closely related open-chain and cyclic tetrathia ether ligands (3,6,10,13-tetrathiapentadecane and 1,4,8,11-tetrathiacyclotetradecane, respectively)[28] which represent the systems with the highest and lowest Cu(II)/(I) potentials among this series. For these two systems it was postulated that the difference in potential was largely attributable to a difference in the number of sulfur donor atoms remaining coordinated to the copper atom when reduced to Cu(I), although greater coordinative distortion in the Cu(I) complex of the cyclic ligand system may also be a contributing factor.

We now direct attention to the influence of structure upon the kinetic aspects of electron-transfer reactions as reflected in the outer-sphere self-exchange reaction:

$$Cu^{II}L + *Cu^{I}L \xrightleftharpoons{k_{11}} Cu^{I}L + *Cu^{II}L \qquad (1)$$
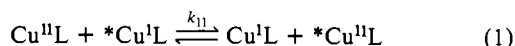
The values of the self-exchange electron-transfer rate constant, $k_{11}$, have been evaluated from carefully selected cross-exchange electron-transfer reactions involving both oxidation and reduction with known outer-sphere reagents.[27] For the majority of copper–polythiaether complexes studied, the $k_{11}$ values appear to be in the vicinity of $10^2$ M$^{-1}$ s$^{-1}$ despite apparent differences in coordination geometry, potentials, and related properties of the Cu(II) and Cu(I) species. However, for the only copper system studied involving a cyclic pentathia ether ligand, 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS$_5$),
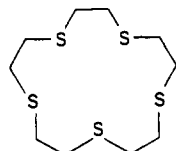


an apparent $k_{11}$ value of $3 \times 10^4$ M$^{-1}$ s$^{-1}$ was resolved. This represents the largest self-exchange rate constant reported for any low molecular weight copper system[29] (other than for the tetrahedral CuCl$_4^{2-/3-}$ system[30]).

In this paper we report the structures of Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$ and Cu$^I$([15]aneS$_5$)(ClO$_4$) as determined by X-ray diffractometry on single crystals. In both complexes the perchlorates are found to be noncoordinating and only thia ether sulfur donor atoms are located in the inner-coordination sphere of the copper atom. In fact, these complexes represent the first known example of a Cu(II)/(I) redox couple in which all inner-sphere sites are occupied by the same donor atom other than the aquo- and chlorocopper systems. The implications of the resolved molecular structures for the chemical behavior of this system are examined.

## Experimental Section

**Ligand Synthesis.** In a significant improvement over the previously published synthetic procedure,[31] [15]aneS$_5$ was prepared through the

cesium ion template-mediated cyclization of 2-mercaptoethyl sulfide (Aldrich M 400-7) with the bimesylate of the 3,6-dithia-1,8-octanediol (Aldrich 23, 522-4) in DMF by adaptation of the general procedure of Kellogg.[32] DMF was purified by distillation from calcium hydride. Cesium carbonate was obtained from Research Organic/Inorganic Chemical Company, Belleville, NJ. The 3,6-dithiaoctane-1,8-diyl bis(methanesulfonate) was prepared from the 3,6-dithia-1,8-octanediol by adaption of the Crossland–Servis mesylation procedure.[33] The mesylate was prepared immediately before use and, except for stripping off the last traces of methylene chloride by vacuum agitation at 0.1 torr for 3 h in a Kugelrohr apparatus, was used without further purification. Proton NMR analysis indicated that the reactant was >95% pure. Analysis of the commercial lot of 2-mercaptoethyl sulfide indicated it to be >98% pure. The cyclization was then effected on approximately a 0.15-mol scale. In a water-cooled, jacketed 500-mL pressure-equalizing dropper funnel, 23.5 g (0.15 mol) of 2-mercaptoethyl sulfide and 53.5 g (0.15 mol) of the mesylate were dissolved in 250 mL of anhydrous DMF. This solution, maintained below 20 °C, showed little reaction over the addition period. The solution was added dropwise over 48 h to 81.5 g (0.25 mol) of finely milled anhydrous Cs$_2$CO$_3$ suspended in 2.2 L of anhydrous DMF. The reaction vessel was maintained at 85 °C and vigorously stirred under a nitrogen atmosphere through the course of the reaction. After stirring for an additional 6 h, the reaction was cooled and filtered to remove salts, and solvent was removed by rotary evaporation. The thick oil residue was taken up in 1 L of methylene chloride and successively washed with 500-mL volumes of water, 5% NaOH, and saturated brine.

After drying with MgSO$_4$, the solvent was rotary vacuum evaporated to yield 52 g of a nearly colorless oil, which solidified on standing at room temperature. TLC analysis in 20% ethyl acetate–hexane on silica gel indicated only traces of starting dithiol and a series of oligomeric cyclic products. The two most mobile components were the [15]aneS$_5$ and the larger [30]aneS$_{10}$. These were resolved by elution chromatography with 20% ethyl acetate–hexane on 60–200 mesh Baker Analyzed silica gel set up in a 6 × 70 cm column. The initial 3 L of eluant yielded 22 g of [15]aneS$_5$ uncontaminated by larger products. An additional 16 g of mixture comprising both [15]aneS$_5$ and [30]aneS$_{10}$ was recovered with 5 L of solvent. In like fashion, an additional 10.5 g of [15]aneS$_5$ was recovered by rechromatography of the mixed fraction. The combined 32.5 g of crude [15]aneS$_5$ was recrystallized from 500 mL of absolute ethanol after clarification with charcoal to yield 23.5 g (52% yield) of fine white crystalline product, mp 99–100 °C, which was identical with a sample prepared by the earlier procedure.[31] A second crop of crystals of 4.7 g was obtained in like manner after concentration of the mother liquor.

**Crystal Preparations.** Pure Cu(ClO$_4$)$_2$ was prepared from CuO and HClO$_4$ and recrystallized twice from water. Crystals of the Cu(II) complex were prepared by adding roughly stoichiometric amounts of hydrated Cu(ClO$_4$)$_2$ and [15]aneS$_5$ in 80% methanol (w/w) and allowing the resulting solution to evaporate slowly. The material crystallized in the form of a deep red mass with an empirical formula corresponding to Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$. From this mass was cut a single crystal of approximate dimensions 0.14 × 0.18 × 0.35 mm. This crystal was mounted on a glass fiber with epoxy cement.

The corresponding Cu(I) complex was prepared by exhaustive controlled-potential electrolysis of a deaerated Cu(II)–ligand solution (prepared as above) under nitrogen atmosphere. This solution was then slowly evaporated under a flow of scrubbed nitrogen. Small colorless crystals were obtained having an empirical formula corresponding to Cu$^I$([15]aneS$_5$)(ClO$_4$). A suitable crystal was selected and sealed in a glass capillary with a portion of the mother liquor.

**Diffraction Measurements.** For both crystals all diffraction data were collected at ambient temperature on a Syntex P2$_1$ automated diffractometer. Intensity data were collected by the $\theta$–$2\theta$ technique with Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å) diffracted from a highly oriented graphite monochromator in a parallel mode with a takeoff angle of 4°. Initial examination by axial and rotation photographs and by preliminary data sets established the symmetry and yielded approximate lattice constants.

In collecting the diffraction data, three standard reflections were measured every 97 reflections. These were statistically constant for the Cu(I) compound but indicated a 5% decrease in the Cu(II) compound during the data collection (with individual fluctuations of up to ±2%) and a step correction was made for this decrease.

The data were reduced to $|F_o|$ and $\sigma|F_o|$ values. Standard deviations were assigned by the formula

$$\sigma(I) = [\sigma_c(I)^2 + (pI)^2]^{1/2}$$

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where

$$\sigma_c = (I + K^2B)^{1/2}$$

In these equations $I$ represents the net intensity, $B$ the background counts, $K$ the ratio of time spent scanning to the time spent measuring backgrounds (5.0, 2.5, or 2.0 in the present measurements), and $p$, assigned a value of 0.05 for these structures, ensures that strong reflections are not overly weighted in the least-squares calculations.

Standard computer programs modified for local use were employed.[34] Correction for Lorentz and polarization effects were made on both compounds. Absorption corrections were also made on the Cu(II) compound by the analytical method (Table I, footnote c) with $\mu = 19.0$ cm$^{-1}$ with minimum and maximum corrections of 1.24 and 1.52, respectively. For both compounds, the atomic positional parameters and thermal parameters of all non-hydrogen atoms were refined by full-matrix least-squares techniques. The 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 Cu, Cl, and S atoms was applied. Discrepancy factors were defined as follows:

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

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

The experimental scan ranges, scan rates, and other pertinent data for both compounds are summarized in Table I.

## Results

**Structure Determination of Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$.** A primitive monoclinic system was indicated by axial photographs and the space group $P2_1/c$ was confirmed by the structural analysis. The structure was solved by direct methods yielding the locations of all heavy atoms plus eight of the carbon atoms from the resulting $E$ map. The remaining atoms were found from a Fourier difference map. Least-squares refinement with anisotropic thermal parameters resulted in convergence with $R = 0.046$ and $R_w = 0.063$. Fixed hydrogen atom contributions were included for positions calculated assuming a C–H distance of 0.95 Å, tetrahedral H–C–H angles, and local $C_{2v}$ symmetry.

A difference Fourier map calculated at this stage showed, in the vicinity of atom Cl(2), appreciable electron density of 1.5 e/Å$^3$, or 30–40% of an oxygen atom. In addition, the thermal parameters for the oxygens attached to Cl(2) (i.e., O(5)–O(8)) were very high compared to those attached to Cl(1) (O(1)–O(4)). A more satisfying model was obtained by refining orientations for two groups of oxygen atoms, each assigned a 50% occupancy and constrained to tetrahedral symmetry. When these orientations were known, the constraints were released and a group occupancy factor was refined with final value 0.72 (1). Atoms O(5) through O(8), representing 72% of the oxygen atoms in the crystal bonded to Cl(2), were assigned anisotropic temperature factors on the basis of a further difference Fourier calculation while atoms O(5A) through O(8A), representing the 28% of oxygen atoms in an alternate perchlorate orientation, were left with isotropic thermal parameters. (The occupancy factor of 0.72 is somewhat sensitive to whether the oxygen atoms were refined isotropically or anisotropically.)

The overall effect of allowing for perchlorate ion disorder was to lower the discrepancy factors to $R = 0.039$ and $R_w = 0.051$ with the addition of only 17 extra parameters, making the ratio of observed data to number of parameters: 2763/252 = 11/1. The highest peaks in a difference Fourier map were, at this point, 0.6–0.7 e/Å$^3$ or about 15% of an oxygen atom, still in the region

**Table I.** Crystal Parameters and Experimental Data for X-ray Diffraction Measurements on Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$ and Cu$^{I}$([15]aneS$_5$)(ClO$_4$)

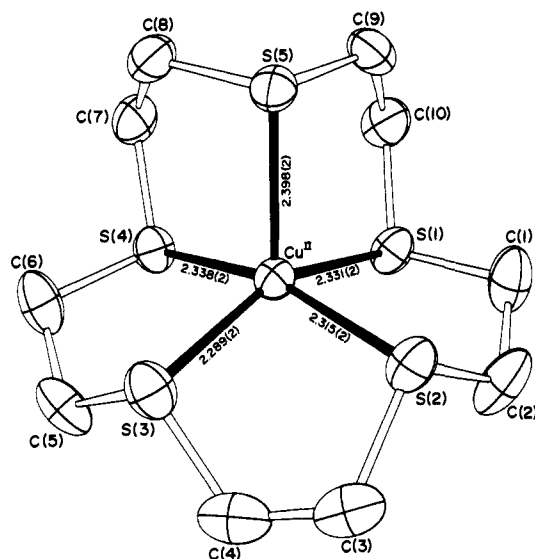| parameter | Cu$^{II}$L(ClO$_4$)$_2$ | Cu$^{I}$L(ClO$_4$) |
|---|---|---|
| lattice type | monoclinic | monoclinic |
| space group | $P2_1/c$ | $P2_1/n$ |
| cell dimensions | | |
| $a$, Å | 17.966 (5) | 11.354 (7) |
| $b$, Å | 9.908 (5) | 14.759 (9) |
| $c$, Å | 11.230 (6) | 11.749 (6) |
| $\beta$, deg | 90.66 (2) | 113.16 (4) |
| cell volume, Å$^3$ | 1999 (2) | 1810 (2) |
| empirical formula | CuC$_{10}$H$_{20}$S$_5$Cl$_2$O$_8$ | CuC$_{10}$H$_{20}$S$_5$ClO$_4$ |
| formula weight | 563.02 | 463.56 |
| $Z$ | 4 | 4 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.874 | 1.701 |
| $F(0,0,0)$ electrons | 1148 | 952 |
| scan method | $\theta-2\theta$ | $\theta-2\theta$ |
| scan range,[a] deg | K$\alpha_1$ – 1 (0.9) to K$\alpha_2$ + 1 (0.9) | K$\alpha_1$ – 1 to K$\alpha_2$ + 1 |
| scan rate, deg min$^{-1}$ | 1.0–4.0 | 2.0 |
| background as fraction of scan time[a] | 0.40 (0.50) | 0.20 |
| collection region | $+h,+k,\pm l$ | $\pm h,+k,+l$ |
| $2\theta$ limits,[a] deg | 0–45 (45–50) | 2–45 |
| reflections measd | 3585 | 2806 |
| standard reflctns | (930), (254), (44$\bar{4}$) | ($\bar{2}\bar{2}3$), ($\bar{2}23$), (013) |
| no. of data between standard reflctns | 97 | 97 |
| decay | 5% | negligible |
| correctns applied | Lp and decay | Lp |
| $\sigma(F_o^2)$[b] | $[\sigma_c^2 + 0.05F_o^2]^{1/2}$ | $[\sigma_c^2 + 0.05F_o^2]^{1/2}$ |
| no. of obsd reflctns | 2763 | 1303 |
| criteria for obsd reflctns | $>2\sigma$ | $>2\sigma$ |
| linear absorp coeff | | |
| $\mu$, cm$^{-1}$ | 19.0 | 19.2 |
| correctn made | yes[c] | no |
| absorption factors | 1.24–1.52 | |
| solution method | MULTAN and $(F_o - F_c)$ Fourier | MULTAN and $F_o$ Fourier |
| calcd H atom positions | yes | yes |
| calcd C–H bond distance, Å | 0.95 | 0.95 |
| calcd H atom temp factor | $B_H = B_C$ | $B_H = 1.10B_C$ |
| variable parameters | 252 | 159 |
| $R, R_w$[d] | 0.039, 0.051 | 0.083, 0.092 |
| $S$[e] | 1.50 | 2.18 |
| $\Delta\rho_{max}$, e$^-$ Å$^{-3}$ | 0.70 | 1.06 |
| unusual features | disorder in second perchlorate group | disorder near S(3), C(4), C(5) |

[a] Values without and within parentheses for Cu$^{II}$L(ClO$_4$)$_2$ refer to the first and second shells of data collection, respectively. [b] $\sigma_c$ is from counting statistics. [c] Correction methods applied were those in: (a) De Meulenaar, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018. (b) Templeton, L. K.; Templeton, D. H. American Crystallogr. Assoc. Meeting: Storrs, CT; Abstr. E-10. [d] $R = \sum ||F_o| - |F_c||/\sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [e] $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $N_o$ is the number of observations and $N_v$ is the number of parameters.

of the disordered perchlorate group.

Final values of the refined parameters are given in Table I. The resultant structure of the Cu$^{II}$([15]aneS$_5$) cation with the atom labeling scheme is shown in Figure 1. The perchlorates, which are noncoordinating, have been omitted from this figure. The atomic coordinates for all non-hydrogen atoms are given in Table II while the interatomic distances and bond angles are listed in Table III.

**Structure Determination of Cu$^{I}$([15]aneS$_5$)(ClO$_4$).** Axial photographs and a preliminary data set showed systematic absences consistent with space group $P2_1/n$.[35] The position of the copper

(34) Local versions of the following computer programs were used: (a) SYNCOR, W. Schmonsees' program for data reduction; (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, D. 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, reciprocal cell dimensions; (k) TRACER, Lawton and Jacobson's program for cell reduction; (l) EQUIV, local program for averaging equivalent reflections.

(35) This nonconventional space group was chosen to maintain $\beta$ closest to 90°.

**Figure 1.** Atom labeling scheme for the Cu$^{II}$([15]aneS$_5$) cation. The copper atom is positioned 0.41 Å above the mean basal plane defined by the S(1), S(2), S(3), and S(4) donor atoms. The S(5) atom is apically coordinated, being bent back 12.8° relative to an axis through the copper atom perpendicular to the basal $S_4$ plane.

**Table II.** Atomic Positional Parameters for Non-Hydrogen Atoms in Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$[a]

| atom[b] | x | y | z |
|---|---|---|---|
| Cu | 0.25010 (3) | 0.23862 (5) | 0.02177 (5) |
| Cl(1) | −0.07714 (6) | 0.27998 (11) | 0.22169 (10) |
| Cl(2) | 0.58721 (8) | 0.15428 (19) | 0.23715 (13) |
| S(1) | 0.30289 (6) | 0.38736 (12) | −0.11412 (9) |
| S(2) | 0.36813 (6) | 0.19919 (13) | 0.09907 (10) |
| S(3) | 0.22317 (7) | 0.02991 (12) | 0.09735 (10) |
| S(4) | 0.13930 (6) | 0.22855 (11) | −0.08917 (10) |
| S(5) | 0.20230 (6) | 0.42153 (11) | 0.13796 (9) |
| O(1) | −0.1485 (2) | 0.2393 (4) | 0.2562 (4) |
| O(2) | −0.0802 (2) | 0.3120 (5) | 0.0971 (4) |
| O(3) | −0.0534 (3) | 0.3957 (5) | 0.2831 (5) |
| O(4) | −0.0261 (3) | 0.1738 (5) | 0.2341 (5) |
| O(5) | 0.6245 (9) | 0.2385 (12) | 0.1784 (12) |
| O(6) | 0.6368 (5) | 0.0262 (11) | 0.2323 (7) |
| O(7) | 0.5273 (6) | 0.0880 (12) | 0.1941 (12) |
| O(8) | 0.5849 (5) | 0.1855 (11) | 0.3616 (7) |
| O(5A) | 0.5486 (12) | 0.3010 (22) | 0.2114 (19) |
| O(6A) | 0.5644 (18) | 0.1397 (33) | 0.3391 (31) |
| O(7A) | 0.5491 (17) | 0.1089 (31) | 0.1366 (25) |
| O(8A) | 0.6592 (12) | 0.1681 (23) | 0.2142 (19) |
| C(1) | 0.3959 (3) | 0.4019 (6) | −0.0530 (5) |
| C(2) | 0.4238 (3) | 0.2632 (6) | −0.0221 (5) |
| C(3) | 0.3740 (3) | 0.0166 (6) | 0.0838 (6) |
| C(4) | 0.3078 (4) | −0.0515 (6) | 0.0505 (7) |
| C(5) | 0.1551 (3) | −0.0280 (5) | −0.0114 (4) |
| C(6) | 0.0965 (3) | 0.0791 (5) | −0.0259 (5) |
| C(7) | 0.0859 (2) | 0.3668 (5) | −0.0293 (4) |
| C(8) | 0.1050 (2) | 0.4064 (5) | 0.0979 (4) |
| C(9) | 0.2368 (3) | 0.5629 (5) | 0.0536 (4) |
| C(10) | 0.2547 (3) | 0.5401 (5) | −0.0768 (5) |

[a] For this and the accompanying tables, the numbers in parentheses represent the standard deviations for the least significant digits listed. [b] Atoms O(5)–O(8) and O(5A)–O(8A) represent alternative orientations of the second perchlorate group. The occupancy factor was allowed to float yielding 72% occupancy in orientation O(5)–O(8) and 28% occupancy in orientation O(5A)–O(8A).

atom was found by direct methods while the positions of the remaining non-hydrogen atoms were obtained from successive difference maps.

The S(3) atom was ill-defined with excessively high thermal parameters suggestive of disorder in this region. At this point two positions were refined for this sulfur, designated as S(3A) and S(3B), each with a fixed occupancy level of 0.5. The adjacent carbon atoms, C(4) and C(5), also appear to be slightly disordered,

**Table III.** Bond Lengths (Å) and Bond Angles (Deg) in Cu$^{II}$([15]aneS$_5$)(ClO$_4$)$_2$ and Cu$^{I}$([15]aneS$_5$)(ClO$_4$)

| | Cu$^{II}$L(ClO$_4$)$_2$ | Cu$^{I}$L(ClO$_4$) |
|---|---|---|
| **Bond Lengths** | | |
| Cu–S(1) | 2.331 (2) | 2.338 (5) |
| Cu–S(2) | 2.315 (2) | 2.243 (5) |
| Cu–S(3A) | 2.289 (2) | 3.442 (12) |
| Cu–S(3B) | | 3.560 (11) |
| Cu–S(4) | 2.338 (2) | 2.245 (5) |
| Cu–S(5) | 2.398 (2) | 2.317 (5) |
| Cl(1)–O(1) | 1.403 (4) | 1.40 (2) |
| Cl(1)–O(2) | 1.435 (4) | 1.40 (1) |
| Cl(1)–O(3) | 1.402 (5) | 1.30 (2) |
| Cl(1)–O(4) | 1.402 (5) | 1.39 (2) |
| Cl(2)–O [mean] | 1.40 | |
| S(1)–C(10) | 1.795 (5) | 1.82 (2) |
| S(1)–C(1) | 1.804 (5) | 1.72 (2) |
| S(2)–C(2) | 1.813 (5) | 1.87 (2) |
| S(2)–C(3) | 1.820 (6) | 1.81 (2) |
| S(3A)–C(4) | 1.805 (6) | 1.88 (4) |
| S(3B)–C(4) | | 1.43 (4) |
| S(3A)–C(5) | 1.812 (5) | 1.12 (3) |
| S(3B)–C(5) | | 1.82 (3) |
| S(4)–C(6) | 1.817 (5) | 1.89 (3) |
| S(4)–C(7) | 1.806 (5) | 1.77 (2) |
| S(5)–C(8) | 1.807 (5) | 1.82 (2) |
| S(5)–C(9) | 1.805 (5) | 1.78 (2) |
| C(1)–C(2) | 1.503 (8) | 1.42 (3) |
| C(3)–C(4) | 1.414 (9) | 1.38 (4) |
| C(5)–C(6) | 1.502 (8) | 1.50 (4) |
| C(7)–C(8) | 1.517 (7) | 1.50 (3) |
| C(9)–C(10) | 1.521 (7) | 1.44 (3) |
| **Bond Angles** | | |
| S(1)–Cu–S(2) | 88.53 (5) | 95.5 (2) |
| S(2)–Cu–S(3) | 84.56 (5) | |
| S(3)–Cu–S(4) | 88.65 (5) | |
| S(4)–Cu–S(5) | 90.81 (4) | 96.0 (2) |
| S(5)–Cu–S(1) | 91.86 (6) | 93.5 (2) |
| S(4)–Cu–S(1) | 91.63 (5) | 112.8 (2) |
| S(1)–Cu–S(3) | 154.58 (5) | |
| S(2)–Cu–S(4) | 164.36 (5) | 135.6 (2) |
| S(2)–Cu–S(5) | 104.82 (5) | 116.5 (2) |
| S(3)–Cu–S(5) | 113.73 (6) | |
| Cu–S(1)–C(10) | 100.3 (2) | 95.4 (8) |
| Cu–S(1)–C(1) | 100.6 (2) | 97.4 (8) |
| Cu–S(2)–C(2) | 99.8 (2) | 96.1 (7) |
| Cu–S(2)–C(3) | 100.7 (2) | 108.3 (7) |
| Cu–S(3)–C(4) | 96.5 (2) | |
| Cu–S(3)–C(5) | 100.4 (2) | |
| Cu–S(4)–C(6) | 100.8 (2) | 96.3 (6) |
| Cu–S(4)–C(7) | 102.8 (2) | 106.1 (6) |
| Cu–S(5)–C(8) | 98.8 (2) | 97.0 (7) |
| Cu–S(5)–C(9) | 100.0 (2) | 97.8 (7) |
| C(10)–S(1)–C(1) | 106.9 (3) | 104.8 (11) |
| C(2)–S(2)–C(3) | 104.1 (3) | 105.6 (11) |
| C(4)–S(3A)–C(5) | 103.1 (3) | 131 (2) |
| C(4)–S(3B)–C(5) | | 115 (2) |
| C(6)–S(4)–C(7) | 104.1 (3) | 110.4 (12) |
| C(8)–S(5)–C(9) | 105.7 (2) | 104.2 (11) |
| S(1)–C(10)–C(9) | 117.3 (3) | 116 (1) |
| S(1)–C(1)–C(2) | 108.7 (4) | 121 (2) |
| S(2)–C(2)–C(1) | 107.9 (4) | 118 (1) |
| S(2)–C(3)–C(4) | 116.7 (4) | 114 (2) |
| S(3A)–C(4)–C(3) | 114.7 (5) | 126 (3) |
| S(3B)–C(4)–C(3) | | 135 (3) |
| S(3A)–C(5)–C(6) | 108.4 (3) | 149 (3) |
| S(3B)–C(5)–C(6) | | 116 (2) |
| S(4)–C(6)–C(5) | 108.6 (4) | 116 (2) |
| S(4)–C(7)–C(8) | 115.6 (3) | 118 (1) |
| S(5)–C(8)–C(7) | 117.6 (3) | 117 (1) |
| S(5)–C(9)–C(10) | 117.9 (3) | 117 (2) |
| O(1)–Cl(1)–O(2) | 107.9 (3) | 112 (1) |
| O(1)–Cl(1)–O(3) | 111.9 (3) | 105 (1) |
| O(1)–Cl(1)–O(4) | 110.8 (3) | 110 (1) |
| O(2)–Cl(1)–O(3) | 107.9 (3) | 114 (1) |
| O(2)–Cl(1)–O(4) | 106.3 (3) | 107 (1) |
| O(3)–Cl(1)–O(4) | 111.7 (4) | 109 (1) |

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**Table IV.** Atomic Positional Parameters for Non-Hydrogen Atoms in $Cu^I([15]aneS_5)(ClO_4)$

| atom[a] | x | y | z |
|---|---|---|---|
| Cu | 0.4876 (2) | 0.0108 (1) | 0.2342 (2) |
| Cl | 0.0549 (5) | 0.1102 (4) | 0.2826 (5) |
| S(1) | 0.6646 (5) | −0.0856 (4) | 0.2879 (4) |
| S(2) | 0.6014 (5) | 0.1354 (3) | 0.3191 (4) |
| S(3A) | 0.3476 (11) | 0.2115 (8) | 0.0983 (11) |
| S(3B) | 0.4110 (10) | 0.1849 (8) | 0.0068 (10) |
| S(4) | 0.3319 (4) | −0.0242 (3) | 0.0508 (4) |
| S(5) | 0.4004 (5) | −0.0670 (3) | 0.3539 (4) |
| O(1) | 0.0583 (18) | 0.0176 (14) | 0.3093 (18) |
| O(2) | 0.1700 (16) | 0.1401 (11) | 0.2792 (15) |
| O(3) | −0.0432 (20) | 0.1201 (14) | 0.1789 (20) |
| O(4) | 0.0356 (16) | 0.1605 (13) | 0.3742 (17) |
| C(1) | 0.7813 (20) | −0.0050 (16) | 0.3519 (22) |
| C(2) | 0.7562 (16) | 0.0752 (16) | 0.4056 (19) |
| C(3) | 0.6260 (25) | 0.1985 (16) | 0.1985 (22) |
| C(4) | 0.5143 (38) | 0.2279 (25) | 0.1048 (35) |
| C(5) | 0.2684 (30) | 0.1656 (23) | 0.0388 (29) |
| C(6) | 0.2120 (17) | 0.0720 (22) | 0.0121 (19) |
| C(7) | 0.2734 (20) | −0.1200 (14) | 0.1038 (18) |
| C(8) | 0.2634 (19) | −0.1138 (13) | 0.2268 (21) |
| C(9) | 0.5127 (23) | −0.1579 (14) | 0.4007 (19) |
| C(10) | 0.6430 (21) | −0.1370 (15) | 0.4189 (22) |

[a] Atoms S(3A) and S(3B) represent alternative sites for the non-bonded sulfur atom. Each site was given a fixed occupancy factor of 0.5.

but no significant improvement in the refinement was obtained by taking such disorder into account.

The hydrogen atom positions were calculated, except for those attached to C(4) and C(5), by assuming a C–H distance of 0.95 Å, tetrahedral H–C–H angles, and $C_{2v}$ symmetry. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms, except C(4), S(3A), S(3B), and C(5) and the oxygen atoms in the perchlorate group, yielded $R = 0.083$ and $R_w = 0.092$.

Final values for the refined parameters are given in Table I. The resultant structure of the $Cu^I([15]aneS_5)$ cation with the atom labeling scheme is shown in Figure 2. The atomic coordinates for all non-hydrogen atoms are given in Table IV while the interatomic distances and bond angles are included in Table III.

## Discussion

**General Structural Features of $Cu^{II}([15]aneS_5)$.** The geometric arrangement of the copper atom and the four equatorial sulfur atoms in $Cu^{II}([15]aneS_5)$ is strikingly similar to that of the $Cu^{II}([13]aneS_4)$ complex whose structure we recently reported.[36] These similarities include the distance of the Cu(II) atom above the mean equatorial $S_4$ plane (0.41 Å vs. 0.38 Å, respectively); the average deviation of the equatorial sulfur atoms from the mean $S_4$ plane (±0.09 Å vs. ±0.08 Å, respectively); the average equatorial Cu–S bond length (2.32 Å in both complexes); and the size of the "open" S–Cu–S bond angle which in the [15]aneS$_5$ complex is represented by the S(1)–Cu–S(4) angle spanning the bridges to the apical sufur (91.6°) and in the [13]aneS$_4$ complex is the angle spanning the lone propylene bridge (90.9°).

The unique feature in the $Cu^{II}([15]aneS_5)$ complex is the coordination to the apical sulfur, S(5). Since the copper atom lies considerably above the equatorial $S_4$ plane, the C(7)–C(8) and C(9)–C(10) ethylene bridges are unable to span the distance to an apical position directly above the copper atom. As a result, the Cu–S(5) coordinate bond is bent back toward the S(1) and S(4) atoms. The extent of this displacement is best characterized in reference to a plane which is normal to the mean plane of the four equatorial sulfurs and passes through the copper atom and is positioned such that the perpendicular distances of S(1) and S(4) from this plane are nearly equal. Relative to this vertical plane, the S(5) atom is displaced "backward" (i.e., toward S(1)

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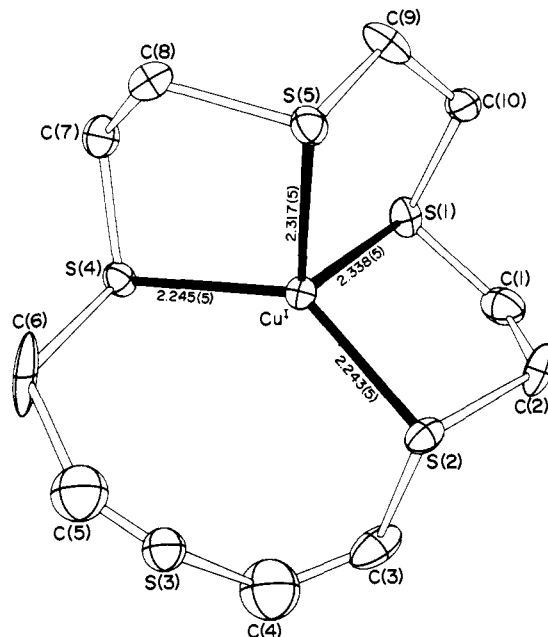


**Figure 2.** Atom labeling scheme for the $Cu^I([15]aneS_5)$ cation. The cationic unit has a nearly twofold axis passing through the copper atom and the bisector of the C(9)–C(10) bond such that S(1) and S(5) as well as S(2) and S(4) are virtually superimposable. The S(3) atom occupies two alternate sites at distances of 3.442 (12) and 3.560 (11) Å from the copper atom.

and S(4)) by 0.526 Å which corresponds to a displacement angle of 12.8°.

The axial coordinate bond in Cu(II) square-pyramidal complexes is generally 0.2–0.6 Å longer than the equatorial bonds,[3b] being accentuated in many instances by the fact that the weakest available donor atom is preferentially located in this site. However, even when all five donor atoms are identical, the apical bond is significantly elongated—as in $Cu(NH_3)_5^{2+}$ where the apical Cu–N bond is 0.17 Å longer than the average of the equatorial bond lengths.[37]

In $Cu^{II}([15]aneS_5)$, however, the axial Cu–S bond length is only 0.08 Å greater than the mean length of the four equatorial Cu–S bonds. Since the radius of sulfur is 0.44 Å greater than oxygen,[36] the 2.40 Å apical Cu–S bond in $Cu^{II}([15]aneS_5)$ is substantially shorter than the 2.15 Å apical Cu–O bond in $Cu^{II}([13]aneS_4)$. This relative foreshortening of the axial Cu–S bond undoubtedly reflects the constraints of the C(7)–C(8) and C(9)–C(10) ethylene bridges. In order to elongate the axial bond significantly, the S(5) atom would have to be bent further away from the perpendicular or else the two ethylene groups would be forced into a more strained conformation. Thus, we may presume that the length and angle of the Cu–S(5) bond represent a compromise of opposing forces.[38]

From resonance Raman measurements,[39] all five Cu–S bonds in $Cu^{II}([15]aneS_5)$ appear to be equivalent in solution. This suggests that the position of the apical sulfur rapidly moves around the ring, presumably by an internal rearrangement. Starting with the conformation shown in Figure 1, the necessary rearrangement can be envisioned by displacing the S(5) atom down into the

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(38) Three other crystal structures have been reported for Cu(II) complexes formed with macrocyclic quinquedentate ligands, each exhibiting square-pyramidal geometry; (a) Drew, M. G. B.; Hollis, S. *Inorg. Chim. Acta* **1978**, *29*, L231–L232. (b) Drew, M. G. B.; Cairns, C.; Nelson, S. M.; Nelson, J. *J. Chem. Soc., Dalton Trans.* **1981**, 942–948. (c) Arnaud-Neu, F.; Schwing-Weill, M. J.; Louis, R.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 2956–2961. Cf. Louis, R.; Agnus, Y.; Weiss, R. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2905–2910.

(39) Ferris, N. S.; Woodruff, W. H., Personal communication. Cf. Ferris, N. S.; Woodruff, W. H.; Rorabacher, D. B.; Jones, T. E.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5939–5942.

equatorial plane and simultaneously moving the S(1) atom into an apical position below the equatorial plane. This concerted movement would also require the inversion of the S(3) atom and the translation of the copper atom through the S(2)–S(3)–S(4) plane to achieve a conformation equivalent to the initial geometry. (From the vantage point of a fixed copper atom, the S(2) and S(4) donor atoms are seen to move "upward", thereby diminishing the extent to which S(5) and S(1) appear to move "downward".) From an alternative viewpoint, the same rearrangement can be effected by moving the S(3) atom to a position *trans* to S(5) while simultaneously inverting the former atom, thereby making S(1) the new apical sulfur. By means of such mechanisms, the necessary rearrangement can move rapidly around the ring so that all five Cu–S bonds may be indistinguishable in solution.

**General Structural Features of Cu$^I$([15]aneS$_5$).** In the Cu$^I$-([15]aneS$_5$) complex, four of the sulfur donor atoms are bonded to the central copper atom in a distorted tetrahedral array. The fifth sulfur is not coordinated being about 3.5 Å distant from the copper atom in either of its two possible orientations. The view shown in Figure 2 and the atom numbering scheme utilized were selected to minimize the apparent differences in structures between the Cu(II) and Cu(I) complexes. From this standpoint, the noncoordinated S(3) atom corresponds to one of the "front" equatorial sulfurs in the Cu(II) complex. A comparison of Figures 1 and 2 shows that all of the remaining coordinated sulfurs have retained their orientations, in terms of the directionality of the unshared electron pairs, upon the reduction of Cu(II) to Cu(I).

By defining an axis running roughly through the S(3) and Cu atoms and the bisector of the C(9)–C(10) bond, a 180° rotation interchanges S(1) and S(5) and also S(2) and S(4). Thus, either S(5) or S(1) can be viewed as the atom which was initially apical in the Cu(II) complex. As a result of this virtual symmetry, the chelate rings Cu–S(1)–C(1)–C(2)–S(2) and Cu–S(4)–C(7)–C-(8)–S(5) are identical whereas the other two chelate rings (Cu–S(5)–C(9)–C(10)–S(1) and Cu–S(2)–C(3)–C(4)–S(3)–C(5)–C-(6)–S(4)) are unique. However, since the rings containing S-(1)–S(5) and S(4)–S(5) are essentially identical in the Cu(II) complex while the ring containing S(1)–S(2) is different, the apparent transformations occurring in each ring upon reduction of Cu(II) to Cu(I) appear to differ slightly in each case, depending upon which Cu–S bond is ruptured.

As revealed in Table III, the S(1)–Cu–S(2) and S(4)–Cu–S(5) bond angles have expanded by a mean value of 6.1° upon reduction of Cu(II) to Cu(I) while the S(5)–Cu–S(1) angle has expanded by only 1.8°, the mean of these three angles being only 95.0° in the Cu(I) complex. The limited increases in these bond angles are obviously mandated by the constraints of the ethylene bridging groups, similar bond angles being observed in the five-membered chelate rings of other Cu(I) complexes.[17b,18]

The S(1)–Cu–S(4) and S(2)–Cu–S(5) bond angles, being relatively unconstrained, have expanded to a mean value of 114.7° in the Cu(I) species. Since these two bond angles are 91.7° and 104.8°, respectively, in the Cu(II) complex (the latter angle being enlarged due to the "bending back" of the S(5) atom), the S-(1)–Cu–S(4) angle appears to have undergone a larger expansion upon reduction of the copper.

The S(2)–Cu–S(4) bond angle, which involves *trans* coordinated sulfurs in the equatorial plane of the Cu(II) complex, decreases from 164.4° to 135.6° upon reduction of Cu(I). Although the other *trans* bond angle, S(3)–Cu–S(1), disappears when the Cu–S(3) bond ruptures upon the reduction of the copper atom, it is interesting to note that the angles formed by the S(3)–Cu–S(5) and S(3)–Cu–S(1) atoms average 133° in the Cu(I) complex being

virtually identical with the angle of the S(2)–Cu–S(4) bond.

For the most part, the Cu–S bond distances are not greatly different in the two Cu complexes. Although Cu(I) is presumably a larger ion than Cu(II), the π-bonding characteristics of sulfur and the reduction in the number of coordinate bonds in Cu(I) relative to Cu(II) doubtless contribute to shortening the average Cu–S bond length in the reduced complex. In fact, the mean Cu–S bond length in the Cu(I) complex is 0.05 Å shorter than in the Cu(II) species, largely reflected in the very short Cu–S(2) and Cu–S(4) bonds, both of which are only 2.24 Å.

**Chemical Implications.** In view of the presumed weakness of the Cu(II)–thia ether sulfur bonds, as indicated by the low stability of the Cu(II)–polythia ether complexes in solution,[24] as well as the apparent strain induced in coordinating all five donor atoms, the bonding of the fifth sulfur atom in the apical site of Cu$^{II}$-([15]aneS$_5$) is somewhat surprising. Nonetheless, both the resonance Raman measurements[39] and recent thermodynamic measurements on perchlorate adduct formation[40] imply that all five sulfurs remain coordinated to Cu(II) in aqueous solution.

At infinite dilution, Cu$^{II}$([14]aneS$_4$) and Cu$^{II}$([15]aneS$_5$) have virtually identical stability constant values (1.0 × 10$^4$ M$^{-1}$ at 25 °C) with very similar enthalpies and entropies.[40] Thus, the advantage of bonding a fifth donor atom appears to be offset by the increased strain in the latter complex (as well as changes in complex solvation). On the basis of experimental formal potential measurements, the stability constant for Cu$^I$([15]aneS$_5$) appears to be 100-fold smaller than for a similar Cu(I) complex formed with a related open-chain tetrathia ether[27] (Et$_2$-2,3,2-S$_4$), the only other polythia ether complex of Cu(I) for which four Cu–S bonds have been reasonably established.[28] These values suggest that internal strain is manifested in both the oxidized and reduced copper complexes formed with [15]aneS$_5$.

**Conclusion**

The similar structures found for Cu$^{II}$([15]aneS$_5$) and Cu$^I$-([15]aneS$_5$) lend support to the hypothesis that the large outer-sphere, self-exchange, electron-transfer rate constant observed for this system[27] reflects, at least in part, a smaller Franck–Condon barrier than normally encountered for low molecular weight copper complexes. In addition, the large open angle in the Cu(I) complex, in the area vacated by the S(3) atom, suggests that this system is also particularly amenable to inner-sphere electron-transfer mechanisms and may serve as a useful model for superoxide dismutase and other copper systems involving direct coordination to the substrate species.

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(41) Zuberbuhler, A. D. In ref 6, pp 237–258 and references therein.