

## Synthesis, spectral, magnetic and electrochemical properties of new binuclear unsymmetrical aminoacid ligands and their Cu(II) complexes with bridging and non bridging motifs

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**Abstract.** The synthesis, spectral, magnetic and electrochemical properties of a series of binuclear Cu(II) complexes of new unsymmetrical binucleating ligands ( $H_2L^1$ ,  $H_2L^2$ ) are described where  $H_2L^1$  = 4-methyl-2-[N-methyl piperazin-1-yl]methyl]-6-[(prolin-1-yl)-methyl] phenol and  $H_2L^2$  = 4-bromo-2-[N-methyl piperazin-1-yl]methyl]-6-[(prolin-1-yl)-methyl] phenol. The exogenous ligands were incorporated into the complexes: hydroxo  $[Cu_2L(OH)(H_2O)_2] ClO_4 \cdot H_2O$  ( $L^1 = 1a$ ,  $L^2 = 1b$ ), acetato,  $[Cu_2L(OAc)_2] \cdot H_2O$  ( $L^1 = 2a$ ,  $L^2 = 2b$ ), nitrito,  $[Cu_2(L(NO_2)_2(H_2O)_2)]$  ( $L^1 = 3a$ ,  $L^2 = 3b$ ), azido,  $[CuL(N_3)_2] \cdot 3H_2O$  ( $L^1 = 4a$ ,  $L^2 = 4b$ ). Complexes 1a, 1b and 2a, 2b contain bridging exogenous groups, while 3a, 3b and 4a, 4b possess only open  $\mu$ -phenolato structures. Both, the ligands and complexes were characterised by spectral studies. The magnetic susceptibility of the complexes have been measured in the temperature range (77–300 K) and the exchange coupling parameter (2J) was determined from least square fitting of the data. The strength of the antiferromagnetic interaction is in the order  $NO_2 = N_3 > OAc > OH$ . The redox behaviour of these complexes in acetonitrile reveal highly quasi reversible behaviour due to chemical or/ and stereochemical changes subsequent to electron transfer. 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.

**Keywords.** Unsymmetrical ligands; dinuclear complexes; synthetic models; exchange interactions; cyclic voltammetry.

### 1. Introduction

The chemistry of binucleating ligands bearing chemically distinct coordination environment is of recent interest to bio-inorganic chemists<sup>1–3</sup>. Such ligands have been classified as compartmental, macrocyclic, side-off and end-off ligands. In the case of the side-off ligands, except a few, the donors to each metal, are identical<sup>4,5</sup>. However in dinuclear metal biosites the metal ions are often found in chemically or geometrically distinct environments. The unsymmetrical nature of the dicopper site in hemocyanin has been demonstrated by the X-ray crystal structure of deoxy hemocyanin<sup>6–7</sup> and sequence homology studies on tyrosinase. While one of the copper sites has been highly conserved throughout evolution, the structure of the second copper site has been variable<sup>7</sup>. For most of the tyrosinases, three histidines are suitably positioned to

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coordinate with each of the copper atoms, but for a few cases  $\text{Cu}_B$  is apparently only coordinated to two histidines. This latter observation led to the suggestion that for modeling studies, unsymmetrical dinucleating ligands should be viewed as desirable targets<sup>2</sup>. Complexes derived<sup>8</sup> from side-off compartmental ligands are of limited use as models for the Cu biosites since they are rigid systems with restricted coordination geometry. The Cu-Cu distance in these complexes is small compared to the biosites, and hence they are unable to support relevant exogenous bridging groups.

End-off compartmental ligands are better candidates for the provision of distinct coordination environment. Many of this sub group dinucleating ligands have been derived from 2,6-disubstituted phenols. Ligands of this type readily form dinuclear transition metal complexes that can coordinate with either one or two exogenous bridging units<sup>9-12</sup>. These ligands strongly favour the formation of dimetallic species because of the enforced ideal distance between the donor sets and the presence of the endogenous bridging phenolato group. These unsymmetrical dinucleating ligands have been prepared by introducing secondary amines, in the presence of formaldehyde activated at 2,6- positions of the *para* substituted phenols<sup>2</sup>.

In the present work, Mannich reaction has been used for introducing a single pentadentate arm into a *para* substituted phenol. The unsymmetrical ligands ( $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$ ) were synthesized by the modified reaction between 4-substituted phenol ( $\text{CH}_3$ , Br), formaldehyde, N-methyl piperazine and proline (scheme 1). Binuclear copper(II) complexes with various bridging units were obtained by the reaction of the metal salt with appropriate ligands (scheme 2). The spectral, magnetic and electrochemical properties of these complexes are reported here.

## 2. Experimental

### 2.1 Physical measurements

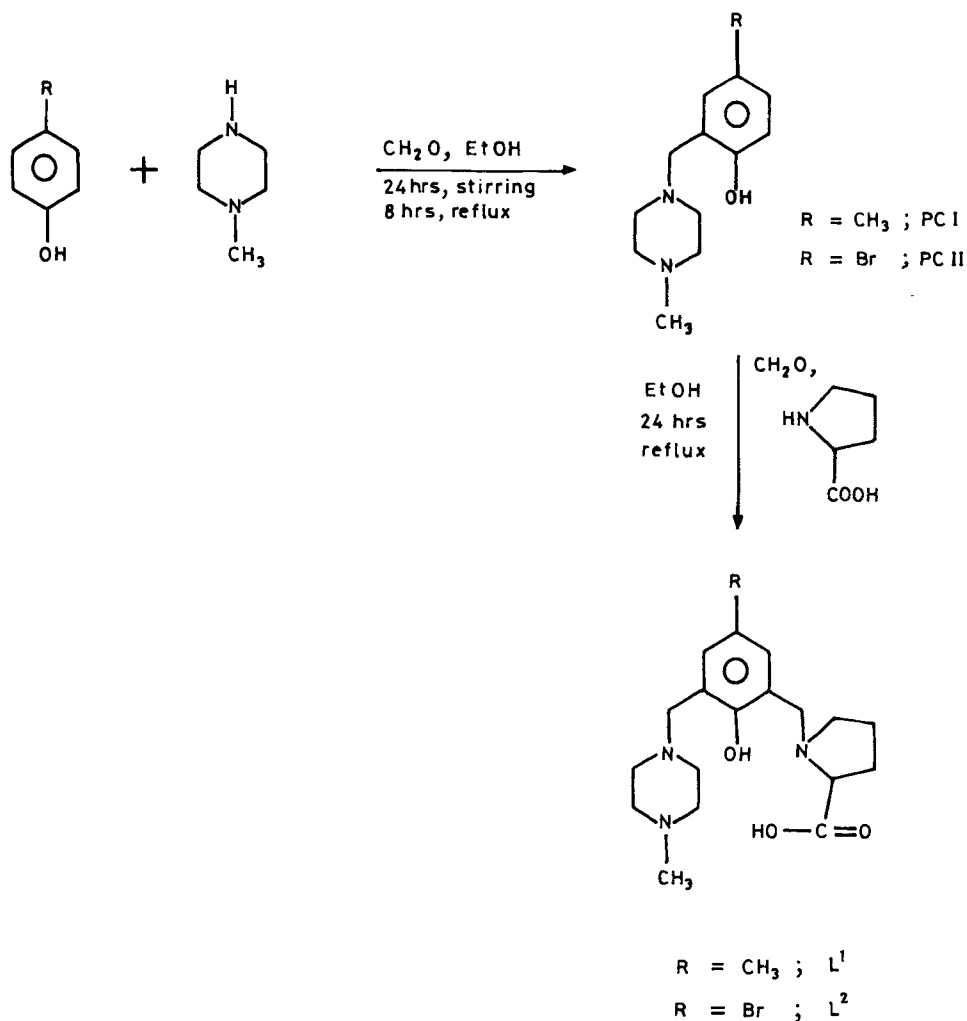
Elemental analysis for C,H,N and Cu were obtained from Indian Institute of Technology, Madras. IR spectra were recorded for KBr pellets on a Shimadzu IR 420 spectrophotometer, electronic spectra on a Hitachi 320 double beam spectrophotometer. Magnetic susceptibilities of powdered samples were measured in the temperature range of 77–300 K on a PAR model 155 vibrating sample magnetometer operating at 5000G and calibrated with metallic nickel. All the data were corrected for diamagnetism using Pascal constants. Cyclic voltammograms were recorded on a PAR 175 universal programmer.

### 2.2 Preparation of ligands

Tetrabutylammonium perchlorate used as the supporting electrolyte in electrochemical measurements was obtained from Fluka and recrystallised from hot water. Acetonitrile (AR grade) was obtained from BDH. All other chemicals and solvents were of reagent grade and were used as received.

#### 2.2a Preparation of Precursor-I (PC-I)<sup>13</sup>: 4-methyl-2-[(N-methyl piperazin-1-yl)methyl] phenol

*p*-cresol (0.05 mol) in ethanol (150 ml) was mixed with N-methyl piperazine (0.05 mol) and cooled in an ice bath as formaldehyde solution (12.5 ml, 0.05 mol) was added



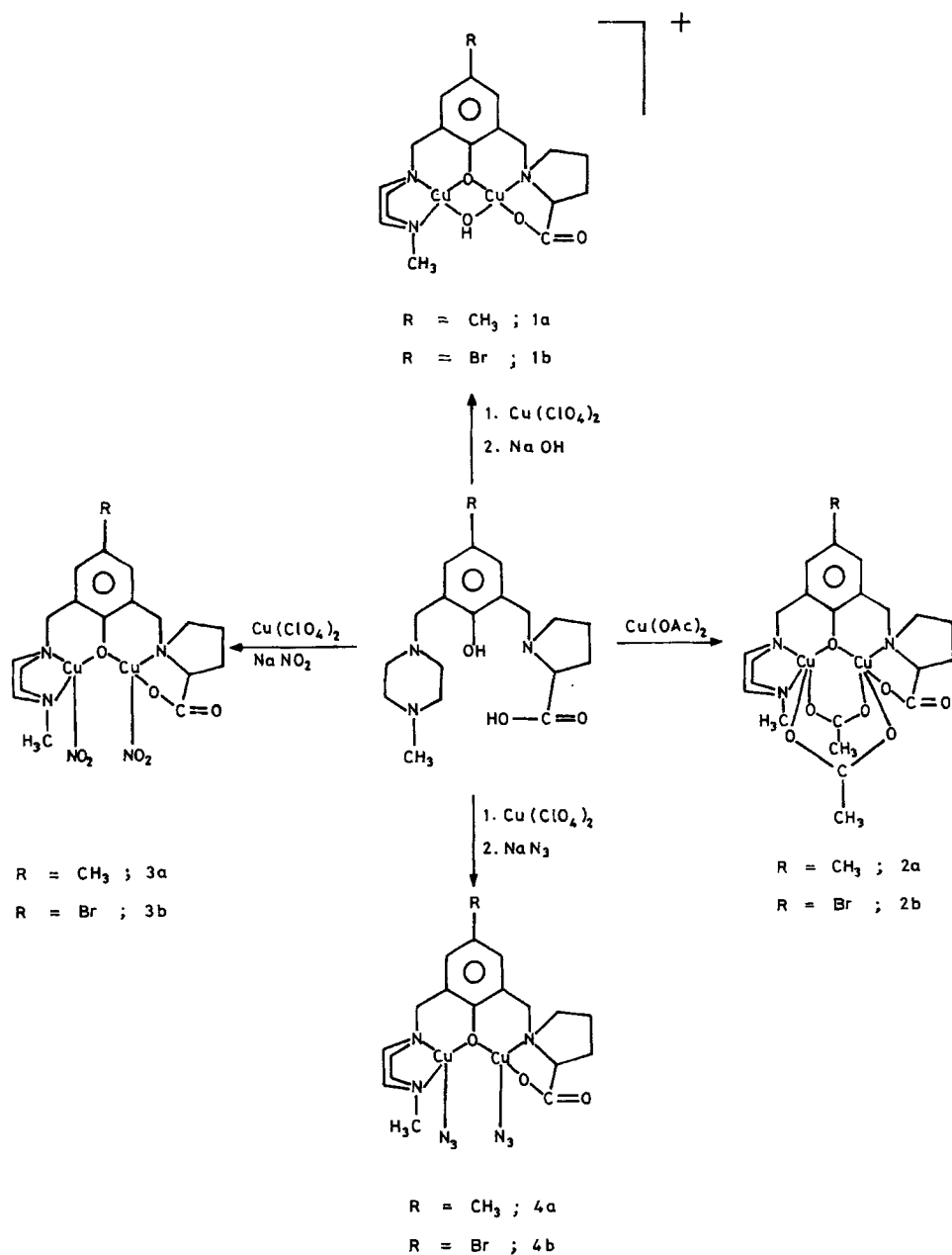
Scheme 1.

dropwise with stirring. The mixture was stirred at room temperature for 24 h and then gently refluxed for 8 h before the ethanol was removed under vacuum. The resulting yellow oil was washed with saturated solution of sodium carbonate and extracted with dichloromethane.

Yield: 70% <sup>1</sup>H NMR in CDCl<sub>3</sub>, δ<sub>ppm</sub>, 2.2 (s, 6H, Ar-CH<sub>3</sub> and N-CH<sub>3</sub>), 3.6 (s, 2H CH<sub>2</sub>-Ph), 2.5 (s, 8H, N-CH<sub>2</sub>), 6.5-7.4 (m, 3H, ArH).

### 2.2b Preparation of Precursor-II (PC-II): 4-bromo-2-[(N-methyl piperazin-1-yl)methyl] phenol

The PC-II was prepared by the same procedure as adopted for PC-I. Yield: 70% <sup>1</sup>H NMR in CDCl<sub>3</sub>, δ<sub>ppm</sub>, 2.3 (s, 3H, N-CH<sub>3</sub>), 3.65 (s, 2H CH<sub>2</sub>-Ph), 2.5 (s, 8H, N-CH<sub>2</sub>), 6.5-7.3 (m, 3H, ArH).



Scheme 2.

### 2.2c Preparation 4-methyl-2-[(N-methyl piperazin-1-yl)methyl]-6-[(prolin-1yl)methyl] phenol ( $\text{H}_2\text{L}^1$ )

PC-I (0.02) in ethanol (75 ml) was mixed with proline (0.02 mol) in ethanol and stirred. Formaldehyde (5 ml, 0.02 mol) was added dropwise with stirring. The mixture

was heated for 24 h. 1.25 ml additions of formaldehyde solution were made at approximately 8 h intervals. The alcohol was evaporated under vacuum and the resulting yellow oil was washed with saturated solution of sodium carbonate and extracted with chloroform, dried with anhydrous  $\text{MgSO}_4$  and filtered before recovery.

Yield: 80%; IR (KBr disc):  $3450\text{ cm}^{-1}$  (br, OH),  $1380\text{ cm}^{-1}$  (N- $\text{CH}_3$ ),  $1690\text{ cm}^{-1}$  (-COO),  $1620\text{ cm}^{-1}$  (aromatic),  $1420\text{ cm}^{-1}$  ( $\text{CH}_3$ )

$^1\text{H NMR}$  in  $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ , 2.3 (s, 6H, Ar- $\text{CH}_3$  and N- $\text{CH}_3$ ), 1.5-3.2 (m, 12H), 3.2-3.6 (br dd, 4H,  $\text{CH}_2$ -Ph), 4.25 (m, 2H), 4.6 (prol. N-H) 6.6-7.4 (m, ArH).

### 2.2d Preparation 4-bromo -2-[(N-methyl piperazin-1-yl)methyl]-6-[(prolin-1yl)methyl] phenol ( $\text{H}_2\text{L}^2$ )

The ligand  $\text{H}_2\text{L}^2$  was prepared in the same way as  $\text{H}_2\text{L}^1$ . The resulting yellow oil was extracted from benzene.

Yield: 80%; IR (KBr disc):  $3450\text{ cm}^{-1}$  (br, OH),  $1360\text{ cm}^{-1}$  (N- $\text{CH}_3$ ),  $1690\text{ cm}^{-1}$  (-COO),  $1618\text{ cm}^{-1}$  (aromatic),  $725\text{ cm}^{-1}$  (Br);  $^1\text{H NMR}$  in  $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ , 2.25 (s, 3H, N- $\text{CH}_3$ ), 1.5-3.2 (m, 12H), 3.3-3.6 (br dd, 4H,  $\text{CH}_2$ -Ph), 4.00 (m, 2H), 4.55 (prol. N-H) 6.42-6.9 (m, ArH).

## 2.3 Preparation of complexes

### 2.3a Preparation of OH bridged complexes

$[\text{Cu}_2\text{L}^1(\text{OH})(\text{H}_2\text{O})_2][\text{ClO}_4]\cdot\text{H}_2\text{O}$  1a.

To an ethanolic solution of the ligand  $\text{H}_2\text{L}^1$  (0.001 mol), sodium hydroxide (0.001 mol) was added, followed by a solution of copper(II)perchlorate hexahydrate (0.002 mol) dissolved in ethanol. The resulting greenish blue solution was refluxed for 4 h and then filtered. Green precipitate was obtained on evaporation of the solution at room temperature for several days. The complex was recrystallised from aqueous ethanol. Found C = 35.45, H = 5.40, N = 6.53, Cu = 19.76. Cal. for  $\text{C}_{19}\text{H}_{28}\text{ClCu}_2\text{N}_3\text{O}_8\cdot 3\text{H}_2\text{O}$ ; C = 35.49, H = 5.53, N = 5.88, Cu = 19.87

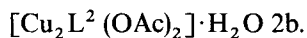
$[\text{Cu}_2\text{L}^2(\text{OH})(\text{H}_2\text{O})_2][\text{ClO}_4]\cdot\text{H}_2\text{O}$  1b.

This complex was prepared by the same procedure as 1a using  $\text{H}_2\text{L}^2$  instead of  $\text{H}_2\text{L}^1$ . Found C = 30.48, H = 4.35, Cu = 17.95, N = 5.93 Cal. for  $\text{C}_{18}\text{H}_{25}\text{ClBrCu}_2\text{N}_3\text{O}_8\cdot 3\text{H}_2\text{O}$ ; C = 30.54, H = 4.41, Cu = 17.89, N = 5.88.

### 2.3b Preparation of bis acetato bridged complexes

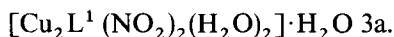
$[\text{Cu}_2\text{L}^2(\text{OAc})_2]\cdot\text{H}_2\text{O}$  2a.

The copper(II) acetate mono hydrate (0.002 mol) was dissolved in warm aqueous ethanol (75 ml). Addition of ethanolic solution of the ligand  $\text{H}_2\text{L}^2$  (0.001 mol) to it led to the formation of a dark green solution. The mixture was then refluxed for 4 h and filtered. Upon concentration, diamond-shaped green crystals were obtained. Found C = 45.30, H = 5.68, Cu = 20.87, N = 6.90. Calc. for  $\text{C}_{23}\text{H}_{33}\text{Cu}_2\text{N}_3\text{O}_7\cdot\text{H}_2\text{O}$ ; C = 45.38, H = 5.79, Cu = 20.58, N = 6.76.

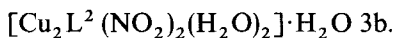


This complex was prepared by the method used for 2a, using  $\text{H}_2\text{L}^2$  in the place of  $\text{H}_2\text{L}^1$ . Found: C = 39.10, H = 4.69, Cu = 18.86, N = 6.23. Calc. for  $\text{C}_{22}\text{H}_{30}\text{BrCu}_2\text{N}_3\text{O}_7\cdot\text{H}_2\text{O}$ : C = 39.23, H = 4.78, Cu = 18.90, N = 6.12.

### 2.3c Preparation of bis nitrito complexes

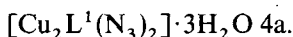


To an ethanolic solution containing the ligand  $\text{H}_2\text{L}^1$  (0.0025) and copper(II) perchlorate hexahydrate (0.005 mol), was added a solution of sodium nitrite (0.0075 mol) dissolved in ethanol (75 ml). The resulting bluish green solution was refluxed for 4 h and filtered. Upon concentration of this solution green black crystals were obtained which were recrystallised from aqueous ethanol. Found: C = 37.28, H = 5.36, Cu = 20.54, N = 11.32. Calc. for  $\text{C}_{19}\text{H}_{31}\text{Cu}_2\text{N}_5\text{O}_9\cdot\text{H}_2\text{O}$ : C = 36.89, H = 5.37, Cu = 20.48, N = 11.37.

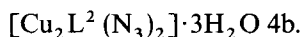


This complex was prepared by adopting the same procedure as 3a using ligand  $\text{H}_2\text{L}^2$  instead of  $\text{H}_2\text{L}^1$ . Found: C = 31.60, H = 4.38, Cu = 18.59, N = 10.24. Calc. for  $\text{C}_{18}\text{H}_{28}\text{BrCu}_2\text{N}_5\text{O}_9\cdot\text{H}_2\text{O}$ : C = 31.63, H = 4.42, Cu = 18.35, N = 10.12.

### 2.3d Preparation of bis azido complexes



An aqueous solution of sodium azide (0.0075 mol) was added to an ethanolic solution containing copper(II) perchlorate hexahydrate (0.005 mol) and ligand  $\text{H}_2\text{L}^1$  (0.0025 mol) whereupon a brown solid of uncertain composition was deposited. After filtration the solution was refluxed for 4 h and slow evaporation of the solution yielded green black precipitate which was recrystallised from aqueous ethanol. Found: C = 37.28, H = 5.36, Cu = 20.81, N = 20.64. Calc. for  $\text{C}_{19}\text{H}_{27}\text{Cu}_2\text{N}_9\text{O}_3\cdot 3\text{H}_2\text{O}$ : C = 37.37, H = 5.44, Cu = 20.71, N = 20.53.



This complex was prepared by adopting the same procedure as 4a with ligand  $\text{H}_2\text{L}^2$  instead of  $\text{H}_2\text{L}^1$ . Found: C = 31.92, H = 4.43, Cu = 18.81, N = 18.66. Calc. for  $\text{C}_{18}\text{H}_{24}\text{BrCu}_2\text{N}_9\text{O}_3\cdot 3\text{H}_2\text{O}$ : C = 32.00, H = 4.47, Cu = 18.75, N = 18.60.

## 3. Results and discussion

### 3.1 Synthesis and characterization

The complexes 1a and 1b are obtained by reaction of copper(II) perchlorate hexahydrate and appropriate ligands in a 2:1 molar ratio in presence of sodium hydroxide. The dinitrito 3a, 3b and bis azido complexes 4a, 4b were prepared in the same way except that an ethanolic solution of sodium nitrite or an aqueous solution of sodium azide was used instead of sodium hydroxide. The bis acetato complexes 2a, 2b were synthesized using copper(II) acetate and ligands in a 2:1 mole ratio.

Spectroscopic techniques were used to elucidate the structure of the complexes. The OH bridged complexes exhibit a broad IR band around  $3480\text{--}3600\text{ cm}^{-1}$  due to OH

**Table 1.** Electrochemical data for complexes 1 and 2 with their conproportionation constants ( $K_{con}$ ) and magnetic susceptibility data for complexes 1, 2, 3 and 4.

Complex	$E_{1/2}^1(\Delta E_p)$	$E_{1/2}^2(\Delta E_p)$	$K_{con}$	$-2J/\text{cm}^{-1}$
1a	-0.75(-0.10)	-1.12(-0.20)	$5.4881 \times 10^7$	101
2a	-0.60(-0.10)	-1.18(-0.30)	$1.5350 \times 10^{10}$	122
1b	-0.60(-0.24)	-0.64(-0.36)	$2.1046 \times 10^{-1}$	—
2b	-0.49(-0.34)	-0.89(-0.58)	$1.7053 \times 10^7$	127
3a	—	—	—	239
4a	—	—	—	165
4b	—	—	—	160

Potentials are in V vs SCE;  $\Delta E_p = E_{pc} - E_{pa}$

-2J values have been calculated using Bleaney-Bower's equation given in the text.

stretching<sup>14,15</sup>. The perchlorate salt shows a strong band near  $1100\text{ cm}^{-1}$  and sharp band around  $620\text{--}625\text{ cm}^{-1}$  indicative of the uncoordinated perchlorate anion<sup>16,17</sup>. The *bis* acetato bridged complexes showed strong  $\nu(\text{COO})$  bands around  $1450$  and  $1583\text{ cm}^{-1}$ . The IR bands due to the nitrite groups were observed around  $1450\text{--}1220\text{ cm}^{-1}$  which on comparison to the one published<sup>18</sup> would suggest a monodentate O bonded mode for the nitrite groups. The  $\text{N}_3$  stretching vibration<sup>19</sup> for  $\text{N}_3$  complexes appears at  $2030\text{--}2096\text{ cm}^{-1}$  and is assigned to monodentate N-coordinated azide groups<sup>20</sup>.

The electronic spectra of these complexes in acetonitrile show a low intensity band in the region  $600\text{--}800\text{ nm}$  indicative of a pyramidal geometry<sup>20</sup>, a medium intensity band occurring between  $360\text{--}480\text{ nm}$  due to phenolato to Cu(II) charge transfer<sup>21</sup>. An intense absorption around  $280\text{--}330\text{ nm}$  has also been observed which probably arises due to the ligand-to-ligand charge transfer transition.

### 3.2 Magnetic properties

Magnetic susceptibilities of powdered samples of the complexes were measured in the temperature range  $77\text{--}300\text{ K}$  by using vibrating sample magnetometer. Analysis were carried out using the following Bleaney-Bowers equation<sup>22</sup>

$$\chi_M = (\text{Ng}^2\beta^2)/(3\text{kT})[1 + (1/3)\exp(-2J/\text{kT})]^{-1}(1 - P) \\ + (\text{Ng}_i^2\beta^2)/(4\text{kT})P + N_a,$$

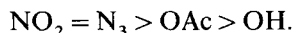
where  $\chi_m$  is the paramagnetic susceptibility per molecule after the correction for diamagnetism,  $P$  is the mole fraction of the paramagnetic impurities (0.05%),  $g_i$  is the average  $g$  factor of the impurity (2.2),  $-2J$  is the singlet-triplet energy separation,  $N_a$  is the temperature independent paramagnetism, assumed to be  $120 \times 10^{-6}$  cgs emu for Cu(II) dimers<sup>23</sup>. Good magnetic simulation was obtained using  $2J = -101\text{ cm}^{-1}$ ,  $g = 1.8354$  and  $N_a = 120 \times 10^{-6}\text{ cm}^{-1}\text{ mol}^{-1}$ . The magnetic parameters are summarised in table 1. Complex 1a exhibits a weak antiferromagnetic interaction. In such cases, very tight Cu-O-Cu angles and short Cu-Cu distances within two coplanar *cis* disposed square pyramidal complexes which contributed to reduced antiferromagnetism. This can be explained by considering a  $\sigma$  type overlap between copper  $dx^2 - y^2$  orbital and the  $p_z$  orbital on oxygen. It was suggested<sup>24</sup> that  $\pi$  type overlap between the out-of-plane copper orbitals and the non bonding pair on oxygen ( $p_x$ ) will be more significant than the  $\sigma$  type overlap and hence gives rise to enhanced antiferromagnetism

in the case of trigonal planar, and reduced antiferromagnetism in the case of pyramidal oxygen. This model has been used in the case of Cr(III) dimers. The suggestion of  $p$  type overlap was based on an empirical model<sup>25,26</sup>.

The nitrito and azido complexes lead to a more negative net  $J$  than do the diacetato bridge in 1b and 2b. It is interesting to note that even though these basal planes have large dihedral angles<sup>27</sup> between them, there is sufficient overlap of each  $\text{Cu}(\text{d}_{x^2-y^2})$  orbital with the phenolate oxygen  $p$  orbital to generate negative  $J$  values i.e.  $-239$  and  $-165 \text{ cm}^{-1}$  in 3a and 4a.

In the acetato bridged complexes, the acetate groups connect basal plane ( $\text{d}_{x^2-y^2}$ ) positions on one copper with apical ( $\text{d}_{z^2}$ ) positions on the other, and this leads to a low overall  $J$  value, probably because of  $J_{\text{ferro}}$  contributions from these pathways. Any contributions from the counter complementary effects of phenolate *vs* acetate bridging orbitals<sup>28</sup> will be small in 1b & 2b because of the relative disposition of the  $\text{Cu}(\text{d}_{x^2-y^2})$  orbitals<sup>10-28,29</sup>.

The final conclusion on the structure/magnetism correlations in this small series of complexes concerns the dependence of  $J$  on Cu–Cu distance and Cu–O–Cu angle. In general, as the Cu–Cu distance and Cu–O–Cu angles increase, so does  $J$  become more negative. However, it must be noted that 1a and 1b have a geometry different from the others, reported in this work and weak overall ferromagnetism has been ascribed largely due to the effect of the pyramidal geometry around the phenolato oxygen atom. Also as described above, the small negative  $J$  value in the *bis*( $\mu$ -acetato) complex reflects the combined effects of the acetate and phenolate super exchange pathways. The magnitude of magnetic interaction of the small series is,



It is interesting to note that for complexes 1b and 2b, 3b and 4b which have comparable unsymmetrical structures, the magnetic properties are essentially the same, indicating that the electron-withdrawing bromine atom does not influence magnetic exchange significantly.

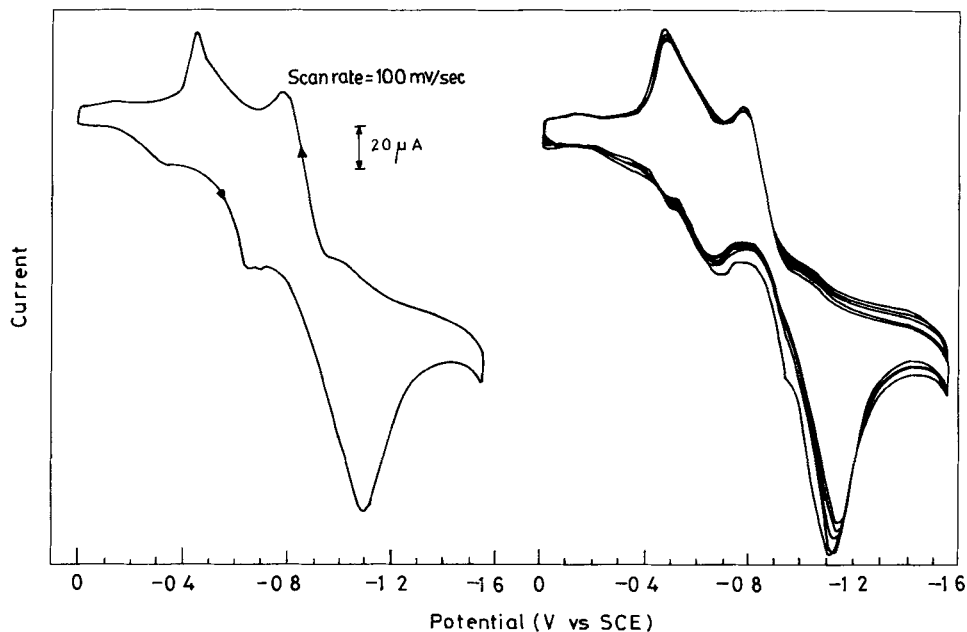
### 3.3 Redox properties

#### 3.3a Hydroxo bridged complexes

Urbach and coworkers<sup>14</sup> and Gagne *et al*<sup>30,31</sup> have reported on the redox properties of copper(II) complexes in which the terminal nitrogen belongs to a pyridine moiety. These complexes exhibit quasi reversible/irreversible behaviour and reduction generally leads to the release of copper metal, possibly through disproportionation of Cu(I) intermediate. The reason for such a behaviour could lie in the poor coordinating ability of hydroxide for Cu(I). This view is supported by the fact that substitution of hydroxide by pyrozoate allows the isolation of stable Cu(I) intermediate.

The cyclic voltammogram of hydroxo bridged of complexes 1 a, 1b undergo a one-electron reduction and oxidation step at different potentials. They are not entirely reversible systems as evident from large  $\Delta E_{\text{pp}}$  values. The reduction of the compounds is in two steps,  $\Delta E_{\text{p}}$  at  $-0.6 \text{ V}$  to  $-1.4 \text{ V}$  vs SCE. Two re-oxidation peaks are present in the range  $-0.4 \text{ V}$  to  $-1.10 \text{ V}$ . After the first scan, the shape of the reduction peak is changed and a new redox couple was observed, around  $\text{Epc}^3 = -0.4 \text{ V}$  to  $-0.6 \text{ V}$  and  $\text{Epa}^3 = -0.1 \text{ V}$  to  $-0.2 \text{ V}$ . The shape of the voltammogram does not change after the





**Figure 1.** Cyclic voltammogram of complex 2a in  $\text{CH}_3\text{CN/TBAP}$  versus SCE at  $25^\circ\text{C}$ . Scan rate =  $100\text{ mV/s}$  and continuous scan.

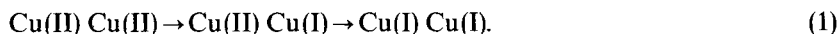
second cycle. These cyclic voltammetric studies reveal a very complex redox behaviour whose analysis is complicated by the quasi reversibility of the electrode process. Nevertheless, several indications can be derived from these results. First, coulometric analysis of the reduction process indicates that two electrons per mole are transferred which suggests the formation of Cu(I) ions. Secondly, two peaks are present which may correspond to sequential one electron oxidation of the Cu(I) species. Moreover, the large difference between  $E_{p_c}$  and  $E_{p_a}$  values suggests that a chemical change is occurring with the electron transfer. It may be due to structural reorganisation of copper coordination sphere. Thirdly, the formation of two redox couples is associated with the different copper structural forms. It is assumed that this form may be derived from some structural distortion of this copper environment, which may contain only endogenous bridging unit. These interpretations of the experimental data are based on a study of occurrence of stereochemical changes<sup>4</sup> and the observation of the ligand loss<sup>32,33</sup> induced by electron transfer in related systems.

### 3.3b Bis acetato bridged complexes

The redox behaviour of acetato bridged complex 2a in acetonitrile is illustrated in figure 1. The large  $\Delta E_p$  values show that the complexes are not reversible systems, the value of cathodic current is larger than the anodic current, showing that the complexes undergo a chemical change after reduction. The voltammogram comprises of two reduction peaks around  $E_{p_c}^1 = -0.5\text{ V}$  to  $0.95\text{ V}$  and  $E_{p_c}^2 = -0.8\text{ V}$  to  $-1.3\text{ V}$  and two re-oxidation peaks around  $E_{p_a}^1 = -0.3\text{ V}$  to  $-0.7\text{ V}$  and  $E_{p_a}^2 = -0.6\text{ V}$  to  $-1.0\text{ V}$ . Both the reductions are monoelectronic as deduced from coulometric analysis. After

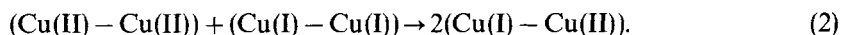
the first cycle, the shape of the main reduction peak is altered and a small reduction peak is observed around  $-0.3$  V to  $-0.5$  V, apart from the main reduction peaks. Thus, after a first complete cycle, the system shows three redox couples. The reduction around  $-0.5$  V to  $-0.95$  V correlates with the oxidation peak observed around  $-0.3$  V to  $-0.7$  V, the reduction around  $-0.8$  V to  $-1.3$  V correlates with oxidation peaks around  $-0.6$  V to  $-1.0$  V and the third reduction around  $-0.3$  V to  $-0.5$  V correlates with the oxidation around  $-0.1$  V to  $-0.2$  V. The third redox couple may be due to the new species generated after the reduction of the original complex. The continuous scan shows that the peak current of the original complex decreases with the increase in the peak current of generated species. A number of important observations follow from the cyclic voltammetric studies. The coulometric analysis of the reduction process indicates that two electrons per mole are transferred suggesting the formation of the Cu(I) ions and its occurrence in a single step electron transfer process. The huge difference between  $E_{pc}$  and  $E_{pa}$  suggests that the system is quasi reversible and a chemical change occurs with electron transfer, resulting in a structural reorganisation of copper coordination sphere. The presence of the new redox couples can be attributed to the formation of a new complex- which may contain the endogenous bridging unit by the first reduction of the original complex. Our results agree with the reports on the stereochemical changes<sup>34</sup> and the observation of the ligand loss<sup>28,35,36</sup> induced by the electron transfer in related complexes.

The electrochemical behaviour in the negative potential range is sensitive to the electron inductive (+I or -I) nature of the substituents at the *para* positions of the benzene rings. For all the complexes, two quasi reversible waves were observed. Coulometric analysis indicated that each of the couples is involved in a one electron transfer process. Therefore it is reasonable to assign the two waves to successive one electron reductions at the metal centres:



From table 1, it is important to note that the replacement of a relatively electron releasing methyl group (1a, 2a,) by an electron withdrawing bromine atom (1a, 2b) shifts the first reduction to more positive potentials. A similar trend has been reported by Lacroix *et al* and Karunakaran *et al*<sup>37,38</sup>.

The stability of the mixed valence Cu(I) Cu(II) complexes is expressed by the conproportionation constant  $K_{con}$  for equilibrium



The  $K_{con}$  values of the complexes have been determined electrochemically using the equation  $\log K_{con} = E_{1/2}/0.059$  (at 25°C), where  $E_{1/2} = E_{1/2}^1 - E_{1/2}^2$ . 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 conproportionation. This situation is the most common and is often observed in several binuclear systems<sup>30,39,40</sup>.

In the present work, we have reported the design, synthesis, and characterization of unsymmetrical binucleating ligands and their Cu(II) complexes with exogenous bridging and non bridging units. Such complexes can also be viewed as models for the dinuclear copper centers in metalloproteins and enzymes.

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