Efficient Oxidation of Various Phenols Catalyzed by Di-μ-hydroxodicopper(II) Complexes of a Hexapyridine Dinucleating Ligand

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The di-μ-hydroxodicopper(II) complexes $[Cu_2(OH)_2(hexpy)](X)_2$ [X = ClO_4 and CF_3SO_3, hexpy: 1,2-bis[2-di-(2-pyridyl)methyl-6-pyridyl]ethane] efficiently catalyze the oxidation of various phenols with H_2O_2.

The activation of dioxygen molecule by copper ions has fascinated chemists and biochemists because of its industrial and biological importance.[1] In industry, copper complexes have been used as catalysts for O_2-oxidation of various phenols to afford phenol polymers which are useful as heat-resistant materials.[2] In biological system, phenols are oxidized to *o*-quinones by tyrosinase which activates dioxygen at its dicopper center.[3] Although biomimetic dicopper complexes have been synthesized to enhance the efficiency of the phenol oxidations, their activity has not been satisfactory as an useful catalysts.[4] Therefore, the search of biomimetic dicopper complexes for the phenol oxidations has been continued.

The hexapyridine dinucleating ligand, 1,2-bis[2-di(2-pyridyl)methyl-6-pyridyl]ethane (hexpy), which has two tripyridylmethane units connected by an ethylene linker has been prepared.[5] The ligand forms di-μ-hydroxodicopper(II) complexes $[Cu_2(OH)_2(hexpy)]X_2$, ($X=ClO_4$ **1a** and CF_3SO_3 **1b**)[6] by the reaction with $Cu(OAc)_2{\bullet}4H_2O$ in MeOH. The structure of **1a** has been characterized by a single crystal structure analysis in the present study.[7] The ORTEP diagram of **1a** is shown in Figure 1. Each copper ion is coordinated by a tripyridylmethane unit and two OH-bridges to take a square pyramidal geometry. The copper coordination structure of **1a** is similar to that of the di-μ-hydroxodicopper(II) complex **2** with a hydrotris(3,5-diisopropyl-pyrazolyl)borate ligand,[8] except for a *syn*-configuration of the two apical *N*-atoms in **1a**. The sterically hindered tridentate ligand in **2** favors an *anti*-configuration which may minimize the steric repulsion between the bulky substituents on the ligand. In **1a**, the ethylene linker in hexpy may force the *syn*-configuration.

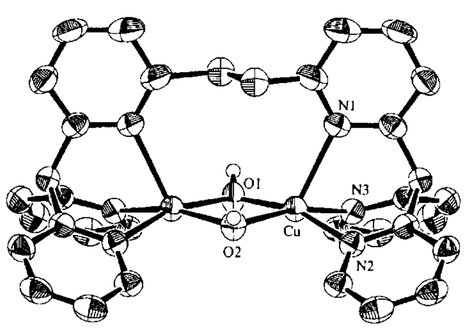


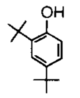
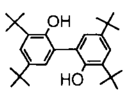
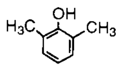
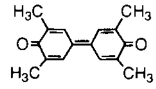
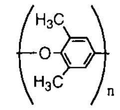
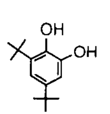
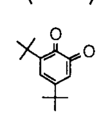
Figure 1. ORTEP view of the cation of **1a**. Selected bond distances (Å) and angles (deg): Cu-Cu 2.989(1), Cu-O(1) 1.931(3), Cu-O(2) 1.937(3), Cu-N(1) 2.362(5), Cu-N(2) 2.020(4), Cu-N(3) 2.026(4), Cu-O(1)-Cu 101.4(2), O(1)-Cu-O(2) 78.7(1), O(1)-Cu-N(1) 111.3(2), O(1)-Cu-N(2) 163.5(2), O(1)-Cu-N(3) 94.7(2).

It is known that **2** reacts with H_2O_2 to give a thermally stable μ-η^2:η^2-peroxodicopper(II) complex, Kitajima's compound, which is a structural model of oxyhemocyanin.[9] However, **1** did not afford its μ-η^2:η^2-peroxodicopper(II) complex by the reaction with H_2O_2, in spite of the structural similarity of **1** to **2**. Considering the fact that the two apical *N*-atoms of the Kitajima's compound adopt an *anti*-configuration, the *syn*-configuration in **1** might be unfavorable for formation of the μ-η^2:η^2-peroxodicopper(II) structure. Interestingly, however, an unique dark purple intermediate, a superoxodicopper(II) complex **3** (Figure 2) was generated in the reaction of **1** with H_2O_2 under Ar. The characterization of **3** will be described elsewhere.[10] In the presence of various phenols, **3** was not generated and very rapid oxidations of the phenols took place.

In a typical reaction, to a CH_2Cl_2-MeCN (3 ml-0.2 ml) solution of 10.6 mg (10 μmol) of **1b** and 10 μl of nitrobenzene as an internal standard were added 103 mg (0.5 mmol) of 2,4-di-*tert*-butylphenol (DBP) and 12 μl of 28% aqueous H_2O_2 with vigorous stirring. The reaction was completed in a few minutes and the reaction mixture was analyzed by GLC. The results are summerized in Table 1.

DBP was oxidized to 3,3',5,5'-tetra-*tert*-butyl-2,2'-dihydroxybiphenyl. This reaction could be repeated several times by further addition of DBP and H_2O_2, the turnover number being increased up to ca. 500 in this case. 3,5-Di-*tert*-

Table 1. Oxidation of various phenols catalysed by **1b**[a]

Substrate	Reaction time/min	Products	Yields/%	Turnover number
	5		86	43
	5		44	22
			45	23
	5		88	44

[a] Although either **1a** or **1b** can catalyse the phenol oxidations, **1b** was adopted as the catalyst because of its higher solubilities in various organic solvents. The typical reaction conditions are shown in the text.

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butylcatechol was oxidized to the corresponding *o*-quinone in the presence of **1b** under air without H_2O_2 and the oxidation was markedly accelerated by addition of H_2O_2.

In order to examine the mechanism for the DBP oxidation catalyzed by the **1b**/H_2O_2 system kinetic study was carried out. The reaction rates were measured by following the change in the electronic absorption spectra of DBP. The concentrations of each component used for the kinetic studys are (1.0-5.0) x 10^{-4}, (0-5.0) x 10^{-2}, and (1.0-5.0) x 10^{-2} M for **1b**, H_2O_2, and DBP, respectively. The concentration dependence of the pseudo first-order rate constants reveals that these reactions are first order with respect to **1b**, H_2O_2, and DBP, indicating that one molecule of an active species generated from a reaction of **1b** with H_2O_2 and one molecule of DBP are involved in the rate determining step. The second-order rate constant for the DBP oxidation was 17 dm^3 mol^{-1} s^{-1}. This value is much larger than those reported for the DBP oxidation catalyzed by μ-η^2:η^2-peroxodicopper(II) complexes[11] or other peroxodicopper(II) complexes.[12] The second-order rate constant for the DBP oxidation catalyzed by a hydroperoxodicopper complex $[Cu_2(O_2H)(pbipl)](ClO_4)_2$ **4** (Hpbipl = 1,5-bis[bis[(1-isopropyl-4-imidazolyl)methyl]amino]-3-pentanol), is 5.3 dm^3 mol^{-1} s^{-1}, the largest one reported so far for the DBP oxidation by dicopper(II) complex/H_2O_2 systems, except for the present work.[12]

The superoxodicopper(II) complex **3** seems to be generated *via* an H-atom abstraction from a hydroperoxodicopper(II) complex which is the initial intermediate in the reaction of **1** with H_2O_2.[10] Namely, we have to consider generation of a strong oxidant **5** to give **3** in the absence of the phenols. This is supported by the fact that the rate constant for the DBP oxidation catalyzed by **1** is three times larger than that by the hydroperoxodicopper(II) complex **4**. The strong oxidant **5** may be a di-μ-oxodicopper(III) complex which is recently demonstrated to be generated from peroxodicopper(II) complex in the copper mediated O_2-activation.[13] Thus, **5** might oxidize the phenol *via* an H-atom abstraction of the phenol (Figure 2). Conclusively, the present dicopper(II) complexes are not only a promising catalyst for the phenol oxidation but also give some insight into the mechanism for the phenol oxidation catalyzed by a dicopper(II) complex with H_2O_2.

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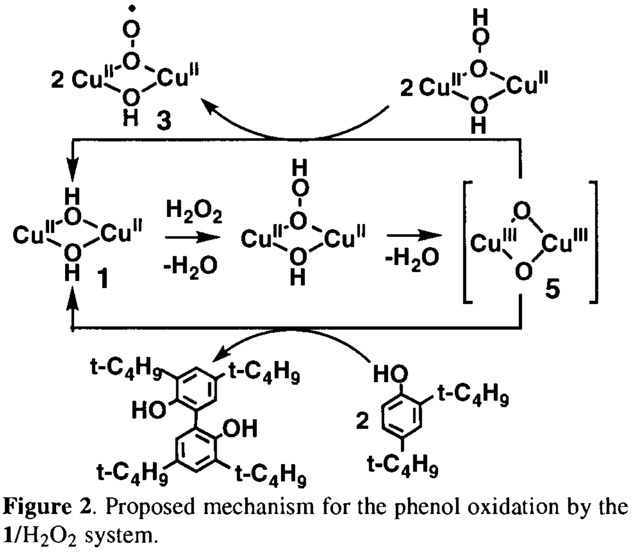

Figure 2. Proposed mechanism for the phenol oxidation by the **1**/H_2O_2 system.

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6 Elemental analysis of **1a**•THF•H_2O: Calc for $C_{38}H_{40}N_6O_{12}Cl_2Cu_2$, C, 47.02; H, 4.15; N, 8.66; Cu, 13.09, Found, C, 47.23; H,4.05; N, 8.83;Cu, 13.18. The solid-state magnetic susceptibilities of **1a**•THF•H_2O were measured at 80-300 K on a Faraday balance. Fitting of the data to the Bleany-Bowers expression for isotropic exchange in Cu(II)-Cu(II) gave a strong anti-ferromagnetic coupling, J = -105 cm^{-1}, which is reasonably explained by the superexchange through the hydroxo bridges. IR (KBr, cm^{-1}) 3600, 3100, 3050, 2930, 1600, 1568, 1475, 1445, 1090; UV-vis [λ_{max}, nm (ε mol^{-1} dm^3 cm^{-1})] (in MeCN/CH_2Cl_2): 270 (29000), 340 (1600), 650 (80). Elemental analysis of **1b**•CH_2Cl_2:Calcd for $C_{37}H_{32}N_6O_8F_6S_2Cl_2Cu_2$: C, 41.74; H, 3.03; N, 7.89; Cu, 11.94%. Found: C, 41.80; H,3.23; N, 8.12, Cu, 11.55%. Other spectral data are almost the same as those of **1a**.

7 Crystal data for **1a**•THF•H_2O: fw = 970.77,orthorhombic, P_{nma}, blue crystal, a = 14.233(4) Å, b = 17.147(2) Å, c = 16.618(3) Å, V = 4055(2) Å^3, Z = 4, R = 0.051, R_w = 0.051 for 2711 observed reflections with $I > 3\sigma(I)$. Compound **1a** has a mirror plane bisecting the molecule at the center of the ethylene linker. Thus, the two carbon atoms of the ethylene linker are disordered to show two ethylene linkers. Both of the two carbon atoms of each linker have a multiplicity of 0.5. Since the actual molecular structure does not have two ethylene spacer, one of which is deleted in the ORTEP diagram to prevent misunderstanding.

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