A Unique Copper(II)-Hydroxide Complex Derived from Copper(II)-Superoxide

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A unique Cu(II)-hydroxide complex, [Cu(tppa)(OH)]-ClO_4 (TPPA = tris[(6-(pivaloylamino)-2-pyridyl)methyl]-amine), has been obtained from the $[Cu^{II}(tppa)(O_2^-)]ClO_4$ complex in a methanol solution and characterized by the electronic absorption, ESR and ESI-MAS spectra and the X-ray diffraction method.

The binding of dioxygen to metal sites is one of the fundamental steps of the oxidation process in biological metalloenzyme systems.[1-3] We have previously succeeded in our studies on model complexes in uptaking dioxygen as a superoxide on mononuclear copper atom by use of a newly designed tripodal tetradentate ligand, TPPA (tris[(6-(pivaloylamino)-2-pyridyl)methyl]amine).[4] In the course of further studies on the stability of the $[Cu(tppa)(O_2^-)]ClO_4$ complex, we found the transformation of this complex to the mononuclear copper(II)-hydroxide complex. Here we describe the characterization of the complex.

The complex $[Cu^{II}(tppa)(O_2^-)]ClO_4$ which is formed in a methanol solution at -78 °C is very stable, as has been reported previously.[4] A detailed analysis of the electronic absorption spectra for the complex in the solution at room temperature, however, indicated it to cause an apparent spectral change in the charge transfer band region: The absorption spectra of the complex after several days gave a new peak at 434 nm (ε = 72) at -78 °C (Figure 1), although the absorption bands in the d-d region (655 nm (ε = 174) and 779 nm (ε = 159)) did not show any noticeable change. This new peak is clearly different from that of the $[Cu(tppa)(O_2^-)]ClO_4$ complex in the solution.[4] The frozen solution ESR spectrum of the complex exhibited a spectral pattern typical to Cu(II) dz^2 ground state ($g_\perp$ = 2.13, $g_{//}$ = 2.03), although that of $[Cu^{II}(tppa)(O_2^-)]ClO_4$ was silent. These findings suggest that the copper atom has a trigonal bipyramidal geometry. Fortunately, standing of the solution at room temperature gave a greenish-blue, needle-like single crystal (**1**) suitable for X-ray structure determination after a few days.

The crystal of the complex **1**[5] is isomorphous with the $[Cu(tppa)(O_2^-)]ClO_4$[4] and $[Cu(tppa)Cl]ClO_4$ complexes[6] previously reported, and the crystal structure, as shown in Figure 2, is almost the same as the structures of the $[Cu(tppa)(O_2^-)]ClO_4$[4] and $[Cu(tppa)Cl]ClO_4$ complexes[6] except for their external axial ligands: The coordination environment around the central copper ion is an axially compressed trigonal bipyramid, as speculated above. The equatorial positions of the trigonal plane are occupied by three pyridine nitrogen atoms (Cu-N(2a) = 2.110(6) Å, Cu-N(2b) = 2.179(6) Å, Cu-N(2c) = 2.161(6) Å), and one of the axial positions is coordinated by the tertiary amine nitrogen atom (Cu-N(1) = 1.990(5) Å). Another axial position is occupied by a monodentate diatomic ligand corresponding to O and H atoms as judged from the electron density, in which the bond parameters around the metal ion (Cu-O(1h) = 1.872(6) Å, O(1h)-H(1h) = 0.67(7) Å, Cu-O(1h)-H(1h) = 98(8)°) lead the ligand to a hydroxide anion.

The coordination of hydroxide anion as a monodentate ligand to the copper(II) ion is extremely unique and it usually plays as bidentate or terdentate ligands because of its own three lone-pair electrons. The present monodentate hydroxyl coordination, to our knowledge, is the rare example in a copper complex with organic ligands.[8] The stability of the hydroxyl coordination is supported by the hydrogen bonds between the two remaining lone pairs of hydroxyl oxygen and two N-H groups of TPPA (O(1h)...N(3a) = 2.81 and O(1h)...N(3c) = 2.82 Å).

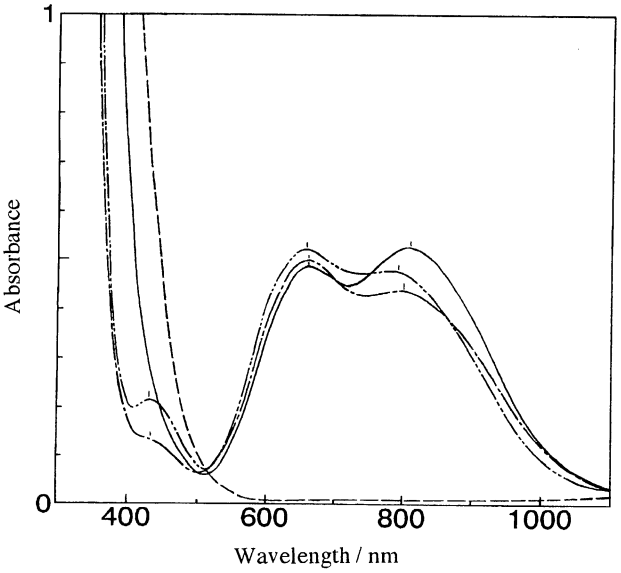

Figure 1. Absorption spectra of complex **1** (——·——) (obtained from $[Cu^{II}(tppa)(O_2^-)]^+$); $[Cu^{II}(tppa)](ClO_4)_2$ + KOH (1:1) (——); $[Cu^{II}(tppa)(O_2^-)]^+$ (———), and Cu(I)-TPPA complex (– – – –); in methanol solution at -78 °C.

The characterization of the complex **1** was further made on the basis of the electronic absorption, ESR, and ESI-MAS spectra and the X-ray analysis for the crystals of $[Cu(tppa)(OH)]ClO_4$ (**2**) that was independently prepared by the reaction of $[Cu(tppa)](ClO_4)_2$ with KOH in 1:1 stoichiometry in a methanol solution. The ESI-MAS spectrum measured for a CH_2Cl_2 solution of the complex **2** gave m/z = 667.3 assignable to $[Cu^{II}(tppa)(OH^-)]^+$. The X-ray crystal structure[7] of the $[Cu(tppa)(OH)]ClO_4$ complex (**2**) (Cu-N(2a) = 2.116(5) Å, Cu-N(2b) = 2.188(5) Å, Cu-N(2c) = 2.173(5) Å, Cu-N(1) = 1.986(5) Å, Cu-O(1h) = 1.871(4) Å, O(1h)-H(1h) = 0.57(6) Å, Cu-O(1h)-H(1h) = 91(5)°) was found to be essentially identical to the complex **1** derived from the $[Cu(tppa)(O_2^-)]ClO_4$ complex. The hydrogen bonding networks were also detected (O(1h)...N(3a) = 2.85 Å, O(1h)...N(3c) = 2.82 Å). The electronic absorption spectra of **2** at -78 °C, as depicted in Figure 1, showed very similar spectral pattern to that of **1**; it exhibited a band at 434 nm (ε = 43) and d-d bands at 661 nm (ε = 165) and 794 nm (ε = 144). The ESR spectra ($g_\perp$ = 2.13 and $g_{//}$ = 2.03) was also very similar to that of the complex **1**. All

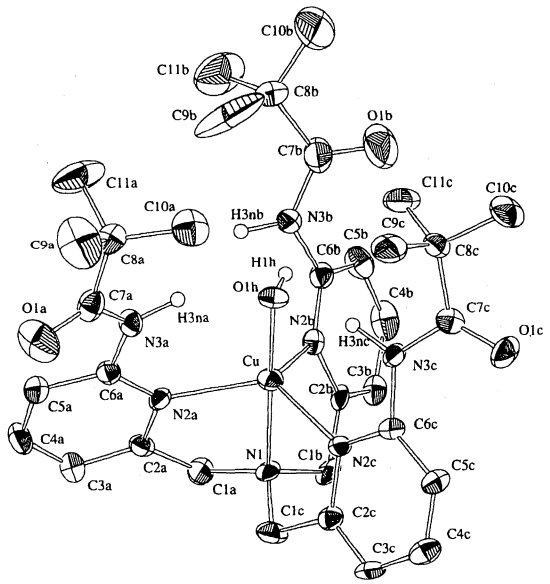

Figure 2. ORTEP drawing of the $[Cu^{II}(tppa)(OH)]^{+}$ cation (**1**) with atom-labeling scheme.

the above findings indicate that the complex **1** derived from $[Cu^{II}(tppa)(O_2^{-})]ClO_4$ is identical to $[Cu^{II}(tppa)(OH)]ClO_4$. Although the mechanism of the formation of the Cu-OH complex is not clear at present, the formation of Cu-OH requires the presence of Cu^{II}-O-O^{-} species. The presence of such a Cu-OH species is sometimes pointed out in biological systems containing copper oxidases such as ascorbate oxidase and laccase, although its origin is not revealed.[9] The further detailed comprehension may contribute to the understanding of metal-related oxygenases in biological system,[3,9] which will be described elsewhere.

References and Notes

1 "*Metal Ion Activation of Dioxygen: Metal Ions in Biology,*" ed by T. G. Spiro, Wiley-Interscience, New York (1980), Vol. 2.

2 L. L. Ingraham, D. L. Meyer, "*Biochemistry of Dioxygen,*" In "*Biochemistry of Elements,*" ed by E. Frieden, Plenum Press, New York (1985), Vol. 4.

3 "*Bioinorganic Chemistry of Copper,*" ed by K. D. Karlin and Z. Tyeklar, Chapman & Hall, New York (1993).

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5 Crystal data for **1**: $C_{33}H_{46}N_7O_8CuCl$, M_w = 767.77, orthorhombic, space group *Pccn*; a = 11.278(2), b = 35.568(3), c = 18.303(7) Å, V = 7341(5) $Å^3$, Z = 8, D_c = 1.39 g cm^{-3}; Cu-Kα (λ = 1.5418 Å); μ = 20.00 cm^{-1}, 2 < 2θ < 120 °. Intensity data collected at room temperature on a Rigaku AFC-5R four-circle diffractometer; structure solved and refined using teXsan program system, absorption correction was applied by DIFABS. 4984 Unique reflections of which 3253 [I > 3σ(I)] were observed. The structure was solved by the heavy-atom method and refined anisotropically. Hydrogen atoms were included in the calculation, but they were not refined except for the hydroxyl hydrogen atom. Final R and R_w values were 0.068 and 0.061, respectively.

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7 Crystal data for **2**: $C_{33}H_{46}N_7O_8CuCl$, M_w = 767.77, orthorhombic, space group *Pccn*; a = 11.285(2), b = 35.59(1), c = 18.340(4) Å, V = 7366(3) $Å^3$, Z = 8, D_c = 1.39 g cm^{-3}; Mo-Kα (λ = 0.71073 Å) ; μ = 7.22 cm^{-1}, 3 < 2θ < 55 °. Intensity data collected at room temperature on an Enraf - Nonius CAD4 - EXPRESS four - circle diffractometer ; structure solved and refined using SDP-MolEN program system, absorption correction was applied by DIFABS. 8143 Unique reflections of which 3531 [I > 3σ(I)] were observed. The structure was solved by the heavy-atom method and refined anisotropically. Hydrogen atoms were included in the calculation, but they were not refined except for the hydroxyl hydrogen atom. Final R and R_w values were 0.065 and 0.078, respectively.

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