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Lateral macrobicyclic tricompartamental ligands: synthetic, spectral, magnetic, electrochemical and kinetic aspects of binuclear copper(II) complexes

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Abstract

New macrobicyclic tricompartamental ligands and their binuclear copper(II) complexes of type $[\text{Cu}_2\text{L}](\text{ClO}_4)_2$ have been synthesized from the precursor compound 3,4:10,11-dibenzo-1,13[*N,N'*-bis(3-formyl-2-hydroxy-5-methyl)benzyl]diazza]-5,9-dioxacycloheptadecane with diamines (like ethylene, propylene and butylene) by template method. These complexes have been characterized by IR, UV–Vis spectral studies. Electrochemical studies of binuclear complexes evidence two quasireversible one electrontransfer reduction waves ($E_{\text{pc}}^1 = -0.75$ to -0.86 V, $E_{\text{pc}}^2 = -0.99$ to -1.29 V). Room temperature magnetic moment studies convey the presence of antiferromagnetic coupling in binuclear complexes (μ_{eff} , 1.52 to 1.59 B.M.) which is also observed from the broad ESR spectra with $g = 2.11$. A variable temperature magnetic susceptibility study of the complex evidences the observed $-2J$ value is 236 cm^{-1} . The calculated initial rate constant values of catalytic reaction of oxidation of catechol to *o*-quinone ranges from 0.97×10^{-2} to $2.30 \times 10^{-2} \text{ min}^{-1}$. It is proposed that a distortion of the copper ion geometry arises as the macrocyclic ring size increases. This is supported by spectral, electrochemical and catalytic studies.

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Keywords: Binuclear copper(II) complexes; Macrobicyclic ligands; Magnetochemistry; Electrochemistry; Catalytic activity

1. Introduction

The synthesis of tailored molecules for the recognition of chemical species is producing diverse classes of macrocyclic and macropolycyclic structures. In particular, special attention is being devoted to the search for ligands capable of promoting the assembly of polynuclear species [1–5]. Binuclear and polynuclear metal complexes are of considerable interest because they provide the opportunity to study the intramolecular binding, magnetic exchange interactions, multi-electron redox reactions and possible activation of small substrate molecules [6–9]. Many metalloenzymes contain two copper ions in their active site that operate cooperatively [10–13] and consequently, complexes with two metal ions in close proximity have drawn a

great deal of attention. In order to determine the modifications in the properties of the complexes caused by the close proximity of two metal centers, we report here the synthesis of phenoxo-bridged compartmental dicopper(II) complexes. In our earlier work we have reported the synthesis and characterization of mononuclear copper(II) complexes [14].

The present work deals with the synthesis of new macrobicyclic tricompartamental binuclear copper(II) complexes, the site preference of the metal ion, and the coordinating behaviour of ligands containing mixed donor atoms. The reported ligand contains 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. The special feature of this ligand is variation of the size of all compartments and coordination ability of each compartment.

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2. Experimental

Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyzer. ^1H 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 27050 spectrophotometer on KBr disks in the range 4000–400 cm^{-1} . Mass spectra were obtained on JEOL DX-303 Mass spectrometer and the electrospray mass spectra of the complexes were recorded on a Micromass Quatro II triple quadrupole mass spectrometer. Molar conductivity was measured by using an Elico model SX 80 conductivity bridge using freshly prepared solution of the complex in CH_3CN . Cyclic voltammograms were obtained on CH instruments electrochemical analyzer. The measurements were carried out under oxygen free condition using a three electrode cell in which glassy carbon electrode was working electrode, saturated Ag/AgCl electrode was reference electrode and platinum wire was used as auxiliary electrode. Ferrocene/ferrocenium (1+) couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fe/Fe^+) couple under the experimental condition is 470 mV in DMF and ΔE_p for Fe/Fe^+ is 70 mV. Tetra(*n*-butyl)ammonium perchlorate was used as supporting electrolyte. 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 as the reference. Kinetic studies were studied using on Hitachi 320 double beam spectrophotometer. 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 quinone at 390 nm and monitoring the increase in the absorbance at this wavelength as a function of time. A plot of $\log(A_\infty/A_\infty - A_t)$ vs. time was made for each complexes and the rate constant for the catalytic oxidation was calculated.

2.1. Materials

5-Methylsalicylaldehyde [15], 3-chloromethyl-5-methylsalicylaldehyde [16] and 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclotetradecane [17,18] were prepared from literature methods. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallised from hot methanol. (Caution! TBAP is potentially explosive; hence care should be taken in handling the compound.) DMF (HPLC) was obtained from E. Merck. All other chemicals and solvents were of analytical grade and were used as received without any further purification.

2.2. Synthesis of precursor compound

This precursor compound (PC) 3,4:10,11-dibenzo-1,13[*N,N'*-bis{(3-formyl-2-hydroxy-5-methyl}benzyl)diaza]-5,9-dioxacycloheptadecane was prepared as explained in our previous report [14].

A mixture of 3,4:5,10,11-dibenzo-1,13-diaza-5,9-dioxacycloheptadecane (2.12 g, 0.0062 mol) and triethylamine (1.250 g, 0.0124 mol) in THF was added slowly to a stirred solution of 3-chloromethyl-5-methyl salicylaldehyde (2.28 g, 0.124 mol) in THF. After the addition was over, the stirring was continued for one more hour. The resulting solution was refluxed using a water bath for 3 h and then it was allowed to cool on standing at room temperature. To this cooled solution, copious amounts of water were added to dissolve any salt. Then the required compound was extracted in organic medium using chloroform. The extraction was repeated two to three times. A pale yellow compound was obtained on evaporation of the solvent: m.p.: 80–82 °C; yield: 3.2 g (82%).

2.3. Synthesis of macrocyclic binuclear copper(II) complexes [Cu_2L^a](ClO_4)₂

To the hot solution of PC (1.08 g, 1.7 mmol) in CHCl_3 was added a methanolic solution of copper(II) perchlorate hexahydrate (0.63 g, 1.7 mmol) followed by the addition of 1,2-diaminoethane (0.102 g, 1.7 mmol) and triethylamine (0.47 g, 3.4 mmol) in methanol. After an hour, another 1 mol of copper(II) perchlorate (0.63 g, 1.7 mmol) was added and the reaction mixture was refluxed on water bath for 24 h. After the reaction was over, the reaction mixture was filtered and allowed to stand at room temperature. After cooling and evaporation of the solvent, the dark green compound obtained was washed with methanol and dried under vacuum. Attempts to obtain crystals were unsuccessful.

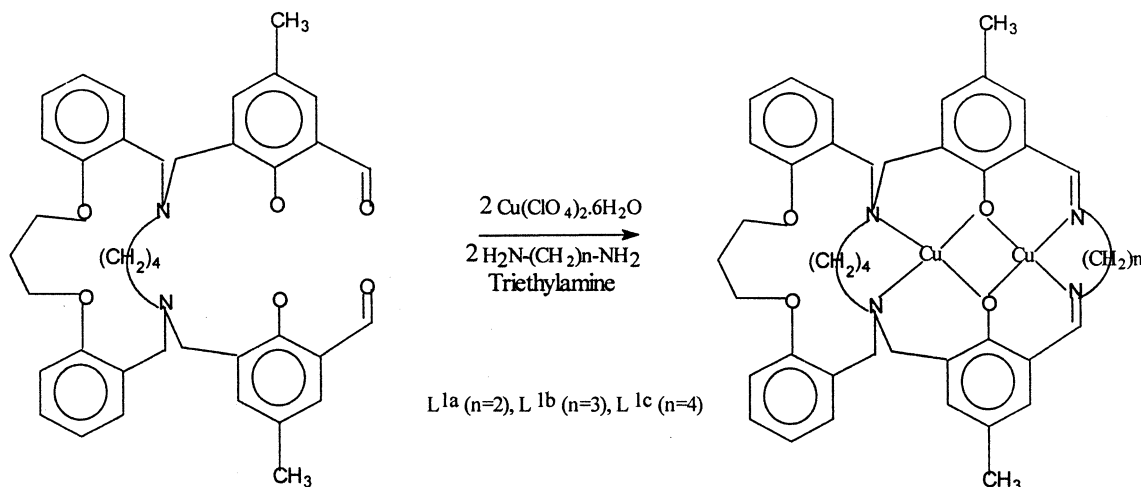
Complexes [Cu_2L^b](ClO_4)₂, [Cu_2L^c](ClO_4)₂ were synthesized by following the above procedure using 1,3-diaminopropane (0.125 g, 1.7 mmol), 1,4-diaminobutane (0.149 g, 1.7 mmol), respectively, instead of using 1,2-diaminoethane (Scheme 1).

2.3.1. [Cu_2L^a](ClO_4)₂

Dark green compound. Analytical data calculated (%) for $\text{C}_{45}\text{H}_{52}\text{Cl}_2\text{N}_6\text{O}_{12}\text{Cu}_2$: C, 50.65; H, 4.87; N, 7.87; Found (%): C, 51.06; H, 4.92; N, 7.96. Selected IR (KBr): 1605, 1100, 1088, 620 cm^{-1} . Conductance ($\Lambda_m/\text{S cm}^2 \text{mol}^{-1}$) in CH_3CN 260. λ_{max} (nm) ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) in CH_3CN 587 (313), 365 (11 200), 275 (27 300). (Mass (EI) $m/z = 1060$ (M^+)).

2.3.2. [Cu_2L^b](ClO_4)₂

Dark green compound. Analytical data calculated (%) for $\text{C}_{46}\text{H}_{54}\text{Cl}_2\text{N}_6\text{O}_{12}\text{Cu}_2$: C, 51.11; H, 5.00; N, 7.77;



Scheme 1. Synthesis of macrocyclic binuclear copper(II) complexes.

Found (%): C, 51.44; H, 5.19; N, 7.96. Selected IR (KBr): 1623, 1100, 1090, 623 cm^{-1} . Conductance ($\Lambda_m/S \text{ cm}^2 \text{ mol}^{-1}$) in CH_3CN 274. λ_{max} (nm) ($\epsilon/M^{-1} \text{ cm}^{-1}$) in CH_3CN 613 (248), 368 (12 300), 270 (28 100).

2.3.3. $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$

Dark green compound. Analytical data calculated (%) for $\text{C}_{47}\text{H}_{56}\text{Cl}_2\text{N}_6\text{O}_{12}\text{Cu}_2$: C, 51.55; H, 5.11; N, 7.67; Found (%): C, 51.76; H, 5.46; N, 7.84. Selected IR (KBr): 1631, 1105, 1096, 624 cm^{-1} . Conductance ($\Lambda_m/S \text{ cm}^2 \text{ mol}^{-1}$) in CH_3CN 292. λ_{max} (nm) ($\epsilon/M^{-1} \text{ cm}^{-1}$) in CH_3CN 648 (266), 375 (10 900), 273 (22 500).

3. Results and discussion

3.1. Spectral studies

All the complexes were characterized by spectral studies. IR spectra of the complexes show a $\nu(\text{C}=\text{N})$ absorption [19] at 1620–1640 cm^{-1} . All the binuclear complexes show a split perchlorate band [20] near 1100 and 1090 cm^{-1} . This splitting could reflect a lowering of the symmetry of the perchlorate group owing to coordination to the copper ion. The electronic spectra of the complexes evince three main transitions: a weak band observed in the range 587–648 nm is assigned to d–d transition of the metal ion. An increase in λ_{max} (red shift) [21] of the d–d transition of Cu(II) ion in the complexes from L^{1a} to L^{1c} was observed for binuclear copper(II) complexes. A moderately intense band observed in the range 365–375 nm is due to a ligand-to-metal charge transfer transition and the strong band observed in the range 270–275 nm is due to an intraligand charge transfer transition [22].

A broad peak centred at $g=2.11$ is obtained for binuclear copper(II) complexes due to the antiferromagnetic interaction between two copper nuclei arises from

the spin–spin coupling of the electrons of both the copper ions. The ESR spectrum of the binuclear copper(II) complex $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$ is shown in Fig. 1.

3.2. Magnetic studies

The observed room temperature magnetic moment for binuclear copper(II) complexes ranges from 1.52 to 1.59 B.M.: $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$, 1.52 B.M.; $[\text{Cu}_2\text{L}^{1b}](\text{ClO}_4)_2$, 1.56 B.M.; $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$, 1.59 B.M. This confirms the presence of an antiferromagnetic interaction between the two copper(II) ions. The calculated room temperature μ_{eff} values of all the complexes are almost same. So, to evaluate the singlet–triplet energy separation ($-2J$), a variable-temperature magnetic study of only one complex $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$ as a reference for the others was carried out in the temperature range 77–300 K and the experimental magnetic susceptibility values were fitted to the modified Bleaney-Bowers equation.

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

In which N_α and g have been fixed as $60 \times 10^{-6} \text{ cm}^3 \text{ M}^{-1}$ and 2.20, respectively. χ_m is the molar magnetic susceptibility corrected for diamagnetism, P is the percentage of monomeric impurities and other symbols have their usual meaning. $-2J$ values were evaluated by a nonlinear regression analysis in which $-2J$, P and g are the variable. Fig. 2 depicts the temperature dependence magnetic properties of complex $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$.

With few exceptions magneto-structural correlations for several phenoxo-bridged [12] dicopper complexes show that the major factor controlling the exchange interactions is the Cu–O–Cu bridge angle; however other factors [23] such as the degree of distortion from planarity [24] and the dihedral angle [25] between two copper planes also have influence on the extent of spin–

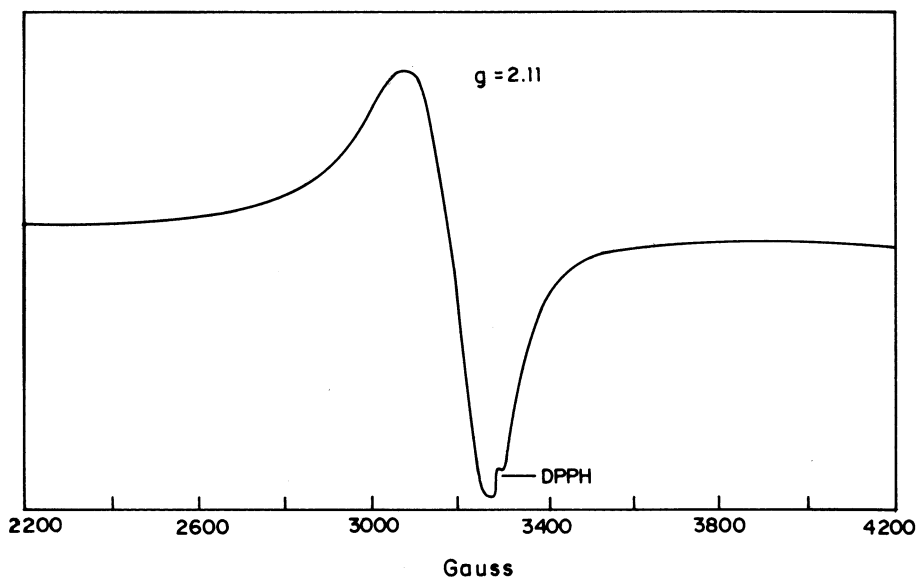


Fig. 1. ESR spectra of $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$.

spin interaction. Generally phenoxo-bridged planar dicopper complexes with $\text{Cu}-\text{O}_{\text{ph}}-\text{Cu}$ 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 ($< 70\text{ cm}^{-1}$) [12]. Thompson et al. reported [12] that for symmetrical planar complexes with bridge angle greater than 99° the $-2J$ values are $\approx 500\text{--}700\text{ cm}^{-1}$. But Okawa et al. [24] 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. For the complex $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$ the observed exchange interaction value ($-2J$) is 236 cm^{-1} . The distortion of the geometry [24] and the deviation from co-planarity [23] may be the possible reasons for this low exchange interaction value.

3.3. Electrochemistry

Conductivity measurements [20] of binuclear copper(II) complexes in acetonitrile indicate that the complexes are 2:1 electrolyte type ($260\text{--}292\text{ }\Lambda_{\text{m}}/\text{S cm}^2\text{ mol}^{-1}$).

The macrocyclic doubly phenoxo-bridged dicopper complexes typically undergo two well-separated one-electron reductions [26–28]. The electronegativity and hard nature of the phenoxide ligands [28] influence the electrochemical properties of the complexes. Electrochemical properties of the complexes reported in the present work were studied by cyclic voltammetry in the potential range -0.2 to -1.5 V in dimethylformamide containing 10^{-1} M tetra(*n*-butyl)ammonium perchlorate and the data are summarized in Table 1. Fig. 3 depicts the cyclic voltammograms for the binuclear

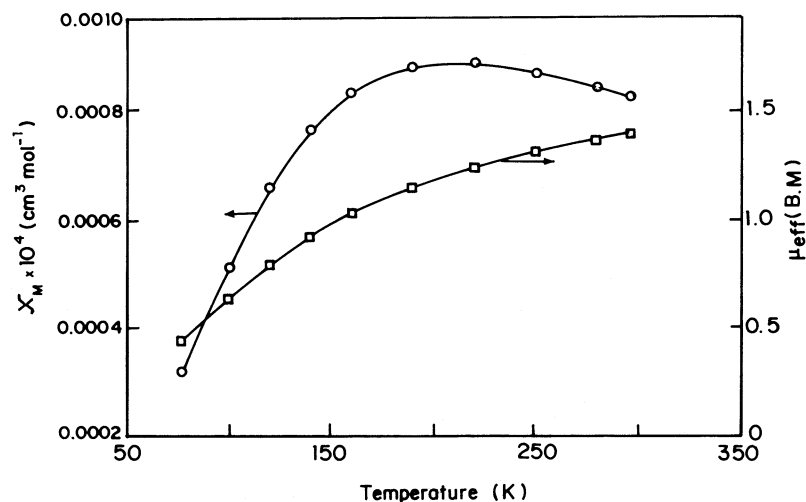


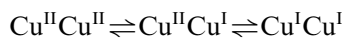
Fig. 2. Temperature dependence magnetic properties of complex $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$.

Table 1
Electrochemical data^a of binuclear copper(II) complexes in DMF medium

Complexes	E_{pc}^1 (V)	E_{pa}^1 (V)	$E^{1/2}$ (V)	ΔE (mV)	E_{pc}^2 (V)	E_{pa}^2 (V)	$E^{1/2}$ (V)	ΔE (mV)	K_{con}
$[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$	-0.86	-0.72	-0.79	140	-1.29	-1.17	-1.23	120	2.78×10^7
$[\text{Cu}_2\text{L}^{1b}](\text{ClO}_4)_2$	-0.81	-0.69	-0.75	120	-1.05	-1.05	-1.10	100	8.36×10^5
$[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$	-0.75	-0.65	-0.70	100	-0.99	-0.89	-0.94	100	1.15×10^4

^a Measured by CV at 25 mV s^{-1} . E vs. Ag/AgCl conditions: GC working and Ag/AgCl reference electrodes; supporting electrolyte TBAP; concentration of complex $1 \times 10^{-3} \text{ M}$, concentration of TBAP $1 \times 10^{-1} \text{ M}$.

complexes. Binuclear complexes are characterized by two well defined quasireversible reductions waves. The first reduction potential ranges from -0.75 to -0.86 V and the second reduction potential lies in the range -0.99 to -1.29 V . Controlled potential electrolysis was also carried out and the experiment reports that the each couple corresponding to one electron transfer process. So, the two redox processes are assigned as follows,



The comproportionation constant for the equilibrium



was calculated using the relationship $\log K_{con} = \Delta E / 0.0591$ [13].

The interesting feature noted for the binuclear complexes is a shift in both first and second reduction potentials towards anodic potential from -0.86 to

-0.75 V and from -1.29 to -0.99 V , respectively, as the chelate ring size is increased. For example the complex $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$ has $E_{pc}^1 = -0.86 \text{ V}$ and $E_{pc}^2 = -1.29 \text{ V}$, which is more negative compared to the complex $[\text{Cu}_2\text{L}^{1b}](\text{ClO}_4)_2$ ($E_{pc}^1 = -0.81 \text{ V}$, $E_{pc}^2 = -1.15 \text{ V}$) which in turn more compared to the complex $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$ ($E_{pc}^1 = -0.75 \text{ V}$, $E_{pc}^2 = -0.99 \text{ V}$). Thus as the chain length of imine compartment increases, the whole macrocyclic ring size increases and becomes more flexible owing to easy reduction [29]. Thus the large size of cavity easily hold the reduced cation and stabilizes the formation of Cu(I) in both the compartments. Hence, there arises problem of assigning the potential of different coordinating sites. Even though the role of planarity and rigidity is well understood, it is not unambiguous to assign which metal ion is reduced first. In our earlier report [14] we have discussed the electrochemistry of corresponding mononuclear copper(II)

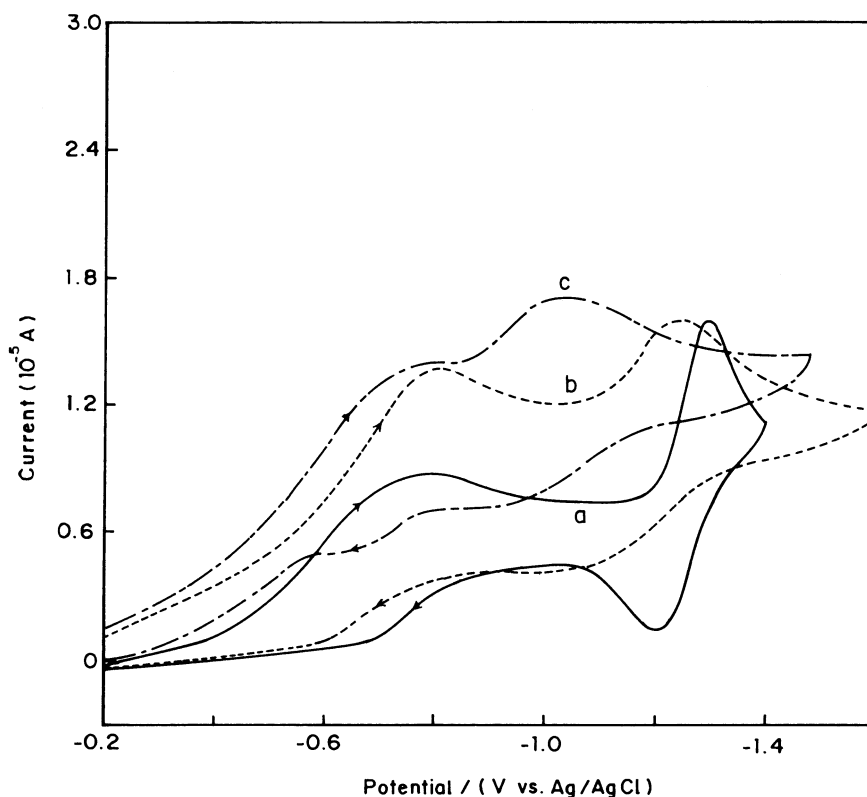


Fig. 3. Cyclic voltammograms of the binuclear copper(II) complexes. (a) $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$ (b) $[\text{Cu}_2\text{L}^{1b}](\text{ClO}_4)_2$ (c) $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$.

complexes. According to the X-ray crystal structure of mononuclear copper(II) complex $[\text{CuL}^{1c}]$ the copper ion presents in the imine nitrogen compartment and during reduction copper(II) ions reduced in the range of -0.80 to -0.90 V. In the case of binuclear the copper(II) complex, the observed first reduction potential lies in the range of -0.75 to -0.86 V and this is almost the same as that observed for mononuclear copper(II) complexes. So between the two compartments in which metal is flanked, the unsaturated imine nitrogen compartment is considered to be reduced first, followed by the saturated nitrogen compartment, according to literature [30]. Though the imine nitrogen compartment has less flexibility, it is assigned to undergo the first reduction. This is mainly because of the presence of unsaturation. This factor reduces the electron density of the metal ion and hence facilitates the easy reduction of the respective metal ion. Thus in assigning the reduction potentials, the imine nitrogen compartment is given first priority followed by the tertiary nitrogen compartment. Another interesting feature that was inferred for these complexes from the calculation of K_{con} values. The decrease in K_{con} value for the complexes of ligands L^{1a} – L^{1c} (2.78×10^7 , 8.36×10^5 , 1.15×10^4 , respectively), indicates that the peak separation between $E_{1/2}^1$ and $E_{1/2}^2$ also decreases. The reduction potential of the second metal ion is highly influenced by the electron density in the first metal ion through exchange interaction in binuclear copper(II) complexes [31]. The increase in ring size around the first metal center produces more distortion of the geometry and the added electron is localized in the first metal ion itself and its impact on the other metal ion is negligible. 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.

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

All the complexes synthesized so far were investigated for catecholase activity. The product *o*-quinone is considerably stable and has a strong absorbance at 390 nm. Therefore, activities and reaction rates, respectively, can be determined using electronic spectroscopy by following the appearance of the absorbance maximum of the quinone. For this purpose, 10^{-3} M $^{-3}$ solutions of the complexes in acetonitrile were treated with 50 equiv. of pyrocatechol in the presence of air.

The course of the reaction was followed by UV–Vis spectroscopy over the first 5–30 min at regular intervals. 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.

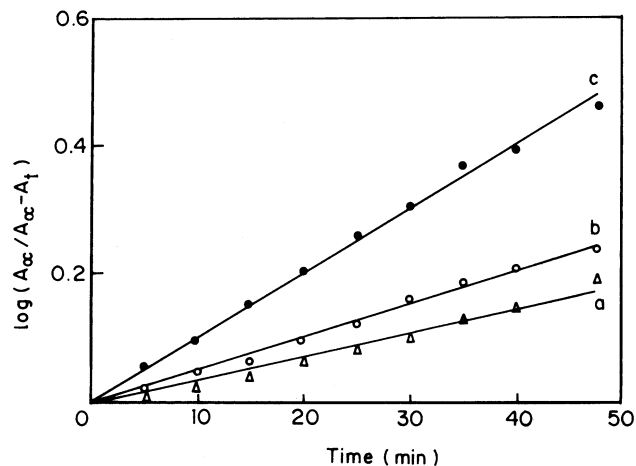


Fig. 4. Catecholase activity of binuclear copper(II) complexes. (a) $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$ (b) $[\text{Cu}_2\text{L}^{1b}](\text{ClO}_4)_2$ (c) $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$.

A plot of $\log(A_{\infty}/A_{\infty} - A_t)$ vs. time for catecholase activity of the complexes are obtained and shown in Fig. 4. The observed initial rate constant value for $[\text{Cu}_2\text{L}^{1b}](\text{ClO}_4)_2$ is $0.97 \times 10^{-2} \text{ min}^{-1}$, for $[\text{Cu}_2\text{L}^{1a}](\text{ClO}_4)_2$ is $1.24 \times 10^{-2} \text{ min}^{-1}$ and for $[\text{Cu}_2\text{L}^{1c}](\text{ClO}_4)_2$ is $2.30 \times 10^{-2} \text{ min}^{-1}$. For binuclear copper(II) complexes the value of rate constant increases from 0.97×10^{-2} to $2.30 \times 10^{-2} \text{ min}^{-1}$ as we move from L^{1a} to L^{1c} . The catalytic activity of the complexes are found to increase as the macrocyclic ring size increases due to the intrinsic flexibility and the same was supported by both spectral and electrochemical studies.

4. Conclusion

New lateral macrobicyclic tricompartamental binucleating ligands and their binuclear copper(II) complexes have been synthesized and characterized. From these studies it is understood that a small variation in ring size induces a greater influence on structural, magnetic, electrochemical and catalytic properties of the complexes. An extension of this work involving the synthesis of another series of binuclear and polynuclear complexes is currently explored.

Acknowledgements

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