

Oxidation

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Specific Enhancement of Catalytic Activity by a Dicopper Core: Selective Hydroxylation of Benzene to Phenol with Hydrogen Peroxide

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Abstract: A dicopper(II) complex, stabilized by the bis(*tpa*) ligand 1,2-bis[2-[bis(2-pyridylmethyl)aminomethyl]-6-pyridyl]ethane (6-hpa), $[\text{Cu}_2(\mu\text{-OH})(6\text{-hpa})]^{3+}$, was synthesized and structurally characterized. This complex catalyzed selective hydroxylation of benzene to phenol using H_2O_2 , thus attaining large turnover numbers (TONs) and high H_2O_2 efficiency. The TON after 40 hours for the phenol production exceeded 12000 in MeCN at 50 °C under N_2 , the highest value reported for benzene hydroxylation with H_2O_2 catalyzed by homogeneous complexes. At 22 % benzene conversion, phenol (95.2 %) and *p*-benzoquinone (4.8 %) were produced. The mechanism of H_2O_2 activation and benzene hydroxylation is proposed.

Phenol is one of the most important chemical intermediates used to manufacture various industrial chemicals.^[1] However, industrial phenol production is dominated by inefficient three-step cumene methods where overall the yield of phenol from benzene is 5 %, using O_2 as oxidant.^[2] Development of efficient catalysts for selective hydroxylation of benzene to phenol with a cheap oxidant, such as O_2 or H_2O_2 , has been one of the most important targets for industry.^[3]

Recently, great progress has been made in direct oxidation of benzene to phenol with H_2O_2 when catalyzed by heterogeneous systems.^[4] However, such reactions have not been mechanistically clarified because of the difficulty in spectroscopic observation of solid-surface reactions. More recently, monometal complexes have been developed as homogeneous catalysts for benzene hydroxylation using H_2O_2 , and mechanistically clarified. The turnover number (TON) of $[\text{Ni}(\text{tepa})]^{2+}$ [tepa = tris(2-pyridyl)ethylamine] was reported to be 749 after 216 hours in MeCN at 60 °C,^[5] and that of $[\text{Cu}(\text{tmpa})]^{2+}$ [tmpa = tris(2-pyridyl)methylamine], incorpo-

rated into a mesoporous material, was reported as 4320 after 112 hours in acetone at 30 °C where a hydroperoxyl radical ($\cdot\text{O}_2\text{H}$) was detected as the active oxidant.^[6]

Dicopper biosites are known to catalyze oxidations of various hydrocarbons, such as aromatic compounds and alkanes.^[7] Various dicopper complexes have been developed for O_2 binding,^[8] but are less studied as catalysts for the oxidation of methane and benzene.^[9] Herein, it was found that a dicopper complex with the dinucleating ligand 1,2-bis[2-[bis(2-pyridylmethyl)aminomethyl]-6-pyridyl]ethane^[10] (6-hpa), $[\text{Cu}_2(\mu\text{-OH})(6\text{-hpa})](\text{ClO}_4)_3$ (**1**), exhibits high catalytic activity in selective hydroxylation of benzene with H_2O_2 .

The complex **1** was synthesized and structurally characterized. The ORTEP view (Figure 1) of **1** shows that the dicopper(II) core with a $\mu\text{-OH}$ bridge is encapsulated by the 6-hpa ligand. The dicopper core of **1** is stable in a solution as shown by the ESI MS spectrum (see Figure S1 in the Supporting Information).

Both **1** and $[\text{Cu}(\text{MeCN})(\text{tmpa})](\text{ClO}_4)_2$ (**2**) were used to compare their catalytic activities for the benzene hydroxylation. In a typical reaction, 10 mL of 30 % aqueous H_2O_2 (120 mmol) was added to an MeCN (20 mL) solution of 60 mmol of benzene, 1 μmol of **1**, and 5 μmol of Et_3N , with vigorous stirring under N_2 at 50 °C. For the reaction of **2**, 2 μmol of **2** and 10 μmol of Et_3N were used under the same reaction conditions. The reaction products were analyzed using GC, GC-MS, and ^1H NMR spectroscopy. Small amounts of phenol were produced in the absence of catalyst, but less than 1 % of the amount formed in the presence of **1**.

Time courses of phenol production catalyzed by **1** and **2** are shown in Figure 2. **1** showed a turnover frequency (TOF)

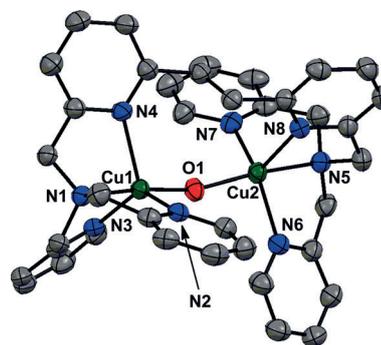


Figure 1. ORTEP view (ellipsoids shown at 50 % probability) of the cationic portion of **1**.^[18] Selected bond distances [Å] and angle [°]: Cu1...Cu2 3.799, Cu1–O1 1.922(3), Cu1–N1 2.029(4), Cu1–N2 2.071(4), Cu1–N3 2.056(4), Cu1–N4 2.225(4), Cu2–O1 1.941(3), Cu2–N5 2.028(4), Cu2–N6 2.051(4), Cu2–N7 2.054(4), Cu2–N8 2.238(4); Cu1–O1–Cu2 158.18(19).

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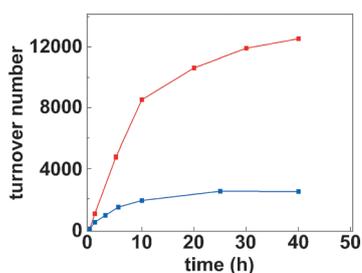


Figure 2. Time courses of phenol production through the oxidation of benzene (60 mmol) with H_2O_2 (10 mL of 30% aqueous H_2O_2 , 120 mmol) catalyzed by **1** (1 μmol ; red) and **2** (2 μmol ; blue) in the presence of Et_3N (5 μmol for **1** and 10 μmol for **2**) in MeCN (20 mL) at 50°C.

[mol phenol (mol catalyst) $^{-1}$ h $^{-1}$] of 1010 and an overall TON of 12000 after 40 hours. These are the largest values yet reported for benzene hydroxylation with H_2O_2 by homogeneous catalysis.^[5,6] After 40 hours, 22% of benzene was converted into phenol (95.2%) and *p*-benzoquinone (4.8%), and H_2O_2 efficiency [(mol phenol + mol *p*-benzoquinone \times 2) (mol H_2O_2 consumed) $^{-1}$] was 45%.^[11] The molar ratio of phenol and *p*-benzoquinone was determined by ^1H NMR spectroscopy (see Figure S2). After completion of the reaction, 1.10 grams (11.7 mmol) of phenol were isolated from the reaction mixture. In comparison, **2** showed a TOF of 444 and an overall TON of 2260 after 40 hours, and 8% of benzene was converted into phenol (91.3%) and *p*-benzoquinone (8.7%), and the H_2O_2 efficiency was 6%.^[11] The overall TON of **1** after 40 hours is 5.3-fold larger than that of **2**. This demonstrates the superiority of the catalyst **1** over **2**, and may be due to the dinuclear structure of **1** enhancing the catalytic activity, selectivity, and H_2O_2 efficiency.

Isotope-labeling experiments using $\text{H}_2^{18}\text{O}_2$ were carried out, showing that ^{18}O -incorporation into phenol is $95 \pm 2\%$ and $91 \pm 4\%$, when catalyzed by **1** and **2**, respectively. This result demonstrated that the O atom of H_2O_2 was incorporated into the phenol. Using a 1:1 mixture of C_6H_6 and C_6D_6 as substrates, kinetic isotope effects (KIE) were estimated as 1.04 and 1.40 for **1** and **2**, respectively, from peak intensity ratios [($\text{C}_6\text{H}_5\text{OH}$) ($\text{C}_6\text{D}_5\text{OH}$) $^{-1}$] using the GC-MS data (see Figure S3). This data showed that C–H bond cleavage of benzene is not involved in the rate-limiting step, and that the active species in the reaction of **1** is not a hydroxyl radical ($\cdot\text{OH}$) because the KIE value of a Fenton-type reaction is generally in the range of 1.7–1.8.^[12]

A radical-chain reaction of $\cdot\text{O}_2\text{H}$ was proposed for the reaction of **2**,^[6] and may explain the low H_2O_2 efficiency of **2** because the $\cdot\text{O}_2\text{H}$ radical decomposes by disproportionation to O_2 and H_2O_2 . Therefore, to examine participation of $\cdot\text{O}_2\text{H}$ in the reaction employing **1**, 5,5'-dimethyl-1-pyrroline *N*-oxide (DMPO; 0.50 and 5.0 mM) was added as a radical trapping reagent. The resulting reaction of **1** was not affected by DMPO (see time courses of phenol production shown in Figure S4). Thus, the radical-chain mechanism by $\cdot\text{O}_2\text{H}$ can be excluded from consideration for the reaction of **1**, thus indicating that the dicopper core enables formation of alternative active species.

Kinetic studies were carried out for benzene oxidation with H_2O_2 , catalyzed by **1**. The initial rates were determined

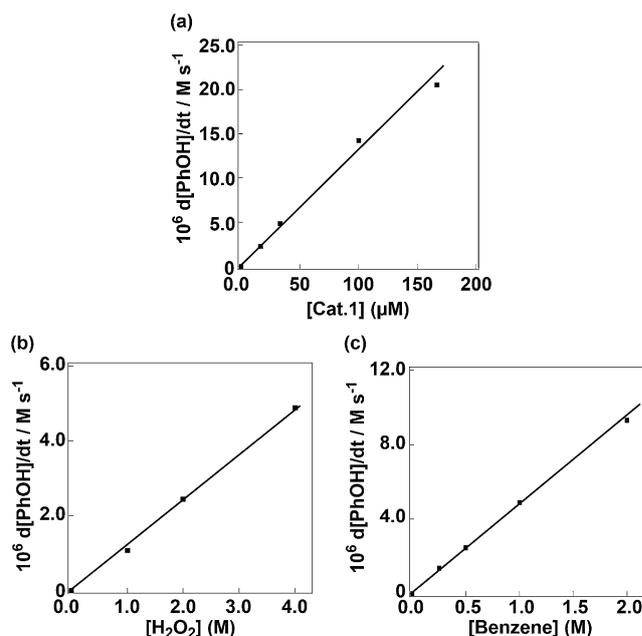


Figure 3. a) Dependence of the initial rate of phenol production estimated from the TOF (h^{-1}) at 50°C ($d[\text{PhOH}]/dt$) on the concentration of **1** ($[\text{I}] = 0\text{--}170 \mu\text{M}$, $[\text{C}_6\text{H}_6] = 1.0 \text{ M}$, $[\text{H}_2\text{O}_2] = 4.0 \text{ M}$). b) Dependence of $d[\text{PhOH}]/dt$ on the concentration of H_2O_2 ($[\text{H}_2\text{O}_2] = 0\text{--}4.0 \text{ M}$, $[\text{I}] = 33 \mu\text{M}$, $[\text{C}_6\text{H}_6] = 1.0 \text{ M}$). c) Dependence of $d[\text{PhOH}]/dt$ on the concentration of C_6H_6 ($[\text{C}_6\text{H}_6] = 0\text{--}2.0 \text{ M}$, $[\text{I}] = 33 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 4.0 \text{ M}$).

from TOFs of phenol production under the typical reaction conditions, and were found to be proportional to concentrations of **1**, H_2O_2 , and benzene, as shown in Figures 3 a–c. The rate equation for the phenol formation is derived on the basis of these kinetic studies and is shown in the Supporting Information. In the case of **2**, however, it was reported that the initial rate was proportional to the square root of the concentration of **2**.^[6] This rate showed that 2 equivalents of $\cdot\text{O}_2\text{H}$ were formed from 1 equivalent of **2** by formation of hydroperoxocopper(II) in equilibrium with **2** and H_2O_2 .

To the reaction mixture of **1**, NaBPh_4 and Et_2O were added, and yielded green crystals after standing for several days at 0°C. The X-ray analysis revealed the structure of a diphenoxodicopper(II) complex, $[\text{Cu}_2(\text{PhO})_2(6\text{-hpa})\text{-(BPh}_4)_2]$ (**3**) (see ORTEP view in Figure S5). The structure shows that a phenoxide ion binds to each copper site, and that 6-hpa is kept intact in the recovered complex.

Besides benzene, nitrobenzene, toluene, and phenol were used as substrates for the reaction, catalyzed by **1**, to examine reactivity of the active species (Table 1). Time courses for oxidation of these substrates are shown in Figure S6. In the case of toluene, *o*- and *p*-cresol and benzaldehyde were produced as major products with a total TON of 4380 after 40 hours. The ratio of aromatic to aliphatic oxidations was 2.6:1.0. In the case of nitrobenzene, *o*-nitrophenol was the major product with *m*- and *p*-nitrophenol as minor products, and the total TON after 40 hours was 860. In the case of phenol, *p*-benzoquinone was the sole detectable product up to 10 hours, with a TON of 1630, after which catechol formation occurred, presumably because of a structural change to the catalyst. Phenol may also inhibit H_2O_2 activation by binding

Table 1: Product analysis in oxidation of benzene and its derivatives catalyzed by **1**.

Entry ^[a]	Substrate	Products [%] ^[b] (<i>o/p/m</i>) ^[c]	TOF ^[d] (h ⁻¹)	TON ^[e]
1	Benzene	Phenol [95.2], <i>p</i> -benzoquinone [4.8]	1010	12550
2	Benzene	Phenol [93.2], <i>p</i> -Benzoquinone [6.8]	540	6250
3	Toluene	Cresol [72] (57:43:trace) Benzaldehyde [26]	380	4320
4	Phenol	<i>p</i> -Benzoquinone [99]	350	1630 ^[f]
5	Nitrobenzene	Nitrophenol [99] (91:4:5)	72	860

[a] Reaction conditions: entry 1: benzene (60 mmol), H₂O₂ (10 mL of 30% aqueous H₂O₂, 120 mmol), **1** (1.0 μmol), and TEA (5.0 μmol) in MeCN (20 mL) at 50 °C under N₂. Entries 2, 3, 4, 5: 30 mmol of substrate was added under the same reaction conditions as entry 1. [b] Product yield based on substrate consumed after 40 h for Entries 1–3 and 5, and after 10 h for Entry 4. [c] Product ratio of hydroxylation at *ortho*-, *meta*-, and *para*-position in cresol and nitrophenol. [d] Turnover frequency of all product after 1 h. [e] Turnover number of all product after 40 h. [f] Turnover number of all product after 10 h.

to Cu^{II} as shown in the crystal structure of **3**, thus explaining the relatively low TON. Selective *p*-benzoquinone production in this reaction system suggests that the oxidation occurred at the *para*-position of a copper-bonded phenoxide, which is more reactive because of the radical character than free phenol, where *ortho*-positions did not react as a result of the steric hindrance of the 6-hpa.^[13] The relative reactivity order estimated from the initial rate (TOF, see Table 1) is phenol ≈ toluene ≫ nitrobenzene, and increases with increasing electron density of the aromatic ring, thus indicating an electrophilic character of the active species. The regioselectivity is *ortho* and *para* for toluene, *ortho* for nitrobenzene, and *para* for phenol, therefore indicating a radical character of the active species. Thus, based on these results, the active species may have an electrophilic radical character such as a metal-bonded oxyl radical, which was previously proposed as the active species in the reactions of Co, Ni, Cu, and Ru complexes with various oxidants.^[14]

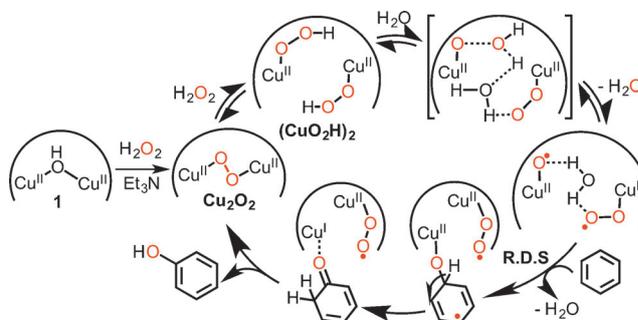
Two intermediates were spectroscopically detected in the reaction of **1** with H₂O₂ and provide insight into the mechanism of H₂O₂ activation. When 1 equivalent of H₂O₂ was added to **1** in the presence of Et₃N in MeCN at -40 °C, clear bands, which are typical of an end-on *trans*-peroxodicopper(II) (Cu₂O₂) complex, appeared at λ = 520 nm,^[15] and decayed with a half-life of 1200 s as shown in Figure S7. In contrast, upon addition of excess amounts of H₂O₂, the Cu₂O₂ complex that once formed rapidly decayed to give a new species that showed a band at λ = 380 nm, close to the band at λ = 379 nm for the hydroperoxocopper(II) (CuO₂H) complex.^[16] The Cu₂O₂ complex decayed with a half-life of 10 seconds in the presence of 100 equivalents of H₂O₂ at -40 °C. The reaction rate showed saturation kinetics with an increase of concentration of H₂O₂, as shown in Figure S8. The resonance Raman spectra of the Cu₂O₂ complex and the as-prepared new species showed clear bands at 821 and 846 cm⁻¹, respectively, and the corresponding

isotope shifts were 43 and 53 cm⁻¹ when H₂¹⁸O₂ was used (see Figure S9). These values are similar to bands at 827 (44) and 847 (55) cm⁻¹ attributed to O–O stretching bands for the Cu₂O₂ and CuO₂H complexes, respectively.^[15,16] Thus, the data confirm that the second intermediate contains a peroxo ligand and we hypothesize that it is a dihydroperoxodicopper(II) (CuO₂H)₂ complex, which is in equilibrium with the Cu₂O₂ complex and H₂O₂.

Here, we propose a mechanism (Scheme 1) for the H₂O₂ activation and benzene hydroxylation catalyzed by **1** and it is based on the relative reactivity and regioselectivity in oxidation of substituted benzenes, the spectroscopic studies of reaction intermediates, and DFT calculations. The reaction pathway is estimated by DFT calculations, and we confirmed the interaction between the Cu–O moiety of the active species and benzene in the transition state. The details are shown in Figures S11 and S12. The (CuO₂H)₂ complex is shown to be a precursor of the active species with an electrophilic radical character shown in the oxidation of substituted benzenes. The (CuO₂H)₂ complex releases H₂O reversibly with the assistance of H₂O to give a copper-bound oxyl and peroxy radical which is stabilized by hydrogen-bonding interactions with H₂O. Here, it reacts with benzene in the rate-limiting step. This reactivity is consistent with kinetic results for the phenol production. It is also not a radical-chain reaction as discussed previously. The active species may then react with DMPO to undergo decomposition, but does not form a stable radical, such as a ·O₂H-adduct, and this may be the reason why DMPO did not inhibit phenol production. The present mechanism is one of many possible pathways, and further studies are needed for clarification.

In a mechanism reported for benzene hydroxylation catalyzed by **2**,^[6] it was shown that ·O₂H was generated as an active oxygen species by O–O bond scission of the CuO₂H species, a step which is energetically unfavorable.^[17] In contrast, in the case of **1**, the active species is formed by a more energetically favorable intramolecular dehydration of the (CuO₂H)₂ complex as shown by DFT calculations, where the two CuO₂H moieties are encapsulated by 6-hpa. Therefore, it is concluded that the dinuclear structure of **1** is favorable for the formation of the active species to specifically enhance the catalytic activity.

In summary, a new dicopper complex with the dinucleating ligand 6-hpa, which specifically stabilizes a dinuclear

**Scheme 1.** Proposed mechanism of H₂O₂ activation and benzene hydroxylation catalyzed by **1**.

structure, enhances catalytic activity, selectivity, and H₂O₂ efficiency in selective hydroxylation of benzene to phenol with H₂O₂. This reactivity is clearly shown in the comparison with a monocopper complex. Moreover, the mechanism of H₂O₂ activation and benzene hydroxylation is consistently supported by kinetic studies of phenol production, product analysis of benzene derivatives, spectroscopic studies of reaction intermediates, and DFT calculations. Such a unique feature of the dicopper complex may provide a new concept around which future catalysts for the direct benzene hydroxylation may be developed.

Experimental Section

Catalytic reactions. A solution of **1** (1.0 μmol), Et₃N (5.0 μmol), substrate (30 or 60 mmol) in MeCN (20 mL) was placed in a flask, and quickly degassed with N₂ gas. 10 mL of 30% aqueous H₂O₂ (120 mmol) was added under N₂ atmosphere with stirred at 50 °C. After passing the reaction mixture through an alumina column (eluent: CHCl₃, CDCl₃ in the case of ¹H NMR analysis and assays), a fraction of the solution was analyzed and assayed by ¹H NMR spectroscopy, as well as GC and GC-MS on the basis of nitrobenzene or *o*-dichlorobenzene as an added standard.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arenes · copper · oxidation · reaction mechanisms · structure elucidation

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- [18] CCDC 1551785 (**1**) and 1551786 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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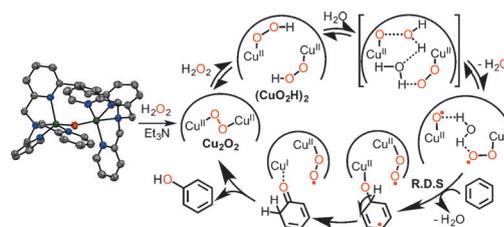
Communications



Oxidation

T. Tsuji, A. A. Zaoputra, Y. Hitomi,
K. Mieda, T. Ogura, Y. Shiota,
K. Yoshizawa, H. Sato,
M. Kodera*     

Specific Enhancement of Catalytic Activity
by a Dicopper Core: Selective
Hydroxylation of Benzene to Phenol with
Hydrogen Peroxide



Doubled up: A new dicopper complex with a dinucleating ligand, which specifically stabilizes a dinuclear structure, displays enhanced catalytic activity, selectivity, and H_2O_2 efficiency in the

selective hydroxylation of benzene to phenol using H_2O_2 . The dinuclear structure is favorable for the formation of the active species that specifically enhance the catalytic activity.