Dinuclear complexes [NAPH (Cu^{II})$_2$ (μ-X) (bipy)$_2$]ClO$_4$: synthesis, characterization and Tyr-like activity

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Abstract

Four μ-X-bridged dicopper(II) complexes have been synthesized, namely [NAPH Cu$_2$ (μ-X) (bipy)$_2$]ClO$_4$ (X = OH (**1**), OAc (**2**), Cl (**3**) and Br (**4**); NAPH denotes 1,8-naphthalate dianion). NAPH was found to have the ability to form dinuclear complexes with X as an additional ligand. Based on the elemental analysis, infrared and electronic spectra, these complexes were found to have heterocyclic structure with both DPHA and μ-X as bridging ligands. The temperature dependence of magnetic susceptibilities of complexes **1** and **4** have been studied, giving the exchange integral of $J = -189.7$ and $-187.9 \, \text{cm}^{-1}$, respectively. This result is in agreement with proposed μ-X-bridged structure. In methanolic solution and excess dioxygen, these complexes were found to be effective catalysts for catechol oxidizing to benzoquinone. The rate constant for these complexes is in the order of 1 > 2–3 > 4. The oxidation is first order in Cu$_2$ complex and zero in substrate. In the same conditions and in the presence of sodium ethoxide, the rates of catalytic reactions for these complexes were found to be 2–4 times greater than for the formal oxidation. On the basis of these observations, a catalytic scheme based on the dicopper(II) complex as the initial active species is proposed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dicopper(II) complexes; Synthesis method; Structure characterization; Catalytic oxidation; Catechol; Benzoquinone

1. Introduction

Dinuclear copper(I) (Cu(I)) complexes are of current interest due to their occurrence in natural system and particular, because of their biological function in protein [1]. These complexes can react with dioxygen to form μ-peroxo bridged dicopper(II) complexes [2] which are relevant to bio-mimetic approach and have potential use in organic synthesis of real catalytic processes [3], since dioxygen is a cheap resource of oxidant. Chemists and biochemists alike have tried to understand the coordination or binding behavior of copper and dioxygen in this system, as a consequence many dicopper complex system based on acyclic, linear and macrocyclic ligand systems have been synthesized and investigated for oxygen uptake [4,5]. Spectroscopic and structural evidences have shown that the activated dioxygen can bind between the two metal ions in μ-1, 2 and μ-η^2, η^2 fashions and in some cases the dioxygen complex is stable enough to be isolated [6–8]. For all these studies, emphasis has been placed on dicopper(I) complexes synthesized as the model complexes or complex catalysts, however, the dicopper(II) complex are the indispensable

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intermediate species in the catalytic cycle [9] for oxidation of the substrate as catechol and phenols, and furthermore in some cases [10] when the dicopper(II) complex is an initiator reveal more higher catalytic reactivity than the dicopper(I) species.

Our previous work [11] in this regard has investigated the μ-dihydroxo-bridged dicopper(II) complex as model complex in examining their catalytic properties as Tyr-like model complex. Spectroscopic and kinetic studies have corroborated that the μ-dihydroxo bridged dicopper(II) complex is an intermediate in the catalytic oxidation of catechol. In the current investigation μ-X-bridged dicopper(II) complex have been prepared and examined for their reactivity. The use of the extended bridging ligand NAPH [12] is expected to support the μ-X bridged dicopper(II) structure as a building unit and so doing making possible the binding of the substrate to form catechol dicopper complex, and the binding of dioxygen to form stable peroxo-complex. This report presents the reactivity studies of these complexes under the assistance of sodium ethoxide as co-catalyst.

2. Experimental

2.1. Preparation of [NAPH Cu$_2$ (μ-OH) (bipy)$_2$](ClO$_4$) (1)

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

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(ClO$_4$)$_2$·6H$_2$O (148.2 mg, 0.4 mmol) in methanol (15 ml) was added and kept under magnetic stirring, then bipy (62.5 mg, 0.4 mmol) was added, a bluish-green solution was obtained. To this solution was added 0.4 mmol sodium ethoxide and a green colored solution with a green suspension was obtained and turned into blue after the mixture was exposed to dioxygen and stirred for 2 h. After no color change could be observed, the final product was separated, washed with absolute methanol and diehtyl ether three times and dried in vacuum to give a satisfactory analysis data. Found: C, 47.3; H, 2.96; N, 6.84; Cu, 7.5, calc. For C$_{32}$H$_{23}$N$_4$O$_9$ClCu$_2$·2H$_2$O: C, 47.7; H, 3.4; N, 6.82; Cu, 7.9%.

2.2. Preparation of [NAPH Cu$_2$ (μ-OAc) (bipy)$_2$](ClO$_4$) (2), [NAPH Cu$_2$ (μ-Cl) (bipy)$_2$] (ClO$_4$) (3) and [NAPH Cu$_2$ (μ-Br) (bipy)$_2$](ClO$_4$) (4)

Following a similar reaction procedure as stated in the previous section, but using NaOAc, NaCl and NaBr rather than NaOEt. Different shad of green–blue microcrystals were obtained, respectively, and satisfactory analysis data were given for all these complexes.

2.3. Composition and structure characterization

Analysis for C, H and N, were carried out on a Perkin-Elmer analyzer, Model 240 and metal contents were determined by EDTA titration. The infrared spectra were recorded with a Perkin-Elmer IR spectrophotometer, Model 983G, using KBr-disks. Electronic spectra (in methanol) were measured on a shimdze UV-240 spectrophotometer. Solution electrical conductivity measurements were made 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 $\mu_{\text{eff}} = 2.828 \, (\chi_M T)^{1/2}$. The products of oxidations were identified by ^{1}H spectroscopy, melting point determination. NMR spectra were measured in CDCl$_3$ on a Varian XL 200FT spectrometer. Chemical shifts are reported relative to tetramethylsilane (TMS) as an internal standard.

2.4. Measurement of catalytic behaviors

The catalytic oxidation of catechol to quinone with these complexeswas carried out under aerobic condition and in the presence of co-catalyst NaOEt, whereas stoichimetric reactions were carried out under an atmosphere of argon. The reaction flask that was thermostated at 25°C was equipped with an inlet and outlet adapter for argon and oxygen purging and evacuation. The reaction solutions were prepared as following: ca. 8.0 mg Cu$_2$ complex was dissolved in 25 ml of methanol to give a 4.0×10^{-4} M solution, and than equal volume of substrate solution (0.05 M) was added. The ratio of Cu$_2$ complex:catechol = 1:125.

Table 1
Physical data for complexes **1–4**

Complex	Λ_M ($\Omega^{-1} cm^2 mol^{-1}$) in MeOH	ν_{as} (COO⁻)	IR (cm⁻¹) ν_s (COO⁻)	μ-X	UV (×10^3 cm⁻¹) d–d λ_{max} (nm)	CT λ_{max} (nm); ε (M⁻¹ cm⁻¹)
1				3500		228 (69058)
	87	1550	1400	1110	615 (153)	298 (27404)
						330 (2646)
2				1582		228 (106000)
	104	1582	1420	1420	630 (152)	298 (50350)
						335 (7950)
3				660		225 (978500)
	110	1580	1420	440	685 (124)	298 (41200)
						328 (5150)
4				650		225 (69058)
	110	1580	1420	430	725 (204)	292 (36444)
						325 (3836)

All reactions were carried out in a reaction vessel connected to a quartz 1.0 cm flow cell. The reaction vessel and cell holder were thermostated at 25°C and the formation of benzoquinone was analyzed by visible spetroscopy as it has a strong absorption at 395 nm. Standard solutions for preparing calibration curves were prepared by a series of nine solutions varying in concentration from 0.05 to 1.5×10^{-3} M with absolute methanol. Observed initial rates were expressed as M s⁻¹ by taking the volume of the solution (50 ml) into account and calculated from the maximum slope of curves describing evolution of quinone versus time. Plots of the initial rates versus the concentration of catechol and Cu₂ complex allowed the determination of the reaction order for both reactants.

3. Results and discussion

3.1. Composition and structure

Satisfactory elemental analysis data were obtained for all these subject complexes synthesized. The molar conductance values fall in the expected range for different types of electrolyte (Table 1) [13].

The signification bands in the IR spectra of the complexes are all given. In the IR region of the spectrum, complex **1** exhibited show two sharp strong band at 3500 and 1100 cm⁻¹, which can be attributed to bridged hydroxo [14]. In low frequency, strong band at 754 cm⁻¹, were diagnostic of the presence of Cu–(OH)–Cu.

In the IR spectrum for **1–4** complexes, the complexes exhibited two characteristic strong and broad bands in the 1600–1300 cm⁻¹ region attributed to the ν_{as} (COO⁻) and ν_s (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 **1–4** are all smaller than 200 cm⁻¹ suggesting a bidentate mode for both carboxylato groups [15]. For these complexes, the unsplited ClO₄⁻ vibration at 1095 is present indicating non-coordinated mode [16]. These data are consistent with the molar conductance measurement.

The electronic spectrum of these complexes are given as Fig. 1. In visible range, a weak and broad band was discovered for these complexes at 615, 630, 675 and 725 nm for complexes **1–4**, respectively, and the order is OH > OAc > Cl > Br, which is consistent with the crystal field parameter for these ligands. At higher energy a shoulder at ca. 330 nm was observed. The high-energy transition is due to μ-X → Cu(II), ligand to metal charge transfer (LMCT). Other two CT bands were also observed at ca. 300 and 230 nm, which can be attributed to N → Cu(II) and O → Cu(II) transfer. These data indicated a five-coordinated Cu(II) chromophore with distorted square-pyramidal

Fig. 1. Electronic spectra of complexes **1–4**.

Fig. 3. Temperature variation of susceptibility and magnetic moment of complex **1**.
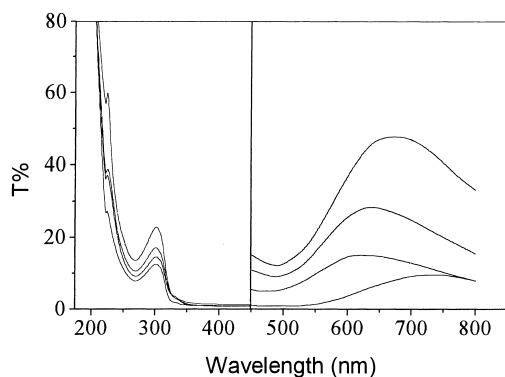
configuration, supported by well established electronic spectrum for Cu(II) complexes [17].

Based on the discussion above, complexes **1–4** are proposed to have μ-X bridged dinuclear structure with NAPH as a supporting fragment. In these complexes NAPH connects two Cu(II) ions in a bis-bidentate fashion and metal ions in a square pyramidal environment bridged by μ-X ligand forming a heterocyclic structure (Fig. 2).

3.2. Magnetic properties and magneto structural correlations

Our formal investigation [12] indicated that the extended bridging ligand NAPH could form stable dinuclear complex giving small spin-coupling integral ($|J| < 1\,cm^{-1}$). Since the additional single atom bridging structure have formed, the magnetic interaction between the Cu(II) ions should expected to be
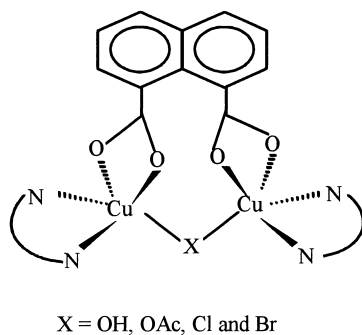
increased significantly. It's this specific coordination structure of these complexes has given us a unique opportunity to study the magneto-structural correlation. The detailed temperature-dependent magnetic studies of complexes **1** and **4** in solid state were undertaken to elucidate the extent of magnetic coupling in this system.

Variable-temperature magnetic susceptibility data was collected in the range of 4.2–300 K. The μ_{eff} versus T plots are shown in Figs. 3 and 4. The magnetic moments decrease with decreasing temperature, implying the existence of an antiferromagnetically coupling of Cu(II)–Cu(II) pairs. In order to quantitatively understand the spin-exchange interaction, the analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator $\mathcal{H} = -J\mathcal{S}_1\mathcal{S}_2$. The molar susceptibility of the

X = OH, OAc, Cl and Br

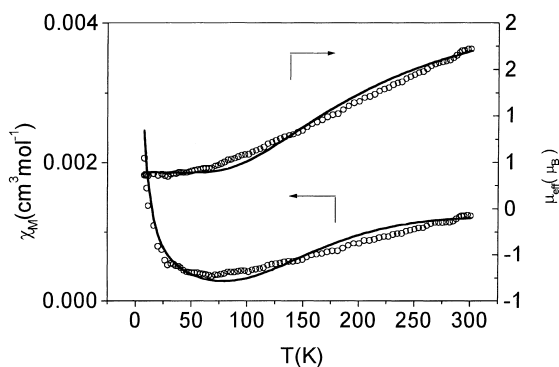Fig. 2. Structure of the hydroxo-bridged dicopper(II) complex.

Fig. 4. Temperature variation of susceptibility and magnetic moment of complex **2**.

Cu–Cu ($S_1 = S_2 = 1/2$) system was calculated by the Bleaney–Bower equation [18]:

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

where χ_M denotes the susceptibility per binuclear complex, N_α is the temperature-independent paramagnetism, ρ the percentage of mononuclear impurity (not participate in the spin-coupling), and other symbols have their usual meaning. As shown in Figs. 3 and 4 good fit to the experimental data were attained. The magnetic parameters, thus, determined are $J = 189.7$, $g = 1.99$, $\rho = 0.5\%$, $N_\alpha = 60 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ for complex **1** and $J = 187.9$, $g = 2.01$, $r = 0.5\%$, $N_\alpha = 10 \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ for complex **4**. This result indicated that NAPH connected Cu(II) ions undergo very strong spin-coupling between the adjacent metal ions when bridged by μ-OH and μ-Br ligand, since the exchanging integral of the extending ligand is negligible. The extent for complex **1** is comparable to related system [19].

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 band angles at the bridging atom, the dihedral angle between the planes containing the Cu(II) ions and the metal-bridging ligand bond lengths [20]. Even though out effort to obtain single-crystal of these complexes were unsuccessful, the quantitatively difference of the spin-coupling between the complexes **1, 4** and [Cu$_2$ NAPH (bipy)$_4$](ClO$_4$)$_2$ is a strong support of the structure proposed.

3.3. Tyr-like activity and kenetic studies

As we know, catalytic oxidation of catechol is one of the functions of tyrosinase. Kida and co-workers have studied a number of Cu(II) complexes and have shown that binuclear system can catalyze the reaction while mononuclear species are either not efficient or inactive [21]. In order to investigate the intermediates involved in the catalytic process, we studied the μ-X-bridged dicopper(II) complexes.

During this oxidation process, three different reaction conditions were chosen to elucidate the catalytic

process as: (a) Cu(II) complexes under argon; (b) Cu(II) complex under excess dioxygen; (c) Cu(II) complex under excess dioxygen and NaOEt. Only one kind of oxidation product was found. Fig. 5A–D show the plot of absorbance versus time for the first 30 min of these reactions.

In order to determine the pseudo-first-order rate of the complexes, the substrate in 125 folds excess was used. The linear relationship between time and absorbance were found, however, with two slopes before and after the time point of ca. 10 min. For curve a, Cu(II) catalyzed oxidations were carried out in the absence of dioxygen, the Cu(I) complex that would be formed could not caused any further oxidation of the substrate, the greatest slopes denotes the rate of dicopper(II) complex.

In the presence of an excess of dioxygen, the results (curve b) indicated that, from the two slopes, there are at least two processes occurring consecutively. The initial gradient is considered to arise from the slow oxidation by Cu(II). Since the reaction occurs in the presence of excess dioxygen any Cu(I) formed as a consequence of this oxidation is capable of absorbing dioxygen and forming a Cu(I) dioxygen complex. It is this species combined with Cu(II), which performed oxidation on the substrate. Thus, the second slope represents the catalytic rate of Cu(I) and Cu(II) dinuclear complex as a whole. The initial rate and turnover numbers for complex **1** are shown in Table 2.

As seen from the results above, complex **1** is the most active catalyst for the oxidation of catechol and **4** comparatively the most inert catalyst. These phenomenon can be interpreted as follow: for complex **1**, OH is a basic ligand and readily react with catechol when leaving the dinuclear moiety; for complex **2**, bridging ligand OAc is more labile compared with complexes **3** and **4**, thus, in the reaction solution, the acetate ligand is easier to leave the Cu(II) ions and so forming coordination unsaturated dicopper(II) cavity.

In order to verify this hypothesis, NaOEt was used as co-catalyst. In the same process as mentioned above, NaOEt solution was added (Cu$_2$ complex:NaOEt = 1:5). The experimental results were compiled in Table 3. The data presented that NaOEt can promote all the four complex catalysts in oxidation yet in different scales. From the experimental results we concluded that the μ-X ligand dissociated from the Cu$_2$ complex must be prior the
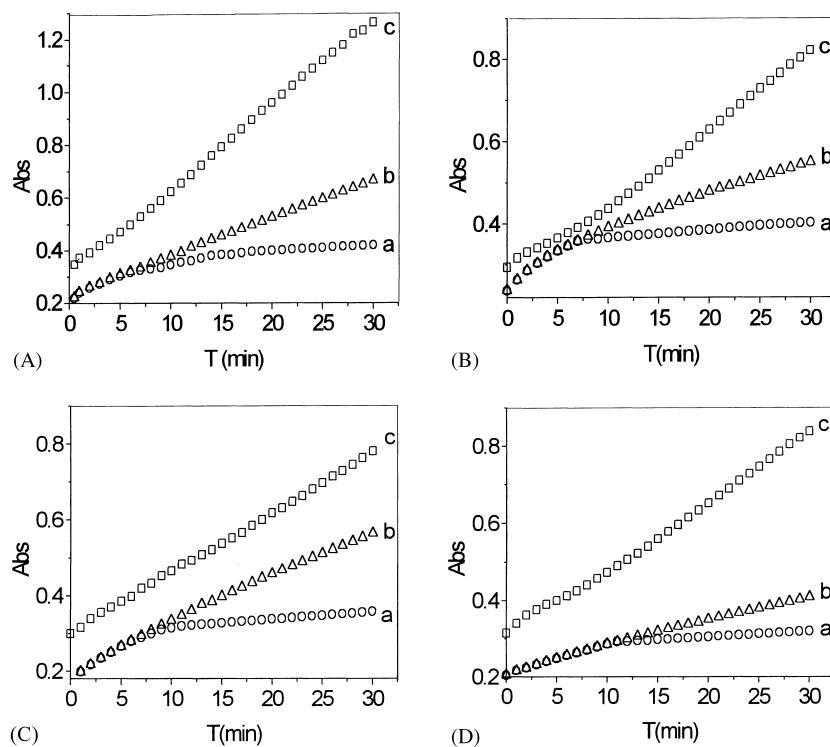
Fig. 5. Time dependence of the catalytic formation of benzoquinone for complexes **1**, **2**, **3** and **4** (2.0×10^{-4} M) under the conditions of (A) under argon; (B) excess of dioxygen and (C) excess dioxygen + co-catalyst.

Table 2
Catalytic activity of complex **1** in oxidation

Conditions	Turnover number (h)	Time of reaction (min)	Initial pseudo-first-order rate (M/s)
Cu(II) complex under argon	2.6	30	7.0×10^{-6}
Cu(II) complex in dioxygen	5	30	9.5×10^{-6}
Cu(II) complex + co-catalyst	11	30	2.1×10^{-5}

Table 3
Comparison of the activity with and without co-catalyst for complex **1–4**

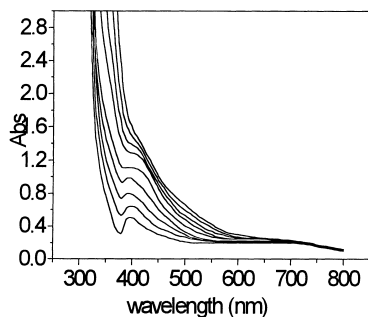| Complex	Rate 1 (under dioxygen)	Rate 2 (with co-catalyst)	r_2/r_1	T_1[a] (h^{-1}) (under dioxygen)	T_2 (h^{-1}) (with co-catalyst)	T_2/T_1
1	9.5×10^{-6}	2.1×10^{-5}	2.2	4.7	11	2.3
2	4.3×10^{-6}	1.3×10^{-5}	3.0	3.0	6.2	2.1
3	5.6×10^{-6}	1.3×10^{-5}	2.4	4.1	6.1	1.5
4	8.0×10^{-6}	1.1×10^{-5}	1.4	4.2	5.8	1.4

[a] Turnover numbers.

Fig. 6. Spectroscopic presentation of oxidation of catechol for complex **4** (2.0×10^{-4}) promoted by NaOEt under excess dioxygen.
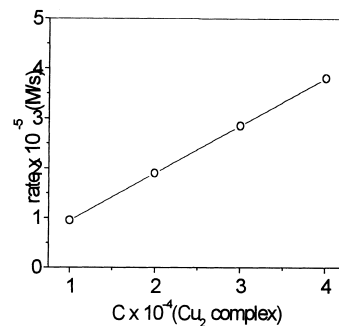

Fig. 7. Initial rates vs. concentration for complex **1**.

formation of catecholate complex. For complex **1**, the OH ligand can react with the substrate and this process can be promoted by strong base NaOEt. Subsequently the complexation process and two-electron redox reaction occurs. In coordination to the substrate, extended bridge DPHA hold the Cu(II) ions together, thus, two proximate metal sites revealed. Spectral changes accompanying the oxidation of catechol with complex and co-catalyst under excess dioxygen were illustrated in Fig. 6.
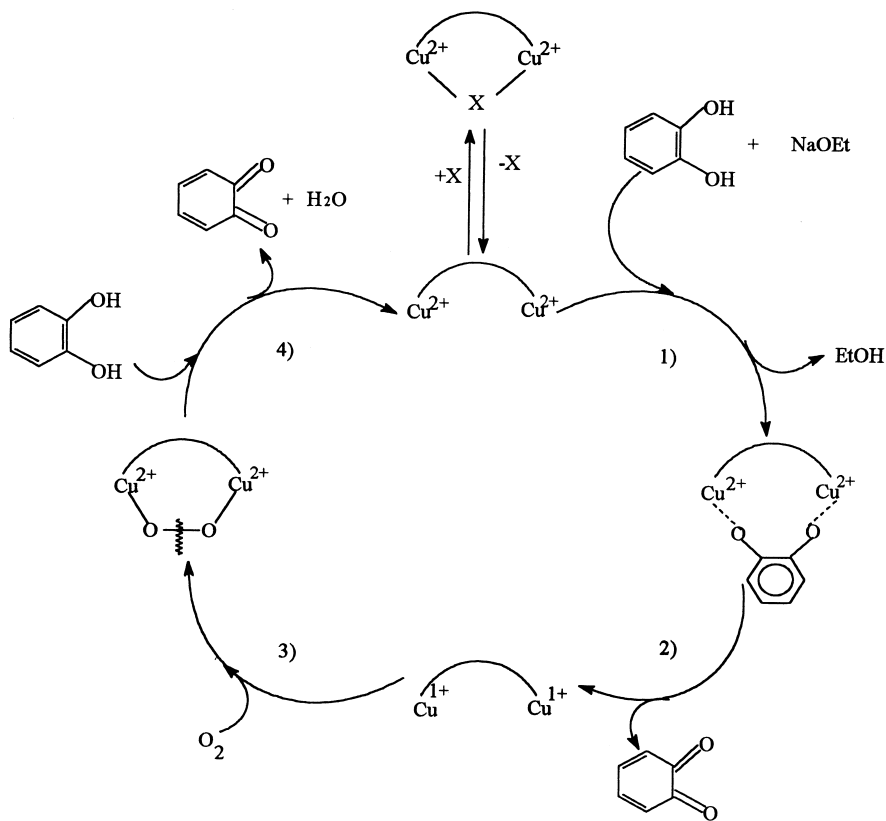
Scheme 1. Catalytic cycle of the oxidation reaction.

The dependence of initial rates of quinone was examined with varying concentration of complex **1** and catechol. In the first experiment, the catechol concentration was kept constant ($C_0 = 0.05$ M) and the concentration of the complex was varied from 0.1×10^{-4} to 2×10^{-4} M. Plots of the initial rates versus catalyst concentration (Fig. 7) indicated that the reaction was first order in complex concentration. In the second experiment, the catalyst concentration was kept constant at 1.0×10^{-4} M and the catechol concentration was varied between 0.01 and 0.1 M. The reaction was zero order in the substrate.

A typical mechanism for the catalytic reaction of is indicated in Scheme 1. When the initiator is the μ-X dicopper(II) complex, the essential steps involve: (1) the leaving of the μ-X bridging ligand which reacts with the deprotonated catechol to form catecholate dicopper(II) complex. This process can be promoted by OH or OEt; (2) the oxidation of catechol to produce benzoquinone and reduced Cu(I) complex; (3) the dicopper(I) complex formed absorbs oxygen to form the peroxo complex [22]; (4) binding of the substrate to the peroxo complex and its oxidation to produce quinone and Cu(II) complex, hence, the cyclic process is continued. The water produced in step (4) is expected to react with the sodium ethoxide to form hydroxy ligand which could bridge the two Cu(II) ions to form the initial complex catalyst.

This work reports the first attempt to correlate the structure of μ-X-bridged dicopper(II) complex as model complex of Tyr-like enzyme and their catalytic activity during oxidation of catechol. We have shown that this activity can be finely turned by modification at the bridging ability of the Cu(II) ions. An absolute requirement is the presence of an exchangeable coordination site that allowed the oxidant to bind the metal center and form bridged structure. With complexes **1** and **2** high turnover number and good yields were obtained with only a limited inactivation of the catalyst. This supports the present biomimetic strategy, based on binuclear rather than mononuclear complexes, which was used to design new oxidizing system. Moreover, preliminary mechanism studies suggested that catechol dianion are intermediates during the oxidation process. Strong base as OH and OR group could facilitate this species and, thus, promote the whole reaction. The greatest contrast with the literature reported was the catalytic center was dicopper(II) cavity other than dicopper(I) species as initial species reported recently, in that case the reaction rate of Cu(I) complexes are several-fold of Cu(II) complexes, however, the Cu(I) dinuclear complexes are not easily to be stabilized in air condition. In our work the catalytic rate can be matched with the effective dicopper(I) complexes reported. We are currently trying to use this stable and effective catalytic system in specific real catalytic reaction.

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