A Stable Cu_2O_2 Complex Supported by an Asymmetric Dinucleating Pentapyridine Ligand Involving an Amide Linkage

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We have synthesized an asymmetric dinucleating ligand connecting the N_3 and N_4 coordination sites with an amido linkage and characterized the corresponding dicopper(I) complex by spectroscopic methods. The dicopper(I) complex reacted with O_2 at low temperature to yield a (μ-peroxo)Cu_2 species with a μ-η^1:η^2-binding mode. We also explored an effect of this amide linkage that contributed to stabilizing a μ-η^1:η^2-Cu_2O_2 adduct.

Active oxygen species on metal centers are ubiquitous and have been explored in many fields. Continuous efforts in Cu_2/O_2 chemistry have provided the *trans*-1,2-μ-peroxodicopper(II),[1] μ-η^2:η^2-peroxodicopper(II),[2] and bis(μ-oxo)copper(III) species,[3] allowing investigations into structures and reactivities.

We have focused on studying the chemistry of a Cu/O_2 adduct prepared by combining a Cu^I complex and O_2 using an asymmetric ligand to yield a novel μ-peroxodicopper(II) species with a μ-η^1:η^2-binding mode.[4,5] The new asymmetric pentapyridine ligand linked by an amide linkage (Figure 1) was designed and synthesized in order to stabilize the μ-η^1:η^2-peroxodicopper(II) species and explore the ligand effect.

Dicopper(I) complex was obtained by the treatment of dinucleating pentapyridine ligand $^{m,e}\mathbf{L}^{Me}$ with two equivalents of $[Cu^I(MeCN)_4](PF_6)$ in MeCN under anaerobic conditions (in a glovebox, $[O_2] < 1$ ppm). Formation of the expected dicopper(I) complex $[Cu^I{}_2(^{m,e}\mathbf{L}^{Me})](PF_6)_2$ ($^{m,e}\mathbf{1}^{Me}$) has been confirmed by high-resolution mass spectrometry, infra-red spectroscopy, and elemental analysis. In order to examine the redox activity of the dicopper(I) complex, electrochemical behavior of the copper(I) complexes has been examined. The cyclic voltammogram of $^{m,e}\mathbf{1}^{Me}$ in acetone containing 0.1 M (^{n}Bu)$_4$NPF$_6$ was compared with those of $[Cu^I(TPA)(MeCN)](PF_6)$ (corresponding to the N_4 site) and $[Cu^I(^e\mathbf{L}^{Bz})](PF_6)$ (corresponding to the N_3 site) (For $^e\mathbf{L}^{Bz}$, see Figure S1).[8] $^{m,e}\mathbf{1}^{Me}$ exhibits two redox couples, at 0.53 and 0.06 V vs. SCE (Figure 2). The peak position of the positive couple is almost the same to that of $[Cu^I(^e\mathbf{L}^{Bz})](PF_6)$ (0.52 V), whereas that of the other redox couple is slightly more positive than that of $[Cu^I(TPA)(MeCN)](PF_6)$ (0.01 V). In case of the N_3 site, Karlin and his co-workers have reported that $[Cu^I(^e\mathbf{L}^{Bz})]^+$ has a three coordinate T-shaped structure.[6] Thus, the structure of the copper(I) site at the N_3 site in $^{m,e}\mathbf{1}^{Me}$ must be the same as that in $[Cu^I(^e\mathbf{L}^{Bz})]^+$. In the case of the N_4 site, the difference in the redox potential of copper(I) at the N_4 site in $^{m,e}\mathbf{1}^{Me}$ from that of $[Cu^I(TPA)(MeCN)](PF_6)$ may be attributed to the absence of the external ligand MeCN in $^{m,e}\mathbf{1}^{Me}$. We expect that coordination geometry of copper(I) at the N_4 site is trigonal pyramidal without any external ligand since the electrochemical measurements were performed in acetone.

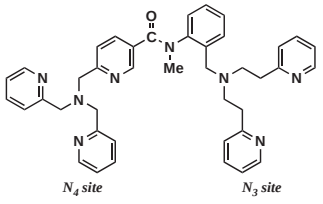

Figure 1. The dinucleating pentapyridine ligand ($^{m,e}\mathbf{L}^{Me}$).

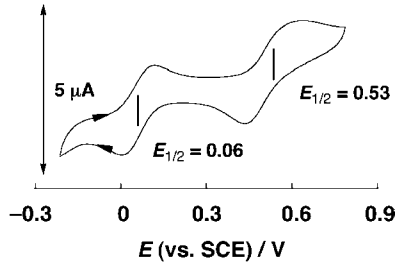

Figure 2. Cyclic voltammogram of $[Cu^I{}_2(^{m,e}\mathbf{L}^{Me})](PF_6)_2$ ($^{m,e}\mathbf{1}^{Me}$) (1.0×10^{-3} M) in acetone containing 0.1 M N(^{n}Bu)$_4$PF$_6$; working electrode Pt, counter electrode Pt, reference electrode Ag/0.01 M $AgNO_3$ (potentials are converted into those with respect to SCE), scan rate 20 mV/s.

Treatment of $^{m,e}\mathbf{1}^{Me}$ with dioxygen (in acetone, at $-94\,^\circ$C) also resulted in the formation of the (μ-η^1:η^2-peroxo)dicopper(II) complex $^{m,e}\mathbf{2}^{Me}$ (Figure S2).[8] The absorption band at 477 nm ($\varepsilon = 6302\,M^{-1}\,cm^{-1}$) readily developed, obeying first-order kinetics ($k_{obs} = 0.41\,s^{-1}$, inset of Figure S2).[8]

The oxygenated intermediate exhibited an isotope-sensitive resonance Raman band at 816 cm^{-1} with $^{16}O_2$, which shifted to 773 cm^{-1} upon $^{18}O_2$ substitution. Thus, the observed isotope shift, $\Delta(\nu_{16} - \nu_{18})$, was 43 cm^{-1}. These Raman data are very similar to those of $^{e,e}\mathbf{L}^{Py}$,[4] confirming the formation of the same type of dicopper(II)peroxo species with the μ-η^1:η^2-binding mode. The ESR silence of $^{m,e}\mathbf{2}^{Me}$ solution was also consistent with that of a dicopper(II)peroxo complex.

These spectroscopic features (UV–vis, resonance Raman, and ESR silence) are very close to those of the (μ-η^1:η^2-peroxo)dicopper(II) complex $^{e,e}\mathbf{2}^{Py}$ supported by the pentapyridine ligand $^{e,e}\mathbf{L}^{Py}$,[4] as well as to those of the structurally characterized (μ-η^1:η^2-peroxo)dicobalt(III) complex, where $\lambda_{max} = 507$ nm ($\varepsilon = 1900\,M^{-1}\,cm^{-1}$) and $\nu_{16} = 839\,cm^{-1}$ {$\Delta(\nu_{16} - \nu_{18}) = 43\,cm^{-1}$}.[5] Thus, we presumed that the peroxo ligand involved in $^{m,e}\mathbf{2}^{Me}$ has a μ-η^1:η^2-binding mode as in the case of $^{e,e}\mathbf{2}^{Py}$.[4]

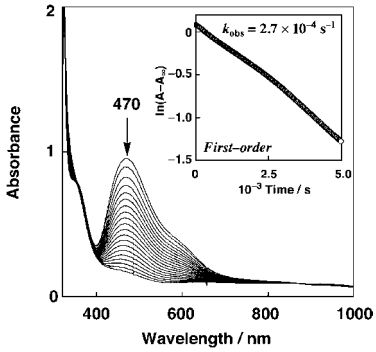

Figure 3. Spectral change for the decomposition of $^{m,e}\mathbf{2}^{Me}$ at 0 °C in acetone. Interval 250 s. Inset: first-order plot based on the absorption change at 470 nm.

Unfortunately, single crystals suitable for X-ray crystallographic analysis have yet to be obtained.

Surprisingly, the thermal stability of $^{m,e}\mathbf{2}^{Me}$ improved significantly compared to that of $^{e,e}\mathbf{2}^{Py}$. No appreciable decay was observed at −70 °C ($t_{1/2} \gg$ at least 15 h, Figure S6).[8] It survived for a couple of hours even at 0 °C in Figure 3 ($k_{obs} = 2.7 \times 10^{-4}$ s^{-1}, $t_{1/2} = 43$ min).

Note that the reaction of $^{m,e}\mathbf{1}^{Me}$ and O_2 in EtCN also provided the (μ-η^1:η^2-peroxo)dicopper(II) complex $^{m,e}\mathbf{2}^{Me}$ (Figure S3).[8] This result clearly suggests that both copper(I) sites in $^{m,e}\mathbf{1}^{Me}$ are protected from solvent coordination even in EtCN,[4b] allowing it to react with O_2 readily. Introduction of a methyl substituent to the amide group of the ligand may prohibit free rotation around the amide linkage, making the metal-binding pocket more rigid.[7] This molecular rigidity may contributed to the high stability of $^{m,e}\mathbf{2}^{Me}$.

Thus, novel unsymmetrical pentapyridine ligand $^{m,e}\mathbf{L}^{Me}$ has been synthesized, and the corresponding dicopper(I) complex $^{m,e}\mathbf{1}^{Me}$ obtained. Detailed electrochemical analyses of the dicopper(I) complex have unambiguously demonstrated that the metal ions are ligated unsymmetrically as expected. On the basis of the redox potentials of the known mononuclear copper(I) complexes supported by tetradentate and tridentate (2-pyridyl)alkylamine ligands, we have discussed the coordination geometries of the copper(I) centers in the dicopper(I) complexes in detail.

In the case of 2,5-pyridine spacer as $^{e,e}\mathbf{L}^{Py}$,[4] all attempted combinations of pyridylalkylamine makes μ-η^1:η^2-peroxo species not only unstable ($k_{obs} = 1.7 \times 10^{-4}$ s^{-1}, $t_{1/2} = 68$ min at −80 °C for $^{e,e}\mathbf{L}^{Py}$)[4] but also yields no active oxygen species. Since 2,5-pyridine spacer caused structural strain, we could not obtain any active oxygen species stabilized by the pyridylalkylamine side arm. In this study, the phenylamidepyridine spacer released the constrained structure to enfold and stabilize the Cu_2O_2 core in the ligand structure as show in Figure 4. A rough correlation between the LMCT transition energies and the ν(O–O) frequencies of peroxo species are useful in elucidating the steric and/or electronic nature of the peroxo core depending on the supporting ligands.[1b] The corresponding values of μ-η^1:η^2-peroxo species are plotted together with those of μ-1,2-peroxo species[1b] as show in Figures S6 and S7.[8] These systems are classified into the less strained ligand architecture.

It should be noted that stability of the (μ-η^1:η^2-peroxo)dicopper(II) complexes are significantly improved when ligand

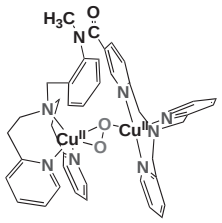

Figure 4. Estimated structure of Cu_2O_2 complex ($^{m,e}\mathbf{2}^{Me}$) supported by $^{m,e}\mathbf{L}^{Me}$ in the (μ-η^1:η^2-peroxo)dicopper(II)-binding mode.

$^{m,e}\mathbf{L}^{Me}$ is employed, and the (μ-η^1:η^2-peroxo)dicopper(II) complex ($^{m,e}\mathbf{1}^{Me}$) can survive even at 0 °C for a while. Thus, we have determined that the stability of the (μ-η^1:η^2-peroxo)dicopper(II) complexes was altered significantly by subtle ligand modification. We are now trying to isolate single crystals of $^{m,e}\mathbf{2}^{Me}$ for further characterization of the (μ-η^1:η^2-peroxo)dicopper(II) complex. In addition, further studies on the detail of reactivity toward external substrates are in progress.

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