

Synthesis, characterization, electrochemical studies and catecholase-like activity of a series of mononuclear Cu(II), homodinuclear Cu(II)Cu(II) and heterodinuclear Cu(II)Ni(II) complexes of a phenol-based compartmental ligand

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Abstract

A series of previously reported mononuclear Cu(II) and homodinuclear Cu(II)Cu(II) complexes, as well as, novel mononuclear Cu(II), homodinuclear Cu(II)Cu(II), and heterodinuclear Cu(II)Ni(II) complexes of a phenol-based dinucleating ligand with two different N(amine)₂O₂ and N(imine)₂O₂ coordination sites, were synthesized and characterized by elemental analyses, infrared and electronic absorption spectroscopies and conductivity measurements. The electrochemical behavior and catecholase-like activity of the complexes were also studied using cyclic voltammetry and UV–vis spectrophotometry, respectively. Our results show that the dinuclear complexes are more effective catalysts in the oxidation of catechol to the corresponding quinone than the mononuclear complexes. Furthermore, the homodinuclear Cu(II)Cu(II) complexes show greater catalytic activity compared to the corresponding heterodinuclear Cu(II)Ni(II) complexes.

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1. Introduction

The chemistry of dinucleating ligands and especially their heterodinuclear complexes has unceasingly and deservedly gained great attraction during the past decade [1–4]. The presence of two metal ions in close proximity at the active site of several metallo-proteins and metallo-enzymes has simulated interest in the synthesis and study of dinuclear complexes. In particular, the recent recognition of heterodinuclear cores at the active sites of purple acid phosphatase [5] and human calcineurin (FeZn) [6], and human protein phosphatase 1 (MnFe) [7] has encouraged the design of heterodinuclear complexes for functional and structural model studies. Another interest in such bimetallic complexes lies in the area of magnetochemistry. The magnetic interaction between the metal ions of the dinuclear complexes has intro-

duced them as being suitable candidates for molecule-based magnets [8–10]. There is also continuing interest in mechanistic studies on the catalytic oxidation of catechols by transition metal complexes because this reaction plays key role in the metabolism of aromatic compounds. Copper-containing metallo-proteins and metallo-enzymes are involved in a variety of biological processes in living systems. Hemocyanin, tyrosinase and catechol oxidase proteins have dinuclear copper(II) centers at their active sites [11,12]. Catechol oxidases, like tyrosinase, oxidize phenolic compounds to the corresponding quinones in the presence of oxygen. During the past decade or so, a very large number of binucleating ligands and their complexes have been synthesized and studied. Among many different types of dinucleating ligands, the phenol-based compartmental ligands (Fig. 1) have attracted particular attention [13–16].

In the course of this study, Okawa and his co-workers have reported the synthesis of homodinuclear and heterodinuclear complexes of a phenol-based compartmental lig-

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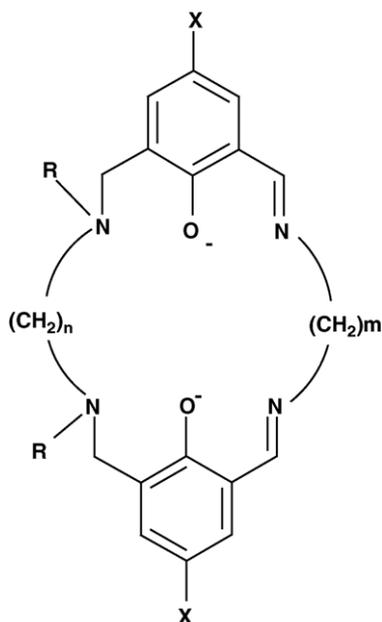


Fig. 1. Structure of phenol-based compartmental ligands.

and in which the $N(amine)_2O_2$ coordination site is provided by two phenolic oxygen atoms and the nitrogen atoms from $(CH_3)NCH_2CH_2N(CH_3)$ [13]. Karunakaran and Kandaswamy have also reported [15] the synthesis of related macrocycles containing piperazine entity to provide the nitrogen atoms of the $N(amine)_2O_2$ coordination site. They have reported the synthesis of homodinuclear $Cu(II)Cu(II)$ complexes but they did not study heterodinuclear complexes of their ligands. Based on the above, we decided to synthesize novel mononuclear $Cu(II)$, homodinuclear $Cu(II)Cu(II)$ and heterodinuclear $Cu(II)Ni(II)$ complexes. The catalytic reactivity of these complexes, as well as four other previously reported mononuclear and homodinuclear complexes, is also studied in the aerobic oxidation of catechol to the corresponding quinone.

2. Experimental

All the reactions were performed under aerobic conditions unless otherwise noted. N,N' -Pyrazinebis(5-bromo-3-formyl-2-hydroxybenzylamine) (H_2L'), the mononuclear complexes $[CuL^{1,3}]$, the dinuclear complexes [14] $[Cu_2L^{1,3}]$ and *meso*-stilbenediamine [17] were synthesized as described elsewhere. All the other materials were used as received. Analyses for carbon, hydrogen and nitrogen were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). Analyses for the metal ions were conducted using a Varian AA-220 spectrophotometer. IR spectra of KBr pellets of the ligands and the complexes were recorded on an ABB Bomem MB series spectrophotometer in the range of 400–4000 cm^{-1} . Electronic spectra were recorded using a Cary 100 Bio Varian UV/Vis spectrom-

eter. Conductivity measurements were performed using a Jenway-4010 conductivity meter. All electrochemical experiments were done using a setup comprised of a PC PII Pentium 300 MHz microcomputer equipped with a data acquisition board (PCL-818PG, PC-Labcard Co.) and a custom made potentiostat [18].

2.1. Typical procedure for the preparation of mononuclear complexes $[CuL^{1-4}]$

2.1.1. Preparation of CuL^2

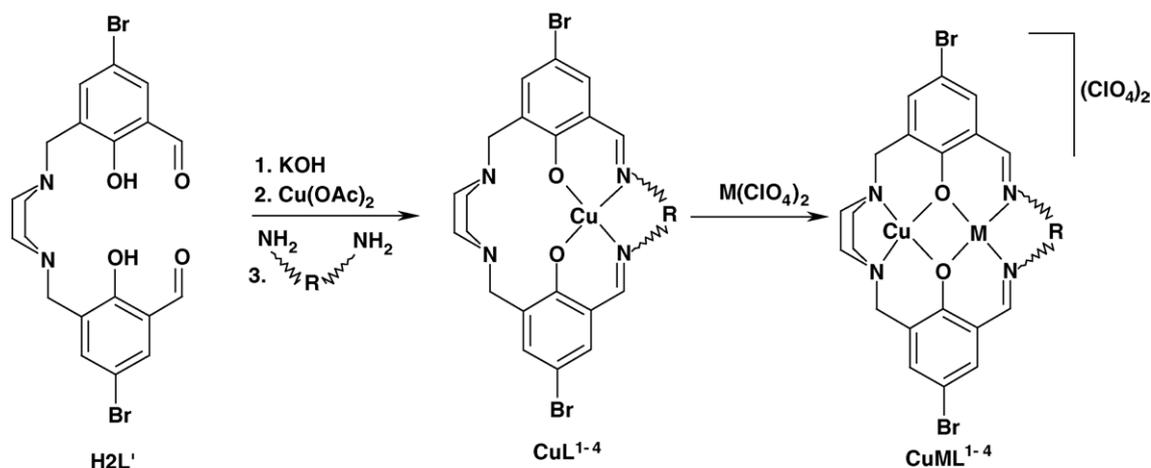
The synthesis route for this complex and the other complexes is shown in Fig. 2. H_2L' (0.5 g, 1 mmol) was dissolved in 30 mL of aqueous solution of KOH (0.11 g, 2 mmol) and the reaction mixture was stirred at room temperature until a clear yellow solution was obtained. To the resulting solution was added an aqueous solution of $Cu(OAc)_2 \cdot H_2O$ (0.2 g, 1 mmol in 20 mL of water) to form a green precipitate. The resulting precipitate was collected by suction filtration and washed successively with water and ether and dried in vacuo. The resulting solid was suspended in 30 mL of methanol and to this mixture was added dropwise a solution of *meso*-stilbenediamine (0.21 g, 1 mmol) in 20 mL of methanol and the reaction mixture was refluxed for about 3 h. The resulting solid was collected by suction filtration and washed successively with water and diethyl ether and dried in vacuo. The complex was obtained as a green powder and the yield was 0.71 g, 92%. Analytically calculated for $C_{34}H_{30}Br_2CuN_4O_2$ (%): C, 54.4; H, 4.0; Cu, 8.5; N, 7.5. Found (%): C, 54.3; H, 4.1; Cu, 8.4; N, 7.4. Selected IR data (ν , cm^{-1} KBr): 1623 ($\nu_{C=N}$). UV-vis [λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)]: 604 (140), 378 (3700), and 368 (4750) in acetonitrile.

2.1.2. CuL^4

This complex was obtained as a green precipitate following the previously described procedure for CuL^2 except 1,3-diamino-2-hydroxypropane was used instead of *meso*-stilbenediamine. The yield was 0.60 g, 95%. Analytically calculated for $C_{23}H_{24}Br_2CuN_4O_3$ (%): C, 43.9; H, 3.8; Cu, 10.2; N, 8.9. Found (%): C, 43.8; H, 3.7; Cu, 10.3; N, 9.0. Selected IR data (ν , cm^{-1} KBr): 1621 ($\nu_{C=N}$). UV-vis [λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)]: 610 (132), 378 (3900), and 367 (4880) in CH_3CN .

2.1.3. Cu_2L^2

To a hot suspension of the mononuclear complex CuL^2 (0.39 g, 0.5 mmol) in 30 mL of methanol was added a methanolic solution of copper(II) perchlorate hexahydrate (0.10 g, 0.5 mmol). A deep green solution was obtained while the amount of the solid mononuclear complex was being decreased. The resulting solution was once filtered to separate any insoluble materials and the filtrate was evaporated to dryness. The residue was re-dissolved in a minimum of methanol and was left undisturbed until the desired product was obtained. The resulting deep green precipitate was collected by suction filtration and washed with water and diethyl



CuML^{1-4} : M = Cu for $\text{Cu}_2\text{L}^{1-4}$ and M = Ni for CuNiL^{1-4}

CuL^1 , Cu_2L^1 and CuNiL^1 : R = $-\text{CH}_2\text{CH}_2-$

CuL^2 , Cu_2L^2 and CuNiL^2 : R = $-\text{CH}(\text{Ph})(\text{Ph})\text{CH}-$

CuL^3 , Cu_2L^3 and CuNiL^3 : R = $-\text{CH}_2\text{CH}_2\text{CH}_2-$

CuL^4 , Cu_2L^4 and CuNiL^4 : R = $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$

Fig. 2. Reaction pathway for the synthesis of the complexes.

ether successively and dried in vacuo. The yield was 0.13 g, 26%. Analytically calculated for $\text{C}_{34}\text{H}_{30}\text{Br}_2\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{10}$ (%): C, 40.5; H, 2.8; Cu, 12.6; N, 5.5. Found (%): C, 40.4; H, 2.7; Cu, 12.4; N, 5.6. Selected IR data (ν , cm^{-1} KBr): 1630 ($\nu_{\text{C}=\text{N}}$), 1100 (ν_{ClO_4} , sym.), 630 (ν_{ClO_4} , diss.). UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 597 (205), 399 (3400), and 368 (3750) in acetonitrile. Molar conductance [Λ_{m} , $\text{S cm}^2\text{mol}^{-1}$]: 215 in acetonitrile.

2.1.4. Cu_2L^4

This complex was obtained as a green precipitate following the previously described procedure for Cu_2L^2 but the mononuclear complex CuL^4 was used in the preparation instead of CuL^2 . The yield was 0.14 g, 26%. Analytically calculated for $\text{C}_{23}\text{H}_{24}\text{Br}_2\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{11}$ (%): C, 31.0; H, 2.7; Cu, 14.3; N, 6.3. Found (%): C, 31.1; H, 2.8; Cu, 14.5; N, 6.4. Selected IR data (ν , cm^{-1} KBr): 1638 ($\nu_{\text{C}=\text{N}}$), 1100 (ν_{ClO_4} , sym.), 628 (ν_{ClO_4} , diss.). UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 594 (764), 384 (3600), and 368 (3990) in acetonitrile. Molar conductance [Λ_{m} , $\text{S cm}^2\text{mol}^{-1}$]: 220 in acetonitrile.

2.1.5. CuNiL^1

This complex was obtained as a green precipitate following the previously described procedure for Cu_2L^2 except CuL^1 and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were used in the preparation instead of CuL^2 and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, respectively. The yield was 0.15 g, 28%. Analytically calculated for

$\text{C}_{22}\text{H}_{22}\text{Br}_2\text{Cl}_2\text{CuN}_4\text{NiO}_{10}$ (%): C, 30.9; H, 2.6; Cu, 7.4; N, 6.5; Ni, 6.9. Found (%): C, 31.0; H, 2.7; Cu, 7.5; N, 6.4; Ni, 6.7. Selected IR data (ν , cm^{-1} KBr): 1638 ($\nu_{\text{C}=\text{N}}$), 1100 (ν_{ClO_4} , sym.), 620 (ν_{ClO_4} , diss.). UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 594 (764), 384 (3600), and 368 (3990) in acetonitrile. Molar conductance [Λ_{m} , $\text{S cm}^2\text{mol}^{-1}$]: 220 in acetonitrile.

2.1.6. CuNiL^2

This complex was obtained as a brown precipitate following the previously described procedure for CuNiL^1 but the mononuclear complex CuL^2 was used in the preparation instead of CuL^1 . The yield was 0.14 g, 26%. Analytically calculated for $\text{C}_{34}\text{H}_{30}\text{Br}_2\text{Cl}_2\text{CuN}_4\text{NiO}_{10}$ (%): C, 40.5; H, 3.0; Cu, 6.3; N, 5.6; Ni, 5.8. Found (%): C, 40.4; H, 3.1; Cu, 6.2; N, 5.5; Ni, 5.9. Selected IR data (ν , cm^{-1} KBr): 1638 ($\nu_{\text{C}=\text{N}}$), 1092 (ν_{ClO_4} , sym.), 630 (ν_{ClO_4} , diss.). UV-vis [λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 594 (150), 404 (3400), and 368 (3740) in acetonitrile. Molar conductance [Λ_{m} , $\text{S cm}^2\text{mol}^{-1}$]: 215 in acetonitrile.

2.1.7. CuNiL^3

This complex was obtained as a brown precipitate following the previously described procedure for CuNiL^1 but the mononuclear complex CuL^3 was used in the preparation instead of CuL^1 . The yield was 0.14 g, 26%. Analytically calculated for $\text{C}_{23}\text{H}_{24}\text{Br}_2\text{Cl}_2\text{CuN}_4\text{NiO}_{10}$ (%): C, 31.7; H, 2.8; Cu, 7.4; N, 6.4; Ni, 6.8. Found (%): C, 31.6; H, 2.7; Cu,

7.5; N, 6.5; Ni, 6.6. Selected IR data (ν , cm^{-1} KBr): 1638 ($\nu_{\text{C}=\text{N}}$), 1100 (ν_{ClO_4} , sym.), 630 (ν_{ClO_4} , diss.). UV–vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 594 (764), 384 (3600), and 368 (3990) in acetonitrile. Molar conductance [Λ_{m} , $\text{S cm}^2 \text{mol}^{-1}$]: 220 in acetonitrile.

2.1.8. CuNiL^4

This complex was obtained as a brown precipitate following the previously described procedure for CuNiL^1 but the mononuclear complex CuL^4 was used in the preparation instead of CuL^1 . The yield was 0.14 g, 26%. Analytically calculated for $\text{C}_{23}\text{H}_{24}\text{Br}_2\text{Cl}_2\text{CuN}_4\text{NiO}_{11}$ (%): C, 31.1; H, 2.7; Cu, 7.2; N, 6.3; Ni, 6.7. Found (%): C, 31.2; H, 2.8; Cu, 7.3; N, 6.4; Ni, 6.5. Selected IR data (ν , cm^{-1} KBr): 1638 ($\nu_{\text{C}=\text{N}}$), 1100 (ν_{ClO_4} , sym.), 630 (ν_{ClO_4} , diss.). UV–vis [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 590 (160), 410 (3250), and 370 (3700) in acetonitrile. Molar conductance [Λ_{m} , $\text{S cm}^2 \text{mol}^{-1}$]: 215 in acetonitrile.

3. Results and discussions

3.1. Preparation and spectroscopic studies of the complexes

The mononuclear complexes $\text{CuL}^{1,3}$ and the dinuclear complexes $\text{Cu}_2\text{L}^{1,3}$ have already been prepared by Kandaswamy and Karunakaran [14]. The other novel mononuclear complexes $\text{CuL}^{2,4}$ as well as homodinuclear complexes $\text{Cu}_2\text{L}^{2,4}$ and heterodinuclear complexes CuNiL^{1-4} were also prepared following the general procedures [13,14]. The mononuclear complexes were readily prepared by the reaction of the ligand ($\text{H}_2\text{L}'$) with copper(II) acetate followed by the reaction with the diamines (Fig. 2). The reaction of the mononuclear complexes with copper(II) and nickel(II) perchlorates resulted in the synthesis of the corresponding dinuclear complexes (Fig. 2). Okawa and his co-workers have reported the synthesis of Cu(II)M(II) complexes of a phenol-based dinucleating ligand (CuM means that Cu is in the $\text{N(amine)}_2\text{O}_2$ coordination site and M is in the $\text{N(imine)}_2\text{O}_2$ coordination site) and their coordination position isomeric M(II)Cu(II) complexes. They have studied thermodynamic stability of their complexes and have shown that the Cu(II)M(II) complexes are more stable compared to the coordination position isomeric M(II)Cu(II) complexes. They have shown that the M(II)Cu(II) isomers are electrochemically and thermodynamically converted to their Cu(II)M(II) isomers [16]. They have actually shown that upon heating their M(II)Cu(II) complexes in DMSO at 70°C , The UV–vis spectrum shows characteristic absorptions of Cu(II)M(II) coordination position isomers. Besides, during the cyclic voltammetry of the M(II)Cu(II) complexes, the cyclic voltammograms show the characteristic of the Cu(II)M(II) complexes. This stability is due to the fact that the Cu(II) metal ion is better stabilized in the more flexible

$\text{N(amine)}_2\text{O}_2$ coordination site. Accordingly and according to the similarity of the spectroscopic and electrochemical data of our complexes with that of Cu(II)Ni(II) complex, reported by Okawa and co-workers, we propose that these complexes have Cu(II)Ni(II) structures (Fig. 2). Besides, it is obvious that Ni(II) better resists in the square planer $\text{N(imine)}_2\text{O}_2$ coordination site. In the IR spectra of the ligand $\text{H}_2\text{L}'$ an intense band centered at 1675 cm^{-1} is indicative of the presence of a carbonyl group which disappears upon the reaction with the diamines in the synthesis of complexes. The disappearance of this band and the appearance of another band centered around $1620\text{--}1640 \text{ cm}^{-1}$ is a good indication of the Schiff base condensation of the diamines and the carbonyl group of the $\text{H}_2\text{L}'$. This new band in the IR spectra of the mononuclear complexes is centered around 1620 cm^{-1} , which shifts to higher wave numbers upon coordination to the second metal ions. Furthermore, the appearance of two new bands around 1100 and 630 cm^{-1} is indicative of the presence of un-coordinated perchlorate ions. The UV–vis spectra of the complexes show three major bands. The intense bands centered around 370 nm is due to the $\pi\text{--}\pi^*$ transition associated with the azomethine group. Another intense band is common for all of the complexes around 380 nm , which could be attributed to the metal to ligand charge transfer. The other weaker bands in the spectra of the complexes are attributed to the d–d transitions of the metal ions. These weaker bands in the UV–vis spectra of the mononuclear and homodinuclear complexes, are centered around 600 nm , which are due to the d–d transitions occurring in the copper centers. In the UV–vis spectra of the heterodinuclear complexes, this band is centered around 570 nm and is representative of the d–d transitions in the Ni centers. Molar conductance of the dinuclear complexes in acetonitrile is in the range of $210\text{--}225 \text{ S cm}^2 \text{mol}^{-1}$ that is indicative of 2:1 electrolytic nature of these complexes.

3.2. Electrochemistry

Cyclic voltammetry is an important tool for the characterization of dinuclear complexes. The cyclic voltammogram of the mononuclear and dinuclear complexes show reduction potential waves at negative potentials because of the hard nature of the phenoxide atoms in the ligands. The cyclic voltammetry of the complexes in this work was studied in the potential range from 0 to -1.5 V in acetonitrile at room temperature and the data are summarized in Table 1. The cyclic voltammograms of the homodinuclear complex Cu_2L^4 is also shown in Fig. 3. The cyclic voltammograms of the mononuclear complexes show one quasi-reversible reduction wave, which is due to the reduction of Cu(II) to Cu(I) .

In the cyclic voltammograms of the homodinuclear complexes two quasi-reversible reduction potential waves are observed and these two redox potentials are assigned as follows:

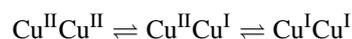


Table 1
Electrochemical data for the complexes in acetonitrile^a

Complexes	E_{pc}	E_{pa}	$E^{1/2} = (E_{pc} - E_{pa})/2$	E_{pc}	E_{pa}	$E^{2/2} = (E_{pc} - E_{pa})/2$
CuL ²	-0.72	-0.46	-0.59	—	—	—
CuL ⁴	-0.65	-0.43	-0.54	—	—	—
Cu ₂ L ²	-0.69	-0.46	-0.57	-1.30	-1.18	-1.24
Cu ₂ L ⁴	-0.61	-0.47	-0.54	-1.29	-1.17	-1.23
CuNiL ¹	-0.78	-0.65	-0.71	—	—	—
CuNiL ²	-0.77	-0.63	-0.70	—	—	—
CuNiL ³	-0.74	-0.62	-0.69	—	—	—
CuNiL ⁴	-0.72	-0.60	-0.66	—	—	—

^a Unit: V vs. Ag/Ag⁺. Conditions: gold ultramicroelectrodes working, Pt auxiliary and Ag/Ag⁺ reference electrodes. Scan rate: 100 mV/s. Concentration of the complexes: (10⁻³ M). At room temperature supporting electrolyte: tetra-*n*-butylammoniumhexafluoroborate (0.1 M).

The cyclic voltammograms of the heterodinuclear complexes show one reduction potential wave in the applied potential range, which is also assigned to the reductions at the copper centers. The reduction in the nickel centers was not observed in the applied potentials.

3.3. Catecholase-like activity studies

Although some deliberate studies [11,20,21] has been directed towards the understanding of the factors affecting the catecholase-like activity of copper-containing complexes; the exploration of the oxidation chemistry of the dinuclear complexes is still necessary to fully understand parameters affecting their catecholase-like activity. In our review in the literature we found that little or no attention has been paid to the study of compartmental heterodinuclear complexes as catalyst in the oxidation of catechols to the corresponding quinones. Having this in our mind and in continuing our interest in the oxidation of organic compounds under mild conditions [22,23], we decided to study the catecholase-like activity of our complexes. The product *o*-quinone is considerably stable and has a strong absorption band at 390 nm. A linear relationship between the concentration of the complexes and the initial rate of the oxidation was observed for all of the complexes, which indicates a first-order dependence on

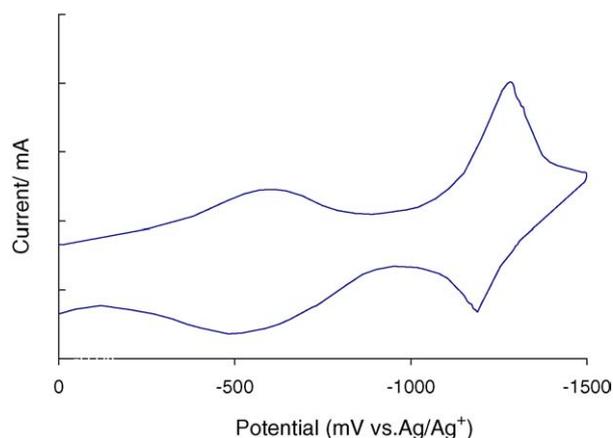


Fig. 3. Cyclic voltammogram of Cu₂L⁴ (10⁻³ M), scan rate: 100 mV/s.

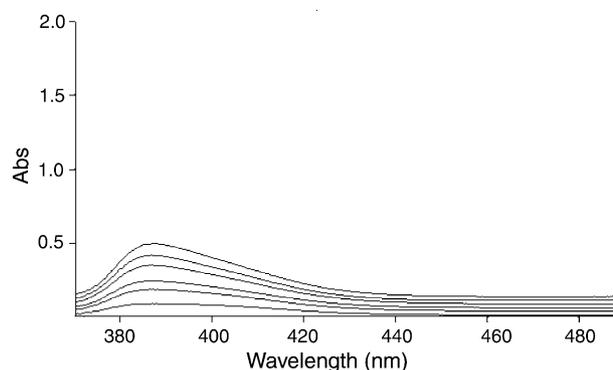


Fig. 4. UV-vis spectra of the 10 min interval oxidation of catechol by Cu₂L⁴.

the complex concentrations. Typically, 20 mL of 10⁻³ molar solution of the complexes were treated with 50 equivalent of catechol in the presence of air at room temperature. The initial rate for the catechol oxidation was determined by monitoring the growth of the band at 390 nm of the product *o*-quinone at 5 min intervals (Fig. 4). A plot of $\log[A_{\infty}/(A_{\infty} - A_t)]$ versus time is shown in Figs. 5–7, respectively, for the mononuclear, homodinuclear and heterodinuclear complexes. A plot of $\log[A_{\infty}/(A_{\infty} - A_t)]$ versus time is also shown in Fig. 8 to compare the catalytic results for the mononuclear CuL⁴, CuNiL⁴ and Cu₂L⁴. Our results (Figs. 5–7) show that as the ring size at the iminic compartment increases, an increase in the catalytic activity of the complexes is also observed.

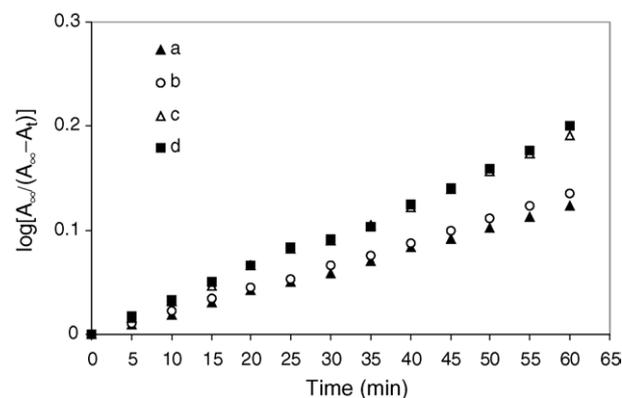


Fig. 5. Catecholase-like activity of mononuclear complexes: (a) CuL¹; (b) CuL²; (c) CuL³; (d) CuL⁴.

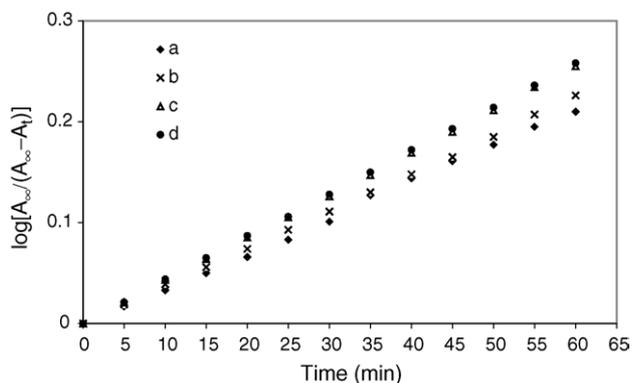


Fig. 6. Catecholase-like activity of heterodinuclear complexes: (a) CuNiL^1 ; (b) CuNiL^2 ; (c) CuNiL^3 ; (d) CuNiL^4 .

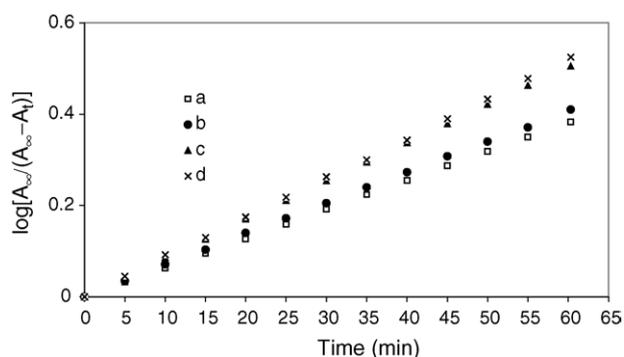


Fig. 7. Catecholase-like activity of homodinuclear complexes: (a) Cu_2L^1 ; (b) Cu_2L^2 ; (c) Cu_2L^3 ; (d) Cu_2L^4 .

This is most probably due to the fact that as the macrocyclic size increases, the metal ions easily get reduced, because of the increased flexibility of the macrocycle [24]. The results (Fig. 8) also show that the homodinuclear Cu(II)Cu(II) complexes are the most effective catalyst in the oxidation of catechol to the corresponding quinone compared to the other complexes. The lowest catalytic activities of the mononuclear complexes suggest that the presence of two metallic

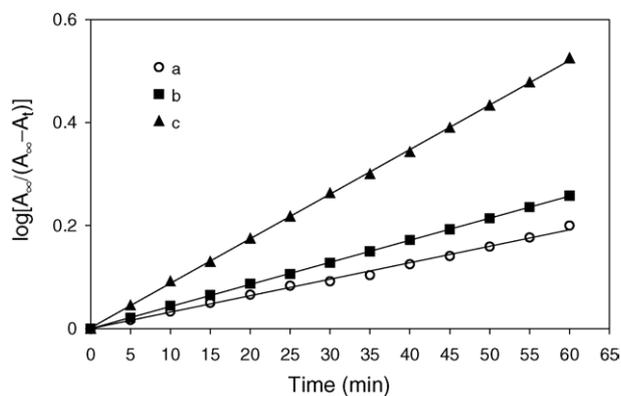


Fig. 8. Comparison of the catecholase-like activity of homodinuclear, heterodinuclear and homodinuclear complexes: (a) CuL^4 ; (b) CuNiL^4 ; (c) Cu_2L^4 .

centers in close proximity is necessary to increase the catalytic activity of these catalysts in the oxidation of catechols. Comparison of the catalytic activity of the homodinuclear complexes with the corresponding heterodinuclear complexes (Fig. 8) reveals that the presence of two easily reduced metallic centers is necessary for obtaining the best results.

This result is consistent with the previously reported mechanism in which both metallic centers are reduced from M(II) to M(I) upon reaction with catechols to form quinones [19]. Cyclic voltammetry of the complexes shows that in the homodinuclear complexes the two metallic centers could be more easily reduced and therefore it results in the better catalytic activity of the homodinuclear complexes.

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References

- [1] H. Okawa, H. Furutachi, D.E. Fenton, *Coord. Chem. Rev.* 174 (1998) 51.
- [2] M. Suzuki, H. Okawa, H. Furutachi, *Coord. Chem. Rev.* 200–202 (2000) 105.
- [3] M. Sakamoto, K. Manseki, H. Okawa, *Coord. Chem. Rev.* 219–221 (2001) 379.
- [4] P. Zanello, S. Tamburini, P.A. Vigato, G.A. Mazzocchin, *Coord. Chem. Rev.* 77 (1987) 165.
- [5] N. Sträter, T. Klabunde, P. Tucker, H. Witzel, B. Krebs, *Science* 13 (1995) 1489.
- [6] C.R. Kissinger, H.E. Parge, D.R. Knighton, C.T. Lewis, L.A. Pelletier, A. Tempczyk, V.J. Kalish, K.D. Tucker, R.E. Showalter, E.W. Moomaw, L.N. Gastinel, N. Habuka, X. Chen, F. Maldonado, J.E. Barker, R.J. Bacquet, E. Villafranca, *Nature (London)* 378 (1995) 641.
- [7] M-P. Egloff, P.T.W. Cohen, P. Reinemer, D. Bradford, *J. Mol. Biol.* 254 (1995) 942.
- [8] S. Sailaja, K.R. Reddy, M.V. Rajasekharan, C. Hureau, E. Riviere, J. Cano, J.-J. Girerd, *Inorg. Chem.* 42 (2003) 180.
- [9] H. Miyasaka, R. Clerac, K. Mizushima, K.-I. Sugiura, M. Yamashita, W. Wernsdorfer, C. Colun, *Inorg. Chem.* 42 (2003) 8203.
- [10] A. Hori, Y. Mitsuka, M. Ohba, H. Okawa, *Inorg. Chim. Acta* 337 (2002) 113.
- [11] K. Selmezi, M. Reglier, M. Giorgi, G. Speier, *Coord. Chem. Rev.* 245 (2003) 191.
- [12] C. Fernandes, A. Neves, A.J. Bortoluzzi, A.S. Mangrich, E. Rentschler, B. Szpoganiez, E. Schwingle, *Inorg. Chim. Acta* 320 (2001) 12.
- [13] M. Yonemura, M. Ohba, H. Furutachi, Y. Matsumura, H. Okawa, D.E. Fenton, *Inorg. Chem.* 36 (1997) 2711.
- [14] S. Karunakaran, M. Kandaswamy, *J. Chem. Soc., Dalton Trans.* (1994) 1595.
- [15] M. Yonemura, M. Ohba, K. Takahashi, H. Okawa, D.E. Fenton, *Inorg. Chim. Acta* 283 (1998) 72.
- [16] M. Yonemura, K. Arimura, K. Inoue, N. Usuki, M. Ohba, H. Okawa, *Inorg. Chem.* 41 (2002) 582.
- [17] M.N.H. Irving, R.M. Parkins, *J. Inorg. Nucl. Chem.* 27 (1965) 270.

- [18] P. Norouzi, M. Namazian, A. Badiei, *Anal. Sci.* 20 (2004) 519.
- [19] M. Loulodi, K. Mitopoulou, E. Evaggelou, Y. Deligiannakis, N. Hadjiliadis, *J. Mol. Catal. A: Chem.* 198 (2003) 231.
- [20] P. Gentshev, N. Moller, B. Krebs, *Inorg. Chim. Acta* 300–302 (2000) 442.
- [21] C.-H. Kao, H.-H. Wei, Y.-H. Liu, G.-H. Lee, Y. Wang, C.-J. Lee, *J. Inorg. Biochem.* 84 (2001) 171.
- [22] D.M. Boghaie, S. Mohebi, *Tetrahedron* 58 (2002) 5357.
- [23] D.M. Boghaie, S. Mohebi, *J. Mol. Catal. A: Chem.* 179 (2002) 41.
- [24] M. Thirumavalavan, P. Akilan, M. Kandaswamy, C. Kandaswamy, G.S. Kumar, H.K. Fun, *Inorg. Chem.* 42 (2003) 3308.