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Chemistry and Crystal Structures of Mixed-Valence Copper Dithioether Complexes with All-Tetrahedral Copper

Sir:

The idea of an entatic state in biological molecules is based on the premise that metal-ion-mediated electron-transfer processes will be most rapid when structural variations between oxidation states of the metal are small.[1,2] In plastocyanin[3] the copper has tetrahedral coordination, but this geometry is rare for Cu(II), especially in nonbiological molecules.[4] We report here the preparation, properties, and crystal structure of all-tetrahedral, mixed-valence copper complexes of 2,5-dithiahexane (2,5-DTH). The stoichiometry of the complexes is $Cu_2{}^{I}Cu^{II}(2,5\text{-}DTH)_6(X)_4$ ($X = ClO_4$ and BF_4).[5] *The perchlorate salt is both shock and heat sensitive.* These deep green, mixed-valence complexes are unusual in that the preparation and crystal structures of both the red-brown, planar all-copper(II) complex of 2,5-DTH and the colorless, tetrahedral all-copper(I) complex have already been reported.[6] [Actually the structure of the 3,6-dithiaoctane (3,6-DTO) complex of copper(I) was reported owing to problems in obtaining a good crystal of the 2,5-DTH complex.]

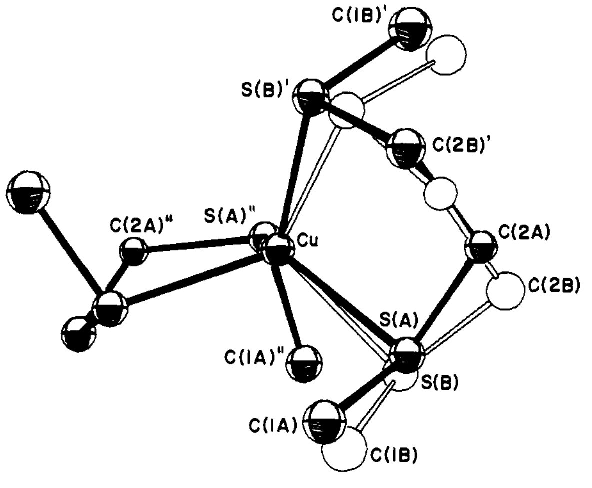

Figure 1. An ORTEP drawing of the $Cu(2,5\text{-}DTH)_2$ cation showing 15% thermal ellipsoids. The disorder in one of the ligands is shown by the unshaded atoms. The $\bar{4}$ axis bisects a line between C(2B) and C(2B)′ and passes through Cu.

The red-brown, planar Cu(II) complex was originally prepared by Flint and Goodgame[7] by treating 2,5-DTH with $Cu(ClO_4)_2$ in *ethanol* in a ratio of 3:1. Under these conditions $Cu(2,5\text{-}DTH)_2(ClO_4)_2$ precipitates immediately. Subsequent workers have followed this recipe.[8] By contrast, when the reaction is carried out in *methanol* at ~0.01 M $Cu(ClO_4)_2$ with a 2,5-DTH to copper ratio of $\leqslant 4{:}1$, the initial solution turns deep green. Then slowly, deep green, lustrous crystals of the mixed-valence complex are deposited. An X-ray diffraction study of these crystals was carried out to confirm the stoichiometry, to determine the local geometry of copper, and to see whether a cluster was present.[9]

The results for the perchlorate salt (the tetrafluoroborate is similar) reveal a local tetrahedral geometry about each copper and no distinction between Cu(I) and Cu(II) complexes. That is, Cu(I) and Cu(II) must be randomly distributed in a disordered way, and the average oxidation state of copper is 1.33. This follows because the 12 copper atoms in the unit cell must occupy one set of special positions of point symmetry $\bar{4}$ (space group $I\bar{4}3d$, cubic). In this space group the $\bar{4}$ axis passing through copper bisects the C-C bonds, and the dihedral angle between S-Cu-S planes is required to be 90°. During the solution of the structure it became apparent that the ligand either undergoes large thermal motion or is disordered. Refinement carried out with anisotropic thermal parameters for S,C(1) and C(2) yields an R index similar to that obtained for a disordered model assuming a double set of atoms assigned weights of 0.5. In a formal sense our data do not permit a distinction to be made between static and dynamic disorder. However, since the distance between disorder positions for the C atoms is only ~0.5 Å, it is unlikely that a barrier exists which would cause a static disorder. We therefore assume the disorder to be dynamic. In any event, the two models yield identical averaged geometries, and we emphasize that this disorder in no way weakens the conclusion that there is a tetrahedral arrangement of sulfur atoms about copper. Packing forces have a well-known ability to influence the coordination geometry of Cu(II) complexes and apparently that is the case here, with Cu(II) trapped in a tetrahedral lattice site. The disordered configurations observed correspond to a twist of the C-C bond and a sideways displacement of the ligand, but little motion of the sulfur. This is illustrated for one of the two ligands in Figure 1. The internal S(A)-Cu-S(B) angle is 95 (1)°, and the external angles range from 111 to 123°. The observed angle between S-Cu-S planes is 90.2°. The average Cu-S distance is 2.28 (2) Å.

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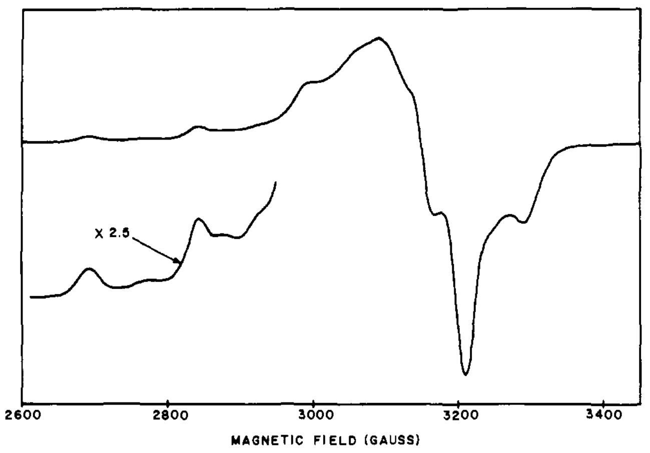

Figure 2. ESR spectrum of polycrystalline $Cu_2{}^ICu^{II}(2,5\text{-DTH})_6(ClO_4)_4$ at 77 K and frequency of 9033 MHz.

The chlorine atom of perchlorate is located at a different special position such that the 16 anions per unit cell have a 3-fold symmetry. These anions are not considered coordinated to copper since the closest approach of an oxygen to a copper atom is 3.80 (6) Å. That there is no direct copper–copper interaction is evident from the long distance [8.08 (2) Å] from a given copper atom to its eight nearest neighbors.

The chemistry of these mixed-valence complexes is also unusual. They are stable in air. The perchlorate salt dissolves in refluxing methanol with or without the exclusion of water or air to give a pale green solution. On cooling, the deep green crystals are recovered with negligible decomposition. However if excess ligand is added, or if the original reaction mixture has a 2,5-DTH to copper ratio of >4:1, the colorless copper(I) complex forms rapidly.

The visible spectrum of $Cu_2{}^ICu^{II}(2,5\text{-DTH})_6(ClO_4)_4$ as a mull exhibits a broad band with a maximum near 450 and a shoulder near 600 nm and tails into the infrared. A 10^{-2} M solution in *methanol* is completely transparent in the visible region except for end absorption in the ultraviolet. The near-infrared region is essentially transparent with only very weak absorption at ~850 nm (ϵ 15). In acetone, decomposition occurs and colorless $Cu(2,5\text{-DTH})_2ClO_4$ is isolated on evaporation.

The spectrum of planar red-brown $Cu(2,5\text{-DTH})_2(ClO_4)_2$ as a mull is somewhat similar except that the absorbance at 440 nm is more intense. $Cu(2,5\text{-DTH})_2(ClO_4)_2$ is insoluble in methanol, but after prolonged refluxing, dissolution occurs. On cooling, the mixed-valence complex precipitates. In acetone $Cu(2,5\text{-DTH})_2(ClO_4)_2$ exhibits an intense band at 430 nm (ϵ 8100) and a series of shoulders from 530 to 600 nm. However, the intensity of the 430-nm band slowly decreases suggesting that decomposition is occurring.

A most interesting phenomenon occurred when we tried to dissolve the mixed-valence complex in CH_2Cl_2. The complex initially appeared to be insoluble, but slowly the solution became brown and then turbid, and $Cu(2,5\text{-DTH})_2(ClO_4)_2$ settled out. The colorless solution was decanted from the solid and evaporated to give colorless crystals of $Cu(2,5\text{-DTH})_2ClO_4$. Thus, CH_2Cl_2 causes fractionation of the mixed-valence complex into a mixture of Cu(II) and Cu(I) complexes.

The magnetic moment of the perchlorate salt at room temperature is 1.04 μ_B; the tetrafluoroborate salt is 0.88 μ_B. The low-temperature (77 K) ESR spectrum of the perchlorate salt is shown in Figure 2.[10] The spectrum is entirely different from that of the red-brown copper(II) complex[11] and bears a strong resemblance to that of the copper proteins.[12] Further analysis of these observations is in progress.

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Supplementary Material Available: Tables of atomic positions and isotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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