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Fine Tuning of the Interaction between the Copper(I) and Disulfide Bond. Formation of a Bis(μ-thiolato)dicopper(II) Complex by Reductive Cleavage of the Disulfide Bond with Copper(I)

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Reactivity of transition-metal ions is finely tuned to accomplish a variety of chemical functions by changing the ligand environments. In recent model studies of non-heme metalloenzymes, great efforts have so far been focused on the development of novel ligands that can reproduce not only the structures and physicochemical properties but also the chemical functions of the enzyme active centers.[1−3] The most prominent example of fine-tuning of the ligand causing a drastic change in the structure and metal oxidation state is found in copper/dioxygen chemistry with TPA [tris(2-pyridylmethyl)amine] derivatives as the ligands. The reaction of the copper(I) complex of TPA itself afforded a (μ-1,2-peroxo)dicopper(II) complex in the reaction with O_2 at a low temperature,[4] while introduction of the 6-methyl group into two of the three pyridine nuclei of the ligand (Me_2TPA, bis(6-methyl-2-pyridinyl-methyl)(2-pyridinylmethyl)amine) resulted in formation of a bis(μ-oxo)dicopper(III) complex under similar reaction conditions.[5] In this case, a small perturbation in the ligand triggers a drastic change in the oxidation state of metal center (II or III) and oxygen (peroxo or oxo). A similar situation may also be expected for copper/thiolate or copper/sulfide chemistry, since both copper(I)−disulfide and bis(μ-thiolato)dicopper(II) complexes are known to be formed depending on different types of thiolate ligands.[6−8] Although the former case is commonly observed,[6,7] the latter is extremely rare and only one example is known for a bis(μ-thiolato)dicopper(II) complex.[8] A thiolate-bridged mixed-valance dicopper(I,II) complex has also merited considerable interest as a model of the Cu_A biological electron-transfer site of cytochrome *c* oxidase (*Cc*O) and nitrous oxide reductase (N_2OR).[9,10] However, there has so far been no example of a small perturbation in the disulfide ligand causing a drastic change in the oxidation state of copper from a dicopper(I) complex bridged by a disulfide group to a bis(μ-thiolato)dicopper(II) complex.

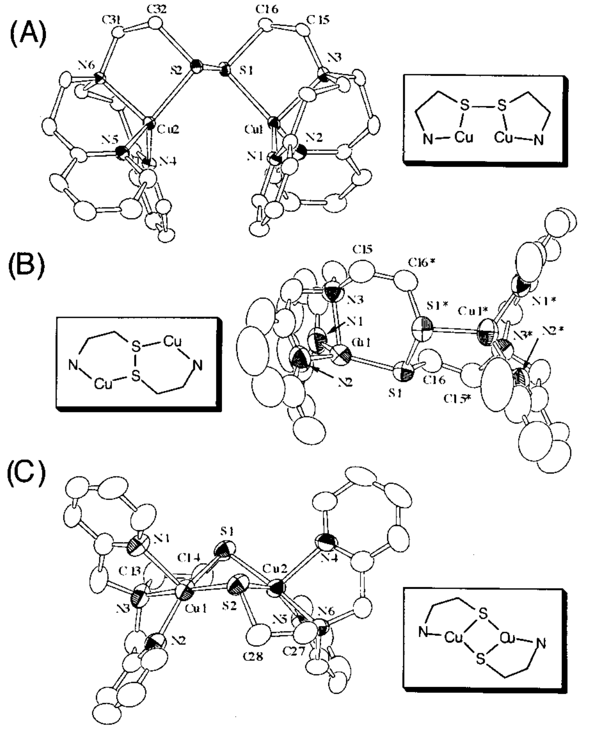
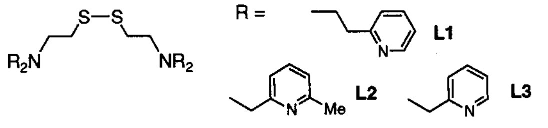


Figure 1. ORTEP drawings of the cationic part of **1** (A), **2** (B), and **3** (C). The counteranions and hydrogen atoms are omitted for clarity.

Chart 1



Herein we report such an example in the redox interaction between the copper(I) and disulfide group using a series of dinucleating ligands **L1**−**L3** leading to a drastic change in the redox states of the sulfur atoms (disulfide vs thiolate) and the metal ions [Cu(I) vs Cu(II)] as well as the coordination geometry of the metal centers depending on the structure of the metal-binding sites. The bis(μ-thiolato)dicopper(II) core of complex **3** generated by using **L3** is regarded as a model for the Cu_A site of cytochrome *c* oxidase (*Cc*O) and nitrous oxide reductase (NOR),[10] the spectroscopic features of which are compared to those of the reported model complex.[8]

Treatment of the ligands with 2 equiv of $[Cu^I(MeCN)_4]ClO_4$ in acetonitrile (MeCN) under anaerobic conditions gave three different types of dinuclear copper complexes **1**−**3**.[11] Complex **1** is a dinuclear copper(I) complex in which the two Cu(I) ions are bridged by the disulfide unit as shown in Figure 1A. It has an approximate *C*2 symmetry and both copper ions have a distorted tetrahedral geometry. The S−S distance in **1** is 2.07 Å, which is a little longer than that of aliphatic disulfide (2.04 Å),[12] while the Cu−S bond lengths are 2.27 and 2.26 Å, which are slightly shorter than the reported Cu−S distances of 2.28−2.40 Å in

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disulfide copper(I) complexes.[7] The dihedral angle of C(16)−S(1)−S(2)−C(32) is 82.2°, which is somewhat smaller than the typical value of aliphatic disulfides (ca. 90∼100°).[12] The overall structure of **1** is fairly close to that of the dicopper(I)−disulfide complex recently reported by Ohta et al.[6]

A significant structural change of the copper(I)−disulfide complex was observed when ligand **L2** was employed (Figure 1B). Complex **2** has a *C2* symmetry, but the coordination mode of the disulfide moiety to the copper ions is totally opposite to the case of complex **1**. Namely, each Cu(I) is coordinated by one of the sulfur atoms of the disulfide group at the distal position, making two six-membered chelation rings [Cu(1)−N(3)−C(15)−(C16*)−S(1*)−S(1) and Cu(1*)−N(3*)−C(15*)−(C16)−S(1)−S(1*)]. In this case, the S−S bond is further elongated to 2.08 Å, while the Cu−S bonds are slightly shortened (2.20 Å) as compared to complex **1** (2.27 and 2.26 Å). As a result, the tetrahedral geometry of the copper(I) center is further distorted to reach a distorted trigonal pyramidal structure, in which the basal plane consists of two pyridine nitrogen atoms [N(1) and N(2)] and one of the sulfur atoms [S(1)] and the axial position is occupied by the tertiary amine nitrogen [N(3)]. The dihedral angle of C(16)−S(1)−S(1*)−C(16*) decreases further to be 64.4°. Although there seems to be no direct interaction between Cu(1) and S(1*) or between Cu(1*) and S(1) (the distance of Cu(1)···S(1*) is 3.30 Å), complex **2** looks like an intermediate in going from complex **1** to complex **3** (vide infra).

In contrast to **L1** and **L2**, the S−S bond in **L3** was reductively cleaved to afford a bis(μ-thiolato)dicopper(II) complex as shown in Figure 1C. The distance of the two sulfur atoms is 3.18 Å and the two copper ions come closer to each other: the Cu···Cu distance is 2.96 Å, which is significantly shorter than those of **1** (3.91 Å) and **2** (5.16 Å). The bis(μ-thiolato)dicopper(II) core is bent about 36° along the S−S axis, and the geometry of the copper center is distorted square pyramidal ($\tau = 0.34$ and 0.36 for Cu(1) and Cu(2), respectively),[13] where each basal plane consists of one of the pyridine atoms [N(2), N(5)], a tertiary amine nitrogen [N(3), N(6)], and two bridging sulfur atoms [S(1) and S(2)] and the axial position is occupied by another pyridine nitrogen [N(1), N(4)]. The two Cu−N axial bonds are adopted to a *cis* configuration. The overall structure of **3** resembles that of the bis(μ-thiolato)-dicopper(II) complex (**4**) with the 2-(4,7-diisopropyl-[1,4,7]-triazonan-1-yl)ethanethiol ligand reported by Tolman et al as a model for the Cu$_A$ site of C*c*O and NOR.[8]

Complexes **1**−**3** are ESR inactive but show distinct NMR spectra.[14] Diamagnetism of the dinuclear copper(II) complex (**3**) is consistent with an expected strong magnetic interaction between the two cupric ions in the bis(μ-thiolato)dicopper(II) core (Figure 1C). The dicopper(I) complexes **1** and **2** exhibit no characteristic absorption band in the visible region, whereas an acetone solution of bis(μ-thiolato)dicopper(II) complex **3** (1.0×10^{-4} M) affords a strong absorption band at 366 nm ($\epsilon = 8000$ M^{-1} cm^{-1}) together with two broad bands at 556 (500 M^{-1} cm^{-1}) and 884 nm (1200 M^{-1} cm^{-1}). The UV−vis spectral features of **3** are somewhat different from that of **4** [$\lambda_{max} = 274$ ($\epsilon = 3600$ M^{-1} cm^{-1}), 338 (3100), 382 (3600), 646 nm (670)].[8] The broad low-energy absorption band of complex **3** (884 nm) can be attributed to a thiolate-to-copper(II) charge-transfer transition.[15] The lower energy of this band (884 nm) as compared to **4** (646 nm) suggests that the coordinative interaction between the copper ion and the thiolate is stronger in **3** than in **4**, which is reflected in the shorter Cu−S bond of **3** (2.30 Å) as compared to **4** (2.33 Å).

Thus, three totally different dinuclear copper complexes **1**−**3** have been obtained in the reactions of copper(I) and a similar type of dinucleating ligands **L1**−**L3**. Complexes **1** and **2** are dicopper(I) species retaining the disulfide group of the parent ligands, but the coordination modes of the disulfide group to the two cuprous ions are significantly different (type **A** and type **B** in Figure 1). With respect to the S−S bond length and the dihedral angle of C−S−S−C, the structure of the disulfide moiety in complex **1** is fairly close to that of simple alkyl disulfides,[12] while that of complex **2** is rather distorted from the normal structure of alkyl disulfides. In the case of **L2**, where the ethylene linker between the tertiary amine nitrogen and the pyridine nucleus is replaced by the methylene linker, the type **A** coordination becomes unstable probably due to the steric repulsion between the 6-methyl groups on the pyridine nuclei of each copper binding site. In such a case, type **B** coordination would be more preferable.

Removal of the 6-methyl groups from **L2** gives **L3**, in which the donor ability of the pyridine nitrogen is increased to enhance the electron transfer from the copper(I) to the disulfide bond leading to the S−S bond scission.[16] Then, an intramolecular rearrangement occurs to produce complex **3** containing a bis(μ-thiolato)dicopper(II) core that can be regarded as a good model of the Cu$_A$ electron-transfer site of C*c*O and NOR. It is interesting to note that the structure of **2** (the type **B** coordination) looks like a snapshot of the intermediate in going from type **A** to type **C**. Interconversion between disulfides (RSSR) and two molecules of the corresponding thiolate (2 RS$^-$) has been widely utilized as a reversible redox process not only in development of functional materials but also in several biological systems. Present results will provide valuable information for the development of transition-metal sulfur clusters exhibiting biological and industrial significance.[17]

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Supporting Information Available: Experimental details including synthetic procedures of the ligand and the copper complexes, X-ray structural determination, summary of X-ray crystallographic data (Table S1), selected bond lengths and angles (Table S2), ESI-MS (Figure S1), UV-vis (Figure S2), and cyclic voltammograms (Figure S3) of the complexes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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