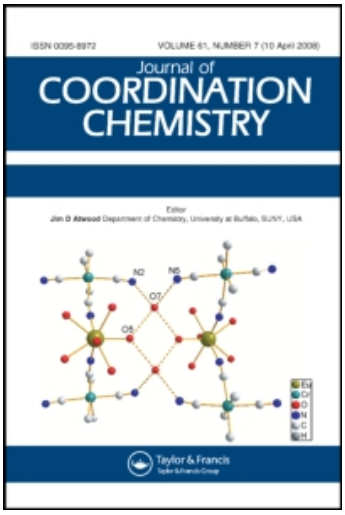

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N-functionalized, cyclam-based unsymmetrical dicompartmental binuclear copper(II) complexes containing 4- and 6-coordination sites: electrochemical, magnetic, catalytic, and antimicrobial studies

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N-functionalized, cyclam-based unsymmetrical dicompartmental binuclear copper(II) complexes containing 4- and 6-coordination sites: electrochemical, magnetic, catalytic, and antimicrobial studies

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A series of unsymmetrical dicompartmental binuclear copper(II) complexes have been prepared by Schiff-base condensation of 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-l,4,8,11-tetraazacyclotetradecane (L) with aliphatic and aromatic diamines, copper(II) perchlorate and triethylamine. The complexes were characterized by elemental and spectral analysis. Electronic spectra of the complexes show d–d transitions in the range 663–786 nm. Electrochemical studies of the complexes in DMF show two irreversible one electron reduction processes $E^1_{pc} = -0.62$ to -0.77 V and $E^2_{pc} = -0.94$ to -1.17 V. Cryomagnetic investigations of the binuclear complexes show $-2J$ values in the range of 154 to 236 cm^{-1}. The rate constants for hydrolysis of 4-nitrophenylphosphate are in the range of 2.27×10^{-2} to 9.21×10^{-2} min^{-1} and for catecholase activity in the range of 3.06×10^{-2} to 8.35×10^{-2} min^{-1}. All the complexes were screened for antifungal and antibacterial activity.

Keywords: Dicompartmental ligand; Cyclam; Copper(II) complexes; Catecholase; Cyclic voltammetry; Antifungal activity

1. Introduction

Aza-macrocyclic compounds bearing pendant coordination side arms receive considerable attention because their selectivity for certain metal ions may be quite different from those of the unsubstituted parent macrocycles [1]. In particular, N-functionalized cyclam-containing dicarbonyl components give rise to versatile ligands including mono-, di-, and tricompartmental macrocycles. Understanding of N-substitution of the ligand on the coordination mode remains an important field of research with

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applications in enzyme mimicking studies, redox catalysts, antibacterial agents, MRI reagents, and fluorescent probes [2–5].

Transition metal complexes with unsymmetrical dicompartmental ligands have importance in biological processes as active sites in metalloproteins and enzymes, interesting catalytic properties, and ability to stabilize unusual oxidation states and mixed-valence compounds, with possibilities for magnetic interaction between the two metal ions [6–8]. Phenoxo bridged copper(II) complexes are the beacon in modeling, serving as models in enzymatic reactions and in catalytic and synthetic oxidation reactions [9, 10]. Since unsymmetrical dicompartmental ligands are of importance for providing discrete homo and heterodinuclear core complexes, various types of compartmental ligands have been prepared and their structures and reactivities reported [11]. Such ligands contain two compartments: one six coordinate (N4O2) and the other four coordinate N2O2.

The present work deals with the influence of ligand modification on spectral, electrochemical, magnetic, and catalytic studies, reporting synthesis and characterization of unsymmetrical macrocyclic dicompartmental binuclear copper(II) complexes containing hexa (amine compartment) and tetra (imine compartment) coordination sites.

2. Experimental

2.1. *Analytical and physical measurements*

Elemental analyses of the complexes were obtained using a Haereus CHN rapid analyzer. ^{1}H NMR spectra were recorded using a JEOL GSX 400 MHz NMR spectrometer. Electronic spectral studies were obtained on a Hitachi 320 spectrophotometer from 200 to 1100 nm. IR spectra were recorded on a Shimadzu FTIR 8300 series spectrophotometer on KBr disks in the range 4000–400 cm^{-1}. Molar conductivities were measured using an Elico digital conductivity bridge model CM-88 using freshly prepared solutions of the complex in DMF. Atomic absorption spectra were recorded using a Varian spectra AA-200 model atomic absorption spectrophotometer. Mass spectra were obtained on a JEOL SX-102 (FAB) mass spectrometer. Cyclic voltammograms were obtained on a CHI-600A electrochemical analyzer. The measurements were carried out under oxygen-free conditions using a three-electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode, the reference electrode, and a Pt wire as the auxiliary electrode. The ferrocene/ferrocenium (1+) couple was used as an internal standard with $E_{1/2}$ couple of 470 mV under experimental conditions. Tetra(*n*-butyl)ammonium perchlorate (TBAP) was used as the supporting electrolyte. Variable-temperature magnetic studies were performed on a PAR model 155 vibrating sample magnetometer in the temperature range 77–300 K, and the instrument was calibrated using metallic Ni as supplied with the instrument. X-band ESR spectra were recorded in DMF at liquid nitrogen temperature on a Varian EPR-E 112 spectrometer with diphenylpicrylhydrazine (DPPH) as the reference. The catalytic oxidation of catechol to *o*-quinone and hydrolysis of 4-nitrophenylphosphate by the copper(II) complexes were studied in 10^{-3} M DMF. The reaction was followed spectrophotometrically by choosing the

strongest absorption band of *o*-quinone at 390 nm and monitoring the increase in the absorbance; hydrolysis of 4-nitrophenylphosphate was monitored by following the UV absorbance change at 420 nm (assigned to the 4-nitrophenolate anion) as a function of time. A plot of $\log(A\alpha/(A\alpha - A_t))$ *versus* time was made for each complex and the rate constants for the catalytic oxidation and the hydrolysis of 4-nitrophenylphosphate were calculated.

2.1.1. Chemicals and reagents. 5-Bromo salicylaldehyde [12], 3-chloromethyl-5-bromo salicylaldehyde [13], and 1,4,8,11-tetraazatricyclo[9.3.1.1^{4,8}]hexadecane [14] were prepared by literature methods. 1,8-[Bis(3-formyl-2-hydroxy-5-bromo)benzyl]-4,11-diazaniatricyclo[9.3.1.1^{4,8}]hexadecane dichloride was prepared by literature method [15] using 3-chloromethyl-5-bromo salicylaldehyde instead of 3-chloromethyl-5-methyl salicylaldehyde. Analytical grade methanol, acetonitrile, and dimethylformamide were purchased from Qualigens and used as received. TBAP used as supporting electrolyte in electrochemical measurement was purchased from Fluka and recrystallized from hot methanol.

Caution! TBAP is potentially explosive; hence, care should be taken in handling the compound). All other chemicals and solvents were of analytical grade and were used as received.

2.2. *Synthesis of ligand (L)*

2.2.1. Synthesis of 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-l,4,8,11-tetraazacyclotetradecane (L). The compound 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-4,11-diazaniatricyclo[9.3.1.1^{4,8}]hexadecane dichloride (1 g, 0.0014 mol) was dissolved in 200 mL of an aqueous NaOH (0.3 M) with stirring. After stirring for 4 h, the solution was extracted with $CHCl_3$ (5×30 mL). The combined $CHCl_3$ extracts were dried with anhydrous $MgSO_4$ and concentrated under vacuum to give 1,8-[bis(3-formyl-2-hydroxy-5-bromo)benzyl]-l,4,8,11-tetraazacyclotetradecane. Yield: 75%; m.p.: 300°C (dec); Analytical data for $C_{26}H_{34}N_4O_4Br_2$: Calculated: C, 49.86; H, 5.47; N, 8.95. Found: C, 49.78; H, 5.42; N, 8.87. Selected IR (KBr): 3407 cm^{-1}, 3289 cm^{-1}, 1680 cm^{-1}; ^{1}H NMR δ (ppm in $CDCl_3$): 1.49 (q, 4H, β-CH_2), 2.56 (br, s, 2H, NH), 2.38 (m, 8H, α-CH_2), 3.39 (s, 8H, H_2C–N–CH_2), 4.1 (s, 4H, N–CH_2–Ar), 7.76 (d, 4H, Ar–H), 10.20 (s, Ar–CHO), 12.64 (br, s, Ar–OH). ^{13}C NMR δ (ppm in DMSO-d_6): 29.8, 49.7, 53.7, 55.0, 55.6, 61.6 122.6, 124.8, 126.0, 131.0, 136.1, 159.0, 196. λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF: 289 (22, 760).

2.3. *Synthesis of the macrobicyclic binuclear copper(II) complexes*

[$Cu_2L^{1a}(ClO_4)$](ClO_4). Copper(II) perchlorate hexahydrate (0.74 g, 0.002 mol) in methanol (50 mL) was added to a hot solution of ligand L (1.00 g, 0.002 mol) in methanol, followed by addition of 1,2-diaminoethane (0.12 g, 0.002 mol) and triethylamine (0.41 g, 0.004 mol) in methanol (50 mL). After 1 h, another one equivalent of copper(II) perchlorate (0.74 g, 0.002 mol) was added and the solution was refluxed for 24 h. The resulting solution was filtered whilst hot and allowed to stand at room temperature. After

slow evaporation of the solvent at 25°C, the dark green compound was collected by filtration, recrystallized from acetonitrile and dried in vacuum.

Dark green compound, Yield: 1.07 g (69%). Analytical data for $C_{28}H_{36}N_6O_{10}Cl_2Br_2Cu_2$: Calculated (%): C, 34.51; H, 3.72; N, 8.63; Cu, 13.04. Found (%): C, 34.49; H, 3.70; N, 8.61; Cu, 13.00. Conductance (Λ_m, S cm^2 mol^{-1}) in DMF: 87. Selected IR data (KBr) (ν/cm^{-1}): 3300 ν(NH), 1610 [s, ν(C=N)], 1103, 1085 (w) [$\nu(ClO_4^-)$ coordinated], 1093 (w) [$\nu(ClO_4^-)$ uncoordinated], 626 (s). λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF: 663 (123), 357 (14 200), 295 (19 100). g: 2.10, μ_{eff}: 1.45 B.M.

The complexes $[Cu_2L^{1b}(ClO_4)](ClO_4)$, $[Cu_2L^{1c}(ClO_4)](ClO_4)$, $[Cu_2L^{1d}(ClO_4)](ClO_4)$, and $[Cu_2L^{1e}(ClO_4)](ClO_4)$ were synthesized by following the synthesis procedure of $[Cu_2L^{1a}(ClO_4)](ClO_4)$ using the ligand L and 1,3-diaminopropane (0.15 g, 0.002 mol), 1,4-diaminobutane (0.18 g, 0.002 mol), 1,2-diaminobenzene (0.22 g, 0.002 mol), and 1,8-diaminonaphthalene (0.32 g, 0.002 mol), respectively, instead of 1,2-diaminoethane.

$[Cu_2L^{1b}(ClO_4)](ClO_4)$. Dark green compound. Yield: 0.96 g (61%). Analytical data for $C_{29}H_{38}N_6O_{10}Cl_2Br_2Cu_2$: Calculated (%): C, 35.24; H, 3.88; N, 8.50; Cu, 12.86. Found (%): C, 35.20; H, 3.35; N, 8.49; Cu, 12.83. Conductance (Λ_m, S cm^2 mol^{-1}) in DMF: 87. Selected IR data (KBr) (ν/cm^{-1}): 3295 ν(NH), 1614 [s, ν(C=N)], 1105, 1091 (w) [$\nu(ClO_4^-)$ coordinated], 1097 (w) [$\nu(ClO_4^-)$ uncoordinated], 628 (s). λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF: 721 (142), 378 (13 600), 298 (20 200). g: 2.10, μ_{eff}: 1.45 B.M.

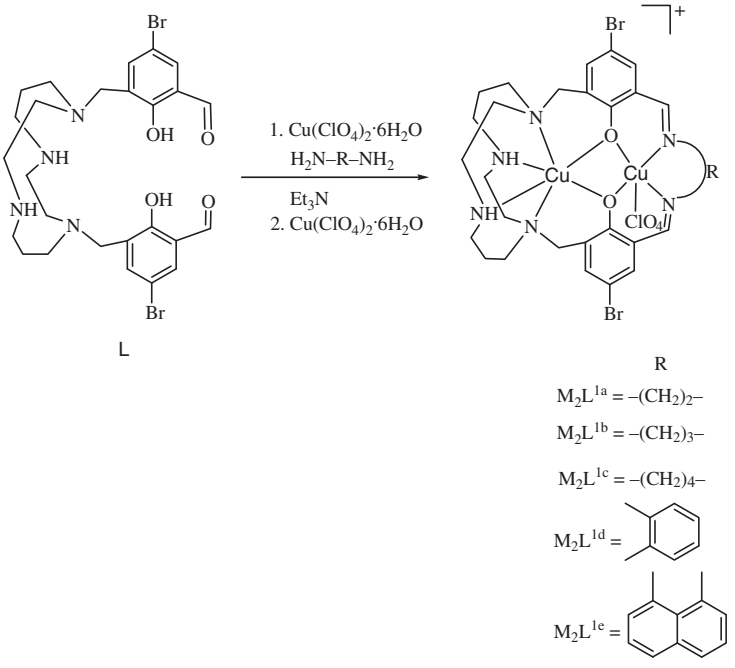
$[Cu_2L^{1c}(ClO_4)](ClO_4)$. Dark green compound. Yield: 1.00 g (63%). Analytical data for $C_{30}H_{40}N_6O_{10}Cl_2Br_2Cu_2$: Calculated (%): C, 35.94; H, 4.02; N, 8.38; Cu, 12.68. Found (%): C, 35.90; H, 3.99; N, 8.37; Cu, 12.65. FAB mass (m/z) (%): $[Cu_2L^{1c}]^+$ 804. Conductance (Λ_m, S cm^2 mol^{-1}) in DMF: 90. Selected IR data (KBr) (ν/cm^{-1}): 3283 ν(NH), 1620 [s, ν(C=N)], 1090, 1097 (w) [$\nu(ClO_4^-)$ coordinated], 1100 (w) [$\nu(ClO_4^-)$ uncoordinated], 624 (s). λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF: 748 (162), 400 (12 100), 319 (18 300). g: 2.10, μ_{eff}: 1.45 B.M.

$[Cu_2L^{1d}(ClO_4)](ClO_4)$. Dark green compound. Yield: 0.97 g (61%) Analytical data for $C_{32}H_{36}N_6O_{10}Cl_2Br_2Cu_2$: Calculated (%): C, 37.57; H, 3.55; N, 8.22; Cu, 12.43. Found (%): C, 37.55; H, 3.53; N, 8.19; Cu, 12.41. Conductance (Λ_m, S cm^2 mol^{-1}) in DMF: 95. Selected IR data (KBr) (ν/cm^{-1}): 3275 ν(NH), 1629 [s, ν(C=N)] 1103, 1091 (w) [$\nu(ClO_4^-)$ coordinated], 1095 (w) [$\nu(ClO_4^-)$ uncoordinated], 624 (s). λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF: 695 (98), 405 (11 500), 328 (18 300). g: 2.11, μ_{eff}: 1.47 B.M.

$[Cu_2L^{1e}(ClO_4)](ClO_4)$. Dark green compound. Yield: 0.95 g (55%) Analytical data for $C_{36}H_{38}N_6O_{10}Cl_2\ Br_2Cu_2$: Calculated (%): C, 40.32; H, 3.57; N, 7.84; Cu, 11.85. Found (%): C, 40.28; H, 3.55; N, 7.82; Cu, 11.83. FAB mass (m/z) (%): $[Cu_2L^{1e}ClO_4]^+$ 973. Conductance (Λ_m, S cm^2 mol^{-1}) in DMF: 99. Selected IR data (KBr) (ν/cm^{-1}): 3283 ν(NH), 1625 [s, ν(C=N)], 1106, 1089 (w) [$\nu(ClO_4^-)$ coordinated], 1095 (w) [$\nu(ClO_4^-)$ uncoordinated], 629 (s). λ_{max}, nm (ε, M^{-1} cm^{-1}) in DMF: 786 (109), 385 (1400), 278 (17 100). g: 2.09, μ_{eff}: 1.45 B.M.

3. Results and discussion

A series of macrobicyclic binuclear copper(II) complexes were synthesized by Schiff-base condensation of L with diamines in the presence of metal ion. The synthetic



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

pathway is shown in scheme 1. In all the copper(II) complexes, one copper(II) in the amine compartment is six coordinate and the other in the imine compartment is five coordinate. All attempts to grow single crystals of the complexes (e.g. by the diffusion of diethyl ether vapor into DMF solutions or recrystalization of the complexes from acetonitrile) failed and only dark green powder or micro crystals were obtained. Spectral, electrochemical, magnetic, catalytic, and antimicrobial activities of the complexes were carried out.

3.1. *Spectroscopic studies*

FT-IR spectra of binuclear copper(II) complexes show bands in the region 3327–3353 cm^{-1}, assigned to NH. The IR spectra of L show a band at 1680 cm^{-1} due to C=O (−CHO). All the complexes show a sharp band in the region 1618–1629 cm^{-1}, assigned to C=N stretching. The disappearance of C=O (aldehyde group) and the appearance of new strong C=N absorption indicate Schiff-base condensation between the aldehyde of L and diamines [16–18]. All binuclear copper(II) complexes showed two sharp peaks near 1100 cm^{-1}, assigned to perchlorate [19]. Among the two peaks, one peak shows splitting and the other does not [20]. Splitting is due to coordinated perchlorate, while the other peak indicates uncoordinated perchlorate ion [21]. Apart from this an additional peak is observed in the range 624–630 cm^{-1}, characteristic for perchlorate [22] bending, and does not show any splitting even if it coordinates. New bands from 1530–1558 cm^{-1} in all the complexes suggest bridging phenoxide [23].

Electronic spectra of the copper(II) complexes in DMF exhibit three main features. One or two peaks in the range 278–325 nm are assigned to intra-ligand transitions (π–π^*). An intense peak in the range 319–405 nm is due to ligand-to-metal charge transfer, and the d–d transition for the copper(II) complexes are at 663–786 nm with a shoulder at 822 nm, characteristic of Cu^{2+} five or six coordination environment [24]. The red shift of the d–d transition of copper(II) for L^{1a} to L^{1c} and L^{1d} to L^{1e} indicates that the coordination geometry around copper is distorted. This is due to the flexibility of the macrocyclic ring upon increasing the chain length of the imine compartment, causing more distortion [21, 22].

3.2. *ESR and magnetic studies*

A broad ESR spectrum with g values in the range 2.09–2.11 indicates antiferromagnetic interaction [25] between the two copper centers. The room temperature magnetic moments of the binuclear copper(II) complexes are in the range 1.45 to 1.47 B.M., less than the total spin-only values due to antiferromagnetic coupling by super-exchange through the phenolic oxygens [26–29]. To evaluate the singlet–triplet energy separation ($-2J$), variable temperature magnetic studies for the binuclear copper(II) complexes $[Cu_2L^{1a-1e}(ClO_4)](ClO_4)$ were performed from 77 to 298 K, and the experimental magnetic susceptibility values were fitted to the modified Bleaney–Bowers equation [26b]

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

Plots of χ_{cu} *versus* T and μ_{Cu} *versus* T for the complexes $[Cu_2L^{1c\&e}(ClO_4)](ClO_4)$ are shown in figures 1 and 2. The observed $-2J$ values are in the range 154–236 cm^{-1}.

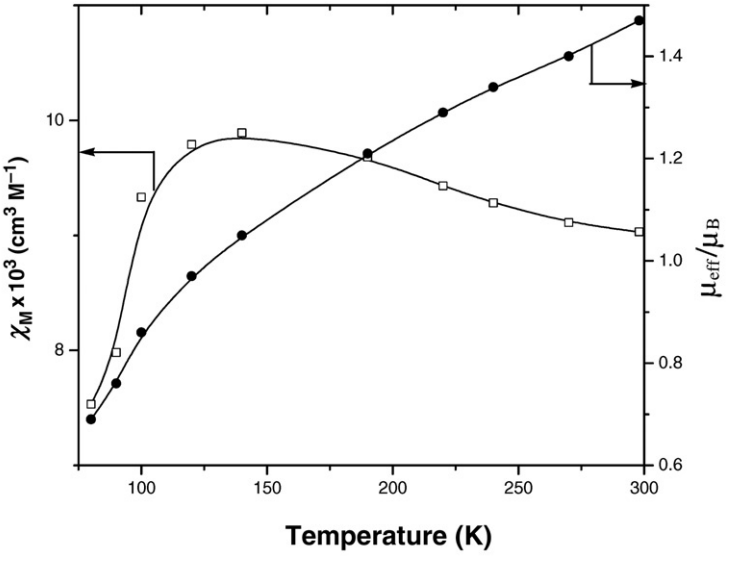


Figure 1. Temperature-dependence magnetic properties for $[Cu_2L^{1c}(ClO_4)](ClO_4)$, where • is μ_{eff}/μ_B and □ is χ_M.

Comparing magnetic properties of the copper(II) complexes based on increasing chain length of the imine compartment is important to discover the effect on spin exchange interactions in the complexes. As observed in the electrochemical studies, a smaller $-2J$ value is observed for $[CuL^{1a–c}(ClO_4)]ClO_4$ ($-2J = 172, 160$, and 154) compared to $[Cu_2L^{1d\&e}(ClO_4)](ClO_4)$ ($-2J = 212$ and $236\,cm^{-1}$). This may be due to the distorted geometry around copper as a result of the increasing chain length of the imine compartment, causing more distortion [29]. Reports suggest that both distortion from planar geometry [29] and reduction in electron density on copper [30] are less favorable for effective spin exchange interaction, and hence smaller exchange integral values were observed for the complexes of $L^{1a–c}$ compared to $L^{1d–e}$. The most probable reason for the strong antiferromagnetic exchange interaction in $L^{1d–e}$ complexes may be the greater planarity due to the presence of aromatic diimine ($-2J = 212$ and $236\,cm^{-1}$). Further, the electron-withdrawing group (Br) in the para position of the phenolic ring in the complexes reduces the electron density on the copper centers, weakening the Cu–O bond and reducing the spin exchange interaction. Hence, smaller exchange values are observed for $[Cu_2L^{1a–e}(ClO_4)](ClO_4)$ than the complexes which contain electron donating para substituent (CH_3) [29, 31].

3.3. *Electrochemical properties of the complexes*

Electrochemical behavior of the complexes was studied by molar conductance and cyclic voltammetry in DMF containing 10^{-1} M tetra(*n*-butyl)ammonium perchlorate. All the complexes show molar conductance in the range 87–99 $\Lambda_m/S\,cm^2\,mol^{-1}$, indicating 1 : 1 electrolytes [32], showing that one perchlorate is coordinated.

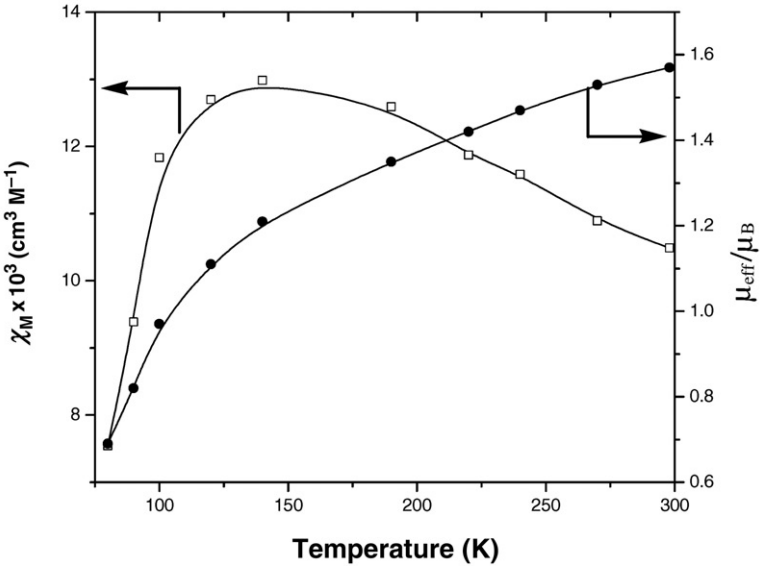


Figure 2. Temperature-dependence magnetic properties for $[Cu_2L^{1e}(ClO_4)](ClO_4)$, where • is μ_{eff}/μ_B and □ is χ_M.

3.4. *Reduction process at negative potential*

Electrochemical data are summarized in table 1. The electrochemical behavior was studied by cyclic voltammetry in DMF containing 10^{-1} M TBAP from 0 to −1.4 V. Cyclic voltammograms for the complexes are shown in 'Supplementary material'. All complexes show two irreversible reduction waves in the cathodic potential region. The first reduction potential ranges from −0.62 to −0.77 V and the second from −0.94 to −1.17 V. Controlled potential electrolysis shows that each couple corresponds to a one-electron transfer process. The two reduction processes are assigned as follows:

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

The first reduction potential of the Cu^{2+}/Cu^{+} couple of $[CuL^{1a-c}(ClO_4)]ClO_4$ complexes in the range −0.64 to −0.77 (table 1) is attributed to reduction of the four-coordinate copper(II) (imine compartment) and the second from −0.94 to −1.03 V is attributed to the reduction of copper(II) in the cyclam compartment. Electrochemical studies of similar complexes with hexa- and tetra-coordination sites [33] suggest that the second reduction potential may be assigned to six-coordinate metal.

The first and second reduction potentials of the L^{1a-c} complexes shift anodic, from −0.77 to −0.64 V and from −1.03 to −0.94 V, respectively, as the chain length of the imine compartment increases [34, 35]. The first and second reduction potentials for $[Cu_2L^{1c}(ClO_4)](ClO_4)$ ($E^1_{pc} = -0.60$ V and $E^2_{pc} = -0.94$ V) are less negative than those of $[Cu_2L^{1b}(ClO_4)](ClO_4)$ ($E^1_{pc} = -0.64$ V and $E^2_{pc} = -1.00$ V) which, in turn, are less negative than those of $[Cu_2L^{1a}(ClO_4)](ClO_4)$ ($E^1_{pc} = -0.78$ V and $E^2_{pc} = -1.09$ V). This shows that increasing chain length increases flexibility of the entire macrocyclic ring, which causes easier reduction. Reduction of complexes of L^{1d} and L^{1e} is rather difficult compared to reduction of complexes of L^{1a-1c} due to rigidity [36].

Further, the electron-withdrawing substituent (Br) at the para position to phenoxide oxygen in the phenyl ring eases the reduction [31, 37, 38] due to lower electron density on copper as a result of poor electron-donating nature of bromide. Literature reports [37] also suggest that the complexes containing electron-withdrawing groups at the para position of the phenoxide get reduced at less negative potential than complexes containing electron-donating (CH_3) substituent [31]. The same trend was also observed for complexes of L^{1d-e}. Whatever the precise interpretation of the bimetallic reduction

Table 1. Electrochemical[a] (reduction at cathodic potential) hydrolysis of 4-nitrophenylphosphate[b] and catecholase[b] activity data of the copper(II) complexes.

			Rate constant (k) ($\times 10^{-2}$) min^{-1}	
Complexes	E^1_{pc} (V)	E^2_{pc} (V)	NPP	Catecholase
$[Cu_2L^{1a}(ClO_4)](ClO_4)$	−0.77	−1.03	5.63	6.24
$[Cu_2L^{1b}(ClO_4)](ClO_4)$	−0.70	−1.00	7.05	7.39
$[Cu_2L^{1c}(ClO_4)](ClO_4)$	−0.64	−0.94	9.21	8.35
$[Cu_2L^{1d}(ClO_4)](ClO_4)$	−0.73	−1.20	2.27	3.06
$[Cu_2L^{1e}ClO_4)](ClO_4)$	−0.62	−1.17	4.31	4.17

[a]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 1×10^{-3} M, concentration of TBAP 1×10^{-1} M.
[b]Measured spectrophotometrically in DMF. Concentration of the complexes: 1×10^{-3} M. Concentration of 4-nitrophenylphosphate: 1×10^{-1} M.

process, it is clear that magnitude varies due to changes caused by the nature of the ligand, geometry, and by the presence of the other metal.

3.5. *Kinetic studies*

3.5.1. Hydrolysis of 4-nitrophenylphosphate. The catalytic activities of the copper(II) complexes for hydrolysis of 4-nitrophenylphosphate were determined spectrophotometrically, similar to our earlier report [36, 39]. Plots of $\log(A_\alpha/A_\alpha - A_t)$ *versus* time for hydrolysis of 4-nitrophenylphosphate activity of the copper(II) complexes are shown in figure 3. The observed initial rate constant values for all the copper(II) complexes, given in table 1, are in the range $2.27 \times 10^{-2}\,\mathrm{min}^{-1}$ to $9.21 \times 10^{-2}\,\mathrm{min}^{-1}$.

3.5.2. Oxidation of pyrocatechol (catecholase activity). The catecholase activity of the copper(II) complexes was carried out using pyrocatechol as the model substrate for identification of functional models for the metalloenzymes by following our earlier reports [36, 40, 41].

Plots of $\log(A_\alpha/A_\alpha - A_t)$ *versus* time for catecholase activity of the binuclear copper(II) complexes are shown in figure 4. The observed initial rate constants for copper(II) complexes are given in table 1. $[Cu_2L^{1c}(ClO_4)](ClO_4)$ has higher catalytic activity ($8.35 \times 10^{-2}\,\mathrm{min}^{-1}$) than $[Cu_2L^{1b}ClO_4)](ClO_4)$ ($7.39 \times 10^{-2}\,\mathrm{min}^{-1}$), which is higher than $[Cu_2L^{1a}ClO_4)](ClO_4)$ ($6.24 \times 10^{-2}\,\mathrm{min}^{-1}$). The rate of oxidation of catechol to *o*-quinone increases as the macrocyclic chain length increases [42a]. The catecholase activity of distorted complex is higher than that of the less distorted complex [42b]; increase in flexibility due to increase in the ring size of macrocycle is the possible reason for the observed higher rate constant value of the complexes.

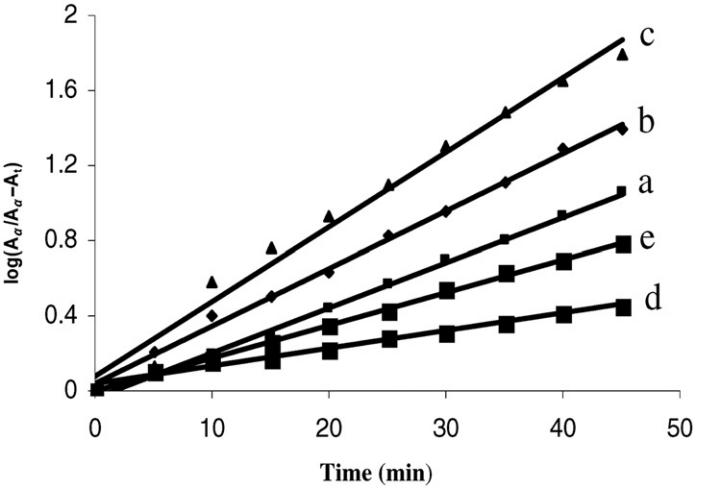


Figure 3. Hydrolysis of 4-nitrophenylphosphate by binuclear copper(II) complexes: (a) $[Cu_2L^{1a}(ClO_4)](ClO_4)$, (b) $[Cu_2L^{1b}(ClO_4)](ClO_4)$, (c) $[Cu_2L^{1c}(ClO_4)](ClO_4)$, (d) $[Cu_2L^{1d}(ClO_4)](ClO_4)$, (e) $[Cu_2L^{1e}(ClO_4)](ClO_4)$.

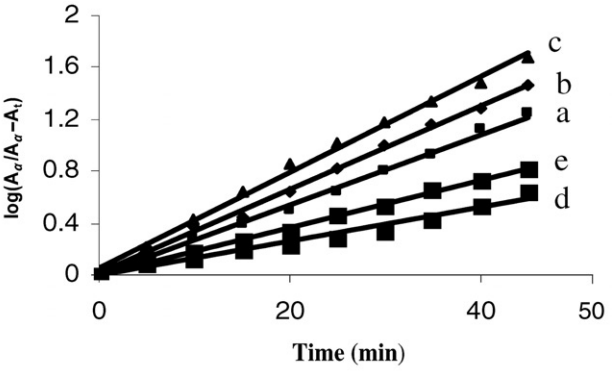


Figure 4. Catecholase activity of the copper(II) complexes: (a) $[Cu_2L^{1a}(ClO_4)](ClO_4)$, (b) $[Cu_2L^{1b}(ClO_4)](ClO_4)$, (c) $[Cu_2L^{1c}(ClO_4)](ClO_4)$, (d) $[Cu_2L^{1d}(ClO_4)](ClO_4)$, (e) $[Cu_2L^{1e}(ClO_4)](ClO_4)$.

Table 2. Antibacterial and antifungal screening data of complexes.

	Representation zone of inhibition ($100\,\mu g\,mL^{-1}$)					
	Antibacterial					Antifungal
Compound	*S.a*	*B.s*	*K.p*	*P.a*	*E.c*	*C.a*
$Cu(ClO_4)_2 \cdot 6H_2O$	–	–	–	–	–	7
Ligand (L)	8	7	10	10	9	10
$[Cu_2L^{1a}(ClO_4)](ClO_4)$	10	9	11	12.5	9	10
$[Cu_2L^{1b}(ClO_4)](ClO_4)$	12	13	15	15	11	12
$[Cu_2L^{1c}(ClO_4)](ClO_4)$	13	13	15	16	11	9.5
$[Cu_2L^{1d}(ClO_4)](ClO_4)$	16	15	17.5	19	12	18
$[Cu_2L^{1e}ClO_4)](ClO_4)$	15	15.5	17	17	13	21

S.a – Staphylococcus aureus; *B.s – Bacillus subtilis*; *K.p – Klebsiella pneumonia*; *P.a – Pseudomonas aeruginosa*; *E.c – Escherichia coli*; *C.a – Candida albicans*.

Further, the para substituent of the phenoxide to the phenyl ring is also one of the factors for the observed higher catecholase and hydrolysis activity of the complexes. If the reduction potential is too negative, the complex has decreased catalytic activity due to more difficult reduction to copper(I), and a less negative reduction potential of the complex gives higher catalytic activity since the donors stabilize copper(I) [43]. The complexes containing Br^- at the para position to the phenoxide oxygen in the phenyl ring get reduced at less negative potential than complexes with CH_3 [38, 44] and show higher catalytic activity. Literature reports [44] also show that the complexes containing electron-withdrawing groups show higher catalytic activity than complexes with electron-donating substituents. The same trend was also observed for complexes of $L^{1d–e}$.

3.6. *Antimicrobial activities*

We have evaluated the antifungal activity of all the copper(II) complexes against the phytopathogenic fungus *Candida albicans*. The screening data are reported in table 2.

All tested complexes show some antifungal activity, comparable with N-substituted tetraazamacrocycles [36, 45].

The complexes have also been screened for their *in vitro* antimicrobial activity against the human pathogenic bacteria Gram (−) *Escherichia coli* (ATCC 11775), *Pseudomonas aeruginosa* (ATCC 10145), *Bacillus subtilis* (ATCC 6633), *Klebsiella pneumonia* (ATCC 13883) and Gram (+) *Staphylococcus aureus* (ATCC 12600) using the agar dilution method (table 2). All the copper(II) complexes are highly potent against *P. aeruginosa*, *B. subtilis*, *K. pneumonia* and Gram (+) *S. aureus*, and moderate activity against *E. coli*. The complexes show superior activity to the ligand L and the copper(II) perchlorate salt. Complexes containing aromatic diimines show higher activity than complexes containing aliphatic diamines. The presence of cyclam may enhance the activity of the complexes. However, further studies are needed to understand the functions responsible for antifungal and antibacterial activities of the tested complexes.

4. Conclusion

Variations in the chain length of the imine compartment and the para substituent of the phenoxide to the phenyl ring influence the electrochemical, magnetic, and catalytic properties of the copper(II) complexes. All the complexes show good antimicrobial activity.

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