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Interconversion between Bis(μ-thiolato)dicopper(II) and Disulfide-Bridged Dicopper(I) Complexes Mediated by Chloride Ion

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Transition metal−sulfur bonds are ubiquitous not only in metalloenzymes but also in man-made functional materials and catalysts.[1] The majority of the sulfur atoms serve as terminal or bridging ligands for transition metal ions to construct various types of M_mS_n molecular architectures (M = transition metal).[1−3] Thus, regulation of the structure and reactivity of M_mS_n has long been an important and attractive subject in both biochemical and industrial researches.[1] With this view, electronic effects of the sulfur ligands on the structures and redox properties of the metal centers have been studied extensively.[1] However, little attention has thus far been focused on the redox chemistry of the sulfur ligands themselves in such systems.[4]

We report herein an unprecedented clean interconversion between a novel bis(μ-thiolato)dicopper(II) complex and a disulfide-bridged dicopper(I) complex mediated by chloride ion, providing a new redox chemistry in the M_mS_n systems (Scheme 1).[5] The bis(μ-thiolato)dicopper(II) core structure in compound **1** is relatively rare among the M_mS_n complexes and has recently attracted much attention as a model compound of the Cu_A sites of cytochrome *c* oxidase (C*c*O) and nitrous oxide reductase (N_2OR).[6−13]

Treatment of ligand 2L with 2 equiv of $[Cu^I(CH_3CN)_4](ClO_4)$ in acetone under anaerobic conditions (Ar) gave an air-sensitive dark brown-colored dicopper complex **1** in 81% yield.[14] The crystal structure of **1** is shown in Figure 1, which definitely confirms the bis(μ-thiolato)dicopper(II) structure.[15] Thus, the disulfide bond of ligand 2L is reductively cleaved by the reaction with two cuprous ions to generate the bis(μ-thiolato)dicopper(II) core. Complex **1** has a C_2 symmetry, and the cupric ion exhibits four-coordinate square planar geometry.[16] The Cu_2S_2 core is largely bent along the S−S axis (angle of the two least-squares planes consisted of Cu(1)−N(1)−N(2)−S(1)−S(1)* and Cu(1)*−N(1)*−N(2)*−S(1)−S(1)* is 115.5 °), and the distances between the two sulfur atoms and two cupric ions are 3.13 and 2.80 Å, respectively. These structural features of the Cu_2S_2 core of **1** is similar to those of the reported bis(μ-thiolato)dicopper(II) complexes with N_3 capping ligands, although the copper(II) center in those cases exhibits a distorted five-coordinate square pyramidal geometry.[9,13] Compound **1** is EPR-silent[17] and exhibits characteristic absorption bands at 351 nm ($\epsilon = 12\,300$ M^{-1} cm^{-1}), 516 (1200), and 813 (2400) (Spectrum a in Figure 2). The low-energy absorption band at 813 nm can be attributed to a thiolate-to-copper(II) charge-transfer transition.[18,19]

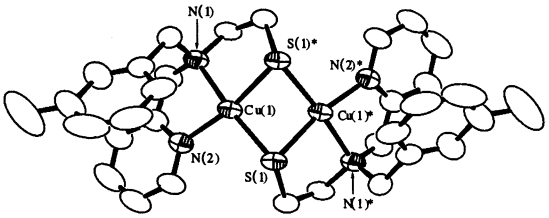


Figure 1. ORTEP drawing of **1** showing 50% probability thermal-ellipsoid. The counteranions and hydrogen atoms are omitted for clarity.

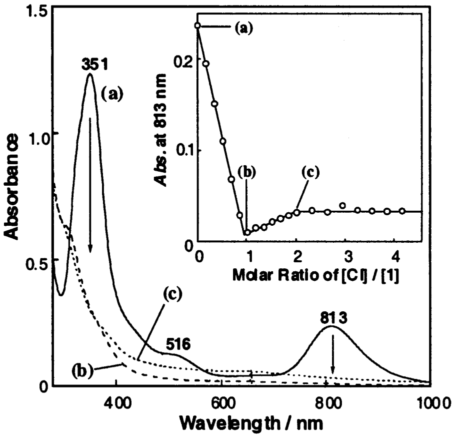
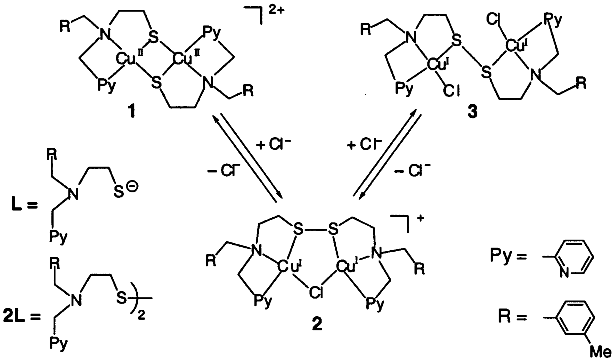


Figure 2. Spectral change for the titration of complex **1** (1.0×10^{-4} M) with $Me_4N^+Cl^-$ in CH_2Cl_2 at 25 °C: (a) spectrum of **1**, (b) Cu:Cl = 2:1, (c) Cu:Cl = 2:2. (Inset) Absorbance change at 813 nm.

Scheme 1



Addition of an external ligand such as chloride ion into a CH_2Cl_2 solution of **1** resulted in color change from dark brown to pale yellow. In Figure 2 is shown the spectral change for the titration of complex **1** with $Me_4N^+Cl^-$. Spectrum a due to **1** was converted to spectrum b, when 1 equiv of Cl^- relative to complex **1** (thus, Cu:Cl = 2:1) was added. Addition of another 1 equiv of Cl^- (totally 2 equiv, thus Cu:Cl = 2:2) gave spectrum c, whereas further addition of Cl^- did not affect spectrum c as shown in the inset of Figure 2. From the final reaction mixture of a preparative scale experiment, the product exhibiting spectrum c was successfully isolated.[14]

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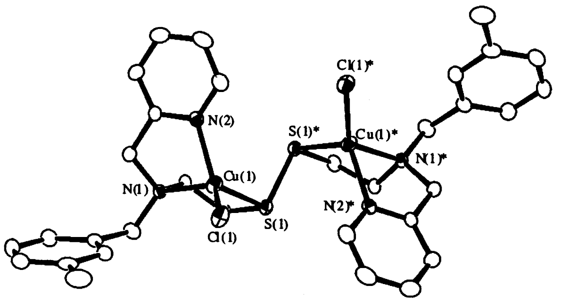

Figure 3. ORTEP drawing of **3** showing 50% probability thermal-ellipsoid. The hydrogen atoms and acetone molecules are omitted for clarity.

The product was a disulfide-bridged dicopper(I) complex [(Cu^{I}-Cl)$_2$(2L)] (**3**) as shown in Figure 3, demonstrating that the disulfide bond originally existed in the starting ligand 2L was regenerated in **3** by oxidative coupling of the thiolate groups of **1**, while the two cupric ions in **1** are reduced to the dicopper(I) state in **3**. This is reflected on the disappearance of the characteristic LMCT bands of **1** as shown in Figure 2 (spectrum c). The complex **3** also has a C_2 symmetry, and the copper(I) ions, separated by 4.11 Å each other, exhibit a distorted tetrahedral geometry with a N_2SCl donor set. The S−S and the Cu−S bond lengths are 2.07 and 2.36 Å, respectively, which are nearly the same to those of the reported disulfide copper(I) complexes.[13,20,21]

Although crystal structure of intermediate **2** has yet to be obtained, the stoichiometry of Cu:Cl = 2:1 for generation of **2** as well as the complete disappearance of the absorption bands in the visible region (spectrum b in Figure 2) suggest that it is a disulfide-bridged (μ-chloro)dicopper(I) complex as illustrated in Scheme 1.[22] In fact, the ESI-MS analysis of intermediate **2** gave a set of prominent peaks with a mass and isotope distribution pattern that is consistent with the molecular formulation of $[Cu^{I}_2(Cl)(2L)]^+$.[14]

Notably, the disulfide−dicopper(I) complex **3** was converted stepwise into the bis(μ-thiolato)dicopper(II) complex **1** through intermediate **2**, when **3** was treated with $AgBF_4$ in acetone.[23] Thus, spectrum c due to **3** was first converted to the spectrum of **2** (b in Figure 2), which further changed to the spectrum of **1** (a in Figure 2) by the gradual addition of $AgBF_4$ into an acetone solution of **3**. In this case, Ag^+ withdraws Cl^- first from **3** giving **2** and then from the resulting intermediate **2** to give **1** as indicated in Scheme 1. Thus, the conversion between **1** and **3** through **2** is reversible (Scheme 1).

Although the mechanism of each process has yet to be investigated in detail, the present result is the first example of a clean interconversion between $2RS^-$ and RSSR on a distinct dicopper unit. Coordination of the external ligand such as Cl− to the cupric ion in **1** may induce a geometric change of the copper from the square planar to tetrahedral by kicking out one of the sulfur atoms of the thiolato ligands. This may induce electron transfer from the thiolate group to Cu(II), resulting in formation of the disulfide-bridged (μ-chloro)dicopper(I) complex **2**.[22] Further addition of Cl^- to **2** gives the disulfide−dicopper(I) complex **3**. The interconversion between **1** and **3** is reminiscent of the one between the bis(μ-oxo)dicopper(III) and the (μ-η^2:η^2-peroxo)-dicopper(II) complexes, a key process in copper/dioxygen chemistry.[24,25] Thus, these results clearly demonstrate that a small perturbation in the coordination environment of the dicopper units can induce the drastic changes in the structure and redox state of the bridging sulfur and oxygen ligands.

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Supporting Information Available: Experimental details about the synthetic procedures of the ligand (2L) and the copper complexes, X-ray structural determination, summary of X-ray crystallographic data (Tables S1 and S3), selected bond lengths and angles (Tables S2 and S4), ESI-MS (Figure S1), and cyclic voltammogram of complex **1** (Figure S2) (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Synthetic procedures for the ligand and copper complexes as well as the analytical data of the products are presented in Supporting Information.
(15) There are two independent molecules of compound **1** in the unit cell of the single crystal (see, Table S2 and CIF file).
(16) The perchlorate anions exist at a position below the two copper ions in their axial direction ($Cu-O_{ClO4}$ = 2.93 and 3.07 Å for the two independent molecules of **1**, respectively).
(17) The ^1H NMR signals of **1** appear within a range between δ 1.8−16.0, indicating the antiferromagnetic nature of the dicopper(II) complex. Detailed signal assignment was, however, hampered by significant broadening of the signals.
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(19) Complex **1** exhibits reduction peaks at −0.17 and −0.49 V and oxidation peaks at 0.08 and −0.30 V vs ferrocene/ferrocenium (Figure S2). These peaks may correspond to the redox couples of Cu(II)Cu(II)/ Cu(I)Cu(II) and Cu(I)Cu(II)/Cu(I)Cu(I) of the dicopper complex, respectively.
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(22) In support of the proposed structure of **2**, the disulfide-bridged (μ-chloro)-dicopper(I) complex has been obtained using a very similar disulfide ligand (2L′); see Supporting Information (Tables S2 and S4).
(23) To dissolve $AgBF_4$ into acetone, a small amount of 18-crown-6 was added.
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