Crystal Structure and Reversible O_2-Binding of a Room Temperature Stable μ-η^2:η^2-Peroxodicopper(II) Complex of a Sterically Hindered Hexapyridine Dinucleating Ligand

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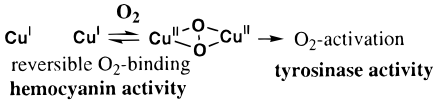
Oxyhemocyanin (oxyHc)[1] and oxytyrosinase (oxyTy)[2] have a similar μ-η^2:η^2-peroxodicopper(II) (Cu_2O_2) structure[2] in the active sites but show different functions, reversible O_2-binding[3] and O_2-activation,[4] respectively (see Scheme 1). On the basis of the large

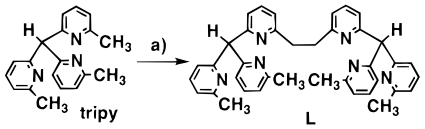
Scheme 1



difference of the Cu−Cu distances, 4.6 and 3.6 Å, for deoxy- and oxyHc, respectively, it is supposed that O_2 is released from oxyHc when the Cu−Cu distance is elongated.[2] The reaction of the μ-η^2:η^2-Cu_2O_2 complex may be directed by various factors, such as the Cu−Cu distance, the Cu coordination geometry, and the electronic effect of the nitrogen donor ligand. However, despite excellent mechanistic studies on the reaction of the μ-η^2:η^2-Cu_2O_2 complex,[5] what determines the direction, reversible O_2-binding or O_2-activation, has not been clearly shown.[2,6] Thermally stable μ-η^2:η^2-Cu_2O_2 complexes $[Cu(HB(3,5\text{-}Me_2pz)_3)]_2(O_2)$ (**1**)[7a,b] and $[Cu(HB(3,5\text{-}^iPr_2pz)_3)]_2(O_2)$ (**2**)[7c] were reported by Kitajima et al. as structural models of oxyHc and oxyTy but their O_2-binding is irreversible. Therefore, to clarify the relationship between the structure of the μ-η^2:η^2-Cu_2O_2 complex and the reversibility in the O_2-binding a thermally stable μ-η^2:η^2-Cu_2O_2 complex which realizes the reversible O_2-binding is necessary.[8]

First, we prepared a sterically hindered tripyridylmethane ligand, tris(6-methyl-2-pyridyl)methane (tripy).[9] Its μ-η^2:η^2-Cu_2O_2 complex $[Cu(tripy)]_2O_2\cdot(PF_6)_2$ (**3**) is prepared by O_2 addtion to a Cu(I) complex of tripy, but not stable at room temperature. Then, tripy is converted to 1,2-bis[2-(bis(6-methyl-2-pyridyl)methyl)-6-pyridyl]ethane (L), which has two sterically hindered tripyridylmethane units connected by an ethylene spacer (see Scheme 2). L forms the μ-η^2:η^2-Cu_2O_2 complex $[Cu_2O_2(L)](PF_6)_2$ (**4**).[10]

Scheme 2



[a] *t*-BuLi in dry THF/1,2-dibromoethane.

The half-life time of **4** in CH_2Cl_2 at 25 °C is 25.5 h. To our knowledge, **4** is the most stable in all μ-η^2:η^2-Cu_2O_2 complexes reported so far. Although many dinucleating ligands[11] have been synthesized with the expectation that those having six donor sets similar to imidazole groups in the active site of Hc would stabilize the μ-η^2:η^2-Cu_2O_2 structure, such a high stability as **4** has never been attained. **4** is the first example of the room-temperature stable μ-η^2:η^2-Cu_2O_2 complex with a dinucleating ligand. Here, we describe the synthesis, crystal structure, and reversible O_2-binding of **4**.

4 was prepared either by reaction of di-μ-hydroxodicopper(II) complex $[Cu_2(OH)_2(L)](PF_6)_2$ (**5**) with H_2O_2 or by O_2 addition to dicopper(I) complex $[Cu_2(MeCN)_2(L)]$ $(PF_6)_2$ (**6**), isolated as a purple solid by concentration of the reaction mixture at −20 °C, and purified by recrystallization from CH_2Cl_2/$PhCH_3$ at −50 °C. Physicochemical properties[10] of **4** are similar to those of oxyHc.[1] Slow recrystallization gave crystals of **4**·$3CH_2Cl_2$ suitable for X-ray crystal structure analysis.[12] As shown in Figure 1, **4** has a discrete dicopper(II) unit bridged by a peroxide in the μ-η^2:η^2-mode. L stabilizes **4** by encapsulating the μ-η^2:η^2-Cu_2O_2 core

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(10) A satisfactory elemental analysis was obtained for **4** dried under vacuum. Anal. Calcd for $C_{38}H_{36}N_6O_2P_2F_{12}Cu_2$: C, 44.53; H, 3.54; N, 8.20; Cu, 12.29. Found: C, 44.45; H, 3.52; N, 8.24; Cu, 12.14. UV−vis (CH_2Cl_2, 25 °C): 360 (ϵ 24700), 532 nm (1530). Resonance Raman (Me_2CO, 25 °C): ($^{16}O-^{16}O$) 760 cm^{-1}, ($^{18}O-^{18}O$) 719 cm^{-1}. ESI MS (CH_2Cl_2, 25 °C): *m*/*z* 881 $\{[Cu_2O_2(L)](PF_6)]\}^+$. ^1H NMR [$(CD_3)_2CO$, −30 °C, δ, ppm (TMS)]: 3.18 (s, 12H, Me), 4.30 (bs, 4H, CH_2), 6.77 (s, 2H, CH), 7.64 (d, 4H, 5-py), 7.81 (d, 2H, 5-pr′), 7.97 (d, 4H, 3-py), 8.12−8.15 (d, 2H, 3-py′, t, 4H, 4-py), 8.27 (t, 2H, 4-py′). ESR: silent in CH_2Cl_2 at 77 K.

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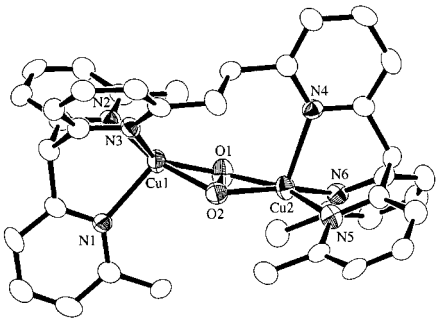

Figure 1. ORTEP view (40% probability) of the crystal structure of **4**·3CH_2Cl_2. Unlabeled atoms (open circles) represent carbon atoms. Selected interatomic distances (Å) and angles (deg) are as follows: Cu(1)−O(1), 1.924(6); Cu(1)−O(2), 1.907(6); Cu(1)−N(1), 2.136(7); Cu(1)−N(2), 1.977(7); Cu(1)−N(3), 2.043(7); Cu(2)−O(1), 1.913(6); Cu(2)−O(2), 1.888(6); Cu(2)−N(4), 2.265(7); Cu(2)−N(5), 1.970(7); Cu(2)−N(6), 1.992(7); Cu···Cu, 3.477(7); O(1)−O(2), 1.485(8); Cu(1)−O(1)−Cu(2), 130.0(3); Cu(1)−O(2)−Cu(2), 132.8(3); the dihedral angle between the Cu(1), O(1), O(2) and Cu(2), O(1), O(2) planes is 162.92.

with the four 6-methyl groups and the ethylene spacer, which may also enhance the stability of **4** entropically by connecting two Cu(tripy) moieties as a kind of chelate effect. The Cu−Cu distance 3.477 Å of **4** is slightly shorter than 3.560 Å[7] of **2**. On the other hand, the O−O bond length 1.485 Å of **4** is slightly longer than 1.412 Å[7] of **2**. Overall structural features (O_2-bridging mode, bond lengths about the Cu_2O_2 core, and anti-configuration of the two axial Cu−N bonds) of **4** are similar to those of oxyHc and **2**.[7] Different from **2**, however, **4** has no symmetric center. Furthermore, the bond angles about the Cu atoms in **4** are much more distorted than those in **2**; the Cu−O_2−Cu of **4** is slightly bent and the τ values,[13] 0.29 and 0.11, of **4** are much larger than the 0.02 value of **2**. These indicate that the square pyramidal geometry around the Cu atoms in **4** is much more distorted than that in **2**.

As shown in Figure 2, the reversible O_2-binding of **4** was observed, where **4** releases O_2 in MeCN−CH_2Cl_2 (0.001:3, v/v) at 80 °C in vacuo and is regenerated by refilling with O_2 at room temperature. After three cycles of the reversible O_2-binding, the irreversible decomposition is less than 30% of **4** used. It was reported that upon reaction with CO or $P(Ph)_3$ **1** releases O_2 to form $[Cu_2(CO)(HB(3,5\text{-}Me_2pz)_3)]^+$ or $[Cu_2(P(Ph)_3)(HB(3,5\text{-}Me_2pz)_3)]^+$,[7] which are too stable to react with O_2, and **1** is not regenerated. In the present O_2-binding experiments, MeCN contained in the solvent system is substituted for O_2 when O_2 is released from **4** to form **6**. With a similar experiment with **1** and **3**, however, the reversible O_2-binding was not observed. Since the neutral hexapyridine ligand **L** better stabilizes the Cu^I_2 state than the anionic hydrotrispyrazolyl borate ligand $\{HB(3,5\text{-dialkylpz})_3\}^-$, the reversible O_2-binding between **4** and **6** may be

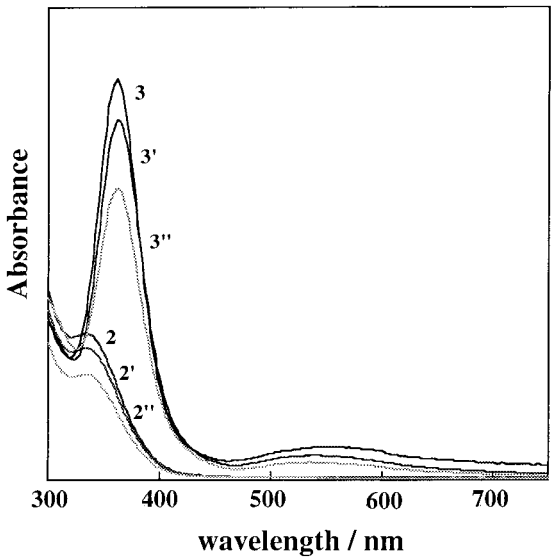

Figure 2. Reversible O_2-binding with **4** in MeCN−CH_2Cl_2 (0.001:3, v/v) at room temperature. Spectrum 3 was obtained with the solution of **4** in MeCN−CH_2Cl_2 (0.001:3, v/v). Spectrum 2 was obtained after degassing the solution by freeze and thaw, and heating the solution at 80 °C. Spectrum 3′ was obtained after O_2 addition to the resultant solution. Spectra 2′, 3″, and 2″ were obtained after the second and third cycles of the repetition of this reversible O_2-binding experiment.

partly owing to the easy accessibility of the Cu^I_2 state from the $Cu^{II}_2O_2$ state.

It is supposed that distortion introduced to the Cu−O_2 bond in oxyHc by elongation of the Cu−Cu distance decreases O_2-affinity of oxyHc so that oxyHc easily releases O_2 to attain reversible O_2-binding.[2] On the other hand, the reversible O_2-binding in the present system may be attained owing to the large distortion of the Cu_2O_2 core in **4**. Karlin and Solomon et al. showed that the distortion of butterfly type μ-η^2:η^2-Cu_2O_2 complexes,[14] which attain the reversible O_2-binding at low temperature, plays an important role in their reactivity.[15] Therefore, we suggest that distortion of the Cu_2O_2 core in the μ-η^2:η^2-Cu_2O_2 complex may be important for controlling aspects of the reversible O_2-binding of the μ-η^2:η^2-Cu_2O_2 complex and the Cu−Cu distance, 3.477 Å, of **4** may be long enough to bind O_2 reversibly because of the distortion of the Cu_2O_2 core.

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Supporting Information Available: Tables S1−S4, crystallographic experimental details, final atomic coordinates, thermal parameters, and full bond distances and angles for **3**, and synthesis and spectroscopic data of ligand L and complexes **1** and **2** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) **4**·3CH_2Cl_2 ($C_{41}H_{42}N_6O_2P_2F_{12}Cu_2Cl_6$, MW 1280.56) crystallized in the triclinic space group *P*1 with $a = 14.003(3)$ Å, $b = 15.695(3)$ Å, $c = 12.600(4)$ Å, $\alpha = 98.56(2)°$, $\beta = 96.49(2)°$, $\gamma = 69.32(2)°$, $V = 2556(1)$ Å^3, $Z = 2$, $R(Rw) = 0.080(0.114)$, GOF = 1.62.

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