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Structural Diversity in Copper–Sulfur Chemistry: Synthesis of Novel Cu/S Clusters through Metathesis Reactions

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With the ultimate goal of understanding the Cu_4S cluster in nitrous oxide reductase, studies of the fundamental chemistry of nitrogen-donor ligand-supported copper–sulfur species have been pursued. Reactions of $Cu^{II}X_2$ ($X = Cl^-$ or $CF_3SO_3^-$), *N*,*N*,*N′*,*N′*-tetramethyl-*trans*-(1*R*,2*R*)-diaminocyclohexane, and Li_2S or Na_2S_2 yielded clusters that contain $[Cu_2(\mu\text{-}S_2)_2]^{2+}$, $[Cu_3(\mu\text{-}S)_2]^{3+}$, $[Cu_4(\mu\text{-}S_2)_2]^{4+}$, and/or $[Cu_6(\mu\text{-}S_2)_4]^{4+}$ cores, depending on the specific reaction conditions, notably the nature of X and the sulfur source used. Copper(II) and/or Copper(III) and variable sulfur oxidation levels, including S^{2-}, S_2^{2-}, and $S_2^{-\bullet}$, were identified by X-ray crystallography and spectroscopy.

The synthesis and characterization of metal−sulfur clusters is an important area of research because of the importance of such structures in biological systems and their potential applications in catalysis.[1,2] While clusters containing iron and molybdenum have received the most attention, the discovery of the novel $[(His)_7Cu_4(\mu_4\text{-}S)]$ center in the active site of nitrous oxide reductase[3] and provocative proposals for its redox[4] and catalytic reactivity[5] have stimulated investigations of copper−sulfur complexes supported by nitrogen-donor ligands.[6,7] We have been interested in copper−sulfur species with copper at an oxidation state greater than 1+ because of the significance of mixed-valence states in the N_2OR active site; copper(I) sulfides are more common, albeit rarely with nitrogen-donor ligands.[8] The few reported structural motifs for higher oxidation state CuS compounds include $[Cu^{II}_2(\mu\text{-}S_2^{2-})]$ cores supported by bi- and tridentate nitrogen donors,[6a,d,7a,c−e] a $[Cu^{II}_2(\mu\text{-}S_2^{-\bullet})_2]^{2+}$ complex with *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (Me_4eda),[6c] and delocalized mixed-valent $[Cu^{III}Cu^{II}_2(\mu\text{-}S^{2-})_2]^{3+}$ moieties supported by Me_4eda and *N*,*N*,*N′*,*N′*-tetramethyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (Me_4chd).[6b] Similar procedures (with one exception) involving the reaction of S_8 with a suitable Cu^I precursor were used to prepare these compounds, but in certain instances, the product isolated depended dramatically on the nature of the counterion. For example, the reactions of S_8 with $[(Me_4eda)Cu(MeCN)]X$ yielded solely the $[Cu^{III}Cu^{II}_2(\mu\text{-}S^{2-})_2]^{3+}$ core for $X = SbF_6^-$ but only the $[Cu^{II}_2(\mu\text{-}S_2^{-\bullet})_2]^{2+}$ unit for $X = CF_3SO_3^-$, which were found to be coordinated to the Cu^{II} ions in the solid state.

Herein we report the results of studies using a different synthetic approach, wherein 1:1 mixtures of Me_4chd and $Cu^{II}X_2$ ($X = Cl^-$ or $CF_3SO_3^-$) salts were treated with Li_2S or Na_2S_2. Novel copper sulfide clusters of varying nuclearity were obtained, with the nature of the counterion and the sulfur source dramatically influencing the observed products.

Treatment of a 1:1 mixture of $Cu(CF_3SO_3)_2$ and Me_4chd (L, Scheme 1) in CH_2Cl_2 with either Li_2S (4 equiv) or Na_2S_2

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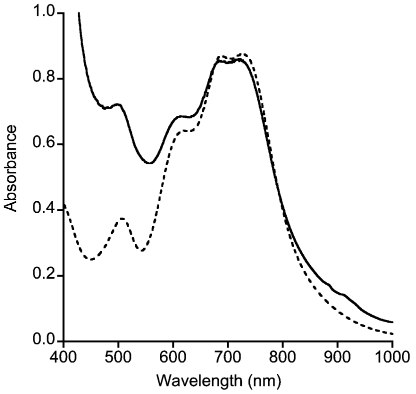
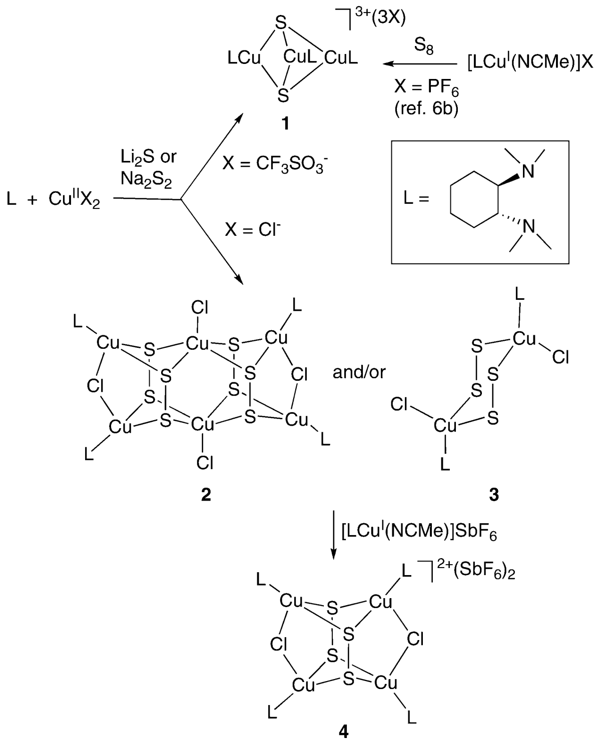


Figure 1. UV−vis spectra of the crude reaction mixtures from the reactions of L, $CuCl_2$, and Li_2S (solid line) or Na_2S_2 (dashed line). The absorbance scales are arbitrarily set so as to render the main feature at ca. 700 nm similarly intense.

Scheme 1



(2 equiv) yielded a deep-blue-green solution. Filtration followed by vapor diffusion of pentane at −20 °C yielded dark-green crystals, which were identified as $[L_3Cu_3(\mu\text{-}S^{2-})_2](CF_3SO_3)_3$ (**1**) on the basis of X-ray crystallography (Figure S1 in the Supporting Information) and CHN analysis. The structural parameters and UV−vis spectrum (Figure S2 in the Supporting Information) of **1** closely match those of the previously reported analogue with PF_6^- counterions prepared from the reaction of [LCu^I(MeCN)]PF_6 with S_8.[6b]

Different results were obtained when the above reactions were repeated using $CuCl_2$ as the metal ion source. In this case, a deep-blue solution was obtained over the course of 1 h. UV−vis spectra of the crude solutions from the reactions with Li_2S and Na_2S_2 were similar (Figure 1), suggesting that they contained comparable species in solution. The blue species were unstable at ambient temperature and decomposed with precipitation of a dark insoluble solid if allowed to react for prolonged times (>1−2 h). When the reaction time was limited and pentane was allowed to diffuse into the reaction solution at −20 °C, a mixture of dark-blue and colorless crystals was obtained. Unfortunately, this hindered isolation of the blue materials in analytically pure form. Nonetheless, X-ray structural data were acquired on selected crystals from each reaction (Figure 2).

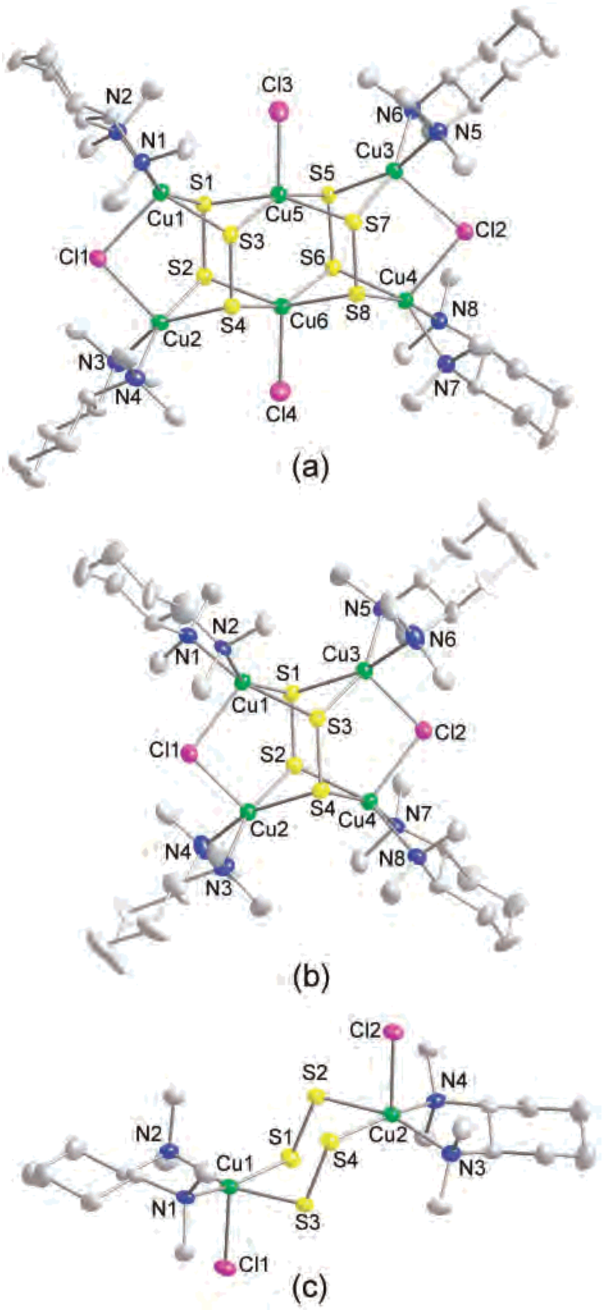


Figure 2. Molecular structures of (a) **2**, (b) the cationic portion of **4**, and (c) **3** (50% thermal ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å): For **2**: S1−S2, 2.0032(13); S3−S4, 2.0028(13); S5−S6, 2.0070(13); S7−S8, 2.0011(13); Cu1−S1, 2.3277(10); Cu1−S3, 2.3320(10); Cu1−N1, 2.148(3); Cu1−N2, 2.140(3); Cu1−Cl1, 2.4621(10). For **4**: S1−S2, 1.984(5); S3−S4, 2.008(5); Cu1−S1, 2.363(4); Cu1−S3, 2.361(4); Cu2−S2, 2.329(4); Cu2−S4, 2.384(4); Cu3−S1, 2.360(4); Cu3−S3, 2.380(4); Cu4−S2, 2.378(4); Cu4−S4, 2.358(4); Cu1−N1, 2.146(12); Cu1−N2, 2.141(11); Cu1−Cl1, 2.396(4). For **3**: S1−S2, 1.9546(19); S3−S4, 1.9528(19); Cu1−Cl1, 2.4849(15); Cu2−Cl2, 2.4780(15); Cu1−N1, 2.065(4); Cu1−N2, 2.047(4); Cu2−N3, 2.085(4); Cu2−N4, 2.020(5).

The novel cluster $[L_4Cu_6(\mu\text{-}S_2)_4Cl_4]$ (**2**) was obtained from the reaction with Li_2S (Figure 2a). The six copper ions present in **2** are coordinated in a distorted square-pyramidal fashion; four are ligated by a Me_4chd ligand, while the other two are bonded to four S_2^{2-} ligands and one chloride. All six Cu−S bond lengths are ∼2.31−2.38 Å, with those of the face-centered copper ions being slightly longer than those with Me_4chd ligation. Two chloride ions bridge between two copper centers, and two are terminally bound to a single copper ion. The S_2 moieties have S−S bond lengths of ∼2.00 Å. While somewhat short, these are most consistent with a single-bonded S_2^{2-} species (typical S−S single bonds range from 2.01 to 2.06 Å).[9] The four S_2^{2-} anions are each coordinated to four different copper centers, a configuration for S_2^{2-} units seen previously in transition-metal complexes[10] that, to our knowledge, has not been reported for copper.[11] Given the presence of four S_2^{2-} and four chloride anions, the six copper ions are all in the 2+ oxidation state. Indeed, the average Cu−N bond length of ∼2.14 Å is consistent with this assignment.[6c]

In order to form each disulfide S−S bond in **2** from the reaction with Li_2S, two electrons must be lost. Thus, for each equivalent of **2** formed, eight electrons are consumed, likely through the concomitant reduction of Cu^{II} to Cu^{I}. Indeed, the loss of $^4/_7$ of the Cu^{II} ions through such a process is consistent with the low yield of the formation of **2** (crudely estimated at ∼25%). In support of this hypothesis, X-ray crystallographic analysis of a colorless crystal obtained from the reaction mixture showed it to be the three-coordinate compound $(Me_4chd)Cu^{I}Cl$ (Figure S3 in the Supporting Information). The observed disproportionation to form both S_2^{2-} and Cu^{I} could also explain the formation of cluster **1** in the reaction of $Cu(CF_3SO_3)_2$ with Li_2S, which could derive from condensation of a putative $[(Me_4chd)Cu^{I}]^+$ species containing a weakly associated $CF_3SO_3^-$ ion with a $[Cu_2S_2]^{2+}$ dimer. Such adduct formation may be inhibited by the more strongly bound chloride in $(Me_4chd)Cu^{I}Cl$, thus leading to isolation of **2** in this case. Taking a cue from this notion, a lower nuclearity cluster $[L_4Cu_4(\mu\text{-}S_2)_2Cl_2]^{2+}$ (**4**) was obtained by treating the preformed crude solution of L, $CuCl_2$, and Li_2S with 4 equiv of $[LCu^{I}(MeCN)]SbF_6$ (Figure 2b). The structural parameters of **4** are similar to those of **2**, with average S−S bond lengths of 1.99 Å and Cu−N bond lengths of ∼2.11 Å consistent with S_2^{2-} and Cu^{II} oxidation states, respectively.

Interestingly, despite the similar UV−vis features in the crude reaction solutions for the reactions of $CuCl_2$ with Li_2S and Na_2S_2, a blue crystal from the reaction with Na_2S_2 was identified as $[L_2Cu_2(\mu\text{-}S_2)_2Cl_2]$ (**3**; Figure 2c). Complex **3** is analogous to that previously reported for $[(Me_4eda)_2Cu_2(\mu\text{-}S_2)_2](CF_3SO_3)_2$,[6c] having short S−S bond lengths of 1.955(2) and 1.953(2) Å that are most consistent with $S_2^{\bullet-}$ moieties bridging two Cu^{II} centers.[12] Similarly, long Cu−N bonds (∼2.02−2.09 Å) are also consistent with a Cu^{II} oxidation state and not Cu^{III} bridged by S_2^{2-} anions. However, resonance Raman spectra (λ_{ex} values from 457 to 647 nm) of the crude reaction solutions in CH_2Cl_2 contain ν(S−S) features in variable ratios at ∼560 and ∼602 cm^{-1} (Figure S4 in the Supporting Information). The former is consistent with a $\mu\text{-}S_2^{2-}$ moiety, while the latter is indicative of the $[Cu^{II}_2(\mu\text{-}S_2^{-\bullet})_2]^{2+}$ core.[6c] Accordingly, these values closely agree with those predicted from input of the S−S distances from the X-ray crystal structures of **2** and **3** into a recently determined Badger's rule relationship (564 and 607 cm^{-1}, respectively).[6d] Taken together, the experimental evidence suggests that when either preparative procedure is followed, both **2** and **3** are present in solution.[13]

In summary, the synthetic methodology toward $Cu^{II}S$ complexes supported by nitrogen-donor ligands has been extended to include reactions of Me_4chd + Cu^{II} salts with Li_2S and Na_2S_2. This work has demonstrated that such reactions can result in the isolation of clusters having two-, three-, four-, and six-copper cores and sulfur in variable oxidation levels (S^{2-}, S_2^{2-}, and $S_2^{-\bullet}$), with the nature of the counteranion, nitrogen donor, and sulfur source impacting the predominant products obtained. The isolation of high-nuclearity nitrogen-donor-ligated CuS clusters represents important progress toward the synthesis of an accurate model of the Cu_Z site of N_2OR, which nonetheless remains a challenging target for future research.

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Supporting Information Available: Detailed experimental descriptions, spectroscopic data, and a drawing of the X-ray structure of **1** and X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] In further corroboration of this conclusion, analysis by UV-vis and resonance Raman spectroscopy of the solutions obtained by dissolution of the crystalline product mixtures from both reactions showed both compounds to be present (Figures S4−S7 in the Supporting Information).