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Dicopper–Dioxygen Complex Supported by Asymmetric Pentapyridine Dinucleating Ligand

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A dicopper(I) complex supported by a novel asymmetric pentapyridine dinucleating ligand, consisting of tetradentate and tridentate metal-binding sites, has been synthesized and characterized. The dicopper(I) complex reacted with molecular oxygen at a low temperature to give an unprecedented μ-peroxo dicopper(II) complex presumably having a μ-η^1:η^2 binding mode, the spectroscopic features and the reactivity of which have been explored in detail.

Active oxygen species generated by the reaction of copper(I) complexes and O_2 have attracted a great deal of attention as reactive intermediates of the oxidation and oxygenation reactions catalyzed by copper complexes and copper enzymes.[1−3] Copper(I) complexes supported by *tetradentate* ligands generally provide (*trans*-μ-1,2-peroxo)dicopper(II) complex **A**,[4−8] whereas copper(I) complexes with *tridentate* ligands tend to give (μ-η^2:η^2-peroxo)dicopper(II) complex **B** (Chart 1).[9−15] The side-on peroxo dicopper(II) complex **B** is well-established to be a common intermediate of the dinuclear copper proteins such as hemocyanin, tyrosinase, and catechol oxidase.[1]

Chart 1

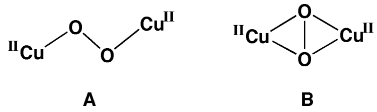
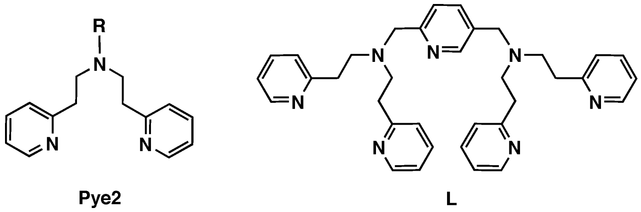


Chart 2



Bis[2-(2-pyridyl)ethyl]amine *tridentate* ligands (Pye2, Chart 2) have played very important roles in copper−dioxygen chemistry.[2,3,13,14] Karlin and co-workers have developed a series of dinucleating ligands involving the Pye2 tridentate metal binding units to accomplish reversible

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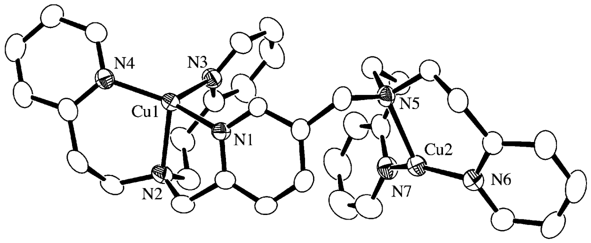

Figure 1. ORTEP diagram of dicopper(I) complex Cu^{I}_2L showing 50% probability thermal ellipsoids. Hydrogen atoms and counteranions are omitted for clarity.

dioxygen binding (functional model of hemocyanin) and aromatic ligand hydroxylation reaction by the side-on peroxo complex **B**.[3,13] We have also demonstrated the aliphatic ligand hydroxylation reaction as well as the oxygenation of phenols (model reaction of tyrosinase) by using a simple mononuclear copper(I) complex of Pye2 as the starting material.[14]

As our continuing efforts in exploring the effects of ligands on Cu_2/O_2 chemistry, we herein developed a new asymmetric pentapyridine ligand L by connecting the metal-binding unit (Pye2) directly to the 2- and 5-positions of pyridine via a methylene linker as shown in Chart 2.[16] The compound is designed to act as a dinucleating ligand, where the left-hand of the compound serves as a N_4-*tetradentate* metal-binding site and the right-hand acts as a N_3-*tridentate* ligand (see Chart 2). Thus, the copper complex prepared by using this ligand is expected to provide an asymmetric dicopper unit that should afford a novel Cu_2/O_2 complex upon oxygenation. Because most of the dinuclear metalloenzymes in nature have asymmetric metal binding sites,[17] it is highly desired to study the dioxygen reactivity of such asymmetrically coordinated dinuclear transition-metal complexes in the model system.[18]

Treatment of ligand L with 2 equiv of $[Cu^{I}(CH_3CN)_4](PF_6)$ in acetonitrile under anaerobic conditions (in a glovebox, $[O_2] < 1$ ppm) gave the corresponding dicopper(I) complex $[Cu^{I}_2(L)](PF_6)_2$ (Cu^{I}_2L).[16] Single crystals of Cu^{I}_2L suitable for X-ray crystallographic analysis were obtained by recrystallization using a liquid/liquid diffusion method between acetone and Et_2O. In Figure 1 is shown the crystal structure of the cationic part of Cu^{I}_2L.[19] One of the copper(I) ions, Cu(1), exhibits a four-coordinate distorted trigonal pyramidal geometry involving three pyridine nitrogen atoms, N(1), N(3), and N(4), in the trigonal basal plane and the amine nitrogen atom, N(2), as the axial ligand, whereas another copper(I) ion, Cu(2), exhibits a three-coordinate T-shaped trigonal planar geometry containing the amine nitrogen atom, N(5), and two pyridine nitrogen atoms, N(6) and N(7). Thus, the two copper(I) ions in Cu^{I}_2L exhibit different coordination geometries as we expected.

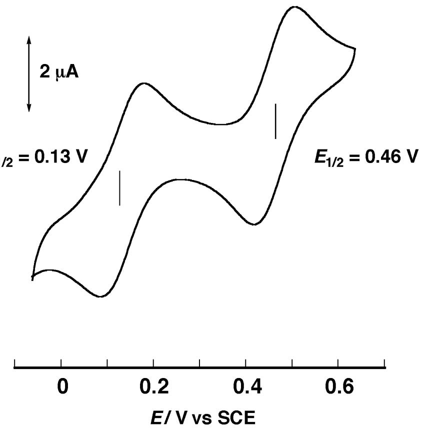

Figure 2. Cyclic voltammogram of $[Cu^{I}_2(L)](PF_6)_2$ (2.0 mM) in acetone containing 0.1 M $TBAPF_6$; scan rate = 20 mV/s.

Figure 2 shows the cyclic voltammogram of Cu^{I}_2L in acetone under anaerobic conditions (Ar).[16] The complex exhibits two reversible redox peaks at 0.13 and 0.46 V vs SCE. The lower and higher redox peaks are assigned to the redox reactions of copper centers at the *tridentate* (N_3) and *tetradentate* (N_4) metal binding sites, respectively, on the basis of the $E_{1/2}$ values of mononuclear copper(I) complexes supported by related tridentate and tetradentate ligands.[20] Existence of the two redox couples clearly demonstrates that the asymmetric coordination geometry of Cu^{I}_2L is maintained in solution.

Dicopper(I) complex Cu^{I}_2L readily reacted with dioxygen in a 2:1 ratio (determined by manometry) in acetone at a low temperature (−94 °C), resulting in a color change of the solution from pale yellow to dark brown. A typical spectral change for the oxygenation reaction of Cu^{I}_2L is shown in Figure 3, where a strong absorption band is observed at 483 nm ($\epsilon = 4300$ M^{-1} cm^{-1}).[21] The resonance Raman spectra of the brown species in acetone-d_6 taken at −90 °C with 413.1 nm excitation are given in the inset of Figure 3. A characteristic Raman band at 828 cm^{-1} with $^{16}O_2$ is exhibited that shifted to 784 cm^{-1} upon $^{18}O_2$ substitution. Thus, the observed isotope shift of $[\nu(^{16}O_2) - \nu(^{18}O_2)]$ is 44 cm^{-1}, which is in good agreement with the expected shift for the diatomic harmonic oscillator, $[\nu(^{16}O_2) - \nu(^{18}O_2)] = 47$ cm^{-1}, of a peroxo ligand. Moreover, the brown solution was ESR-silent, indicating the diamagnetism of the oxygenated intermediate.

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(16) The experimental details for the syntheses and the measurements are described in the Supporting Information.

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(19) Details of the crystallographic data of Cu^{I}_2L are provided in the Supporting Information as a CIF file.

(20) Osako, T.; Ohkubo, K.; Taki, M.; Tachi, Y.; Fukuzumi, S.; Itoh, S. *Inorg. Chem.* **2001**, *40*, 6604−6609. Details of the electrochemical analyses of Cu^{I}_2L and the related dicopper(I) complexes will be reported elsewhere.

(21) The time course of the oxygenation reaction was followed by monitoring the absorption change at 483 nm. It became apparent that the reaction was biphasic; $k_{obs(1)} = 4.7 \times 10^{-3}$ s^{-1} and $k_{obs(2)} = 2.8 \times 10^{-3}$ s^{-1}. The biphasic kinetics indicates that the peroxo intermediate is formed via at least two steps, although the mechanistic details are not known at present.

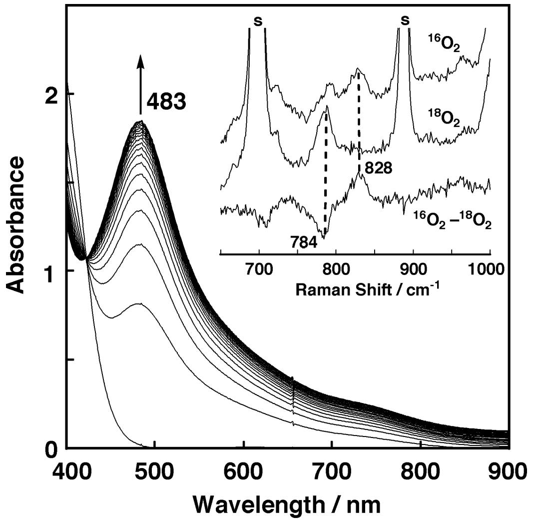
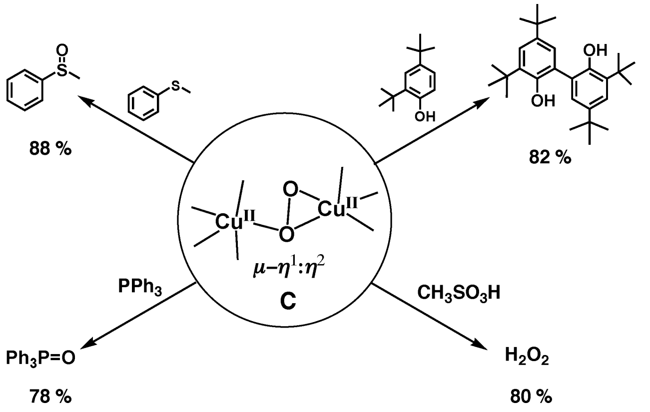


Figure 3. Spectral change observed upon introduction of O_2 gas into an acetone solution of $Cu^{I}_{2}L$ (4.5×10^{-4} M) at −94 °C. Interval = 100 s. Inset: Resonance Raman spectra of the intermediate generated in the reaction of $Cu^{I}_{2}L$ with $^{16}O_2$ (top) and $^{18}O_2$ (middle) and their difference spectrum (bottom) obtained with an excitation wavelength of 413.1 nm in acetone-d_6 at −90 °C. Note: The peaks indicated by (s) are due to the acetone-d_6.

The Cu-to-O_2 stoichiometry (2:1) and the ESR silence, as well as the resonance Raman features, clearly demonstrate that the oxygenated intermediate is a (μ-peroxo)dicopper(II) species. The UV−vis spectrum of the intermediate (λ_{max} = 483 nm, ϵ = 4300 M^{-1} cm^{-1}) shown in Figure 3 is, however, significantly different from that of the well-characterized (μ-peroxo)dicopper(II) complexes such as (*trans*-μ-1,2-peroxo)dicopper(II) complex **A** [435 nm (1700 M^{-1} cm^{-1}), 524 (11300), 615 (5800), 1035 (180)][4] and (μ-η^2:η^2-peroxo)dicopper(II) complex **B** [349 (21000), 551 (790)],[9] suggesting that the peroxo intermediate obtained in this study has a different binding mode of the peroxo ligand as described below.

As stated above, the oxygenation reaction of the copper(I) complexes supported by tetradentate ligands provides the end-on μ-η^1:η^1-peroxo dicopper(II) complex **A** (Chart 1), whereas the copper(I) complexes with tridentate ligands Pye2 give the side-on μ-η^2:η^2-peroxo dicopper(II) complex **B**. Thus, the μ-peroxo dicopper(II) complex supported by ligand L, which contains both the tetradentate and tridentate metal-binding sites, should have a μ-η^1:η^2 binding mode **C** as illustrated in Scheme 1. In fact, the resonance Raman feature of the oxygenated intermediate is fairly close to that of the structurally characterized (μ-η^1:η^2-peroxo)dicobalt(III) complex; $\nu(^{16}O_2)$ = 839 cm^{-1} [$\Delta\nu(^{16}O-^{18}O)$ = 43 cm^{-1}].[22] Although (μ-η^1:η^2-peroxo) dinuclear transition metal complexes have been reported for $Co^{III}-Co^{III}$,[22] $Fe^{III}-Cu^{II}$,[23] $V^{V}-V^{V}$,[24] $Rh^{I}-Rh^{I}$,[25] and $Pd^{II}-Pd^{II}$,[26] the peroxo complex obtained in this study is the first example of $Cu^{II}-Cu^{II}$ complex containing the μ-η^1:η^2-binding mode.

Scheme 1



Despite our great efforts, we could not isolate the (μ-η^1:η^2-peroxo)dicopper(II) complex **C** for further structural characterization. Nonetheless, the reactivity of **C** toward some external substrates has been examined in acetone at a low temperature (−80 °C). The peroxo complex **C** immediately decomposed with evolving H_2O_2 (80%) when a protic acid such as CH_3SO_3H (10 equiv) was added to the solution. This seems to indicate that the peroxo intermediate **C** exhibits a nucleophilic character similar to that of the end-on peroxo complex **A**.[27,28] On the other hand, the reactivity of **C** toward Ph_3P, PhSMe, and ArOH is rather similar to that of the side-on peroxo complex **B** to give the corresponding oxidation products $Ph_3P{=}O$ (78%), Ph(Me)S=O (88%), and the C−C coupling dimer of phenol (82%), respectively, demonstrating an electrophilic nature of **C**.[27,28] Thus, it is apparent that the peroxo complex **C** exhibits the reactivities of both the end-on and side-on peroxo complexes.[27] Mechanistic details of the oxidation reactions are now under investigation.

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Supporting Information Available: Experimental details of the syntheses and characterizations of the ligand L and the dicopper(I) complex as well as product analyses of the reactions between peroxo intermediate **C** and the external substrates. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] It was reported that the (μ-η^2:η^2-peroxo)dicopper(II) complex **B** did not react with protic acids, whereas the oxidation reactions of Ph_3P and phenols did not proceed with the (*trans*-μ-1,2-peroxo)dicopper(II) complex **A**.[27]