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Polyhedron 22 (2003) 3483–3492

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# Synthesis of mono and binuclear copper(II) complexes using new macrobicyclic tricompartmental unsymmetrical ligands: magnetic, electrochemical and catalytic studies

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Received 7 July 2003; accepted 5 September 2003

## Abstract

A series of new mono and binuclear copper(II) complexes $[CuL^{1a-e}H_2](ClO_4)_2$ and $[Cu_2L^{1a-e}(ClO_4)](ClO_4)$, where L is a macrobicyclic tricompartmental ligand obtained from the condensation of the precursor compound (PC) 3,4:10,11-dibenzo-1,13[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl) benzyl}diaza]-5,9-dioxocyclohexadecane with various diamines have been synthesized. In this system, there are three compartments: the first compartment ($N_2O_2$) comprises two ether oxygens and two tertiary nitrogens, the second compartment ($N_2O_2$) contains two tertiary nitrogens and two phenolic oxygens and the third compartment ($N_2O_2$) is composed of two phenolic oxygens and two imine nitrogens. In mononuclear complexes the geometry of copper(II) ion present in the phenolic oxygen and imine nitrogen compartment is distorted square planar and in binuclear complexes the geometry of Cu(II) ion present in imine nitrogen and phenolic oxygen compartment is distorted square planar and the another Cu(II) ion present in phenolic oxygen and tertiary nitrogen compartment is square pyramidal. The synthesized complexes were characterized by spectroscopic (IR, UV–Vis and ESR) techniques. Electrochemical studies of the complexes reveal that all the mononuclear copper(II) complexes show a single quasireversible one-electron transfer reduction wave ($E_{pc} = -0.76$ to $-0.84$ V) and the binuclear complexes show two quasireversible one-electron transfer reduction waves ($E^1_{pc} = -0.86$ to $-1.01$ V, $E^2_{pc} = -1.11$ to $-1.43$ V) in the cathodic region. The ESR spectra of the mononuclear complexes show four lines with nuclear hyperfine splittings with the observed $g_\parallel$ values in the range 2.20–2.28, $g_\perp = 2.01$–$2.06$ and $A_\parallel = 125$–$273$. The binuclear complexes show a broad ESR spectra with $g = 2.10$–$2.11$. The room temperature magnetic moment values for the mononuclear complexes are in the range [$\mu_{eff} = (1.70$ to $1.72)$ BM] and for the binuclear complexes the range is [$\mu_{eff} = (1.46$ to $1.59)$ BM]. Variable temperature magnetic susceptibility study of the binuclear complex $[Cu_2L^{1d}(ClO_4)](ClO_4)$ shows that the observed $-2J$ value is 225 $cm^{-1}$. The calculated initial rate constant values for oxidation reaction of catechol to *o*-quinone ranges from $8.52 \times 10^{-3}$ to $3.08 \times 10^{-2}$ $min^{-1}$. The catalytic activity of binuclear copper(II) complexes ($1.65 \times 10^{-2}$ to $3.08 \times 10^{-2}$ $min^{-1}$) is higher than the mononuclear copper(II) complexes ($8.52 \times 10^{-3}$–$9.67 \times 10^{-3}$ $min^{-1}$).

*Keywords:* Macrobicyclic copper(II) complexes; Tricompartmental ligands; Magnetic properties; Electrochemical properties; Catalytic activity

## 1. Introduction

The design and synthesis of new macrocyclic ligands with mixed donor sites (or) atoms and their metal complexes have been one of the most studied groups of compounds and received much attention [1–5]. 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 and constitutes the active sites in metalloproteins and enzymes [6–11]. Copper is an essential trace element [12] for life processes, and several copper-containing proteins have been identified [13–15]. Especially dinuclear copper(II) complexes with two metal ions in close proximity have received a great deal of attention [16]. In physicochemical

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doi:10.1016/j.poly.2003.09.004

aspects these dicopper complexes have noteworthy significance as new inorganic materials of showing various magnetic properties with anti-ferromagnetic coupling depending upon the bridge angle and degree of distortion [17–19] and redox properties depending upon the macrocyclic ring size [17a,20–23] and they show redox driven translocation mechanism. Dinuclear copper containing proteins play an important role in biology, including dioxygen transport or activation, electron transfer, reduction of nitrogen oxides and hydrolytic chemistry [24]. As a consequence, the design and synthesis of unsymmetrical binucleating ligands has to satisfy a number of conditions such as metal–metal distance, geometry, electronic and magnetic features [25–29].

Mono and binuclear copper(II) complexes using the precursor compound (PC) 3,4:10,11-dibenzo-1,13[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}diaza]-5,9-dioxocycloheptadecane have been already explored in our previous work [30,31]. In continuation of our earlier work [30,31], here we report the synthesis of new macrobicyclic tricompartmental ligands that contain N and O donor atoms and their mono and binuclear copper(II) complexes using slightly varied precursor compound 3,4:10,11-dibenzo-1,13[*N*,*N*′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}diaza]-5,9-di-oxocyclohexa-decane. The advantage of already reported and reporting macrocyclic system is that the size of a particular compartment is varied by keeping the other compartments fixed. The spectral, magnetic properties, electrochemical and catalytic studies of mono and binuclear copper(II) complexes have been discussed.

## 2. Experimental

Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. $^1$H NMR spectra were recorded using FX-80-Q Fourier transition NMR spectrometer. Electronic spectral studies were carried out on a Hitachi 320 spectrophotometer in the range 200–800 nm. IR spectra were recorded on a Hitachi 270–50 spectrophotometer on KBr disks in the range 4000–250 cm$^{-1}$. Mass spectra were obtained on JEOL model DX-303 mass spectrometer and the electrospray mass spectra of the complexes were recorded on a Micromass Quatro II triple quadrupole mass spectrometer. The cyclic voltammograms were obtained on a model CHI600A electrochemical analyzer. The measurements were carried out under oxygen free condition using a three-electrode cell in which a glassy carbon electrode was the working electrode, saturated Ag/AgCl electrode was the reference electrode and platinum wire was used as the auxiliary electrode. Ferrocene/ferrocenium (1+) couple was used as an internal standard; and the value $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc$^+$) couple, under the experimental conditions is 470 mV in DMF and $\Delta E_p$ value for Fc/Fc$^+$ is 70 mV. Tetra(*n*-butyl)ammonium perchlorate was used as supporting electrolyte. (*Caution! TBAP* is potentially explosive; hence care should be taken in handling the compound). Room temperature magnetic moment was measured on a PAR vibrating sample magnetometer Model-155. X-band ESR spectra were recorded at 25 °C on a Varian EPR-E 112 spectrometer using diphenylpicrylhydrazine (DPPH) as the reference. The catalytic oxidation of catechol to *o*-quinone by the complexes was studied in a $10^{-3}$ M 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. A plot of log $(A_\infty/A_\infty - A_t)$ versus time was made for each complexes and the initial rate constant for the catalytic oxidation was calculated.

### 2.1. Materials

5-Methylsalicylaldehyde [32], 2-chloromethyl-4-methyl-6-formylphenol [33] and 3,4:10,11-dibenzo-1,13-diaza-5,9-dioxacyclohexadecane [34,35] were prepared from the literature methods. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallized from hot methanol. DMF and $CH_3CN$ were obtained from E. MERCK and purified [36]. All other chemicals and solvents were of analytical grade and were used as received without any purification.

### 2.2. Synthesis of precursor compound

#### 2.2.1. 3,4:10,11-dibenzo-1,13[N,N′-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}diaza]-5,9-dioxa-cyclohexadecane

A mixture of 3,4:10,11-dibenzo-1,13-diaza-5,9-dioxacyclohexadecane (1.043 g and 3.2 mmol) and triethylamine (1.32 g and 6.4 mmol) in THF was added slowly to a stirred solution of 2-chloromethyl-4-methyl-6-formyl phenol (1.16 g and 6.4 mmol) in THF. After the addition was over the stirring was continued further for one more hour. The resulting solution was refluxed on water bath for 3 h and then it was allowed to cool on standing at room temperature. To this cooled solution, copious water was added to dissolve any salt. Then the required compound was extracted in organic medium using chloroform. The extraction was repeated for 2–3 times. A pale yellow compound was obtained on removal of the solvent by rotary evaporator. The compound was recrystallized from chloroform. Yield: 1.38 g (70%), m.p.: 78 °C. *Anal.* Calc. for $C_{38}H_{42}O_6N_2 \cdot CHCl_3$: C, 73.31; H, 6.75; N, 4.50. Found: C, 73.41; H, 6.87; N, 4.62%. IR data ($\nu$ cm$^{-1}$): 1672 ($\nu$C=O, s), 3420 (OH, br). $^1$H NMR ($\delta$ ppm in $CDCl_3$): 10.0 (s, 2H, CHO protons), 7.1 (m, 12H, aromatic protons), 4.6 (m, 4H, methylene protons attached to oxygen atom), 3.6 (m, 8H, benzylic protons), 3.2 (brs, 4 H, methylene protons attached to nitrogen atom), 2.3 (s, 6H, protons of $CH_3$ group attached to aromatic ring), 2.1(brs, 4 H, $CH_2$ protons attached to alkyl chain). $^{13}C$ NMR ($\delta$ ppm in $CDCl_3$): 20.2 (q, $CH_3$), 23.6 (t, $NCH_2–CH_2–CH_2N$), 50.6 (t, $CH_2–CH_2–N$), 51.9 (t, $Ar–CH_2–N$), 54.9 (t, $Ar–CH_2–N$), 65.8 (t, $OCH_2$), 110–135.8 (d, Ar–CH), 157–159 (s,Cq), 190.8 (d, CHO). Mass (EI) *m/z*: 622 ($m^+$).

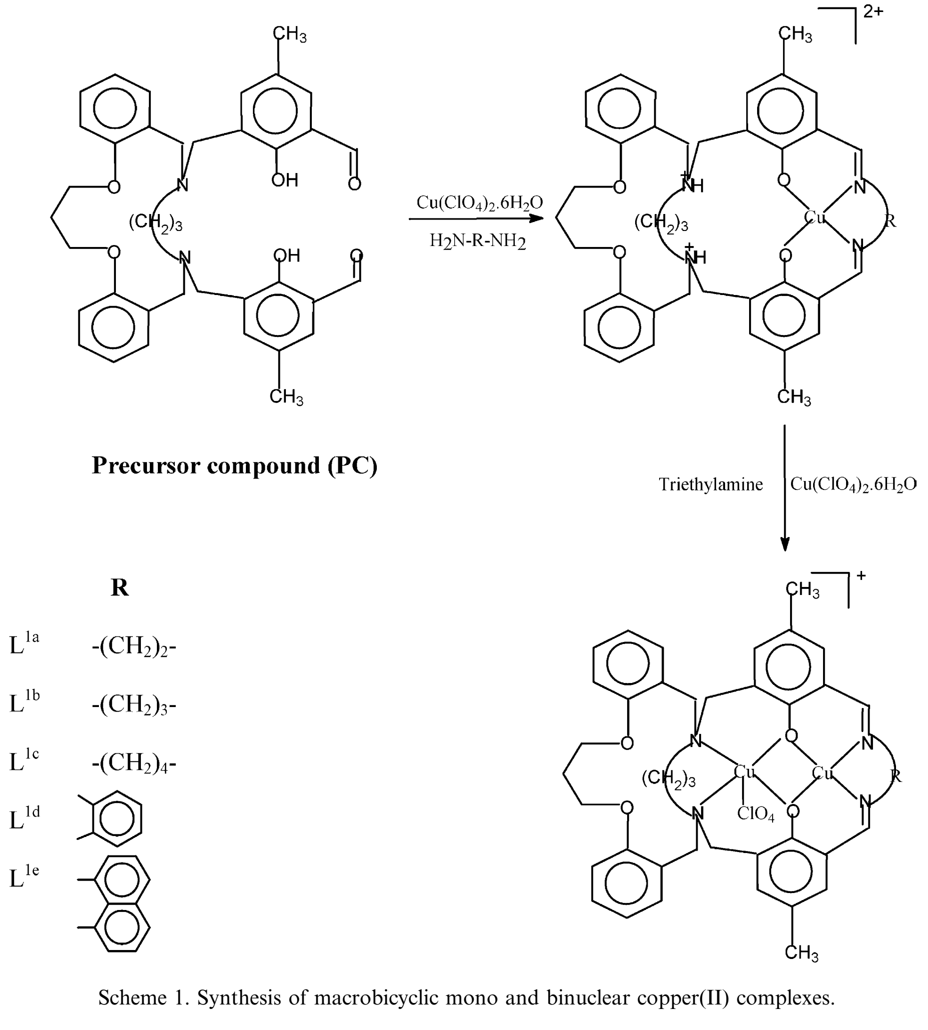
### 2.3. Synthesis of macrobicyclic mononuclear copper(II) complexes $[CuL^{1a}H_2](ClO_4)_2$

A methanolic solution (20 ml) of copper(II) perchlorate hexahydrate (0.741 g and 2.0 mmol) was added to the hot solution of PC (1.244 g and 2.0 mmol) in $CHCl_3$ (30 ml) followed by the addition of 1,2-diaminoethane (0.120 g and 2.0 mmol) in methanol (20 ml). The solution was refluxed on water bath for 24 h. The resulting solution was then filtered at hot condition and allowed to stand at room temperature. Dark green compound was obtained on slow evaporation of the solvent and recrystallized from $CH_3CN$. Yield: 1.59 g (80%). *Anal.* Calc. for $C_{44}H_{52}O_{12}N_6Cl_2Cu$: C, 53.35; H, 5.25; N, 8.48; Cu, 6.42. Found: C, 53.46; H, 5.32; N, 8.52; Cu, 6.52%. Selected IR (KBr): 1627 (s), 1099 (s), 623 (s) $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2 mol^{-1}$) in $CH_3CN$: 248. $\lambda_{max}$ (nm) ($\varepsilon$/$M^{-1} cm^{-1}$) in $CH_3CN$: 580 (163), 353 (18 000), 270 (29 000), $g_{\parallel} = 2.20$, $g_{\perp} = 2.01$ and $A_{\parallel} = 273$; $\mu_{eff} = 1.70$ BM.

Complexes $[CuL^{1b}H_2](ClO_4)_2$, $[CuL^{1c}H_2](ClO_4)_2$, $[CuL^{1d}H_2](ClO_4)_2$, $[CuL^{1e}H_2](ClO_4)_2$ were synthesized by following the above procedure using 1,3-diaminopropane, 1,4-diaminobutane, 1,2-diaminobenzene and 1,8-diaminonapthalene, respectively, instead of using 1,2-diaminoethane. The synthetic route is shown in Scheme 1.

#### 2.3.1. $[CuL^{1b}H_2](ClO_4)_2$

Dark green compound. Yield: 1.63 g (81%). *Anal.* Calc. for $C_{45}H_{54}O_{12}N_6Cl_2Cu$: C, 53.80; H, 5.38; N, 8.37; Cu, 6.33. Found: C, 53.90; H, 5.90; N, 8.39; Cu, 6.59%. Selected IR (KBr): 1627 (s), 1099 (s), 625 (s) $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2 mol^{-1}$) in $CH_3CN$: 256. $\lambda_{max}$ (nm) ($\varepsilon$/$M^{-1} cm^{-1}$) in $CH_3CN$: 590 (113), 350 (15 700),



Scheme 1. Synthesis of macrobicyclic mono and binuclear copper(II) complexes.

255 (23 000), $g_{\parallel} = 2.28$, $g_{\perp} = 2.06$ and $A_{\parallel} = 250$; $\mu_{\mathrm{eff}} = 1.70$ BM.

### 2.3.2. $[CuL^{1c}H_2](ClO_4)_2$

Dark green compound. Yield: 1.65 g (81%). *Anal.* Calc. for $C_{46}H_{56}O_{12}N_6Cl_2Cu$: C, 54.24; H, 5.50; N, 8.25; Cu, 6.24. Found: C, 54.58; H, 5.62; N, 8.36; Cu, 6.51%. Selected IR (KBr): 1620 (s), 1085 (s), 626 (s) $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$: 260. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 615 (173), 350 (13 500), 252 (18 200), $g_{\parallel} = 2.22$, $g_{\perp} = 2.05$ and $A_{\parallel} = 220$; $\mu_{\mathrm{eff}} = 1.71$ BM.

### 2.3.3. $[CuL^{1d}H_2](ClO_4)_2$

Dark green compound. Yield: 1.63 g (78%). *Anal.* Calc. for $C_{48}H_{52}O_{12}N_6Cl_2Cu$: C, 55.51; H, 5.01; N, 8.09; Cu, 6.12. Found: C, 56.01; H, 5.11; N, 8.10; Cu, 6.41%. Selected IR (KBr): 1625 (s), 1100 (s), 626 (s) $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$: 245. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 595 (117), 422 (21 400), 355 (34 300), 300 (39 600), 250 (22 100), $g_{\parallel} = 2.24$, $g_{\perp} = 2.06$ and $A_{\parallel} = 137$; $\mu_{\mathrm{eff}} = 1.72$ BM.

### 2.3.4. $[CuL^{1e}H_2](ClO_4)_2$

Dark green compound. Yield: 1.60 g (73%). *Anal.* Calc. for $C_{52}H_{54}O_{12}N_6Cl_2Cu$: C, 57.37; H, 4.96; N, 7.72; Cu, 5.84. Found: C, 57.41; H,4.99; N, 7.86; Cu, 5.98%. Selected IR (KBr): 1629 (s), 1100 (s), 623 (s) $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$: 253. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 600 (174), 362 (15 200), 340 (37 400), 260 (21 600), $g_{\parallel} = 2.20$, $g_{\perp} = 2.01$ and $A_{\parallel} = 125$; $\mu_{\mathrm{eff}} = 1.71$ BM.

### 2.4. Synthesis of macrobicyclic binuclear copper(II) complexes $[Cu_2L^{1a}(ClO_4)](ClO_4)$

A methanolic solution (20 ml) of copper(II) perchlorate hexahydrate (0.750 g and 2.0 mmol) was added to the hot solution of PC (1.25 g and 2.0 mmol) in $CHCl_3$ (20 ml) followed by the addition of 1,2-diaminoethane (0.121 g and 2.0 mmol) and triethylamine (0.405 g and 4.0 mmol) in methanol (20 ml). After 1 h further quantity of copper(II) perchlorate (0.750 g and 2.0 mmol) was added and the resulting solution was refluxed on water bath for 24 h. The solution was then filtered and allowed for standing at room temperature (25 °C). After slow evaporation of the solvent at 25 °C, a dark green compound obtained washed with methanol and dried in vacuum. The dark green crystals were obtained on recrystallization from $CH_3CN$. Yield: 1.60 g (75%). *Anal.* Calc. for $C_{44}H_{52}O_{12}N_6Cl_2Cu_2$: C, 50.14; H, 4.93; N, 7.97; Cu, 12.06. Found: C, 50.21; H, 4.98; N, 7.21; Cu, 12.19%. Selected IR (KBr): 1630 (s),1087, 1099 (w), 626 (s) $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$: 144. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$: 589 (205), 364 (7500), 271 (23 400), $g = 2.10$, $\mu_{\mathrm{eff}} = 1.48$ BM.

Complexes $[Cu_2L^{1b}(ClO_4)](ClO_4)$, $[Cu_2L^{1c}(ClO_4)](ClO_4)$,$[Cu_2L^{1d}(ClO_4)](ClO_4)$,$[Cu_2L^{1e}(ClO_4)](ClO_4)$ were synthesized by the above procedure using the following diamines: 1,3-diaminopropane, 1,4-diaminobutane, 1,2-diaminobenzene and 1,8-diaminonapthalene, respectively, instead of using 1,2-diaminoethane. The synthetic route is as shown in Scheme 1.

### 2.4.1. $[Cu_2L^{1b}(ClO_4)](ClO_4)$

Dark green compound. Yield: 1.65 g (77%). *Anal.* Calc. for $C_{45}H_{54}O_{12}N_6Cl_2Cu_2$: C, 50.60; H, 5.06, N, 7.87; Cu, 11.90. Found: C, 50.71; H, 5.13; N, 7.90; Cu, 12.04%. Selected IR (KBr): 1624, 1087, 1095, 626 $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$ 150. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$ 618 (176), 354 (11 300), 270 (31 200), $g = 2.11$, $\mu_{\mathrm{eff}} = 1.54$ BM.

### 2.4.2. $[Cu_2L^{1c}(ClO_4)](ClO_4)$

Dark green compound. Yield: 1.55 g (71%). *Anal.* Calc. for $C_{46}H_{56}O_{12}N_6Cl_2Cu_2$: C, 51.06; H, 5.18, N, 7.77, Cu, 11.75. Found: C, 51.10; H, 5.25; N, 7.96; Cu, 11.95%. Selected IR (KBr): 1626, 1082, 1093, 626 $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$ 155. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$ 165 (166), 349 (10 900), 268 (20 100), $g = 2.11$, $\mu_{\mathrm{eff}} = 1.59$ BM.

### 2.4.3. $[Cu_2L^{1d}(ClO_4)](ClO_4)$

Dark green compound. Yield: 1.62 g (73%). *Anal.* Calc. for $C_{48}H_{52}O_{12}N_6\ Cl_2Cu_2$: C, 52.30; H, 4.69, N, 7.29,Cu, 11.84. Found: C, 52.57; H, 4.73; N, 7.29; Cu, 11.85%. Selected IR (KBr): 1627, 1081, 1096, 626 $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$ 152. $\lambda_{max}$(nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$ 580 (198), 410 (22 300), 350 (13 800), 330 (15 200), 268 (20 100), $g = 2.10$, $\mu_{\mathrm{eff}} = 1.51$ BM.

### 2.4.4. $Cu_2L^{1e}(ClO_4)](ClO_4)$

Dark green compound. Yield: 1.66 g (72%). *Anal.* Calc. for $C_{52}H_{54}O_{12}N_6\ Cl_2Cu_2$: C, 54.20; H, 4.69, N, 7.29,Cu, 11.04. Found: C, 54.31; H, 4.74; N, 7.60; Cu, 11.27%. Selected IR (KBr): 1625, 1084, 1096, 626 $cm^{-1}$. Conductance ($\Lambda_m$/S $cm^2\,mol^{-1}$) in $CH_3CN$ 143. $\lambda_{max}$ (nm) ($\varepsilon/M^{-1}\,cm^{-1}$) in $CH_3CN$ 595 (217), 405 (25 400), 340 (12 800), 310 (18 600), 250 (21 400), $g = 2.11$, $\mu_{\mathrm{eff}} = 1.46$ BM.

All the complexes obtained were only in microcrystalline nature. Various attempts to obtain the crystals suitable for X-ray analysis were unsuccessful.

## 3. Results and discussion

### 3.1. Spectral studies

The mono and binuclear complexes were characterized by spectral studies. IR spectra of the complexes show a new peak in the range 1620–1630 cm$^{-1}$. The formation of this new peak [37] and the disappearance of the peak around 1680 cm$^{-1}$ $\nu$(C=O) in the complexes, indicate the effective Schiff's base $\nu$(C=N) condensation of aldehyde groups with the appropriate amines. For the mononuclear complexes the sharp peaks observed around 1100 and 628 cm$^{-1}$ are assigned to perchlorate ion [38]. There is no splitting in the peak at 1100 cm$^{-1}$, which indicates that the $ClO_4^-$ ion is not coordinated to the metal ion [30]. All the binuclear complexes show splitting of two peaks near 1100 cm$^{-1}$. This clearly explains that the splitting is due to the presence of coordinated perchlorate ion [39]. Apart from this an additional peak is also observed around 626 cm$^{-1}$, which is characteristic of perchlorate ion.The electronic spectra of the complexes evince three main transitions [40]: a weak band observed in the range 580–650 nm is assigned to d–d transition [41] of the metal ion, a moderate intensive band observed in the range 343–422 nm is due to ligand to metal charge transfer transition and the strong band observed in the range 250–270 nm is due to intraligand transition. From the electronic spectral studies it was inferred that an increase in $\lambda_{max}$ (red shift) of the d–d transition of Cu(II) ion in the complexes is observed as moving from complexes of ligand $L^{1a}$ to $L^{1c}$ and $L^{1d}$ to $L^{1e}$. This is due to distortion in the geometry of the complexes due to the increase in macrocyclic ring size from 19 to 21membered ring, which causes more distortion of the geometry [42].

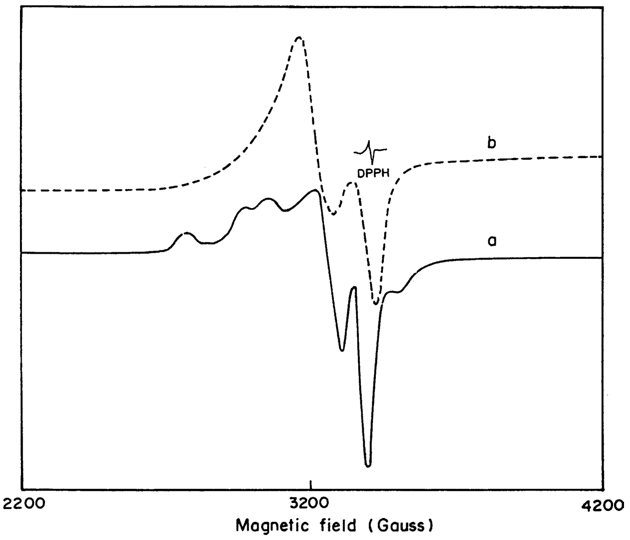


Fig. 1. ESR spectra of: (a) $[CuL^{1a}H_2](ClO_4)_2$, (b) $[Cu_2L^{1c}(ClO_4)](ClO_4)$.

The room temperature (25 °C) solid-state X-band ESR spectra of the mono nuclear copper(II) complexes show four lines [43] with nuclear hyperfine spin 3/2 due to hyperfine splitting. The observed $g_{\parallel}$ values are in the range 2.20–2.28, $g_{\perp} = 2.01$–$2.06$ and $A_{\parallel}$ values vary in the range 125–273. The ESR spectra of the binuclear copper(II) complexes show a broad band centered at g; 2.10–2.11. The broad ESR spectra of the complexes indicate the presence of anti-ferromagnetic interaction [44] between two copper(II) ions in the complexes. The ESR spectra of mono and binuclear copper(II) complex of $[CuL^{1a}H_2](ClO_4)_2$ and $[Cu_2L^{1c}(ClO_4)](ClO_4)$ are shown in Fig. 1 and the data are given in Table 1.

### 3.2. Magnetic studies

The magnetic moment values of mono and binuclear complexes were calculated at room temperature. The magnetic moment values for mononuclear copper(II) complexes are in the range of (1.70–1.72 BM), which are very close to that of spin only value (1.73 BM) expected for complexes having one copper(II) ion [45] with single unpaired electron sited in an essentially $d_{x^2-y^2}$ orbital. The observed magnetic moment values of binuclear copper(II) complexes lie in the range from 1.46 to 1.59 BM and the data are given in the Table 1. This confirms the presence of anti-ferromagnetic interaction between the two copper(II) ions. To evaluate the singlet-triplet energy separation ($-2J$), variable-temperature magnetic study of the complex $[Cu_2L^{1d}(ClO_4)](ClO_4)$ was carried out in the temperature range 77–300 K and the experimental magnetic susceptibility values were fitted to the modified Bleany–Bowers equation [46].

Table 1
ESR spectral and room temperature magnetic moment data of mono and binuclear copper(II) complexes

| Complexes | $g_{\parallel}$ | $g_{\perp}$ | $g$ | $A_{\parallel}$ | $\mu_{eff}$ (BM) |
|---|---|---|---|---|---|
| $[CuL^{1a}H_2](ClO_4)_2$ | 2.20 | 2.01 | | 273 | 1.70 |
| $[CuL^{1b}H_2](ClO_4)_2$ | 2.28 | 2.06 | | 250 | 1.71 |
| $[CuL^{1c}H_2](ClO_4)_2$ | 2.22 | 2.05 | | 220 | 1.71 |
| $[CuL^{1d}H_2](ClO_4)_2$ | 2.24 | 2.06 | | 137 | 1.72 |
| $[CuL^{1e}H_2](ClO_4)_2$ | 2.20 | 2.01 | | 125 | 1.71 |
| $[Cu_2L^{1a}(ClO_4)](ClO_4)$ | | | 2.10 | | 1.48 |
| $[Cu_2L^{1b}(ClO_4)](ClO_4)$ | | | 2.11 | | 1.54 |
| $[Cu_2L^{1c}(ClO_4)](ClO_4)$ | | | 2.11 | | 1.59 |
| $[Cu_2L^{1d}(ClO_4)](ClO_4)$ | | | 2.10 | | 1.51 |
| $[Cu_2L^{1e}(ClO_4)](ClO_4)$ | | | 2.11 | | 1.46 |

$$\chi_m = (Ng^2\beta^2/3kT)[3+\exp(-2J/kT)]^{-}1(1-P) + 0.45P/T + N_\alpha,$$

in which $N_\alpha$ and $g$ have been fixed as $60 \times 10^{-6}$ $cm^3$ $M^{-1}$ and 2.20, respectively. $\chi_m$ is the molar magnetic susceptibility corrected for diamagnetism, $P$ is the percentage of monomeric impurities and other symbols have their usual meaning. The singlet–triplet energy separation ($-2J$) values were evaluated by a nonlinear regression analysis in which $-2J$, $P$ and $g$ are the variables. Fig. 2 depicts the temperature dependence magnetic properties of the complex $[Cu_2L^{1d}(ClO_4)](ClO_4)$.

The general phenomenon observed in unsymmetrical dicopper(II) complexes is weak exchange interaction [47]. This is due to the different geometries, which effect lack of coplanarity between the copper planes. With few exceptions magneto-structural correlations [33] for several phenoxo bridged dicopper complexes show that the major factor controlling the exchange interactions is the Cu–O–Cu bridge angle; however, other factors [48] such as degree of distortion from planarity [17a] and the dihedral angle [18] between two copper planes also have influence on the extent of spin–spin interaction. Generally phenoxo-bridged planar dicopper complexes with $Cu–O_{ph}–Cu$ bridge angles greater than 99° show exchange coupling values greater than 420 $cm^{-1}$ and for the complexes with bridge angles less than 99° the exchange interaction is less ($<70$ $cm^{-1}$) [49,50]. Thompson et al. reported [51] that for symmetrical planar complexes with bridge angle greater than 99° the $-2J$ values are $\approx$500–700 $cm^{-1}$. But Okawa et al. [17] reported for the distorted copper(II) complexes the $-2J$ values is 220 $cm^{-1}$. This low value is due to the distortion of the geometry of one of the Cu(II) ion, which causes deviation from co-planarity [48,52]. For the complex $[Cu_2L^{1d}(ClO_4)](ClO_4)$ the observed exchange interaction value ($-2J$) is 225 $cm^{-1}$. The distortion of the geometry [17] and the deviation from co-planarity [42] may be the possible reasons for this low exchange interaction value.

### 3.3. Electrochemistry

Electrochemical properties of both mono and binuclear copper(II) complexes were studied by cyclic voltammetry technique in dimethylformamide solvent containing $10^{-1}$ M tetra(*n*-butyl)ammonium perchlorate in the potential range 0 to −1.5 V and the electrochemical data are summarized in Table 2. All the mononuclear copper(II) complexes show a single quasireversible one-electron transfer reduction process in the cathodic potential region. The cyclic voltammograms for the mononuclear complexes are shown in Fig. 3. Each voltammogram shows one quasireversible reduction wave at negative potential in the range −0.76 to −0.84 V. The reduction potential of the mononuclear copper(II) complexes of ligands $L^{1a}$ to $L^{1c}$ displays a shifts towards anodic, as the number of methylene group between imine nitrogens is increased and in turn increases the macrocyclic ring size. This causes for more flexibility [20,53–55] in the macrocyclic ring and tries to stabilize copper(I) complex. In the case of $L^{1d}$ to $L^{1e}$ the reduction potential of the complexes entails a shift towards more anodic from −0.81 to −0.79 V. The complexes with aromatic diimines reduced at somewhat higher potential than that of the complexes with aliphatic diimines due to the more planar nature. Transition metal ions have been shown to be translocated reversibly between the non-equivalent compartments of macrocyclic ditopic ligands by an input of pH or redox potential. For redox-driven translocation, the moveable metal center should possess two consecutive oxidation states of comparable stability. The stereochemical variation accomplished with the change of the electronic configuration of the metal ion oxidation or reduction

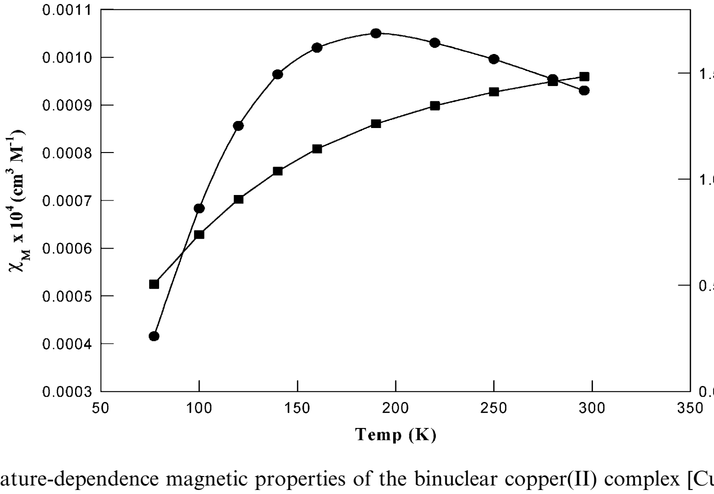


Fig. 2. Temperature-dependence magnetic properties of the binuclear copper(II) complex $[Cu_2L^{1d}(ClO_4)]$ $(ClO_4)$.

Table 2
Electrochemical data[a] of mono and binuclear copper(II) complexes in DMF medium

| Complexes | $E^1_{pc}$ (V) | $E^1_{pa}$ (V) | $E^1_{1/2}$ (V) | $\Delta E$ (mV) | $E^2_{pc}$ (V) | $E^2_{pa}$ (V) | $E^2_{1/2}$ (V) | $\Delta E$ (mV) | $K_{con}$ |
|---|---|---|---|---|---|---|---|---|---|
| $[CuL^{1a}H_2](ClO_4)_2$ | −0.84 | −0.69 | −0.76 | 150 | | | | | |
| $[CuL^{1b}H_2](ClO_4)_2$ | −0.80 | −0.69 | −0.74 | 110 | | | | | |
| $[CuL^{1c}H_2](ClO_4)_2$ | −0.76 | −0.66 | −0.71 | 100 | | | | | |
| $[CuL^{1d}H_2](ClO_4)_2$ | −0.81 | −0.70 | −0.75 | 110 | | | | | |
| $[CuL^{1e}H_2](ClO_4)_2$ | −0.79 | −0.69 | −0.74 | 100 | | | | | |
| $[Cu_2L^{1a}(ClO_4)](ClO_4)$ | −0.95 | −0.79 | −0.87 | 160 | −1.36 | −1.17 | −1.26 | 190 | $3.97 \times 10^6$ |
| $[Cu_2L^{1b}(ClO_4)](ClO_4)$ | −0.90 | −0.75 | −0.82 | 150 | −1.20 | −1.04 | −1.12 | 160 | $1.19 \times 10^5$ |
| $[Cu_2L^{1c}(ClO_4)](ClO_4)$ | −0.86 | −0.73 | −0.79 | 130 | −1.11 | −1.00 | −1.05 | 110 | $2.50 \times 10^4$ |
| $[Cu_2L^{1d}(ClO_4)](ClO_4)$ | −1.01 | −0.89 | −0.95 | 120 | −1.43 | −1.24 | −1.33 | 190 | $2.69 \times 10^6$ |
| $[Cu_2L^{1e}(ClO_4)](ClO_4)$ | −0.92 | −0.73 | −0.86 | 110 | −1.20 | −1.03 | −1.11 | 170 | $1.69 \times 10^4$ |

[a] Measured by CV at 50 mV/s. E vs. Ag/AgCl conditions: GC working and Ag/AgCl reference electrodes; supporting electrolyte TBAP; concentration of complex $1 \times 10^{-3}$ M, concentration of TBAP $1 \times 10^{-1}$ M.

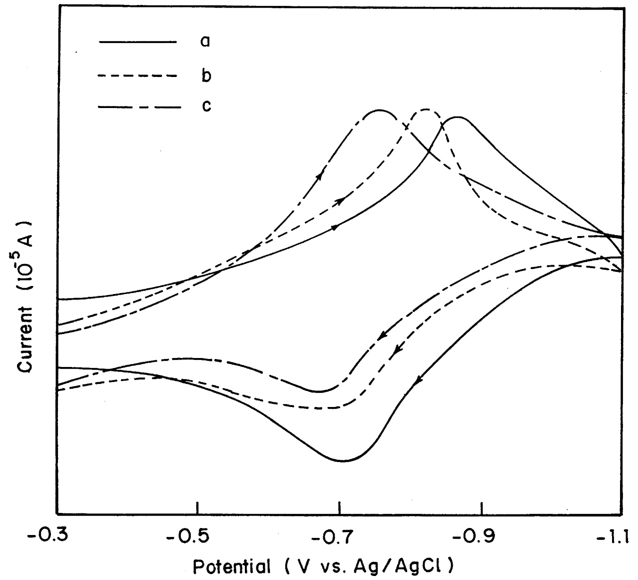


Fig. 3. Cyclic voltammograms of the mononuclear copper(II) complexes ($1 \times 10^{-3}$ M): (a) $[CuL^{1a}H_2](ClO_4)_2$, (b) $[CuL^{1b}\ H_2](ClO_4)_2$, (c) $[CuL^{1c}\ H_2](ClO_4)_2$.

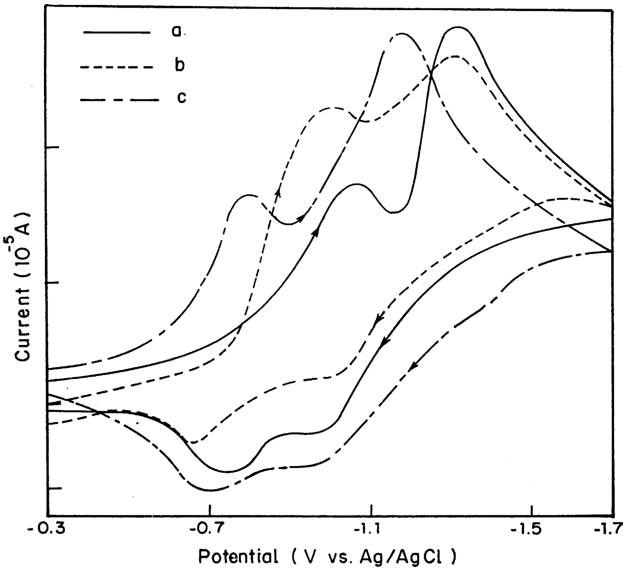


Fig. 4. Cyclic voltammograms of the binuclear copper(II) complexes ($1 \times 10^{-3}$ M): (a) $[Cu_2L^{1a}(ClO_4)](ClO_4)$, (b) $[Cu_2L^{1b}(ClO_4)](ClO_4)$, (c) $[Cu_2L^{1c}(ClO_4)](ClO_4)$.

produces mechanical work at the molecular level [56]. In this case the copper(II) ion present in the rigid and hard imine nitrogen compartment gets reduced [30] while an input voltage is applied and the reduced Cu(I) ion prefers tetrahedral geometry and hence the resulting reduced ion is translocated to soft tertiary nitrogen compartment where it can find flexible coordination compartment [30]. During reverse scan the Cu(I) ion gets oxidized to Cu(II) and it enters into the hard imine compartment. On moving from the complexes of the ligand $L^{1a}$ to $L^{1c}$ when methylene group in the imine nitrogen is increased, the whole macrocyclic ring size increases and the macroyclic ring becomes more flexible. Hence the movement of ion from imine nitrogen compartment to tertiary nitrogen compartment and vice versa becomes easy. This explanation solely depends upon only the electrochemical data and not upon the structural data.

The macrocyclic doubly phenoxo-bridged dicopper complexes typically undergo two well-separated one-electron reductions [21,57]. Fig. 4 represents the cyclic voltammograms of the binuclear complexes. It is observed that all the binuclear complexes show two quasireversible reduction waves in the cathodic potential region. The first reduction potential ranges from −0.85 to −1.05 V and the second reduction potential lies in the range −1.10 to −1.45 V. Controlled potential electrolysis also carried out and the experiment reports that the each couple corresponding to one-electron transfer process.

The two redox processes are assigned as follows:

$$Cu^{II}Cu^{II} \rightleftharpoons Cu^{II}Cu^{I} \rightleftharpoons Cu^{I}Cu^{I}$$

The conproportionation constant for the equilibrium

$$Cu^{II}Cu^{II} + Cu^{I}Cu^{I} \overset{K_{con}}{\rightleftharpoons} 2Cu^{II}Cu^{I}$$

was calculated using the relationship $\log K_{\mathrm{con}} = \Delta E/0.0591$ (where as $\Delta E = E^2_{1/2} - E^1_{1/2}$).

The interesting feature observed for the binuclear complexes of ligand $L^{1a}$ to $L^{1c}$ there is shifting of both first and second reduction potentials towards anodic from $E^1_{\mathrm{PC}} = -0.95$ to $-0.86$ V and values of $E^2_{\mathrm{PC}} = -1.36$ to $-1.11$ V, respectively, as the number of methylene group is increased. For example the complex $[Cu_2L^{1a}(ClO_4)](ClO_4)$ has $E^1_{\mathrm{PC}} = -0.95$ V and $E^2_{\mathrm{PC}} = -1.36$ V, which is more negative compared to the complex $[Cu_2L^{1b}(ClO_4)](ClO_4)$ ($E^1_{\mathrm{PC}} = -0.90$ V, $E^2_{\mathrm{PC}} = -1.20$ V), which in turn more compared to the complex $[Cu_2L^{1c}(ClO_4)](ClO_4)$ ($E^1_{\mathrm{PC}} = -0.86$ V, $E^2_{\mathrm{PC}} = -1.11$ V). Thus as the chain length of imine compartment increases, the whole macrocyclic ring becomes more flexible which causes easy reduction. Thus the large size of cavity easily holds the reduced cation and stabilizes the formation of Cu(I) in both the compartment. Another interesting feature was inferred for the binuclear copper(II) complexes from the calculation of $K_{\mathrm{con}}$ values. The decrease in $K_{\mathrm{con}}$ value for the complexes of ligands $L^{1a}$ to $L^{1c}$ ($L^{1a} = 3.97 \times 10^6$, $L^{1b} = 1.19 \times 10^5$, $L^{1c} = 2.50 \times 10^4$) indicates that the potential difference between $E^1_{1/2}$ and $E^2_{1/2}$ also decreases moving from $L^{1a}$ to $L^{1c}$ and the same tendency is observed for the complexes of ligands $L^{1d}$ to $L^{1e}$. This may be due to the reason that as the ring size increases, the stability of the mixed-valent species formed as a result of the one-electron reduction of complexes decreases. The reduction potential of the second metal ion is highly influenced by the electron density in the first metal ion through exchange mechanism [20] in binuclear copper(II) complexes. The reason is that the increase in ring size produces more distortion of the geometry around the metal center and the added electron is localized in the first metal ion itself and its impact on the second metal ion is decreased. Thus the interaction between the two metal ions present in the distorted geometry is minimized and hence the reduction of second metal ion becomes easy.

An attempt was made to compare the results of the present work with some of the complexes of previous work [30] and this leads to an interesting result that increase in macrocyclic ring size in ether oxygen site has no much influence on redox properties of the complexes. For example it can be seen that the redox potential of the complexes reported in our earlier work [30] is found to be almost similar that of the complexes reported in the present and these complexes differ in macrocyclic ring size in ether oxygen site.

### *3.4. Kinetic studies of oxidation of catechol (catecholase activity)*

Efforts have also been made to investigate the catecholase activity of both mono and binuclear copper(II) complexes using 3,5-ditertiarybutylcatechol as a convenient model substrate for the identification of functional models for the metalloenzymes [58]. All the mono and binuclear copper(II) complexes synthesized were subjected for catecholase activity. The course of the reaction was followed spectrophotometrically at 390 nm nearly for 45 min at regular time interval of 5 min. The slope was determined by the method of initial rates by monitoring the growth of 390 nm band of the product *o*-quinone. A linear relationship for initial rate and the complex concentration obtained for all the complexes shows a first-order dependence on the complex concentration for the systems.

A plot of $\log (A_\infty/A_\infty - A_t)$ versus time for catecholase activity of the mono and binuclear complexes are obtained and shown in Figs. 5 and 6. The observed initial rate constant value for mononuclear and binuclear copper(II) complexes are given in Table 3. The initial rate constant value of mononuclear complexes increases from $8.76 \times 10^{-3}$ to $9.67 \times 10^{-3}$ min$^{-1}$ and for binuclear copper(II) complexes increases from $1.82 \times 10^{-2}$ to $3.08 \times 10^{-2}$ min$^{-1}$ as we move from $L^{1a}$ to $L^{1c}$. The catalytic activity of the mono and binuclear complexes are found to increase as the macrocyclic ring size increases [59,60] due to the intrinsic flexibility and distortion in the geometry because of which the copper(II) ion gets reduced easily and in turn oxidize the substrate.

The catalytic activities of the complexes of ligands $L^{1d}$ and $L^{1e}$ containing the aromatic diimines are found to be comparatively lower than that of the complexes containing aliphatic diimines. The reason may be due to the planarity and the electronic properties that are

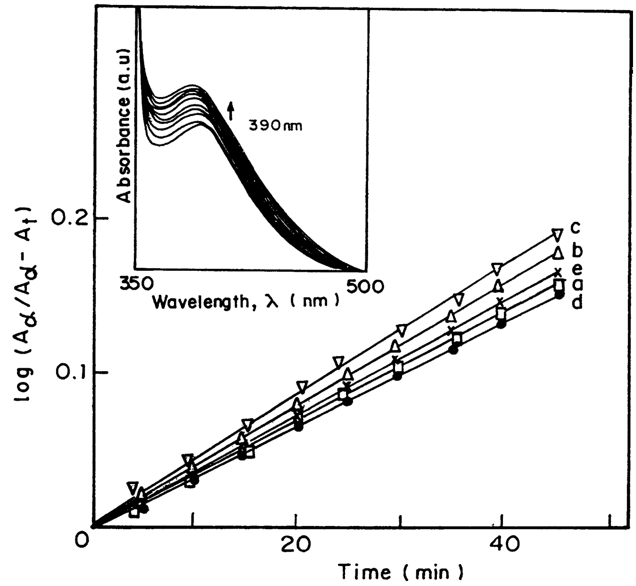


Fig. 5. Catecholase activity of mononuclear copper(II) complexes: (a) $[CuL^{1a}H_2](ClO_4)_2$, (b) $[CuL^{1b}H_2](ClO_4)_2$, (c) $[CuL^{1c}H_2](ClO_4)_2$, (d) $[CuL^{1d}H_2](ClO_4)_2$, (e) $[CuL^{1e}H_2](ClO_4)_2$. Inset: Absorbance maximum at 390 nm with time for 5–45 min.

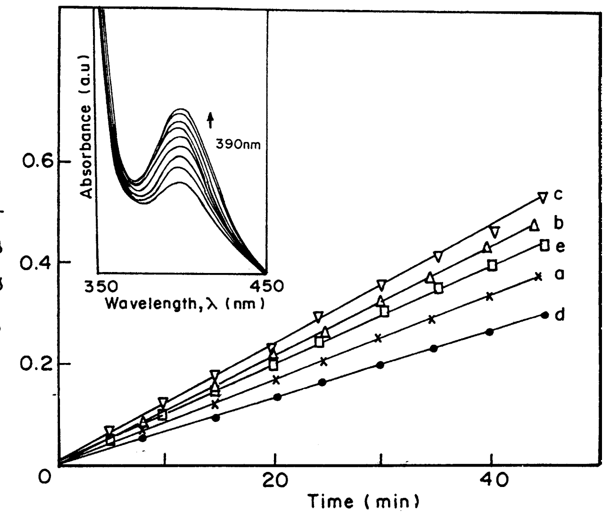


Fig. 6. Catecholase activity of of the binuclear copper(II) complexes: (a) $[Cu_2L^{1a}(ClO_4)](ClO_4)$, (b) $[Cu_2L^{1b}(ClO_4)](ClO_4)$, (c) $[Cu_2L^{1c}(ClO_4)](ClO_4)$, (d) $[Cu_2L^{1d}(ClO_4)](ClO_4)$, (e) $[Cu_2L^{1e}(ClO_4)](ClO_4)$. Inset: Absorbance maximum at 390 nm with time for 5–45 min.

Table 3
Catecholase activity[a] of mono and binuclear copper(II) complexes

| Complexes | Rate constant ($k$), $min^{-1}$ |
|---|---|
| $[CuL^{1a}H_2](ClO_4)_2$ | $8.76 \times 10^{-3}$ |
| $[CuL^{1b}H_2](ClO_4)_2$ | $9.44 \times 10^{-3}$ |
| $[CuL^{1c}H_2](ClO_4)_2$ | $9.67 \times 10^{-3}$ |
| $[CuL^{1d}H_2](ClO_4)_2$ | $8.52 \times 10^{-3}$ |
| $[CuL^{1e}H_2](ClO_4)_2$ | $9.21 \times 10^{-3}$ |
| $[Cu_2L^{1a}(ClO_4)](ClO_4)$ | $1.82 \times 10^{-2}$ |
| $[Cu_2L^{1b}(ClO_4)](ClO_4)$ | $2.34 \times 10^{-2}$ |
| $[Cu_2L^{1c}(ClO_4)](ClO_4)$ | $3.08 \times 10^{-2}$ |
| $[Cu_2L^{1d}(ClO_4)](ClO_4)$ | $1.65 \times 10^{-2}$ |
| $[Cu_2L^{1e}(ClO_4)](ClO_4)$ | $2.00 \times 10^{-2}$ |

[a] Measured spectrophotometrically at 390 nm in $CH_3CN$ medium. Concentration of the complexes: $1 \times 10^{-3}$ M, concentration of 3,5-ditertiarybutylcatechol: $1 \times 10^{-1}$ M.

associated with aromatic ring impart the less catalytic efficiency due to the rigidity of the systems.

The binuclear copper(II) complexes show higher catalytic activity [61,62] compared to mononuclear copper(II) complexes. Thus it is proposed that a determining factor is the presence of two metal centers located in close proximity to facilitate the binding of two oxygen atoms of the catechol prior to the electron transfer.

## Acknowledgements

Financial support received by authors P.A. and M.T. from UGC (New Delhi) major project sanctioned to M.K. and CSIR (New Delhi) is gratefully acknowledged.

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