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A Structurally Characterized Mononuclear Copper(II)−Superoxo Complex

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Copper plays an important role in catalytic oxidation reactions in biological systems through the interaction with dioxygen (O_2). Copper proteins contain mono-, di-, tri-, or multinuclear centers according to their function.[1] In each case, the formation of a 1:1 Cu−O_2 adduct is probably important as an intermediate in the reaction of dioxygen with copper enzymes, yet few such intermediates have been characterized.[2] In order to investigate the interaction and reactivity of dioxygen with a single copper ion, appropriate ligand designs have been developed by many chemists,[3] and the formation of Cu−O_2 1:1 species has been revealed chemically and/or spectroscopically from either Cu(I)/O_2[3] or Cu(II)/O_2^- reactions.[4] However, the distinct structural characterization of a superoxo complex has not yet been confirmed. We independently designed and prepared the copper complex with a new tripodal tetradentate ligand, tris[(6-(pivaloylamino)-2-pyridyl)methyl]ammine (TPPA), for this purpose.[5] In this communication, we describe the successful uptake of dioxygen by the mononuclear copper complex with TPPA. The spectroscopic characterization and X-ray crystal structure analysis establish this as the first example of an isolated copper−superoxo species.

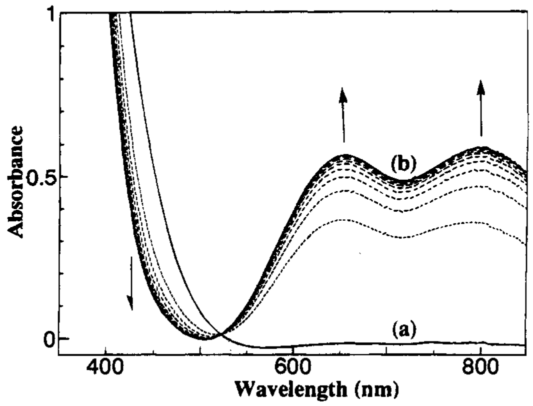

Figure 1. Electronic absorption spectral changes upon addition of O_2 (b) to the Cu(I)−TPPA complex (a) in MeOH at −80 °C.

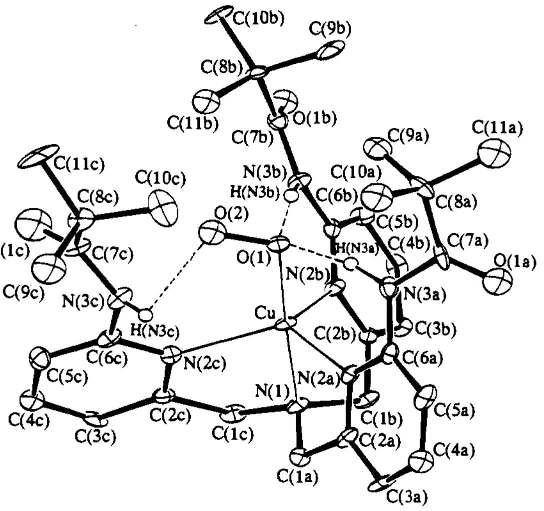

Figure 2. ORTEP drawing of the $[Cu(tppa)(O_2)]^+$ complex with the atomic labeling scheme.

The direct O_2 addition to the Cu(I)−TPPA complex prepared from $[Cu(CH_3CN)_4]ClO_4$ and TPPA (1:1) in methanol solution at −80 °C results in an immediate spectral change (Figure 1). The presence of two weak, well-separated absorptions in the d−d region (λ = 657 (ϵ = 100 M^{-1} cm^{-1}) and 803 nm (ϵ = 120 M^{-1} cm^{-1})) suggests that the oxidation state of the copper ion is divalent. A shoulder peak assignable to $O_2^- \rightarrow$ Cu(II) LMCT band also occurred at ca. 315 nm ($\epsilon \sim 4000$ M^{-1} cm^{-1}). Moreover, the spectrum is very similar to that for the [Cu(tris(2-pyridylmethyl)ammine)]−O_2 adduct previously reported by Karlin et al.[3d,e] The solution of the complex at −80 °C was simultaneously shown to be EPR silent. We attribute this apparent diamagnetism to a strong magnetic coupling between the copper(II) ion and the superoxide. Similar spectroscopic results were also observed in THF solution.

To clarify the structure of the complex, we were able to analyze its crystal structure. Allowing a solution of the complex to stand in a freezing room for several days gave a greenish-blue crystal suitable for X-ray diffraction measurements. The crystal structure of the complex,[6] shown in Figure 2, is very similar to the $[Cu(tppa)Cl]ClO_4$ complex previously reported: the coordination environment around the central copper atom is an axially compressed trigonal bipyramid. The equatorial positions of trigonal plane are occupied by three pyridine nitrogen atoms (Cu−N(2a) = 2.109(4) Å, Cu−N(2b) = 2.139(4) Å, Cu−N(2c) = 2.169(4) Å), and one of the axial positions is coordinated by the tertiary amine nitrogen atom (Cu−N(1) = 1.992(4) Å). Interestingly, the other axial position is occupied by a diatomic molecule in an end-on configuration. We assigned this ligand as a superoxide ion, judging from the bond

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[1] (a) *Metal Ion Activation of Dioxygen: Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980; Vol. 2. (b) Ingraham, L. L.; Meyer, D. L. Biochemistry of Dioxygen. In *Biochemistry of the Elements*; Frieden, E., Ed.; Plenum Press: New York, 1985; Vol. 4. (c) *Bioinorganic Chemistry of Copper*, Karlin, K. D., Tyeklár, Z., Eds.; Chapman & Hall: New York, 1993.

[2] (a) Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344. (b) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3−68. (c) Kurtz, D. M. *Chem. Rev.* **1990**, *90*, 585. (d) Que, L., Jr. *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, 1993; pp 261−315. (e) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 521−542.

[3] (a) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057−4059. (b) Thompson, J. S. In *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guiderland, NY, 1986; Vol. 2, pp 1−10. (c) Tahir, M. M.; Karlin, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 7600−7601. (d) Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 5868−5870. (e) Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Niklaus, P.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1993**, *115*, 9506−9514. (f) Wei, N.; Murthy, N. N.; Chen, Q.; Zubieta, J.; Karlin, K. D. *Inorg. Chem.* **1994**, *33*, 1953−1965.

[4] (a) Nappa, M.; Valentine, J. S.; Miksztal, A. R.; Schugar, H. G.; Isied, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 7744−7746. (b) O'Young, C.-L.; Lippard, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 4920−4924. (c) Nishida, Y.; Unoura, K.; Watanabe, I.; Yokomizo, T.; Kato, Y. *Inorg. Chim. Acta* **1991**, *181*, 141−143. (d) Cabelli, D. E.; Bielski, B. H.; Holcman, J. *J. Am. Chem. Soc.* **1987**, *109*, 3665−3669. (e) Bailey, C. L.; Bereman, R. D.; Rillema, D. P. *Inorg. Chem.* **1986**, *25*, 3149−3153. (f) Weinstein, J.; Bielski, B. H. *J. Am. Chem. Soc.* **1980**, *102*, 4916−4919.

[5] Harata, M.; Jitsukawa, K.; Masuda, H.; Einaga, H., submitted for publication.

[6] Crystal data: $C_{33}H_{45}N_7O_9CuCl$, MW = 782.76, orthorhombic, space group *Pccn*; *a* = 11.253(1), *b* = 35.238(5), and *c* = 18.201(2) Å, *V* = 7217.2 Å^3, *Z* = 8, D_c = 1.441 g cm^{-3}; Mo Kα (λ = 0.710 73 Å); μ = 8.09 cm^{-1}, $3 < 2\theta < 55°$. 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. Of 8081 unique reflections, 5127 [$I > 3\sigma(I)$] are observed. The structure was solved by the heavy-atom method and refined anisotropically. The ClO_4^- anion lay on the crystallographic twofold axis symmetry with one-half occupancies. All hydrogen atoms were located from difference Fourier maps, and their parameters were refined with isotropic thermal parameters. Final *R* and R_w factors were 0.0681 and 0.0956, respectively.

length (O(1)−O(2) = 1.235(9) Å) and the bond angle (Cu−O(1)−O(2) = 108(1)°). The presence of the superoxo group, furthermore, is evidenced from the direction of three N−H bond vectors and hydrogen-bonding distances between them: O(1)⋯N(3a) = 2.84 Å, O(1)⋯N(3b) = 2.82 Å, and O(2)⋯N(3c) = 2.21 Å.

Bubbling CO gas into a CH_3OH/THF/EtCN (4:3:3) solution of the superoxo species at −80 °C led to a significant color change from yellow-green to pale yellow. The absorption spectra, when alternate bubblings of O_2 and CO to the solution were carried out, clearly exhibited a reversible change with an isosbestic point at 521 nm. The high anodic potential value of the Cu(I) complex measured previously by cyclic voltammetry, +0.225 V vs Ag/AgCl,[5] supports the above results.

The results given here indicate that the newly designed $[Cu(tppa)]^+$ complex successfully reacts with the dioxygen to generate $[Cu(tppa)(O_2)]^+$, which has been characterized on the basis of electronic absorption and EPR spectra, X-ray structure analysis, and the reversible spectral changes by alternate addition of O_2 and CO. It may be that the N−H hydrogen-bonding and hydrophobic *tert*-butyl groups in the present Cu−TPPA complex are important for stabilizing bound dioxygen as a superoxo species. We believe that this result has been achieved by molecular recognition with a combination of noncovalent bonding groups, and we hope this work will become a starting point for the further study of the metal−oxygen interaction in copper oxygenase chemistry.

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Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and torsion angles (11 pages); listing of observed and calculated structure factors (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.