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Formation of (μ-Hydroxo)(μ-azido) Dinuclear Copper Complex from μ-η^2:η^2-Peroxo Complex

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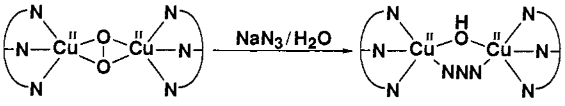
Hemocyanin (Hc) is a copper protein which functions as an oxygen carrier for invertebrates. Based on synthetic model studies, we have been demonstrating that dioxygen is bound to the dinuclear copper site as μ-η^2:η^2-peroxide.[1] Very recently, Magnus et al. have determined the crystal structure of oxyHc from *Limulus*, which supports our hypothesis.[2] The peroxide coordination in oxyHc, however, had been believed to be *cis*-μ-1,2, with the existence of an endogenous bridging ligand, most likely hydroxide. This was deduced mainly from extensive spectroscopic studies on metHcs, particularly met-azideHc, which led to the conclusion that met-azideHc adopts a (μ-hydroxo)(μ-1,3-azido) bridging structure.[3] Since met-azideHc is derived from oxyHc upon azide treatment, given the coordination mode of peroxide in oxyHc as μ-η^2:η^2, it is a problem of controversy how the (μ-hydroxo)(μ-1,3-azido) bridging unit can be constructed. To address this question, we have explored the reaction of the model complex $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(O_2)$ (**1**) with azide ion.

When a CH_2Cl_2 solution of **1** was mixed with aqueous NaN_3 (2 equiv) under argon for 5 min, the color of the CH_2Cl_2 phase turned into intense blue from deep purple. From the solution, $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)(N_3)$ (**2**) was isolated almost quantitatively (Scheme I).[4] Complex **2** was also obtained by the reaction of $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)_2$ (**3**) with excess aqueous NaN_3 (1.5–10 equiv). Although both reactions were carried out in the presence of an excess amount of azide, no detectable amount of $[Cu(N_3)(HB(3,5\text{-}iPr_2pz)_3)]_2$[5] was formed. Thus the formation of **2** is a thermodynamically favorable reaction. The slow recrystallization of **2** from CH_2Cl_2 at −20 °C gave single crystals of **2**·3(CH_2Cl_2) suitable for X-ray diffractions.[6] The molecular structure of **2** is shown in Figure 1, which represents a novel (μ-hydroxo)(μ-1,3-azido) bridging core. This is the first example of such a structure, while a (μ-hydroxo)(μ-1,1-azido) dinuclear copper complex was reported previously.[7] The molecule sits on a C_2 axis, and the geometry of each copper ion is best described as square-pyramidal with one nitrogen atom from the tris(pyrazolyl) borate as an apical ligand (N2). Accordingly, the hydroxo and azido bridging ligands occupy the basal positions. The Cu⋯Cu separation of 3.71 Å is slightly longer than that found in **1** (3.56 Å) and close to the value estimated for met-azideHc by EXAFS (3.66 Å).[8]

Scheme I



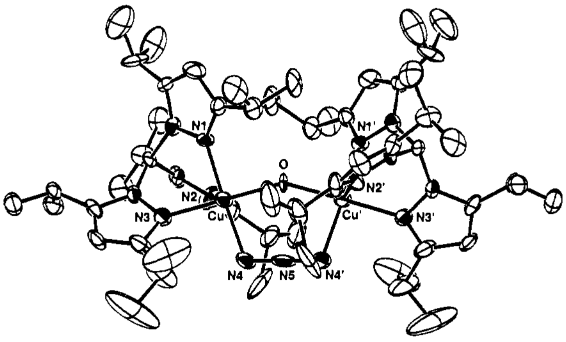


Figure 1. ORTEP view of $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(OH)(N_3)$ (**2**). The molecule sits on a C_2 axis. The CH_2Cl_2 molecules of crystallization are omitted for clarity. The selected bond distances (Å) and angles (°): Cu⋅⋅Cu, 3.713(4); Cu–O, 1.929(4); Cu–N1, 1.99(1); Cu–N2, 2.21(1); Cu–N3, 2.01(1); Cu–N4, 2.06(1); N4–N5, 1.19(1); N1–Cu–N2, 94.6(5); N1–Cu–N3, 88.2(4); N1–Cu–O, 91.2(5); N1–Cu–N4, 163.4(7); N2–Cu–N3, 89.6(5); N2–Cu–O, 95.6(3); N2–Cu–N4, 100.4(4); N3–Cu–O, 174.7(4); N3–Cu–N4, 92.4(4); O–Cu–N4, 86.7(5); Cu–N4–N5, 110(1); Cu–O–Cu′, 148.4(8).

Complex **2** exhibits three characteristic bands at 340 (19 000), 380 (sh) and 605 (810) nm. The Gaussian resolution of the band at 605 nm indicates the overlapping of a band at ca. 680 nm which is assigned to the d–d band. In a *cis*-μ-1,3 coordination mode, $N_3\pi_\sigma^{nb} \rightarrow Cu(II)$ transition is theoretically predicted to split into two due to the dipole interaction.[9] Such a split is observed for several *cis*-μ-1,3-azide complexes bridged with a phenoxide[10] or an alkoxide:[11] they give the bands at ca. 370 and 400–500 nm. Hence, the bands at 380 and 605 nm are assignable to the $N_3\pi_\sigma^{nb} \rightarrow Cu(II)$ LMCT bands. The assignment of the intense band at 340 nm is not clear at the present stage but may be ascribed to the pyrazole nitrogen-to-copper LMCT band.[12] Complex **2** is EPR silent, suggesting a strong antiferromagnetic property by the superexchange coupling between the two copper ions predominantly mediated through the hydroxo bridge. Accordingly, ^1H NMR spectrum and variable-temperature magnetic susceptibilities indicate that **2** is diamagnetic ($-2J > 600$ cm^{-1}) at room temperature. The $\nu_{asym}(N_3)$ of **2** (2028 cm^{-1}) may be compared

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(1) (a) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 151. (b) Kitajima, N.; Fujisawa, K.; Moro-oka, Y.; Toriumi, K. *J. Am. Chem. Soc.* **1989**, *111*, 8975. (c) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664. (d) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277. (e) Kitajima, N. *Adv. Inorg. Chem.* **1992**, *39*, 1. (f) Kitajima, N.; Moro-oka, Y. *J. Chem. Soc., Dalton Trans.*, in press.

(2) Magnus, K.; Ton-That, H. *J. Inorg. Biochem.* **1992**, *47*, 20.

(3) (a) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378. (b) Pate, J.; Thamann, T. J.; Solomon, E. I. *Spectrochim. Acta* **1986**, *42A*, 313. (c) Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; p 116.

(4) Anal. Calcd for $C_{54}H_{93}N_{15}B_2Cu_2O$: C, 58.06; H, 8.39; N, 18.81. Found: C, 57.84; H, 8.54; N, 18.71. IR(KBr, cm^{-1}): ν(OH) 3631; ν(BH) 2538; $\nu(N_3)$ 2028. UV–vis (in CH_2Cl_2, nm, ϵ/cm^{-1} M^{-1}): 340 (19 000), 380 (sh, 6300), 605 (810). ^1H NMR (270 MHz, in toluene-d_8 at 25 °C): 5.80 (s, 6H, pz), 3.83 (m, J = 6.8 Hz, 6H, C*H*Me$_2$), 3.58 (m, J = 6.8 Hz, 6H, C*H*Me$_2$), 1.23 (d, J = 6.8 Hz, 36H, CH*Me*$_2$), 1.18 (d, J = 6.8 Hz, 36H, CH*Me*$_2$), −5.63 (s, 1H, O*H*).

(5) The dinuclear structure of the azido complex was established by X-ray crystallography. The details will be reported elsewhere.

(6) X-ray quality crystals of **2** were obtained from CH_2Cl_2 in a solvated form. **2**·3(CH_2Cl_2) crystallized in the monoclinic space group $C_{2/c}$ with a = 29.244(8) Å, b = 13.630(2) Å, c = 20.340(7) Å, β = 114.63(2)°, V = 7369(7) Å^3, and Z = 4. The structure was solved by the Patterson method. All non-hydrogen atoms except the ones on the solvent molecules were refined anisotropically by the block-diagonal least-squares method. Hydrogen atoms were calculated and included isotropically. The current $R(R_w)$ factor converged with 9.86(8.20)% for 2719 reflections collected at −45 °C ($I > 5\sigma(I)$, $3 < 2\theta < 45°$).

(7) Kahn, O.; Sikorav, S.; Gouteron, J.; Jeannin, S.; Jeannin, Y. *Inorg. Chem.* **1983**, *22*, 2877.

(8) Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. I.; Spiro, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 86.

(9) Pate, J. E.; Ross, P. K.; Thamann, T. J.; Reed, C. A.; Karlin, K. D.; Sorrell, T. N.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 5198.

(10) Sorrell, T. N.; O'Conner, C. J.; Anderson, O. P.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 4199.

(11) (a) McKee, V.; Dagdigian, J. V.; Bau, R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 7000. (b) McKee, V.; Zvagulis, M.; Dagdigian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765.

(12) A similar intense band is observed at ca. 350 nm for **1** and $[Cu(HB(3,5\text{-}iPr_2pz)_3)]_2(S_2)$, while in the former case the band is dominated by $O_2^{2-} \rightarrow Cu(II)$ LMCT transition: Baldwin, M. J.; Root, D. E.; Pate, J. E.; Fujisawa, K.; Kitajima, N.; Solomon, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 10421. This band may include the hydroxo–Cu(II) LMCT transition, but its contribution is predicted to be small since **3** gives only a weak band at 340 (1800) nm.

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to 2042 cm^{-1} reported for met-azideHc from *Busycon*.[3b] Thus, the properties of **2** are reasonably similar to those known for met-azideHc,[13] while there is slight inconsistency in absorption spectra which may reflect the small geometrical change around the copper. In fact, met-azideHcs from different species give variable UV–vis spectra.[3]

When **1** was reacted with NaN_3 dissolved in $H_2{}^{18}O$, the ν(OH) originally observed at 3631 cm^{-1} was shifted to 3619 cm^{-1}, indicating the incorporation of $^{18}OH^-$ into **2** from the water. Since the isotopic substitution between the hydroxide in **2** and water is fast, two plausible interpretations are suggested for the incorporation of the hydroxide from water into **2**. One possibility is that **2** is directly formed from **1** via O–O bond cleavage of the μ-η^2:η^2-peroxide with the addition of azide ion. The subsequent fast ligand replacement of the hydroxo bridge results in formation of the ^{18}O derivative. The other interpretation is that **1** decomposes to the bis(μ-hydroxo) complex **3** isotopically substituted at the initial stage of the reaction, from which ^{18}O-labeled **2** is generated. While we cannot conclude the definite mechanism for the formation of **2**, the present experimental results clearly demonstrate that the μ-η^2:η^2-peroxide bridge in oxyHc can be converted into a (μ-hydroxo)(μ-1,3-azido) unit in the presence of azide ion, where the hydroxide is originated from water.

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Supplementary Material Available: Experimental and crystallographic details, atomic coordinates, isotropic and anisotropic thermal parameters of non-hydrogen atoms, and bond distances and bond angles, and electronic spectrum of **2** (9 pages); observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(13) Met-azideHc from *Busycon*: UV–vis; 380 (1220), 480 (sh) nm; IR $\nu(N_3)$, 2042 cm^{-1}; diamagnetic.[3b] Met-azideHc from *Limulus*: UV–vis, <375 (>2000), 500 (600); diamagnetic.[3a]