

## New unsymmetrical $\mu$ -phenoxo bridged binuclear copper(II) complexes

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### Abstract

A series of binuclear  $\text{Cu}^{\text{II}}$  complexes  $[\text{Cu}_2\text{XL}]^{n+}$  having two copper(II) ions bridged by different motifs ( $\text{X} = \text{OH}^-$ ,  $\text{MeCO}_2^-$ , or  $\text{Cl}^-$ ) have been prepared using the ligands:  $\text{H}_2\text{L}^1 = 4\text{-methyl-2-[N-(2-(dimethylamino)ethyl-N'-methylaminomethyl)-6-(prolin-1-yl)methyl]phenol}$ ,  $\text{H}_2\text{L}^2 = 4\text{-nitro-2-[N-(2-(dimethylamino)ethyl-N'-methylaminomethyl)-6-(prolin-1-yl)methyl]phenol}$ ,  $\text{H}_2\text{L}^3 = 4\text{-methyl-2-[N-(2-(diethylamino)ethyl-N'-ethylaminomethyl)-6-(prolin-1-yl)methyl]phenol}$  and  $\text{H}_2\text{L}^4 = 4\text{-nitro-2-[N-(2-(diethylamino)ethyl-N'-ethylaminomethyl)-6-(prolin-1-yl)methyl]phenol}$ . The complexes have been characterized by spectroscopic, analytical, magnetic and electrochemical measurements. Cryomagnetic investigations (80–300 K) revealed anti-ferromagnetic exchange between the  $\text{Cu}^{\text{II}}$  ions ( $-2J$  in the range  $-50$  to  $-182 \text{ cm}^{-1}$ ). The strength of anti-ferromagnetic coupling lies in the order:  $\text{OAc} > \text{OH} > \text{Cl}$ . Cyclic voltammetry revealed the presence of two redox couples, assigned to  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}$ . The first reduction potential is sensitive to electronic effects from the aromatic ring substituents and steric effect on the donor nitrogens (side arm) of the ligand systems.

### Introduction

The chemistry of dinucleating ligands with dissimilar coordination environments is of current interest to bioinorganic chemists. Complexes derived from these ligands may serve as corroborative models for the active site of metalloenzymes such as hemocyanin [1], tyrosinase [2] and bovine erythrocyte SOD [3]. With a few exceptions [4–6], most ligands so far prepared for mimicking the properties of these biosites have provided identical donor environments to the metal centers. However, in binuclear transition metal biosites the metal ions are often found in chemically or geometrically distinct environments. For instance, the unsymmetrical nature of the dicopper site in hemocyanin is demonstrated in the crystal structure of deoxyhemocyanin [7] and sequence homology studies on tyrosinases have shown that whilst one of the copper sites is highly conserved, the structure of the second copper site is quite variable. For most of the tyrosinases, three histidines are suitably positioned to co-ordinate each of the copper ions, but in a few cases  $\text{Cu}_B$  is apparently only co-ordinated to two histidines and this latter observation led to the suggestion that for modeling

studies, unsymmetrical binucleating ligands [8] should be viewed as desirable targets.

In the present investigation, we have synthesized unsymmetrical dinucleating ligands derived from proline, using the Mannich base reaction between *para*-substituted phenols, formaldehyde, secondary amines (*N,N,N'*-trialkylethylenediamine) and proline. Binuclear copper(II) complexes  $[\text{Cu}_2\text{LX}]^{n+}$  with various bridging motifs ( $\text{X} = \text{OH}$ ,  $\text{OAc}$ , and  $\text{Cl}$ ) were obtained by reacting the metal salts with appropriate ligands. The spectral, magnetic and electrochemical properties of the complexes are reported and discussed.

### Experimental

#### Materials

All chemicals and solvents were reagent grade and were used without further purification, except for those used for electrochemical measurement and ligand synthesis. EtOH was refluxed over CaO for 3 h and the middle fraction was distilled onto 3 Å molecular sieves. MeCN was dried by stirring over  $\text{K}_2\text{CO}_3$  for 24 h and stored over 3 Å sieves. *n*- $\text{Bu}_4\text{NClO}_4$  used as the supporting electrolyte in electrochemical measurements, was prepared from *n*- $\text{Bu}_4\text{NBr}$ ,  $\text{HClO}_4$  and  $\text{NaHCO}_3$ . Recrystallisation was performed from hot EtOH and further drying was carried out in a vacuum desiccator.

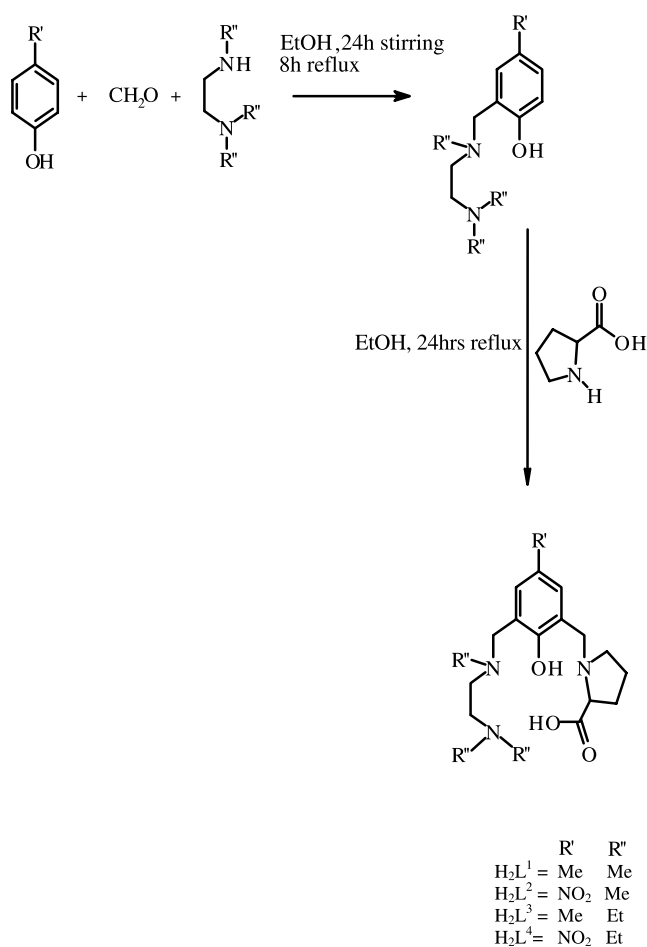
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## Physical measurements

$^1\text{H}$ - and  $^{13}\text{C}$ -n.m.r. spectra were recorded on a JEOL FX-400 FT-NMR spectrometer in  $\text{CDCl}_3$  solution, using TMS as the internal standard. Abbreviation used; s: singlet; d: doublet; t: triplet; m: multiplet. FAB mass spectra were recorded at room temperature a JEOL SX 102 1DA-6000 mass spectrometer/data system using Ar/Xe (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV. Electronic absorption spectra were obtained in MeCN solution with a Hitachi 320 UV-visible double beam spectrometer using 1 cm quartz cells and a solution concentration of  $10^{-3}$  mol  $\text{dm}^{-3}$ . I.r. spectra were recorded on a Perkin-Elmer IR 598 spectrophotometer using KBr disks. Elemental (C, H and N) analysis was performed with a Heraeus rapid analyzer. Cu was estimated by AAS using a model 2380 Perkin-Elmer spectrophotometer. Molar conductance ( $\Lambda_{\text{M}}$ ) values were measured using a control dynamics conductivitymeter in a MeCN solvent. Variable temperature magnetic susceptibility data of the powdered samples were measured in the 80–300 K range using a Princeton Applied Research Model 155 VSM instrument in a 5000 G magnetic field. Diamagnetic susceptibility corrections for ligand susceptibility were made using Pascal's constants. Effective magnetic moments were calculated using the formula  $\mu_{\text{eff}} = 2.828(\chi_{\text{m}} T)^{1/2}$ , where  $\chi_{\text{m}}$  is the corrected molar susceptibility. The instrument was calibrated using metallic Ni. C.v. was performed at room temperature using an AUTO LAB PGSTAT 12 instrument controlled by a general purpose electrochemical system software (GPES) running under MS-Windows 95. The supporting electrolyte was  $0.1$  mol  $\text{dm}^{-3}$   $n\text{-Bu}_4\text{NClO}_4$  in MeCN freshly distilled from  $\text{P}_2\text{O}_5$  and deaerated by purging with  $\text{N}_2$ . A standard three-electrode system was used comprising a Pt disc working electrode, Pt electrode auxiliary electrode and a saturated Ag/AgCl reference electrode (SCE). The ligands were prepared by a modified procedure [9] based on the Mannich base reaction of *para*-substituted phenols (Scheme 1).

*4-Methyl-2-[N-(2-{dimethylamino}ethyl-N'-methyl)-aminomethyl]phenol [PC<sup>1</sup>]*

*p*-Methylphenol (0.001 mol) in EtOH (75  $\text{cm}^3$ ) was mixed with *N,N,N'*-trimethylethylenediamine (0.001 mol) and cooled in ice. Aqueous HCHO (7  $\text{cm}^3$  0.001 mol) was then added dropwise with stirring. The mixture was stirred at room temperature for 24 h and then refluxed for 8 h. The EtOH was removed under vacuum and the resulting oily liquid was neutralized with a saturated  $\text{Na}_2\text{CO}_3$  solution and extracted with  $\text{CHCl}_3$ . An oily yellow liquid was obtained. Yield: 83%.  $^1\text{H}$ -n.m.r. (400 MHz) in  $\text{CDCl}_3$ :  $\delta$  6.7–7.3 (m, 3H, ArH); 3.6 (s, 2H, benzylic  $\text{CH}_2$ ); 2.2 (s, 3H,  $\text{NCH}_3$ ); 2.5–2.9 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ); 2.2 (Two close peak s, 3H,  $\text{ArCH}_3$ ; s, 6H,  $\text{N}(\text{CH}_3)_2$ ).  $^{13}\text{C}$ -n.m.r. (100 MHz) in  $\text{CDCl}_3$ :  $\delta$  20.4 (q); 42.2 (q); 45.6 (q); 54.5 (t); 56.8 (t); 58.3 (t); 116.0 (d); 123.7 (s); 128.2 (d); 129.4 (d); 153.4 (s); 155.7 (s). I.r. (KBr disc):  $1452$   $\text{cm}^{-1}$  (Aromatic);  $1313$   $\text{cm}^{-1}$  ( $\text{N}-\text{CH}_3$ );  $2900$ –



Scheme 1.

$2800$   $\text{cm}^{-1}$  (C–H aliphatic);  $3400$ – $3500$  (br, OH).  $m/z = 222$  (M + 1).

The precursors  $\text{PC}^2$ ,  $\text{PC}^3$  and  $\text{PC}^4$  were synthesized in similar way to  $\text{PC}^1$  with the appropriate phenols and secondary amines.

*4-Nitro-2-[N-(2-{dimethylamino}ethyl-N'-methyl)-aminomethyl]phenol [PC<sup>2</sup>]*

A yellow solid was obtained. Yield: 87%; M.p:  $112$   $^\circ\text{C}$ ;  $^1\text{H}$ -n.m.r. (400 MHz) in  $\text{CDCl}_3$ :  $\delta$  6.8–8.1 (m, 3H, ArH); 3.6 (s, 2H, benzylic  $\text{CH}_2$ ); 2.2 (s, 3H,  $\text{NCH}_3$ ); 2.6–2.7 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ); 2.4 (s, 6H,  $\text{N}(\text{CH}_3)_2$ ).  $^{13}\text{C}$ -n.m.r. (100 MHz) in  $\text{CDCl}_3$ :  $\delta$  42.2 (q); 44.7 (q); 53.3 (t); 55.8 (t); 57.2 (t); 102.6 (d); 117.1 (s); 123.5 (d); 125.6 (d); 152.6 (s); 165.2 (s). I.r. (KBr disc):  $1452$   $\text{cm}^{-1}$  (Aromatic);  $1317$   $\text{cm}^{-1}$  ( $\text{N}-\text{CH}_3$ );  $2900$ – $2850$   $\text{cm}^{-1}$  (C–H aliphatic);  $3400$ – $3600$  (br, OH).  $m/z = 253$  (M + 1).

*4-Methyl-2-[N-(2-{diethylamino}ethyl-N'-ethyl)-aminomethyl]phenol [PC<sup>3</sup>]*

An oily yellow liquid was obtained. Yield: 79%.  $^1\text{H}$ -n.m.r. (400 MHz) in  $\text{CDCl}_3$ :  $\delta$  6.7–7.9 (m, 3H, ArH); 3.7 (s, 2H, benzylic  $\text{CH}_2$ ); 2.6 (m, 4H,  $\text{NCH}_2\text{CH}_2\text{N}$ ); 2.4–2.5

(q, 6H, NCH<sub>2</sub>CH<sub>3</sub>); 2.2 (s, 3H, ArCH<sub>3</sub>); 1.0–1.1 (t, 3H, NCH<sub>2</sub>CH<sub>3</sub>); 0.9–1.0 (t, 6H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C-n.m.r (100 MHz) in CDCl<sub>3</sub>: δ 11.4 (q); 11.6 (q); 20.5 (q); 46.9 (t); 47.3 (t); 50.3 (t); 50.8 (t); 57.2 (t); 115.9 (d); 127.5 (s); 128.6 (d); 128.9 (d); 129.3 (s); 155.6 (s). I.r. (KBr disc): 1456 cm<sup>-1</sup> (Aromatic); 1368 cm<sup>-1</sup> (N—CH<sub>2</sub>); 2900–2760 cm<sup>-1</sup> (C—H aliphatic); 3400–3550 (br, OH). *m/z* = 264.

*4-Nitro-2-[N-(2-{diethylamino}ethyl-N'-ethyl)-aminomethyl]phenol [PC<sup>4</sup>]*

Yellow solid was obtained. Yield: 88%; M.p: 80 °C; <sup>1</sup>H-n.m.r. (400 MHz) in CDCl<sub>3</sub>: δ 6.8–8.1 (m, 3H, ArH); 3.6 (s, 2H, benzylic CH<sub>2</sub>); 2.4–2.7 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N); 2.3 (t, 9H, NCH<sub>2</sub>CH<sub>3</sub>); 2.2 (q, 6H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C-n.m.r (100 MHz) in CDCl<sub>3</sub>: δ 10.6 (q); 11.3 (q); 46.6 (t); 47.6 (t); 50.5 (t); 50.8 (t); 54.8 (t); 117.0 (d); 123.3 (s); 124.3 (d); 126.3 (d); 138.9 (s); 166.1 (s). I.r. (KBr disc): 1454 cm<sup>-1</sup> (Aromatic); 1370 cm<sup>-1</sup> (N—CH<sub>2</sub>); 2920–2800 cm<sup>-1</sup> (C—H aliphatic); 3400–3500 (br, OH). *m/z* = 295 (M + 1).

*4-Methyl-2-[N-(2-{dimethylamino}ethyl-N'-methyl)-aminomethyl]-6-[(prolin-1-yl)methyl]phenol [H<sub>2</sub>L<sup>1</sup>]*

4-Methyl-2-[N-(2-{dimethylamino}ethyl-N'-methyl)aminomethyl]phenol [PC<sup>1</sup>] (0.02 mol) in EtOH (75 cm<sup>3</sup>) was mixed with L-proline (0.02 mol) in EtOH (50 cm<sup>3</sup>) with constant stirring. HCHO (14 cm<sup>3</sup>, 0.02 mol) was added slowly with stirring and the reaction mixture was heated to reflux for 24 h. During this time, HCHO (*ca.* 1.25 cm<sup>3</sup>) was added twice, at *ca.* 8 h intervals. EtOH was removed by evaporation under vacuum and the resulting oily liquid was neutralized with saturated Na<sub>2</sub>CO<sub>3</sub> solution and extracted with CHCl<sub>3</sub>, dried with anhydrous MgSO<sub>4</sub> and separated into a yellow oily liquid on evaporation CHCl<sub>3</sub>. (Yield: 76%.) <sup>1</sup>H-n.m.r. (400 MHz) in CDCl<sub>3</sub>: δ 6.7–7.3 (m, 2H, ArH); 4.5–4.6 (t, 1H, proline CH); 3.5, 3.6 (s, 4H, benzylic CH<sub>2</sub>); 2.2–2.6 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N, 4H, proline, 3H, ArCH<sub>3</sub>, 9H, NCH<sub>3</sub>). <sup>13</sup>C-n.m.r (100 MHz) in CDCl<sub>3</sub>: δ 20.5 (q); 29.2 (t); 31.6 (t); 42.1 (q); 45.6 (q); 53.1 (t); 55.7 (t); 57.0 (t); 60.6 (t); 66.6 (t); 67.0 (s); 121.7 (s); 123.6 (s); 127.5 (d); 128.6 (d); 129.3 (s); 153.2 (s); 190.0 (s). I.r. (KBr disc): 1472 cm<sup>-1</sup> (Aromatic); 1323 cm<sup>-1</sup> (N—CH<sub>3</sub>); 1610 cm<sup>-1</sup> (—COO); 2970–2800 cm<sup>-1</sup> (C—H aliphatic); 3400–3500 (br, OH). *m/z* = 349 (M<sup>+</sup>).

Ligands H<sub>2</sub>L<sup>2</sup>, H<sub>2</sub>L<sup>3</sup> and H<sub>2</sub>L<sup>4</sup> were synthesized in the same way as H<sub>2</sub>L<sup>1</sup>.

*4-Nitro-2-[N-(2-{dimethylamino}ethyl-N'-methyl)-aminomethyl]-6-[(prolin-1-yl)methyl]phenol [H<sub>2</sub>L<sup>2</sup>]*

A yellow solid was obtained. Yield: 74%; M.p: 89 °C; <sup>1</sup>H-n.m.r. (400 MHz) in CDCl<sub>3</sub>: 6.8 (m, 2H, ArH); 4.6 (t, 1H, proline CH); 3.6 (t, 2H, proline CH<sub>2</sub>); 3.5 (s, 4H,

benzylic CH<sub>2</sub> two close peaks); 2.6 (m, 4H, NCH<sub>2</sub>—CH<sub>2</sub>N); 2.2–2.3 (m, 4H, proline, 9H, NCH<sub>3</sub>). <sup>13</sup>C-n.m.r (100 MHz) in CDCl<sub>3</sub>: δ 15.0 (t); 30.9 (t); 42.3 (q); 44.7 (q); 53.3 (t); 55.6 (t); 56.8 (t); 62.9 (t); 66.4 (t); 67.1 (t); 117.2 (s); 123.6 (s); 125.7 (d); 126.3 (d); 139.1 (s); 165.6 (s); 190.3 (s). I.r. (KBr disc): 1482 cm<sup>-1</sup> (Aromatic); 1320 cm<sup>-1</sup> (N—CH<sub>3</sub>); 1607 cm<sup>-1</sup> (—COO); 2940–2810 cm<sup>-1</sup> (C—H aliphatic); 3430–3600 (br, OH). *m/z* = 380 (M<sup>+</sup>).

*4-Methyl-2-[N-(2-{diethylamino}ethyl-N'-ethyl)-aminomethyl]-6-[(prolin-1-yl)methyl]phenol [H<sub>2</sub>L<sup>3</sup>]*

An oily yellow liquid was obtained. Yield: 75%. <sup>1</sup>H-n.m.r. (400 MHz) in CDCl<sub>3</sub>: δ 6.6–7.3 (m, 2H, ArH); 4.6 (t, 1H, proline CH); 4.4 (t, 2H, proline CH<sub>2</sub>); 3.5, 3.6 (s, 4H, benzylic CH<sub>2</sub>); 2.51–2.53 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N, 4H, proline CH<sub>2</sub>); 0.9–1.2 (m, 15H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C-n.m.r (100 MHz) in CDCl<sub>3</sub>: δ 10.4 (q); 15.0 (q); 20.5 (q); 23.8 (t); 30.5 (t); 46.9 (t); 47.8 (t); 48.5 (t); 50.3 (t); 54.8 (t); 59.2 (t); 67.4 (t); 70.2 (t); 119.2 (s); 122.7 (s); 124.6 (d); 126.2 (d); 140.3 (s); 162.8 (s). I.r. (KBr disc): 1470 cm<sup>-1</sup> (Aromatic); 1382 cm<sup>-1</sup> (N—CH<sub>2</sub>); 1611 (—COO); 2910–2830 cm<sup>-1</sup> (C—H aliphatic); 3400–3620 (br, OH).

*4-Nitro-2-[N-(2-{diethylamino}ethyl-N'-ethyl)-aminomethyl]-6-[(prolin-1-yl)methyl]phenol [H<sub>2</sub>L<sup>4</sup>]*

A crystalline yellow solid was obtained. Yield: 67%; M.p: 63 °C; <sup>1</sup>H-n.m.r. (400 MHz) in CDCl<sub>3</sub>: δ 6.7–6.8 (m, 2H, ArH); 4.6 (t, 1H, proline CH); 4.4 (t, 2H, proline CH<sub>2</sub>); 3.5 (s, 4H, benzylic CH<sub>2</sub> two close peaks); 2.4–2.5 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>N, 4H, proline CH<sub>2</sub>); 1.0–1.1 (m, 15H, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C-n.m.r (100 MHz) in CDCl<sub>3</sub>: δ 10.6 (q); 11.3 (q); 23.6 (t); 29.2 (t); 46.1 (t); 47.2 (t); 48.9 (t); 49.1 (t); 54.5 (t); 58.4 (t); 67.1 (t); 69.7 (t); 117.2 (s); 123.4 (s); 124.4 (d); 125.7 (d); 138.5 (s); 166.7 (s). I.r. (KBr disc): 1467 cm<sup>-1</sup> (Aromatic); 1375 cm<sup>-1</sup> (N—CH<sub>2</sub>); 1588 (—COO); 2910–2840 cm<sup>-1</sup> (C—H aliphatic); 3450–3600 (br, OH). *m/z* = 422 (M + 1).

*Bis acetato-bridged complexes: [Cu<sub>2</sub>L<sup>1</sup>(OAc)<sub>2</sub>] · H<sub>2</sub>O (1a); [Cu<sub>2</sub>L<sup>2</sup>(OAc)<sub>2</sub>] · H<sub>2</sub>O (1b); [Cu<sub>2</sub>L<sup>3</sup>(OAc)<sub>2</sub>] · H<sub>2</sub>O (1c) and [Cu<sub>2</sub>L<sup>4</sup>(OAc)<sub>2</sub>] · H<sub>2</sub>O (1d)*

H<sub>2</sub>L<sup>1</sup> (0.001 mol) was dissolved in 75 cm<sup>3</sup> of distilled MeOH · Cu(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (0.002 mol) in MeOH was added followed by NaOAc (0.001 mol) dissolved in 5 cm<sup>3</sup> of H<sub>2</sub>O:MeOH (1:4). The resulting dark green solution was boiled under reflux for 4 h and then filtered. A green precipitate was obtained on evaporation of MeOH at room temperature during several days. The complex thus formed (1a) was recrystallized from aqueous MeOH. The analytical data for these complexes are given in Table 1. Complexes (1b), (1c)

Table 1. Analytical data for the copper complexes

Complex	Found (calcd.)%			
	C	H	N	Cu
(1a) [Cu <sub>2</sub> L <sup>1</sup> (OAc) <sub>2</sub> ]·H <sub>2</sub> O	45.2 (45.2)	6.2 (6.1)	6.9 (6.8)	20.9 (20.8)
(1b) [Cu <sub>2</sub> L <sup>2</sup> (OAc) <sub>2</sub> ]·H <sub>2</sub> O	41.2 (41.2)	5.3 (5.3)	8.8 (8.7)	19.9 (19.8)
(1c) [Cu <sub>2</sub> L <sup>3</sup> (OAc) <sub>2</sub> ]·H <sub>2</sub> O	44.1 (44.0)	5.9 (5.8)	8.2 (8.1)	18.7 (18.6)
(1d) [Cu <sub>2</sub> L <sup>4</sup> (OAc) <sub>2</sub> ]·H <sub>2</sub> O	47.9 (47.8)	6.8 (6.6)	6.5 (6.4)	19.5 (19.5)
(2a) [Cu <sub>2</sub> L <sup>1</sup> (OH)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	36.5 (36.4)	5.5 (5.5)	6.7 (6.7)	20.3 (20.2)
(2b) [Cu <sub>2</sub> L <sup>2</sup> (OH)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	32.9 (32.9)	4.9 (4.8)	8.7 (8.5)	19.4 (19.3)
(2c) [Cu <sub>2</sub> L <sup>3</sup> (OH)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	36.1 (36.0)	5.4 (5.3)	8.1 (8.0)	18.2 (18.1)
(2d) [Cu <sub>2</sub> L <sup>4</sup> (OH)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	39.6 (39.5)	6.2 (6.0)	6.4 (6.3)	19.1 (18.9)
(3a) [Cu <sub>2</sub> L <sup>1</sup> (Cl)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	35.3 (35.4)	5.2 (5.1)	6.6 (6.5)	19.8 (19.7)
(3b) [Cu <sub>2</sub> L <sup>2</sup> (Cl)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	32.0 (31.9)	4.6 (4.4)	8.4 (8.3)	18.9 (18.8)
(3c) [Cu <sub>2</sub> L <sup>3</sup> (Cl)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	35.2 (35.1)	5.1 (5.0)	7.9 (7.8)	17.8 (17.7)
(3d) [Cu <sub>2</sub> L <sup>4</sup> (Cl)(H <sub>2</sub> O) <sub>2</sub> ]ClO <sub>4</sub>	40.2 (40.1)	6.1 (5.9)	6.5 (6.4)	19.4 (19.3)

and (1d) were prepared by the same procedure as (1a) using H<sub>2</sub>L<sup>2</sup>, H<sub>2</sub>L<sup>3</sup> and H<sub>2</sub>L<sup>4</sup> respectively instead of H<sub>2</sub>L<sup>1</sup> (Scheme 2).

*Hydroxo-bridged complexes:* [Cu<sub>2</sub>L<sup>1</sup>(OH)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (2a); [Cu<sub>2</sub>L<sup>2</sup>(OH)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (2b); [Cu<sub>2</sub>L<sup>3</sup>(OH)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (2c) and [Cu<sub>2</sub>L<sup>4</sup>(OH)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (2d)

To a MeOH solution of H<sub>2</sub>L<sup>1</sup> (0.001 mol), NaOH (0.001 mol) was added, followed by a MeOH solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.002 mol). The resulting greenish blue solution was boiled under reflux for 4 h and then filtered. Evaporation of the solution at room temperature during 7 days obtained a green compound, which was recrystallized from MeOH. The complex (2b), (2c) and (2d) were prepared as per (2a) using H<sub>2</sub>L<sup>2</sup>, H<sub>2</sub>L<sup>3</sup> and H<sub>2</sub>L<sup>4</sup> instead of H<sub>2</sub>L<sup>1</sup>.

*Chloro-bridged complexes:* [Cu<sub>2</sub>L<sup>1</sup>(Cl)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (3a); [Cu<sub>2</sub>L<sup>2</sup>(Cl)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (3b); [Cu<sub>2</sub>L<sup>3</sup>(Cl)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (3c) and [Cu<sub>2</sub>L<sup>4</sup>(Cl)(H<sub>2</sub>O)<sub>2</sub>]ClO<sub>4</sub> (3d)

To a solution of H<sub>2</sub>L<sup>1</sup> (0.001 mol) in MeOH (75 cm<sup>3</sup>) was added Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.002 mol) followed by NaCl (0.001 mol) with constant stirring. The resulting dark brown solution was refluxed for 4 h and then filtered. The resulting solution was evaporated to dryness and the crude product was recrystallized from MeOH. The complexes (3b), (3c) and (3d) were prepared as was (3a) using H<sub>2</sub>L<sup>2</sup>, H<sub>2</sub>L<sup>3</sup> and H<sub>2</sub>L<sup>4</sup> instead of H<sub>2</sub>L<sup>1</sup>.

## Results and discussion

### Characterization

The ligands were synthesized using a Mannich base reaction. Both <sup>1</sup>H-n.m.r. as well as <sup>13</sup>C-n.m.r. spectra

are very informative with regard to the unsymmetrical nature of these ligands and are very distinct from their symmetric analogues. Both types of spectrum show the methylenic CH<sub>2</sub> group in the aminomethylated phenol. The methylenic H-atoms give a single resonance in the 3.6–3.8 p.p.m. region. In the <sup>13</sup>C-n.m.r spectra the methylenic carbon resonance are in the 56–63 p.p.m. region [10]. Moreover different resonance for the two sets of protons and carbons at the benzylic positions are observed.

The OH-bridged complexes exhibit a broad i.r. band at ca. 3450–3475 cm<sup>-1</sup> due to OH stretching [11, 12]. The acetato-bridged complex [13] show strong ν<sub>COO</sub> bands at ca. 1603 and 1455 cm<sup>-1</sup>. The binding nature of the acetate ions in (1a–d) has been determined from the difference in energy (Δ) between the asymmetric and symmetric carboxylate stretching frequencies. In general, Δ for a monodentate acetate is greater than 150 cm<sup>-1</sup> and for a bidentate acetate it is less than 100 cm<sup>-1</sup>, whereas for bridging acetate Δ is close to 150 cm<sup>-1</sup> [12]. For the four acetate complexes Δ varies from 129–148 cm<sup>-1</sup>, suggesting the presence of bridging acetate. The hydroxo- and chloro-bridged compounds exhibit strong bands at 1100 cm<sup>-1</sup> and sharp bands at 629 cm<sup>-1</sup> assigned to perchlorate. The characteristic Cu–O, Cu–N and Cu–Cl vibrations for the complexes were observed as sharp peaks in the regions 475, 270, and 320 cm<sup>-1</sup> [14]. The important i.r. stretching frequencies and their assignments are given in Table 2.

The electronic spectra of the complexes in MeCN (Table 3) showed a low intensity band in the 611–680 nm region and a medium intensity band at ca. 346–404 nm, due to phenolate-to-copper(II) charge-transfer [15]. An intense absorption band which may arise from ligand to ligand charge-transfer was observed around ca. 245 nm. A red shift in the λ<sub>max</sub> values of the d–d band observed for the complexes of the ligands H<sub>2</sub>L<sup>3</sup> and H<sub>2</sub>L<sup>4</sup> when compared to the complexes of the ligands H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup> suggests that the coordination geometry in the former is more distorted than the latter (Figure 1).

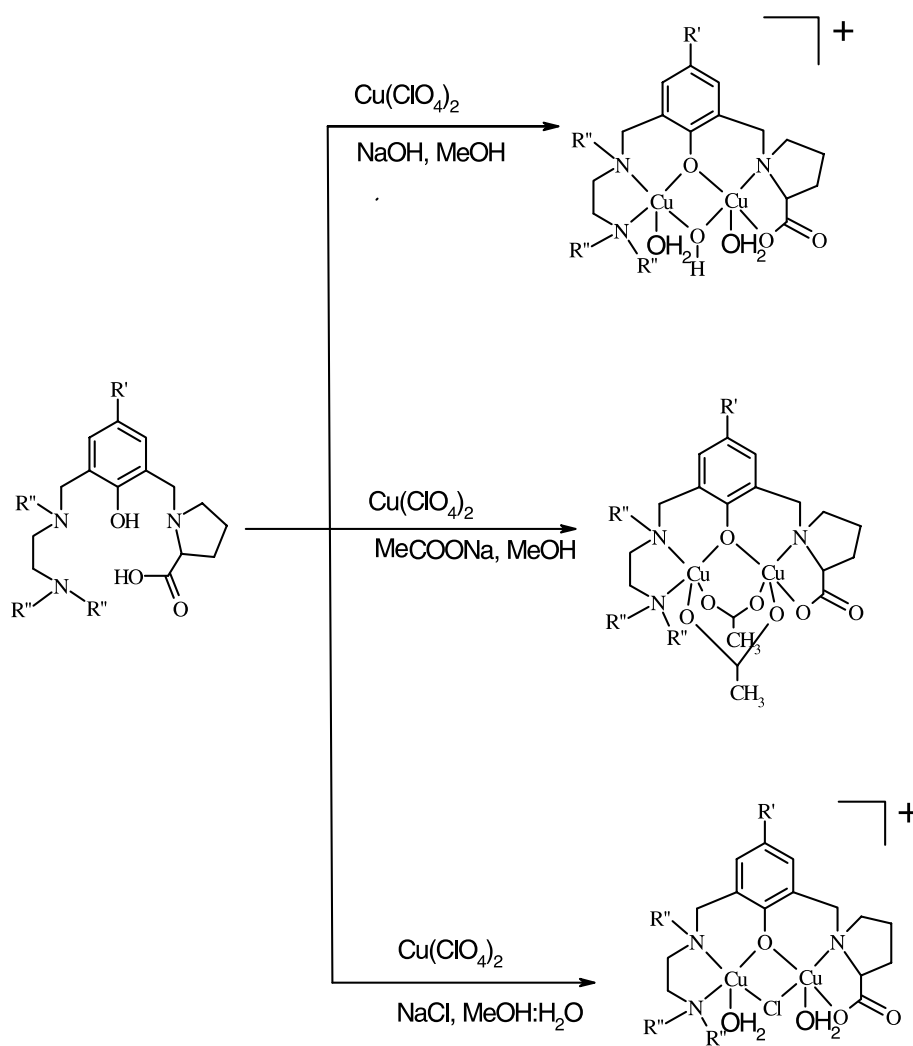


Table 2. Major i.r. spectral data for Cu(II) complexes ( $\text{cm}^{-1}$ )

Complex	$\nu_{\text{OH}}$	$\nu_{\text{COO}}$	$\nu_{\text{ClO}_4}$	$\nu_{\text{Cu-N}}$	$\nu_{\text{Cu-Cl}}$	$\nu_{\text{Cu-O}}$
(1a)	–	1603, 1455	–	480	–	285
(1b)	–	1597, 1467	–	480	–	286
(1c)	–	1603, 1470	–	483	–	280
(1d)	–	1596, 1467	–	480	–	282
(2a)	3458	–	1084, 629	478	–	280
(2b)	3450	–	1091, 627	480	–	280
(2c)	3466	–	1099, 629	480	–	285
(2d)	3472	–	1089, 629	482	–	282
(3a)	–	–	1092, 628	482	320	280
(3b)	–	–	1111, 629	486	320	285
(3c)	–	–	1099, 629	480	318	282
(3d)	–	–	1088, 629	485	322	288

#### Solution conductivities and magnetic properties

Molar conductance ( $\Lambda_{\text{M}}$ ) values of the complexes were measured in MeCN at room temperature (Table 3). We observed 1:1 electrolyte behavior [16] for the hydroxo- and chloro-bridged complexes, whereas the acetato-bridged complexes are non-electrolytes.

The magnetic behavior of all the complexes was studied in the temperature range 80–300 K. The magnetic susceptibility data were fitted using the Bleaney–Bowers equation (1) [17]

$$\chi_{\text{m}} = \{Ng^2\beta^2/kT\} [3 + \exp(-2J/kT)]^{-1} (1 - p) + (Ng^2\beta^2/4kT)\rho + N_x \quad (1)$$

Table 3. Electronic, magnetic and conductivity data of the complexes:  $\lambda_{\text{max}}/\text{nm}$  ( $\epsilon$ ,  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) in MeCN

Complex	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon$ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ )			$g$	Conductivity <sup>b</sup> ( $\Lambda_{\text{m}}/\text{S cm}^2 \text{M}^{-1}$ )
	Charge-transfers	d-d	$-2J^{\text{a}}$		
(1a)	226, 294, 346	641 (46)	-184	1.903	29
(1b)	277, 404	611 (61)	-168	2.018	24
(1c)	249, 281, 371	656 (55)	-140	2.084	30
(1d)	304, 384	650 (50)	-104	2.047	27
(2a)	244, 373	647 (44)	-126	2.016	131
(2b)	245, 376	651 (43)	-88	1.918	125
(2c)	247, 280, 381	657 (55)	-92	2.001	128
(2d)	242, 288, 383	652 (90)	-84	2.068	121
(3a)	207, 227, 304	680 (72)	-118	1.905	158
(3b)	246, 378	653 (55)	-72	2.024	140
(3c)	227, 306, 405	658 (66)	-80	2.018	149
(3d)	223, 304, 381	656 (61)	-50	1.992	137

<sup>a</sup>  $-2J$  values have been calculated using Bleaney-Bower's equation; <sup>b</sup> expected range 120–160 (1:1) and 220–300 (1:2) electrolyte in  $\text{CH}_3\text{CN}$ .

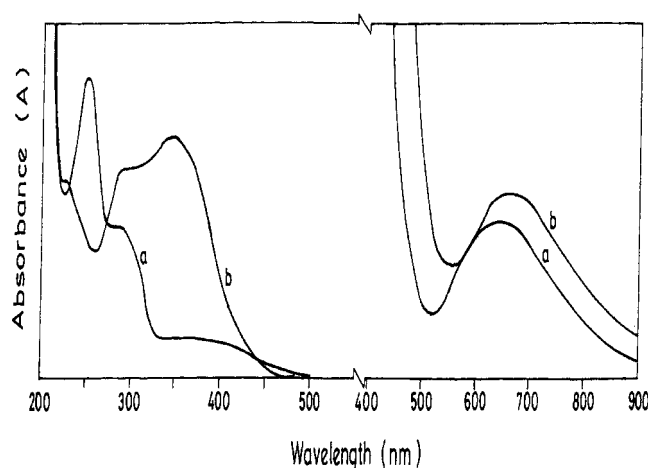


Fig. 1. U.v.-vis. spectra of complexes (a)  $[\text{Cu}_2\text{L}^1(\text{OAc})_2] \cdot \text{H}_2\text{O}$  (1a); (b)  $[\text{Cu}_2\text{L}^3(\text{OAc})_2] \cdot \text{H}_2\text{O}$  (1c) in  $\text{CH}_3\text{CN}$ .

where ( $\chi_{\text{m}}$ ) is the paramagnetic susceptibility per molecule after the correction for diamagnetism, ( $\rho$ ) is the paramagnetic impurities;  $-2J$  is the singlet-triplet energy separation, ( $N_{\text{g}}$ ) is the temperature independence paramagnetism (TIP) assumed to be  $60 \times 10^{-6} \text{cm}^3 \text{mol}^{-1}$  for copper (II) dimers [18]. Figure 2 shows plots of  $\chi_{\text{Cu}}$  and  $\mu_{\text{eff}}$  versus  $T$  for complexes (1a) and (3c). Good magnetic simulation was obtained for (1a) using  $2J = -184 \text{cm}^{-1}$ ,  $g = 1.903$  and for (3c)  $2J = -80 \text{cm}^{-1}$ ,  $g = 2.018$ . The  $\mu_{\text{eff}}$  decreases with decreasing temperature, indicating an anti-ferromagnetic interaction between two copper(II) ions. It is interesting to note that a general trend emerges from the data in Table 3. Variation in the exogenous bridging group chloro- and hydroxo-bridged compounds show weak anti-ferromagnetic coupling compared to the acetato-bridged complexes. The moderate  $J$  values observed for the bis acetate-bridged complexes are possibly due to the counter-complementary nature of the overlap of the magnetic orbitals involving three atom bridging ligands [19].

Magneto-structural correlations for several dinuclear copper(II) complexes [20–22] show that the major factors controlling the exchange interactions are the

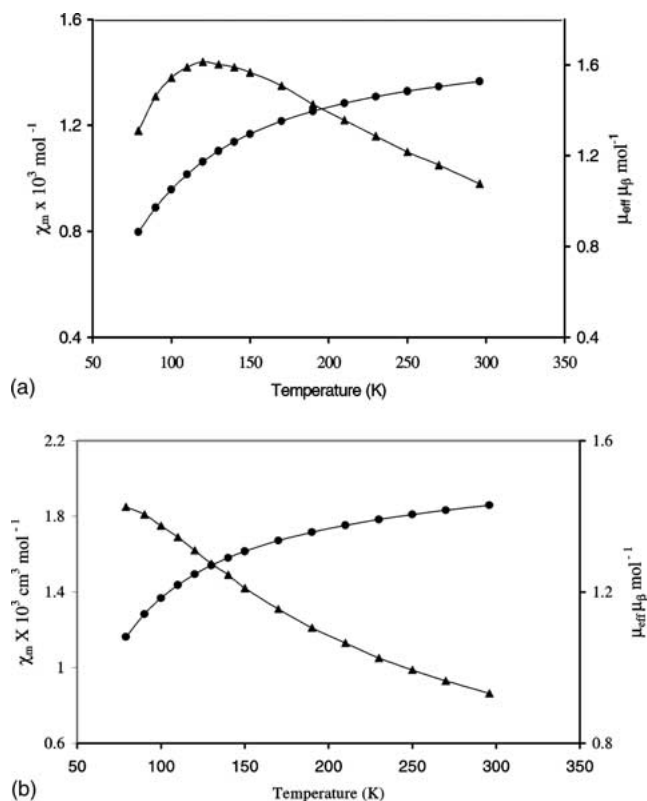


Fig. 2. Plots of  $\chi_{\text{m}}$  versus  $T$  and  $\mu_{\text{eff}}$  versus  $T$  for complexes (1a) (A) and (3c) (B). The solid line represents the least square fitting of the data using the Bleaney-Bower's equation.

Cu—Cu distance and Cu—O—Cu angle; however, other factors such as electronegativity of bridging atoms, electronic perturbation by remote substituents, degree of distortion from planar geometry and dihedral angle between two copper planes also have considerable influence on the extent of magnetic spin-spin interactions. For the present complexes, the observed  $-2J$  values are greatest for the acetato-bridged complexes, smaller for the hydroxo-bridged complexes and smallest of all for the chloro-bridged complexes. It has been reported [23] that very tight Cu—O—Cu angles and short Cu—Cu distance within two coplanar cis disposed

square pyramidal complexes contribute to reduced anti-ferromagnetism. This can be explained by considering a  $\sigma$  type overlap between the copper  $d_{x^2-y^2}$  orbital and the  $p_x$  and/or  $p_y$  orbital on oxygen. In general, it is reported that as the Cu—Cu distance and Cu—O—Cu angle increases, so does  $J$  become more negative [24, 25]. Since, the electron-donating nature of the exogenous donor ligands follows the order  $\text{OAc} > \text{OH} > \text{Cl}$ , the electron density on the copper atom will decrease in the same order; consequently, the super-exchange interaction decreases in the same order [26–28].

The observed magnetic integrals,  $-2J$ , for the complexes of  $\text{H}_2\text{L}^3$  and  $\text{H}_2\text{L}^4$  are substantially less than those of  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$ . The lowering of  $J$  for the former can be assigned to geometrical distortion around the copper(II). As explained below, the electron-withdrawing effect of the  $\text{NO}_2$  group may generate electro-positive character at the metals and the steric effect of the ethyl groups may distort the copper coordination geometry in the complexes of the ligands  $\text{H}_2\text{L}^3$  and  $\text{H}_2\text{L}^4$ . Reports suggest that both these factors, i.e. reduction in electron density [29] on the copper atom and distorted structure [30] are less favorable for effective coupling, resulting in a lower  $-2J$  value for the complexes of the ligand  $\text{H}_2\text{L}^3$ ,  $\text{H}_2\text{L}^4$  compared to  $\text{H}_2\text{L}^1$  and  $\text{H}_2\text{L}^2$ .

### Redox properties

The cyclic voltammograms of the complexes were recorded in acetonitrile. The electrochemical data are summarized in Table 4. The electrochemical behavior in the negative potential range is sensitive to the inductive ( $+I$  or  $-I$ ) nature of the *para*-substituted benzene rings and the steric effects of the ligand substituent. We observed that (i) the  $\Delta E_p$  increases with increasing scan rate and exceeds 60 mV, (ii) the  $E_{pc}$  and  $E_{pa}$  values change with scan rate, (iii) the cathodic ( $I_c$ ) and anodic ( $I_a$ ) peak currents were unequal, indicating the quasi-reversible nature of the electron transfer process. Therefore it is reasonable to assign the two waves to successive one-electron reactions at the metal centers, i.e.  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}$ . Replacement of one N—Me substituent by the bulkier N—Et or the electron-withdrawing  $\text{NO}_2$  group shifts the first reduction to less negative potential. A similar trend has been observed previous studies [31–33].

The reduction potentials for the bridged complexes follow the order:  $\text{OAc} > \text{OH} > \text{Cl}$ . This may be due to a reduction in electron density on the copper atoms as a result of decreasing electron-donating nature of the exogenous ligand. The stabilities of the mixed valence complexes are expressed by the conproportionation constant,  $K_{\text{con}}$  for the following equilibrium



The  $K_{\text{con}}$  values were determined electrochemically using the equation  $\log K_{\text{con}} = E_{1/2}/0.059$  (at 25 °C) where

Table 4. Electrochemical data with their conproportionation constants ( $K_{\text{con}}$ ) for the complexes in MeCN at room temperature<sup>a</sup>

Complex	$E_{pc}$	$E_{pa}$	$E_{1/2}$	$K_{\text{con}}$
(1a)	-0.72 -0.96	-0.43 —	-0.57 —	—
(1b)	-0.66 -0.98	0.00 -0.17	-0.33 -0.58	$1.909 \times 10^4$
(1c)	-0.64 -0.87	-0.09 -0.44	-0.36 -0.66	$1.102 \times 10^5$
(1d)	-0.63 -1.17	-0.44 -0.63	-0.54 -0.90	$1.414 \times 10^6$
(2a)	-0.62 -1.23	-0.59 -0.71	-0.58 -0.97	$3.746 \times 10^6$
(2b)	-0.55 -1.14	-0.14 -0.67	-0.34 -0.91	$3.492 \times 10^9$
(2c)	-0.53 -1.48	-0.18 -0.65	-0.35 -1.06	$1.011 \times 10^{12}$
(2d)	-0.49 -0.94	-0.41 -0.59	-0.45 -0.77	$2.056 \times 10^5$
(3a)	-0.41 -1.17	-0.56 -0.93	-0.48 -1.05	$3.702 \times 10^9$
(3b)	-0.39 -0.90	-0.12 -0.30	-0.26 -0.59	$5.237 \times 10^5$
(3c)	-0.30 -1.05	-0.47 -0.65	-0.39 -0.85	$6.826 \times 10^7$
(3d)	-0.29 -1.03	-0.08 -0.43	-0.19 -0.73	$1.541 \times 10^9$

<sup>a</sup> Potential ( $V$ ) versus Ag/AgCl; supporting electrolyte: TBAP;  $E_{1/2} = 0.5(E_{pc} + E_{pa})$  where  $E_{pc}$  and  $E_{pa}$  are the cathodic and anodic peak potentials.

$E_{1/2} = E_{1/2}^1 - E_{1/2}^2$ . From Table 3, the  $K_{\text{con}} > 4$ , which indicate that the  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  mixed valence species is stable with respect to disproportionation. This situation is the most common and has been observed in several binuclear systems [34, 35]. A coulometric experiment conducted at 100 mV more negative than the second reduction peak consumed two electrons per molecule.

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