

Novel μ -X Bridged Dicopper(II) Complex System: Synthesis, Structural Characterization and Catalytic Activity

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Three NAPH (1,8-naphthalate dianion) bridged dicopper(II) complexes have been synthesized, namely $[\text{NAPHCu}_2(\mu\text{-X})_2\cdot 2\text{H}_2\text{O}]\cdot n\text{H}_2\text{O}$, X = OH⁻ (**1**), OAc⁻ (**2**) and Cl⁻ (**3**). NAPH was found to have the ability to form a dinuclear core with μ -X as additional ligand. Based on IR, elemental analysis and electronic spectra, these complexes were found to have heterocyclic structure with both NAPH and μ -X as bridging ligands. The temperature dependence of magnetic susceptibilities of **1** has been studied, giving the exchange integral of $J = -216 \text{ cm}^{-1}$, $g = 2.09$. This result is in agreement with proposed dihydroxo-bridged structure of **1**, since Cu_2O_2 unit normally undergoes a strong anti-ferromagnetic interaction. Significantly, these complexes were found to exhibit catalase-like activity.

Key words: dicopper(II) complexes, bridging ligand, hydrogen peroxide, catalase-like activity

Transition metal dinuclear complexes with extended bridged structures are currently an interesting topic, due to the spin-coupling and charge transfer between metal ions and the bridging-ligand in the domain of metalloenzymes [1]. Meanwhile, single atomic (O²⁻, OH⁻, OR⁻ and Cl⁻) [2–5] bridged dinuclear complexes are also investigated intensively in recent years, mainly because they are active species in both biomimetic and real catalysis processes. Our interests lie in the design of cavity-containing dinuclear framework as complex catalyst, which can be used in specific reaction.

Dinuclear cores, bridged by one oxygen-containing (oxo, hydroxo or water) and one or two carboxylate groups, are widely known in biosites such as hamerythrin [6], ribonucleotide reductase [7] and phospholipase C [8], *etc.* A similar dinuclear core is proposed for the active site of Mn–CAT [9]. Model system of μ -phenoxo-bis(μ -carboxylato) dinuclear complexes, relevant to μ -oxo-bis(μ -carboxylato) cores are found to have catalase activity [10].

In this study, dinucleating ligand NAPH with two metal-binding sites was used to synthesize dicopper(II) core structure, which allow the involvement of oxygen-containing bridge (μ -OH or μ -OAc) between a pair of metal ions. Significantly, these

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complexes are found to present catalase-like activity, comparable to a similar Mn-CAT model system [11].

EXPERIMENTAL

All reagent used are of analytical grade and purchased from the Peking Chemical Company.

Preparation of [NAPHCu₂(μ-OH)₂·2H₂O]·0.5H₂O (1): In dinitrogen-flushed methanol solution (10 ml) containing 1,8-naphthalic acid (43.2 mg, 0.2 mmol) and triethylamine (0.4 mmol), a solution of Cu(ClO₄)₂·6H₂O (148.2 mg, 0.4 mmol) in methanol (15 ml) was added and kept under magnetic stirring. A green solution and few green microcrystals were obtained. To this solution sodium ethoxide (0.4 mmol) was added by injection with a syringe. A colorless solution with a deep-green suspension was obtained and turned into white-green after the mixture was stirred in air condition for 2 h. After no further color change could be observed, the final product was separated, washed with absolute methanol and diethyl ether three times and dried in vacuum. Yield, 62 mg (80%).

Preparation of [NAPHCu₂(μ-OAc)₂·2H₂O] (2): Following a similar reaction procedure as stated above, using NaOAc instead of NaOEt, white-blue microcrystals were obtained. Yield, 69 mg (75%).

Preparation of [NAPHCu₂(μ-Cl)₂·2H₂O] (3): Following a similar reaction procedure as stated above, but using NaCl instead of NaOEt, yellow-green microcrystals were obtained. Yield, 72.5 mg (88%).

Study of catalase-like activity: All reactions were carried out at 20° and in a 50 ml reactor containing a stirring bar under air. Acetonitrile (13 ml) was added to the complex (2 μmol, 0.13 μmol/L) and the flask was closed with a rubber septum. Hydrogen peroxide (4.0 mmol, 450 μl) was injected through the septum with a syringe. The reactor was connected to a graduated burette filled with water and dioxygen evolution was measured volumetrically at time intervals during 1 min. Observed initial rates were expressed as mol L⁻¹ s⁻¹ by taking the volume of the solution (15 ml) into account and calculated from the maximum slope of curve describing evolution of O₂ versus time.

Physical measurement: Chemical analyses confirmed the compositions given. The infrared spectra were recorded with a Perkin-Elmer spectrophotometer, model 983G, using KBr-disks. Electronic spectra (in methanol) were measured on a Shimadzu UV-240 spectrophotometer. The electrical conductivity measurements were performed with a DDS-11A conductometer. Variable-temperature magnetic susceptibilities were measured on a SQUID susceptometer (sensitivity $m = 10^{-6}$ emu). Diamagnetic correction were made with Pascal's constants for all the constituent atoms and the magnetic moment were calculated using $\mu_{\text{eff}} = 2.828(X_M T)^{1/2}$.

RESULTS AND DISCUSSION

IR spectroscopic characterization: The molar conductance values fall in the expected range for different types of electrolyte [12] (Table 1).

Table 1. Physical and chemical data for complexes 1–3.

Complex	Λ_M		IR (cm ⁻¹)		UV ($\times 10^3$ cm ⁻¹)	
	(Ω^{-1} cm ² mol ⁻¹)	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	μ -X	d-d λ_{max} , nm	CT λ_{max} , nm
	in MeCN					
1	55	1560	1430	3500, 1120	680(36)	292(66800)
2	102	1560	1420	1560, 1440 940	680(12)	292(84000)
3	60	1540	1430	940, 660 440	660(21)	292(17560)

In the IR spectrum for 1–3 complexes, two characteristic strong and broad bands in the 1600 – 1300 cm^{-1} region were recorded, attributed to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching vibration of the carboxylato groups of NAPH. In addition, the separation between ν_{as} and ν_{s} has often been used to diagnose the coordination models of the carboxylato groups. The separation values between ν_{as} and ν_{s} for complexes 1–3 are smaller than 200 cm^{-1} , suggesting a bidentate mode for both carboxylato groups [13]. For these complexes, no ClO_4^- vibration at 1095 is observed. These data are consistent with the molar conductance measurement.

In regard to the μ -X ligand, for complex 1, two sharp strong bands at 3500 cm^{-1} and 1100 cm^{-1} could be attributed to bridged hydroxo [14]. In low frequency, a strong band at 754 cm^{-1} was diagnostic of the presence of Cu–O–Cu. For complex 2, the band at 1560 cm^{-1} becomes stronger, as compared with other two complexes; meanwhile new bands at 1440 cm^{-1} and 940 cm^{-1} were observed, which can be attributed to bridged acetate groups. For complex 3, bands at 900 , 660 and 440 cm^{-1} were discovered, which could be tentatively assigned to Cu–Cl–Cu vibration.

Visible absorption spectra of copper(II) complexes: The electronic spectra of these complexes are given in Fig. 1. In the visible range, a weak and broad band was discovered for these complexes at 680 , 680 and 660 nm for complexes 1, 2 and 3 respectively. At higher energy a shoulder at *ca.* 330 nm was observed. This transition is typical of μ -X \rightarrow Cu(II), ligand to metal charge transfer (LMCT) [15]. Another CT band was also observed at *ca.* 300 and can be attributed to N \rightarrow Cu(II) or O \rightarrow Cu(II) transfer. These data indicated a five coordinate Cu(II) chromophore with distorted square-pyramidal configuration, supported by well established electronic spectrum for copper(II) complexes [16].

Based on the discussion above, complexes 1–3 are proposed to have μ -X bridged dinuclear structure with NAPH as a supporting fragment. In these complexes NAPH connects two copper(II) ions in a bis-bidentate fashion and metal ions in a square pyramidal environment, resulting a heterocyclic structure shown in Fig. 2.

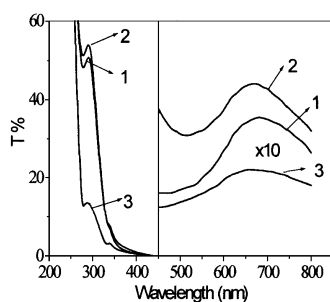


Figure 1. Electronic spectra of complexes 1–3.

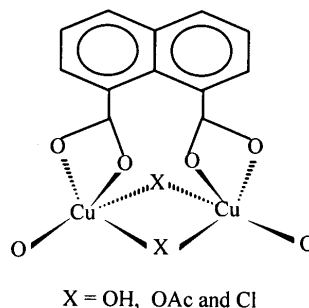


Figure 2. Proposed structures of the complexes.

Magnetic properties and magnetic structural correlations: Specific coordination structure of these complexes has given us an unique opportunity to study the magneto-structural correlation. The detailed temperature-dependent magnetic studies of complex **1** in solid state was undertaken to elucidate the extent of magnetic coupling in this system.

Variable-temperature magnetic susceptibility data was collected in the 77–300 K range. The M versus T plot is shown in Figure 3. The magnetic moments decrease with decreasing temperature, implying the existence of an antiferromagnetically coupling of Cu(II)–Cu(II) pairs.

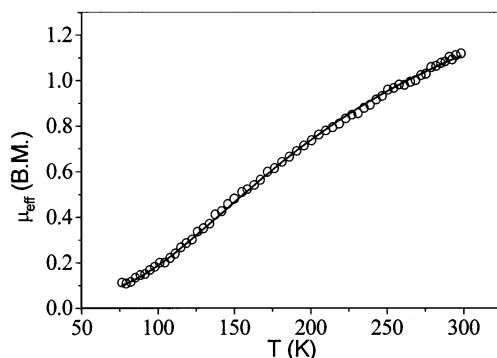


Figure 3. Temperature variation of the magnetic moment of complex **1**.

In order to understand quantitatively the spin-exchange interaction, the analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator $H = -J \cdot S_1 \cdot S_2$. The molar susceptibility of the Cu–Cu ($S_1 = S_2 = 1/2$) system was calculated by the Bleaney-Bower equation [17]:

$$\chi_M = \frac{2Ng^2\beta^2}{kT} [3 + \exp(-2J/kT)]^{-1} (1 - \rho) + \frac{Ng^2\beta^2}{2kT} \rho + N_\alpha$$

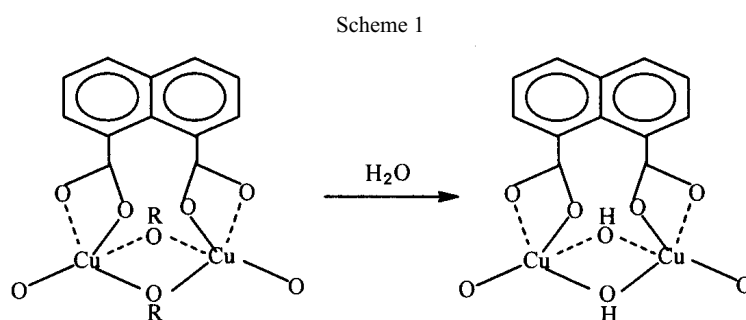
where χ_M denotes the susceptibility per binuclear complex, N_α is the temperature-independent paramagnetism ($120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$), ρ denotes the fraction of mononuclear paramagnetic impurity. Other symbols have their usual meaning. As shown in Fig 3, a good fit to the experimental data was attained. The magnetic parameters, thus determined, are $J = -216 \text{ cm}^{-1}$, $g = 2.09$, $\rho = 0.005$ for complex **1**. This result indicates that bis- μ -OH bridged dinuclear complexes undergo a very strong spin-coupling between the adjacent metal ions, since the exchanging integral of the extending ligand is negligible [18] and the extent is comparable to the related μ -OH [19] system.

It is well established, that the type and magnitude of magnetic exchange interactions in dinuclear complexes depend on bridge identity, the distance between metal ions, the bond angles at the bridging atom, the dihedral angle between the planes containing the copper(II) ions, and the metal-bridging ligand bond length [20]. Even though the effort to obtain a single-crystal of complex **1** was unsuccessful, the quanti-

tative difference of the spin-coupling between the complex **1** and $[\text{Cu}_2\text{NAPH}(\text{bipy})_2](\text{ClO}_4)_2$ [21] is easy to illustrate. For the latter, two metal ions are separated by an extended bridge, hence undergo a weak interaction. While for complex **1**, two copper(II) ions in two planes are connected by μ -X bridge, when the metal ions move towards the same plane, the overlap between the metal based $d_{x^2-y^2}$ orbitals and the oxygen-based sp^2 hybrid orbitals is increased, the enhanced overlap should increase the strong antiferromagnetic interaction.

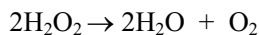
Conversion from dialkoxyl to dihydroxo bridged dicopper(II) complexes:

In the synthesis of dihydroxo bridged complexes, sodium ethoxyl was used instead of sodium hydroxy, we speculated that dialkoxyl bridged complex was formed first, undergoing a ligand-exchange reaction (Scheme 1):



A water ligand comes from metal salt $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Interestingly, when 4 equivalent of sodium ethoxy was added, the blue or purple colored dihydroxo complexes converted to its original green colored complexes, which, however, quickly transformed into the dihydroxo complexes when exposed to air. This phenomenon suggests that in this system, the bridge ligand of alkoxy/hydroxo is very active and readily participates in acid and base related reactions.

Catalytic activity: The catalase-like activity was tested by measuring the dioxygen evolution with a Cu_2 complex: H_2O_2 ratio of 1:2000 and a catalyst concentration of 0.13 mmol/L. These conditions were found to be optimal in terms of reaction yields. The amount of residual hydrogen peroxide (measured by iodometric titration) was compared with the amounts of dioxygen formed (as calculated by volumetry) and found to satisfy the stoichiometry implied by:



The time course of oxygen evolution for the catalysis by complex **1** is given in Fig. 4. The evolved dioxygen linearly increased first but tended to saturate after 8 min and then a more rapid evolution occurred after 40 min and ceased after 140 min. At this stage the evolved dioxygen corresponds to 100% decomposition of hydrogen peroxide. The evolution profile suggests the involvement of a slow catalytic process, occurring at the initial stage (1) and a faster catalytic process (2), appearing after a lag phase. Complex **2** and **3** showed the similar evolution profiles (Fig. 5), however, at

relatively low reaction rates. The observed initial rates for these complexes are summarized in Table 2.

The disproportionation process of H_2O_2 by these complexes has also been monitored by visible spectroscopy (Fig. 6). For complex **1**, just after the addition of H_2O_2 , the solution was almost colorless (a) and when the fast catalytic process started, the solution became yellowish colored (b) and displayed copper(I)-dioxygen [μ -peroxo-dicopper(II)] features [22] in the visible range. This phenomenon can be assigned to a ligand-metal charge transfer band from oxo ion to Cu^{2+} . To our knowledge these are the first dicopper(II) complexes with μ -X bridging ligand, which exhibit a catalase-like reactivity.

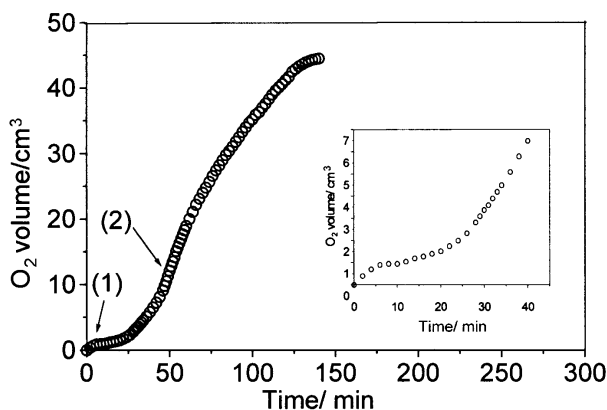


Figure 4. Time course of oxygen evolution in the disproportionation of H_2O_2 by complex **1**.

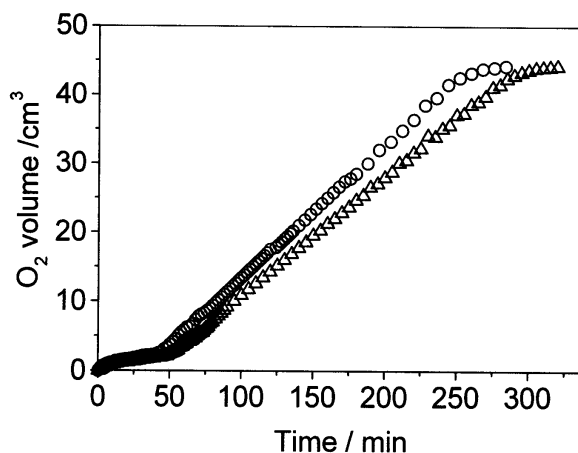
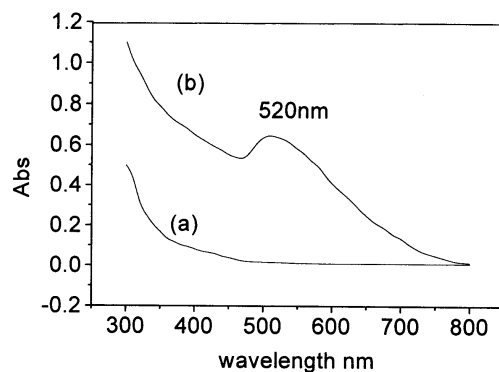


Figure 5. Time course of oxygen evolution in the disproportionation of H_2O_2 by complex **2** (O) and **3** (Δ).

Table 2. Reaction rates for disproportionation of H_2O_2 by complexes 1–3.

Complex	Rate ($\text{mol}/\text{dm}^3 \text{ s}$)
1	4.0×10^{-5}
2	1.0×10^{-5}
3	8.4×10^{-6}

**Figure 6.** Visible spectral changes in the catalytic reaction of H_2O_2 by complex 1. (a), At the initial stage of the catalytic reaction. (b), Fast catalytic process after lag time.

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