Synthesis and characterization of dihydroxo-bridged dicopper(II) complex and its catalytic properties for catechol oxidation

Jian Gao, Shun-he Zhong*

College of Chemical Engineering and Technology, University of Tianjin, Tianjin 300072, People's Republic of China

Abstract

Three dihydroxo-bridged dicopper(II) complex catalysts have been synthesized, namely $[Cu_2(\mu\text{-}OH)_2L_2](ClO_4)_2$ [L=phen (**1a**), NO_2-phen (**1b**) and bipy (**1c**)]. Diphenic acid dianion (DPHA) was found to have the ability to form mononuclear complex of [CuDPHA] (**2a**), dinuclear complex of $[Cu_2DPHA(phen)_2](ClO_4)_2.2H_2O$ (**2b**) and dihydroxo-bridged dicopper(II) complex of $[Cu(\mu\text{-}OH)_2DPHA(H_2O)_2]$ (**2c**). Based on IR, elemental analysis and electronic spectra, complexes **1a**, **1b** and **1c** were supposed to have dihydroxo-bridged dinuclear planar structure and consist of two copper(II) ions in planar square environment, **2b** was supposed to have extended DPHA-bridged structure with two copper(II) ions in saturated five-fold coordination environment, whereas **2c** was found to have a heterocyclic structure with both DPHA and dihydroxo as bridging ligands. The temperature dependence of magnetic susceptibilities of **2b** and **2c** has been studied, giving the exchange integral of $J=-1.5$ cm^{-1} and $J=-120$ cm^{-1}, respectively. This result is in agreement with proposed dihydroxo-bridged structure of **2c**, since complex **2b** was weakly antiferromagnetically coupled by DPHA ligand and Cu_2O_2 unit normally undergoes strong antiferromagnetic interaction as a rule. In methanol solution, catalytic properties of these complexes were investigated for the oxidation of catechol, revealing that **2c** is an effective catalyst for the oxidation of catechol to benzoquinone. Complexes **1a**, **1b** and **1c** are also capable of catalyzing this reaction, but at a low reaction rate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Dicopper(II) complex catalyst; Bridging ligand; Ligand exchange reaction; Catechol; Catalytic oxidation

1. Introduction

Transition metal dinuclear complexes with extended bridged structure are currently an interesting topic due to the spin-coupling and charge transfer between metal ions and bridging ligand in the domain of metalloenzymes [1]. Meanwhile, single atomic (O^{2-} OH^- OR^- Cl^-) [2–5] bridged dinuclear complexes are also investigated energetically in recent years mainly because they are active species in both biomimetic and real catalysis processes. Tyrosinase (Tyr) is a dinuclear copper(II)-containing protein that binds or activates dioxygen and functions as a monooxygenase that hydroxylates monophenols and further oxidizes the *O*-diphenol to an *O*-quinone [6].

Significant progress has been made in the chemical modeling of Tyr-like monooxygenase activity. Karlin et al. reported [7] the first model consisting of a binucleating ligand having a *m*-xylyl spacer between the two tridentate coordination units. Another group [8] has also developed Schiff bases system involving hydroxylation process, and providing only two *N*-coordinations per copper(II). Menif et al. [9] demonstrated the first successful use of xylyl-based macrocyclic ligand derived from diethylenetriamine to bring about aromatic ring hydroxylation.

* Corresponding author.

Concerning the literature reports: (1) dihydroxo-bridged dicopper(II) complexes are the stable reaction products of dicopper(I) complex and dioxygen at room temperature and air condition [10]; (2) bis-alkoxy-bridged dicopper(II) complex is either the possible intermediate in the oxidation of *O*-diphenol by dicopper(I) complex dioxygen adduct [11], or the complex catalyst synthesized to fulfill the catalytic oxidation; and (3) ligand diphenic acid dianion (DPHA) has the ability of forming dinuclear complexes with little spin-exchange between the adjacent metal ions [12], we initiated a program to systematically investigate the dihydroxo-bridged dicopper(II) complexes with or without extended bridging ligand DPHA that is capable of providing only two *O*-coordinations to each copper(II) site.

In this paper, detailed account of synthesis and characterization process is provided. The coordination ability of DPHA to form mono- and dinuclear complexes, in open and cyclic fashion, was studied thoroughly. Spectroscopic and magnetic results suggested that dihydroxo dicopper(II) structure can be stabilized by ligand DPHA. Special emphasis was given to illustrate the functions of metal ions, hydroxo ligands and bridging ligand DPHA in the catalytic oxidation process. In addition, proposed catalytic reaction mechanism was also given, trying to understand the catalytic procedure of copper-containing enzyme Tyr.

2. Experimental

All reagents used were of analytical grade and purchased from Peking Chemical.

2.1. Preparation of $[Cu_2(\mu\text{-}OH)_2(phen)_2](ClO_4)_2$ (**1a**)

In dinitrogen-flushed CH_3OH (10 ml), solid $Cu(ClO_4)_2 \cdot 6H_2O$ (148.2 mg, 0.4 mmol) was added and kept under magnetic stirring. The terminal ligand phen (79.2 mg, 0.4 mmol) was dissolved in methanol (5 ml) under a dinitrogen atmosphere and then added to the metal salt solution by a cannula; blue precipitate was formed immediately. An ethanol solution (1.4 ml) of NaOEt (0.4 mmol) was injected through the septum with a syringe; deep green compound thus formed and transformed into white–blue precipitate

when exposed to the atmosphere for 30 min. The final product was collected by filtration, washed three times with absolute methanol and dried in vacuum. Found: C, 40.0; H, 2.5; N, 7.8; Cu, 21.0. Calc: for $C_{24}H_{18}N_4O_2Cl_2Cu_2$: C, 40.0; H, 2.5; N, 7.8; Cu, 21.5%. IR (KBr, cm^{-1}, selected peaks): 3520 (m, $\nu(OH)$), 955 (m, $\nu(OH)$), 1100 and 620 (s, $\nu(ClO_4^-)$), 760 (m, $\nu(Cu-O)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 240$ Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [λ_{max}, nm (ε, M^{-1} cm^{-1})]: in CH_3CN, 610 (117), 354 (4600).

2.2. Preparation of $[Cu_2(\mu\text{-}OH)_2(NO_2\text{-}phen)_2]$-$(ClO_4)_2$ (**1b**) and $[Cu_2(\mu\text{-}OH)_2(bipy)_2](ClO_4)_2$ (**1c**)

Following a similar reaction procedure as stated in the previous section, but using NO_2-phen and bipy rather than phen, white–blue and purple microcrystals were obtained respectively, and satisfactory analysis data were given. For complex **1b**, IR (KBr, cm^{-1}, selected peaks): 3520 (m, $\nu(OH)$), 955 (m, $\nu(OH)$), 1100 and 630 (s, $\nu(ClO_4^-)$), 758 (m, $\nu(Cu-O)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 249$ Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [λ_{max}, nm (ε, M^{-1} cm^{-1})]: in CH_3CN, 610 (132), 354 (3590). For complex **1c**, IR (KBr, cm^{-1}, selected peaks): 3510 (m, $\nu(OH)$), 960 (m, $\nu(OH)$), 1100 and 620 (s, $\nu(ClO_4^-)$), 760 (m, $\nu(Cu-O)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 244$ Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [λ_{max}, nm (ε, M^{-1} cm^{-1})]: in CH_3CN, 615 (89), 356 (5300).

2.3. Preparation of mononuclear complex [CuDPHA] (**2a**)

This complex was prepared by adding a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (148.2 mg, 0.4 mmol) in absolute methanol (5 ml) to a solution of methanol (10 ml) containing diphenic acid (96.8 mg, 0.4 mmol) and triethylamine (0.8 mmol). Blue microcrystals were formed, separated and recrystallized from methanol, washed with absolute methanol and diethyl ether three times and vacuum-dried. Found: C, 55.2: H, 2.2; Cu, 20.5. Calc.: for $C_{14}H_8O_4Cu$: C, 55.4; H, 2.6; Cu, 20.9%. IR (KBr, cm^{-1}, selected peaks): 1580 (s, $\nu_{as}(COO^-)$), 1410 (m, $\nu_s(COO^-)$), 748 (m, $\nu(Cu-O)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 49$ Ω^{-1}

cm^2 mol^{-1}. Absorption spectrum [λ_{max}, nm (ε, M^{-1} cm^{-1})]: in CH_3CN, 620 (160), 275 (7630).

2.4. Preparation of [Cu₂DPHA(phen)₂](ClO₄)₂.2H₂O (2b)

To a stirred solution of methanol (10 ml) containing diphenic acid (48.4 mg, 0.2 mmol) and triethylamine (0.4 mmol) and phen (158.6 mg, 0.8 mmol) in absolute methanol (5 ml), a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (148.2 mg, 0.4 mmol) in absolute methanol (5 ml) was added, green microcrystal was formed immediately. This solid complex was separated, washed several times with methanol and diethyl ether, and dried in vacuum to give a satisfactory analysis data. Found: C, 56.0; H, 3.6; N, 9.0; Cu, 9.6. Calc.: for $C_{62}H_{40}N_8O_{12}Cl_2Cu_2.H_2O$, C, 56.3; H, 3.4; N, 8.5; Cu, 9.6%. IR (KBr, cm^{-1}, selected peaks): 1580 (s, $\nu_{as}(COO^-)$), 1370 (m, $\nu_s(COO^-)$), 1095 and 630 (s, $\nu(ClO_4^-)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 265$ Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [λ_{max}, nm (ε, M^{-1} cm^{-1})]: in CH_3CN, 676 (91), 283 (8540).

2.5. Preparation of [Cu₂(μ-OH)₂DPHA(H₂O)₂] (2c)

In dinitrogen-flushed methanol solution (10 ml) containing diphenic acid (48.2 mg, 0.2 mmol) and triethylamine (0.4 mmol), a solution of $Cu(ClO_4)_2.6H_2O$ (148.2 mg, 0.4 mmol) in methanol (15 ml) was added and kept under magnetic stirring; a bluish-green solution was obtained. To this solution was added sodium ethoxide (0.4 mmol) by injection with a syringe; a green solution with a green suspension was obtained and turned into a blue solution after the mixture was exposed to dioxygen for 2 h. After no color change could be observed, the final product was separated, washed with absolute methanol and diethyl ether three times and dried in vacuum to give a satisfactory analysis data. Found: C, 37; H, 3.1; Cu, 27.6. Calc.: for $C_{14}H_{10}O_6Cu_2.3H_2O$: C, 36.9; H, 3.5; Cu, 28%. IR (KBr, cm^{-1}, selected peaks): 3520 and 1110 (s, ν(bridged OH)), 1580 (s, $\nu_{as}(COO^-)$), 1400 (m, $\nu_s(COO^-)$), 752 (m, $\nu(Cu–O)$). Conductivity (CH_3CN, 10^{-3} M solution at 298 K): $\Lambda_M = 265$ Ω^{-1} cm^2 mol^{-1}. Absorption spectrum [λ_{max}, nm (ε, M^{-1} cm^{-1})]: in CH_3CN, 676 (91), 283 (8540).

2.6. Measurement

Analysis for C, H and N was 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 PPS-11A conductometer. Variable-temperature magnetic susceptibilities were measured on a SQUID susceptometer (sensitivity $m = 10^{-6}$ emu). Diamagnetic correction was made with Pascal's constants for all the constituent atoms, and the magnetic moment was calculated using $\mu_{eff} = 2.828$ $(X_M T)^{1/2}$.

2.7. Catalytic oxidation

Catalytic oxidation of catechol was carried out under aerobic condition as following: complexes (**1a**, **1b** and **1c**, **2a**, **2b** and **2c**, 0.3 μmol) were dissolved in a solution of 3 ml methanol containing 0.3 mmol of catechol. The ratio of Cu_2 complex to catechol = 1:1000. The kinetics of the reaction was studied spectrophotometrically at the wavelength of $\lambda_{max} = 390$ nm. Formation of quinone was monitored by the increase of absorbance as a function of time.

3. Results and discussion

3.1. Composition and IR spectroscopic characterization

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. The signification bands in the IR spectra of the complexes are all given. In the IR region of the spectrum, complexes **1a**, **1b** and **1c** exhibited two sharp, strong bands at 3520 and 955 cm^{-1}; those can be attributed to bridged hydroxo. In low frequency, strong band at 754 cm^{-1} was diagnostic of the presence of Cu–O–Cu.

In the IR spectrum of complexes **2a**, **2b** and **2c**, 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 DPHA. 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 **2a** and **2c** are smaller than 200 cm^{-1}, suggesting a bidentate mode for both carboxylato groups [13]. For complex **2b**, the unsplit ClO$_4^-$ vibration at 1095 is present indicating non-coordinated mode [14]. For complex **2c**, strong and sharp bands at 3520 and 1110 cm^{-1} suggested the formation of dihydroxo-bridged dicopper(II) structure. Bands at 748 and 752 cm^{-1} for complexes **2a** and **2c** attribute to Cu–O vibration. The data are consistent with the molar conductance measurement.

3.2. Visible absorption spectra of the copper(II) complexes

The electronic spectrum of **1a** shows a broad and weak ligand field band at 610 nm; at higher energy, an intense peak at 354 nm was observed. The high-energy transition is due to OH–Cu(II) ligand-to-metal charge transfer. These data suggest that each copper(II) center is four-coordinated with dihydroxo bridging ligand [10]. Complex **2c** exhibits two bands; one weak at ca. 670 nm was assigned to d–d transition; at higher energy, an intense peak at 356 was observed, typical of an OH–Cu(II) charge-band transfer [15]. These data indicated five-coordinated copper(II) chromophores with distorted square-pyramidal configuration, supported by well-established electronic spectrum for copper(II) complexes [16]. The spectral behavior of **2b** (d–d transition at 676 nm and a strong CT band at 283 nm) suggests that each copper(II) center is five-coordinated.

Based on the discussion above, complexes **1a**, **1b** and **1c** are proposed to have dihydroxo-bridged structure; complex **2a** to have a mononuclear structure; complex **2b** to have extended DPHA-bridged structure, in which DHPA bridges are in a bis-monodentate fashion and metal ions are in a square-pyramidal environment. Meanwhile, for complex **2c**, a heterocyclic structure was proposed (shown in Fig. 1)
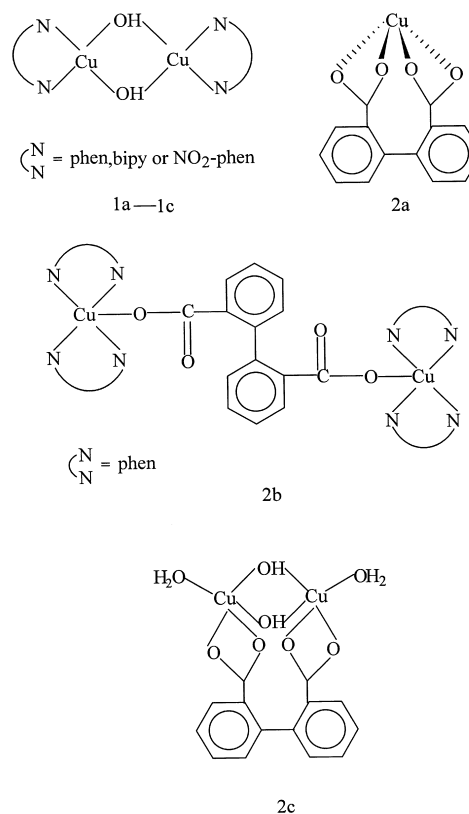

Fig. 1. Proposed structures of the complexes.

3.3. Magnetic properties and magneto-structural correlations

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 **2b** and **2c** in solid state were undertaken to elucidate the extent of magnetic coupling in this system. Variable-temperature magnetic susceptibility data were collected in the 4.2–300 K range. The μ_{eff} versus T plots are shown in Fig. 2. The magnetic moments decrease with decreasing temperature, implying the existence of an antiferromagnetic 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 $H = -JS_1S_2$.
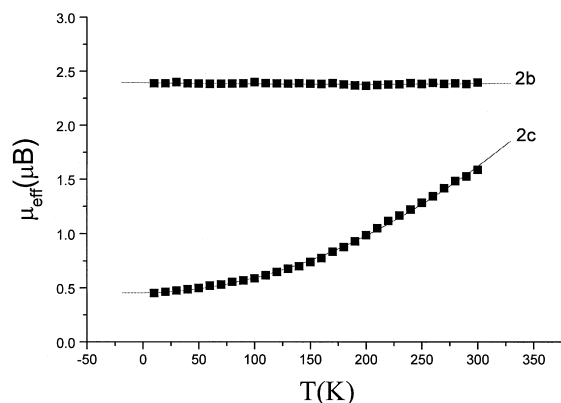
Fig. 2. Temperature variation of the μ_{eff} of complexes **2b** and **2c**.

The molar susceptibility of the Cu–Cu ($S_1 = S_2 = 1/2$) system was calculated by the Bleaney–Bower equation [17]

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

where χ_M denotes the susceptibility per binuclear complex, $N\alpha$ is the temperature-independent paramagnetism (120×10^{-6} cm^3 mol^{-1}) and other symbols have their usual meaning. As shown in Fig. 3, good fit to the experimental data was attained. The magnetic parameters thus determined are $J = -1.5$ cm^{-1}, $g = 1.98$ for complex **2b** and $J = -120$ cm^{-1}, $g = 2.00$ for **2c**. This result indicated that extended bridge DPHA undergoes very weak spin-coupling

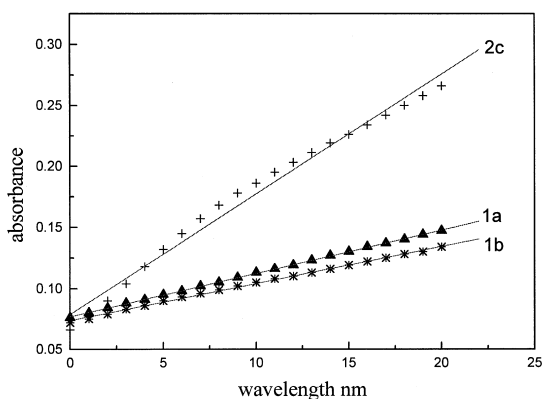

Fig. 3. UV–Vis absorbance versus time for complexes of **1a**, **1b** and **2c** (1.0×10^{-4} M).

between the adjacent metal ions, which is consistent with our former investigation [12]; whereas for dihydroxo-bridged complex **2c**, there exists a strong antiferromagnetic interaction and the extent is comparable to related systems [18,19].

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 copper(II) ions, and the metal–bridging ligand bond lengths. Even though our effort to obtain single crystal of **2c** was unsuccessful, the qualitative difference of the spin-coupling between the complexes **2b** and **2c** is easy to illustrate. For complex **2b**, two metal ions are separated by extended bridge, hence undergo weak interaction, whereas for complex **2c**, two copper(II) ion sites in two planes are connected by dihydroxo bridges. When the metal ions move towards the same plane, the overlap between the metal-based $d_{x^2-y^2}$ orbits and the oxygen-based sp^2 hybrid orbits are increased; the enhanced overlap should increase the strong antiferromagnetic interaction.

3.4. Conversion from dialkoxy- to dihydroxo-bridged dicopper(II) complexes

In the synthesis of dihydroxo-bridged complexes, where sodium ethoxyl was used other than sodium hydroxy, we speculated that dialkoxy-bridged complex was formed first, which underwent a ligand-exchange reaction (Scheme 1). Water ligand comes from metal salt Cu(ClO$_4$)$_2$.6H$_2$O. Interestingly, when four equivalents of sodium ethoxy were added, the blue or purple dihydroxo complexes converted to their original green complexes; however, when exposed to or in air condition, they quickly transformed into the dihydroxo complexes. This phenomenon suggested that in the system, the bridge ligand of alkoxy/hydroxo is very active and readily participates in the reaction.
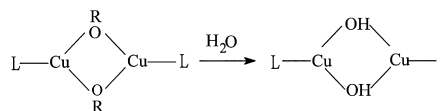
Scheme 1. Bridging ligand exchange reaction.

Table 1
Kinetic data of selected complexes

| Complexes	Turnover number (h)	Time of reaction	Initial pseudo-first-order rate (M/s)
2c	4.2	20	3.34×10^{-4}
1a	1.5	20	1.19×10^{-4}
1b	1.3	20	1.04×10^{-4}

3.5. Catalytic properties for catechol oxidation

As we know, catalytic oxidation of catechol is one of the function of Tyr. In order to understand the catalytic process, we studied dihydroxo bridge di-copper(II) complexes with or without extra extended ligand. Kida et al. [20] have studied a number of copper(II) complexes and have shown that binuclear system catalyzes the reaction while mononuclear species are either not efficient or inactive. Fig. 3 shows the plot of absorbance versus time for the first 20 min of the reaction for complexes **1a**, **1b** and **2c**. Initial rate and turnover number for complexes are shown in Table 1. Complexes **1a**, **1b** and **1c** were less active and **2c** was the most active catalyst for the oxidation of catechol to quinone that can be explained by assuming that in the oxidation of catechol, dissociation of the dihydroxo bridging groups must occur prior to the complexation of the substrate. Subsequently, the two-electron redox reaction occurs. In coordination to supposed intermediate, complexes **1a**, **1b** and **1c** transfer into mononuclear species (Scheme 2), whereas for complex **2c**, extended bridge DPHA holds the copper(II) ions together, thus two proximate metal sites revealed (Scheme 3). This is why complex **2c** is said to be the most efficient catalyst.

According to the phenomenon, supposed mechanism was illuminated as Scheme 4. In order to testify this hypothesis, the function of dihydroxo bridging ligands was testified. In the catalytic process of **2c**,
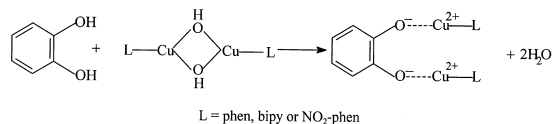
Scheme 2. Initial stage of the catalytic oxidation reaction for complexes **1a**, **1b** and **1c**.
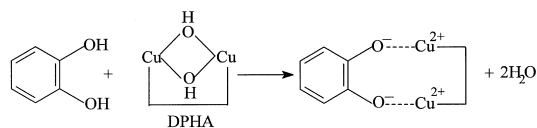
Scheme 3. Initial stage of the catalytic oxidation reaction for complex **2c**.
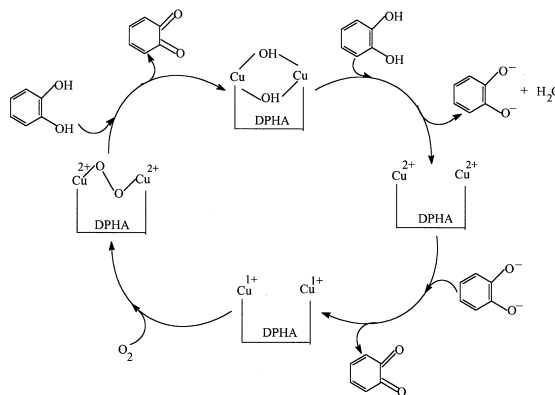
Scheme 4. Catalytic oxidation mechanism of complex **2c**.

when two equivalents of $HClO_4$ were added, no catalytic oxidation reaction was observed.

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