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# A New Class of ($\mu$-$\eta^2$:$\eta^2$-Disulfido)dicopper Complexes: Synthesis, Characterization, and Disulfido Exchange

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Rare examples of ($\mu$-$\eta^2$:$\eta^2$-disulfido)dicopper complexes have been prepared from Cu(I) and Cu(II) complexes of $\beta$-diketiminate and anilido–imine supporting ligands. A novel byproduct derived from sulfur functionalization of the methine position of a $\beta$-diketiminate ligand was identified. DFT calculations on $[(LCu)_2X_2]$ (L = $\beta$-diketiminate, X = O or S) complexes rationalize the absence of a bis($\mu$-sulfido)dicopper isomer, $[Cu_2(\mu\text{-}S)_2]^{2+}$, in the synthetic reactions, yet predict that a $[Cu_2(\mu\text{-}S)_2]^0$ core is a stable product of 2-electron reduction of the $[Cu_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}S_2)]^{2+}$ unit. Exchange of the disulfido ligand was discovered upon reaction of a ($\mu$-$\eta^2$:$\eta^2$-disulfido)dicopper complex with a Cu(I) reagent.

Copper−sulfur coordination in metallobiomolecules is generally limited to copper−thiolates, as exemplified by the ubiquitous class of $Cu^{I,II}$−SR electron transfer sites (cupredoxins)[1] and the $Cu^{I}_x(SR)_y$ clusters found in metallothioneins.[2] Synthetic models of these various sites have provided extensive fundamental insights into the chemistry of Cu−SR units in a variety of supporting ligand contexts.[3] Recently, a unique, redox active tetracopper−sulfide cluster was identified in the bacterial denitrification enzyme nitrous oxide reductase ($N_2OR$)[4] and shown to be the site of $N_2O$ reduction.[5] This discovery of the first example of a multiple valence state $Cu_x(\mu\text{-}S)$ unit in biology raises many fundamental questions concerning the properties and redox behavior of discrete copper−sulfide complexes. Indeed, $Cu_x(\mu\text{-}S)$ compounds that feature low coordinate, N-donor supported copper ions with oxidation states $> +1$,[6] as found in the $N_2OR$ active site, are unknown. Likewise, synthetic protocols for disulfido complexes $[Cu_x(\mu\text{-}S_2)]$ are poorly developed, with examples limited to preparations of ($\mu$-$\eta^1$:$\eta^1$-disulfido)- and ($\mu$-$\eta^2$:$\eta^2$-disulfido)dicopper(II,II) compounds supported by tetra- and tridentate N-donors, respectively.[7−9] Herein we present preliminary results of a systematic exploratory study aimed at the preparation and characterization of high valent copper−sulfide complexes supported by low denticity N-donor ligands. We have developed preparative routes to a new class of $\mu$-$\eta^2$:$\eta^2$-disulfido complexes with bidentate N-donor ligation, examined aspects of their bonding via DFT calculations, and discovered an intriguing

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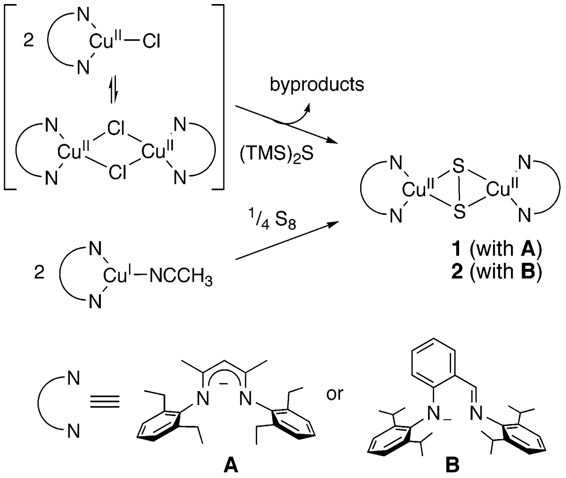
reaction between members of the class and an added $Cu^I$ complex involving exchange of the $\mu$-$S_2^{2-}$ unit.

Initial syntheses involved treatment of the complexes $[LCu^{II}Cl]_n$[10] with $(TMS)_2S$ in $CH_3CN$, using a $\beta$-diketiminate **A** or a backbone-protected analogue **B**[11] as supporting ligand L (Scheme 1). Instead of isolating targeted product(s) with Cu($\mu$-S)Cu units, however, we isolated $[(LCu)_2(\mu\text{-}S_2)]$ (**1** and **2**) in low yields (17% and 29% based on copper, respectively). Formation of the disulfido bond suggests a redox process between $Cu^{II}$ and the sulfur ligand(s). This notion was corroborated by identification of $LCu^I(CH_3CN)$[12] as a coproduct for the case L = **B** and by isolation of a small amount of a novel byproduct for the case L = **A** that was identified by X-ray crystallography (Figure 1). This byproduct (**3**) results from reduction of copper and addition of sulfur to the central methine carbon of the $\beta$-diketiminate ligand, yielding a $Cu^I_4(SR)_4$ cluster where R is a diimine−thiolate. Related derivatizations at the methine position of $\beta$-diketiminates have been reported,[13] which may be avoided by using ligands such as **B**.

**Scheme 1.** Syntheses of Complexes



Complexes **1** and **2** were more efficiently prepared by addition of $^1/_8$ equiv of $S_8$ to $LCu(CH_3CN)$[10a,12] in $CH_3CN$ (Scheme 1), providing the products in 54% and 59% isolated yields, respectively. X-ray crystal structures of both complexes (**2**, Figure 2; **1**, Figure S3, Supporting Information) show 4-coordinate, square planar metal centers with similar Cu−Cu distances (3.799(5) Å for **1** and 3.8446(16) Å for **2**) and S−S′ distances consistent with a single bond (2.2007(11) Å for **1** and 2.165(3) Å for **2**), yet longer than the S−S′ distance in the only other reported ($\mu$-$\eta^2$:$\eta^2$-disulfido)-dicopper(II,II) complex (2.073(4) Å).[8] UV−vis spectra of **1** and **2** (Figures S5 and S6, Supporting Information) contain multiple intense features tentatively ascribed to ligand based $\pi \rightarrow \pi^*$ and/or $S_2^{2-} \rightarrow Cu^{II}$ LMCT transitions,[9] but exact assignments await more detailed analysis.[14] Both **1** and **2** are EPR silent and exhibit sharp $^1$H NMR spectra, indicative of strong antiferromagnetic coupling between the $Cu^{II}$ ions.

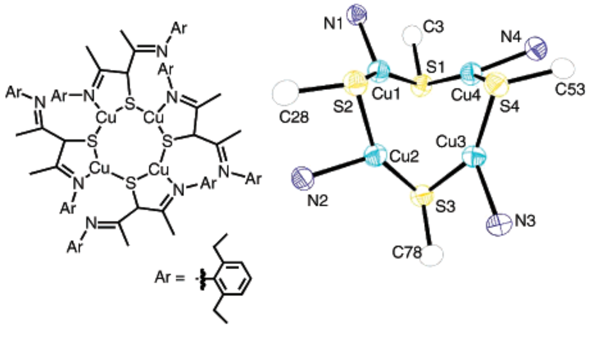


**Figure 1.** Drawing of **3** and a representation of its heteratom core from an X-ray crystal structure, shown as 50% thermal ellipsoids. See Supporting Information for interatomic distances and angles.

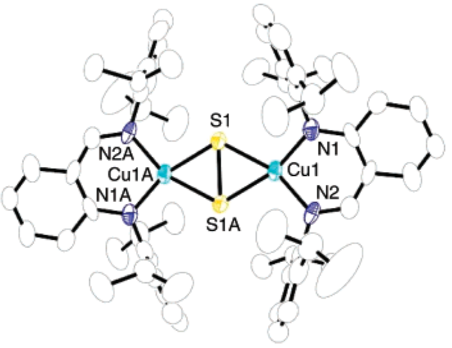


**Figure 2.** Representation of the X-ray crystal structure of **2**, with all non-hydrogen atoms shown as 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1−S1, 2.2011(17); Cu1−S1A, 2.2113(18); Cu1−N1, 1.880(5); Cu1−N2, 1.922(5); Cu1···Cu1A, 3.8446(16); S1−S1A, 2.165(3); S1−Cu1−N1, 103.5(17); S1−Cu1−N2, 158.8(17); S1A−Cu1−N1, 162.2(17); S1A−Cu1−N2, 100.1(17); N1−Cu1−N2, 97.7(2); S1−Cu1−S1A, 58.8(8); Cu1−S1−Cu1A, 121.2(7); S1A−S1−Cu1, 60.9(7).

In contrast to previous findings for oxygen analogues,[15] $[Cu_2(\mu\text{-}S)_2]^{2+}$ isomers of the $[Cu_2(\mu\text{-}S_2)]^{2+}$ cores of **1** and **2** were notably absent from the aforementioned synthetic reactions. In order to shed light on this structural preference, DFT calculations on the series $[(LCu)_2X_2]$ were performed, for X = O or S and L = the simplified $\beta$-diketiminate $HN(CH)_3NH^-$.[16,17] Two energetic minima were found for X = O, corresponding to different O−O distances (1.44 and 2.36 Å), in agreement with previous experimental and theoretical results[15] that indicate similar stabilities for some ($\mu$-$\eta^2$:$\eta^2$-peroxo)- and bis($\mu$-oxo)dicopper cores. For X = S, however, only one minimum energy structure was found with a short S−S = 2.18 Å, in close agreement with the S−S distances in **1** and **2**. This result suggests an intrinsic

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(10) (a) $[(\mathbf{A})CuCl]_n$ and $[(\mathbf{A})Cu(CH_3CN)]$: Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307. (b) $[(\mathbf{2})CuCl]_n$ exists as a 3-coordinate monomer ($n = 1$) by X-ray crystallography, but formation of a dimer at low temperature is indicated by EPR spectroscopy (Figure S4, Supporting Information).

(11) Hayes, P. G.; Welch, G. C.; Emslie, D. J. H.; Noack, C. L.; Piers, W. E.; Parvez, M. *Organometallics* **2003**, *22*, 1577.

(12) $(\mathbf{B})Cu(CH_3CN)$ was independently synthesized and fully characterized, including by an X-ray crystal structure. See Supporting Information for details.

(13) Yokota, S.; Tachi, Y.; Itoh, S. *Inorg. Chem.* **2002**, *41*, 1342 and references therein.

(14) **1**: UV−vis (THF) [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)]: 284 (16600), 328 (41400), 432 (24200), 541 (900), 806 (300). **2**: UV−vis (THF) [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$)]: 287 (31900), 448 (31600), 633 (1300), 865 (400).

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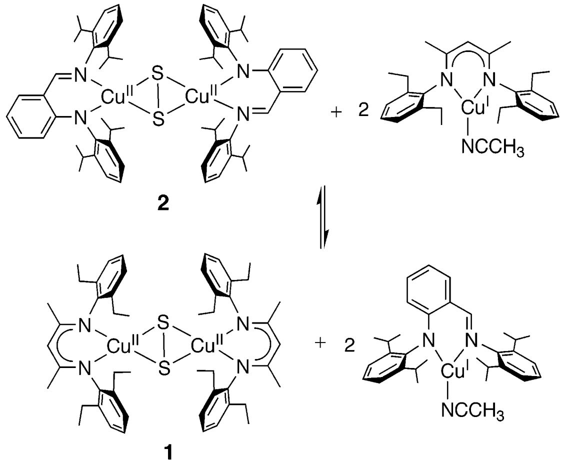
(16) See Supporting Information for details.

(17) A more complete discussion of the calculations will be presented elsewhere: Aullón, G.; Alvarez, S. Submitted for publication.

**Scheme 2.** Disulfido Exchange Reaction



instability for the $[Cu_2(\mu\text{-}S)_2]^{2+}$ core, an intriguing contrast to what has been found for isoelectronic complexes with group 10 metals.[18] On the other hand, future synthetic efforts are inspired by the additional finding that 2-electron reduction of $[(LCu)_2(\mu\text{-}S_2)]$ results in scission of the S−S bond (S−S = 3.24 Å) to yield a $[Cu_2(\mu\text{-}S)_2]^0$ core as the energetic minimum, with structural parameters (Cu−Cu = 3.34 Å, Cu−S = 2.32 Å) that are similar to those of known bis($\mu$-thiolato)dicopper(II,II) complexes (Cu−Cu = 3.34 Å, Cu−S = 2.33 Å).[19]

Finally, in an initial exploration of the reactivity of the new disulfido complexes, we discovered that treatment of **2** with (**A**)Cu($CH_3CN$) in $CH_3CN$ at room temperature cleanly generated **1** and (**B**)Cu($CH_3CN$) (Scheme 2). The unanticipated exchange process is drawn as an equilibrium because of the observation of incomplete formation of **1** when <4 equiv of (**A**)Cu($CH_3CN$) or different solvents (that solubilize all the involved species) were used. To our knowledge, the reaction in Scheme 2 is unprecedented in copper chemistry, although it resembles a recently reported[20] metal−metal exchange reaction of a ($\mu$-disulfido)dimanganese complex.[21]

In conclusion, synthetic protocols for a new class of ($\mu$-$\eta^2$:$\eta^2$-disulfido)dicopper(II,II) complexes have been developed, the lack of isomeric bis($\mu$-sulfido)dicopper(III,III) products in these reactions has been rationalized through DFT calculations, and a new disulfido exchange reaction has been discovered. Further spectroscopic, mechanistic, and reactivity studies are planned, with a view toward developing preparative routes toward $\mu$-sulfido species relevant to the $N_2OR$ active site.

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**Supporting Information Available:** Experimental details, spectroscopic data, representations of the X-ray structures of (**B**)-Cu($CH_3CN$), (**B**)CuCl, and **1**, perspective views of theoretically optimized structures, cross sections of potential energy surfaces (PDF), and X-ray crystallographic information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Adams, R. D.; Captain, B.; Kwon, O.; Miao, S. *Inorg. Chem.* **2003**, *42*, 3356.

(21) Insertion of metal units into the S−S bond of disulfido ligands is more common. For example, see: (a) Cowie, M.; DeKock, R. L.; Wagenmaker, T. R.; Seyferth, D.; Henderson, R. S.; Gallagher, M. K. *Organometallics* **1989**, *8*, 119. (b) Kuwata, S.; Mizobe, Y.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 8499. (c) Adams, R. D.; Kwon, O.; Smith, M. D. *Inorg. Chem.* **2002**, *41*, 1658. (d) Adams, R. D.; Miao, S. *Organometallics* **2003**, *22*, 2492.