

Synthesis and physiochemical studies on binuclear Cu(II) complexes derived from 2,6-[(N-phenylpiperazin-1-yl)methyl]-4-substituted phenols

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Abstract. Preparation of the ligands $HL^1 = 2,6-[(N\text{-phenylpiperazin-1-yl)methyl}]\text{-}p\text{-ethylphenol}$; $HL^2 = 2,6-[(N\text{-phenylpiperazin-1-yl)methyl}]\text{-}p\text{-methoxyphenol}$ and $HL^3 = 2,6-[(N\text{-phenylpiperazin-1-yl)methyl}]\text{-}p\text{-nitrophenol}$ are described together with their Cu(II) complexes with different bridging units. The exogenous bridges incorporated into the complexes are: hydroxo $[\text{Cu}_2\text{L}(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ($L^1 = \mathbf{1a}$, $L^2 = \mathbf{1b}$, $L^3 = \mathbf{1c}$), acetato $[\text{Cu}_2\text{L}(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($L^1 = \mathbf{2a}$, $L^2 = \mathbf{2b}$, $L^3 = \mathbf{2c}$) and nitrito $[\text{Cu}_2\text{L}^1(\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ($L^1 = \mathbf{3a}$, $L^2 = \mathbf{3b}$, $L^3 = \mathbf{3c}$). Complexes $\mathbf{1a}$, $\mathbf{1b}$, $\mathbf{1c}$ and $\mathbf{2a}$, $\mathbf{2b}$, $\mathbf{2c}$ contain bridging exogenous groups, while $\mathbf{3a}$, $\mathbf{3b}$, $\mathbf{3c}$ possess only open *m*-phenolate structures. Both the ligands and complexes were characterized by spectral studies. Cyclic voltammetric investigation of these complexes revealed that the reaction process involves two successive quasireversible one-electron steps at different potentials. The first reduction potential is sensitive to electronic effects of the substituents at the aromatic ring of the ligand system, shifting to positive potentials when the substituents are replaced by more electrophilic groups. EPR studies indicate very weak interaction between the two copper atoms. Various covalency parameters have been calculated.

Keywords. Unsymmetrical ligands; dinuclear complexes; synthetic models; cyclic voltammetry.

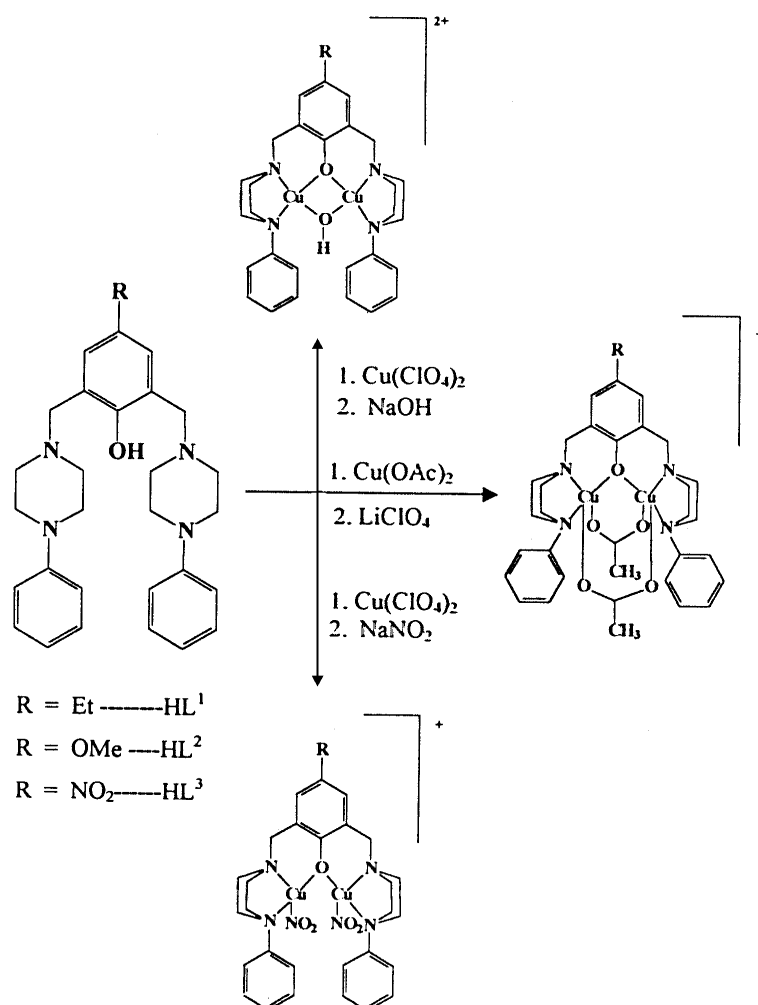
1. Introduction

Studies on the geometry around the metal centre by electronic spectra and magnetic properties of the metal ions present in the active site of metallo-biomolecules are rather difficult owing to the fact that metal ions in active sites are embedded in the protein polymer backbone. Hence, design and synthesis of model compounds that mimic the physical and chemical properties of the active site present in the metallo-biomolecules are very essential. Most of the binuclear copper(II) complexes are prepared from macrocyclic, side-off and end-off ligands. Complexes derived¹ from side-off ligands are limited in their use as models for the Cu biosites as they are rigid systems with restricted coordination geometry. The M–M distance is very small compared to the biosite and hence they are unable to support relevant exogenous bridging groups.

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End-off compartment ligands are better candidates for the provision of distinct coordination environments. Many of these sub-group dinucleating ligands have been derived from 4- (or) 3,4-disubstituted phenols. Ligands of this type readily form dinuclear transition metal complexes that can coordinate with either one or two exogenous bridging units²⁻⁵. These ligands strongly favour the formation of bimetallic species because of the enforced ideal distance between the donor sites and the presence of the endogenous bridging phenolato group. These end-off dinucleating ligands have been prepared by introducing secondary amines, in the presence of formaldehyde, activated at the 2,6-positions of the para- (or) 3,4-disubstituted phenols⁶.

The present study describes the preparation and characterisation of a series of end-off binucleating ligands and their Cu(II) complexes in which the copper centres are bridged by OH, OAc and NO₂ moieties (scheme 1). The spectral, electrochemical and EPR studies of these complexes are reported and discussed here.



Scheme 1.

2. Experimental

2.1 Physical measurements

Elemental analyses for C, H, N and Cu were obtained from the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Chennai. IR spectra were recorded on a Shimadzu FTIR 8300/8700 instrument by the KBr pellet technique, electronic spectra on a Hitachi U-2000 spectrophotometer and ^1H NMR spectra recorded using CDCl_3 on an EM-390, 90 MHz NMR spectrometer. EPR spectra were recorded using a JES-TE 100 ESR spectrometer and cyclic voltammograms were measured using BASCV-50 W electrochemical analyser in acetonitrile solution containing tetra-*n*-butyl ammonium perchlorate (TBAP) as the supporting electrolyte. Electro spray mass spectra were recorded on a Micromass Quattro II Triple Quadrupole Mass Spectrometer. The samples were dissolved in methanol and introduced into the ESI source through a syringe pump at the rate of 5 μl per min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V unless stated otherwise. The spectra were collected in 6 s scans and the print outs are averaged spectra of 6–8 scans.

2.1a *Materials*: Tetrabutylammonium perchlorate used as the supporting electrolyte in electrochemical measurements was obtained from Fluka and recrystallised from methanol. Acetonitrile (HPLC grade) was obtained from SD Fine Chemicals and dried by distillation over P_2O_5 and KMnO_4 .

2.2 Preparation of the ligands

The ligands were synthesized by a modified procedure⁷ based on Mannich base reaction of *p*-substituted phenols, formaldehyde and *N*-phenylpiperazine.

2.2a *Preparation of 2,6[(N-phenylpiperazin-1-yl)methyl]-p-ethylphenol (HL¹)*: 6.108 g (0.05 mol) of *p*-ethylphenol was completely dissolved in 100 ml of distilled ethanol. Then 15.3 ml (0.1 mol) of *N*-phenylpiperazine, followed by 12.5 ml of formaldehyde, was added drop by drop with constant stirring. The resulting solution was stirred at room temperature for half an hour and refluxed for 24 h. 2.5 ml of formaldehyde was added at approximately 8-hour intervals. After refluxing, ethanol was removed by distillation under vacuum. The precipitate obtained was collected and dried. The product was recrystallized from ethanol.

m.p. = 167°C; Yield: 80%; IR (KBr disc): 3390 cm^{-1} (*br*, OH), 1600 cm^{-1} (N-Ph), 1600 cm^{-1} (aromatic), 1458 cm^{-1} (CH_3); ^1H NMR in CDCl_3 , δ ppm: 1.2 (*t*, 3H, CH_3), 2.65 (*q*, 2H, CH_2 -Ph), 2.7–3.2 (*dd*, 16 H N- CH_2), 3.7 (*s*, 4H, benzyl CH_2), 6.9–7.3 (*m*, 12H, ArH).

The ligands HL^2 and HL^3 were prepared by adopting the same procedure as that used for HL^1 .

2.2b *Preparation of 2,6[(N-phenylpiperazin-1-yl)methyl]-p-methoxyphenol (HL²)*: m.p. = 183°C; Yield: 80%; IR (KBr disc): 3435 cm^{-1} (*br*, OH), 1600 cm^{-1} (N-Ph), 1600 cm^{-1} (aromatic), 1224 cm^{-1} (CH_3); ^1H NMR in CDCl_3 δ ppm: 2.8–3.3 (*dd*, 16H, N- CH_2), 3.7 (*s*, 4H, CH_2), 3.8 (*s*, 3H, OCH_3), 6.9 (*m*, 10H, Ph) and 7.3 (*s*, 2H, ArH).

2.2c Preparation of 2,6[(*N*-phenyl piperazin-1-yl)methyl]-*p*-nitrophenol (HL^3): Yield: 80%; IR (KBr disc): 3440 cm^{-1} (br, OH), 1600 cm^{-1} (N-Ph), 1600 cm^{-1} (aromatic), 1498 cm^{-1} (NO_2) ^1H NMR in CDCl_3 δ ppm: 2.8–3.3 (*dd*, 16H, N- CH_2), 3.7 (*s*, 4H, CH_2), 6.9–7.0 (*m*, 12H ArH).

2.3 Preparation of the complexes

2.3a Preparation of the hydroxo bridged complexes: (i) $[\text{Cu}_2L^1(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1a**) – To the methanolic solution of the ligand (1 mmol), sodium hydroxide (1 mmol) was added, followed by copper(II) perchlorate hexahydrate (2 mmol) dissolved in methanol. The resulting greenish blue solution was refluxed for one hour and then filtered. A green precipitate was obtained on evaporation at room temperature for several days, which yielded a dark green compound which was recrystallized from aqueous methanol. (Found: C = 41.52, H = 5.05, N = 6.41, Cu = 14.32%. Cal. for $\text{C}_{30}\text{H}_{42}\text{Cl}_2\text{N}_4\text{O}_{12}\text{Cu}_2 \cdot \text{H}_2\text{O}$: C = 41.57, H = 5.08, N = 6.46, Cu = 14.67%.)

(ii) $[\text{Cu}_2L^2(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1b**), $[\text{Cu}_2L^3(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1c**) – These complexes were prepared by the same procedure as **1a** using HL^2 or HL^3 instead of HL^1 . (Found: C = 40.01, H = 4.80, N = 6.47, Cu = 14.60%. Cal. for $\text{C}_{29}\text{H}_{40}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{13} \cdot \text{H}_2\text{O}$: C = 40.09, H = 4.83, N = 6.45, Cu = 14.64%; Found: C = 37.99%, H = 4.39, N = 7.86, Cu = 14.12; Cal. for $\text{C}_{28}\text{H}_{37}\text{Cl}_2\text{Cu}_2\text{N}_5\text{O}_{14} \cdot \text{H}_2\text{O}$: C = 38.05, H = 4.41, N = 7.92, Cu = 14.39%.)

2.3b Preparation of the bis acetato bridged complexes: (i) $[\text{Cu}_2L^1(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2a**) – Copper(II) acetate monohydrate (0.002 mol) was dissolved in methanol (75 ml). Addition of the methanolic solution of the ligand (0.001 mol) and (0.002 mol) of lithium perchlorate to it, led to the formation of a dark green solution. The mixture was refluxed for one hour and filtered. The filtrate was allowed slowly to evaporate at room temperature. A dark green solid was obtained, washed with methanol and left to dry in air at room temperature. (Found: C = 49.12, H = 5.40, N = 6.71, Cu = 15.20%; Cal. for $\text{C}_{34}\text{H}_{43}\text{ClCu}_2\text{N}_4\text{O}_9 \cdot \text{H}_2\text{O}$: C = 49.06, H = 5.41, N = 6.73, Cu = 15.28%.)

(ii) $[\text{Cu}_2L^2(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2b**), $[\text{Cu}_2L^3(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2c**) – These complexes were prepared by the same procedure as **2a** using HL^2 or HL^3 instead of HL^1 . (Found: C = 47.59, H = 4.98, N = 6.69, Cu = 15.21%; Cal. for $\text{C}_{33}\text{H}_{41}\text{ClCu}_2\text{N}_4\text{O}_{10} \cdot \text{H}_2\text{O}$: C = 47.50, H = 5.15, N = 6.71, Cu = 15.24%; Found: C = 45.21, H = 4.71, N = 8.12, Cu = 14.81%; Cal. for $\text{C}_{32}\text{H}_{38}\text{ClCu}_2\text{N}_5\text{O}_{11} \cdot \text{H}_2\text{O}$: C = 45.25, H = 4.71, N = 8.24, Cu = 14.97%.)

2.3c Preparation of the bis nitrito bridged complexes: (i) $[\text{Cu}_2L^1(\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**3a**) – A solution of sodium nitrite (0.003 mol) dissolved in methanol (75 ml) was added to the methanolic solution containing the ligand (0.001 mol) and copper (II) perchlorate hexahydrate (0.002 mol). The resulting bluish green solution was refluxed for 4 h and filtered. Upon concentration of this solution green black crystals were obtained, which were recrystallised from aqueous methanol. (Found: C = 42.68, H = 5.02, N = 9.80, Cu = 15.01%; Cal. for $\text{C}_{30}\text{H}_{41}\text{ClCu}_2\text{N}_6\text{O}_{11} \cdot \text{H}_2\text{O}$: C = 42.77, H = 5.10, N = 9.98, Cu = 15.10%.)

(ii) $[\text{Cu}_2L^2(\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**3b**), $[\text{Cu}_2L^3(\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**3c**) – These complexes were prepared by the same procedure as **3a** using HL^2 or HL^3 instead of HL^1 . (Found: C = 41.23, H = 4.61, N = 9.82, Cu = 15.01% Cal. for $\text{C}_{29}\text{H}_{39}\text{ClCu}_2\text{N}_6\text{O}_{12}$.

H₂O: C = 41.25, H = 4.80, N = 9.95, Cu = 15.06%; Found: C = 39.01, H = 4.36, N = 11.20, Cu = 14.63%; Cal. for C₂₈H₃₆ClCu₂N₇O₁₃.H₂O: C = 39.13, H = 4.42, N = 11.41, Cu = 14.80%).

3. Results and discussion

3.1 Synthesis and characterization

Complexes **1a**, **1b** and **1c** were prepared by using the ethanolic solution of ligand and copper(II) perchlorate hexahydrate 1 : 2 molar ratio in the presence of sodium hydroxide. The *bis* acetato complexes **2a**, **2b** and **2c** were synthesized from the reaction of the ligands with copper(II) acetate monohydrate and lithium perchlorate. The dinitrito **3a**, **3b** and **3c** complexes were obtained using a 1 : 2 molar ratio of the ligand and copper perchlorate in the presence of sodium nitrite in aqueous ethanol.

Spectroscopic techniques were used to elucidate the structure of the complexes. The OH-bridged complexes exhibit a broad IR band around 3480–3600 cm⁻¹ due to the OH stretching^{8,9}. The perchlorate salts show a strong band near 1100 cm⁻¹ and sharp band around 620–630 cm⁻¹ indicative of the uncoordinated perchlorate anion^{10,11}. The *bis* acetato bridged complexes showed¹² strong $\nu(\text{COO})$ bands around 1485 and 1583 cm⁻¹. IR bands due to the nitrite groups were observed around 1240–1495 cm⁻¹ which on comparison to the one published¹³ would suggest a monodentate O-bonded mode for the nitrite groups.

The electronic spectra of these complexes in methanol show a low intensity band in the region 600–800 nm indicative of pyramidal geometry¹⁴, a medium intensity band occurring between 360 and 480 nm due to charge transfer from phenolato to Cu(II)¹⁵. An intense absorption band around 280–330 nm has also been observed which probably arises due to the ligand-to-ligand charge transfer transition.

3.2 Redox properties

The electrochemical properties of the complexes were studied by cyclic voltammetry. The cyclic voltammetric measurements were performed in dry acetonitrile. TBAP was used as supporting electrolyte. The solutions were deoxygenated by purging dry nitrogen for 10 min before taking measurements. A three-electrode cell configuration with a platinum disc as the working, a platinum rod as the counter and saturated LiCl–Ag/AgCl as the reference electrodes were employed.

All the complexes undergo two one-electron reduction and oxidation at two different potentials. Figure 1 shows the cyclic voltammogram of **1b**. The electrochemical data are summarized in table 1.

Electrochemical behaviour in the negative potential range is sensitive to the electron inductive (+ *I* (or) – *I*) nature of the substituents at the para position of the benzene rings. It has been observed that (i) the E_{pc} and E_{pa} values change with the scan rate. (ii) the ΔE_p increases with increase of scan rate and was found to be more than 60 mV and (iii) the cathodic (*I_c*) and anodic (*I_a*) peak currents were not equal. This indicates the quasi-reversible nature of the electron transfer process. Coulometric experiments indicated that each of the couples was involved in a one-electron transfer process. Therefore it is reasonable to assign the two waves to successive one-electron reactions at the metal centres.

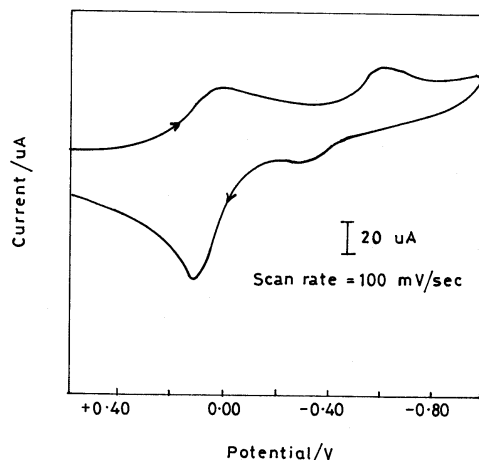
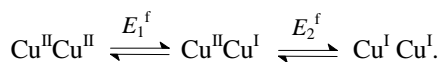


Figure 1. Cyclic voltammogram of $[\text{Cu}_2\text{L}^2(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1b**) in CH_3CN .

Table 1. Electrochemical data for complexes with their conproportionation constants (K_{con}) and conductivity data.

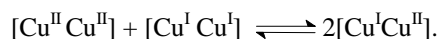
Complex ^a	$E_{1/2}^1(\Delta E_p)^b$	$E_{1/2}^2(\Delta E_p)$	K_{con}	Equivalent conductance ($\text{ohm cm}^2 \text{mol}^{-1}$)	Type of electrolyte
1a	+0.19 (+0.46)	-0.28 (+0.20)	8.96×10^7	180	1 : 2
1b	-0.01 (+0.26)	-1.22 (+0.38)	2.97×10^{20}	180	1 : 2
1c	+0.22 (+0.52)	-0.42 (+0.38)	6.74×10^{10}	200	1 : 2
2a	+0.11 (+0.18)	-0.57 (+0.38)	3.20×10^{11}	110	1 : 1
2b	+0.23 (+0.30)	-0.82 (+0.54)	5.80×10^{17}	110	1 : 1
3a	+0.14 (+0.22)	-0.66 (+0.70)	3.40×10^{13}	100	1 : 1
3b	+0.21 (+0.34)	-0.25 (+0.70)	6.60×10^7	100	1 : 1
3c	-0.67(+0.06)	-1.14(+0.08)	8.90×10^7	100	1 : 1

^a1 mmol of the complexes in CH_3CN (0.1 M TBAP) was used; ^b $(\Delta E_p) = E_{\text{Pc}} - E_{\text{Pa}}$; $E_{1/2} = E_{\text{Pc}} + E_{\text{Pa}}/2$; $\log K_{\text{con}} = E_{1/2}^1 - E_{1/2}^2/0.0591$.



In table 1, it is important to note that the replacement of a relatively electron-releasing (ethyl) group by an electron-withdrawing NO_2 group shifts the first reduction to more negative potentials. A similar trend has been observed by Lacroix *et al*¹⁶ and Sujatha *et al*¹⁷.

The stability of the mixed valent complexes is expressed by the conproportionation constant K_{con} for the following equilibrium,



The K_{con} values of the complexes have been determined by electrochemically using the equation, $\log K_{\text{con}} = E_{1/2}/0.059$ (at 25°C), where $E_{1/2} = E^1_{1/2} - E^2_{1/2}$. From table 1, it is evident that the large K_{con} values indicate that the addition of a second electron is more difficult than that of the first electron, and the Cu(II)–Cu(I) mixed valence species is stable with respect to comproportionation. This situation is more common and is often observed in several binuclear systems^{18–20}. Coulometric experiments conducted at –1.0 V which confirm the consumption of 2 electrons per molecule.

3.3 Conductivity studies

Conductances of the complexes have been studied using methanol as solvent. The type of electrolyte is 1 : 1 for acetate and nitrite and 1 : 2 for hydroxo complexes. The conductance data are given in table 1.

3.4 Electron paramagnetic resonance

EPR studies have been carried out only on powder samples as we could not get well-shaped single crystals suitable for EPR studies. Samples were nicely powdered and the spectra were recorded in a quartz tube to avoid lines from impurities like Fe^{3+} and Mn^{2+} .

Complex **1a** gave an axially symmetric EPR spectrum with $g_{\parallel} = 2.208$, $A_{\parallel} = 18.2$ mT, $g_{\perp} = 2.115$ and $A_{\perp} = 3.4$ mT. EPR spectra of complexes **1b** and **1c** are shown in figure 2 and the spin Hamiltonian parameters calculated from the spectra are given in table 2. For these three complexes (**1a**, **1b** and **1c**) the parallel values are close, whereas the perpendicular values differ slightly. The complex **1b** behaves slightly different compared to **1a** and **1c**. The hyperfine values indicate very weak coupling between the two copper ions and one can say that the unpaired electron is mainly localized on one copper ion.

We have also recorded the EPR spectra for complexes **2a**, **2b** and **2c**. The spin Hamiltonian parameters have been calculated and are also given in table 2. Here also complexes **2a** and **2c** have similar g and A values where as complex **2b** has slightly different values, especially the A_{\perp} value. The EPR spectra for the complex **2c** are shown in figure 3. The complexes **3a**, **3b** and **3c** have two nitrite groups as compensating ions.

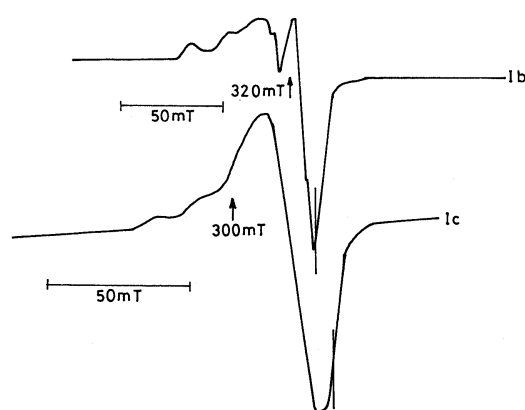
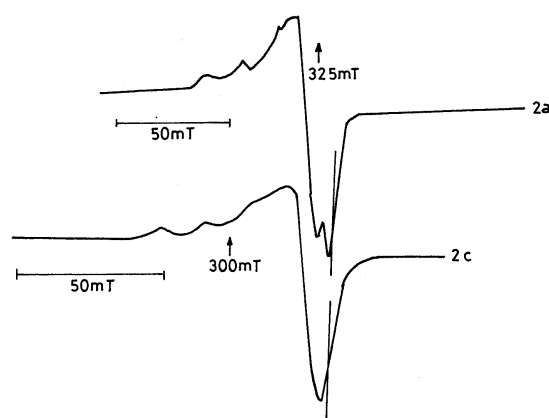


Figure 2. EPR spectrum of hydroxo-bridged $[\text{Cu}_2\text{L}^2(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1b**) and hydroxo-bridged $[\text{Cu}_2\text{L}^3(\text{OH})(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1c**).

Table 2. EPR spectral data for Cu(II) complexes.

Complexes	g_{\parallel}	g_{\perp}	A_{\parallel} (mT)	A_{\perp} (mT)
1a	2.208	2.115	18.2	3.4
1b	2.275	2.074	18.8	2.1
1c	2.216	2.131	17.9	4.3
2a	2.215	2.145	18.2	4.7
2b	2.225	2.100	19.0	3.1
2c	2.208	2.115	19.0	4.3
3a	2.217	2.089	18.9	2.9
3b	2.231	2.095	19.3	3.1
3c	2.210	2.112	19.6	4.1

**Figure 3.** EPR spectrum of acetato bridged $[\text{Cu}_2\text{L}^1(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2a**) and acetato bridged $[\text{Cu}_2\text{L}^3(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2c**).

We have recorded the EPR spectra for these complexes and the calculated spin Hamiltonian parameters are included in table 2. For these three complexes, the g_{\perp} and A_{\perp} values are slightly lesser than for the 1 and 2 series. EPR spectra for a few nitrite bridged complexes are shown in figure 4. In one of our previous studies¹⁷ dealing with hydroxo, acetate and nitrite-bridged complexes, we noticed a substantial decrease in A values for nitrite complexes compared to the other two. That observation has been explained on the basis of a weak interaction between the two copper ions. However, in the present case, we did not notice any such reduction.

Using the spin Hamiltonian parameters, covalency parameters (\mathbf{a}^2 , \mathbf{a}' , \mathbf{b}_1^2) have been calculated using the standard formula²¹. The equations are

$$\mathbf{a}^2 = (A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + (3/7)(g_{\perp} - 2.0023) + 0.04, \quad (1)$$

$$\mathbf{a}' = (1 - \mathbf{a}^2)^{1/2} + \mathbf{a}S, \quad (2)$$

$$g_{\parallel} = 2.0023 - 8r[\mathbf{a}b_1 - (1/2)\mathbf{a}'(1 - \mathbf{b}_1^2)^{1/2}T(n)], \quad (3)$$

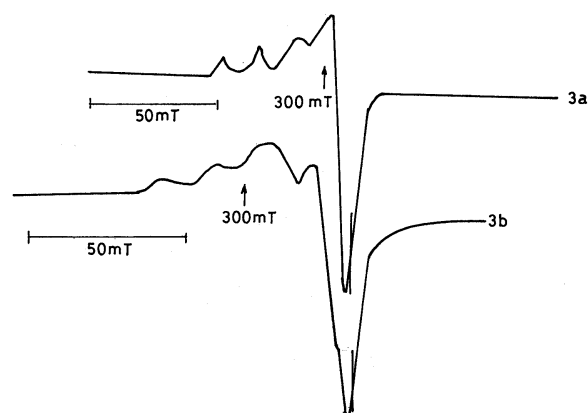


Figure 4. EPR spectrum of nitrito-bridged $[\text{Cu}_2\text{L}^1(\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**3a**) and nitrito-bridged $[\text{Cu}_2\text{L}^2(\text{NO}_2)_2(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**3b**).

Table 3. Optical transition and covalency parameter for Cu(II) complexes.

Complexes	I_{max} (nm)	a^2	a	a'	b_1
1a	636	0.791	0.889	0.524	0.80
1b	661	0.872	0.934	0.428	0.86
1c	661	0.760	0.872	0.555	0.82
2a	680	0.821	0.906	0.491	0.92
2b	671	0.834	0.913	0.476	0.79
2c	663	0.822	0.907	0.489	0.76
3a	658	0.819	0.905	0.493	0.76
3b	650	0.844	0.919	0.463	0.81
3c	670	0.812	0.901	0.501	0.78

where a denotes the in-plane s bonding, a' is normalizing condition on the ground state orbital, S is overlap integral between ground state orbital and normalized ligand orbital, b_1^2 is a direct measure of the covalency of the in-plane p bonding, $r = I_0 a b_1 / \Delta E$ where I_0 is spin-orbit coupling constant for the free ion and ΔE is the transition energy between 2B_1 and 2B_2 states. We can assume $S = 0.076$, $I_0 = -828 \text{ cm}^{-1}$ if the ligands are oxygen or nitrogen donors. $T(n)$ is a function involving metal–ligand distance, hybridization constant (n) and effective nuclear charges for the ligand $2s$, $2p$ and the metal d orbitals. $T(n)$ is assumed as 0.220²². Using optical and EPR data, we have calculated the parameters a^2 , a' and b_1^2 for all copper complexes and the results are given in table 3. It is clear from the table that the covalency parameters have a trend similar to that similar trend noticed with the spin Hamiltonian parameters. However complexes **1b**, **2b** and **3b** behave slightly differently from other members of the series.

Since the copper hyperfine values are slightly lower for nitrite-bridged complexes, we can arrange these complexes for the metal–metal interaction roughly in the order



Table 4. Electrospray mass spectral data.

Complex	<i>m/z</i>	Peak assignment
1a	309 (base)	[C ₂₀ H ₂₅ ON ₂] ⁺
	471 (HL ¹)	[C ₃₀ H ₃₉ ON ₄] ⁺
	597	[Cu ₂ L ¹] ⁺
	614	[Cu ₂ L ¹ (OH)] ⁺
	632	[Cu ₂ L ¹ (OH)(H ₂ O)] ⁺
	865(M)	[Cu ₂ L ¹ (OH)(H ₂ O) ₃ (ClO ₄) ₂] ⁺
2a	309	[C ₂₀ H ₂₅ ON ₂] ⁺
	471(HL ¹)	[C ₃₀ H ₃₉ ON ₄] ⁺
	597	[Cu ₂ L ¹] ⁺
	656	[Cu ₂ L ¹ (CH ₃ COO)] ⁺
	713(base)	[Cu ₂ L ¹ (CH ₃ COO) ₂] ⁺ -3H ⁺
	716	[Cu ₂ L ¹ (CH ₃ COO) ₂] ⁺
	755	[Cu ₂ L ¹ (CH ₃ COO)(ClO ₄)] ⁺
	831(M)	[Cu ₂ L ¹ (OAc) ₂ (ClO ₄)(H ₂ O)] ⁺
3a	309(base)	[C ₂₀ H ₂₅ ON ₂] ⁺
	471(HL ¹)	[C ₃₀ H ₃₉ ON ₄] ⁺
	535	[CuL ¹] ⁺
	597	[Cu ₂ L ¹] ⁺
	714	[Cu ₂ L ¹ (ClO ₄)(H ₂ O)] ⁺
	760	[Cu ₂ L ¹ (NO ₂)(ClO ₄)(H ₂ O)] ⁺
	788	[Cu ₂ L ¹ (NO ₂) ₂ (ClO ₄)] ⁺
	796	[Cu ₂ L ¹ (NO ₂) ₂ (ClO ₄)(H ₂ O) ₃] ⁺
	841(M)	[Cu ₂ L ¹ (NO ₂) ₂ (ClO ₄)(H ₂ O) ₃] ⁺

The above order is purely logical and based on an approximate approach. This order can be confirmed by studying these systems at low temperatures and single crystal EPR may shed better light on the behaviour of these complexes.

3.5 Electrospray mass spectra

Electrospray mass spectral analyses were carried out for the complexes **1a**, **2a** and **3a**. Base peaks for the complexes **1a** and **3a** occur at *m/z* 309. This results from the loss of one of the N-phenylpiperazine arms from the ligands and we use this peak as diagnostic for the presence of N-phenylpiperazine arms. At lower mass units (i.e *m/z* less than 470) there are many similarities in the spectrum to that found for the ligand HL¹ and these peaks are identified as those from ligand fragmentations. Moreover these complexes show peaks indicative of their binuclear nature along with peaks derived from fragmentations to the mononuclear species. Important peak assignments and their corresponding *m/z* values are given in table 4. The electrospray mass spectrum of the complex **2a** is given in figure 5.

4. Conclusions

We have prepared three new ligands with an N₄O donor set and their copper complexes. These complexes have some biological significance in bioinorganic chemistry. All the complexes show quasireversible nature of the electron transfer mechanism. The large

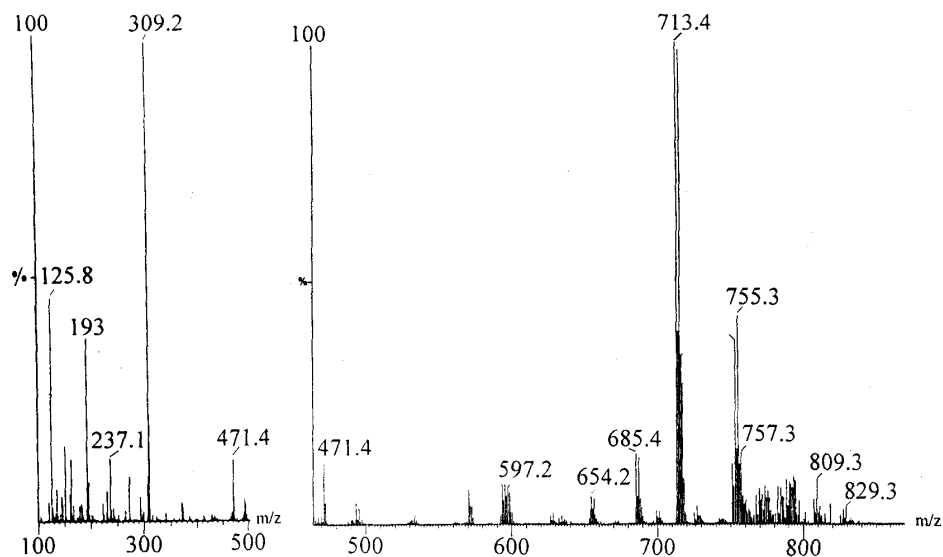


Figure 5. Electrospray mass spectrum of $[\text{Cu}_2\text{L}^1(\text{OAc})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**2a**).

K_{con} values indicate that the addition of the second electron is more difficult. During the course of EPR investigations, we observed that copper hyperfine values are slightly lower for nitrite-bridged complexes. Hence, we can arrange all the complexes based on M–M interaction roughly in the order $\text{NO}_2 \geq \text{OAc} > \text{OH}$. The electrospray mass spectral analysis data indicate the presence of a binuclear core in these complexes.

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This paper is dedicated to Prof J Subramanian on the occasion of his sixtieth birthday.

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