

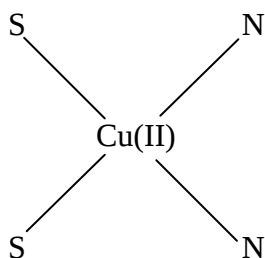
University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track
Written Qualifying Exam
June 18, 2007

Inorganic Chemistry I

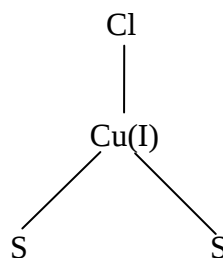
Questions are directly related to the examination paper:

“Adamantane-like Cluster Complexes of Mixed-Valent Copper-Copper and Nickel-Copper Thiolates” Matthew L. Miller, Said A. Ibrahim, Melissa L. Golden, and Marcetta Y. Darensbourg. *Inorganic Chemistry*, **2003**, 42(9), 2999-3007.

1. In the complex $\text{Cu}_6\text{S}_4\text{adam}$ the structure (see p. 5) consists of two $\text{N}_2\text{S}_2\text{Cu(II)}$ monomers bridged by four Cu(I)Cl moieties. The X-ray diffraction data suggests that the Cu(II)-S and Cu(I)-S bond distances are statistically identical. What do the authors suggest as a possible reason for this observation?
2. The authors present two ball and stick drawings side-by-side in a figure. On one side is the adamantane C_{10} core and on the other is the bridging core of the Cu_6S_4 complexes. The average bond distance in the adamantane is 1.536(5) Å with C-C-C bond angles of 109.4(7) deg. The geometries of the Cu_6S_4 core in $\text{Cu}_6\text{S}_4\text{adam}$ vary considerably from adamantane: Cu-S distance averages 2.25(2) Å and five sets of angles range (S-Cu-S and Cu-S-Cu) from 94.9 deg. to 130 deg. Give a reasonable explanation for the asymmetry of the Cu_6S_4 core.
3. In the $\text{Cu}_6\text{S}_4\text{adam}$ complex there are three metal centers with two being virtually identical. The ball and stick representations shown in figure 2 of the paper are presented below.



Cu(II) in $\text{Cu}_6\text{S}_4\text{adam}$

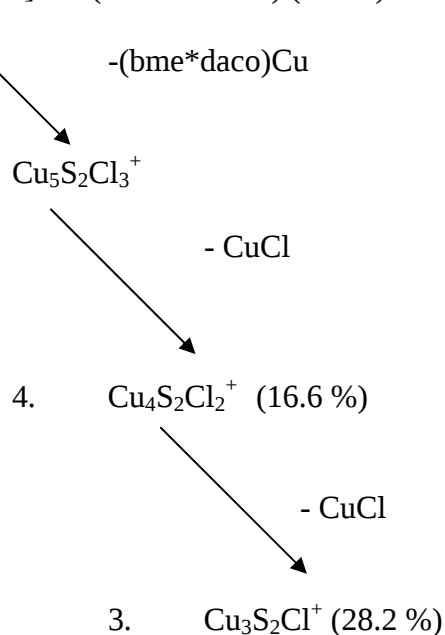
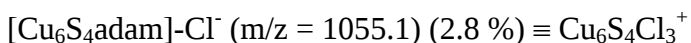


Cu(I) in $\text{Cu}_6\text{S}_4\text{adam}$

Assume that both structures are planar and that the Cu-N and Cu-S bond distances are identical. In the Cu(II) structure the both S-Cu(II)-N angles are 87.6 deg. In the Cu(I) structure the S-Cu(I)-Cl angles are identical (123 deg.).

- (a) What is the point group symmetry of each structure?
- (b) What is the point group symmetry of an ideal square planar structure (AX_4 type)?

- (c) What is the point group symmetry of an ideal triangular planar structure (AX_3 type)?
4. The X-ray structures of Cu_6S_4adam and $Ni_2Cu_4S_4adam$ are both monoclinic in space group $P2_1$. Besides solvent molecules of crystallization, both solids have two independent molecules within their asymmetric units. The number of molecules per unit cell, Z , is listed as 4. Does this mean that there are four complex molecules of each complex per unit cell? Explain?
5. Electrospray (electron spray) ionization mass spectra of the complexes are discussed. Fragmentation pathways are easily established by the isotopic patterns. The pathway is illustrated in scheme 2 for Cu_6S_4adam . One branch is shown below.



- (a) Is this a degradation or aggregation process?
- (b) What do the numbers (4 and 3) indicate in the scheme?
- (c) What do the authors suggest as a structure for the $Cu_3S_2Cl^+$? Hint: The authors use a shorthand notation for $[Cu_6S_4adam]-Cl^-$. Thus, a species written as $Cu_3S_2Cl^+$ does have a $(bme*daco)Cu$ moiety present and can also be noted as $Cu_3(bme*daco)Cl^+$.
- (d) Write the alternative formula (see part (c) above) for $Cu_4S_2Cl_2^+$?

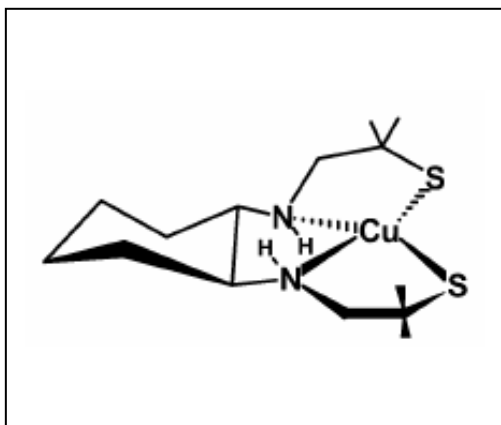
6. The bulk magnetic susceptibility of the metal complexes was measured by the Evans method in MeCN solution and verified by the Guoy method on the solid complexes.
- Give a brief explanation of the Evans and Guoy methods for measuring the magnetic susceptibility of materials?
 - The $\text{Ni}_2\text{Cu}_4\text{S}_4\text{adam}$ cluster was found to be diamagnetic. Why did the authors expect such a result? Hint: Ni(II) is strong field with square planar geometry.
 - For the $\text{Cu}_6\text{S}_4\text{adam}$ cluster the measured magnetic moment is $2.51 \mu_B$ or $1.26 \mu_B$ per Cu(II) where μ_B is the Bohr Magnetron, a standard unit of magnetic measurements. What is the spin-only magnetic moment (μ_{eff}) for a Cu(II) ion?
 - What do the authors suggest is the reason for the $1.26 \mu_B$ moment per Cu(II) measured for the complex than the larger spin-only value?
7. The electronic spectra of $\text{Cu}_6\text{S}_4\text{adam}$, a deep red solution in MeCN is described as having the following absorbance maxima:

$$\left. \begin{array}{l} 198 \text{ nm } (\epsilon = 9500 \text{ cm}^{-1}) \\ 352 \text{ nm } (\epsilon = 7000 \text{ cm}^{-1}) \end{array} \right\} L \rightarrow M \text{ charge transfer bands}$$

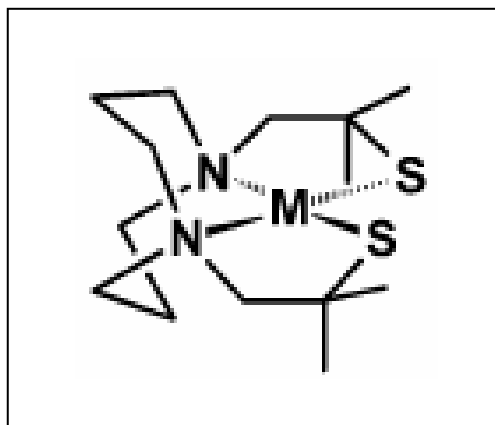
$$504 \text{ nm } (\epsilon = 590 \text{ cm}^{-1}) \left. \right\} \text{ligand field transfer}$$

- What does the term $L \rightarrow M$ charge transfer bands mean and why do these have greater extinction coefficients than the 504 band?
- What is meant by the term ligand field transition? To what metal ion might this be ascribed?
- In the complexes studied there are three metal ions Cu(I), Cu(II), and Ni(II). Which ion shows no absorbance in the typical electronic spectral range for transition metal complexes? Why doesn't this ion absorb electromagnetic radiation in this region?

8. When one examines the cyclic voltammograms of (bme*daco)Cu and the N₂S₂Cu Schugar complexes in MeCN vs NHE there is a considerable difference in their Cu(II)/Cu(I) reduction potentials. Both complexes have similar atom donors to the metal ion but the (bme*daco)Cu(II) is reduced at a more negative potential than the N₂S₂Cu(II) Schugar complex (-1.07 V versus -0.55 V respectively).



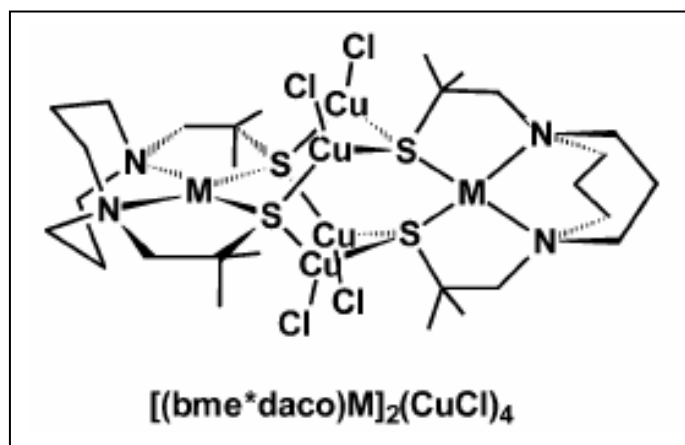
Schugar N₂S₂Cu(II) Complex



(bme*daco)Cu(II) Complex (M = Cu²⁺)

- (a) Which copper(I) complex is the better oxidizing agent?
 - (b) How do the authors explain the difference in redox behavior of the two complexes?
 - (c) In the cluster complex Cu₆S₄adam there are two reversible Cu(II)/Cu(I) reduction waves centered at -0.63 V and -0.49 V. These are assigned to Cu within the N₂S₂ coordination sphere. What does this imply about the about the two Cu(II) centers?
9. (a) At the beginning of the paper there is the following sentence, “This results in three bonds to copper(I) and divalent, bridging sulfur sites, μ_2 -SR.” What does the μ_2 mean?
- (b) Structure A in the paper is described as a tetrahedron of copper atoms that is edge-bridged by thiolate sulfur donors, i.e., producing an octahedron of S atoms inscribed onto a tetrahedron of Cu atoms. How many Cu atoms and S atoms are contained in this cluster?
10. (Green Chemistry Question) In the synthesis aspect of this work do you feel that the authors made a good attempt at preserving the tenets of green chemistry? Give a specific example to support your conclusion to the last question?

A helpful structural for reference:



When $M = Cu$ the complex is abbreviated Cu_6S_4adam or $[(bme^*daco)Cu]_2(\mu-CuCl_4)$.

When $M = Ni$ the complex is abbreviated Ni_2Cu_4adam or $[(bme^*dacoNi)]_2(\mu-CuCl_4)$.