A Superoxodicopper(II) Complex Oxidatively Generated by a Reaction of Di-μ-hydroxodicopper(II) Complex with Hydrogen Peroxide

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Di-μ-hydroxodicopper(II) complex with a hexapyridine dinucleating ligand, $[Cu_2(OH)_2(hexpy)](CF_3SO_3)_2$ (hexpy = 1,2-bis[2-(bis(2-pyridyl)methyl)-6-pyridyl]ethane), reacts with H_2O_2 in $MeCN/CH_2Cl_2$ to give a superoxodicopper(II) complex.

Dicopper dioxygen complexes[1-3] and their O_2-activation[4-8] are currently attracting the interests of chemists from the bioinorganic and industrial points of view. Karlin et al. reported that a superoxodicopper complex was generated by the reaction of a mixed valent dicopper(I, II) complex with O_2.[13] However, there is no example for the superoxodicopper complex generated oxidatively. In this paper, we describe a superoxodicopper(II) complex generated by the reaction of a di-μ-hydroxodicopper(II) complex having a hexapyridine dinucleating ligand with H_2O_2.

We prepared a hexapyridine dinucleating ligand (hexpy) which has two tripyridylmethane units connected by an ethylene linker.[9] The ligand forms the di-μ-hydroxodicopper(II) complex $[Cu_2(OH)_2(hexpy)](CF_3SO_3)_2$ **1**.[10] The crystal structure of $[Cu_2(OH)_2(hexpy)](ClO_4)_2$ shows that the Cu(II) ions are bridged by two hydroxide ions to take a square pyramidal geometry, while the apical *N* atoms adopt a *syn*-configuration which is forced by the hexpy ligand.[10]

A dark purple complex **2** was generated upon addition of aqueous H_2O_2 to a $MeCN/CH_2Cl_2$ (1:9, v/v) solution of **1** at -20 °C. The UV-vis spectrum (Figure 1) of **2** showed two bands at 370 (ε 11000 M^{-1} cm^{-1}) and 550 nm (530). The spectrum of **2** is similar to that reported for the hydroperoxodicopper(II) complex of 2,6-bis[bis((2-pyridylethyl)amino)methyl]phenoxide **3**, 395 (ε 8000 M^{-1} cm^{-1}) and 620 nm (450)[11], and to that for a μ-η^2:η^2-peroxodicopper(II) complex with a hydrotris(3,5-di-isopropyl-pyrazolyl)borate ligand (355 (ε 18000 M^{-1} cm^{-1}) and 542 nm (1040)).[12] These aspects suggest that **2** has a Cu_2O_2 core structure and one or two of the bridging oxygen atoms are provided by the dioxygen moiety. The origin of the dioxygen moiety in **2** is H_2O_2, since **2** was generated under Ar. Compound **2** decomposed to a structurally unknown green complex at higher temperature. The hexpy ligand was recovered quantitatively by demetallation of the green complex.

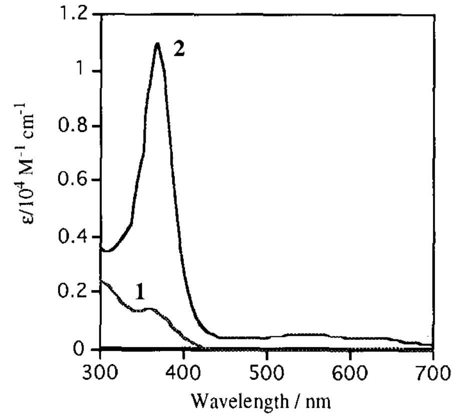

Figure 1. UV-vis spectra of **1** and **2** in $MeCN/CH_2Cl_2$ (1:9, v/v) at -40°C.

Compound **1** was ESR silent because of the strong anti-ferromagnetic coupling between the two Cu(II) ions.[10] The ESR

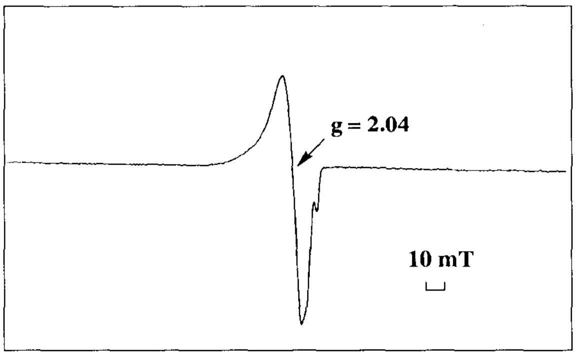

Figure 2. ESR spectrum of **2** in $MeCN/CH_2Cl_2$ (1:9, v/v) at 77K.

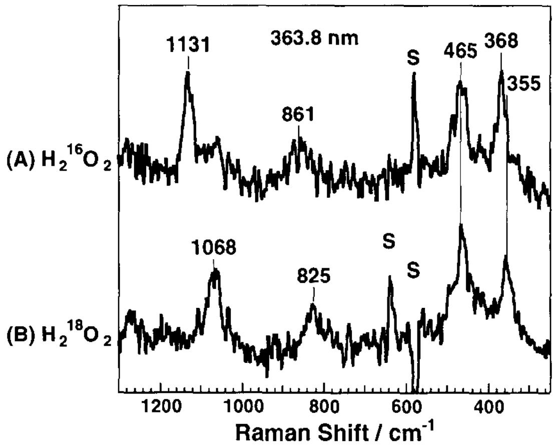

Figure 3. Resonance Raman spectra of **2** generated by the reaction of **1** with (A) $H_2{}^{16}O_2$ and (B) $H_2{}^{18}O_2$ in MeCN/ CH_2Br_2 (1:9, v/v) at -30°C. S denotes solvent (CH_2Br_2) bands.

spectrum (77 K, $MeCN/CH_2Cl_2$, 1:9, v/v) of **2** shows a broad band at g = 2.04 (Figure 2) which is similar to but sharper than that reported for the superoxodicopper(II) complex,[13] suggesting coupling to the two Cu(II) ions, but the delocalization of the unpaired electron in the coordinated superoxide of **2** is less than that of the superoxodicopper complex reported by Karlin et al.[13] The peak intensity was calibrated using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl. About 80 % of **1** was converted to **2**. Upon addition of the spin-trapping reagent M_4PO (3,3,5,5-tetramethyl-1-pyrroline *N*-oxide) to the solution of **2** a sharp triplet centered at g = 2.010 (A_N = 11 G) appeared in the ESR spectrum (see supplementary material), indicating the formation of a superoxo-M_4PO adduct similar to the Karlin's one.[13]

Resonance Raman spectrum (Figure 3) of **2** (-30 °C, $MeCN/CH_2Br_2$, 1:9, v/v) with 364 nm exitation exhibits a band at 1131 cm^{-1} which is close to 1112 cm^{-1} of the $\nu(O\text{-}O^-)$ band for a mononuclear superoxocopper(II) complex of hydrotris(3,5-di-*tert*-butylpyrazoly)borate.[14] Compound **2** has two other bands at 465 and 368 cm^{-1}. The band at 1131 cm^{-1} shifted to 1068 cm^{-1} upon isotope-labelling with $H_2{}^{18}O_2$. The observed isotopic shift of $\{\nu({}^{16}O_2{}^-) - \nu({}^{18}O_2{}^-)\} = 63$ cm^{-1} is in good agreement with the expected shift for a diatomic harmonic oscillator: $\{\nu({}^{16}O_2{}^-) - \nu({}^{18}O_2{}^-)\} = 65$ cm^{-1}. Thus, the band at 1131 cm^{-1} is assigned to $\nu(O\text{-}O^-)$ of the superoxide moiety in **2**.

ESI mass spectrum of **2** reveals the bridging ligands. A parent peak [829 (m/z)] and the isotope peaks due to $\{[Cu_2(OH)_2hexpy](CF_3SO_3)\}^+$ of **1** disappeared upon addition of H_2O_2 to a $MeCN/CH_2Cl_2$ (1:9, v/v) solution of **1** and a new parent peak appeared at 844 (m/z) which is assignable to $\{[Cu_2(OH)(O_2{}^-)hexpy](CF_3SO_3)\}^+$ of **2**. Although the isotope peaks for **2** were overlapped with isotope peaks due to $\{[Cu_2(OH)(O_2H)hexpy](CF_3SO_3)\}^+$ of the hydroperoxodicopper(II) complex **4**, an isotopic distribution of **2** was clearly observed by the difference spectra, and fits the caluculated one (see supplemetary material). Compound **4** might be an intermediate in the reaction of **1** with H_2O_2 and/or a product generated by a hydrogen atom addition to **2** during the ESI mass measurement. These results show that two Cu(II) ions in **2** are bridged by OH^- and $O_2{}^-$. The two resonance Raman bands at 465 and 368 cm^{-1} seem to arise from $\nu(Cu\text{-}(OH)\text{-}Cu)$ and $\nu(Cu\text{-}(O_2{}^-)\text{-}Cu)$, respectively, since the former band does not shift with $H_2{}^{18}O_2$ significantly but the latter shifts to 355 cm^{-1}.

The resonance Raman spectrum also showed a minor band at 861 cm^{-1} which shifted to 825 cm^{-1} with $H_2{}^{18}O_2$. The minor band is assignable to $\nu(O\text{-}OH)$ in **4**. The band at 861 cm^{-1} decreased gradually during the reaction, while the band at 1131 cm^{-1} relatively increased. This indicates that **4** is the precursor of **2** in the present system.

These spectral data demonstrate that **2** is formulated as a superoxodicopper(II) complex $[Cu_2(OH)(O_2{}^-)hexpy](CF_3SO_3)_2$ in which the $O_2{}^-$ moiety is provided by H_2O_2. The chemical structure of **2** is proposed in Figure 4. In this structure, the $O_2{}^-$ moiety takes the μ-1,1-terminal bridging mode similar to O_2H in **3**. Such a structure can interpret the similarity in the UV-vis spectra of **2** and **3**. The structure also explains the singlet band of the ESR spectrum of **2**. Since the unpaired electron of the terminal oxygen atom of the $O_2{}^-$ moiety is less delocalized in this structure, the electron spin of the oxygen radical is weakly coupled to the nuclear spin of two Cu(II) ions. The ESI mass spectrum shows that the two Cu(II) ions in **2** are bridged by the OH and $O_2{}^-$ anions. Therefore, the structure shown in Figure 4 is consistent with all of the present spectral data of **2**.

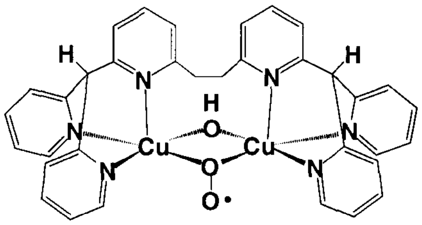

Figure 4. Proposed chemical structure of **2**.

Study on the mechanism for the oxidative generation of **2** is now in progress. One possibility is that the hydroperoxodicopper(II) complex **4** is converted to a strong oxidant to oxidize **4** to **2**.

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