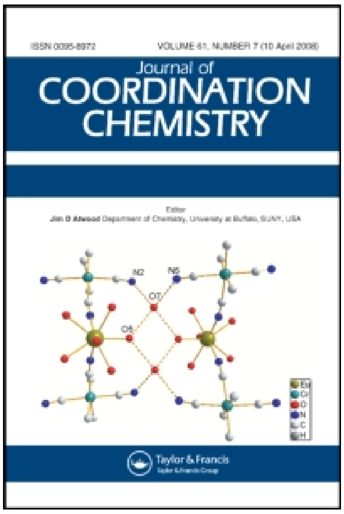

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Synthesis, characterization, electrochemical studies and catecholase-like activity of dinuclear copper(II) complexes of a phenol-based compartmental ligand

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Synthesis, characterization, electrochemical studies and catecholase-like activity of dinuclear copper(II) complexes of a phenol-based compartmental ligand

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The new dinuclear copper(II) complexes, Cu(II)M(II) (M = Mn, Co, Ni, Cu), of a phenol-based compartmental ligand, having dissimilar N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ coordination sites have been synthesized. In this system there are two different compartments, one has piperazinyl nitrogens and phenolic oxygens and the other compartment has meso-stilbenediamine nitrogens and phenolic oxygens as coordinating sites. The complexes were characterized by elemental analysis, IR and electronic spectra as well as conductivity measurements. Dinuclear complexes were prepared through the Cu^{II}Pb^{II} precursor complex by transmetalation of the Pb(II) for the M(II) ion. The electrochemistry and catecholase-like activity of the complexes were also studied using cyclic voltammetry and UV–Vis spectrophotometry, respectively. Electrochemical studies of the dinuclear complexes reveal that Cu^{II}M^{II} (M=Co, Ni, Cu) complexes undergo two quasi-reversible couples, $E^1_{pc} = -0.57$ to -0.59 V and $E^2_{pc} = -0.90$ to -1.05 V, whereas the Cu^{II}Mn^{II} complex shows one quasi-reversible couple, $E_{pc} = -0.80$ V. Our results show that the homodinuclear Cu^{II}Cu^{II} complex shows higher catalytic activity in oxidation of cathecol to the corresponding quinone compared to the other complexes. The molar conductances in acetonitrile solutions indicate that the complexes are 1 : 2 electrolytes.

Keywords: Dinuclear complexes; Compartmental ligand; Cyclic voltammetry; Catecholase-like activity; Copper(II)

1. Introduction

The design and synthesis of dinucleating ligands having dissimilar coordination environments and especially their heterodinuclear complexes have received increasing attention [1–4]. Particularly the chemistry of transition metal ion complexes with unsymmetrical dicompartmental ligands has become a rapidly growing area of research because of their importance in biological processes, constituting the active sites in metalloproteins and enzymes [5–9]. Heterodinuclear metal complexes with two different metal ions in close proximity are of interest because of the unique physicochemical properties that arise from the metal-metal interaction [10, 11]. In particular, recent

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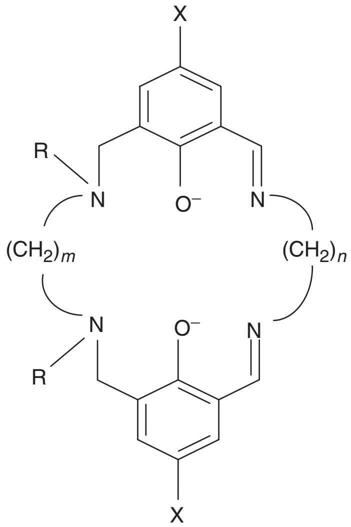


Figure 1. Structure of phenol-based compartmental ligands with two dissimilar N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ metal-binding sites.

recognition of heterodinuclear cores at the active sites of purple acid phosphatase (FeZn) [9], human calcineurin (FeZn) [12], and human protein phosphatase 1 (MnFe) [13] has stimulated interest in heterodinuclear metal complexes. In order to provide discrete heterodinuclear core complexes phenol-based dinucleating macrocycles with two dissimilar N(amine)$_2$O$_2$ and N(imine)$_2$O$_2$ metal-binding sites, sharing two phenolic oxygens, (figure 1) have been developed [14–17].

Copper is an essential trace element [18] for life processes, and several copper-containing metallo-proteins and metallo-enzymes are involved in a variety of biological processes in living systems [19, 20]. Hemocyanin, tyrosinase, and catechol oxidase proteins have dinuclear copper(II) centers at their active sites [21]. Catechol oxidases, like tyrosinase, oxidize phenolic compounds to the corresponding quinones in the presence of oxygen.

Dinuclear copper(II) complexes with two metal ions in close proximity have significance as new inorganic materials showing various magnetic properties and suitable candidates for molecule-based magnets [22, 23]. There is also continuing interest [24] in mechanistic studies on the catalytic oxidation of catechols by transition metal complexes because this reaction plays the key role in metabolism of aromatic compounds.

Since the pioneering work of Robson [25–27] on the synthesis of dinucleating ligands, a number of macrocyclic metal complexes have been synthesized and their properties studied [4, 28, 29]. Okawa and co-workers [30] synthesized homo and heterodinuclear complexes of a phenol-based compartmental ligand. Kandaswamy [14, 31–33] also reported related macrocycles containing the piperazine entity to provide nitrogen atoms of the N(amine)$_2$O$_2$ coordination site. Based on the importance of dinuclear metal complexes, we planned to synthesize dinuclear copper(II) complexes, Cu(II)M(II) (M = Mn, Co, Ni, Cu), of a phenol-based compartmental ligand having two different compartments, one with piperazinyl nitrogens and phenolic oxygens and the other

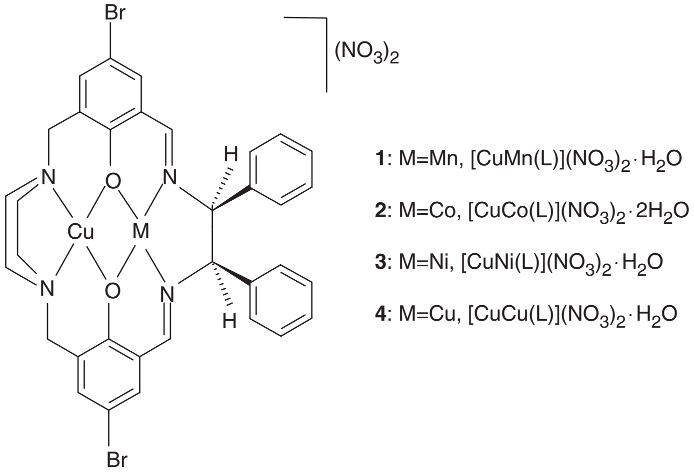


Figure 2. Dinuclear copper(II) complexes, Cu(II)M(II) (M = Mn, Co, Ni, Cu), of a phenol-based compartmental ligand.

compartment with meso-stilbenediamine nitrogens and phenolic oxygens as the coordinating sites (figure 2). The complexes were prepared through the $Cu^{II}Pb^{II}$ precursor complex by transmetalation of the Pb(II) for the M(II) ion. Electrochemical behavior and catecholase-like activity of the complexes were also studied using cyclic voltammetry and UV–Vis spectrophotometry, respectively.

2. Experimental

2.1. *Materials and measurements*

All chemicals and solvents were reagent grade, obtained from either Merck or Fluka and used without further purification. *N*,*N*′-pyrazinebis(5-bromo-3-formyl-2-hydroxy-benzylamine) (H_2L') [30], the mononuclear complex [CuL′] [30], and meso-stilbenediamine [34] were synthesized as described elsewhere.

Elemental analyses were performed using a Heraeus Elemental Analyzer CHN-O-Rapid (Elementar-Analysesysteme, GmbH). Analyses for metal ions were conducted using a Varian AA-220 spectrophotometer. IR spectra were recorded on a FT–IR JASCO 460 spectrophotometer with KBr pellets. Electronic spectra were recorded in DMSO solution using a CARY 100 Bio VARIAN UV–Vis spectrophotometer. Melting points were found on a BUCHI Melting point B-540. Conductivity measurements were performed in acetonitrile solution using a Jenway-4010 conductivity meter. Cyclic voltammograms were recorded using a Metrohm model 746 VA Trace Analyzer. The working, auxiliary and reference electrodes were glassy carbon, platinum wire and AgCl/Ag, respectively. Electrochemical measurements were performed in acetonitrile at room temperature (scan rate: $100\,mV\,s^{-1}$), in the potential range 0 to $-1.5\,V$ with $10^{-1}\,M$ tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. The catalytic oxidation of catechol to *o*-quinone by the complexes was studied in acetonitrile solution. The reaction was followed spectrophotometrically by choosing the strongest absorbance of the quinone at 390 nm and monitoring the increase in the absorbance at this wavelength as a function of time.

2.2. *Synthesis of the [CuPb(L)](NO_3)$_2$ (Precursor complex)*

A methanol solution (10 cm^3) of lead(II) nitrate (0.33 g, 1 mmol) was added to a hot suspension of [Cu(L′)] (0.58 g, 1 mmol) in a chloroform-methanol mixture (20 : 80 in volume, 30 cm^3). Then a methanol solution (10 cm^3) of meso-stilbenediamine (0.21 g, 1 mmol) was added dropwise to the resulting green solution to give a dark-green powder, which was filtered, washed with diethylether, and dried *in vacuo* (yield: 75%); m.p. 318°C. Anal. Calcd (found) for $C_{34}H_{30}Br_2CuPbN_6O_8$ (%): C, 37.77 (37.82); H, 2.80 (3.01); N, 7.77 (7.55); Cu, 5.9 (5.8); Pb, 19.2 (19.4). Selected IR data (KBr, cm^{-1}): 3453 (H_2O), 2857 (aliph., C–H), 1618 (–C=N), 1533 (Ph–C–C=N), 1387 (uncoordinated NO_3^-). UV–Vis [λ_{max}, nm (ε, $M^{-1} cm^{-1}$)] in DMSO: 350 (7300), 550 (210). Molar conductance ($\Lambda_M/\Omega^{-1} mol^{-1} cm^2$) 274 in acetonitrile.

2.3. *Synthesis of dinuclear copper(II) complexes [CuM(L)](NO_3)$_2$ · nH_2O*

A solution of metal(II) sulfate salt (0.6 mmol) in dry methanol (10 cm^3) was added to a suspension of [CuPb(L)](NO_3)$_2$ (0.65 g, 0.6 mmol). The mixture was stirred for 4 h resulting in the precipitation of $PbSO_4$, was filtered and the filtrate was evaporated to dryness. The residue was extracted with dry acetonitrile, and the extract was filtered to separate $PbSO_4$. Then the acetonitrile solution was left overnight at room temperature. The dark-green precipitate obtained was filtered, washed with water and diethyl ether, and dried *in vacuo*.

2.3.1. [CuMn(L)](NO_3)$_2$ · H_2O (1). A green powder formed (yield: 48%); m.p. 352°C. Anal. Calcd (found) for $C_{34}H_{30}Br_2CuMnN_6O_8 \cdot H_2O$ (%): C, 43.12 (42.91); H, 3.41 (3.57); N, 8.88 (8.61); Mn, 5.8 (5.6); Cu, 6.7 (6.8). Selected IR data (KBr, cm^{-1}): 3407 (H_2O), 2846 (aliph., C–H), 1621 (–C=N), 1546 (Ph–C–C=N), 1384 (uncoordinated NO_3^-). UV–Vis [λ_{max}, nm (ε, $M^{-1} cm^{-1}$)] in DMSO: 333 (9570), 620 (180). Molar conductance ($\Lambda_M/\Omega^{-1} mol^{-1} cm^2$) 285 in acetonitrile.

2.3.2. [CuCo(L)](NO_3)$_2$ · 2H_2O (2). A green powder formed (yield: 50%); m.p. 292°C. Anal. Calcd (found) for $C_{34}H_{30}Br_2CuCoN_6O_8 \cdot 2H_2O$ (%): C, 42.14 (41.93); H, 3.54 (3.28); N, 8.68 (8.81); Co, 6.1 (6.2); Cu, 6.6 (6.8). Selected IR data (KBr, cm^{-1}): 3438 (H_2O), 2850 (aliph., C–H), 1627 (–C=N), 1546 (Ph–C–C=N), 1390 (uncoordinated NO_3^-). UV–Vis [λ_{max}, nm (ε, $M^{-1} cm^{-1}$)] in DMSO: 335 (8320), 607 (160). Molar conductance ($\Lambda_M/\Omega^{-1} mol^{-1} cm^2$) 278 in acetonitrile.

2.3.3. [CuNi(L)](NO_3)$_2$ · H_2O (3). A green powder formed (yield: 55%); m.p. 352°C. Anal. Calcd (found) for $C_{34}H_{30}Br_2CuNiN_6O_8 \cdot H_2O$ (%): C, 42.95 (43.07); H, 3.40 (3.11); N, 8.84 (8.68); Ni, 6.2 (6.1); Cu, 6.7 (6.8). Selected IR data (KBr, cm^{-1}): 3407 (H_2O), 2846 (aliph., C–H), 1630 (–C=N), 1546 (Ph–C–C=N), 1384 (uncoordinated NO_3^-). UV–Vis [λ_{max}, nm (ε, $M^{-1}cm^{-1}$)] in DMSO: 340 (9350), 544 (180), 590 (140). Molar conductance ($\Lambda_M/\Omega^{-1}mol^{-1}cm^2$) 280 in acetonitrile.

2.3.4. [CuCu(L)]$(NO_3)_2 \cdot H_2O$ (4). A green powder formed (yield: 56%); m.p. 284°C. Anal. Calcd (found) for $C_{34}H_{30}Br_2Cu_2N_6O_8 \cdot H_2O$ (%): C, 42.73 (42.90); H, 3.38 (3.06); N, 8.80 (8.51); Cu, 13.3 (13.4). Selected IR data (KBr, cm^{-1}): 3407 (H_2O), 2846 (aliph., C–H), 1620 (–C=N), 1546 (Ph–C–C=N), 1380 (uncoordinated NO_3^-). UV–Vis [λ_{max}, nm (ε, $M^{-1}cm^{-1}$)] in DMSO: 330 (9640), 610 (210). Molar conductance ($\Lambda_M/\Omega^{-1}mol^{-1}cm^2$) 264 in acetonitrile.

3. Results and discussion

3.1. *Preparation and spectral studies*

The dinuclear copper(II) complexes [CuM(L)]$(NO_3)_2$ (M = Mn, Co, Ni, Cu), **1–4**, were prepared through the $Cu^{II}Pb^{II}$ precursor complex [30] by transmetalation of Pb(II) for the M(II) ion as shown in figure 3. The complexes were characterized by elemental analysis, IR and electronic spectra as well as conductivity measurements. The results of elemental analysis support the proposed structure.

The two N_2O_2 metal-binding sites of the macrocycle (H_2L) share the two phenolic oxygens, but are not equivalent with respect to the aminic or iminic nature of the donor nitrogens. In order to prepare such unsymmetrical macrocycles it is recommended [30] to use an appropriate acyclic precursor in the template reaction. For the present purpose acyclic ligand (H_2L') was adopted as the precursor, which was obtained in a tolerable yield by the Mannich reaction of 5-bromosalicylaldehyde, paraformaldehyde, and piperazine in ethanol. The mononuclear complex [Cu(L′)] was readily prepared [30] by the reaction of copper(II) acetate and the ligand (H_2L') in 1 : 1 molar ratio. In [Cu(L′)] the Cu is bound at the $N(amine)_2O_2$ site judged from the presence of a ν(CO) (formyl) mode at 1670 cm^{-1} in the IR spectrum. The reaction of [Cu(L′)] with meso-stilbenediamine in the presence of lead(II) nitrate formed a Cu(II)Pb(II) complex [CuPb(L)]$(NO_3)_2$, which is a good precursor for the preparation of the heterodinuclear

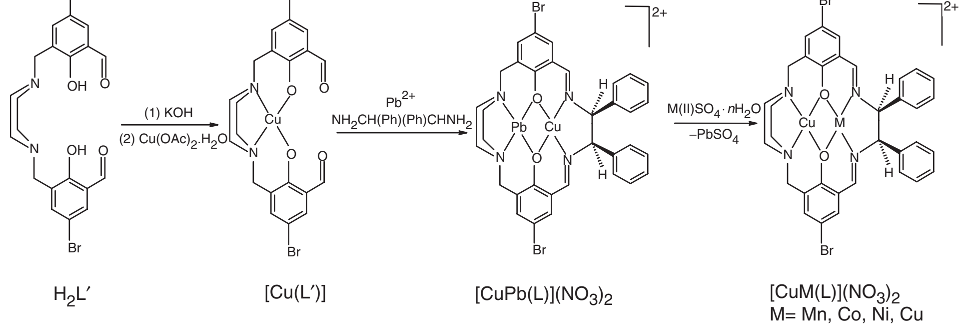


Figure 3. The reaction pathway for the synthesis of dinuclear complexes through the $Cu^{II}Pb^{II}$ precursor by transmetalation of Pb(II) for M(II).

$Cu^{II}M^{II}$ complexes. Transmetalation of Pb(II) for M(II) was achieved [30] by reaction of $[CuPb(L)](NO_3)_2$ with a metal(II) sulfate salt in acetonitrile. In this reaction Pb(II) is eliminated from the reaction mixture as $PbSO_4$'s. X-ray crystallography studies for the analogous complexes [30, 35] proved that in the CuPb precursor the Cu(II) resides at the $N(imine)_2O_2$ site and the Pb(II) at the $N(amine)_2O_2$ site, demonstrating that a migratory transmetalation occurred and that the Cu(II) shifted from the $N(amine)_2O_2$ site of $(L')^{2-}$ to the $N(imine)_2O_2$ site of $(L)^{2-}$ in the cyclization process. X-ray crystallography [30] established migration of the Cu(II) ion from the $N(imine)_2O_2$ in the CuPb complex, to the $N(amine)_2O_2$ site in the Cu(II)M(II) complexes to accommodate the M^{II} in the iminic site. According to previous studies [30], the driving force in the initial reaction involving Cu(II) and Pb(II) may be related to the nature of the donor compartments. The Cu(II) migrates to occupy the relatively rigid $N(imine)_2O_2$ site, which provides the preferred square coplanar environment, and the larger Pb(II) is then accommodated in the more flexible $N(amine)_2O_2$ site. The site selectivity observed in the Cu(II)M(II) complexes [30] shows that a reversal of the migratory transmetalation has occurred with the Cu(II) reverting to the $N(amine)_2O_2$ site. This process may be related to further flexibility of the $N(amine)_2O_2$ site, and so able to accommodate distortions imposed at the Cu(II) by the Jahn–Teller effect. Based on the similarity of the spectroscopic and electrochemical data of our complexes with that for $Cu^{II}M^{II}$ complexes [30, 36], we proposed that these complexes have the Cu(II)M(II) structure (figure 2). The molar conductance measured in acetonitrile of 10^{-3} M solutions of the complexes is in the range of 264–285 $\Omega^{-1}\,mol^{-1}\,cm^2$, indicative of the 1 : 2 electrolyte [37] nature of these complexes. The complexes give fine powders and a goal to prepare single crystals suitable for X-ray diffraction measurements has been unsuccessful.

IR spectrum of the mononuclear complex [Cu(L′)] shows a peak at 1670 cm^{-1} due to the ν(C=O) peak. The effective Schiff-base condensation of the meso-stilbenediamine and carbonyl group of the [Cu(L′)] is confirmed by the disappearance of the ν(C=O) peak at 1670 cm^{-1}, and the appearance of the another intense ν(C=N) band [38] around 1618–1630 cm^{-1}. A shift in the absorption of the ν(C=N) frequency in the case of the complexes suggests coordination through >C=N. The IR spectra of the complexes show a broad band due to water centered at 3400 cm^{-1}, and also a medium band in the range of 2846–2857 cm^{-1} due to the aliphatic C–H stretch. The appearance of a broad band at 1380–1390 cm^{-1} is indicative of the presence of uncoordinated nitrate ions [39]. IR spectra of all complexes show a medium-strong band at 1546 cm^{-1} due to vibration of the (Ph–)C–C(=N) bond [40]. Some important IR (cm^{-1}) spectral data of the complexes are given in table 1.

Table 1. Some IR (cm^{-1}) and electronic [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)] spectral data of the complexes.

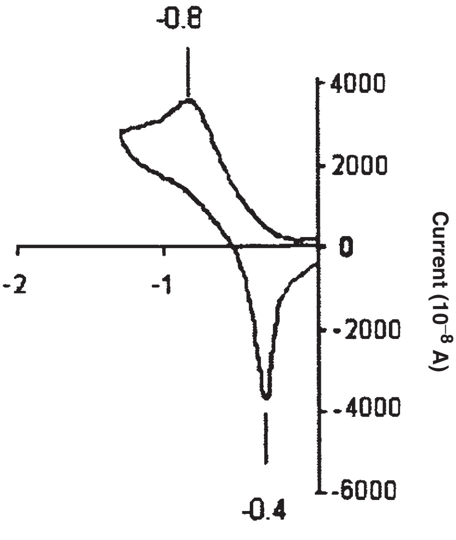
Complexes	IR frequencies (cm^{-1})			UV–Vis data [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]	
	$\nu_{(C=N)}$	$\nu_{(uncoordinated\ NO_3^-)}$	$\nu_{((Ph–)C–C(=N))}$	π–π*	d–d
$[CuPb(L)](NO_3)_2$	1618	1387	1533	350 (7300)	550 (210)
1	1621	1384	1546	333 (9570)	620 (180)
2	1627	1390	1546	335 (8320)	607 (160)
3	1630	1384	1546	340 (9350)	544 (180), 590 (140)
4	1620	1380	1546	330 (9640)	610 (210)

Electronic spectra, recorded in DMSO solution, show two major bands. An intense band around 330-350 nm is assigned to the π–π* transition associated with the azomethine linkage (imine π–π* transition) [41]. The other weak band is seen for the precursor complex, $[CuPb(L)](NO_3)_2$, at 550 nm and for the dinuclear copper(II) complexes **1**–**4** around 590–620 nm due to d–d transitions of the Cu(II) ion in the iminic [42] and aminic [43] sites, respectively. In the case of the Cu(II)Ni(II) complex, an additional weak absorption band is observed at 544 nm, that is characteristic of the d–d transition in the Ni^{II} center [44]. For the other complexes (**1**, **2**, and **4**) the d–d bands due to M^{II} are not resolved because of a low extinction coefficient. Electronic spectral data of the complexes are given in table 1.

3.2. *Electrochemistry*

Cyclic voltammetry is an effective technique for the characterization and the differing [36] $Cu^{II}M^{II}$ (Cu^{II} at the amine site), and $M^{II}Cu^{II}$ (Cu^{II} at the imine site) dinuclear complexes. Reports [36] show that the Cu^{II} should indicate a quasi-reversible couple around −1.05 V and −0.58 V due to the Cu^{I}/Cu^{II} process at the iminc and aminic sites, respectively. Therefore, the reduction potential for Cu^{II} at the aminic site is high relative to those of the Cu^{II} at the iminic site, indicating that the $\{CuN(amine)_2O_2\}$ chromophore is flexible [45] enough to allow a distorted geometry preferred for Cu^{I}.

Electrochemical properties of the dinuclear copper(II) complexes **1**–**4** were studied by cyclic voltammetry in acetonitrile containing 10^{-1} M tetra(*n*-butyl)ammonium perchlorate at room temperature in the potential range 0 to −1.5 V. The cyclic voltammograms of the dinuclear copper(II) complexes **1**–**4**, are shown in figures 4–7, respectively and the data are summarized in table 2.



Potential (V vs. Ag/AgCl)

Figure 4. Cyclic voltammogram of dinuclear Cu(II)Mn(II) complex **1** in acetonitrile.

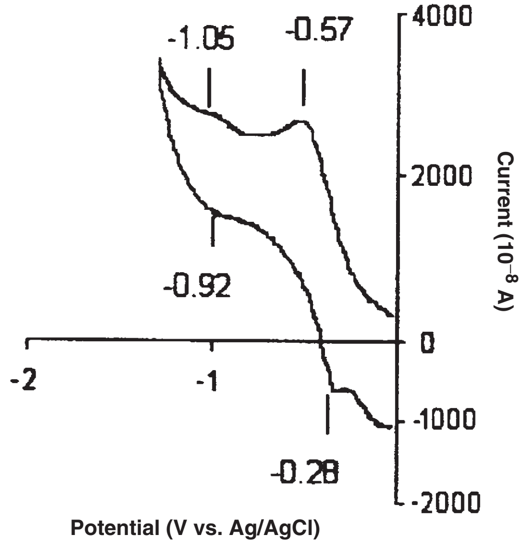


Figure 5. Cyclic voltammogram of **2** in acetonitrile.

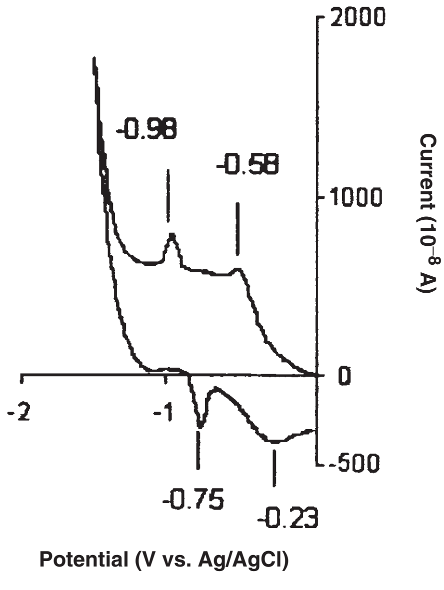


Figure 6. Cyclic voltammogram of the Cu(II)Ni(II) complex **3** in acetonitrile.

The cyclic voltammograms of the dinuclear complexes Cu(II)M(II) (M = Co, Ni, Cu), **2**–**4**, show two quasi-reversible couples. The first couple, $E^1_{pc} = -0.57$ to -0.59 V, and the second couple at the lower potential, $E^2_{pc} = -0.90$ to -1.05 V, are attributed to the the Cu(II) reduction at the aminic site [30, 36], and the M(II) reduction at the iminic site [30, 36, 46], respectively. The dinuclear complex Cu(II)Mn(II), **1**, shows a quasi-reversible couple, $E_{pc} = -0.80$ V, due to the Cu(II) reduction at the aminic [30, 47] site.

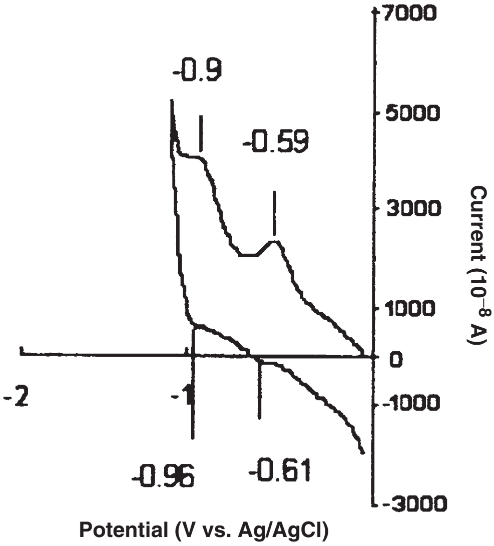


Figure 7. Cyclic voltammogram of **4** in acetonitrile.

Table 2. Electrochemical data of dinuclear copper(II) complexes **1**–**4** in acetonitrile.

Complexes	E^1_{pa} (V)	E^1_{pc} (V)	$E^1_{1/2}$ (V)	ΔE_p (mV)	E^2_{pa} (V)	E^2_{pc} (V)	$E^2_{1/2}$ (V)	ΔE_p (mV)
1	−0.40	−0.80	−0.60	0.40	–	–	–	–
2	−0.28	−0.57	−0.42	0.29	−0.92	−1.05	−0.98	0.13
3	−0.23	−0.58	−0.40	0.35	−0.75	−0.98	−0.86	0.23
4	−0.61	−0.59	−0.60	0.02	−0.96	−0.90	−0.93	0.06

The cyclic voltammograms of the dinuclear complexes in this work, **1**–**4**, were compared in figure 8.

3.3. *Kinetic studies of the oxidation of catechol (catecholase-like activity)*

Efforts have also been made to investigate the catecholase-like activity of dinuclear copper(II) complexes using catechol and its derivatives as the convenient model substrates for identification of functional models for metalloenzymes [24]. Little attention has been paid to compartmental dinuclear complexes as catalysts in the oxidation of catechols to the corresponding quinones. Continuing our interest in oxidation of organic compounds under mild conditions [48], we decided to examine the catecholase-like activity of the dinuclear copper(II) complexes. The oxidation product is *o*-quinone, which is 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, indicating a first-order dependence on the complex concentration. The course of the reaction was followed spectrophotometrically at 390 nm nearly for 115 min at regular time interval of 5 min. The initial rate for

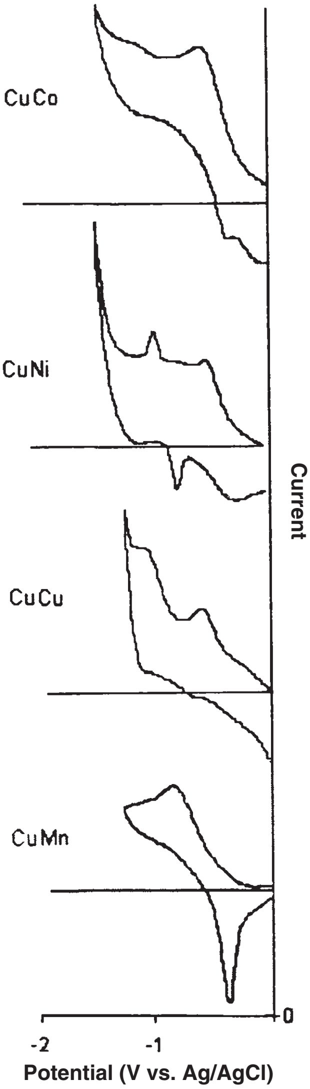


Figure 8. Comparative cyclic voltammograms of **1**–**4**.

the catechol oxidation was found by monitoring the increase in the intensity of the band at 390 nm of the product *o*-quinone at 5 min intervals as shown in figure 9.

Plots of $\log(A_\infty/(A_\infty - A_t))$ *versus* time for the catecholase-like activity of **1**–**4** are obtained, and shown in figure 10. The initial rate constant values for the dinuclear copper(II) complexes were obtained from the slope of the plot of $\log(A_\infty/(A_\infty - A_t))$ *versus* time, and are given in table 3. The initial rate constant value increases from 1.7×10^{-3} to $5.4 \times 10^{-3}\,\mathrm{min}^{-1}$ as we move from complex **1** to complex **4**. Our results show that the homodinuclear $\mathrm{Cu^{II}Cu^{II}}$ complex shows higher catalytic activity in oxidation of cathecol to the corresponding quinone compared to the other complexes. The lowest catalytic activity of the Cu(II)Mn(II) complex, **1**, suggests that the presence

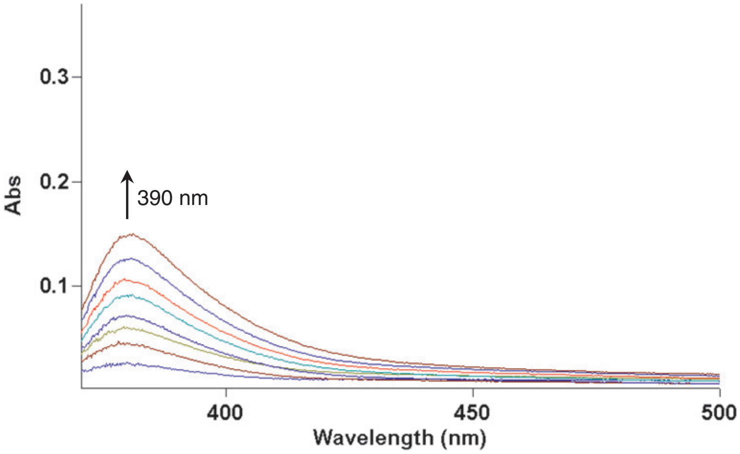


Figure 9. UV–vis spectra of the increase in intensity of the band at 390 nm of *o*-quinone in oxidation of catechol by the $Cu^{II}Co^{II}$ complex **2**.

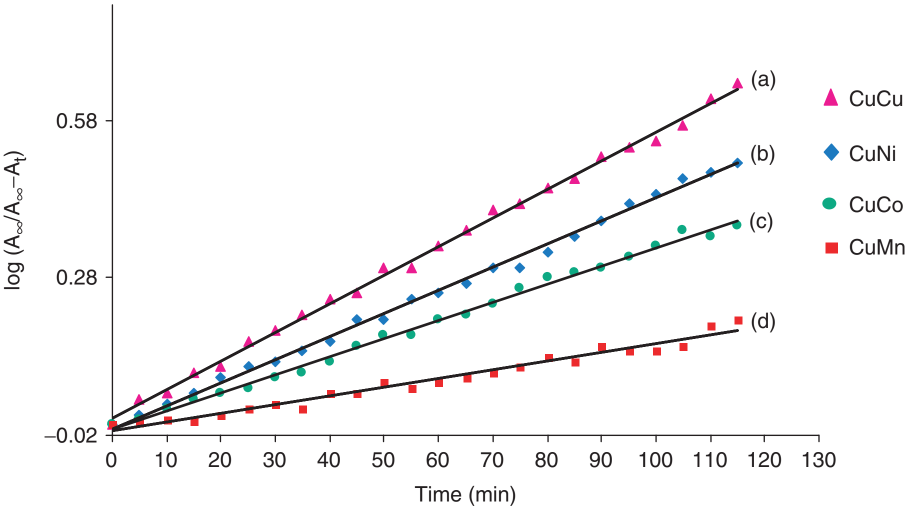


Figure 10. The catecholase-like activity of **1**–**4**: (a) CuCu; (b) CuNi; (c) CuCo and (d) CuMn.

Table 3. The catecholase-like activity[a] of **1**–**4**.

Complex	Rate constant, k (min^{-1})
1	1.7×10^{-3}
2	3.5×10^{-3}
3	4.4×10^{-3}
4	5.4×10^{-3}

[a] Measured spectrophotometrically at 390 nm in the acetonitrile solution. The concentration of the complexes: 10^{-3} M and catechol: 10^{-1} M 115 min.

of the easily reduced metal centers located in close proximity is important to increase the catalytic activity of the dinuclear complexes in the oxidation of the cathecol to the corresponding quinine. This result is consistent with the previously reported [49] mechanism, in which both metallic centers are reduced from M(II) to M(I) upon reaction with catechols to form quinones.

4. Conclusion

New dinuclear copper(II) complexes **1**–**4**, Cu(II)M(II) (M = Mn, Co, Ni, Cu), of a phenol-based compartmental ligand, having dissimilar $N(amine)_2O_2$ and $N(imine)_2O_2$ coordination sites have been prepared through the $Cu^{II}Pb^{II}$ precursor complex by transmetalation of Pb(II) for M(II). Dinuclear copper(II) complexes in this study have two different compartments as coordination sites, one compartment has piperazinyl nitrogens and phenolic oxygens and the other has meso-stilbenediamine nitrogens and phenolic oxygens. The complexes were characterized by elemental analysis, IR and electronic spectra as well as conductivity measurements. The molar conductances in acetonitrile indicate that the complexes are 1 : 2 electrolytes. Electrochemical studies of the dinuclear complexes reveal that the $Cu^{II}Mn^{II}$ complex shows one quasi-reversible couple, $E_{pc} = -0.80\,V$, whereas $Cu^{II}M^{II}$ (M = Co, Ni, Cu) complexes undergo two quasi-reversible couples, $E^1_{pc} = -0.57$ to $-0.59\,V$ and $E^2_{pc} = -0.90$ to $-1.05\,V$. The higher catalytic activity in oxidation of the cathecol to the corresponding quinone of the homodinuclear $Cu^{II}Cu^{II}$ complex compared to the other complexes suggests that the presence of an easily reduced metal center located in close proximity is important to increase the catalytic activity of the dinuclear complexes, consistent with the previously reported mechanism, in which both metallic centers are reduced from M(II) to M(I) upon the oxidation of catechols to the corresponding quinones.

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