

## Imidazolidine ring as a reduced heterocyclic spacer in a new all-N-donor *m-bis*(bidentate) Schiff base ligand: Synthesis, characterization and electron transfer properties of imidazolidine-bridged dicopper complexes

MANINDRANATH BERA, PRASANT KUMAR NANDA, UDAY MUKHOPADHYAY and DEBASHIS RAY\*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India  
e-mail: dray@chem.iitkgp.ernet.in

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**Abstract.** Low-temperature stoichiometric Schiff base reaction in air in 3 : 1 mole ratio between benzaldehyde and triethylenetetramine (trien) in methanol yields a novel tetraaza *m-bis*(bidentate) acyclic ligand L. It was characterized by elemental analysis, IR, EI mass and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) spectra. The formation of a five-membered imidazolidine ring from the ethylenediamine backbone as a spacer-cum-bridging unit gives rise to a new type of imidazolidine-bridged ligand. A geometric optimisation was made of the synthesized ligand and its complexes by the method of molecular mechanics (MM2) method in order to establish the stable conformations. This hitherto unknown tetraaza acyclic ligand affords new cationic dicopper(I/I) and dicopper(II/II) complexes in good yield. Dicopper(II/II) complex displays weak *d-d* transition bands in the visible region, while dicopper(I/I) complex displays strong MLCT band in the same region. Both the dinuclear complexes are of non-intimate nature and show interesting solution electrochemical behaviour. EPR spectral study of *m-bis*(imidazolidino) bridged dicopper(II/II) complex also supports the non-communicative nature of the two copper centres within the same molecule.

**Keywords.** Schiff base; dicopper (II/II) complexes; imidazolidine-bridged; molecular mechanics; cyclic voltammetry; EPR.

### 1. Introduction

The design and synthesis of new dinuclear complex requires good agreement between the stereochemical requirements of the metal and the special features of the ligand such as geometry of the available donor groups and spacers between the coordination groups.<sup>1</sup> Among various products from the condensation of aromatic aldehydes with *a,w*-tetramine containing both primary and secondary amino groups is a binucleating Schiff base with an in-built spacer imidazolidine ring, which can take up two same or different metal ions.<sup>2</sup> Recently we reported X-ray structural characterization of one such heterodinuclear complex of copper(II)–zinc(II) held by an imidazolidine ring.<sup>3</sup> The use of binucleating ligands for the synthesis of new family of di-3*d*-metal complexes has been receiving considerable attention in

recent years following the identification of similar catalytically active biosites in living systems. In case of dicopper complexes, during complex formation, the  $d^{10}\text{Cu}^{1+}$  ion can assemble two molecules of any *m-bis*(bidentate) ligand in tetrahedral geometry. Similar helical assembly is not feasible for  $d^9$  ion copper(II) because its geometrical preference is different. Instead the copper(II) ions change the ligand arrangement according to their choice for a tetragonal coordination. The in-built unsubstituted imidazolidine spacer, on the other hand, does not allow the mononuclear  $\text{N}_4$  coordination around a single copper(II) ion. Two *m-bis*(bidentate) ligands can accommodate two copper ions in two cavities.

The *p*-acceptor features of the coordinating nitrogen atoms of the new ligand 2-phenyl-2,3-*bis*-[3'-aza-4-(2''-phenyl)-prop-4'-en-1'-yl]-1,3-imidazolidine, L stabilize the  $\text{Cu}^{\text{I}}$  state, while the phenyl substituted imidazolidine spacer keeps the two metal centres apart in a 2 : 2 metal–ligand stoichiometry. This promotes the formation of the stable dicopper(I/I)

\*For correspondence

entity  $[\text{Cu}_2^{\text{I/I}}\text{L}_2]^{2+}$  for **2b**. The corresponding  $\text{Cu}^{\text{II}}$  centres are only stabilized in a square ligating environment, again in a dinuclear assembly. Therefore, the reversible ligand twisting around the spacer imidazolidine ring can accommodate both the copper(I) and copper(II) centres within the same molecule. The  $[\text{Cu}_2^{\text{I/I}}\text{L}_2]^{2+}$  and  $[\text{Cu}_2^{\text{II/II}}\text{L}_2]^{4+}$  species are stable both in solution and in the solid state. In case of a double-helical arrangement the flexible imidazolidine ring is folded somewhat to introduce the required twist in the ligand backbone for metal binding through tetrahedral coordination, whereas for a non-helical case it remains in planar form. Dicopper(I/I)-promoted activation of molecular dioxygen and subsequent hydroxylation reaction and mechanism of the nearby phenyl ring is an important area of research<sup>4-9</sup> using synthetic dicopper complexes. The ineffectiveness of the imidazolidine bridges in importing any magnetic communication between the two copper(II) centres has also been here established through EPR study.

## 2. Experimental

Triethylenetetramine (trien) was obtained from SD Fine Chem, India. Benzaldehyde was purchased from Qualigens, India. Cupric perchlorate hexahydrate was prepared by treating copper(II) carbonate with 1 : 1  $\text{HClO}_4$  and crystallizing after concentration on a water bath. Dry acetonitrile was prepared by the published method.<sup>10</sup>  $[\text{Cu}(\text{MeCN})_4]\text{ClO}_4$  was also prepared by a published procedure.<sup>11</sup> The preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work was performed as reported in the literature.<sup>12</sup> Microanalyses (C, H, N) were carried out using a Perkin-Elmer 240 C elemental analyser. The solution electrical conductivity and electronic spectra were obtained using a Unitech type U131C digital conductivity meter with a solute concentration of about  $10^{-3}$  M and a Shimadzu UV 3100 UV-Vis-NIR spectrophotometer respectively. Mass spectra were obtained with a Finnigan MAT 8200 (electron ionisation, EIMS) instrument. Room temperature magnetic susceptibilities in the solid state were measured using a home-built Gouy balance fitted with a polytronic DC power supply. The experimental magnetic susceptibilities were corrected for the diamagnetic response using Pascal's constants. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer. X-band EPR spectra were recorded on a Varian E-109C spectrometer fitted with a

quartz Dewar flask for measurements at 77 K (liquid nitrogen). The spectra were calibrated with diphenylpicrylhydrazyl(dpph) ( $g = 2.0037$ ). The microwave power level was maintained at  $\approx 0.2$  mW. Electrochemical measurements were made using a PAR model 173 potentiostat/galvanostat, 175 universal programmer, 178 electrometer, and 377-cell system. A planar Beckman 39273 platinum-disk working-electrode, a platinum-wire auxiliary-electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. A digital series 2000 Omni Graphic recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. Conformational analysis was done by using Allinger's MM2 method.<sup>13</sup>

### 2.1 Synthesis of ligand L

A solution of triethylenetetramine (5 g, 34.2 mmol) in methanol (15 ml) was added drop wise to an ice-cold methanolic solution (30 ml) of benzaldehyde (10 g, 102.7 mmol) with stirring the yellow solution was stirred for 1 h and the solvent was evaporated in air. The yellow solid was separated by filtration through G4 sintered bed and washed thoroughly with hexane and water. Finally the isolated compound was dried *in vacuo* over  $\text{P}_4\text{O}_{10}$ . Yield 8.4 g (60%), m.p. 75–77°C. Analysis Calc. for  $\text{C}_{27}\text{H}_{30}\text{N}_4$ : C, 78.99; H, 7.36; N, 13.65%. Found: C, 78.76; H, 7.49; N, 13.89%. Mass spectrum (EI):  $m/z$  410 ( $M^+ = L^+$ ). Infrared spectrum ( $\text{cm}^{-1}$ , KBr disk): 1639 (*vs*,  $n_{\text{C}=\text{N}}$ ).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $d_{\text{ppm}}$ : 2.5–2.9 (8H, *m*,  $\text{H}_8$  and  $\text{H}_9$ ), 3.47–3.66 (4H, *m*,  $\text{H}_{10}$  and  $\text{H}_{11}$ ), 3.73 (H, *s*,  $\text{H}_{12}$ ), 7.25–7.28 (3H, *m*,  $\text{H}_{15}$ ,  $\text{H}_{16}$  and  $\text{H}_{17}$ ), 7.34–7.36 (8H, *m*,  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_3$ ,  $\text{H}_{14}$  and  $\text{H}_{18}$ ), 7.66–7.67 (6H, *m*,  $\text{H}_4$ ,  $\text{H}_5$  and  $\text{H}_6$ ), 8.17 (2H, *s*,  $\text{H}_7$ ).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ )  $d_{\text{ppm}}$ : 51.86 ( $\text{C}_{10}$  and  $\text{C}_{11}$ ), 53.35 ( $\text{C}_9$ ), 60.61 ( $\text{C}_8$ ), 89.55 ( $\text{C}_{12}$ ), 96.14 ( $\text{C}_1$ ,  $\text{C}_5$ ,  $\text{C}_{14}$  and  $\text{C}_{18}$ ), 127.81 ( $\text{C}_2$ ,  $\text{C}_4$ ,  $\text{C}_{15}$  and  $\text{C}_{17}$ ), 128.05 ( $\text{C}_{16}$ ), 128.44 ( $\text{C}_3$ ), 136.26 ( $\text{C}_6$ ), 161.70 ( $\text{C}_7$ ).

### 2.2 Synthesis of the complexes

$[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  (**2a**): An aqueous solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.542 g, 1.46 mmol) was slowly added drop wise at ambient temperature to a stirred methanolic solution (15 mL) of L (0.6 g, 1.46 mmol) over a period of 0.5 h. The blue coloured compound that formed was separated immediately. The mixture was stirred for 1 h at room temperature and the blue

precipitate was filtered through a glass frit, washed with water followed by ethanol and hexane and finally dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. The yield of the compound was 0.69 g (70%). Analysis Calc. for C<sub>54</sub>H<sub>60</sub>N<sub>8</sub>O<sub>16</sub>Cl<sub>4</sub>Cu<sub>2</sub>: C, 48.19; H, 4.49; N, 8.32; Cu, 9.44%. Found: C, 48.32; H, 4.66; N, 8.57, Cu, 9.58%. Infrared spectrum (cm<sup>-1</sup>, KBr disk): 1617 (*vs*,  $\nu_{C=N}$ ). Molar conductance,  $\Lambda_M$ : (MeCN solution) 560 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. UV-Vis spectra [ $I_{max}$ , nm ( $\epsilon$ , l mol<sup>-1</sup> cm<sup>-1</sup>): (MeCN solution) 576 (380), 277 (9875), 244 (25440)]. Mass spectrum (FAB):  $m/z$  1247 ( $M^+ = [Cu_2^{II/II}(m-L)_2](ClO_4)_3^+$ ).

[Cu<sup>II</sup>(*m*-L)<sub>2</sub>] (ClO<sub>4</sub>)<sub>2</sub> (**2b**): Solid [Cu(MeCN)<sub>4</sub>]ClO<sub>4</sub> (0.32 g, 0.978 mmol) was added in portions to the degassed acetonitrile (20 mL) solution of L (0.976 mmol) in nitrogen atmosphere. Immediately a yellow compound separated and the mixture was stirred for 15 min. The compound was filtered, washed and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. A second crop of the compound was obtained by evaporating the yellow filtrate at reduced pressure. The yield of the compound was 0.34 g (60%). Analysis Calc. for C<sub>54</sub>H<sub>60</sub>N<sub>8</sub>O<sub>8</sub>Cl<sub>2</sub>Cu<sub>2</sub>: C, 56.54; H, 5.27; N, 9.77; Cu, 11.08%. Found: C, 56.17; H, 5.22; N, 9.52, Cu, 11.02%. Infrared spectrum (cm<sup>-1</sup>, KBr disk): 1611 (*vs*,  $\nu_{C=N}$ ). <sup>1</sup>H NMR (200 MHz, *d*<sub>6</sub>-DMSO)  $d_{ppm}$ : 2.49–3.45 (8H, *m*, H<sub>8</sub> and H<sub>9</sub>), 3.51–3.68 (4H, *m*, H<sub>10</sub> and H<sub>11</sub>), 3.84 (H, *s*, H<sub>12</sub>), 7.33–7.39 (3H, *m*, H<sub>15</sub>, H<sub>16</sub> and H<sub>17</sub>), 7.45–7.59 (8H, *m*, H<sub>1</sub>, H<sub>2</sub>, H<sub>3</sub>, H<sub>14</sub> and H<sub>18</sub>), 7.93–8.07 (6H, *m*, H<sub>4</sub>, H<sub>5</sub> and H<sub>6</sub>), 8.62 (2H, *s*, H<sub>7</sub>). Molar conductance,  $\Lambda_M$ : (MeCN solution) 255 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>. UV-Vis spectra [ $I_{max}$ , nm ( $\epsilon$ , l mol<sup>-1</sup> cm<sup>-1</sup>): (MeCN solution) 400 (4700), 257 (24330), 241 (24035)].

**Caution!** Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities with care.

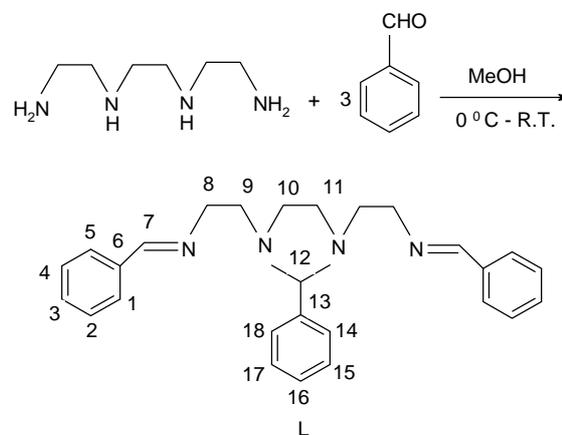
### 3. Results and discussion

The ligand used in this work belongs to a new class of *m*-*bis*(bidentate) type with a semi-rigid substituted five-membered imidazolidine spacer and has easy synthetic accessibility. The five-membered imidazolidine ring is introduced inside the tetradentate precursor to act as a spacer-cum-bridging-cum-backbone unit. The synthesis and characterization of tribenzylidinetriethylenetetramine (L) ligand and its dicopper(II/II) and (I/I) complexes are described in

this work. The ligand with *bis* imine groups separated by a flexible semi rigid imidazolidine ring can behave as a good *bis*(bidentate)-N,N' donor ligand to two metal ions for discrete binuclear metal compounds. The conformationally and geometrically well-defined phenyl substituted imidazolidine linker can guide *bis* imine subunits to create a particular coordination pocket for metal ion binding. Discrete binuclear assembly of copper(II) ions as against polynuclear assembly is formed in quantitative yields. The ligand does not use all its coordination sites to bind a single metal centre. Each copper(II) centre is bonded to two different molecules of the ligand in a CuN<sub>4</sub> coordination mode. The preference of the copper(II) ions for a tetragonal four-coordinate geometry and the semirigidity of the imidazolidine coordinating-cum-spacer group forces the ligand to act as a *bis*(bidentate) rather than a tetradentate one. The situation is also favourable for the formation of an infinite self-assembly<sup>1</sup> which is not achieved with our ligand system. These single imidazolidine-bridged dimetal complexes are less intimate and show magnetic features typical of mononuclear complexes only. This non-phenolic all-N-donor ligand system is effective in stabilizing the dicopper(I/I) complex also. Both the complexes show interesting electron-transfer behaviour as revealed by cyclic voltammetry.

In a one-pot reaction the ligand was prepared by the condensation of 1 equivalent of trien and 3 equivalents of benzaldehyde (scheme 1).

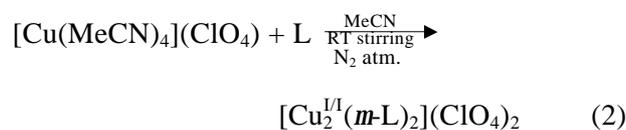
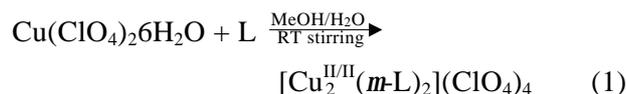
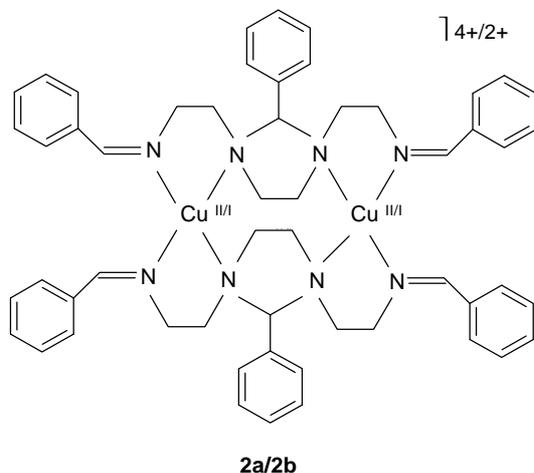
Ligand L has been characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectral analyses. In IR spectrum a strong band at 1639 cm<sup>-1</sup> indicates the  $\nu_{C=N}$



**Scheme 1.** 2-Phenyl-2,3-*bis*-[3'-aza-4-(2''-phenyl)-prop-4'-en-1'-yl]-1,3-imidazolidine, L.

stretching frequency. The  $^1\text{H}$  NMR spectrum of L in  $\text{CDCl}_3$  shows a characteristic signal of the imidazolidine ring proton ( $\text{H}_{12}$ ) at 3.73 ppm. The aromatic protons appear as a multiplet centred in the range of 7.25–7.67 ppm. The imine protons are observed at 8.17 ppm ( $\text{H}_7$ ). In the  $^{13}\text{C}$  NMR spectrum the imine carbons ( $\text{C}_7$ ) appear at 161.70 ppm indicating the characteristic imine carbons. In the mass spectrum the molecular ion peak ( $m/z$ ) is observed at 410 which indicates the formation of the desired imidazolidino  $\text{N}_4$  Schiff base ligand. The EI mass spectra of the ligand is shown in figure 1.

The reaction of the methanolic solution of ligand L with aqueous copper(II) perchlorate hexahydrate in 1 : 1 mole ratio at room temperature in air leads to the formation of a blue dicopper(II/II) complex (see (1) below). The same ligand on reaction with tetrakis(acetonitrile)copper(I) perchlorate in 1 : 1 mole ratio at room temperature in dinitrogen atmosphere and dry MeCN, gives an orange dicopper(I/I) complex ((2) below). Analytical, spectral and room temperature magnetic moment values establish that the dinuclear complexes are of composition  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  (**2a**) and  $[\text{Cu}_2^{\text{I/I}}(\text{m-L})_2](\text{ClO}_4)_2$  (**2b**) respectively. The complex  $[\text{Cu}_2^{\text{I/I}}(\text{m-L})_2](\text{ClO}_4)_2$  was also characterized by solution ( $d_6$ -DMSO)  $^1\text{H}$  NMR spectra. The characteristic signals are slightly shifted toward higher ppm values from their free ligand values. The imine  $\text{CH}=\text{N}$  peaks are seen at 8.62 (8.17) ppm. In dicopper(I/I) complex ethylene hydrogen resonances of the amine back bone are observed at 2.49–3.45  $\delta$  and are broad in nature. Imidazolidine proton signal is seen at 3.84 ppm and slightly shifted downfield compared to the free ligand position. The aromatic proton signals also show downfield shift in the range 7.33–8.07 ppm.



### 3.1 MM2 calculation

Geometric optimisation of the synthesized ligand and its complexes was done by the method of molecular mechanics (MM2)<sup>13</sup> in order to establish their stable conformations. The data for the most stable conformations of the ligand and the complexes are listed in table 1. These three energy minimized conformations are shown in figure 2. The total energy for the stable conformation of ligand is calculated to be  $-4.384$  kcal/mol and the total energies for the corresponding stable conformations of two complexes  $[\text{Cu}_2^{\text{I/I}}(\text{m-L})_2](\text{ClO}_4)_2$  and  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  are calculated to be 53.568 kcal/mol and 82.725 kcal/mol respectively. The analysis of the total energies for all the conformations have shown that the energies are primarily due to the torsional strain and van der Waals interactions.

### 3.2 Conductivity measurement and IR spectra

All the crystalline complexes are soluble in MeCN, DMF and DMSO. In acetonitrile solution the electrical conductivities of the blue and orange solutions of the complexes are close to the values for 1 : 4 and 1 : 2 (560 and 255  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ) electrolytic types respectively. IR spectra of the complexes show strong  $\text{C}=\text{N}$  stretching frequency of the terminal imine functions at  $\sim 1630 \text{ cm}^{-1}$  which is shifted from the free ligand value (for free ligand it is at  $1639 \text{ cm}^{-1}$ ). The strong unsplit band ( $\nu_{\text{ClO}_4^-}$ ) at around  $1091 \text{ cm}^{-1}$  suggests absence of coordination of perchlorate ions.<sup>14</sup>

### 3.3 Electronic absorption and mass spectra

The  $[\text{Cu}_2^{\text{I/I}}(\text{m-L})_2](\text{ClO}_4)_2$  complex is orange in colour and shows a rather intense absorption band centred at  $\lambda_{\text{max}} = 400 \text{ nm}$  (MLCT transition,  $\epsilon = 4700 \text{ M}^{-1} \text{cm}^{-1}$ ), whereas the  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  complex is blue (metal-centred transition,  $\lambda_{\text{max}} = 576 \text{ nm}$ ,  $\epsilon = 380 \text{ M}^{-1} \text{cm}^{-1}$ ).

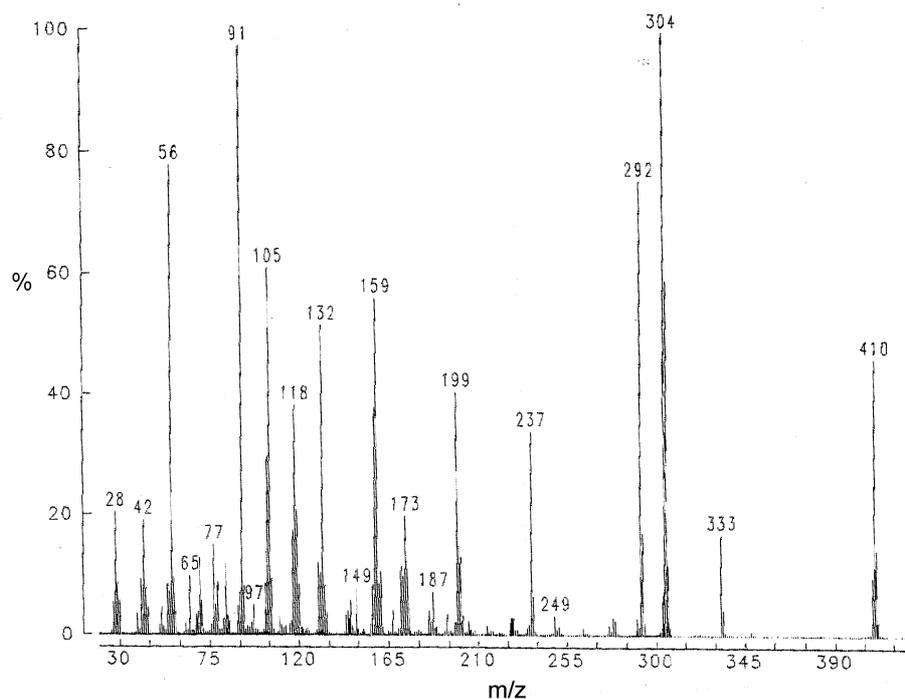


Figure 1. EI mass spectrum of the ligand, L.

Table 1. Energies of the most stable conformations of the ligand and the complexes from the MM2 force field calculations (energies in kcal/mol).

Molecule	Total	Stretch bend	Angle	Torsional (dihedral)	van der Waals	Stretch	Electrostatic
Ligand	-4.384	0.245	9.449	-33.364	17.639	1.099	0.547
Complex <b>2a</b>	82.725	0.474	63.052	-2.224	27.052	5.680	-11.484
Complex <b>2b</b>	53.569	0.433	34.689	-16.171	25.276	3.798	5.442

The FAB mass spectrum of the compound **2a** shows the molecular ion peak at  $m/z$  1247 for  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_3^+$  corresponding to dinuclear formulation  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  for the dicopper(II/II) complex.

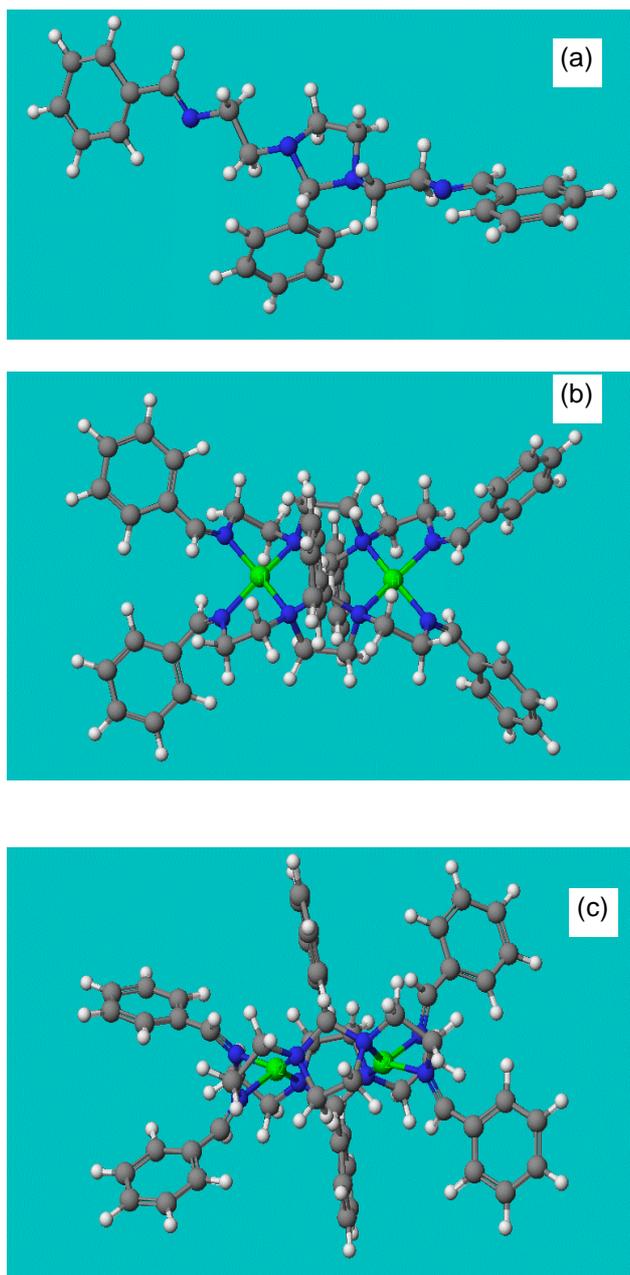
### 3.4 Magnetic susceptibility measurements

Effective magnetic moment value of complex **2a** in the powdered state is  $2.42 m_B$  ( $1.71 m_B/\text{Cu}$ ) at room temperature which is very close to the spin only value ( $1.73 m_B$ ). This suggests that no spin exchange is operative between the two metal centres in the solid state.<sup>15</sup> This is possibly due to the fact that the imidazolidine group is not expected to contribute to the magnetic exchange interaction in this molecule. A diamagnetic correction of  $278.43 \times 10^{-6}$  cgsu per complex, as calculated from the Pascal constants,<sup>16</sup> was used. The orange complex **2b** is diamagnetic in nature.

### 3.5 EPR spectra

The polycrystalline EPR spectrum of  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  at 296 K is typical for mononuclear copper(II) complexes with no internuclear magnetic interaction. The spectrum is axial with  $g_{\parallel} > g_{\perp}$  ordering for a  $d_{x^2-y^2}^2$  ground state and this configuration has high strain energy as obtained from MM2 calculations. The absence of any signal at  $g \approx 4$ , around 1500 G also shows that there is no weak exchange interaction between the copper centres. The results obtained are summarized as follows:  $g_{\parallel} = 2.21$ ,  $g_{\perp} = 2.02$ ,  $g_{\text{iso}} = 2.03$ ,  $A_{\parallel} = 122.0 \text{ G}$ .<sup>17-19</sup> Two imidazolidine bridges per molecule do not impart any magnetic communication between the two copper(II) centres giving only spectra characteristic for mononuclear ones. The frozen (77 K) MeCN-toluene spectrum is also axial. Both the polycrystalline and frozen solution spectra at 296 K and 77 K

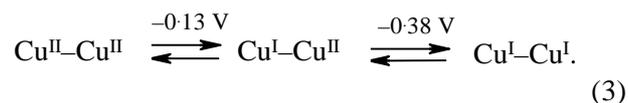
(shown in figure 3), are typical of a mononuclear copper(II) complex. In both the cases the  $g_{\parallel}$  resonance is split by the hyperfine coupling between the unpaired electron on  $\text{Cu}^{\text{II}}$  and the  $I = 3/2$  nuclear spin of copper. The large line width in the  $g_{\perp}$  region indicates that the copper centre is in a distorted (rhombic) environment.



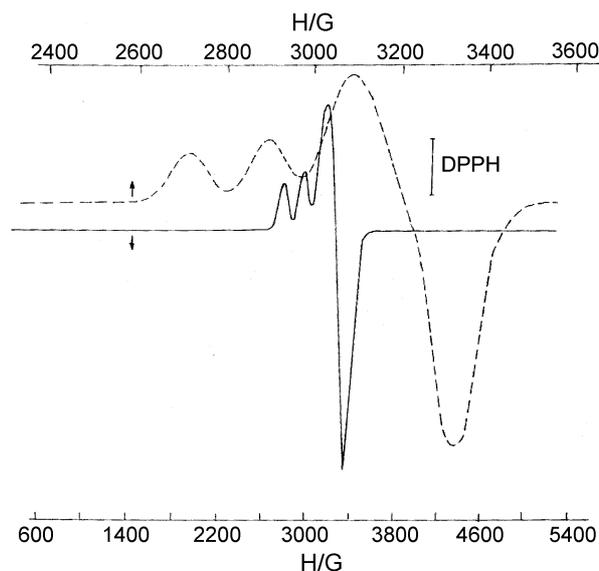
**Figure 2.** Calculated (MM2) conformation for (a) ligand L (total strain energy  $-4.384$  kcal/mol); (b) compound  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  (total strain energy =  $82.725$  kcal/mol); (c) compound  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_2$  (total strain energy =  $53.569$  kcal/mol).

### 3.6 Electrochemistry

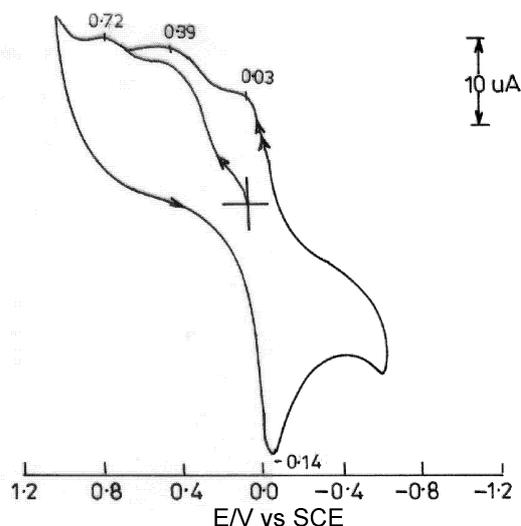
The electrochemical behaviour of both the  $\text{Cu}_2^{\text{II/II}}$  and  $\text{Cu}_2^{\text{I/I}}$  complexes was investigated in dimethylformamide by cyclic voltammetry. In the cathodic potential range (0 to  $-1.2$  V) the  $\text{Cu}_2^{\text{II/II}}$  complex exhibits two reduction waves at  $E_p = -0.13$  V and  $-0.38$  V vs SCE. This suggests that the reduction processes may involve the following steps,



No other reduction wave is observed at a more negative potential region due to any kind of reduction of  $\text{Cu}^{\text{I}}-\text{Cu}^{\text{I}}$  to  $\text{Cu}^0-\text{Cu}^0$  and subsequent deposition of copper metal on the electrode surface. The responses observed are irreversible in nature. This irreversible nature of reductions observed may be attributed to the fact that after reduction of  $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$  there may be a change in the coordination geometry. In two cases, almost superimposable profiles are seen for the cupric and cuprous complexes of the same ligand, and very similar profiles, as regards shape and number of signals. Use of glassy carbon electrode does not change the trace. For both the complexes the initial potential was chosen at  $0.0$  V to check the identical electron-transfer behaviour. The successive addition of one electron to two



**Figure 3.** X-band (9.10 GHz) EPR spectrum of  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  in solid state at 296 K.



**Figure 4.** Cyclic voltammogram (scan rate  $50 \text{ mVs}^{-1}$ ) of  $[\text{Cu}_2^{\text{I/II}}(\text{m-L})_2](\text{ClO}_4)_2$  in dimethylformamide using tetraethyl ammonium perchlorate as supporting electrolyte at a platinum electrode at 298 K.

noncommunicating redox sites of a molecule should lead to two essentially overlapping reduction processes, the expected separation in redox potentials being 36 mV.<sup>20</sup> The voltammetric profile (figure 4) for **2b** on first scan displays two consecutive (one electron transfer) oxidation waves at 0.39, 0.72 V, which appear to be completely irreversible (i.e., these lack corresponding return waves), while a separate, irreversible reduction at  $-0.14 \text{ V}$  (again without its corresponding oxidation wave) is observed for two-electron transfer. The lack of corresponding return waves in either direction is visualized from the large separation in  $\Delta E_p$  value. The  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$  reduction step is followed by a very fast helical turn of the ligands and the  $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$  oxidation process occurs in two discrete steps for two metal centres. The arrangement with coordinatively unsaturated copper(II) ions allows one-step two-electron transfer, whereas for the saturated copper(I) case two discrete single electron transfer steps are observed. The electronic interaction between the two centres is the major source of wave splitting.<sup>21</sup>

#### 4. Conclusions

The electrochemical process is believed to be reversible, as there is no sign of dicopper(I/I) complex catalysed activation of molecular dioxygen for ring hydroxylation of the pendant phenyl ring on each

ligand. The change in metal oxidation state on the other hand causes the transformation of planar dicopper(II/II) complex to dicopper(I/I) complex with some distortion from planarity. The change in ligand conformation around the two metal ions is achievable from the ligand consisting of two imine halves linked by a 2-phenyl-1,3-imidazolidine spacer. The coordinatively unsaturated copper(II) centres in  $[\text{Cu}_2^{\text{II/II}}(\text{m-L})_2](\text{ClO}_4)_4$  can bind any suitable fluorescent probe at the fifth coordination sites for quenching/revival of a fluorescent signal during definite change in ligand shape through change in oxidation states of the metal centres. The new metal containing assembly undergoing a change to two different molecular topologies during electron transfer. Absence of any bridging donor group on the imidazolidine ring of the ligand results in such controllable motion in two different oxidation states of copper. Work is now in progress in order to find other ligands not featuring the terminal imine moieties but capable of giving a similar molecular arrangement on changing the oxidation state of the coordinated copper cation.

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