# Communications

### **Bioinorganic Chemistry**

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## A $\mu$ - $\eta^2$ : $\eta^2$ -Disulfide Dicopper(II) Complex from Reaction of S<sub>8</sub> with a Copper(I) Precursor: Reactivity of the Bound Disulfur Moiety\*\*

Matthew E. Helton, Debabrata Maiti, Lev N. Zakharov, Arnold L. Rheingold, John A. Porco, Jr., and Kenneth D. Karlin\*

Copper chalcogenide compounds including clusters are of continuing interest in structural, synthetic, and materials chemistry,<sup>[1,2]</sup> while examples of copper/inorganic-sulfur

[*]	Dr. M. E. Helton, D. Maiti, Prof. K. D. Karlin Department of Chemistry Johns Hopkins University 3400 North Charles Street, Baltimore, MD 21218 (USA)
	Fax: (+ 1) 410-516-7044 E-mail: karlin@jhu.edu
	L. N. Zakharov, <sup>[+]</sup> Prof. A. L. Rheingold <sup>[+]</sup> Department of Chemistry and Biochemistry University of Delaware Newark, DE 19716 (USA)
	Prof. J. A. Porco, Jr. Department of Chemistry and Center for Chemical Methodology and Library Development Boston University Boston, MA 02215 (USA)
[+]	Current address: Department of Chemistry and Biochemistry University of California San Diego La Jolla, CA 92093 (USA)

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active-site entities in biology were recently discovered in the case of two metalloenzymes.<sup>[3,4,5]</sup> Nitrous oxide reductase (N<sub>2</sub>OR) has an active-site {(histidine)<sub>7</sub>Cu<sub>4</sub>S} cluster (called Cu<sub>z</sub>), where nitrous oxide binds and is reduced in the terminal step in bacterial denitrification (N<sub>2</sub>O + 2e<sup>-</sup> + 2H<sup>+</sup> $\rightarrow$ H<sub>2</sub>O + N<sub>2</sub>).<sup>[3,4]</sup> The other case occurs in the active site of aerobic organism carbon monoxide dehydrogenase (CO + H<sub>2</sub>O $\Rightarrow$ CO<sub>2</sub>+2H<sup>+</sup>+2e<sup>-</sup>), with a molybdopterin and copper containing Mo-S-Cu<sup>I</sup>-S<sub>cysteine</sub> moiety.<sup>[5]</sup> With these findings, there has been a surge of interest in relevant copper coordination chemistry, with goals including 1) the generation of discreet and tractable copper sulfide complexes, 2) the elucidation of their structure and spectroscopy, and 3) determination of copper sulfide compound chemistry, that is, redox and/or atom-transfer reactivity patterns.

Our own interests are focused towards chemistry potentially relevant to N<sub>2</sub>OR. We previously reported the use of elemental sulfur as a reagent to generate new copper sulfide complexes with nitrogen containing co-ligands. In the reaction of a copper(I) complex of tris(2-pyridylmethyl)amine (TMPA) with  $S_8$ , the first example of an end-on bound  $\mu$ -1,2disulfido dicopper(II) complex was discovered.<sup>[6,7]</sup> Herein, we report rather that, with a tridentate ligand, N,N-bis{2-[2methylamine (*N'*,*N'*-4-dimethylamino)pyridyl]ethyl}  $((MePY2)^{Me_2N})$ , and S<sub>8</sub> a side-on bound  $\mu$ - $\eta^2$ : $\eta^2$ -disulfido dicopper(II) compound is formed, [{Cu<sup>II</sup>(MePY2)<sup>Me<sub>2</sub>N</sup>}<sub>2</sub>- $(S_2^{2-})^{2+}$  (1). It is notable that the pattern of structures, endon versus side-on binding with a tetradentate versus tridentate ligand for copper, exactly follows that already known for peroxo dicopper(II) complexes formed in ligand-Cu<sup>I</sup>/O<sub>2</sub> reactivity investigations.<sup>[8,9]</sup> We also report the reactivity of 1 towards exogenous substrates; (reversible) displacement of bound sulfur can be effected by a number of reagents, and substrate-sulfur-atom transfer can also be demonstrated. Kitajima, Fujisawa, and co-workers have also generated a side-on bound analogue of 1 using a tridentate hydrotris(3,5diisopropyl-1-pyrazolyl)borate (HB $(3,5-iPr_2pz)_3$ ) ligand; the disulfide moiety formed through thermal decomposition (through C-S bond cleavage and follow-up chemistry) of a thiolate copper(II) complex.<sup>[10]</sup> More recently, Tolman, Alvarez, and co-workers employed bidentate β-diketiminate and anilido imine supporting ligands and ligand-copper(I) reactions with either trimethylsilylsulfide or S<sub>8</sub> to form µ- $\eta^2$ : $\eta^2$ -disulfido dicopper(II) compounds.<sup>[11]</sup> The study presented herein complements this investigation, but 1 shows a considerably more diverse reactivity than has been previously known.

The X-ray crystal structure of  $1-[B(C_6F_5)_4]_2 \cdot 2 CH_2Cl_2$ (Figure 1) reveals that the copper ions in the centrosymmetric binuclear complex are pentacoordinate, in slightly distorted square-pyramidal environments ( $\tau = 0.06$ );<sup>[12]</sup> both pyridyl nitrogen atoms (N(1) and N(4)) and the disulfur unit are equatorial ligands. The remaining alkylamino nitrogen N(3) is in the axial position. The nonbonding Cu···Cu (3.9336(10) Å) distance and the S–S (2.117(2) Å) bond in **1** fall in the middle of a relatively narrow range of values seen for the other known disulfido dicopper(II) complexes.<sup>[6,10,11]</sup>

The UV/Vis absorption spectrum of  $1-[B(C_6F_5)_4]_2 \cdot CH_2Cl_2$ in acetone at reduced temperature contains multiple features



**Figure 1.** X-ray structure of the cation of  $1-[B(C_6F_5)_4]_2 \cdot 2CH_2CI_2$  (hydrogen atoms are omitted for clarity; yellow S, green Cu, blue N, gray C). Selected bond lengths [Å] and angles [°]: S(1)–S(1A) 2.117(2), Cu(1)–S(1) 2.2249(12), Cu(1)–S(1A) 2.2420(12), Cu(1)–N(1) 1.978(4), Cu(1)–N(3) 2.225(4), Cu(1)–N(4) 1.978(4). Cu(1A)-··Cu(1) 3.9336(10); N(1)-Cu(1)-S(1) 96.53(12), N(3)-Cu(1)-S(1) 105.18(10), N(4)-Cu(1)-S(1) 151.30(11), N(1)-Cu(1)-S(1A) 147.50(12), N(3)-Cu(1)-S(1A) 104.59(10), N(4)-Cu(1)-S(1A) 98.93(11), S(1A)-S(1)-Cu(1) 62.12(5), S(1)-Cu(1)-S(1A) 56.57(5), S(1A)-S(1)-Cu(1A) 61.31(6), Cu(1)-S(1)-Cu(1A) 123.43(5).

 $\lambda \max [nm]$  ( $\varepsilon$ ,  $M^{-1}$  cm<sup>-1</sup>) at 315 (13900), 395 (3700), 460 (1850), and 630 (460). There is a noticeable difference in the charge-transfer energy and intensity for these transitions of complex **1** relative to Kitajima's<sup>[10]</sup> and Tolman's<sup>[11]</sup> complexes, most likely because the (MePY2)<sup>Me<sub>2</sub>N</sup> ligand is neutral whereas the other systems have ligands with a -1 charge.

As mentioned above, an understanding of the reactivity of copper sulfur (disulfide in this case) complexes is of considerable interest, but almost no information is yet available. Preliminary studies, the first of their kind, are described below. The reaction of 1 with PPh<sub>3</sub> leads to nearly quantitative yields of triphenylphosphine sulfide (S=PPh<sub>3</sub>; Scheme 1), assuming the reaction leads to formal "release" of zero-valent



Scheme 1. Reactivity of the {Cu<sub>2</sub>S<sub>2</sub>} core in 1 towards exogenous substrates.

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sulfur and reduction of copper ion to give  $[Cu^{I}(MePY2)^{Me_2N}]^+$ . With excess (4 equiv) PPh<sub>3</sub>, the copper(I) is trapped as the phosphine complex  $[Cu^{I}(MePY2)^{Me_2N}(PPh_3)]^+$  (2; Scheme 1). Sulfur atom transfer from 1 also occurs in a near quantitative manner (GC and GC/MS analysis) when treated with 2,6dimethylphenylisocyanide, leading to the corresponding isothiocyanate (Scheme 1). Such chemistry is known for other metal sulfur compounds.<sup>[13]</sup>

Interestingly, there is no reaction of **1** with benzyl bromide (Scheme 1). This observation, combined with the results of the PPh<sub>3</sub> and isocyanide reactivity, indicates that the disulfur moiety in **1** is electrophilic. In fact, this reactivity directly contrasts with what we otherwise observe for an end-on  $\mu$ -1,2-disulfido complex where nucleophilic chemistry occurs; with a modified TMPA ligand, TMPA<sup>R</sup>, we observe that [{Cu<sup>II</sup>-(TMPA<sup>R</sup>)}<sub>2</sub>(S<sub>2</sub>)]<sup>2+</sup>+2PhCH<sub>2</sub>Br→2[Cu<sup>II</sup>(TMPA<sup>R</sup>)Br]<sup>+</sup>+

PhCH<sub>2</sub>SSCH<sub>2</sub>Ph. Thus, our findings with ligand–Cu<sup>1</sup>/S<sub>8</sub> reactivity appear to parallel those for ligand–Cu<sup>1</sup>/O<sub>2</sub> chemistry, as side-on bound peroxo dicopper(II) complexes are generally electrophilic compared to end-on bound peroxides (e.g., as with TMPA) which are nucleophilic towards exogenous substrates.<sup>[8,14]</sup>

Other reactions also provide insight concerning the nature of the Cu<sup>II</sup> disulfide moiety in **1**. Dioxygen displaces the disulfur moiety in 1, leading to the already well established µ- $\eta^2: \eta^2$ -peroxo complex  $[{(Cu^{II}(MePY2)^{Me_2N})_2(O_2^{2-})}]^{2+} (\lambda_{max} =$ 360 nm; Scheme 1).<sup>[15]</sup> When CO is bubbled through an acetone solution of 1, the reddish color is bleached as a result of the formation of the previously reported<sup>[15]</sup> carbonyl  $[Cu<sup>I</sup>(MePY2)<sup>Me<sub>2</sub>N</sup>(CO)]^+$ complex,  $(v_{\rm CO} = 2077 \, {\rm cm}^{-1})$ (Scheme 1). That elemental sulfur is reformed in the reaction of 1 with CO is indicated by the reversible nature of the reaction. Application of a vacuum/Ar purge to the solution (which removes the carbon monoxide) leads to a change from colorless back to reddish as concomitant growth in the absorption features arising to 1 occurs. This carbonylation/ sulfur-release/CO-removal cycle can be repeated several times.

Addition of the tetradentate ligand TMPA to a THF solution of **1** causes an immediate color change to purple, the solution exhibiting a UV/Vis feature at 568 nm ascribed to the known complex [ $\{Cu^{II}(TMPA)\}_2(S_2^{2-})\}^{2+}$  (Scheme 1).<sup>[6,7]</sup> This result implies the greater thermodynamic stability of [ $\{Cu^{II}(TMPA)\}_2(S_2^{2-})\}^{2+}$  compared to [ $\{Cu^{II}(MePY2)^{Me_2N}\}_2(S_2^{2-})\}^{2+}$  (**1**) and may reside with the tetradentate (versus tridentate) nature of the ligand. Tolman and co-workers have also demonstrated related disulfide exchange reactions.<sup>[11]</sup>

In conclusion, a {Cu<sub>2</sub>S<sub>2</sub>} core with bound side-on  $\mu$ - $\eta^2$ : $\eta^2$ -S<sub>2</sub><sup>2-</sup> moiety has been synthesized and characterized and the reactivity with exogenous substrates has been explored. This represents the first example of a sulfur atom-transfer reaction from a copper sulfur moiety to substrates. Striking analogies between copper dioxygen and copper sulfur chemistry appear to be emerging. The use of elemental sulfur in reactions with ligand–copper(t) complexes seems to be a lucrative avenue for future generation of copper sulfur entities. Future investigations will include further structural–spectroscopic interrogations and elaboration of the scope of sulfur atom-transfer reactivity of this and other dicopper disulfide moieties. Redox

chemistry, including reduction of 1 or analogues, could lead to new copper sulfide species capable of  $N_2O$  reduction chemistry.<sup>[3,16]</sup>

### **Experimental Section**

Preparation of 1-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: Solid elemental sulfur (0.0045 g,  $1.75 \times 10^{-5}$  mol) was added to a stirred solution of [{Cu<sup>I</sup>- $((MePY2)^{Me_2N}][B(C_6F_5)_4]$  (0.150 g,  $1.40 \times 10^{-4}$  mol) prepared in dry/ deoxygenated CH<sub>2</sub>Cl<sub>2</sub> (5 mL). The color of the solution changed from near-colorless to dark red-brown over the course of a few hours; this solution was allowed to stir for at least 1 day. Addition of dry/ deoxygenated pentane (75 mL) precipitated dark colored solid 1 which was collected by filtration through a coarse porosity Schlenk filter-frit. The solid was redissolved in CH2Cl2 and filtered through a KimWipe plugged pipette and then the solvent was removed under vacuum, and this process was repeated 5 times to confirm the removal of all residual S<sub>8</sub>. The product was finally precipitated out with pentane. After collection by filtration, the solid product [{Cu<sup>II</sup>- $(MePY2)^{Me_2N}_2(S_2^{2-})][B(C_6F_5)_4]_2 \cdot CH_2Cl_2 (0.080 g; 50\%)$  was dried under vacuum. Elemental analysis (%) calcd for  $C_{87}H_{60}B_2Cl_2Cu_2F_{40}N_{10}S_2$ : C 45.65, H 2.64, N 6.12; found: C 45.97, H 2.72, N 6.11.

X-ray crystal structure analysis of **1**-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>·2 CH<sub>2</sub>Cl<sub>2</sub>: A red crystal suitable for X-ray diffraction was obtained from dichloromethane layered with pentane. Crystal data: C<sub>88</sub>H<sub>62</sub>B<sub>2</sub>Cl<sub>4</sub>Cu<sub>2</sub>F<sub>40</sub>N<sub>10</sub>S<sub>2</sub>,  $M_r = 2374.10$ , triclinic, space group  $P\bar{1}$  (no. 2), a = 11.3778(7), b = 14.9669(9), c = 15.8101(9) Å, a = 106.7870(10),  $\beta = 103.6420(10)$ ,  $\gamma = 107.3320(10)^\circ$ , V = 2302.9(2)C<sup>3</sup>, Z = 1,  $\rho_{calcd} = 1.712$  g cm<sup>-3</sup>,  $\mu = 0.758$  mm<sup>-1</sup>, Mo<sub>Ka</sub> radiation ( $\lambda = 0.71070$  Å), T = 173 K,  $R_1 = 0.074$ ,  $R_w = 0.088$ . CCDC-283434 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

PPh<sub>3</sub> reactions: <sup>31</sup>P NMR spectroscopy of the reaction mixture of **1**-[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sub>2</sub>·2 CH<sub>2</sub>Cl<sub>2</sub> with 4 equiv PPh<sub>3</sub> in CDCl<sub>3</sub> with P(Mes)<sub>3</sub> as reference: (400 MHz); δ = 43.92 (S=PPh<sub>3</sub>), -1.69 (**2**), -4.62 (PPh<sub>3</sub>), -35.91 ppm (P(Mes)<sub>3</sub>). On the basis of integration, the ratio of S= PPh<sub>3</sub>/[**2**+PPh<sub>3</sub>] ≈ 1:1.2 showed the reaction yield was 91 %. <sup>31</sup>P NMR, **2** in CDCl<sub>3</sub> with P(Mes)<sub>3</sub> as reference (400 MHz): δ = -1.72(**2**), -35.92 ppm (P(Mes)<sub>3</sub>). <sup>1</sup>H NMR, **2** in CDCl<sub>3</sub> (400 MHz): δ = 7.8 (2H, d, *J* = 6.0 Hz), 7.41–7.34 (15H, m, PPh<sub>3</sub>), 6.29 (2H, d, *J* = 2.8 Hz), 6.25 (2H, d, *J* = 6.4 Hz), 2.97 (8H, m), 2.57 (8H, m), 2.26 ppm (3H, s). Elemental analysis (%) calcd for [Cu<sup>1</sup>(MePY2)<sup>Me<sub>2</sub>N</sup>(PPh<sub>3</sub>)]-(B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>)·(C<sub>5</sub>H<sub>12</sub>)<sub>0.9</sub>: C 56.30, H 3.95, N 5.01; found: 56.24, H 3.82, N 4.89.

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