

## Synthesis of flexible ligands for assembling two metals in close proximity. Magnetic, electrochemical and spectral properties of binuclear copper (II) complexes with different exogenous bridging motifs

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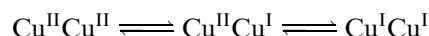
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### Abstract

Binuclear Cu<sup>II</sup> complexes having new flexible heptadentate ligands 2,6-bis{[bis(3,3'-*N,N*-dimethylaminopropyl)amino]methyl}-4-bromophenol [HL<sup>1</sup>], 2,6-bis(3,3'-*N,N*-dimethylaminopropyl)amino]methyl}-4-methylphenol [HL<sup>2</sup>], and 2,6-bis{[bis(3,3'-*N,N*-dimethylaminopropyl)amino]methyl}-4-methoxyphenol [HL<sup>3</sup>], capable of assembling two copper ions in close proximity have been synthesized. Comparisons of the charge-transfer (CT) features, observed in electronic spectra of these complexes, are correlated with the electronic effect on the aromatic ring of the ligand systems. Cyclic voltammetry has revealed the existence of two reduction couples,



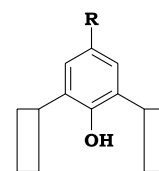
The first is sensitive to the electronic effects of aromatic ring substituents of the ligand system, shifting to more positive potentials when more electrophilic groups replace the existing substituents. The comproportionation constants ( $k_{\text{con}}$ ) for the mixed valent Cu<sup>I</sup>Cu<sup>II</sup> complexes have been determined electrochemically. The magnetic susceptibilities of the complexes have been measured over the 70–300 K range and the exchange coupling parameter ( $-2J$ ) determined by a least squares fit of the data which indicates an antiferromagnetic spin exchange ( $-2J = 94\text{--}172\text{ cm}^{-1}$ ) between the Cu<sup>II</sup> ions with bridging units in the order: N<sub>3</sub> ≈ NO<sub>2</sub> > OAc > OH.

### Introduction

The synthesis of low molecular weight binuclear copper (II) complexes, mimicking hemocyanin activity, has been a challenge for bioinorganic chemists [1, 2]. A large number of copper (II) complexes have been made with macrocyclic, side-off and end-off<sup>1</sup> Schiff base compartmental ligands. Complexes derived [3] from side-off ligands are of limited use as model compounds for the copper biosites, as they are flexible with restricted coordination geometries and contain connected terminal and endogenous bridging ligand types. They are unable to support relevant exogenous bridging groups, since the

Cu–Cu separation in these systems is *ca.* 3.0 Å, compared with 3.5 Å found at the biosites.

The end-off<sup>1</sup> ligands are better candidates for the provision of distinct coordination geometries. Many of these sub-groups of dinucleating ligands are derived from a 2,6-disubstituted phenol.



Donor set-1 Donor set-2

Ligands of this type readily form dinuclear transition metal complexes that can coordinate either one or two exogenous bridging groups [4–7]. They strongly favor the formation of bimetallic species because of the enforced idealised distance between the donor sets and the endogenous phenolate group. Functionalised alkylaminomethyl side arms can be introduced at the activated 2 and 6 positions of phenol by condensation with an appropriate secondary amine and formaldehyde

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<sup>1</sup>Dinucleating ligands have been classified as isolated and compartmental donor sets. In the former, the donor atoms are not shared between the two metal atoms. The later further divided as macrocyclic, side-off and end-off compartmental ligands which form complexes in which the metals share at least one donor atom in species containing adjacent sites, in which the central donor atom (s) provide a bridge. However, in the case of end-off ligands, the metal can form an exogenous bridges, while it is not so in the case of macrocyclic and side-off ligands.

[8]; this variation on the Mannich reaction has been used successfully with a 4-substituted phenol to prepare the desired dinucleating ligand [7].

In the present work, the Mannich reaction was used to introduce a single pentadentate arm into a 2,4 substituted phenol. The heptadentate ligands, HL<sup>1</sup>, HL<sup>2</sup> and HL<sup>3</sup> were synthesized by a modified reaction between 3,3'-iminobis(*N,N*-dimethylpropylamine), formaldehyde and 4-substituted phenol. Binuclear copper (II) complexes [Cu<sub>2</sub>LX]<sup>n+</sup> with various bridging motifs (X = OH, OAc, NO<sub>2</sub> and N<sub>3</sub>) were obtained by reacting the metal salts with appropriate ligands. The spectral, magnetic and electrochemical properties of these complexes are reported and discussed here.

## Experimental

### Physical measurements

U.v.-vis. spectra in MeOH were recorded on a Hitachi 300 spectrometer. I.r spectra were recorded on KBr discs with a Shimadzu FT-IR 8300/8700 spectrometer. <sup>1</sup>H-n.m.r. spectra were recorded on a JEOL FX-400 FT NMR spectrometer in CDCl<sub>3</sub> using Me<sub>4</sub>Si (TMS) as internal standard. <sup>13</sup>C-n.m.r. spectra were recorded on a Bruker DRX300-FT NMR spectrometer. C, H and N were analyzed using Heraeus Carlo Erba 1108 elemental analyzer. Electron impact (EI) mass spectra were taken on a JEOL D-300 mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL SX-102/DA-6000 spectrometer, using *m*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH as a matrix solvent unless otherwise stated. The variable temperature magnetic susceptibility studies were carried out using a Princeton Applied Research Model 155 VSM in 5000 G magnetic field. Calibrations were made using metallic nickel and diamagnetic corrections were evaluated using Pascal's constants. The data were least square fitted to the Bleaney-Bowers equation. Cyclic voltammograms were measured using an Autolab PGSTAT 12 electrochemical analyzer in MeCN solution containing tetra *n*-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte.

### Materials

All chemicals and solvents were reagent grade and were used without further purification, except for those employed for electrochemical measurement and ligand synthesis. Refluxing over CaO for 3 h purified EtOH and then the middle fraction was distilled onto 3 Å molecular sieves. MeCN was dried by stirring over K<sub>2</sub>CO<sub>3</sub> for 24 h and stored over 3 Å sieves. *n*-Bu<sub>4</sub>NClO<sub>4</sub> used as the supporting electrolyte in electrochemical measurement, was prepared from *n*-Bu<sub>4</sub>NBr, HClO<sub>4</sub> and NaHCO<sub>3</sub>. Recrystallisation was performed from hot EtOH and further drying was carried out in a vacuum desiccator.

### Synthesis of ligands

#### 2,6-Bis{[bis(3,3'-*N,N*-dimethylaminopropyl)amino]-methyl}-4-bromophenol [HL<sup>1</sup>]

This ligand was prepared by a modification of the Mannich base reaction [9].

p-BrC<sub>6</sub>H<sub>4</sub>OH (4.3 g, 0.025 mol) was mixed with 3,3'-imino-bis-(*N,N*-dimethylpropylamine) (11 cm<sup>3</sup>, 0.05 mol) and stirred as a HCHO solution (7 cm<sup>3</sup>) was added slowly. The solution was then heated to reflux for 24 h 2.5 cm<sup>3</sup> quantities of formaldehyde being at *ca.* 8 h intervals. The EtOH was then evaporated under vacuum and the resulting oil was washed with aqueous Na<sub>2</sub>CO<sub>3</sub>, extracted with CHCl<sub>3</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. The product, a brownish yellow viscous liquid, was further purified by silicagel column chromatography using CHCl<sub>3</sub>-MeOH (2:1) as the eluent. Yield: 75%. Mass spectrum, *m/z* 570 [C<sub>28</sub>H<sub>55</sub>N<sub>6</sub>OBr]<sup>+</sup>. <sup>1</sup>H-n.m.r. in CDCl<sub>3</sub>: 1.67 (q, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-); 2.20 (s, 24H, N (CH<sub>3</sub>)<sub>2</sub>); 2.23 [t, 8H, CH<sub>2</sub>N (CH<sub>3</sub>)<sub>2</sub>]; 2.51 (t, 8H, N-CH<sub>2</sub>-CH<sub>2</sub>); 3.62 (s, 4H, benzyl CH<sub>2</sub>); 7.19 (s, 2H, aromatic CH) 7.27 (s, 1H, phenolic OH). <sup>13</sup>C-n.m.r. in CDCl<sub>3</sub>: 155.0, 130.8, 130.1, 129.8, 126.1, 110.4 (aryl); 66.5, 65.9 (PhCH<sub>2</sub>); 57.5, 57.2 [(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>]; 51.7, 51.3 (NCH<sub>2</sub>); 45.3, 44.8 [N (CH<sub>3</sub>)<sub>2</sub>]; 24.7, 24.2 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>).

I.r. (KBr disc): 3747 cm<sup>-1</sup> (Ph-OH), 1644 cm<sup>-1</sup> (aromatic), 1457 cm<sup>-1</sup> (N-CH<sub>3</sub>), 755 cm<sup>-1</sup> (Ph-Br). The ligands HL<sup>2</sup> and HL<sup>3</sup> were prepared in similar way to HL<sup>1</sup>.

#### 2,6-Bis{[bis(3,3'-*N,N*-dimethylaminopropyl)amino]-methyl}-4-methylphenol [HL<sup>2</sup>]

Yield: 70%. Mass spectrum, *m/z* 506 [C<sub>29</sub>H<sub>58</sub>N<sub>6</sub>O]<sup>+</sup>. <sup>1</sup>H-n.m.r. in CDCl<sub>3</sub>: 1.68 (q, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-); 2.18 (s, 3H, PhCH<sub>3</sub>); 2.20 (s, 24H, N (CH<sub>3</sub>)<sub>2</sub>); 2.26 (t, 8H, CH<sub>2</sub>-N(CH<sub>3</sub>)<sub>2</sub>); 2.5 (t, 8H, N-CH<sub>2</sub>-CH<sub>2</sub>); 3.63 (s, 4H, benzyl CH<sub>2</sub>); 6.85 (s, 2H, aromatic CH); 7.27 (s, 1H, Ph-OH). <sup>13</sup>C-n.m.r. in CDCl<sub>3</sub>: 154.0, 128.6, 127.3, 123.5 (aryl); 57.8 (PhCH<sub>2</sub>); 55.7, 54.9 [(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>]; 45.4 [N(CH<sub>3</sub>)<sub>2</sub>]; 25.5, 24.8 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 20.3 (PhCH<sub>3</sub>). I.r. (KBr disc): 560 cm<sup>-1</sup> (Ph-OH), 2943 cm<sup>-1</sup> (Ph-CH<sub>3</sub>), 1460 cm<sup>-1</sup> (N-CH<sub>3</sub>) and 1650 cm<sup>-1</sup> (aromatic).

#### 2,6-Bis{[bis(3,3'-*N,N*-dimethylaminopropyl)amino]-methyl}-4-methoxyphenol [HL<sup>3</sup>]

Yield: 78%. Mass spectrum, *m/z* 522 [C<sub>29</sub>H<sub>58</sub>N<sub>6</sub>O<sub>2</sub>]<sup>+</sup>. <sup>1</sup>H-n.m.r. in CDCl<sub>3</sub>: 1.68 (q, 8H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-); 2.19 (s, 24H, N(CH<sub>3</sub>)<sub>2</sub>); 2.23 (t, 8H, CH<sub>2</sub>N (CH<sub>3</sub>)<sub>2</sub>); 2.51 (t, 8H, N-CH<sub>2</sub>-CH<sub>2</sub>); 3.63 (s, 4H, benzylic CH<sub>2</sub>); 3.75 (s, 3H, Ph-O-CH<sub>3</sub>); 6.67 (s, 2H, aromatic CH) 7.28 (s, 1H, Ph-OH). <sup>13</sup>C-n.m.r. in CDCl<sub>3</sub>: 151.9, 149.6, 125.9, 113.6 (aryl); 67.0, 65.6 (PhCH<sub>2</sub>); 58.3, 58.2, 57.6, 57.3, 57.1 [(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>]; 55.5, 55.4, 55.0 (Ph-OCH<sub>3</sub>); 51.8, 51.5, 51.5 (PhCH<sub>2</sub>NCH<sub>2</sub>); 45.4, 45.3, 44.9 [N(CH<sub>3</sub>)<sub>2</sub>]; 24.8, 24.7, 24.5, 24.4 (CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>). I.r. (KBr disc):

3401  $\text{cm}^{-1}$  (Ph—OH), 2946  $\text{cm}^{-1}$  (ph—CH<sub>3</sub>), 1466  $\text{cm}^{-1}$  (N—CH<sub>3</sub>), 1644  $\text{cm}^{-1}$  (aromatic) 1261  $\text{cm}^{-1}$  (C—O—C).

### Binuclear $\text{Cu}^{\text{II}}$ complexes

#### Hydroxo-bridged complexes [10, 11]:

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

A mixture of HL<sup>1</sup> (0.57 g, 1 mmol), Cu (ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (0.74 g, 2 mmol) and NaOH (0.04 g, 1 mmol) in MeOH (75 cm<sup>3</sup>) was stirred at ambient temperature for 30 min. The resulting green solution was then evaporated to dryness and the solid product was recrystallised from MeOH. Yield: 78% (Found: C, 35.9; H, 6.3; N, 8.4; Cu, 12.6. C<sub>30</sub>H<sub>65</sub>N<sub>6</sub>O<sub>13</sub>Cu<sub>2</sub>Cl<sub>2</sub>Br calcd.: C, 36.2; H, 6.9; N, 8.5; Cu, 12.8%).

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

$[\text{Cu}_2\text{L}^3(\text{OH})] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot \text{H}_2\text{O}$  (1c)

These complexes were prepared by the same reaction as HL<sup>1</sup> using HL<sup>2</sup> and HL<sup>3</sup> respectively instead of HL<sup>1</sup>. (1b) Yield: 82% (Found: C, 39.9; H, 7.2; N, 9.0; Cu, 13.7. C<sub>31</sub>H<sub>68</sub>N<sub>6</sub>O<sub>13</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 40.0, H, 7.2, N, 9.0, Cu, 13.8%). FAB Mass, *m/z* 732 (M) [Cu<sub>2</sub>L<sup>2</sup>(OH)] (ClO<sub>4</sub>)<sub>2</sub> · 2MeOH · H<sub>2</sub>O, 607 M—2Cu, 507 (M—(2Cu + 2MeOH + H<sub>2</sub>O + OH), 176 (base peak) 4[N (Me)<sub>2</sub>]<sup>+</sup>. (1c) Yield: 78% (Found: C, 39.5; H, 7.1; N, 8.9; Cu, 13.3. C<sub>31</sub>H<sub>68</sub>N<sub>6</sub>O<sub>14</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 40.0; H, 7.4; N, 9.0; Cu, 13.7%).

#### Acetato-bridged complexes

$[\text{Cu}_2\text{L}^1\text{OAc}] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (2a)

Cu(OAc)<sub>2</sub> · H<sub>2</sub>O (0.39 g, 2 mmol) was dissolved in MeOH (75 cm<sup>3</sup>). Addition of a MeOH solution of the ligand (0.57 g, 1 mmol) and LiClO<sub>4</sub> (2 mmol) led to the formation of a dark green solution. The mixture was stirred at ambient temperature for 30 min. The resulting solution was evaporated to dryness, and the crude product was recrystallised from MeOH to give green microcrystals. Yield: 78% (Found: C, 39.2; H, 7.3; N, 8.7; Cu, 12.6. C<sub>32</sub>H<sub>69</sub>N<sub>6</sub>O<sub>15</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 39.42; H, 7.1; N, 8.6; Cu, 12.9%).

$[\text{Cu}_2\text{L}^2(\text{OAc})] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (2b) and

$[\text{Cu}_2\text{L}^3(\text{OAc})] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (2c)

These complexes were prepared in a similar way to (1a) using HL<sup>2</sup> and HL<sup>3</sup> instead of HL<sup>1</sup>. (2b) Yield: 76% (Found: C, 39.9; H, 7.4; N, 8.8; Cu, 12.5. C<sub>33</sub>H<sub>72</sub>N<sub>6</sub>O<sub>15</sub> · Cu<sub>2</sub>Cl<sub>2</sub>, calcd.: C, 40.0; H, 7.3; N, 8.5; Cu, 12.8%). (2c) Yield: 80%. (Found: C, 39.5; H, 7.1; N, 8.6; Cu, 12.4. calcd.: C<sub>33</sub>H<sub>72</sub>N<sub>6</sub>O<sub>16</sub>Cu<sub>2</sub>Cl<sub>2</sub>: C, 39.4; H, 7.2; N, 8.4; Cu, 12.5%).

#### Nitrito-bridged complexes

$[\text{Cu}_2\text{L}^1(\text{ONO})] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 3\text{H}_2\text{O}$  (3a)

To a solution of HL<sup>1</sup> (0.57 g, 1 mmol) in MeOH (75 cm<sup>3</sup>) was added Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (0.74 g, 2 mmol)

followed by NaNO<sub>2</sub> (0.20 g, 2 mmol) dropwise. After stirring for 30 min, the resulting green solution was kept at room temperature to allow the solvent evaporate slowly. The dark green solid obtained was recrystallised from hot MeOH. Yield: 82% (Found: C, 33.0; H, 6.4; N, 9.2; Cu, 11.9. C<sub>30</sub>H<sub>68</sub>N<sub>7</sub>O<sub>16</sub>Cu<sub>2</sub>Cl<sub>2</sub>Br calcd.: C, 32.9; H, 6.5; N, 9.3; Cu, 12.0%). FAB mass, *m/z* 863 (M) [Cu<sub>2</sub>L<sup>1</sup>(ONO)] (ClO<sub>4</sub>)<sub>2</sub> · 2MeOH · 3H<sub>2</sub>O, 697 (base peak) M—(2MeOH + 3H<sub>2</sub>O + NO<sub>2</sub> + H<sub>2</sub>), 460 M—2H [(CH<sub>2</sub>)<sub>3</sub>—N(Me)<sub>2</sub> + OMe, 176 4[N(Me)<sub>2</sub>]<sup>+</sup>.

$[\text{Cu}_2\text{L}^2(\text{ONO})] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 3\text{H}_2\text{O}$  (3b) and

$[\text{Cu}_2\text{L}^3(\text{ONO})] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 3\text{H}_2\text{O}$  (3c)

The same method was used as for complexes (3b) and (3c) using HL<sup>2</sup> and HL<sup>3</sup> instead of HL<sup>1</sup>. (3b) Yield: 79%. (Found: C, 37.3; H, 7.08; N, 9.7; Cu, 12.6. C<sub>31</sub>H<sub>71</sub>N<sub>7</sub>O<sub>16</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 37.4; H, 7.2; N, 9.9; Cu, 12.8%). (3c) Yield: 83% (Found: C, 36.7; H, 7.0; N, 10.0; Cu, 12.5. C<sub>31</sub>H<sub>71</sub>N<sub>7</sub>O<sub>17</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 36.9; H, 7.1; N, 10.0; Cu, 12.6%).

#### Azido-bridged complexes

$[\text{Cu}_2\text{L}^1(\text{N}_3)] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (4a)

A solution of Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (0.74 g, 2 mmol) in MeOH was added to a MeOH solution of HL<sup>1</sup> (0.57 g, 1 mmol). Addition of NaN<sub>3</sub> (0.13 g, 2 mmol) in MeOH yielded a brown precipitate and the mixture was stirred for 30 min. The precipitate was filtered off and the green filtrate obtained was evaporated under reduced pressure at room temperature for a few days to give green solid, which was recrystallised from MeOH. Yield: 79% (Found: C, 34.7; H, 6.9; N, 12.7; Cu, 12.1. C<sub>30</sub>H<sub>66</sub>N<sub>9</sub> · O<sub>13</sub>Cu<sub>2</sub>Cl<sub>2</sub> · Br calcd.: C, 34.7; H, 7.0; N, 12.7; Cu, 12.2%). FAB mass, *m/z* 840 (M) [Cu<sub>2</sub>L<sup>1</sup>(N<sub>3</sub>)] (ClO<sub>4</sub>)<sub>2</sub> · 2MeOH · 2H<sub>2</sub>O, 697 M—(2CH<sub>3</sub>OH + 2H<sub>2</sub>O + N<sub>3</sub> + H), 176 (base peak) 4[N (Me)<sub>2</sub>]<sup>+</sup>.

$[\text{Cu}_2\text{L}^2(\text{N}_3)] [(\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (4b) and

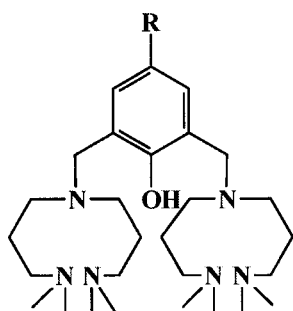
$\text{Cu}_2\text{L}^3(\text{N}_3)] (\text{ClO}_4)_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (4c)

These complexes were prepared in a similar way to (4a) but replacing HL<sup>1</sup> with HL<sup>2</sup> and HL<sup>3</sup> respectively. (4b) Yield: 79% (Found: C, 38.2; H, 7.1; N, 12.9; Cu, 13.0. C<sub>31</sub>H<sub>69</sub>N<sub>9</sub>O<sub>13</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 38.2; H, 7.1; N, 13.0; Cu, 13.1%). (4c) Yield: 85% (Found: C, 37.6; H, 7.0; N, 12.8; Cu, 12.8. C<sub>31</sub>H<sub>69</sub>N<sub>9</sub>O<sub>14</sub>Cu<sub>2</sub>Cl<sub>2</sub> calcd.: C, 37.6; H, 7.0; N, 12.7; Cu, 12.8%).

## Results and discussion

### Synthesis

The ligands were synthesized by the Mannich reaction, *i.e.* refluxing the appropriate phenol and 3,3'-iminobis (*N,N*-dimethylpropylamine) in the presence of formaldehyde in EtOH. The ligands are represented by the notation HL<sup>1</sup>, HL<sup>2</sup> and HL<sup>3</sup>.

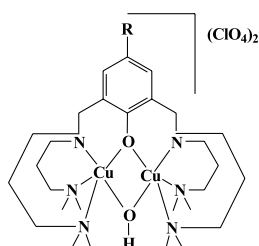


HL<sup>1</sup>; R= Br

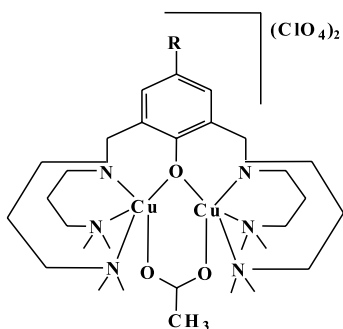
HL<sup>2</sup>; R= Me

HL<sup>3</sup>; R= OMe

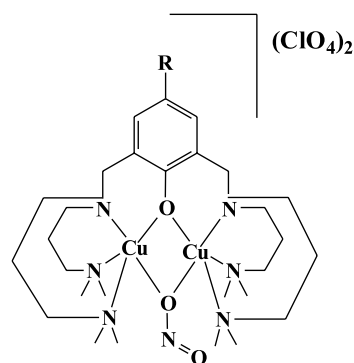
The hydroxo-bridged complexes (*1a*, *1b*, and *1c*) were prepared using a MeOH solution of each ligand and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in a 1:2 molar ratio in the presence of NaOH.



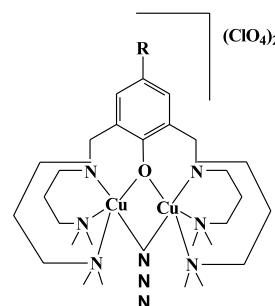
Complexes (*2a*, *2b*, and *2c*), containing bis-acetato bridges were prepared by reacting the appropriate ligands with Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and LiClO<sub>4</sub>.



Complexes (*3a*, *3b* and *3c*) pertaining to the nitrite groups were obtained from a 1:2 molar ratio of the ligand and NaNO<sub>2</sub> in aqueous MeOH.



The azide-bridged complexes (*4a*, *4b* and *4c*), were synthesized according to the standard procedure consisting the addition of the appropriate ligand and NaN<sub>3</sub> to the MeOH solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O.



The structure of the complexes were elucidated using spectroscopic techniques like i.r. and u.v.-vis. in conjunction with FAB mass spectrometry. The FAB mass spectrum of complex (*3a*) is displayed in Figure 1.

All the hydroxo-bridged complexes exhibited a broad band in the 3480–3600 cm<sup>-1</sup> region assigned to the hydroxo stretch on the basis of previous reports [12, 13]. The perchlorate salts show strong bands at 1100 cm<sup>-1</sup> and a sharp band at in 620–625 cm<sup>-1</sup>, indicative of the uncoordinated perchlorate anion [14, 15]. The nature of the binding of the acetate ions in (*2a*), (*2b*) and (*2c*) have been determined from the i.r. spectra by considering the difference in energy (Δ) between the asymmetric

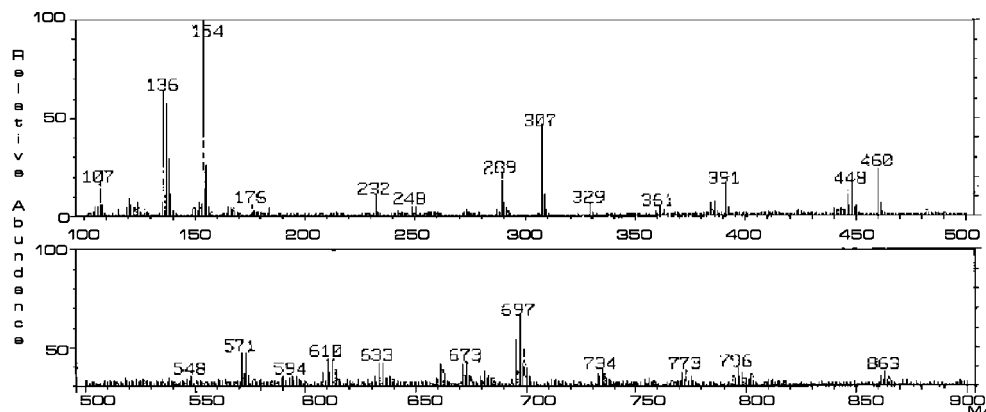


Fig. 1. FAB mass spectrum of complex (*3a*).

and symmetric carboxylate stretching frequencies. In general, for an unidentate acetate,  $\Delta$  is quite  $> 150 \text{ cm}^{-1}$  and for a bidentate acetate it is  $< 100 \text{ cm}^{-1}$ , whereas for bridging acetate  $\Delta$  is not much different from  $150 \text{ cm}^{-1}$  [16]. For all acetate complexes  $\nu(\text{COO})$  are observed at 1582, 1478; 1580, 1470, 1604 and  $1472 \text{ cm}^{-1}$  and their energy difference ( $\Delta$ ) = 104, 110 and  $132 \text{ cm}^{-1}$  suggest the presence of bridging acetate. The bands due to the nitrite group are observed [17] at  $1450\text{--}1220 \text{ cm}^{-1}$  which, by comparison with published work suggest a monodentate O bonded mode for the nitrite groups. The azide stretching vibration for azide complexes appears at  $2030\text{--}2056 \text{ cm}^{-1}$  and is assigned to monodentate N-coordinated azide groups [18]. All the complexes show bands at *ca.*  $488 \text{ cm}^{-1}$  and  $280 \text{ cm}^{-1}$  indicating the presence of Cu–N and Cu–O respectively [19].

The electronic spectra of these complexes in MeOH show a low intensity band in the 600–750 nm region, due to the d–d transition [20]. This indicates that the geometry around copper (II) is five coordinate square pyramidal. A medium intensity band occurring in the 325–460 nm range is due to phenolato-to-copper (II) charge-transfer (CT) [21]. Definitive assignment of this band is provided by substitution of the *para* position with an electron-withdrawing or donating group. Electron donating groups are expected to decrease the Lewis acidity of the copper center thus shifting the phenoxo-to-copper CT band to lower energies, while electron-withdrawing groups are expected to increase the Lewis acidity and shift the phenolato to copper (II) CT band to higher energies [22]. We happened to observe the LMCT band shifts to lower energy (401, 397 nm) (Figure 2) when the *para* position is substituted with an electron-donating group such as –OMe, or –Me. Conversely, when the *para* position is substituted with an electron-withdrawing group such as Br, the LMCT band shifts to higher energy (379 nm).

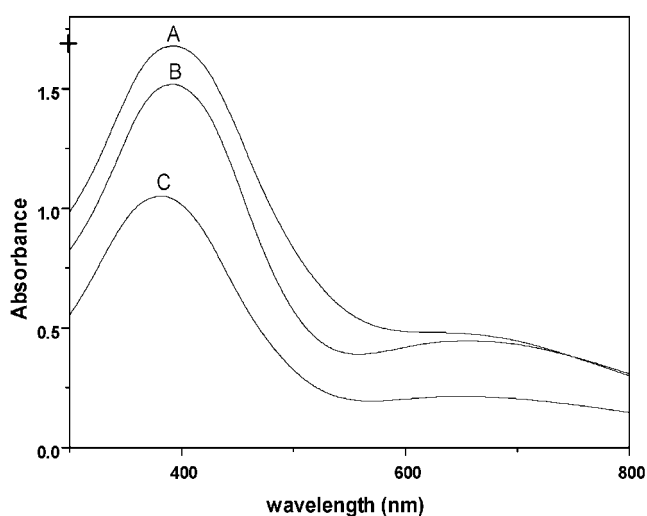


Fig. 2. Visible spectrum of complex  $[\text{Cu}_2(\text{Z-L})(\text{ONO})](\text{ClO}_4)_2$  where Z = OMe (A), Me (B), and Br (C).

Table 1. Electronic absorption spectral data of the dinuclear  $\text{Cu}^{\text{II}}$  complexes in MeOH  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), CT corresponds to charge-transfer band and d–d corresponds to d–d transition

Complex	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	
	CT	d–d
(1a)	356, 261, 221	613 (155)
(1b)	357, 261, 236	619 (205)
(1c)	359, 290, 235	654 (230)
(2a)	349, 246, 207	718 (107)
(2b)	353, 347, 278	677 (80)
(2c)	423, 260, 230	680 (96)
(3a)	379, 290, 230	656 (136)
(3b)	397, 286, 240	626 (104)
(3c)	401, 270, 218	644 (114)
(4a)	330, 267, 220	628 (250)
(4b)	358, 265, 207	622 (114)
(4c)	458, 351, 267	699 (89)

These energy shifts consistent with the expected change in the Lewis acidity at the copper (II) centers. Similar trend has been made in phenoxo – to iron CT bands in related systems [23]. An intense absorption at *ca.* 200–270 nm has also been observed which is probably due to the ligand-to-ligand CT transition (see Table 1).

#### Magnetic properties

The magnetic susceptibilities for complexes (1a), (1c), (2b), (3c) and (4a) were studied in the 80–296 K range. The susceptibility data were fitted to the Bleaney–Bowers equation for an exchange coupled pair of copper (II) ions with  $2J$ . The magnetic exchange parameter in the spin ( $H = -2JS_1S_2$ ),

$$\chi_m = \{Ng^2\beta^2/3kT\}[3 + \exp(-2J/kT)]^{-1}(1 - p) + (Ng_i^2\beta_i^2/4KT)p + N\alpha$$

$-2J$  is the singlet–triplet energy separation and  $g$  as variable parameters, where  $p$  is the fraction of monomeric impurity and  $\chi_m$  is the molar magnetic susceptibility per Cu. Figure 3 shows plots of  $\chi_{\text{Cu}}$  and  $\mu_{\text{eff}}$  versus  $T$  for complexes (1a) (A) and (4a) (B). Good magnetic simulation was obtained: for (1a)  $2J = -94 \text{ cm}^{-1}$ ,  $g = 2.05$  and  $p = 0.003$ ; for (4a)  $2J = -137 \text{ cm}^{-1}$ ,  $g = 2.01$  and  $p = 0.001$ .  $N\alpha = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . The  $\mu_{\text{eff}}$  decreases with decreasing temperature indicating there is an antiferromagnetic interaction between two copper (II) ions. Some interesting general trends emerging from the data in Table 2 are: variation in the exogenous bridging group shows that azide and nitrito groups give stronger antiferromagnetic coupling than OAc and OH. *i.e.* a more negative  $J$ . This is probably as a result of strong field and resonance property [24] providing a more favorable super exchange pathway.

It is interesting to note that in the  $[\text{Cu}_2\text{L}^1(\text{X})]^{n+}$  complexes, which have a compatible structure, relatively

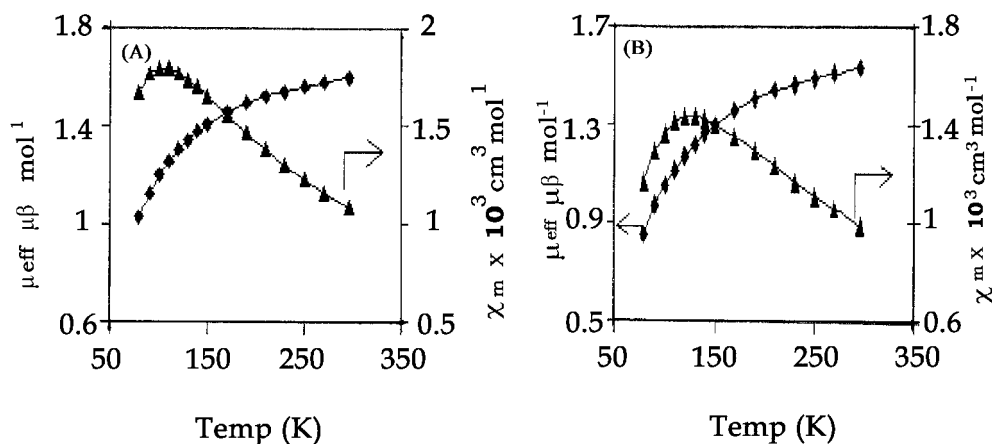


Fig. 3. Plots of the molar susceptibility per molecule ( $\chi_m$ ) versus temperature and of the effective magnetic moment per molecule ( $\mu_{\text{eff}}$ ) versus temperature for complexes (1a) (A) and (4a) (B). The solid lines represent the least square fitting of the data using the magnetic parameters given in Table 3.

Table 2. Magnetic data for  $\text{Cu}^{\text{II}}$  complexes

Complex	$-2J$ ( $\text{cm}^{-1}$ )	$\mu_{\text{eff}}$ per molecule (B.M)		$g$
		79 K	296 K	
(1a)	94.90	1.03	1.60	2.056
(4a)	137.28	0.86	1.53	2.013
(1b)	128.60	0.76	1.56	1.947
(2b)	146.82	0.89	1.48	2.102
(3c)	172.87	0.88	1.46	2.007

$N_z$  fixed at  $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for magnetic simulations. Refer text for the definition of  $g$  and  $P$ .  $-2J$  value calculated using the Bleaney-Bowers equation.

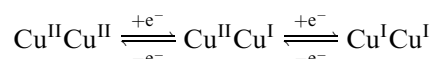
low spin exchange coupling was observed when compared to  $[\text{Cu}_2\text{L}^2(\text{X})]^{n+}$  and  $[\text{Cu}_2\text{L}^3(\text{X})]^{n+}$ . As explained by the electrochemical properties of the complexes, the electron-withdrawing Br atom decreases the electron density on the copper atoms in the complexes  $[\text{Cu}_2\text{L}^1(\text{X})]$ . Reports suggest that factors, *i.e.* reduction in electron density [25] on the copper atom, are less favorable for effective coupling, resulting in a lower  $2J$  value for the complexes of the ligand  $\text{HL}^1$  when compared to  $\text{HL}^2$  and  $\text{HL}^3$ .

The final conclusion on the structure and magnetism of this small series of complexes concerns the dependence of Cu—O—Cu angle, Cu—Cu distance and electronic perturbation by remote substituents. In general, as the Cu—Cu distance and Cu—O—Cu angle increase,  $J$  becomes more negative. The weak overall antiferromagnetism of the hydroxo-bridged complexes has been ascribed largely to the effect of the pyramidal geometry around the phenolato oxygen atom [26–28] and, also, the small negative  $J$  value in bis (acetato) complexes reflects the combined effect of the acetate and phenolate super-exchange pathway [29]. The large  $2J$  values of nitrito and azide complexes, probably due to the resonance property, provide a more favorable super-exchange pathway. The magnitude of magnetic interaction of the small series is:  $\text{N}_3 \approx \text{NO}_2 > \text{OAc} > \text{OH}$ .

### Cyclic voltammetry

The electrochemical properties of complexes (1a)–(4b) were studied by cyclic voltammetry. The electrochemical data are summarized in Table 3.

The cyclic voltammogram of the complexes generally show two quasi-reversible redox processes in the cathodic potential region. Coulometric analysis carried out for the complexes at 100 mV more negative to the second reduction peak consumes two electrons per molecule ( $n = 1.8$ ). These results indicate that reduction of the complexes involve a two step single electron transfer. The schematic pathway for the electron chemical reduction is given below.



The cyclic voltammogram response of the complexes follow the characteristics of a typical [30, 31] quasireversible redox process such as a shift in  $\Delta E_p$  values, broadening of the peak size with scan rate,  $E_{\text{pc}} - E_{\text{pa}} > 60 \text{ mV}$  and  $i_p^a/i_p^c \neq 11$ .

The reduction potentials observed for the acetato-bridged complexes is less negative when compared to the hydroxo and other complexes. This behavior seems to be associated with the increased number of atoms involved in the acetato bridge, which may provide more flexibility for the complexes as against hydroxo, nitrito and azido-bridged complexes.

The electrochemical data show that complexes of the ligand  $\text{HL}^1$  undergo reduction at a less negative potential when compared to the complexes of the ligands  $\text{HL}^2$  and  $\text{HL}^3$ . Since, all the ligands have the same coordination sites, the reduction observed at a less negative potential for the complexes  $[\text{Cu}_2\text{L}(\text{X})]^{n+}$  can be correlated with the electronic effects of the substituents present in the ligand. The electron density on the copper ions of the complexes  $[\text{Cu}_2\text{L}^1(\text{X})]^{n+}$  will

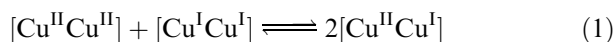
Table 3. Electrochemical data for Cu<sup>II</sup> complexes with their conproportionation constant ( $K_{\text{con}}$ ) in MeCN at room temperature

Complex	$E_{\text{pc}}/V$	$E_{\text{pa}}/V$	$E_{1/2}/V$	$\Delta E_{\text{p}}/V$	$K_{\text{con}}$
(1a)	-0.272	-0.011	-0.142	-0.261	$4.864 \times 10^4$
	-0.533	-0.305	-0.419	-0.228	
(1b)	-0.310	0.010	-0.150	-0.320	$8.359 \times 10^5$
	-0.720	-0.280	-0.500	-0.440	
(1c)	-0.318	-0.250	-0.284	-0.068	$7.823 \times 10^{12}$
	-1.057	-1.034	-1.046	-0.023	
(2b)	-0.149	-0.061	-0.105	-0.088	$4.696 \times 10^3$
	-0.399	-0.245	-0.322	-0.154	
(3a)	-0.201	-0.110	-0.156	-0.091	$9.072 \times 10^4$
	-0.578	-0.319	-0.449	-0.259	
(3b)	-0.428	-0.116	-0.272	-0.312	$1.349 \times 10^3$
	-0.632	-0.282	-0.457	-0.350	
(3c)	-0.465	-0.062	-0.264	-0.403	$4.714 \times 10^2$
	-0.626	-0.217	-0.422	-0.409	
(4a)	-0.148	-0.028	-0.088	-0.120	$9.432 \times 10^4$
	-0.410	-0.354	-0.382	-0.056	
(4b)	-0.463	-0.056	-0.260	-0.407	$2.347 \times 10^{11}$
	-1.050	-0.813	-0.932	-0.237	
(4c)	-0.570	-0.153	-0.362	-0.417	$1.085 \times 10^9$
	-1.139	-0.653	-0.896	-0.486	

Potential  $V$  versus Ag/AgCl; supporting electrolyte: TBAP;  $\Delta E_{\text{p}} = E_{\text{pc}} - E_{\text{pa}}$ ,  $E_{1/2} = 0.5 (E_{\text{pc}} + E_{\text{pa}})$  where  $E_{\text{pc}}$  and  $E_{\text{pa}}$  are the cathodic and anodic peak potentials.

be less, due to the electron-withdrawing effect of bromine atom present on the phenolic residues causing the redox orbital energies to be lower than those for the complexes  $[\text{Cu}_2\text{L}^2(\text{X})]^{n+}$  and  $[\text{Cu}_2\text{L}^3(\text{X})]^+$ . Reports suggest that reduction in electron density on the copper ions [23, 26] will influence the copper (II)  $\rightarrow$  copper (I) conversion at a less negative potential in the complexes of ligand HL<sup>1</sup>.

The stability of the mixed valence species  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  is expressed by the conproportionation constant  $K_{\text{con}}$  for equilibrium (1)



The  $K_{\text{con}}$  values of the complexes have been determined electrochemically using the following equation; the values are given in Table 3.

$$\log K_{\text{con}} = E_{1/2}/0.0591 \quad (\text{at } 25^\circ\text{C}) \quad \text{where } E_{1/2} = E_{1/2}^1 - E_{1/2}^2$$

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