Reaction of Copper(II) Complexes with Na_2S_2. An Alternative Method for the Preparation of Disulfido–Dicopper(II) Complexes

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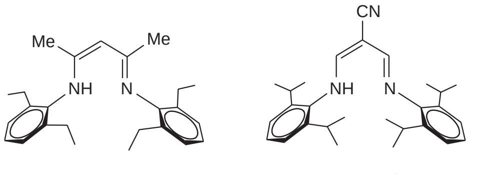
The reaction of copper(II) complexes supported by β-diketiminate ligands with Na_2S_2 has been examined as an alternative method for the preparation of (μ-η^2:η^2-disulfido)dicopper(II) complexes.

The reaction of copper(I) complexes with O_2 has been studied extensively in order to shed light on the dioxygen activation mechanism of copper proteins and numerous copper-catalyzed oxidation reactions.[1] The most frequently obtained are peroxo dicopper(II) complexes both with end-on (*trans*-μ-1,2-) and side-on (μ-η^2:η^2-) binding modes as well as bis(μ-oxo)dicopper(III) complexes (path (i) in Scheme 1).[1b,1c] The side-on peroxo dicopper(II) and the bis(μ-oxo)dicopper(III) complexes can also be generated by the reaction of copper(II) precursors with H_2O_2 in the presence of a base (path (ii) in Scheme 1).[2] The studies on the structure, physicochemical properties, and reactivity of those active-oxygen dicopper complexes have provided significantly important insights into the catalytic mechanism of type-3 copper proteins such as tyrosinase, catechol oxidase, and hemocyanin.[3]

Recently, much attention has also been paid to copper–sulfur chemistry in order to evaluate the structure and chemical functions of biological copper reaction centers involving various Cu/S clusters.[4–11] Notably, disulfido–dicopper(II) complexes (Cu_2S_2) both with the end-on and the side-on binding modes were obtained in the reactions of copper(I) complexes with elemental sulfur S_8 (path (iii) in Scheme 1), demonstrating striking analogies to the dicopper–dioxygen chemistry (path (i) in Scheme 1).[5–11] However, little attention has so far been paid to the reaction between copper(II) complexes and sulfides (reduced sulfur).

In this study, we have found that the reaction of copper(II) complexes with Na_2S_2 also afforded the disulfido–dicopper(II) complexes (Cu_2S_2) (path (iv) in Scheme 1), being analogous to the reaction between copper(II) complexes and H_2O_2 providing the dioxygen–dicopper (Cu_2O_2) complexes (path (ii) in Scheme 1). Since great success has been made in Cu^I/O_2 chemistry as well as in Cu^I/S_8 chemistry by using β-diketiminate ligands,[12] we first examined the β-diketiminate derivatives shown in Chart 1 as the supporting ligands.

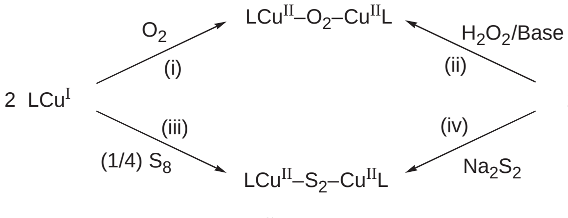


(a) $^{H,Me}L^{Dep}H$ (b) $^{CN,H}L^{Dipp}H$

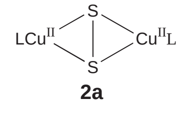
Chart 1.

Tolman and co-workers have recently demonstrated that the reaction of copper(I) complex of ligand $^{H,Me}L^{Dep}$ (deprotonated form of $^{H,Me}L^{Dep}H$) $[Cu^I(^{H,Me}L^{Dep})(CH_3CN)]$ and (1/8)S_8 in CH_3CN provides (μ-η^2:η^2-disulfido)dicopper(II) complex **2a** in a 54% yield (Scheme 2).[8] In this study, we obtained the same product **2a** in a 39% yield, when copper(II) complex $[Cu^{II}(^{H,Me}L^{Dep})(OAc)]$ (**1a**) was treated with 0.5 equiv of Na_2S_2 in CH_3CN under anaerobic conditions (Scheme 2).[13,14] The UV–vis spectrum of the isolated product [$\lambda_{max} = 331$ nm ($\varepsilon = 20500\,M^{-1}\,cm^{-1}$), 432 (8200), 541 (350), and 804 (100)] was identical to that of the reported product,[8] and the IR and the HR-MS data also supported the (μ-η^2:η^2-disulfido)dicopper(II) structure. The low yield of **2a** could be attributed to lability of the central methine carbon of the ligand framework affording hardly soluble by-products.[8,15]

A similar (μ-η^2:η^2-disulfido)dicopper(II) complex **2b** was obtained in a higher yield (78%), when $[Cu^{II}(^{CN,H}L^{Dipp})(OAc)]$ (**1b**) was reacted with Na_2S_2 under the same experimental conditions.[13,16,17] In this case, the central methine carbon of the ligand framework is protected by a cyano group as shown in Chart 1.[18] The crystal structure of **2b** is shown in Figure 1, which clearly confirms the existence of Cu_2S_2 core structure



Scheme 1.



Scheme 2.

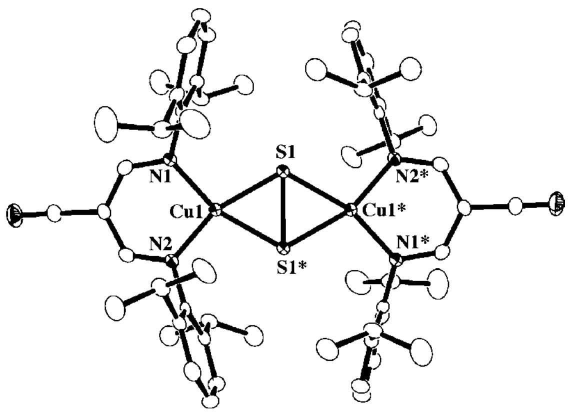


Figure 1. ORTEP drawing of **2b** showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

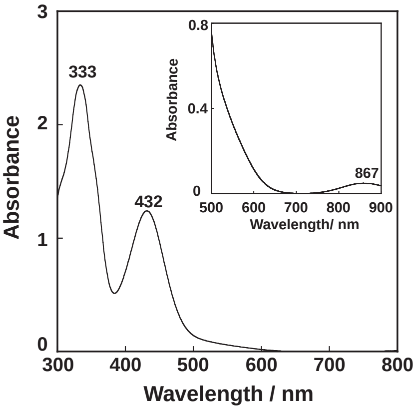


Figure 2. UV–vis spectrum of **2b** (1.0×10^{-4} M) in THF. Inset. UV–vis spectrum of a concentrated THF solution of **2b** (5.0×10^{-4} M).

with Cu–Cu distance of 3.8253(7) Å and S–S distance of 2.1899(15) Å. These values are close to those of the (μ-η^2:η^2-disulfido)dicopper(II) complexes of β-diketiminate type ligands reported by Tolman et al.[8,9]

UV–vis spectrum of **2b** shown in Figure 2 is also similar to those of the Tolman's complexes and contains two intense absorption bands at 333 ($\varepsilon = 24000\,\mathrm{M^{-1}\,cm^{-1}}$) and 432 nm (12500), attributable to the ligand-based π–π^* and/or $S_2{}^{2-}$ to $\mathrm{Cu^{II}}$ LMCT transitions, together with a weak d–d band at 867 nm (150). Compound **2b** was ESR silent and exhibits a sharp ^{1}H NMR spectrum,[16] indicative of strong antiferromagnetic coupling interaction between the two $\mathrm{Cu^{II}}$ ions.

In this study, we have also examined the reaction of $[\mathrm{Cu^{II}(TPA)(CH_3CN)}](\mathrm{ClO_4})_2$ [TPA = tris(2-pyridylmethyl)amine *tetradenate* ligand] with Na_2S_2 in CH_3CN to obtain the end-on (*trans*-μ-1,2-disulfido)dicopper(II) complex, although the reaction mixture contained some unidentified by-products as in the reaction of $[\mathrm{Cu^{I}(TPA)}]^+$ with $(1/8)S_8$ reported by Karlin et al. previously.[5,6] Thus, the present reaction using Na_2S_2 provides an alternative method for the preparation of disulfido–dicopper(II) (Cu_2S_2) complexes. Mechanistic details as well as the ligand effects on the present reaction are now under investigation.[19]

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13 The copper(II) complexes of the β-diketiminate ligand involving acetate ion as an external coligand were synthesized by following the reported procedure.[2d] The structure and purity of the sample were confirmed by elemental analysis and X-ray crystallographic analysis. Experimental details are provided in Supporting Information.

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16 Analytical data for **2b**: IR (KBr) 2207 (C≡N), 1563 (C=N), 505 $\mathrm{cm^{-1}}$ (S–S). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.93 (d, 24H, $J = 7.2$ Hz, CH_3), 1.04 (d, 24H, $J = 6.8$ Hz, CH_3), 2.79 (septet, 8H, $J = 6.8$ Hz C*H*), 6.97 (d, 8H, $J = 7.8$ Hz, aromatic protons at the *m*-position), 7.18 (t, 4H, $J = 7.8$ Hz, aromatic protons at the *o*-position), 7.37 (s, 4H, C*H*); HRMS *m/z* 1019.3955, calcd for $C_{56}H_{73}Cu_2N_6S_2$ 1019.4130. Anal. Calcd for $C_{56}H_{72}N_6Cu_2S_2 \cdot H_2O$: C, 64.77; H, 7.18; N, 8.09%. Found: C, 65.07; H, 7.01; N, 8.12%.

17 Crystallographic data of **2b** have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-652858.

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19 It should be noted that depending on the substituents of the carbon framework as well as of the aromatic groups of β-diketiminate ligands, reduction of $\mathrm{Cu^{II}}$ to $\mathrm{Cu^{I}}$ took place in the reaction with Na_2S_2 under similar experimental conditions.

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