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Macrocyclic Unsymmetrical Binuclear Copper(II) Complexes as Ligands: Spectral, Structural, Magnetic and Electrochemical Studies

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A new series of macrocyclic unsymmetrical binuclear copper(II) complexes was prepared by using [CuL^{a,b}] (L^a = [6,6′-piperazine-1,4-diyldimethylenebis(4-methyl-2-formyl)phenol] and L^b = [6,6′-piperazine-1,4-diyldimethylenebis(4-bromo-2-formyl)phenol]) and [Cu(oxen)](ClO$_4$)$_2$ or [Cu(oxpn)](ClO$_4$)$_2$, where oxen = *N*,*N*′-bis(2-aminoethyl)oxamide and oxpn = *N*, *N*′-bis(3-aminopropyl)oxamide. The binuclear copper(II) complexes contain three different compartments: the first compartment has two piperazinyl nitrogens and two phenolic oxygens (N$_2$O$_2$), the second compartment has two phenolic oxygens and two imine nitrogens (O$_2$N$_2$) and the third compartment has two imine nitrogens and two amide nitrogens (N$_4$) as coordinating sites. Apart from the three compartments the complex has two oxamide oxygen atoms for further coordination. The copper(II) ion in the complex is tetracoordinated with two tertiary nitrogen atoms and two phenoxy oxygen atoms coordinated in the equatorial plane to the copper(II) ion and the geometry around the copper nuclei is distorted square planar. The binuclear copper(II) complexes were characterized by elemental and spectral analysis. Electronic spectra of the complexes show a single broad band for the d–d transition in the region around 585–635 nm. The mono- and binuclear copper(II) complexes show four-line hyperfine splitting in the ESR spectra. For the mononuclear complexes the observed $g_{\|}$ values are in the range 2.21 to 2.31, $g_{\perp}$ values vary from 2.10 to 2.11 and $A_{\|}$ values from 175 to 180 G. For the binuclear complexes the observed $g_{\|}$ values are in the range 2.20 to 2.10, $g_{\perp}$ values vary from 2.06 to 2.01 and $A_{\|}$ values from 165 to 175 G. Room temperature magnetic moments of the mono- and binuclear copper(II) complexes show a μ_{eff} value around 1.72 BM, which is near to the spin-only value of 1.73 BM. Electrochemical studies of the mono- and binuclear copper(II) complexes are discussed. The mononuclear copper(II) complexes show one irreversible reduction wave in the region −0.54 to −0.89 V and the binuclear copper(II) complexes show two irreversible single-step one-electron transfer processes in the range $E^1_{\text{pc}} = -0.35$ to -0.53, $E^2_{\text{pc}} = -0.62$ to -0.78 at the cathodic potential region.

Keywords: Binuclear copper(II) complexes; Crystal structure; Electrochemical studies; Macrocyclic compartmental ligands; Unsymmetrical binucleating ligands

INTRODUCTION

The design and synthesis of macrocyclic unsymmetrical binuclear ligands have been the subject of growing interest during the past few years because of their importance in biomimetic studies of binuclear metal complexes, their capacity to act as catalysts for numerous chemical reactions [1,2], and the possibilities for magnetic interaction between the two metal ions, leading to the design of molecular magnetic materials. Much attention has also been paid to the construction of machine-like supramolecules [3] starting from molecular components and mechanical work can be induced at the molecular level through the controlled motion of a chosen component occurring within a molecular or a supramolecular system. Crown ethers and cyclophanes, for example, have been used extensively as cyclic components in the construction of supramolecular structures. The controllable molecular motion can be induced by variation of a bulk parameter, such as the pH or the redox potential [4]. Transition metal ions can be translocated between two non-equivalent coordinating compartments of a ditopic ligand by varying the pH or redox potential. Enzymes such as haemocyanin [5] or tyrosinase [6]

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have a binuclear copper centre in their active sites. The geometry, the coordination sites, the bridging ligands between the centres, etc., define the properties of the binuclear centres. The synthesis of polymetallic co-ordination complexes that have supramolecular structures is of current interest for inorganic chemists seeking to design new molecular materials with unusual magnetic and electrical properties [7–10]. In addition, the oxamide group can bind exogenous metal ions via the *exo*- oxygen atoms, facilitating the synthesis of polymetallic complexes using an appropriate group. These can be used as "complexes as ligands" [11–13]. In continuation of our earlier work [14,15], we report here the synthesis of a new series of macrocyclic unsymmetrical binuclear copper(II) complexes with oxamide coordination environments. The magnetic and electrochemical behaviour of the phenoxo bridged copper(II) ions that varies with respect to ring size and the substituent at the para position to the phenoxide is discussed.

RESULTS AND DISCUSSION

X-ray Structural Study of the Complex

The molecular structure of the mononuclear copper(II) complex [CuL^a] and its atomic labelling are shown in Fig. 1. Crystal data and structure refinement [16,17] for the complex [CuL^a] are given in Table I. Selected bond lengths and bond angles are summarized in Table II. Half a molecule is present in the asymmetric unit. The final R-value is 0.0434 for 1724 observed reflections [$I > 2\sigma(I)$]. The copper(II) ion in the complex is tetracoordinated and the geometry around the copper nuclei is best described as distorted square planar. Both the phenyl rings are essentially planar, with a maximum deviation of ±0.0044(4) Å. The dihedral angle between the phenyl rings and O1–C1–C2–C8–N1–Cu planes in the same molecules is 23.6(1)°. The piperazine ring adopts a boat conformation, which is confirmed from the puckering parameters of $Q2 = QT = 0.874$; $\theta = 90°$. The best plane passes through the central C atoms, leaving the N and C atoms above and below plane. The molecule is stabilized by two intermolecular C–H···O [C9–H9A···O2: D–A = 3.0765 Å, D–H = 0.9700 Å, H···A = 2.4777 Å, D–H···A = 119.75°, Symmetry = x, $1-y$, $-1/2+z$], [C10–H10B···O2: D–A = 3.0986 Å, D–H = 0.9700 Å, H···A = 2.4777 Å, D–H···A = 121.63°, Symmetry = $-x$, $1-y$, $1-z$] and one intramolecular C–H···O [C5–H5···O1: D–A = 3.3392 Å, D–H = 0.9299 Å, H···A = 2.5601 Å, D–H···A = 141.60°, Symmetry = x, $1-y$, $-1/2+z$] type of interactions.

Spectral Studies

IR spectra of the mononuclear copper(II) complexes CuL^a and CuL^b show peaks at 1670 and 1668 cm^{-1} indicating the characteristic peak for the C═O group. The complexes Cu(oxen) and Cu(oxpn) show bands in the region 3099–3240 cm^{-1} indicating the presence of NH groups, and a characteristic peak for the C═O group in the region 1660–1670 cm^{-1} indicates the oxamide group. All binuclear copper(II) complexes show a strong peak at 1605–1620 cm^{-1} evidenced by the formation of an imine group (C═N) in the macrocyclic complexes [18] by Schiff's base condensation. The binuclear copper(II) complexes show a band in the region 3099–3240 cm^{-1} indicating the presence of NH groups. The broad band at 623 cm^{-1}, 1083–1093 cm^{-1} indicates the presence of an uncoordinated perchlorate ion.

Electronic spectra of all the complexes were obtained in DMF in the range 250–800 nm. The data are given in Table III. The d–d transition was observed for the mononuclear copper(II) complexes in the range 620–635 nm. A broad band was observed for all binuclear complexes in the region

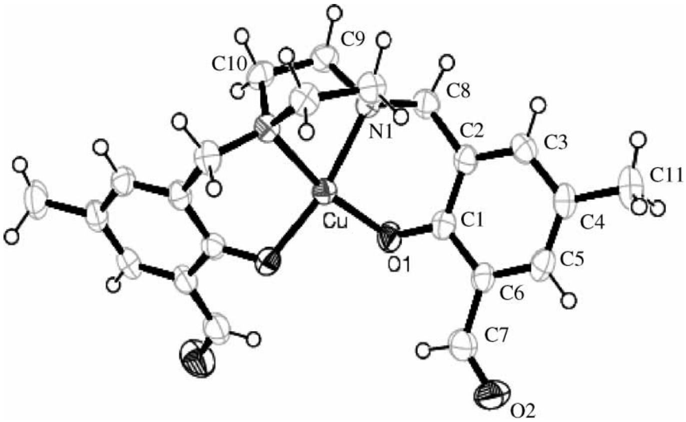


FIGURE 1 ORTEP diagram of the complex [CuL^a].

TABLE I Crystal data and structure refinement for [CuL^a]

Empirical formula	$C_{22}H_{24}N_2O_4Cu$
Formula weight	443.97
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	18.451(3)
b (Å)	9.327(2)
c (Å)	12.411(5)
α (°)	90.00
β (°)	113.93(2)
γ (°)	90.00
Volume (Å^3)	1952.1(9)
Z	4
Density (calculated) (mg m^{-3})	1.511
Absorption coefficient (mm^{-1})	1.133
$F(000)$	924
Crystal size (mm)	0.3 × 0.2 × 0.2
Theta range for data collection (deg)	2.42–24.99
Index ranges	$0 \le h \le 21$, $0 \le k \le 11$, $-14 \le l \le 13$
Reflections collected	1780/1724; $R(\mathrm{int}) = 0.0732$
Absorption correction	Psi-scan
Completeness to $2\theta = 24.99$	99.9%
Max. and min. transmission	0.9986 and 0.5888
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1724/1/136
Goodness-of-fit on F^2	1.038
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0434$, $wR_2 = 0.1147$
R indices (all data)	$R_1 = 0.0571$, $wR_2 = 0.1237$
Largest diff. peak and holes (e Å^{-3})	1.04 and −0.452

585–605 nm and is assigned to the d–d transition of the copper(II) ions [19,20]. Even though the metal ions are present in two different compartments (N_2O_2 and N_4), we observed a broad d–d band that could not be further resolved. The ligand to metal charge transfer (LMCT) transition was observed in the range 368–380 nm and the strong band observed in the range of 268–280 nm is due to a intraligand charge transfer transition.

ESR Spectra

The solid-state ESR spectra of the mononuclear and binuclear copper(II) complexes were recorded at room temperature in the X-band region. Figures 2a and 2b show the ESR spectra of the mono- and binuclear complexes of CuL^a and Cu$_2$L^{1a}. ESR spectra of mononuclear copper(II) complexes show four lines [21] with a nuclear hyperfine spin 3/2. The observed $g_{\|}$ values are in the range 2.21 to 2.31, $g_{\perp}$ values vary from 2.10 to 2.11 and $A_{\|}$ values from 175 to 180. The binuclear complexes show four-line hyperfine splitting due to nuclear spin 3/2 and the observed $g_{\|}$ values are in the range 2.20 to 2.10, $g_{\perp}$ values vary from 2.06 to 2.01 and $A_{\|}$ values from 165 to 175. Hence the observed spectra of the binuclear complexes are similar to the mononuclear complexes. This indicates that the two metal ions are apart from each other and there is no interaction between the two metal ions.

TABLE II Selected bond lengths (Å) and angles (deg) for [CuL^a]

Cu–O(1)	1.898(3)
Cu–O(1a)	1.898(3)
Cu–N(1)	2.017(3)
Cu–N(1a)	2.017(3)
O(1)–Cu–O(1a)	97.0(16)
O(1)–Cu–N(1)	94.9(1)
O(1a)–Cu–N(1)	167.1(1)
O(1)–Cu–N(1a)	167.1(1)
O(1a)–Cu–N(1a)	94.2(1)
N(1a)–Cu–N(1)	73.9(2)

Magnetic Studies

The magnetic moment of the copper(II) complexes was observed at room temperature and the magnetic moment data are listed in Table III. The mononuclear copper(II) complexes gave a μ_{eff} value in the range 1.70 to 1.72 BM with one unpaired electron in the d_{x2-y2} orbital. The binuclear copper(II) complexes also gave a μ_{eff} value in the range 1.70 to 1.72 BM, which is near to the spin-only value of 1.73 BM. This shows the absence of any exchange interaction between the two copper ions.

Electrochemical Studies

The electrochemical properties of the complexes were studied by cyclic voltammetry in the range 0.8 to −1.0 V in DMF using tetra(n-butyl)ammonium perchlorate as the supporting electrolyte. The cyclic

TABLE III Electronic spectral and magnetic moment values for the complexes

Complex	λ_{max}/nm (ε_{max}/dm^{-3} m^{-1} cm^{-1}) d–d	LMCT	μ_{eff}/BM
[CuL^a]	620 (240)	368 (15,800), 274 (62,300)	1.72
[CuL^b]	635 (240)	378 (13,500), 272 (45,500)	1.70
[Cu(oxen)](ClO$_4$)$_2$	625 (235)	280 (18,500)	1.71
[Cu(oxpn)](ClO$_4$)$_2$	630 (395)	270 (16,400)	1.71
[Cu$_2$L^{1a}](ClO$_4$)$_2$	585 (460)	370 (27,200), 268 (70,000)	1.72
[Cu$_2$L^{1b}](ClO$_4$)$_2$	600 (479)	380 (22,500), 272 (63,400)	1.71
[Cu$_2$L^{2a}](ClO$_4$)$_2$	590 (478)	375 (17,100), 276 (27,500)	1.71
[Cu$_2$L^{2b}](ClO$_4$)$_2$	605 (337)	380 (26,700), 273 (23,400)	1.70

voltammograms for the mononuclear complexes of CuL^a and CuL^b are shown in Fig. 3. The cyclic voltammograms for the binuclear copper(II) complexes of Cu$_2$L^{1a} and Cu$_2$L^{1b} are shown in Fig. 4. The electrochemical data are summarized in Table IV.

Reduction Process

Mononuclear Complexes

The cyclic voltammograms for the mononuclear complexes show one irreversible reduction wave in the cathodic region. The copper(II) ion in the complexes CuL^a and CuL^b (N$_2$O$_2$ compartment) reduces at -0.89 and -0.75 V, respectively. The electron-withdrawing bromide ion that is present at the para position to the phenolic group decreases the electron density at the metal centre, leading to easy reduction, and shifts the reduction potential to a less negative potential. The copper(II) ion in the complexes Cu(oxen) and Cu(oxpn) (N$_4$ compartment) reduces at -0.60 and -0.54 V, respectively. The increase in chelate ring size increases the macrocyclic ring size and the macrocycle incorporates more flexibility that tries to stabilize copper(I) ions and causes easy reduction.

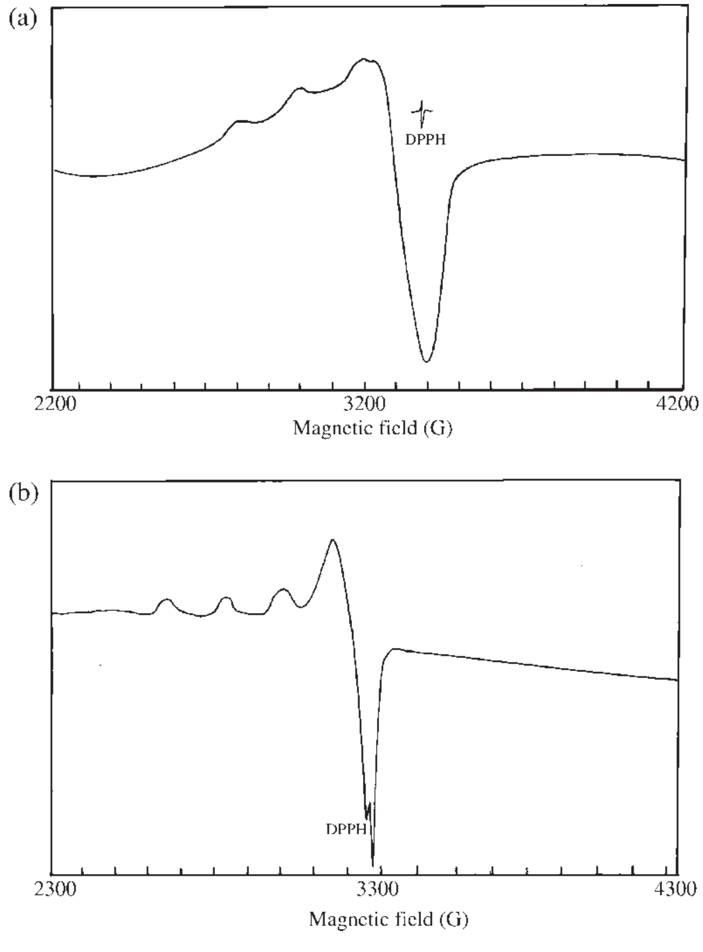


FIGURE 2 ESR spectra of copper(II) complexes (a) [CuL^a] and (b) [Cu$_2$L^{1a}](ClO$_4$)$_2$.

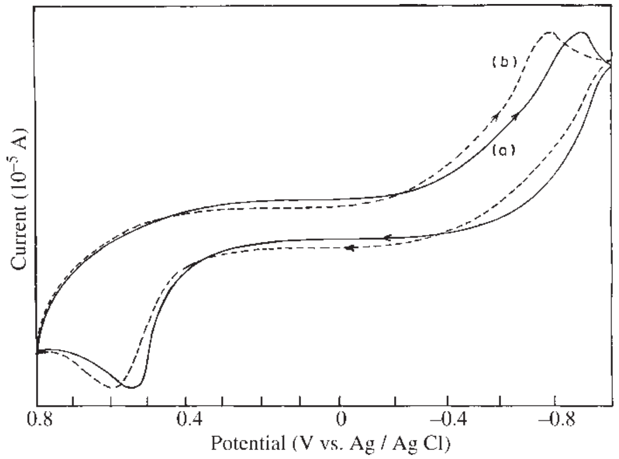


FIGURE 3 Cyclic voltammogram of the mononuclear copper(II) complexes (a) CuL^a and (b) CuL^b.

Binuclear Copper(II) Complexes

All the binuclear complexes show two-step irreversible [22] single-electron transfer processes in the cathodic region. Coulometric studies performed at 100 mV more negative relative to the first reduction wave consumed approximately one electron ($n = 0.89$) and at 100 mV more negative to the second reduction wave consumed two electrons ($n = 1.85$) per molecule, which indicates the involvement of two single-electron transfers in the reduction processes. The reduction process involves the following steps:

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

The first reduction potential ranges from −0.35 to −0.53 V, and the second reduction potential lies in the range −0.62 to −0. 78 V. The first and second reduction potentials shift towards the anode as the chelate ring size increases from the ethylene to the propylene linkage. The increase in the chelate ring size increases the macrocyclic ring size and the macrocycle incorporates more flexibility, which tries to stabilize copper(I) ions and causes easy reduction [23,24]. Moreover, the electron-withdrawing bromide ion that is present at the para position to the phenolic group decreases the electron density at the metal centre leading to easy reduction, and shifts the reduction potential to less negative potential [25,26]. The copper ions present in the oxen and oxpn (N_4) compartments are reduced at a less negative potential than CuL^a and CuL^b (N_2O_2 compartment), which is in good agreement with the mononuclear complexes. Thus in the binuclear copper(II) complexes the first reduction may be due to metal ions present in the N_4 compartment and the second potential corresponds to metal ions present in the N_2O_2 compartment.

Oxidation Process

Mononuclear Complexes

CuL^a and CuL^b (N_2O_2 compartment) oxidize at 0.53 and 0.60 V, respectively. The electron-withdrawing bromide ions that are at the present para position to the phenolic group shift the oxidation potential to a more positive value [27]. Cu(oxen) and Cu(oxpn) (N_4 compartment) oxidize at 0.50 and 0.52 V, respectively.

Binuclear Complexes

The cyclic voltammograms of the binuclear copper(II) complexes show the first oxidation

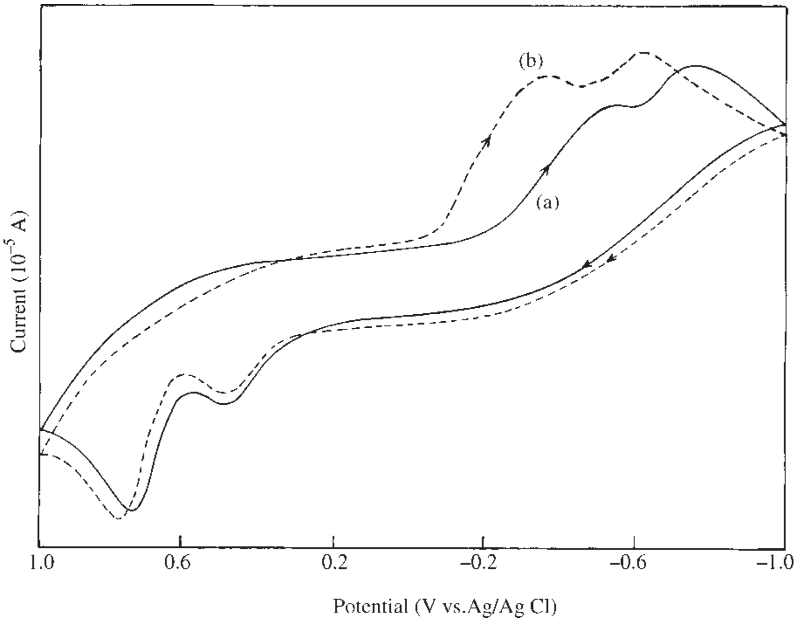


FIGURE 4 Cyclic voltammogram of the binuclear copper complexes (a) $Cu_2[L^{1a}](ClO_4)_2$ and (b) $Cu_2[L^{1b}](ClO_4)_2$.

TABLE IV Electrochemical data for the complexes

	Reduction		Oxidation	
Complex	E^1_{pc} (V)	E^2_{pc} (V)	E^1_{pa} (V)	E^2_{pa} (V)
[CuL^a]	−0.89		0.53	
[CuL^b]	−0.75		0.60	
[Cu(oxen)]$(ClO_4)_2$	−0.60		0.50	
[Cu(oxpn)]$(ClO_4)_2$	−0.54		0.52	
[Cu_2L^{1a}]$(ClO_4)_2$	−0.53	−0.78	0.51	0.75
[Cu_2L^{1b}]$(ClO_4)_2$	−0.36	−0.74	0.50	0.83
[Cu_2L^{2a}]$(ClO_4)_2$	−0.50	−0.76	0.49	0.73
[Cu_2L^{2b}]$(ClO_4)_2$	−0.35	−0.62	0.49	0.78

Measured by CV at scan rate 50 mV s^{-1}. E vs Ag/AgCl conditions: counter and working electrodes were platinum foils and Ag/AgCl reference electrode; supporting electrolyte tetra(*n*-butyl)ammonium perchlorate (TBAP) 1×10^{-1} M; concentration of the complexes 1×10^{-3} M.

potential in the range 0.49 to 0.51 V and the second oxidation potential in the range 0.83 to 0.73 V. The binuclear complexes show two-step single-electron transfer processes. The oxidation process is irreversible in nature. A comparison of the second oxidation potential of Cu_2L^{1a} (0.75 V) and Cu_2L^{1b} (0.83) shows that it shifts towards a more positive value due to the electron-withdrawing bromine, which is present at the *para* position to the phenolic oxygen as substituent. This shift is also seen in the complexes between Cu_2L^{2a} and Cu_2L^{2b}.

New unsymmetrical multidentate macrocyclic binucleating ligands and their mono- and binuclear copper(II) complexes have been synthesized and characterized. ESR and magnetic properties indicate that there is no interaction between the copper(II) ions. From this we infer that the two copper(II) ions are present in the remote (N_2O_2, N_4) compartments among the three compartments (N_2O_2, O_2N_2, N_4) present in the complexes. Small variation in the ligand framework influences the spectroscopic properties and reactivity.

EXPERIMENTAL

Elemental analysis of the complexes was obtained in a Heraeus CHN rapid analyser. The metal content was analysed using a Perkin-Elmer 2380 atomic absorption spectrophotometer. Electronic spectral studies were carried out on a Hitachi 320-model double-beam spectrophotometer in the range 200–800 nm. IR spectra were recorded on a Hitachi 270–50 spectrophotometer on KBr discs in the range 4000–400 cm^{-1}. The electrochemical measurements were performed at room temperature in DMF by using electrochemical system M 263A (EG&G A PAR). The measurements were carried out under oxygen-free conditions using a three-electrode cell in which the counter and working electrodes were platinum foil and a saturated Ag/AgCl electrode was the reference 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 conditions is 470 mV in DMF and ΔE_p for Fc/Fc^+ is 70 mV. Tetra(*n*-butyl)ammonium perchlorate (10^{-1} M) was used as the supporting electrolyte. (**Caution!** TBAP is potentially explosive; hence care should be taken in handling the compound). The concentration of complexes is 10^{-3} M. Room temperature magnetic moment was measured on a PAR vibrating sample magnetometer Model-155. X-band ESR spectra were recorded in the solid state at 25°C on a Varian EPR-E 112 spectrometer using diphenylpicrylhydrazine (DPPH) as the reference.

Materials

N,N′-bis(2-aminoethyl)oxamide, *N,N′*-bis(3-aminopropyl)oxamide, [Cu(oxen]$(ClO_4)_2$ and [Cu(oxpn)]-$(ClO_4)_2$ were prepared by using literature methods [28]. TBAP used as the supporting electrolyte in the electrochemical measurement was purchased from Fluka and recrystallized from hot methanol. DMF (HPLC) was obtained from Merck. All other chemicals and solvents were of analytical grade and were used as received without any further purification. The precursor compound (PC-1) [6,6′-piperazine-1,4-diyldimethylenebis(4-methyl-2-formyl)phenol] and (PC-2) [6,6′-piperazine-1,4-diyldimethylene-bis(4-bromo-2-formyl)phenol] were prepared by using the literature methods [29].

Synthesis of Mononuclear Complexes

[CuL^a]

PC-I (0.382 g, 1 mmol) was dissolved in $CHCl_3$/MeOH (40 ml, 1:1) and added to a solution of copper(II) perchlorate (0.370 g, 1 mmol) dissolved in methanol (25 ml) under boiling conditions and refluxed for 1 h. The green-coloured precipitate formed was collected by filtration, washed with $CHCl_3$ followed by MeOH and then dried. Selected IR data (ν/cm^{-1} using KBr): 3380, 1670.

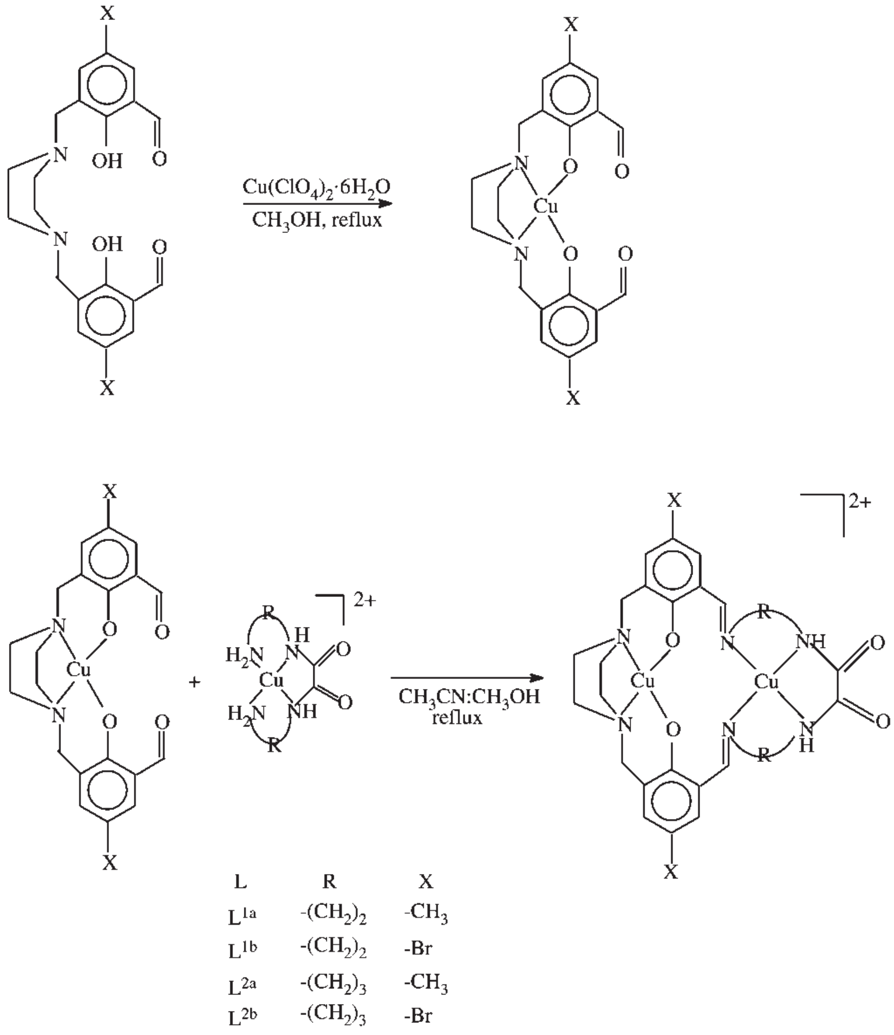
[CuL^b]

This was obtained by following the above procedure using PC-II and copper(II) perchlorate. Selected IR data (ν/cm^{-1} using KBr): 3374, 1668.

Synthesis of Binuclear Complexes

[Cu_2L^{1a}] $(ClO_4)_2 \cdot 2H_2O$ (1)

CuL^a (0.44g, 1 mmol) was dissolved in CH_3CN:CH_3OH (1:2) and added to a solution of [Cu(oxen)]$(ClO_4)_2$ (0.43 g, 1 mmol) dissolved in 15 ml methanol and



L	R	X
L^{1a}	$-(CH_2)_2$	$-CH_3$
L^{1b}	$-(CH_2)_2$	-Br
L^{2a}	$-(CH_2)_3$	$-CH_3$
L^{2b}	$-(CH_2)_3$	-Br

SCHEME 1

refluxed for 24 h. The green solid obtained was filtered, washed with cold methanol and diethyl ether and dried in a vacuum desiccator. Recrystallized in CH_3CN/CH_3OH. Yield (72%). Anal. (%) Calcd. for $C_{28}H_{34}N_6O_4Cu_2(ClO_4)_2{\cdot}2H_2O$: C, 38.20; H, 4.32; N, 9.56; Cu, 14.33. Found: C, 38.23; H, 4.12; N, 9.66; Cu, 14.63. Selected IR data (KBr disc, ν/cm^{-1}): 3450, 3205, 1675, 1614, 1085, 623.

The synthetic route is shown in Scheme 1. All copper complexes given below were synthesized by following the procedure used for the synthesis of complex **1** using the appropriate precursor compound, $[Cu(oxen)](ClO_4)_2$ and $[Cu(oxpn)](ClO_4)_2$.

$[Cu_2L^{1b}](ClO_4)_2{\cdot}2H_2O$ (2)

This complex was prepared by following the above procedure (complex **1**) using CuL^b instead of CuL^a. Yield 0.60 g (68%). Anal. (%) Calcd for $C_{26}H_{28}N_6O_4Br_2Cu_2(ClO_4)_2.2H_2O$: C, 30.98; H, 2.78; N, 8.34; Cu, 12.51. Found: C, 30.75; H, 2.87; N, 8.48; Cu, 12.67. Selected IR data (KBr disc, ν/cm^{-1}): 3380, 3114, 1660, 1616, 1091, 624.

$[Cu_2L^{2a}](ClO_4)_2{\cdot}2H_2O$ (3)

This complex was prepared by following the above procedure using $[Cu(oxpn)](ClO_4)_2$ instead of $[Cu(oxen)](ClO_4)_2$. Yield 0.67 g (75%). Anal. (%) Calcd for $C_{30}H_{38}N_6O_4Cu_2(ClO_4)_2{\cdot}2H_2O$: C, 39.69; H, 4.19; N, 9.26; Cu, 13.89. Found: C, 39.31; H, 4.59; N, 9.34; Cu, 13.58. Selected IR data (KBr disc, ν/cm^{-1}): 3413, 3240, 1660, 1614, 1083, 623.

$[Cu_2L^{2b}](ClO_4)_2{\cdot}2H_2O$ (4)

This complex was prepared by following the above procedure using CuL^b, $[Cu(oxpn)](ClO_4)_2$ instead of CuL^a, $[Cu(oxen)](ClO_4)_2$. Yield 0.64 g (73%). Anal. (%) Calcd for $C_{28}H_{32}N_6O_4Br_2Cu_2(ClO_4)_2{\cdot}2H_2O$: C, 32.46; H, 3.09; N, 8.11; Cu, 12.17. Found: C, 32.64; H, 3.24; N, 8.22; Cu, 12.37. Selected IR (KBr disc, ν/cm^{-1}): 3427, 3099, 1660, 1616, 1093, 623.

SUPPLEMENTARY MATERIAL

Full crystal data and structure refinement details, atomic coordinates, equivalent isotropic displacement parameters, full interatomic distances and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters for complex [CuL^{a}] are available from the Cambridge Crystallographic Data Centre, CCDC No. 200623. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; www.http//www.ccdc.cam.ac.uk).

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