Bioinorganic Chemistry

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Characterization of a Complex Comprising a $\{Cu_2(S_2)_2\}^{2+}$ Core: Bis(μ-S_2^{2-})dicopper(III) or Bis(μ-$S_2^{\bullet-}$)dicopper(II)?[**]

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Copper–sulfur interactions play a critical role in the function of several classes of biological molecules, with the soft, polarizable nature of sulfur being uniquely suited for modulating the electronic structure and reactivity of copper-protein active sites. For example, copper–thiolate bonds with significant covalent character in type 1 monocopper and

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mixed-valent dicopper "Cu$_A$" centers mediate electronic delocalization, which facilitates electron-transfer reactions.[1] The inorganic sulfur recently identified in the "Cu$_Z$" site of nitrous oxide reductase, which features four copper ions linked by a μ$_4$-sulfido ligand and attached to the protein through multiple histidine imidazolyl ligands, has also been postulated to play a role in electronic delocalization.[2,3] To gain insight into the properties of the unique "Cu$_Z$" catalytic cluster through the study of synthetic model complexes, the chemistry of copper–sulfur complexes containing N-donor ligands needs to be developed. In efforts towards this aim, complexes with (μ-η^2:η^2-disulfido(2-))dicopper(II)[4a,b] or (*trans*-μ-1,2-disulfido(2-))dicopper(II)[4c,d] cores have been isolated by using sterically bulky multidentate N-donor coligands. We recently discovered that reactions of the copper(I) complexes [Cu(tmeda)(MeCN)]SbF$_6$ (**1a**) and [Cu(tmchd)(MeCN)]PF$_6$ with S$_8$ yield clusters with fully delocalized mixed-valent {Cu$_3$(μ-S)$_2$}$^{3+}$ cores (Scheme 1).[5,6] Herein, we report that the reaction of [Cu(tmeda)(MeCN)]OTf (**1b**)[5] with S$_8$ instead yields a complex with a heterocyclic {Cu$_2$(μ-1,2-S$_2$)$_2$}$^{2+}$ core,[7] for which an unexpected electronic structure is proposed on the basis of structural and spectroscopic data.

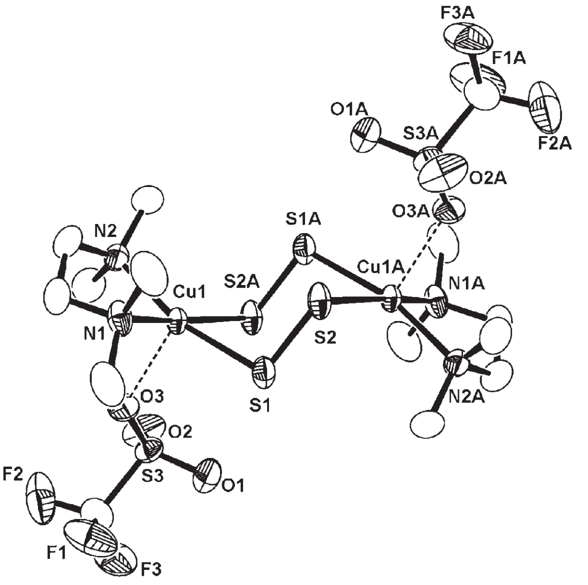
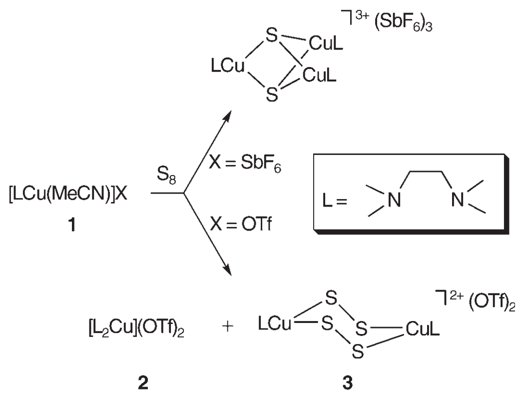


Figure 1. Molecular structure of **3** (50% ellipsoids, H atoms excluded, only heteroatoms labeled). Selected interatomic distances [Å]: S1-S2, 1.9500(13); Cu1-S1, 2.2696(11); Cu1-S, 2.2729(12); Cu1-N1, 2.032(3); Cu1-N2, 2.058(3); Cu1-O3, 2.304(2).



Scheme 1.

The addition of excess elemental sulfur (4 equiv) to a colorless solution of **1b** in THF or CH$_2$Cl$_2$ at room temperature resulted in the gradual development of a deep-blue color. Two products were isolated from the reaction mixture by removal of solvent, filtration, and fractional crystallization/precipitation, and were structurally characterized by X-ray diffraction (Scheme 1).[8] The blue–green complex [Cu(tmeda)$_2$](OTf)$_2$ (**2**, see Supporting Information) is a minor product (13% yield) that apparently derives from partial disproportionation of **1b**, as small amounts of metallic copper were also observed. The dark-blue complex [Cu$_2$(tmeda)$_2$(μ-1,2-S$_2$)$_2$](OTf)$_2$ (**3**, Figure 1) was isolated in 63% yield, and features two square-pyramidal copper centers, each with two S and two N donors occupying equatorial positions and a weakly coordinated axial triflate anion.

In assessing the structural parameters for **3**, two extreme resonance formulations may be considered for its {Cu$_2$(μ-1,2-S$_2$)$_2$}$^{2+}$ core: two Cu$^{\mathrm{III}}$ ions bridged by disulfide(2-) ions (S$_2^{2-}$), or two Cu$^{\mathrm{II}}$ ions bridged by disulfide(•1−) ions (S$_2^{\bullet-}$).[9] Similar resonance forms have been invoked in ruthenium and iron complexes.[7d,10] The Cu–N bond lengths in **3** of 2.032(3) and 2.058(3) Å are significantly longer than those in Cu$^{\mathrm{III}}$ complexes with similar diamine ligands (Cu–N $\approx$1.93 Å),[11] and are more consistent with those in Cu$^{\mathrm{II}}$–N(amine) complexes (Cu–N 2.06–2.17 Å in **2**). The S–S bond length in **3** is 1.950(1) Å, which falls between that of free S$_2$ (S=S 1.892 Å) and H$_2$S$_2$ (S–S 2.055 Å).[12] As a comparison, the S–S bonds in transition-metal μ-1,2-disulfido(2-) complexes typically range from 2.01 to 2.06 Å;[7,10a,b,d,13,14] the only structurally characterized (*trans*-μ-1,2 disulfido(2-))dicopper(II) complex has a S–S bond length of 2.044 Å.[4c] In summary, the X-ray structural data are most consistent with a bis(μ-disulfido-(•1−))dicopper(II) formulation for **3**.

Further insight is provided by spectroscopic data. Complex **3** is EPR silent (X-band, 20 K) and exhibits a sharp, well-resolved ^{1}H NMR spectrum, indicative of a diamagnetic ground state; this is consistent with either resonance formulation if one invokes strong antiferromagnetic coupling in the case of the bis(μ-disulfido(•1−))dicopper(II) species. The UV/Vis spectrum of **3** in THF at 25 °C has intense absorption features at 251 ($\varepsilon = 11\,000\,\mathrm{M^{-1}cm^{-1}}$), 394 ($\varepsilon = 9000\,\mathrm{M^{-1}cm^{-1}}$), and 575 nm ($\varepsilon = 6400\,\mathrm{M^{-1}cm^{-1}}$), which bleach upon exposure to air (Figure 2a). Unlike many *trans*-disulfido(2-)-bridged complexes,[4c,9c,13e,13f,15] **3** exhibits no absorption features generally attributable to the 4-center–6-electron {M$_2$S$_2$} chromophore in the near-IR region of the spectrum. Resonance Raman spectra (Figure 2b) of a frozen solution of **3** in THF obtained by using 514.5-nm laser excitation wavelength reveal strong S-isotope sensitive bands at 613 and 336 cm^{-1} that are consistent with ν(S–S) and ν(Cu–S) vibrations, respectively ($\Delta^{34}\mathrm{S}_{\mathrm{exptl}} = 19$ and 9 cm^{-1}; $\Delta^{34}\mathrm{S}_{\mathrm{calcd}} = 18$ and 7 cm^{-1}). The ν(S–S) vibration at 613 cm^{-1} is at a much higher wavenumber

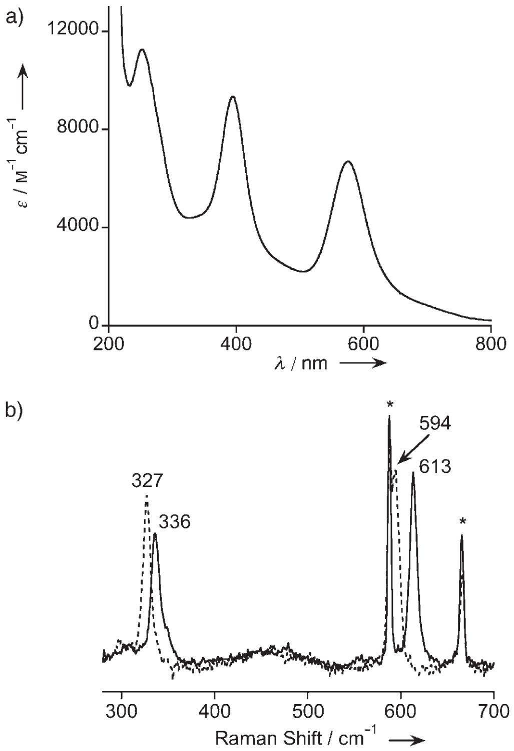


Figure 2. a) UV/Vis spectrum of **3** in THF at 25 °C. b) Resonance Raman spectrum of **3** in THF at −196 °C, $\lambda_{ex} = 514.5$ nm (^{32}S, solid line; ^{34}S, dashed line; asterisks indicate peaks arising from the solvent).

than that normally observed in μ-disulfido(2-) complexes,[9b,g,14c,16] including dicopper examples, which have ν(S–S) vibrations in the range from around 450 to 500 cm^{-1}.[4] Indeed, comparison with published ν(S–S) values for Na_2S_2 (446 cm^{-1}),[17] $S_2^{\bullet-}$ (601 cm^{-1}),[18] and doubly bonded S_2 (718 cm^{-1})[19] clearly supports a $S_2^{\bullet-}$ formulation for the bridging ligands in **3**.

In summary, the combined structural and spectroscopic data indicate that **3** is best described as a bis(μ-disulfido(•1−))dicopper(II) complex,[9] which represents a new motif in copper–sulfur chemistry. The lack of further reduction of the sulfur ligands to yield a bis(μ-disulfido(2-))dicopper(III) species can be rationalized on the basis of the relatively low electronegativity of sulfur (relative to that of oxygen). A further intriguing aspect is the fact that **3** is the major product of the reaction of S_8 with **1b**, but under identical conditions, the reaction with **1a** yields the mixed-valent cluster $[Cu_3S_2(tmeda)_3](SbF_6)_3$.[5] The better coordinating ability of OTf^- relative to that of SbF_6^- may be in part responsible for the divergent reactivity, but the nature of the N-donor ligand also is important, as both the PF_6^- and OTf^- salts of $[Cu(tmchd)(MeCN)]^+$ yield the bis(μ-sulfido)tricopper cluster.[20] Future studies will address this effect of counterion, as well as aspects of the reactivity of **3**.

Experimental Section

All solvents and reagents were obtained from commercial sources and used as received unless noted otherwise. The solvents tetrahydrofuran (THF), pentane, diethyl ether, and dichloromethane were passed through solvent purification columns (Glass Contour, Laguna, CA) prior to use. All metal complexes were prepared and stored in a Vacuum Atmospheres inert-atmosphere glove box under a dry nitrogen atmosphere or were manipulated by using standard Schlenk line techniques. Labeled elemental sulfur (^{34}S, 99 % enrichment) was purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded on a Varian VI-300 or VXR-300 spectrometer. Chemical shifts (δ) for ^{1}H or ^{13}C NMR spectra were referenced to residual protons in the deuterated solvent. UV/Vis spectra were recorded on a HP8453 (190–1100 nm) diode-array spectrophotometer. X-band EPR spectra were recorded on a Bruker E-500 spectrometer with an Oxford Instruments EPR-10 liquid-helium cryostat. Resonance Raman spectra were recorded on an Acton 506 spectrometer by using a Princeton Instruments LN/CCD-11100-PB/UVAR detector and ST-1385 controller interfaced with Winspec software. The spectra were obtained at −196 °C by using a back-scattering geometry. Samples were frozen in an NMR tube by submersion in a dewar flask containing liquid nitrogen. Raman shifts were externally referenced to liquid indene. ESI mass spectra were obtained on a Bruker BioTOF II spectrometer. The ligand tmeda was purchased from Aldrich Chemical Co. and used as received. The complex $[Cu(MeCN)_4]OTf$ was prepared according to a published procedure.[21] Crystallographic information on **2** are listed in the Supporting Information.

[Cu(tmeda)(MeCN)]OTf (**1b**): A solution of tmeda (0.055 g, 0.47 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $[Cu(MeCN)_4]OTf$ (0.160 g, 0.43 mmol) in CH_2Cl_2 (4 mL). The reaction was stirred for 30 minutes, filtered through celite, and the filtrate concentrated under reduced pressure to approximately 2 mL. Addition of pentane (10 mL) resulted in the precipitation of a white solid, which was collected, washed with diethyl ether (3 × 5 mL), and dried under vacuum. Yield: 148 mg (93 %); ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 2.56 (s, 4 H), 2.52 (s, 12 H), 2.23 ppm (s, 3 H); ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 120.7 ($J_{C,F} = 320$ Hz), 115.9, 57.9, 48.1, 2.1 ppm; ESIMS: calcd for $[Cu(tmeda)(MeCN)]^+$: *m/z* 220.0870; found: 220.0853.

$[Cu_2(S_2)_2(tmeda)_2](OTf)_2$ (**3**): Elemental sulfur (0.117 g, 0.46 mmol) was added to a solution of **1b** (0.170 g, 0.46 mmol) in THF (15 mL). The solution was stirred for 18 h at room temperature, during which time it turned deep blue. The solvent was removed by vacuum and the resulting residue was extracted with THF (10 mL) and filtered through celite. The filtrate was placed in a freezer at −20 °C overnight. Two different forms of crystals of **2** were formed, along with excess sulfur, which were collected by filtration and separated mechanically (0.035 g, 13 % yield). Elemental analysis (%) calcd for $C_{14}H_{32}N_4CuS_2O_6F_6$ (**2**): C 28.30, H 5.43, N 9.43; found: C 27.70, H 5.14, N 9.13. The solvent was removed from the filtrate in vacuo to give **3** as a dark blue powder. The solid was washed with diethyl ether (2 × 5 mL) and dried under vacuum. Purple crystals of **3** were grown from a solution in THF by slow diffusion of pentane at −20 °C. Yield: 115 mg (63 %); ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 2.49 (s, 8 H), 2.37 ppm (s, 24 H); UV/Vis (THF): λ_{max} (ε, M^{-1}cm^{-1}) = 251 (11 000), 394 (9000), 575 nm (6400); elemental analysis (%) calcd for $C_{14}H_{32}N_4Cu_2S_6O_6F_6$ (**3**): C 21.40, H 4.10, N 7.13; found: C 21.84, H 4.05, N 6.94.

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[5] Abbreviations used: tmeda = *N,N,N′,N′*-tetramethylethylenediamine; tmchd = *N,N,N′,N′*-tetramethylcyclohexane-1,2-diamine; OTf = trifluoromethanesulfonate.

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[8] X-ray structural analysis of **3**: An X-ray quality crystal was mounted on a Siemens SMART Platform CCD diffractometer for data collection. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.84 Å. The intensity data were corrected for absorption and decay by using SADABS (R. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33). Final cell constants were calculated from the *xyz* centroids of strong reflections from the actual data collection after integration with SAINT (SAINT version 6.2, Bruker Analytical X-ray Systems, Madison, WI, **2001**). The structure was solved by direct methods with SHELXL97 software (SHELXTL version 6.10, Bruker Analytical X-Ray Systems, Madison, WI, **2000**). Full-matrix least-squares/difference Fourier cycles were performed by using SHELXL97 software, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. $C_{14}H_{32}N_4F_6O_6S_6Cu_2$, $M_r = 785.88$, monoclinic, space group $P2(1)/n$, $a = 8.697(5)$, $b = 13.269(5)$, $c = 13.029(5)$ Å, $\beta = 92.481(5)°$, $V = 1502.1(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.737$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71069$ Å, $T = 173(2)$ K, crystal dimensions $0.25 \times 0.25 \times 0.20$ mm^3, $\mu(Mo_{K\alpha}) = 1.906$ mm^{-1}, θ range from 2.19 to 25.06°, 7497 measured reflections, 2651 independent reflections ($R_{int} = 0.0243$), R_1 ($I > 2\sigma(I) = 0.0314$), wR_2 ($I > 2\sigma(I)) = 0.0710$, GOF = 1.027, 172 parameters, final difference map within 0.569 and -0.230 e Å^{-3}. The crystallographic data for the two forms of **2** are given in the Supporting Information. CCDC-282801–282803 contain 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.

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