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Synthesis, spectral, electrochemical and magnetic properties of new phenoxo-bridged dicopper(II) complexes derived from unsymmetrical binucleating ligands

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Abstract

New unsymmetrical binucleating ligands 4-bromo-2-[(4-methylpiperazin-1-yl)methyl]-6-[N-(3,5-dimethyl-2-hydroxy-benzyl)-N-methylaminomethyl]phenol (H_2L^1) and 4-bromo-2-[(4-methyl-piperazin-1-yl)methyl]-6-[N-(3,5-dichloro2-hydroxybenzyl)-N-cyclo-hexylminomethyl] phenol (H_2L^2) and their copper(II) complexes $[Cu_2L^{1\text{-}2}(X)]ClO_4$, (X=OH, Br, OAc) have been prepared. Spectral, electrochenuical and magnetic behaviors have been studied. Electrochemical study of the complexes shows two distinct quasireversible redox peaks. ($E^1_{pc}=-0.35$ to -0.70 V, $E^2_{pc}=-0.75$ to -0.97 V). Variable temperature magnetic susceptibility studies of the complexes show the presence of antiferromagnetic interaction between the copper atoms ($-2J=69$–124 cm^{-1}). A comparison of the electrochemical and magnetic behavior of the complexes derived from both the ligands is discussed on the basis of substitutional steric and electronic effects.

Keywords: Binucleating ligands; Binuclear copper(II) complexes; Electrochemical studies; Magnetic studies

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Synthesis and characterization of new binuclear copper(II) complexes have made an impact on bioinorganic chemistry, since the spectral, electrochemical and magnetic features provide new insight into the structure of naturally occurring dicopper proteins such as hemocyanin, tyrosinase, catechol oxidases, ceruloplasmin etc. [1–5]. In physicochemical aspects these dicopper complexes have noteworthy significance as new inorganic materials capable of showing peculiar magnetic and redox properties and hence these binuclear copper(II) complexes have wealth of applications in magnetochemistry [6–8] and homogeneous catalysis [9]. From Robson's pioneering work on binuclear copper(II) complexes with phenolate endogeneous bridge, a lot of work has been carried out [10,11]. Most of the work is concerned with the studies of symmetrical dicopper complexes and the study on unsymmetrical dicopper complexes is sparse. Synthesis of unsymmetrical binucleating ligands and their copper(II) complexes gains the attention in recent years with the establishment of unsymmetrical nature of the active site of hymocyanin [12] and tyrosinase [13] and the expectation of interesting redox and magnetic behaviours associated with the chemically different coordination environments around the two copper atoms within the molecule. The present work deals with the synthesis of two new unsymmetrical binucleating ligands H_2L^1 and H_2L^2 their copper(II) complexes and the study of their spectral, electrochemical and magnetic behaviors.

1. Experimental

1.1. Materials and methods

All the chemicals and reagents were obtained from commercial sources and used without further purification. 3,4-dihydro-3,6,8-trimethyl-2H-1,3-benzoxazine [14], and 2-cyclohexylaminomethyl-4,6-dichlorophenol [15] were prepared by following the literature procedures. Elemental analyses were carried out using a Carlo Erba Elemental Analyzer Model 1106. ^1H NMR (90 MHz) spectra were recorded in CDCb or DMSO D6 using JOEL FX-90Q Fourier Transform NMR spectrometer. ^{13}C NMR spectrum (100 MHz) of ligand H_2L was recorded on JOEL GSX 400 NMR spectrometer. Mass (EI) spectra were recorded on

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JOEL JMS-DX303 HF Mass spectrometer. IR spectra were recorded on KBr disc using Hitachi 270-50 Spectrophotometer. Electronic spectra were recorded using a Hewlett-Packerd 8452A Spectrophotometer. Conductivity measurements were done using an Elico digital conductivity bridge model CM-88 using freshly prepared solution of the complexes in dmf Cyclic voltammograms were obtained on an apparatus comprising a PAR model 173 potentiostat/galvanostat, model 175 universal programmer, model 176 current/voltage convertor, 179 coulometer and Perkin Elmer Hitachi 057 X–Y recorder using platinum foil as the working electrode and a saturated Ag/AgCl as the reference electrode, using freshly distilled HPLC grade dmf as the solvent. Magnetic susceptibility on powdered samples of the complexes were measured in the temperature range 77–300 K using a PAR model 155 vibrating sample magnetometer and the instrument was calibrated with the use of metallic nickel. Room temperature magnetic moment of the complexes were recorded using a Gucy balance, in which HgIICo(SCN)411 was used as the calibrant. ESR spectra of the complexes were recorded using a Varian EPR-E112 spectrophotometer using DPPH as the reference.

1.2. N-(2-Hydroxy-5-bromobenzyl)-N-(2-hydroxy-3,5-dimethylbenzyl)-N-methylamine ***PC1***

3,4-Dihydro-3,6,8-trimethyl-2H-1,3-benzoxazine (8.85 g, 0.05 mol) and p-bromophenol (8.65 g, 0.05 mol) were mixed by slight warming and kept stoppered at room temperature. After 15 days the viscous mass was diluted with 150 ml of methanol and kept at room temperature for 24 h. Colourless solid separated was filtered off and recrystallized from benzene–methanol (1:1) mixture. m.p. 158°C, Yield 9 g, 48 %. ^{1}H NMR ($CDCl_3$) $\delta = 2.2$ (two close peaks, 9H), 3.7 (s, 4H), 6.7–6.9 (m, 5H). Mass (EI) m/z=336 (M+). Anal (%) calc. for $C_{17}H_{20}BrNO_2$ C, 60.81; H, 5.96; N, 4.17. Found C, 61.18; H, 6.35; N, 4.29.

1.3. N-(2-Hhydroxy-5-bromobenzyl)-N-(2-hydroxy-3,5-dichlorobenzyl)-N-cyclohexylamine ***PC2***

Paraformaldehyde (1.8 g, 0.06 mol) was taken in 75 ml of glacial acetic acid, 2-cyclohexylaminomethyl-4-6-dichlorophenol (13.6 g, 0.05 mol) was added and stirred at room temperature for 24 hours. Then 4-bromophenol (8.65 g, 0.05 mol) was added and stirred for 72 hours. The reaction mixture was neutralized with solid Na_2CO_3 and the residue was dissoluted in 150 ml of methanol. Colourless insoluble solid separated was filtered off and recrystallized from $CHCl_3$. m.p. 179°C. Yield 7 g (69%), ^{1}H NMR (DMSO D_6) $\delta = 1–2$ (two broad multiplets, 10H), 2.5 (br, 1H), 3.6 (s, 2H), 3.7 (s, 2H), 6.7–7.2 (m, 5H). Mass (EI) m/z=460 (M+2) Anal (%) Calc for $C_{20}H_{22}BrCl_2NO_2$ C,52.40; H,4.80; N,3.06. Found C,52.45; H,4.85; N,3.17.

1.4. 4-Bromo-2-[(4-methylpiperazin-1-yl)methyl]-6-[N-(3,5-dimethyl-2-hydroxybenzyl)-N-methylaminomethyl]phenol. $\boldsymbol{H_2L^1}$

Compound PC1 (3.35g, 0.01 mol) was dissolved in 100 ml of ethanol and N-methylpiperazine (1.2 ml, 0.01 mol) was added. To the resulting mixture 37% formalin (1.2 ml, 0.015 mol) was added with cooling and stirred at room temperature for 5 h. The mixture was refluxed on a water bath for 24 h and the solvent was evaporated. The residue was thoroughly washed with water. Column chromatographic separation on silica gel (CH_2Cl_2/MeOH 4:1) offered the compound as yellow oil. Yield 2.2 g (67%), ^{1}H NMR ($CDCl_3$) $\delta = 2.2$ (two close peaks, 9H), 2.3 (s, 3H), 2.6 (br, 8H), 3.6 (two close peaks, 6H), 6.5–6.8 (m, 4H), 9.8 (br. 2H). Mass (EI) m/z=461 (M+1). Anal (%) Calc for $C_{23}H_{30}BrN_3O_2$ C, 60.00; H,6.52; N,9.13. Found C,61.09; 11,6.96; N,9.27.

1.5. 4-Bromo-2-[(4-methylpiperazin-1-yl)methyl]-6-[N-(3,5-dichloro-2-hydroxybenzyl)-N-cyclohexylaminomethyliphenol $\boldsymbol{H_2L^2}$

The procedure adopted for the preparation of the ligand H_2L^2 was same as that of H_2L^1, but instead of ethanol medium the reaction was carried out in THF/ethanol(1:1). After 24 h of refluxion the solvent was evaporated at room temperature. The residue was extracted with CH_2Cl_2 (2× 50 ml). To the extract 50 ml of methanol was added and cooled at 0°C for several days. Solid separated was filtered and recrystallized from ethanol–hexane(1:1). m.p. 87°C, Yield 1.6 g, (34%), ^{1}11 NMR ($CDCl_3$) $\delta = 1–2$ (two broad mutiplets, 10H), 2.3 (s, 3H), 2.6 (br. 9H), 3.6 (s, 2H), 3.65 (s, 2H), 3.7 (s, 2H), 6.6–7.2 (m, 4H). ^{13}C NMR ($CDCl_3$) $\delta = 25.4$, 25.7, 31.5, 47.02, 47.06, 57.68, 58.8, 60.6, 109.7, 117.8, 123.1, 124.7, 126.5, 126.6, 127.3, 127.4, 153.6, 156.4. Mass(EI) m/z=571 (M^+). Anal (%) Calc for $C_{26}H_{34}BrCl_2N_3O_2$ C,54.74; H,5.96; N,7.37. Found C,54.84; H,6.01; N,7.45.

The μ-phenoxo-μ-(X)-dicopper(II) complexes $[Cu_2L^{1-2}(X)]ClO_4$ **(1–6)** were prepared by following the procedure reported by Reed and coworkers [16].

The ligand H_2L^1 or H_2L^2 (1 mmol) was dissolved in 75 ml of distilled methanol by heating. To the resulting solution copper(II) perchlorate hexahydrate (0.74 g, 2 mmol) dissolved in 30 ml of methanol was added and refluxed on a water bath for 3 h. The reaction mixture was then reacted with one equivalent of NaX (X=OH, Br, GAc) dissolved in 5 ml of water–methanol (1:4) and refluxed for further 1 h. Solid compound deposited on slow evaporation of the solvent was filtered, washed with diethyl ether and dried. Various attempts to develope crystals suitable for X-ray diffraction studies such as slow diffusion, crystallisation using mixture of solvents and low temperature crystallisation were unsuccesful.

1.5.1. *[$Cu_2L^1(OH)]ClO_4.2H_2O$* **(1)**

Green solid. Anal (%) calc for $C_{23}BrCl\ Cu_2N_3O_9$ C, 37.35; H,4.74; N,5.68. Found C,37.45; H,4.74; N,5.59. Selected IR (KBr): 3450, 1630, 1100 and 620 cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in dmf 74.</H2>

1.5.2. *[$Cu_2L^1(Br)]ClO_4.H_2O$* **(2)**

Brown solid. Anal (%) calc for $C_{23}H_{32}Br_2Cl\ Cu_2N_3O_7$ C,35.23; H,4.08; N,5.36. Found C,35.11; H,4.13; N,5.28. Selected IR (KBr): 3450, 1630, 1100 and 620 cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in dmf 83.

1.5.3. *[$Cu_2L^1(OAc)]ClO_4.2MeOH$* **(3)**

Green solid. Anal(%) calc for $C_{27}H_{41}BrCl\ Cu_2N_3O_{10}$ C,41.67; H,5.27; N,5.40. Found C,41.45, H,5.24; N,5.48. Selected R(KBr): 1630, 1100 and 620 cm^{-1}. Conductance (Λ_mS cm^2 mol^{-1}) in dmf 78.

1.5.4. *[$Cu_2L^2(OH)]ClO_4.2H_2O$* **(4)**

Green solid. Anal(%) calc for $C_{26}H_{37}Cl_4\ Cu_2N_3O_9$ C,38.81; H,4.60; N,5.22. Found C,38.89; H,4.65; N,5.28. Selected IR (KBr): 3450, 1630, 1100 and 620 cm^{-1}. Conductance (Λ_m/S cm2 mol^{-1}) in dmf 77.

1.5.5. *[$Cu_2L^2(Br)]ClO_4.MeOH$* **(5)**

Brown solid. Anal(%) calc for $Cr_{27}H_{36}BrCl_4\ Cu_2N_3O_7$ C,37.54; H,4.17; N,4.87. Found C,37.69; H,4.14; N,4.98. Selected IR (KBr): 1630, 1100 and 620 cm^{-1}. Conductance (Λm/S cm^2 mol^{-1}) in dmf 85.

1.5.6. *[$Cu_2L^1(OAc)]ClO_4.2H_2O$* **(6)**

Green solid. Anal(%) calc for $C_{28}H_{38}C_{14}\ Cu_2N_3O_8$ C,41.33; H,4.67; N,5.17. Found C,41.33; H,4.45; N,5.12. Selected IR (KBr): 3450, 1630, 1100 and 620 cm^{-1}. Conductance (Λ_m/S cm^2 mol^{-1}) in dmf 79.

2. Results and discussion

2.1. *Synthesis*

Reaction of p-bromophenol and 3,4-dihydro-3,6,8-trimethyl- 2H-1,3-benzoxazine in 1:1 molar ratio offered the intermediate compound PC1, whose X-ray structure has been solved (Fig. 1) [17]. Reaction of p-chromophenol and 2-cyclohexylaminomethyl-4-6-dichlorophenol gave the intermediate PC2. Reaction of PC1 and PC2 with formaldehyde and N-methylpiperazine (1:1:1) offered the ligands H_2L^1 and H_2L^2 respectively. Reaction of the ligands with copper(II) perchlorate and appropriate sodium salt (1:2:1) afibrded the binuclear copper(II) complexes (Fig. 2).

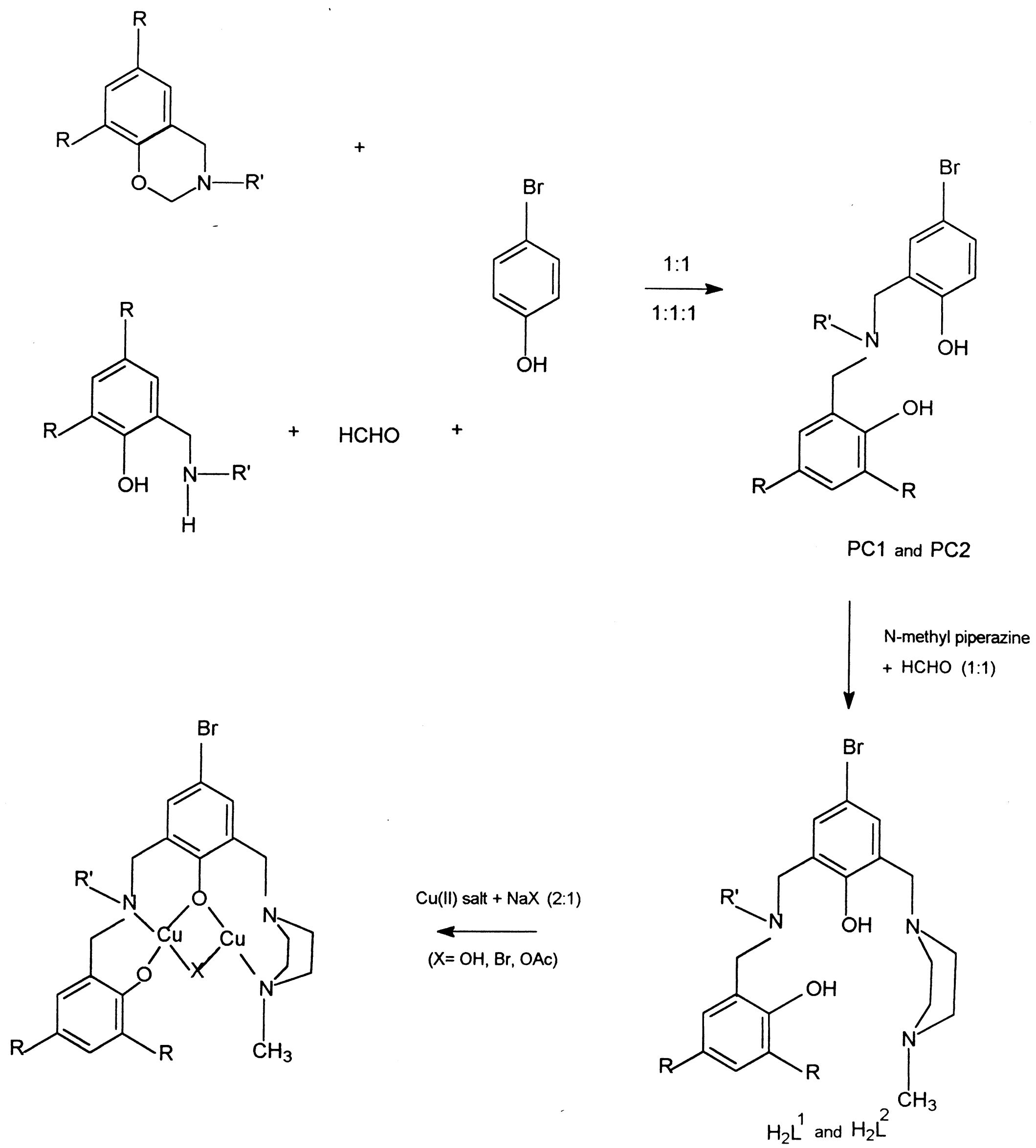
In all the compounds the peaks observed in the region $\delta=2.2$ to 2.3 were assigned to the aromatic methyl and N-methyl protons, peaks observed in the region $\delta=3.6$ to 3.9 were assigned to the benzylic protons, broad observed in the ligands H_2L^1 and H_2L^2 in the region $\delta=2.6$ were assigned to the piperazinyl protons and multiplet observed in the region $\delta=6.6$ to 7.1 were assigned to the aromatic protons. Broad bands observed in the region $\delta=1$–2 and 2.5 for the compound PC2 and ligand H_2L^2 were assigned to the cyclohexyl protons. Appearance of new benzylic peak in the region $\delta=3.6$ and 3.65 and broad peak in the region $\delta=2.6$ in the ligands H_2L^1 and H_2L^2 with respect to their corresponding intermediates clearly indicates the presence of N-methyl piperazinyl residue in the ligands.

IR spectra of the complexes shows a broad band centered around 3400 cm^{-1} indicating the presence of coordinated or lattice water in the complexes along with a strong symmetrical peak for the ClO_4 anion at 1100 cm^{-1}, which indicates that the perchlorate anion is not coordinated to the copper ions. The acetato bridged complexes **3** and **6** shows the characteristic peak for the acetate in the region 1540 cm^{-1}. Electronic spectra of the complexes were studied in dmf and the data are given in Table 1. The electronic spectra of the complexes shows three main features, a weak band in the region around 640–676 nm ($\varepsilon\approx150$ M^{-1} cm^{-1}) for the d–d transition, a peak or shoulder in the region 410–428 nm ($\varepsilon\approx1000$ M^{-1} cm^{-1}) for phenolate to copper charge transfer transition and one or two strong peaks below 300 nm ($\varepsilon\approx7000$ M^{-1} cm^{-1}) for intraligand charge transfer transitions. A red shift in the d–d band for the complexes of the ligand H_2L^2 when compared to the complexes of the ligand H_2L^1 indicates that the coordination geometry around the copper atom of the former complexes is more distorted than the latter complexes.

2.2. *Electrochemical studies*

Electrochemical behavior of the complexes was studied by molar conductance measurement and cyclic voltammetry. All the complexes show a molar conductance in the range 75–85 Λ_m/S cm^2 M^{-1} which indicates that the complexes are 1:1 electrolytes [18] in which the perchlorate is not coordinated to the any of the copper atoms (Table 2). The cyclic voltammogram of the complexes generally show two redox peaks and the data are summarized in Table 2. Cyclic voltammogram for the complexes **1** and **4** are reproduced in Fig. 3.

Coulometric analysis carried out for the complexes **1** and **4** at 100 mV to the first reduction peak consumes one electron per molecule and consumes two electrons per molecule of the complex when it was performed at 100 mV more negative to the second reduction peak. This behaviour indicates that the two reduction peaks are due to two single electron transfers which involves $Cu(II)Cu(II)\leftrightharpoons Cu(II)Cu(I)$ and $Cu(II)Cu(I)\leftrightharpoons Cu(I)Cu(I)$ conversions. The relative stability of the mixed valent species Cu(II)Cu(I) in the equilibrium mixture of Cu(II)Cu(II) and Cu(I)Cu(I) has been calculated using the relationship $\log K_{con}=\Delta E/0.0591$ and the values are given in Table 2. Larger K_{con} values observed for the complexes



PC1 & H_2L^1 — R=R'=CH_3

PC2 & H_2L^2 — R=Cl and R'=C_6H_{11}

Fig. 1. Schematic diagram for the synthesis of the ligands and complexes.

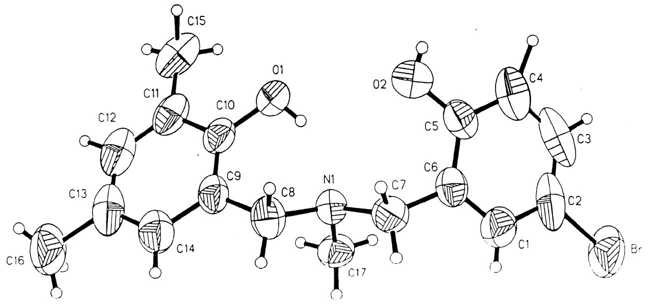


Fig. 2. ORTEP diagram for compound **PC1**.

Table 1
Electronic spectral data for the complexes

Complex	λ_{max}/nm (ε/M^{-1} cm^{-1})	
	d–d	C.T
1	640(148)	420(648), 310(5202), 290(4169)
2	642(191)	410(s), 310(7171), 291(7498)
3	647(160)	410(1121), 320(9202), 293(8167)
4	672(184)	410(700), 313(9152), 298(9093)
5	676(162)	415(765), 3 10(6763), 297(6160)
6	666(178)	410(531), 3 15(7610), 298(8031)

Table 2
Electrochemical data for the complexes

Complex	E_{pc}^{1}/V	E_{pa}^{1}/V	$E_{1/2}^{1}$ (ΔE/mV)	E_{pc}^{2}/V	E_{pa}^{2}/V	$E_{1/2}^{2}/V$ (ΔE/mV)	K_{con}
1	−0.70	−0.52	−0.61(180)	−0.97	−0.85	−0.91(120)	1.19×10^{5}
2	−0.66	−0.54	−0.60(120)	−0.93	−0.62	−0.81(190)	4.32×10^{5}
3	−0.55	−0.45	−0.50(100)	−0.85	−0.66	−0.76(190)	2.50×10^{4}
4	−0.42	−0.32	−0.37(100)	−0.85	–	–	–
5	−0.39	−0.23	−0.31(160)	−0.80	−0.62	−0.72(180)	7.79×10^{3}
6	−0.35	−0.13	−0.24(220)	−0.75	−0.65	−0.70(100)	6.07×10^{7}

Potential V vs Ag/AgCl, Electrodes: Pt vs Ag/AgCl. Sweep rate 50 mV/sec. Supporting electrolyte: TBAP, Concentration: Complex (1×10^{-3} M); TBAP (1×10^{-1} M).

indicates the greater stability of the mixed valent species under electrochemical conditions.

A comparison of the electrochemical data of the complexes of the ligands H_2L^1 and H_2L^2 shows the following interesting feature. Complexes of the ligand H_2L^2 undergo reduction at less negative potential ($E_{pc}^{1}=-0.35$ to -0.42 V and $E_{pc}^{2}=-0.75$ to -0.85 V) when compared to the complexes of the ligand H_2L^1 ($E_{pc}^{1}=-0.55$ to -0.70 V and $E_{pc}^{2}=-0.85$ to -0.97 V). Since, the nature of the donor atoms in both these ligands are the same, the reduction observed at less negative potential for the complexes **4**–**6** can be related to the electronic and steric effect of the substituents of the ligand H_2L^2. The electron withdrawing chlorine atoms positioned on the phenolic residues of H_2L^2 will reduce the electron density on the copper atoms, distortion will be induced in the copper coordination geometry by the relatively bulky cyclohexyl group. Further, cyclohexyl amine of the ligand H_2L^2 is less basic than methyl amine [19] of the H_2L^1, hence the latter will be a better electron donor than the former. Both distortion in the coordination geometry [20] and less electron density on the copper atom [21] in the complexes **4**–**6** of the ligand H_2L^2 will influence easy Cu(II)→Cu(1) conversion at less negative potential relative to the complexes of the ligand H_2L^1.

The electrochemical data indicates that the reduction potential is exogenous donor dependent. The reduction potential follows the order OAc<Br<OH. Although acetate is better electron donor than hydroxide and bromide, reduction was observed at less negative potential. This behavior seems to be associated with the increased number of atoms involved in the acetate bridge, which may offer more flexibility for the acetate bridged complexes as against the bromo and hydroxo bridged complexes. Reduction at less negative potential observed for the bromo bridged complexes when compared to the hydroxide may be due to the poor electron donating nature of the bromide than the hydroxide.

2.3. Magnetic properties

Low room temperature magnetic moment value observed for the complexes suggests the operation of superexchange interaction within the complex molecule. The extent of superexchange interaction has been evaluated by performing variable temperature magnetic moment measurements in the temperature range 77–3000 K and by fitting the data to the Bleaney-Bowers equation [22].

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

where χ_m is the molar magnetic susceptibility of the complex, P is the percentage of monomeric impurities and other symbols have their usual meanings. N_α has been fixed as 120×10^{-6} cm^3 mol^{-1} and g has been fixed at 2.20 for all magnetic simulations. A best fit to the experimental value for the complexes were summarized in Table 3. The temperature dependance of the magnetic properties for the complexes 1 and 5 are shown in Fig. 4.

Poor exchange interaction is the generally observed phenomenon in unsymmetrical dicopper(II) complexes due to ligand induced two different geometries around the two copper atoms within the molecule [23,24], which may result larger dihedral angle between the two copper magnetic orbitals [25]. In accordance with these results, the observed coupling constant values for the complexes are low.

Relatively larger spin exchange coupling values are observed for the complexes of the ligand H_2L^1, when compared to the complexes of the ligand of H_2L^2. This behavior indicates that the extent of spin–spin interactions in the former case is more than the latter. As explained in the electrochemical properties of the complexes of the ligands, generation of electropositive character on the copper atoms due to effective electron withdrawal by the chlorine atoms substituted in the ligand H_2L^2 and the possible distortion in geometry due to the bulky cyclohexyl group of the ligand are the most probable reasons for the observed low −2J values of the complexes of H_2L^2 than $H_2L^{1.}$. Reports suggest both these factors i.e. reduction in electron density on the copper atoms [26] and distorted structure [27–31] are unfavourable for effective coupling, resulting a small −2J value for the complexes of the ligand H_2L^2.

Comparison of the complexes **1**, **3** or **5**, **6** of a particular

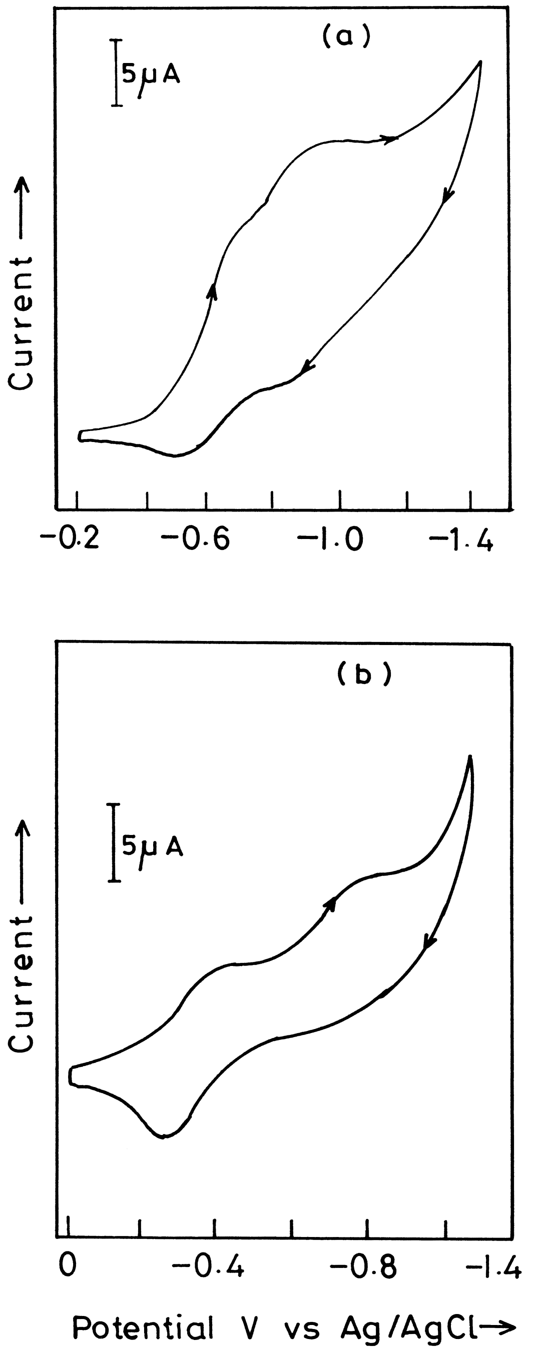


Fig. 3. Cyclic voltammogram for the complexes (a) $[Cu_2L^1(OH)]ClO_4.2H_2O$ **1** and (b) $[Cu_2L^2(OH)]C1O_4.2H_2O$ **4**.

ligand shows that the exchange interaction is influenced by the exogenous donor. A lower −2J value was observed for acetato bridged complexes (**3** and **6**) when compared to the hydroxo or bromo bridged complexes. This behaviour of the acetato complexes is possibly due to the counter-complementary nature of the overlap of the magnetic orbitals involving monciatomic and three atom bridging ligands [32].

Table 3
Magnetic and ESR spectral data for the complexes

Complex	$-2J$ cm^{-1}	μ_{eff} per molecule (B.M.)		g	
		77K	298K		
1	124	1.65	1.98	213	
2	–	–	2.10	225	
3	98	1.96	2.15	219	
4	–	–	2.24	$g_{\|}=2.24$	$g_{\perp}=2.06$
5	85	1.73	2.65	$g_{\|}=2.20$	$g_{\perp}=2.01$
6	69	2.16	2.83	$g_{\|}=2.25$	$g_{\perp}=1.99$

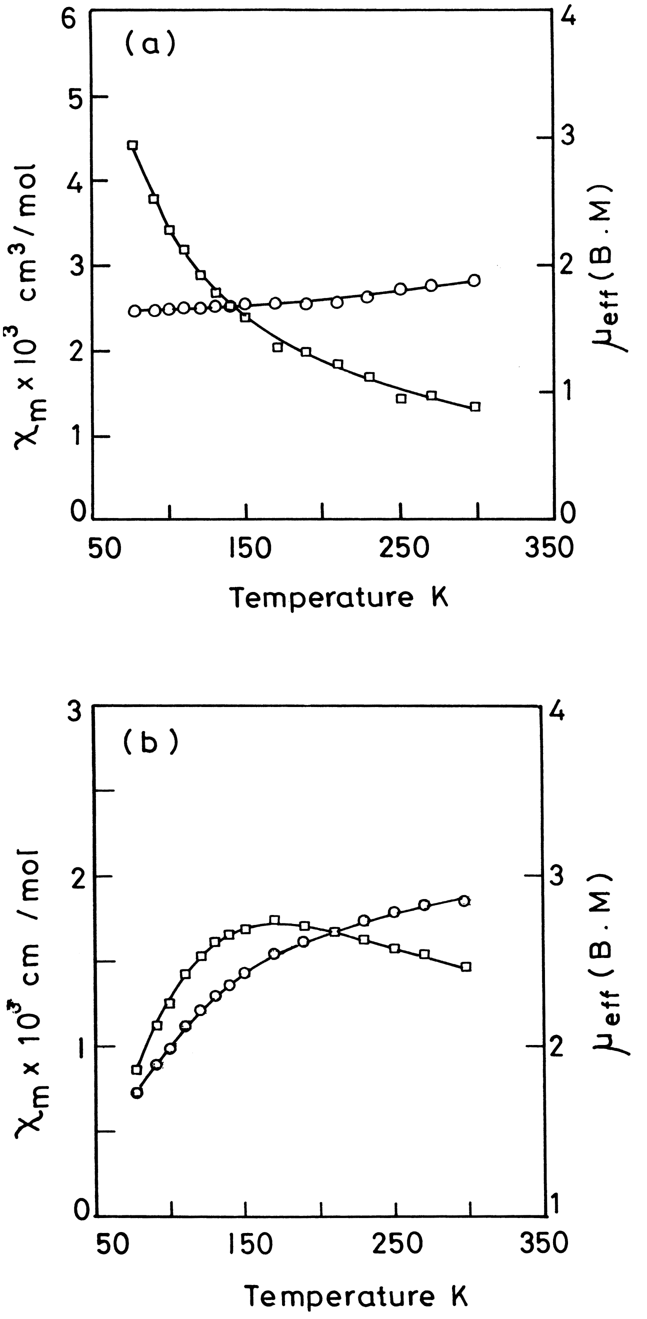


Fig. 4. Temperature dependence magnetic properties of the complex (a) $[Cu_2L^1(OH)]ClO_4.2H_2O$ **1** and (b) $[Cu_2L^2(Br)]ClO_4.MeOH$ **5**.

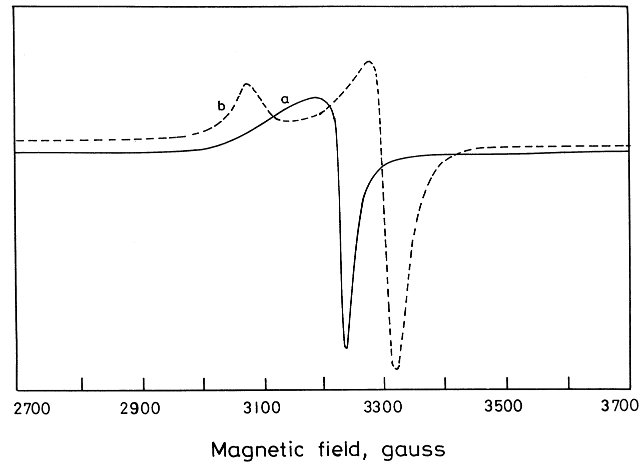


Fig. 5. ESR spectra for the complexes (a) $[Cu_2L^1(OH)]ClO_4.2H_2O$ **1** and (b) $[Cu_2L^2(OH)[ClO_4.2H_2O$ **4**.

2.4. ESR spectra

The ESR spectra of the complexes at 298 K of the complexes were obtained in the X-band region and the g values were evaluated using the relationship $h_\upsilon = g\beta H$ and the g values are given in Table 3 and the ESR spectra of the complexes **1** and **4** are reproduced in Fig. 5. Generally all the complexes of the ligand H_2L^1 shows a broad band and the complexes of the ligand H_2L^2 show broad band with poorly resolved hyperfine splitting signals and the $g_|$ values observed for the complexes are greater than the $g_\perp$ values which indicates that the copper complexes of both ligands display a signal for $|\Delta M_s = 2|$ transition at $g = 4.35$ indicating the presence of spin-exchange interaction in the complexes [33,34]

3. Summary

New unsymmetrical binucleating ligands and their copper(II) complexes have been prepared. Electrochemical study of the complexes indicates that the reduction potentials are strongly dependent on the nature of the exogenous donor atoms and peripheral substuitutents. Variable temperature magnetic and ESR spectral study of the complexes indicates the presence of spin–spin interaction between the copper atoms.

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