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Structural and Spectroscopic Characterization of a Mononuclear Hydroperoxo – Copper(II) Complex with Tripodal Pyridylamine Ligands**

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Hydroperoxo – copper species are key intermediates in biological oxidations catalyzed by copper enzymes, such as dopamine β-hydroxylase (DβH),[1] galactose oxidase (GO),[2] and superoxide dismutase (SOD).[3] Characterization of these hydroperoxo intermediates is very difficult due to their short lifetimes. Hydroperoxo– or alkylperoxo – copper(II) complexes could be used as model compounds of hypothetical reaction intermediates in these oxidations. Recently the spectroscopic characterization of binuclear hydroperoxo – copper(II) complexes and X-ray structural characterization of mononuclear acylperoxo – copper(II) complexes were reported by Karlin et al.[4] and Kitajima et al.[5] However, the thermal instability of these compounds prevented their complete characterization. To confirm the structural characterization of the $Cu^{II}-OOH^-$ species, we prepared a mononuclear copper complex with a newly designed tripodal pyridylamine ligand, bis(6-pivalamide-2-pyridylmethyl)-(2-pyridylmethyl)amine (bppa), and subjected it to reaction with hydrogen peroxide. Here we describe the structural and spectroscopic characterization of the resulting mononuclear hydroperoxo – copper complex cation $[Cu^{II}(bppa)(OOH^-)]^+$, the first example of an isolated copper – hydroperoxo species.

The addition of a large excess of hydrogen peroxide to a MeCN solution of $[Cu^{II}(bppa^-)]ClO_4$ (**1**)[6] or $[Cu^{II}(bppa)(CH_3COO)]ClO_4$ (**2**)[6] at room temperature resulted in a slight color change from greenish blue to green. The absorption spectra of the reaction product **3,** which is stable for a month at room temperature, exhibited well-separated bands in the d – d region at 830 nm ($\varepsilon = 250\,\text{M}^{-1}\text{cm}^{-1}$) and 660 nm ($\varepsilon = 150\,\text{M}^{-1}\text{cm}^{-1}$) and an intense band near 380 nm ($\varepsilon = 890\,\text{M}^{-1}\text{cm}^{-1}$). The ESR spectrum of a solution of **3** is typical of a trigonal-bipyramidal mononuclear copper complex ($g_\parallel = 2.004$, $g_\perp = 2.207$, $A_\perp = 75$, and $A_\parallel = 109$ G at 77 K in MeOH), suggesting that one of the axial positions has been coordinated by an anionic donor ligand such as a deprotonated hydrogen peroxo ion. The resonance Raman spectra of a solution of **3** in MeCN measured at room temperature (laser excitation wavelength 441.6 nm) revealed a strong resonance-enhanced Raman band at 856 cm^{-1}, which shifted to 810 cm^{-1} ($\Delta\tilde{\nu} = 46$ cm^{-1}) when ^{18}O-labeled H_2O_2 was used. This range is characteristic for ν(O–O) vibrations of peroxide species and is in close proximity to those found in free $H_2{}^{16}O_2$ and $H_2{}^{18}O_2$ (873 and 826 cm^{-1}).[7] Interpretation of the vibrational data indicates that the hydroperoxo moiety is bound to the copper(II) ion and the intense absorption band near 380 nm can be assigned to the charge-transfer transition of the hydroperoxo group to copper(II) ion. The ESI mass spectrum of a solution of **3** in MeCN showed positive and negative ions with prominent peak clusters at *m/z* 584 and 784, the observed masses and isotope patterns of which corresponded to the $[Cu^{II}(bppa)(OOH^-)]^+$ and $\{[Cu^{II}(bppa)(OOH^-)](ClO_4)_2\}^-$ ions. The use of ^{18}O-labeled H_2O_2 caused these features to shift, as expected, to *m/z* 588 and 788. The intense green color of **3** is maintained throughout the mass spectroscopic experiment, suggesting that the complex is very stable. It is thus clear from these findings that **3** can be best formulated as $[Cu^{II}(bppa)(OOH^-)]^+$. The electronic absorption, ESR, resonance Raman, and ESI mass spectra, as described above, represent the first evidence for the successful synthesis of a mononuclear hydroperoxo – copper(II) complex in solution.

A solution of **3** in MeCN stored in a cold room produced a dark green crystal suitable for X-ray diffraction measurements. The crystal structure of the complex **3**[8] (Figure 1) revealed that the coordination geometry around the copper(II) ion is an axially compressed trigonal bipyramid. The three pyridine nitrogen atoms are in the equatorial plane (Cu – N(2A) 2.099(5), Cu – N(2B) 2.136(4), Cu – N(2C) 2.051(6) Å), and one of the axial positions is occupied by a nitrogen atom

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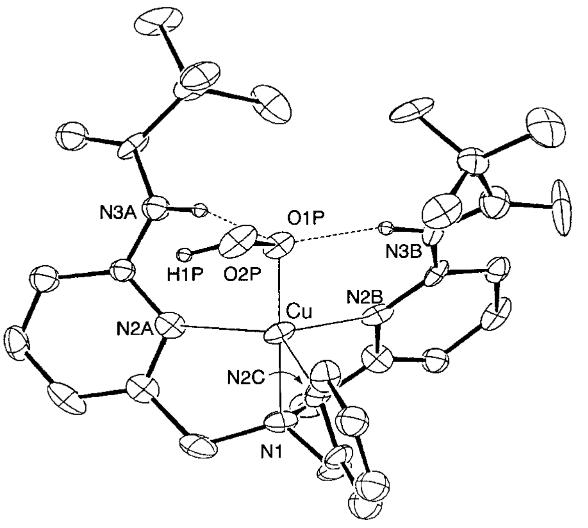

Figure 1. ORTEP representation of the $[Cu^{II}(bppa)(OOH^-)]^+$ cation in **3**. All hydrogen atoms, except for the hydroperoxo hydrogen and those of the amino group, have been omitted for clarity. Selected bond lengths [Å]: Cu–N(1) 1.999(5), Cu–N(2A) 2.099(5), Cu–N(2B) 2.136(4), Cu–N(2C) 2.051(6), Cu–O(1P) 1.888(4), O(1P)–O(2P) 1.460(6).

from the tertiary amine group (Cu–N(1) 1.999(5) Å). Interestingly, the other axial position is occupied by the hydroperoxide anion with a Cu–O(1P) bond length of 1.888(4) Å and a Cu-O(1P)-O(2P) angle of 114.5°. The O–O bond distance of 1.460(6) Å is in good agreement with that of H_2O_2 (1.490 Å),[7] and the O(1P)-O(2P)-H(1P) valence bond angle of 101.8° is similar to that in H_2O_2 (96–102°).[9] As previously demonstrated in Cu^{II}–tppa (tppa = tris(6-pivalamide-2-pyridylmethyl)amine) complexes with small molecules such as OH^- ($[Cu^{II}(tppa)(OH^-)]^+$)[10] and N_3^-, ($[Cu^{II}(tppa)(N_3^-)]^+$),[11] the two amine H atoms stabilize the hydroperoxide group (seen by the direction of two N–H bond vectors and distances between the peroxo oxygen atom and the hydrogen-bonded nitrogen atoms (O(1P)–N(3A) 2.78, O(1P)–N(3B) 2.79 Å).

These results clearly indicate that the novel copper complexes $[Cu^{II}(bppa^-)]ClO_4$ (**1**) or $[Cu^{II}(bppa)(CH_3COO)]ClO_4$ (**2**) react with hydrogen peroxide to generate $[Cu^{II}(bppa)(OOH^-)]^+$ (**3**).[12] It is also apparent that the N–H hydrogen bonding and hydrophobic *tert*-butyl groups contribute significantly to the stabilization of the extremely thermally unstable hydroperoxo species. We have confirmed that a particular arrangement of noncovalently interacting groups is essential for the coordination of small molecules such as HOO^- by metal complexes. These hydroperoxo complexes could serve as models for the active center in biological systems, and the elucidation of their chemistry, in particular the metal–oxygen interactions, will enable us to gain insight into the mechanism of the catalysis by copper oxygenase.

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