Coordination Behaviour of Novel Macrobicyclic Tricompartmental Ligands: Synthesis, Magnetic, Electrochemical and Kinetic Studies of Unsymmetrical Mono- and Binuclear Copper(II) Complexes

M. Thirumavalavan[a]; P. Akilan[a]; M. Kandaswamy[a]

[a] Department of Inorganic Chemistry, University of Madras, Chennai, India

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Coordination Behaviour of Novel Macrobicyclic Tricompartmental Ligands: Synthesis, Magnetic, Electrochemical and Kinetic Studies of Unsymmetrical Mono- and Binuclear Copper(II) Complexes

M. THIRUMAVALAVAN, P. AKILAN and M. KANDASWAMY*

Department of Inorganic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

Several mono- and binuclear copper(II) complexes of general formula [CuL](ClO$_4$) and [Cu$_2$L(ClO$_4$)](ClO$_4$) have been synthesized from macrobicyclic ligands having different compartments originating from their corresponding precursor compound (PC: 3,4:9, 10-dibenzo-1,12[N,N'-bis{(3-formyl-2-hydroxy-5-methyl)-benzyl}diaza]-5,8-dioxacyclohexadecane). Electrochemical studies show that one quasi-reversible reduction wave ($E_{pc} = -0.75$ to -0.83 V) for the mononuclear complexes and two quasi-reversible one-electron transfer reduction waves ($E_{pc}^1 = -0.78$ to -0.86 V, $E_{pc}^2 = -1.01$ to -1.28 V) for the binuclear complexes are obtained in the cathodic region. Room temperature magnetic moment studies indicate the presence of antiferromagnetic coupling in the binuclear complexes ($\mu_{eff} = 1.44-1.56$ BM), which is confirmed by the broad ESR spectra with $g = 2.10-2.11$, whereas the mononuclear complexes show hyperfine splitting in the ESR spectra and have magnetic moment values close to the spin-only value ($\mu_{eff} = 1.69-1.72$ BM). Variable temperature magnetic susceptibility study of the complex finds that the observed $-2J$ values for the binuclear complexes [Cu$_2$L^1(ClO$_4$)](ClO$_4$) and [Cu$_2$L^4(ClO$_4$)]-(ClO$_4$) are 216 cm^{-1} and 236 cm^{-1}, respectively. The observed initial rate constant values for catechol oxidation using the complexes as catalysts range from 6.57×10^{-3} to 4.93×10^{-2} min^{-1} and the values are found to be higher for the binuclear complexes than the corresponding mononuclear complexes. 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.

Keywords: Macrobicyclic ligands; Unsymmetrical copper(II) complexes; Electrochemistry; Magnetic studies; Catalysis

INTRODUCTION

An investigation into the design and synthesis of new macrocyclic ligands with various functionalities is a key factor in the advancement of coordination chemistry. In particular, such strategies have been useful in modifying the coordination ability of transition metals with relevance to their biomimetic properties. The major thrust of the research programme is at the interface of functional models, catalysis and new materials chemistry. Many biochemical transformations as well as important synthetic and industrial processes are catalysed by metal ions. Recent efforts have focused on understanding the mechanism of multicentre metalloproteins, and the design and synthesis of new multinuclear compartmental macrocyclic polyamine ligands are of current interest because they form stable complexes with transition element and heavy metal ions [1]. Current awareness of the asymmetric nature of a number of homo- or heterobinuclear transition metal-derived metallobiosites and of the ability of the individual metal ions to have distinct roles in the functioning of the metalloenzyme concerned has led to a search for carefully designed unsymmetric binucleating ligands that will give binuclear complexes capable of acting as models for the metallobiosites [2–4]. Macrocyclic dicopper(II) complexes [5–13] derived from symmetric binucleating ligands have been prepared and investigated as potential model complexes for metallobiosites,

*Corresponding author. Fax: +91-44-2230-0488. E-mail: mkands@yahoo.com

but polydentate ligand systems that would give necessarily asymmetric binuclear complexes remain rare [4]. More recently, a synthetic route based on the reaction of 3-chloromethyl-5-methylsalicylaldehyde with functionalized secondary amines followed by Schiff base condensation with functionalized secondary amines has provided a further range of unsymmetric proligands [14–17]. In the present work we have prepared the donor precursor compounds for asymmetric compartmental ligands and the asymmetry arising from the mixture of sp^2 and sp^3 N atoms available for metal coordination. These ligands were then treated with copper(II) salts to derive macrobicyclic mono- and binuclear copper(II) complexes.

The new macrobicyclic tricompartmental copper(II) complexes contain nitrogen and oxygen donor atoms. The first compartment (N_2O_2) comprises two ether oxygens and two tertiary nitrogens, the second compartment (N_2O_2) two tertiary nitrogens and two phenolic oxygens, and the third compartment (N_2O_2) two phenolic oxygens and two imine nitrogens. The cavity size and the shape of the host molecule can be varied to study the coordination properties of the ligands.

RESULTS AND DISCUSSION

Macrobicyclic mono- and binuclear copper(II) complexes were synthesized by Schiff's base condensation of the precursor compound with diamines in the presence of metal ion by the template method. In our earlier work we reported the crystal structure of similar types of mono- and binuclear copper(II) complexes [18]. Hence, with respect to this work it is proposed that the geometry around the copper(II) ion in the mononuclear complex is distorted square planar and one of the tertiary nitrogen atoms is protonated. In the binuclear copper(II) complex one copper(II) ion is four coordinated and another copper(II) ion is five coordinated. Conductivity measurements also indicate that both mono- and binuclear copper(II) complexes are 1:1 electrolyte type. The complexes were characterized by spectral, magnetic, electrochemical studies and catalytic studies of the complexes were carried out.

Spectral Studies

IR spectra of the complexes show a ν(C=N) peak [19] at 1620–1630 cm^{-1}. The formation of this new peak and the disappearance of the ν(C=O) peak at 1678 cm^{-1} in the complexes are indicative of effective Schiff base condensation. The mononuclear complexes show peaks near 1100 cm^{-1} and 620 cm^{-1} characteristic of the uncoordinated perchlorate ion. The binuclear complexes show two peaks near
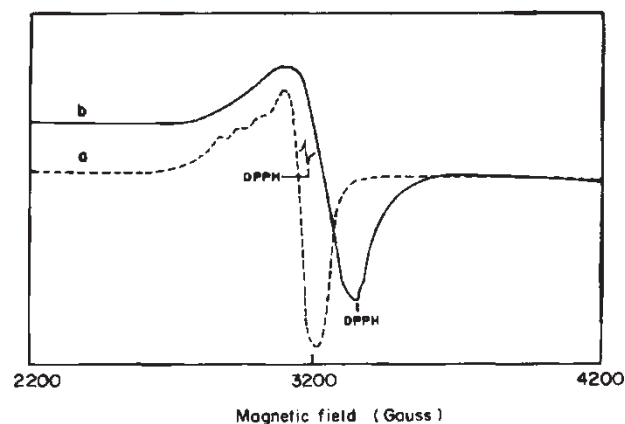

FIGURE 1 ESR spectra of (a) $[CuL^1]ClO_4$ and (b) $[Cu_2L^1(ClO_4)](ClO_4)$.

1100 cm^{-1} and one peak near 620 cm^{-1}. Of the two peaks, one peak is split [20] due to the presence of the coordinated perchlorate ion while the other peak due to the presence of the uncoordinated perchlorate ion does not show any splitting. The electronic spectra of the complexes were observed as three main transitions. A weak band observed in the range 595–655 nm is due to the d–d transition of the metal ion. An increase in λ_{max} (red shift) [21] of the d–d transition of the copper(II) ion in the complexes from L^1 to L^3 and L^4 to L^5 was observed for both mono- and binuclear copper(II) complexes. A moderately intense band observed in the range 357–378 nm is due to a ligand-to-metal charge transfer transition and the strong band observed in the range 263–287 nm is due to an intraligand charge transfer transition [22]. In the case of complexes of ligands L^4 and L^5, additional peaks are observed, which may be due to the presence of the aromatic ring in the imine nitrogen compartment.

The solid-state ESR spectra of the mononuclear copper(II) complexes show four lines with nuclear hyperfine spin 3/2 due to hyperfine splittings. For the mononuclear complexes the observed $g_\parallel$ values fall in the range 2.19 to 2.25 and $g_\perp$ values vary from 2.00 to 2.06. A broad spectrum centred at $g = 2.10$–2.11 is observed for the binuclear copper(II) complexes due to the antiferromagnetic interaction between the two copper ions. Figure 1 shows the ESR spectra of the mono- and binuclear copper(II) complexes of ligand L^1.

Magnetic Studies

The room temperature magnetic studies of the mononuclear copper(II) complexes resulted in magnetic moment values (1.69–1.72 BM) that are very close to the spin-only value (1.73 BM) expected for complexes having one copper(II) ion [23] with a single unpaired electron sited in an essentially d_{x^2/y^2} orbital. The observed room temperature magnetic

TABLE I   ESR spectral and room temperature magnetic moment data of mono- and binuclear copper(II) complexes

Complex	$g_{\parallel}$	$g_{\perp}$	g	μ_{eff} (BM)
$[CuL^1](ClO_4)$	2.25	2.00	–	1.72
$[CuL^2](ClO_4)$	2.23	2.01	–	1.71
$[CuL^3](ClO_4)$	2.19	2.01	–	1.71
$[CuL^4](ClO_4)$	2.23	2.06	–	1.71
$[CuL^5](ClO_4)$	2.21	2.03	–	1.69
$[Cu_2L^1(ClO_4)](ClO_4)$	–	–	2.11	1.48
$[Cu_2L^2(ClO_4)](ClO_4)$	–	–	2.11	1.53
$[Cu_2L^3(ClO_4)](ClO_4)$	–	–	2.10	1.56
$[Cu_2L^4(ClO_4)](ClO_4)$	–	–	2.10	1.39
$[Cu_2L^5(ClO_4)](ClO_4)$	–	–	2.11	1.44

moment values for the binuclear copper(II) complexes range from 1.39 to 1.56 BM confirming the presence of an antiferromagnetic interaction between the two copper(II) ions. Table I shows the ESR spectral and magnetic moment data for the mono- and binuclear copper(II) complexes. To evaluate the singlet-triplet energy separation $(-2J)$, a variable-temperature magnetic study of the binuclear complexes was carried out at the temperature range $77-300$ K and the experimental magnetic susceptibility values were fitted to the modified Bleany–Bowers equation [24]:

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

$$+ 0.45P/T + N_\alpha$$

where N_α and g have been fixed at $60 \times 10^{-6}\,\text{cm}^3\,\text{M}^{-1}$ and 2.20, respectively. χ_m is the molar magnetic susceptibility corrected for diamagnetism, P is the percentage of monomeric impurities and the other symbols have their usual meaning. The $-2J$ values
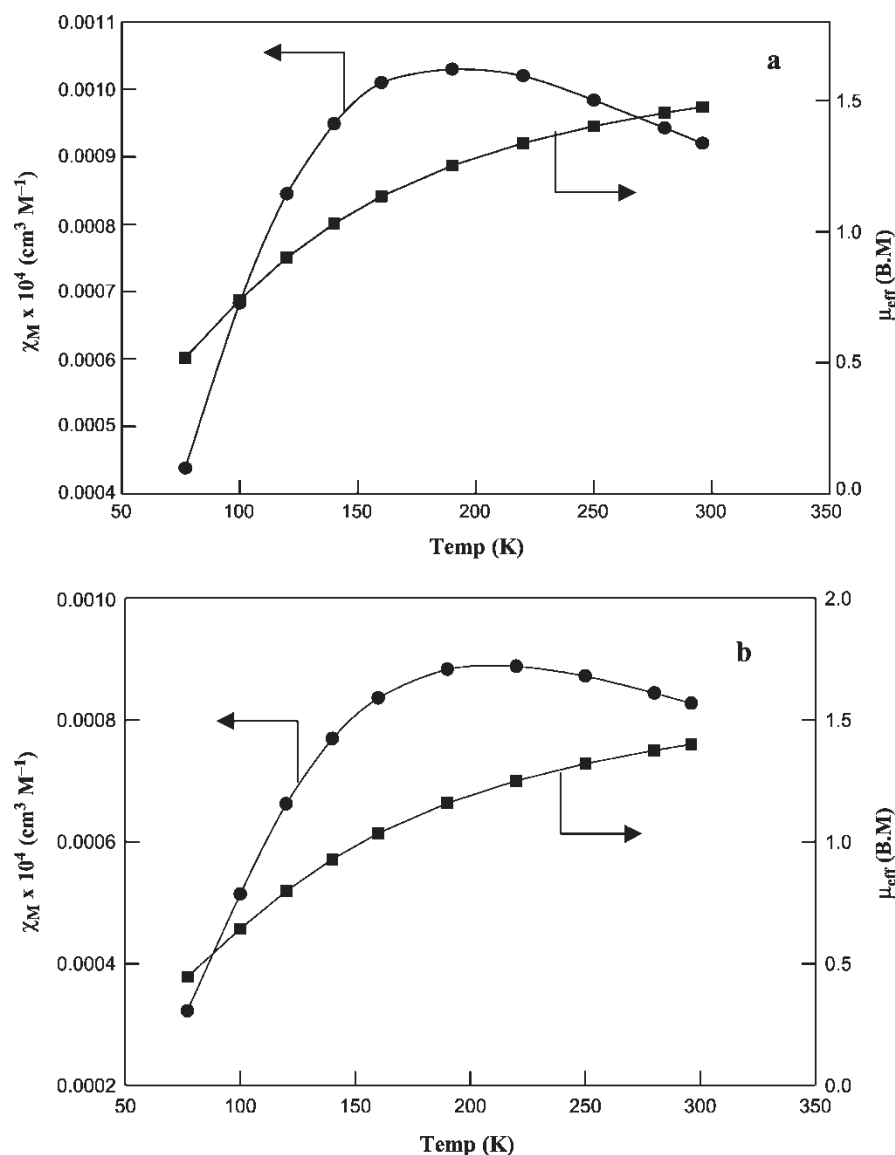
FIGURE 2   Temperature-dependent magnetic properties of complexes $[Cu_2L^{1b}](ClO_4)_2$: (a) $[Cu_2L^1(ClO_4)](ClO_4)$; (b) $[Cu_2L^4(ClO_4)](ClO_4)$.

were evaluated by a nonlinear regression analysis in which $-2J$, P and g are the variables. Figure 2 shows the temperature-dependent magnetic properties of the complexes $[Cu_2L^1(ClO_4)](ClO_4)$ and $[Cu_2L^4(ClO_4)](ClO_4)$.

With few exceptions magneto-structural correlations for several phenoxo bridged [25] dicopper complexes show that the major factor controlling the exchange interactions is the Cu–O–Cu bridge angle; however, other factors [26] such as degree of distortion from planarity [27] and the dihedral angle [28] between the two copper planes also have an 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 ($<70 \, cm^{-1}$) [22]. Thompson *et al.* [25] reported that for symmetrical planar complexes with the bridge angle greater than $99°$ the $-2J$ values are ≈ 500 to $700 \, cm^{-1}$. However, Okawa *et al.* [27] reported that for the distorted copper(II) complexes the $-2J$ value is $220 \, cm^{-1}$. This low value is due to the distortion of the geometry of one of the copper(II) ions, which causes a deviation from co-planarity. For the complexes $[Cu_2L^1(ClO_4)](ClO_4)$ and $[Cu_2L^4(ClO_4)](ClO_4)$ the observed exchange interaction values ($-2J$) are $216 \, cm^{-1}$ and $236 \, cm^{-1}$, respectively. The distortion of the geometry [27] and the deviation from co-planarity [26] may be the reasons for this low exchange interaction value. The observed room temperature magnetic moment values of the binuclear copper(II) complexes containing aromatic diamines are lower than those of complexes containing aliphatic diamines. This is mainly because the planarity of N_2O_2 of the imine nitrogen compartment is greater in the case of complexes containing aromatic diamines. Thus the greater planarity causes the higher exchange interaction and hence the lower magnetic moment values.

Electrochemistry

Conductivity measurements [20] of the mono- and binuclear copper(II) complexes in acetonitrile resulted in values ranging from 128 to $160 \, \Lambda_m / S \, cm^2 \, mol^{-1}$ and this indicates that the complexes are of the 1:1 electrolyte type. Usually phenoxo copper complexes undergo reduction at negative potentials due to the electronegativity and hard nature of the phenoxide atoms in the ligands [29,30]. Electrochemical properties of the complexes reported in the present work were studied by cyclic voltammetry in the potential range 0 to $-1.5 \, V$ in dimethylformamide containing $10^{-1} \, M$ tetra(n-butyl)ammonium perchlorate and the data are summarized in Table II. The cyclic voltammograms for the mononuclear complexes are shown in Fig. 3. Each voltammogram shows one quasi-reversible reduction wave at negative potential in the range -0.75 to $-0.83 \, V$. Controlled potential electrolysis carried out at $100 \, mV$ more negative than the reduction wave ratifies the consumption of one electron per molecule ($n = 0.96$) and the experiment shows that the couple corresponds to a one-electron transfer process. Figure 4 shows the cyclic voltammograms of the binuclear complexes. The binuclear complexes are associated with two quasi-reversible reduction waves. The first reduction potential ranges from -0.79 to $-0.86 \, V$ and the second reduction potential lies in the range -1.01 to $-1.28 \, V$. Controlled potential electrolysis was also carried out and the experiment indicates that each couple corresponds to a one-electron transfer process. Thus, the two redox processes can be 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 $\log K_{con} = \Delta E / 0.0591$.

TABLE II Electrochemical data* of mono- and binuclear copper(II) complexes in DMF

Complex	E^1_{pc} (V)	E^1_{pa} (V)	$E^1_{1/2}$ (V)	ΔE (mV)	E^2_{pc} (V)	E^2_{pa} (V)	$E^2_{1/2}$ (V)	ΔE (mV)	K_{con}
$[CuL^1](ClO_4)$	-0.82	-0.66	-0.74	160	–	–	–	–	–
$[CuL^2](ClO_4)$	-0.79	-0.64	-0.72	150	–	–	–	–	–
$[CuL^3](ClO_4)$	-0.75	-0.61	-0.68	140	–	–	–	–	–
$[CuL^4](ClO_4)$	-0.83	-0.68	-0.76	150	–	–	–	–	–
$[CuL^5](ClO_4)$	-0.75	-0.62	-0.67	130	–	–	–	–	–
$[Cu_2L^1(ClO_4)](ClO_4)$	-0.84	-0.75	-0.80	90	-1.25	-1.16	-1.21	90	8.66×10^6
$[Cu_2L^2(ClO_4)](ClO_4)$	-0.80	-0.72	-0.76	80	-1.12	-1.04	-1.08	80	2.59×10^5
$[Cu_2L^3(ClO_4)](ClO_4)$	-0.78	-0.71	-0.75	70	-1.01	-0.94	-0.98	70	5.28×10^3
$[Cu_2L^4(ClO_4)](ClO_4)$	-0.86	-0.75	-0.81	110	-1.28	-1.18	-1.23	100	1.28×10^7
$[Cu_2L^5(ClO_4)](ClO_4)$	-0.80	-0.70	-0.75	100	-1.19	-1.10	-1.15	90	5.86×10^6

*Measured by CV at $50 \, mV \, s^{-1}$. E vs Ag/AgCl conditions: GC working and Ag/AgCl reference electrodes; supporting electrolyte TBAP; concentration of complex $1 \times 10^{-3} \, M$, concentration of TBAP $1 \times 10^{-1} \, M$.
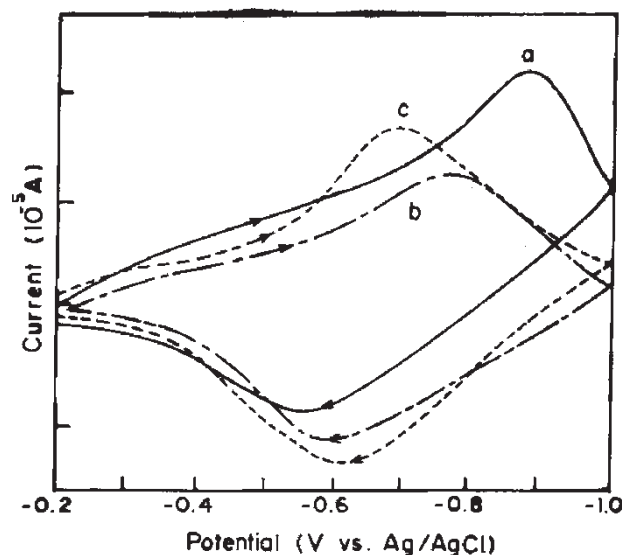
FIGURE 3 Cyclic voltammograms of the mononuclear copper(II) complexes $(1 \times 10^{-3}\,M)$: (a) $[CuL^1](ClO_4)$, (b) $[CuL^2](ClO_4)$ and (c) $[CuL^3](ClO_4)$.

It is of interest to compare the electrochemical behaviour of the complexes. The reduction potential of the mononuclear copper(II) complexes of ligands L^1 to L^3 shifts towards the anode from $-0.83\,V$ to $-0.75\,V$ as the number of methylene group between the imine nitrogens is increased and in turn increases the macrocyclic ring size. This is observed also in the case of L^4 to L^5. This causes more flexibility in the macrocyclic ring [31–34] and helps to stabilize the copper(I) complex. The complexes with aromatic diimines are reduced at a somewhat higher potential than that of the complexes with aliphatic diimines because of the more planar nature. The observed ΔE
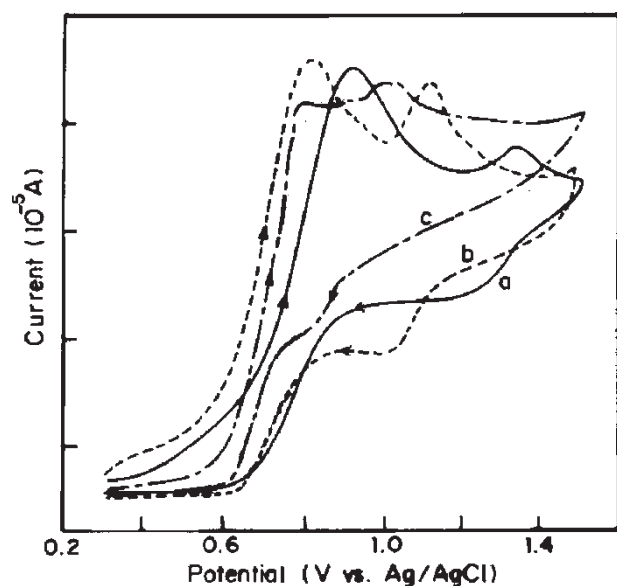

FIGURE 4 Cyclic voltammograms of the binuclear copper(II) complexes $(1 \times 10^{-3}\,M)$: (a) $[Cu_2L^1(ClO_4)](ClO_4)$, (b) $[Cu_2L^2 (ClO_4)](ClO_4)$ and (c) $[Cu_2L^3(ClO_4)](ClO_4)$.

values for the mononuclear complexes are larger than the corresponding binuclear complexes and this may be attributed to the occurrence of electrochemical interconversion (translocation) [35] of reduced cation copper(I) from the rigid imine nitrogen compartment (N_2O_2) to the flexible tertiary nitrogen compartment (N_2O_2), which favours a tetrahedral geometry. The larger ΔE values also indicate that the reduction process is associated with an ECE mechanism, that is when an input voltage is applied the copper(II) ion is reduced first to copper(I) (electron transfer) and this reduced copper(I) is then translocated from the rigid compartment to the flexible compartment (chemical phenomenon), which in turn is oxidized to copper(II) (electron transfer) and finally reverts back to its original position (chemical phenomenon). It is also ratified that the decrease in ΔE as the chain length between the two imine nitrogens increases assists the translocation process and favours the tetrahedral geometry [14] moving from the complexes of ligands L^1 to L^3 and L^4 to L^5. The interesting feature for the binuclear complexes is the shift of both first and second reduction potentials towards the anode from -0.86 to $-0.79\,V$ and from -1.28 to $-1.01\,V$, respectively, as the number of methylene group is increased. For example, the complex $[Cu_2L^1(ClO_4)]$ (ClO_4) has values $E^1_{pc} = -0.84\,V$ and $E^2_{pc} = -1.25\,V$, which are more negative than values for the complex $[Cu_2L^2(ClO_4)](ClO_4)$ $(E^1_{pc} = -0.80\,V, E^2_{pc} = -1.12\,V)$, and for the complex $[Cu_2L^3(ClO_4)](ClO_4)$ $(E^1_{pc} = -0.78\,V, E^2_{pc} = -1.01\,V)$. Thus as the chain length of the imine compartment increases, the whole macrocyclic ring becomes more flexible, which causes easy reduction. Thus the large size of the cavity easily holds the reduced cation and stabilizes the formation of copper(I) in both compartments. Another interesting feature was inferred for the binuclear copper(II) complexes from the calculation of K_{con} values. The decrease in the K_{con} value for the complexes of ligands L^1 to L^3 $(8.66 \times 10^6, 2.59 \times 10^5, 5.28 \times 10^3)$ and of ligands L^4 to L^5 $(1.28 \times 10^7, 5.86 \times 10^6)$ can be explained by the fact 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. This is because the increase in ring size produces more distortion of the geometry around the metal centre and the added electron is localized in the first metal ion 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 takes places more readily.

An attempt was made to compare the results of the present work with previous work [15,18] and this led to the interesting result that an increase in the macrocyclic ring size in the tertiary amine nitrogen site influences the electrochemical properties of

the complexes, whereas an increase in the macro-cyclic ring size in the ether oxygen site has little influence on the redox properties of the complexes. For example, it can be seen that the redox potential of the complexes reported in our earlier work [18] is greater than that of the complexes reported here and these complexes differ in macrocyclic ring size in the tertiary amine nitrogen site. However, comparing the results of the present work with our other previous work [15], the redox potential of the complexes does not differ significantly and these complexes differ in macrocyclic ring size in the ether oxygen site. Hence, it can be stated that, in general, an increase in macrocyclic ring size favours the ease of reduction of the metal ions in the complexes.

Kinetic Studies of Oxidation of Catechol (Catecholase Activity)

All of the complexes synthesized so far were subjected to catecholase activity. The product *o*-quinone is fairly stable and has a strong absorbance at 390 nm. For this purpose, 10^{-3} mol dm^{-3} solutions of complexes in acetonitrile were treated with 50 equivalents of 3,5-di-*tert*-butylcatechol in the presence of oxygen.

The course of the reaction was followed at 390 nm for nearly 45 min at regular time intervals. The slope was determined by the method of initial rates by monitoring the growth of the 390-nm band of the product *o*-quinone. A linear relationship for the initial rate and the complex concentration obtained for all the complexes shows a first-order dependence on the complex concentration for the systems.

Plots of $\log(A_\infty/A_\infty - A_t)$ vs time for catecholase activity of some of the binuclear complexes are shown in Fig. 5, respectively. The rate constant
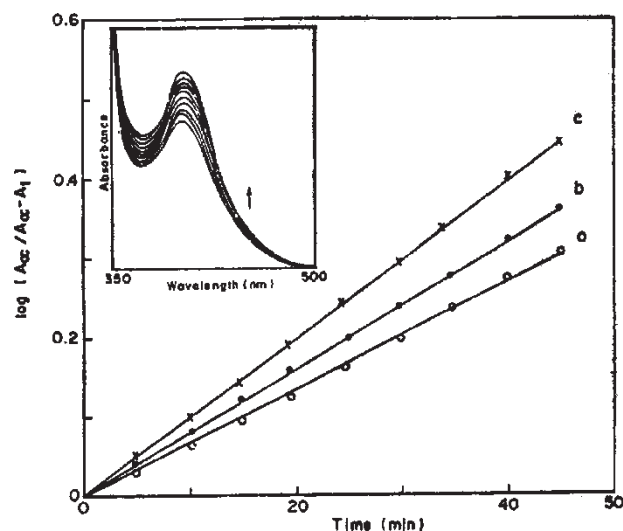
TABLE III Catecholase activity* of mono- and binuclear copper(II) complexes

Complex	Rate constant (min^{-1})
[CuL^1](ClO$_4$)	6.69×10^{-3}
[CuL^2](ClO$_4$)	7.85×10^{-3}
[CuL^3](ClO$_4$)	8.08×10^{-3}
[CuL^4](ClO$_4$)	6.57×10^{-3}
[CuL^5](ClO$_4$)	7.80×10^{-3}
[Cu$_2$L^1(ClO$_4$)](ClO$_4$)	2.53×10^{-2}
[Cu$_2$L^2(ClO$_4$)](ClO$_4$)	3.96×10^{-2}
[Cu$_2$L^3(ClO$_4$)](ClO$_4$)	4.93×10^{-2}
[Cu$_2$L^4(ClO$_4$)](ClO$_4$)	1.77×10^{-2}
[Cu$_2$L^5(ClO$_4$)](ClO$_4$)	2.83×10^{-2}

*Measured spectrophotometrically in CH$_3$CN. Concentration of the complexes: 1×10^{-3} M. Concentration of 3,5-di-*tert*-butylcatechol: 1×10^{-1} M.

values are reported in Table III. The first apparent result was that the reactivities of the complexes differ significantly. The binuclear complexes have higher activities than the mononuclear complexes [36–40]. For example, the binuclear complexes [Cu$_2$L^1(ClO$_4$)](ClO$_4$), [Cu$_2$L^2(ClO$_4$)]-(ClO$_4$), [Cu$_2$L^3(ClO$_4$)](ClO$_4$), [Cu$_2$L^4(ClO$_4$)](ClO$_4$) and [Cu$_2$L^5(ClO$_4$)](ClO$_4$) have the rate constant values 2.53×10^{-2}, 3.96×10^{-2}, 4.93×10^{-2}, 1.77×10^{-2} and 2.83×10^{-2} min^{-1}, respectively, whereas the mononuclear complexes [CuL^1](ClO$_4$), [CuL^2](ClO$_4$), [CuL^3](ClO$_4$), [CuL^4](ClO$_4$) and [CuL^5](ClO$_4$) have the rate constant values 6.69×10^{-3}, 7.85×10^{-3}, 8.08×10^{-3}, 6.57×10^{-3} and 7.80×10^{-3} min^{-1}, respectively. The oxidation of catechol to *o*-quinone requires the presence of two metal ions in close proximity and hence the rate constant values of the binuclear complexes are comparatively high. The catalytic activities of both mono- and binuclear complexes are found to increase as the macrocyclic ring size increases because of the intrinsic flexibility, and therefore the metal ion is readily reduced and binds with the substrate; this was supported by both spectral and electrochemical studies. For the mononuclear complexes the observed variation in the value of the rate constant is very small when compared to that for the binuclear complexes. The rate constant value increases from 6.69×10^{-3} to 8.08×10^{-3} and from 6.57×10^{-3} to 7.80×10^{-3} min^{-1} for the mononuclear copper(II) complexes, and for binuclear complexes the increase is from 2.53×10^{-2} to 4.93×10^{-2} and from 1.77×10^{-2} to 2.83×10^{-2} min^{-1} as we move from L^1 to L^3 and L^4 to L^5. In general, the catalytic activities of the complexes containing aromatic diimines are low compared to those containing aliphatic diimines. The planarity that is associated with the aromatic ring thus imparts less catalytic efficiency because of the rigidity of the systems as observed in the case of the electrochemical reduction of the complexes.

FIGURE 5 Catecholase activity of the binuclear copper(II) complexes: (a) [Cu$_2$L^1(ClO$_4$)](ClO$_4$), (b) [Cu$_2$L^2(ClO$_4$)](ClO$_4$) and (c) [Cu$_2$L^3(ClO$_4$)](ClO$_4$).

A quantitative comparison of the catalytic activity of the complexes reported in the present study and in previously published work [18] also reveals that the increase in the macrocyclic ring size increases the catalytic activity of the complexes. For example, the catalytic activity of the complexes reported here is quantitatively higher than that of the previously reported complexes [18] because the macrocyclic ring size of the current complexes is larger than that of the previously reported complexes [18].

CONCLUSION

New macrobicyclic tricompartmental ligands and their mono- and binuclear copper(II) complexes have been synthesized by varying the diimines. Spectral, magnetic, electrochemical and catalytic studies were carried out. From both present and previous studies it is clear that a small variation in the ligand framework, such as the macrocyclic ring size in the tertiary amine nitrogen site, and the aliphatic and aromatic nature of the diimines influence the electrochemical and catalytic properties of the complexes, whereas variation in the ether oxygen site has no influence on these properties of the complexes.

EXPERIMENTAL

Elemental analysis was carried out on a Carlo Erba Model 1106 elemental analyser. ^{1}H NMR spectra were recorded using an 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 discs in the range 4000–250 cm^{-1}. Mass spectra were obtained on a JEOL DX-303 mass spectrometer. Molar conductivity was measured by using an Elico model SX 80 conductivity bridge using freshly prepared solution of the complex in CH$_3$CN. Cyclic voltammograms were obtained on a CHI600A electrochemical analyser. The measurements were carried out under oxygen-free conditions using a three-electrode cell in which the glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode and a platinum wire was used as the auxiliary electrode. A ferrocene/ferrocenium (1+) couple was used as an internal standard and $E_{1/2}$ of the ferrocene/ferrocenium (Fc/Fc$^+$) couple under the experimental condition is 470 mV in DMF and ΔE_p for Fc/Fc$^+$ is 70 mV. Tetra(n-butyl)ammonium perchlorate was used as the supporting electrolyte. Room temperature magnetic moments were 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 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 initial rate constant for the catalytic oxidation was calculated.

Materials

5-Methylsalicylaldehyde [41], 3-chloromethyl-5-methylsalicylaldehyde [42] and 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclohexadecane [43,44] were prepared by the literature methods. TBAP, used as supporting electrolyte in the electrochemical measurements, was purchased from Fluka and recrystallized from hot methanol. (Caution! TBAP is potentially explosive; care should be taken in handling this compound.) DMF and CH$_3$CN were obtained from Merck. All other chemicals and solvents were of analytical grade and were used as received without any further purification.

Synthesis of Precursor Compounds

3,4:9,10-Dibenzo-1,12[N,N'-bis{(3-formyl-2-hydroxy-5-methyl)benzyl}diaza]-5,8-dioxacyclohexadecane (PC)

A mixture of 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxa-cyclohexadecane (1.043 g, 3.2 mmol) and triethyl-amine (1.32 g, 6.4 mmol) in THF was added slowly to a stirred solution of 3-chloromethyl-5-methylsalicyl-aldehyde (1.16 g, 6.4 mmol) in THF. After the addition was over the stirring was continued for 1 h. The solution was then refluxed on a water bath for 3 h and was allowed to cool on standing at room temperature. Copious water was added to this solution to dissolve any salt obtained. 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 at room temperature (25°C). Pale yellow crystals were obtained on recrystallization from chloroform. Yield: 1.61 g (81%), mp 162°C. Mass (EI) m/z: 622 (m$^+$). Analytical data for C$_{36}$H$_{38}$O$_6$N$_2$·CHCl$_3$: Calculated (%): C, 73.31; H, 6.75; N, 4.50; Found (%): C, 73.50; H, 6.89; N, 4.61. IR data (ν cm^{-1}): 1675 (νC=O, s), 3424 (νOH, br). ^{1}H NMR (δ ppm in CDCl$_3$): ~10.0 (s, 2H, CHO protons), ~7.2 (m, 12H, aromatic protons), ~4.5 (m, 4H, methylene protons attached to oxygen atom) ~3.8 (m, 8H, benzylic protons), ~3.5 (s, 4H, methylene protons attached to

nitrogen atom), ~ 2.5 (s, 6H, aromatic CH_3 protons), ~ 2.0 (s, 4H, CH_2 protons attached to alkyl chain).

Synthesis of Macrobicyclic Mononuclear Copper(II) Complexes

[CuL^1](ClO$_4$)

A methanolic solution of copper(II)perchlorate hexahydrate (0.676 g, 1.8 mmol) was added to the hot solution of PC (1.119 g, 1.8 mmol) in $CHCl_3$ followed by the addition of 1,2-diaminoethane (0.121 g, 1.8 mmol) in methanol. The solution was refluxed on a water bath for 24 h. After the reaction was over, the solution was filtered when hot and then allowed to stand at room temperature. After slow evaporation of the solvent at 25°C, a dark green compound was obtained, washed with methanol and dried in vacuum. Attempts to obtain the crystals were unsuccessful. Yield: 1.20 g (78%). Analytical data for $C_{42}H_{48}O_8N_5ClCu$: Calculated (%): C, 59.29; H, 5.64; N, 8.23; Found (%): C, 59.36; H, 5.74; N, 8.31. Selected IR (KBr): 1620(s), 1099 (s), 624 (s) cm^{-1}. Conductance $(\Lambda_m/S\,cm^2\,mol^{-1})$ in CH_3CN: 144. λ_{max} (nm) $(\varepsilon/M^{-1}\,cm^{-1})$ in CH_3CN: 597 (170), 361 (13 800), 276 (33 700). $g_\parallel = 2.25$, $g_\perp = 2.00$; $\mu_{eff} = 1.72$ BM.

[CuL^2](ClO$_4$)

[CuL^2](ClO$_4$) was synthesized by following the previously described procedure for [CuL^1](ClO$_4$), using 1,3-diaminopropane instead of 1,2-diaminoethane. The compound obtained was dark green. Yield: 1.25 g (80%). Analytical data for $C_{43}H_{50}O_8N_5ClCu$: Calculated (%): C, 59.72; H, 5.78; N, 8.10; Found (%): C, 59.79; H, 5.84; N, 8.17. Selected IR (KBr): 1625 (s), 1096 (s), 625 (s) cm^{-1}. Conductance $(\Lambda_m/S\,cm^2\,mol^{-1})$ in CH_3CN: 160. λ_{max} (nm) $(\varepsilon/M^{-1}\,cm^{-1})$ in CH_3CN: 625 (161), 357 (14 900), 276 (35 900). $g_\parallel = 2.23$, $g_\perp = 2.01$; $\mu_{eff} = 1.71$ BM.

[CuL^3](ClO$_4$)

[CuL^3](ClO$_4$) was synthesized by following the previously described procedure for [CuL^1](ClO$_4$), using 1,4-diaminobutane instead of 1,2-diaminoethane. The compound obtained was dark green. Yield: 1.28 g (81%). Analytical data for $C_{44}H_{52}O_8N_5ClCu$: Calculated (%): C, 60.13; H, 5.92; N, 7.97; Found (%): C, 60.21; H, 5.99; N, 8.04. Selected IR (KBr): 1627 (s), 1095 (s), 625 (s) cm^{-1}. Conductance $(\Lambda_m/S\,cm^2\,mol^{-1})$ in CH_3CN: 139. λ_{max} (nm) $(\varepsilon/M^{-1}\,cm^{-1})$ in CH_3CN: 655 (173), 378 (12 800), 278 (34 300). $g_\parallel = 2.19$, $g_\perp = 2.01$; $\mu_{eff} = 1.71$ BM.

[CuL^4](ClO$_4$)

[CuL^4](ClO$_4$) was synthesized by following the previously described procedure for [CuL^1](ClO$_4$), using *o*-phenylenediamine instead of 1,2-diamino-ethane. The compound obtained was dark green. Yield: 1.31 g (81%). Analytical data for $C_{46}H_{48}O_8N_5ClCu$: Calculated (%): C, 61.46; H, 5.34; N, 7.79; Found (%): C, 61.52; H, 5.41; N, 7.86. Selected IR (KBr): 1620 (s), 1100 (s), 620 (s) cm^{-1}. Conductance $(\Lambda_m/S\,cm^2\,mol^{-1})$ in CH_3CN: 148. λ_{max} (nm) $(\varepsilon/M^{-1}\,cm^{-1})$ in CH_3CN: 620 (146), 420 (15 900), 357 (15 100), 325 (16 000), 287 (35 300). $g_\parallel = 2.23$, $g_\perp = 2.06$; $\mu_{eff} = 1.71$ BM.
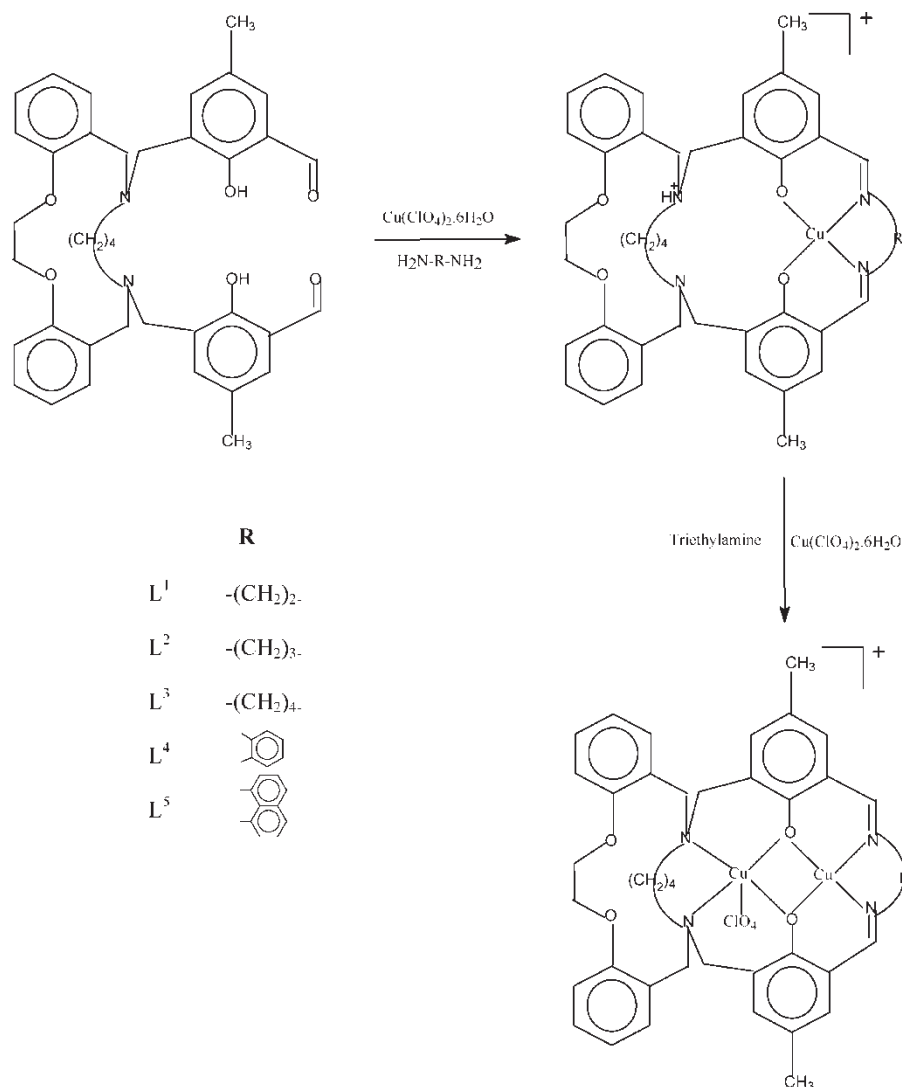
[CuL^5](ClO$_4$)

[CuL^5](ClO$_4$) was synthesized by following the previously described procedure for [CuL^1](ClO$_4$), using 1,8-diaminonaphthalene instead of 1,2-diamino-ethane. The compound obtained was dark green. Yield: 1.28 g (75%). Analytical data for $C_{50}H_{50}O_8N_5ClCu$: Calculated (%): C, 63.29; H, 5.27; N, 7.38; Found (%): C, 63.32; H, 5.33; N, 7.46. Selected IR (KBr): 1622 (s), 1100 (s), 623 (s) cm^{-1}. Conductance $(\Lambda_m/S\,cm^2\,mol^{-1})$ in CH_3CN: 131. λ_{max} (nm) $(\varepsilon/M^{-1}\,cm^{-1})$ in CH_3CN: 630 (151), 361 (15 600), 271 (33 400), 243 (22 800). $g_\parallel = 2.21$, $g_\perp = 2.03$; $\mu_{eff} = 1.69$ BM.

Synthesis of Macrobicyclic Binuclear Copper(II) Complexes

[Cu$_2$L^1(ClO$_4$)](ClO$_4$)

A methanolic solution of copper(II)perchlorate hexahydrate (0.676 g, 1.8 mmol) was added to a hot solution of PC (1.119 g, 1.8 mmol) in $CHCl_3$ followed by the addition of 1,2-diaminoethane (0.121 g, 1.8 mmol) and triethylamine (0.251 g, 1.8 mmol) in methanol. After 1 h copper(II) perchlorate (0.676 g, 1.8 mmol) was added and the reaction mixture was refluxed on a water bath for 24 h. After the reaction was over, the reaction mixture was filtered and allowed to stand at room temperature (25°C). After slow evaporation of the solvent at 25°C, the dark green compound obtained was washed with metha-nol and dried in vacuum. Attempts to obtain the crystals were unsuccessful. Yield: 1.45 g (77%). Analytical data for $C_{44}H_{50}O_{12}N_6Cl_2Cu_2$: Calculated (%): C, 50.23; H, 4.75; N, 7.99; Found (%): C, 50.36; H, 4.88; N, 8.09. Selected IR (KBr): 1628 (s), 1086, 1098, 1100 (w), 625 (s) cm^{-1}. Conductance $(\Lambda_m/S\,cm^2\,mol^{-1})$ in CH_3CN: 136. λ_{max} (nm) $(\varepsilon/M^{-1}\,cm^{-1})$ in CH_3CN: 595 (224), 365 (12 600), 272 (31 760). $g = 2.11$; $\mu_{eff} = 1.48$ BM.

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

$[Cu_2L^2(ClO_4)](ClO_4)$

$[Cu_2L^2(ClO_4)](ClO_4)$ was synthesized by following the previously described procedure for $[Cu_2 L^1(ClO_4)](ClO_4)$, using 1,3-diaminopropane instead of 1,2-diaminoethane. The compound obtained was dark green. Yield: 1.41 g (74%). Analytical data for $C_{45}H_{52}O_{12}N_6Cl_2Cu_2$: Calculated (%): C, 50.70; H, 4.88; N, 7.88; Found (%): C, 50.81; H, 4.97; N, 7.95. Selected IR (KBr): 1624 (s), 1088, 1092, 1101 (w), 625 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH$_3$CN: 129. λ_{max} (nm) (ε/M^{-1} cm^{-1}) in CH$_3$CN: 620 (278), 366 (14 990), 272 (35 400). $g = 2.11$; $\mu_{eff} = 1.53$ BM.

$[Cu_2L^3(ClO_4)](ClO_4)$

$[Cu_2L^3(ClO_4)](ClO_4)$ was synthesized by following the previously described procedure for $[Cu_2 L^1(ClO_4)](ClO_4)$, using 1,4-diaminobutane instead of 1,2-diaminoethane. The compound obtained was dark green. Yield: 1.53 g (79%). Analytical data for

$C_{46}H_{54}O_{12}N_6Cl_2Cu_2$: Calculated (%): C, 51.15; H, 5.00, N, 7.78; Found (%): C, 51.20; H, 5.11; N, 7.88. Selected IR (KBr): 1627 (s), 1085, 1093, 1102 (w), 624 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH$_3$CN: 140. λ_{max} (nm) (ε/M^{-1} cm^{-1}) in CH$_3$CN: 650 (264), 370 (15 940), 272 (32 820). $g = 2.10$; $\mu_{eff} = 1.56$ BM.

$[Cu_2L^4(ClO_4)](ClO_4)$

$[Cu_2L^4(ClO_4)](ClO_4)$ was synthesized by following the previously described procedure for $[Cu_2 L^1(ClO_4)](ClO_4)$, using o-phenylenediamine instead of 1,2-diaminoethane. The compound obtained was dark green. Yield: 1.49 g (75%). Analytical data for $C_{48}H_{50}O_{12}N_6Cl_2Cu_2$: Calculated (%): C, 52.41; H, 4.54, N, 7.64; Found (%): C, 52.57; H, 4.63; N, 7.69. Selected IR (KBr): 1622 (s), 1085, 1096, 1100 (w), 625 (s) cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in CH$_3$CN: 128. λ_{max} (nm) (ε/M^{-1} cm^{-1}) in CH$_3$CN: 635 (229),

420 (16 800), 357 (16 720), 325 (17 200), 270 (33 800). $g = 2.10$; $\mu_{eff} = 1.39$ BM.

$[Cu_2L^5(ClO_4)](ClO_4)$

$[Cu_2L^5(ClO_4)](ClO_4)$ was synthesized by following the previously described procedure for $[Cu_2 L^1(ClO_4)](ClO_4)$, using 1,8-diaminonaphthalene instead of 1,2-diaminoethane. The compound obtained was dark green. Yield: 1.58 g (77%). Analytical data for $C_{52}H_{52}O_{12}N_6Cl_2Cu_2$: Calculated (%): C, 54.30; H, 4.52, N, 7.64, Found (%): C, 54.41; H, 4.66; N, 7.43. Selected IR (KBr): 1625 (s), 1087, 1096, 1103 (w), 624 (s) cm^{-1}. Conductance ($\Lambda_m/$ S cm^2 mol^{-1}) in CH$_3$CN: 133. λ_{max} (nm) ($\varepsilon/$ M^{-1} cm^{-1}) in CH$_3$CN: 650 (245), 360 (17 290), 263 (35 870), 243 (23 500). $g = 2.10$; $\mu_{eff} = 1.44$ BM.

The synthetic route for the mono- and binuclear complexes is shown in Scheme 1.

Acknowledgements

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