

A Monomeric Side-On Superoxocopper(II) Complex: $\text{Cu}(\text{O}_2)(\text{HB}(3\text{-tBu-5-iPrpz})_3)$

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Formation of a monomeric superoxocopper(II) species is suggested as an initial reaction step in a wide variety of chemical/biological oxidations catalyzed by copper.¹ For instance, involvement of such an intermediate is common to all hypothesized reaction mechanisms proposed for copper monooxygenases containing a monomeric site such as dopamine- β -hydroxylase,² phenylalanine hydroxylase,³ and peptidylglycine- α -amidating enzyme.⁴ Despite considerable efforts,⁵ however, no X-ray structure of this type complex has been reported so far.⁶ In this communication, we describe the first example of a side-on superoxocopper(II) complex, which was characterized unambiguously by X-ray analysis.

Since the reaction between dioxygen and a copper(I) complex with $\text{HB}(3,5\text{-iPr}_2\text{pz})_3$ merely results in instantaneous formation of the $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dinuclear copper(II) complex,⁷ our synthetic strategy lies in the employment of a more sterically demanding ligand, $\text{HB}(3\text{-tBu-5-iPrpz})_3$, to prevent the dimerization; note that $\text{HB}(3\text{-tBu-5-iPrpz})_3$ inhibits approach of the metal ions to closer than 4 Å, whereas the $\text{Cu}\cdots\text{Cu}$ distance in the $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ complex is 3.6 Å.⁸ The DMF adduct $\text{Cu}(\text{DMF})(\text{HB}(3\text{-tBu-5-iPrpz})_3)$ (**1**)⁹ was our preferred selection as a copper(I) precursor because of the advantage of its stability against air in a solid state. When complex **1** was dissolved in a noncoordinating solvent, it became reactive for dioxygen binding, presumably because of the DMF dissociation. Thus a pale yellow solution of **1** in CH_2Cl_2 turned to reddish brown

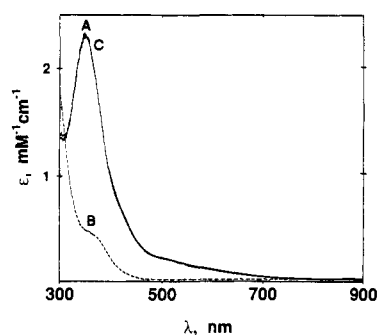


Figure 1. UV-vis spectra demonstrating the reversible dioxygen binding behavior of $\text{Cu}(\text{DMF})(\text{HB}(3\text{-tBu-5-iPrpz})_3)$ (**1**). The spectra were recorded in toluene at room temperature under argon for spectrum B and under 1 atm of O_2 for spectra A and C.

when it was treated with 1 atm of O_2 at $-50\text{ }^\circ\text{C}$ in CH_2Cl_2 . The oxygenated product exhibits two characteristic absorption bands at 352 and 510 nm with a weak shoulder at ca. 660 nm; the absorption coefficients are 2330 and $230\text{ M}^{-1}\text{ cm}^{-1}/\text{Cu}$, respectively. The manometric determination of the O_2 binding stoichiometry suggests the formation of a 1:1 $\text{Cu}\text{-O}_2$ adduct ($\text{Cu}:\text{O}_2 = 0.9$, average of two trials). The reversible formation of this O_2 adduct is demonstrated by a vacuum cycling experiment, and this process can be followed spectroscopically as shown in Figure 1. When the solution of **1** in toluene was treated with 1 atm of O_2 at $-50\text{ }^\circ\text{C}$, a reddish brown solution was obtained, the spectrum being indicated as spectrum A. Evaporation of the solution at room temperature under vacuum to dryness, followed by addition of the same volume of the solvent, afforded the copper(I) precursor, which gave only a shoulder band at 370 nm (see spectrum B). When the solution was re-treated with O_2 at $-50\text{ }^\circ\text{C}$, the O_2 adduct was regenerated (spectrum C). The cycle can be repeated, although a small degree of decomposition occurred.

The O_2 adduct was successfully isolated as reddish brown solids from a saturated solution of **1** in CH_2Cl_2 at $-20\text{ }^\circ\text{C}$ under 1 atm of O_2 .¹⁰ The IR spectrum of the adduct exhibits a characteristic band at 1112 cm^{-1} , which is assignable to $\nu(\text{O}\text{-O})$ of a superoxide ion. While the observation of an expected shift of the band to ca. 1060 cm^{-1} upon $^{18}\text{O}_2$ substitution was hampered owing to the presence of an intense band in the region due to the hydrotris(pyrazolyl)borate ligand, the preliminary resonance Raman exploration with excitation at 364 nm lends support to the assignment (the sample prepared with $^{16}\text{O}_2$ gave rise to a band at 1111 cm^{-1} which was shifted to 1062 cm^{-1} upon isotropic substitution).¹¹ In conjunction with the analytical result, the aforementioned results led to the formulation of the O_2 adduct as $\text{Cu}(\text{O}_2)(\text{HB}(3\text{-tBu-5-iPrpz})_3)$ (**2**). The monomeric superoxo structure is further endorsed by its magnetic property. Since both copper(II) and superoxide ions possess a half spin, one may expect an enormous magnetic coupling in the superoxocopper(II) complex, resulting in a seeming diamagnetism. To evaluate this point, the $^1\text{H-NMR}$ spectrum of the isolated **2** was recorded in CD_2Cl_2 at $-40\text{ }^\circ\text{C}$ under 1 atm of O_2 . The spectrum consists of very sharp signals with a high resolution, indicating that the complex is virtually diamagnetic at this temperature. This is confirmed by the variable temperature magnetic susceptibility measurement by SQUID performed for a solid sample.¹²

(10) Anal. Calcd for $\text{C}_{30}\text{H}_{52}\text{N}_6\text{BCuO}_2$: C, 59.74; H, 8.69; N, 13.93. Found: C, 59.39; H, 8.85; N, 13.39. UV-vis (toluene, $23\text{ }^\circ\text{C}$): 352 (ϵ , $2330\text{ M}^{-1}\text{ cm}^{-1}$), 510 (sh, 230), 660 nm (90). FTIR (cm^{-1} , KBr): $\nu(\text{BH})$ 2564, $\nu(\text{OO})$ 1112. $^1\text{H-NMR}$ (δ/ppm , CD_2Cl_2 , 400 MHz, $-40\text{ }^\circ\text{C}$): 1.19 (d, $J = 6.4\text{ Hz}$, 18H, CHMe_2), 1.66 (s, 27H, CMe_3), 3.36 (m, $J = 6.4\text{ Hz}$, CHMe_2), 6.19 (s, 3H, pz).

(11) T. Kitagawa et al., unpublished result.

(12) E. I. Solomon et al.; the details will be published elsewhere.

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(9) Anal. Calcd for $\text{C}_{33}\text{H}_{59}\text{N}_7\text{BCuO}$: C, 61.52; H, 9.23; N, 15.22. Found: C, 61.10; H, 9.11; N, 15.38. FTIR (cm^{-1} , KBr): $\nu(\text{BH})$ 2530, $\nu(\text{CO})$ 1661. $^1\text{H-NMR}$ (δ/ppm , $\text{DCON}(\text{CD}_3)_2$, 400 MHz, $25\text{ }^\circ\text{C}$): 1.22 (d, $J = 6.7\text{ Hz}$, 18H, CHMe_2), 1.35 (s, 27H, CMe_3), 2.78 (s, 3H, HCONMe_2), 2.95 (s, 3H, HCONMe_2), 3.58 (m, $J = 6.7\text{ Hz}$, 3H, CHMe_2), 5.84 (s, 3H, pz), 8.02 (s, 1H, HCONMe_2).

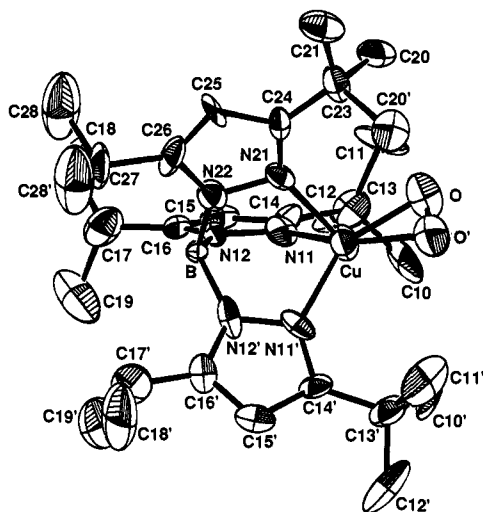


Figure 2. ORTEP view of $\text{Cu}(\text{O}_2)(\text{HB}(3\text{-tBu-5-iPrpz})_3)$ (**2**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu–O, 1.84(1); Cu–N11, 1.99(2); Cu–N21, 2.25(2); O–O', 1.22(3); O–Cu–N11, 111.7(7); O–Cu–N11', 148.8(7); O–Cu–N21, 104.8(7); N11–Cu–N11', 93(1); N11–Cu–N21, 91.4(7); O–Cu–O', 38.7(8); Cu–O–O', 70.6(4).

Finally, the molecular structure of **2** was determined by X-ray crystallography.¹³ The preliminary X-ray structure is given in Figure 2. The O–O bond distance of 1.22(3) Å is typical for superoxide ion bound to transition metal ions, establishing definitely the monomeric superoxo structure. Since the molecule sits on a crystallographically imposed mirror plane, the coordination mode of the superoxide is symmetric side-on. An analogous side-on superoxo complex $\text{Co}(\text{O}_2)(\text{HB}(3\text{-tBu-5-Mepz})_3)$ has been reported.¹⁴ Note that the complex was also

(13) Slow recrystallization of **2** from diethyl ether/2-methyl-2-propanol at -26°C gave crystals of **2** of marginal quality for X-ray diffractions. **2** ($\text{C}_{30}\text{H}_{52}\text{N}_6\text{BCuO}_2$; $M_w = 603.12$) crystallized in the orthorhombic space group $Pnma$, with $a = 20.564(11)$ Å, $b = 16.270(11)$ Å, $c = 10.007(6)$ Å, $V = 3348(3)$ Å³, and $Z = 4$. The X-ray data collection ($5^\circ < 2\theta < 50^\circ$) was carried out at 23°C . The initial structure was solved by the direct method and expanded using Fourier techniques. Because of the low quality of the data, the boron atom could not be refined anisotropically. The other non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method (*TEXSAN*). Hydrogen atoms were included but not refined. The refinement based on 979 observed reflections ($I > 2.0\sigma(I)$) with 193 variable parameters converged to the $R(R_w)$ factor of 11.60% (8.46%). The preparation of single crystals of **2** is extremely difficult to accomplish, and therefore all our attempts to obtain crystals of higher quality have been unsuccessful.

isolated with a highly hindered hydrotris(pyrazolyl)borate as a supporting ligand. While the overall structural features of these Cu and Co complexes are similar, a significant deviation is noteworthy; whereas in the Co complex all Co–N distances are comparable (2.01–2.07 Å), one of the Cu–N bonds (Cu–N21) in **2** is elongated considerably so that N21 serves an apical ligand. Therefore, the coordination geometry of **2** is best described as square-pyramidal. Since the superoxide is located on a basal plane, a large overlapping population between the $d_{x^2-y^2}$ lobe and the π^* orbital of the superoxide is anticipated, accounting for the diamagnetic property observed for **2**. While 3-*tert*-butyl-substituted hydrotris(pyrazolyl)borates work as strong “tetrahedral enforcers”,⁸ the adoption of a five-coordinate side-on superoxo structure rather than a tetrahedral terminal one indicates that the peculiarity of Cu(II) ion to favor a tetragonal geometry gains a more driving force.

With a less sterically demanding hydrotris(pyrazolyl)borate, formation of a monomeric superoxo complex $\text{Cu}(\text{O}_2)(\text{HB}(3,5\text{-Me}_2\text{pz})_3)$ was proposed previously,^{5g} yet the reported properties of the complex are consistent with those of $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ dinuclear complex $[\text{Cu}(\text{HB}(3,5\text{-Me}_2\text{pz})_3)]_2(\text{O}_2)$, arousing suspicion about the structural identification. The present work provides solid evidence that the monomeric superoxocopper(II) complex exhibits characteristic properties distinct from those of the $\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo}$ complex.

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Supplementary Material Available: Summary of X-ray analysis, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for **2** (10 pages); listing of observed and calculated structure factors for **2** (4 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.

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