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Exogenous bridging and nonbridging in Cu(II) complexes of Mannich base ligands: Synthesis and physical properties

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Abstract. Preparation of pentadentate ligands L^1, L^2, L^3 and L^4, where L^1 = 4-chloro-3-methyl-2[(prolin-1-yl)methyl]-6-[N-phenyl piperazin-1-yl)methyl]phenol, L^2 = 4-ethyl-2-[(prolin-1-yl)methyl]-6-[(N-phenyl piperazin-1-yl)methyl]phenol, L^3 = 4-chloro-3-methyl-2-[(prolin-1-yl)methyl]-6-[N-methyl piperazin-1-yl]methyl phenol, L^4 = 4-methoxy-2-[(prolin-1-yl)methyl]-6-[(N-phenyl piperazin-1-yl)methyl]phenol is described together with that of the corresponding Cu(II) complexes with various bridging motifs like OH, OAc and NO_2. The complexes are characterized by elemental analysis, electrochemical and electron paramagnetic spectral studies. Redox properties of the complexes in acetonitrile are highly quasireversible due to the chemical or/and stereochemical changes subsequent to electron transfer. The complexes show resolved copper hyperfine EPR at room temperature, indicating the presence of weak antiferromagnetic coupling between the copper atoms. Strengths of the antiferromagnetic interactions are in the order NO_2 > OAc > OH.

Keywords. Unsymmetrical ligands; dinuclear complex; synthetic models; cyclic voltammetry and electron paramagnetic resonance.

1. Introduction

Study of the synthesis and characterisation of new binuclear copper(II) complexes is highly interesting due to their significance in bioinorganic chemistry, magnetochemistry, materials science, multimetal centre catalysis, superconductivity and multielectron redox chemistry. We have synthesized unsymmetrical dinuclear ligand bearing aminoacid as one of the side arms, using Mannich base reaction between para-3,4-disubstituted phenols, formaldehyde, N-phenylpiperazine and proline (**1**). With this ligand, dinuclear Cu(II) complexes were synthesized having various bridging and non-bridging units.

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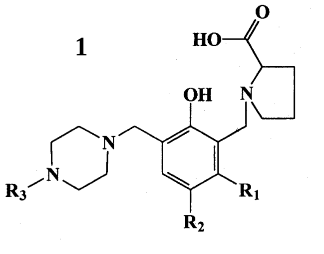

Ligand	R_1	R_2	R_3
L^1	Cl	CH_3	C_6H_5
L^2	C_2H_5	H	C_6H_5
L^3	Cl	CH_3	CH_3
L^4	OCH_3	H	CH_3

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*For correspondence

Hydroxo bridged complexes (**2**) were obtained and characterized by spectral and electrochemical measurements. They exhibit weak antiferromagnetic coupling observed via electron paramagnetic spectral studies.

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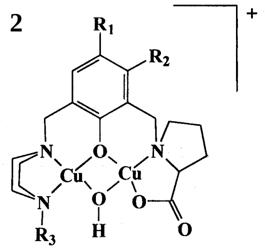

We are interested in inserting exogenous bridging groups, particularly those having two or more atoms and we have come across unusual and unexpected results. In the case of acetate, triply bridged (*m*-phenoxo) *bis*(*m*-acetato) complexes (**3**) were obtained.

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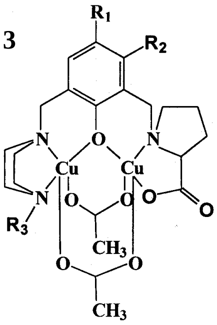

This observation is in contrast with similar studies with other binucleating ligands in which mono (*m*-acetato) copper (II) derivatives are obtained. Interestingly, similar *bis*(*m*-acetato) complexes of Cu(II)[1], Fe(III)[2] and Mn(III)[3] have been reported with other ligands. The bridging unit found in these structures has been proposed by Anderson *et al*[4]. Use of nitrite NO_2^-, as a potential exogenous bridge also leads to the formation of a dinitrite complex (**4**) in which there is no exogenous bridging between the two Cu(II) atoms. The lack of nitrite bridging contrasts with the expected mono(*m*-nitrito, O, N)

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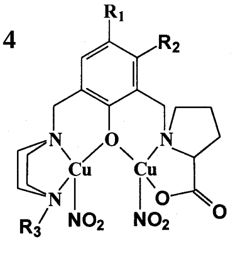


bridging recently reported by Reed *et al*[5] in related systems. These complexes provide another addition to the small groups of binucleating complexes that are now known to possess only an endogenous phenolate (or alcoholate) bridging oxygen atom[6–10]. Suzuki *et al*[6] and Urbach *et al*[10] have used the term ‘open’ structure to describe this bridging mode and have attributed it to a less strained, more relaxed conformation of the binucleating ligand. In this paper, we describe the synthesis, and spectral and electrochemical studies on a series of new binuclear Cu(II) complexes with bridging (OH, OAc) and non-bridging (NO_2^-) units.

2. Experimental

2.1 *Physical measurements*

Elemental analyses for C, H, N and Cu were obtained from the University of Michigan, Ann Arbor, Michigan. Infrared spectra in the range 4000–200 cm^{-1} were obtained on a Perkin–Elmer Model 558. UV-Vis spectra were obtained using a Hitachi 320 double beam spectrophotometer. The ^1H NMR of the ligands were obtained in $CDCl_3$. The instrument used was a 90 MHz NMR spectrophotometer (Model Em 390). Cyclic voltammograms were recorded on a Model POSG.125, Central ElectroChemical Research Institute, Karaikudi. EPR spectra of powdered samples were measured at room temperature on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies, and having a 100 kHz phase modulation to obtain the first derivative EPR spectrum. DPPH with a g value of 2·0036 was used as an internal field marker.

2.2 *Materials*

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

2.3 *Preparation of precursors*

Preparation of 4-chloro-3-methyl-6-[(N-phenyl piperazin-1-yl)methyl]phenol [PC^1] – *p*-Chloro-*m*-cresol (0·01 mol) in ethanol (75 ml) was mixed with *N*-phenyl piperazine (0·01 mol) and cooled in ice. Formaldehyde solution (7 ml, 0·01 mol) was then added dropwise with stirring. The mixture was stirred at room temperature for 24 h and gently refluxed for eight hours. The ethanol was then removed under vacuum. The resulting oil, when washed with sodium carbonate solution and extracted with benzene, yielded white powder. Yield: 80%, ^1H NMR in $CDCl_3$ *d* ppm: 2·29 (*s*, 3H, $-CH_3$), 3·69 (*s*, 2H, benzylic CH_2), 3·2 (*s*, 4H, N-CH_2), 2·65 (*s*, 4H, N-CH_2), 6·3–7·2 (*m*, 7H, aromatic). PC^2, PC^3 and PC^4 were synthesized by similar procedures.

4-Ethyl-6-[(N-phenyl piperazin-1-yl)methyl]phenol[PC^2] – Yield: 80%, ^1H NMR in $CDCl_3$ *d* ppm: 1·199 (*s*, 3H, CH_3), 2·57 (*s*, 4H, N-CH_2), 3·24 (*s*, 4H, N-CH_2), 3·68 (*s*, 4H, benzylic CH_2 and ethyl CH_2), 6·8–7·2 (*m*, 8H, aromatic).

4-Chloro-3-methyl-6-[(N-methyl piperazin-1-yl)methyl]phenol [PC^3] – Yield: 70%, ^{1}H NMR in CDCl$_3$ *d* ppm: 6·6–6·9 (*m*, 2H, ArH), 3·62 (*s*, 2H, benzylic CH$_2$), 1·2 (*s*, 3H Ar-CH$_3$), 2·28 (*s*, 3H, N-CH$_3$), 2·303 (*s*, 8H, N-CH$_2$).

4-Methoxy-6[N-methyl piperazin-1-yl)methyl]phenol [PC^4] – Yield: 90%, ^{1}NMR in CDCl$_3$ *d* ppm: 1·25 (*s*, 3H, OCH$_3$), 2·23 (*s*, 3H, N-CH$_3$), 3·6 (*s*, 2H, CH$_2$-Ph), 2·5 (*s*, 8H, N-CH$_2$), 6·5–7·5 (*m*, 3H, ArH).

2.4 *Preparation of ligands*

Preparation of 4-chloro-3-methyl-2[(prolin-1-yl)methyl]-6-[N-phenyl piperazin-1-yl) methyl]phenol [L^1] – 4-Chloro-3-methyl-6-[(N-phenylpiperazine-1-yl)methyl] phenol (0·02 mol) in chloroform (75 ml) was mixed with L-proline (0·02 mol) in chloroform (75 ml) and stirred. Formaldehyde solution 14 ml (0·02 mol) was added dropwise with stirring. The mixture was then heated to reflux and kept at room temperature for 24 h. Additions of 1·25 ml formaldehyde were made at approximately 8 h intervals. Ethanol was evaporated under vacuum and the resulting oil was washed with saturated sodium carbonate solution, extracted with benzene, dried with anhydrous magnesium sulphate and filtered before recovery.

Yield: 80%, ^{1}NMR in CDCl$_3$ *d* ppm: 6·7–7·2 (*m*, 6H, ArH), 3·6 (*s*, 4H, benzylic CH$_2$), 2·25 (*s*, 3H, CH$_3$), 4·56 (1H, NCH-Pro), 4·12 (NCH$_2$-Pro, 1·65–3·3, *m*, 12H). IR (KBr disc): 3450 cm^{-1} (b, OH), 1690 cm^{-1} (–COO), 1618 cm^{-1} (aromatic), 830 cm^{-1} (Cl), 1420 cm^{-1} (CH$_3$).

Ligands L^2, L^3 and L^4 were prepared in the same way as L^1.

4-Ethyl-2-[(prolin-1-yl)methyl]-6-[(N-phenyl piperazin-1-yl)methyl]phenol [L^2] – Yield: 80%, ^{1}H NMR in CDCl$_3$ *d* ppm: 1·2 (*s*, 3H, CH$_3$) 1·5–3·2 (*m*, 12H), 3·3–3·7 (*m*, 6H, benzylic and ethyl CH$_2$), 4·58 (*t*, N-CH), 4·20 (*m*, 2H), 6·8–7·4 (*m*, 7H aromatic). IR (KBr disc): 3450 cm^{-1} (br, OH), 1690 cm^{-1} (–COO), and 1620 cm^{-1} (aromatic), 2942 cm^{-1} (–C$_2$H$_5$).

4-Chloro-3-methyl-2-[(prolin-1-yl)methyl]-6-[(N-methyl piperazin-1-yl)]methyl]phenol [L^3] – Yield: 70%, ^{1}H NMR in CDCl$_3$ *d* ppm: 1·2 (*s*, 3H, CH$_3$), 2·28 (*s*, 3H, N-CH$_3$), 1·2–2·8 (*m*, 12H), 3·3–3·8 (*m*, 4H, benzylic CH$_2$), 4·4 (*dd*, 2H), 4·69 (*t*, N-CH), 6·6–7·2 (*m*, 2H, ArH). IR (KBr disc): 3450 cm^{-1} (b, OH), 1380 cm^{-1} (N-CH3), 1690 cm^{-1} (–COO), 1620 cm^{-1} (aromatic), 1420 cm^{-1} CH$_3$, 830 cm^{-1} (Cl).

4-Methoxy-2-[(prolin-1-yl)methyl]-6-[(N-methyl piperazin-1-yl)methyl]phenol [L^4] – Yield: 80%, ^{1}H NMR in CDCl$_3$ *d* ppm: 1·25 (*s*, 3H, OCH$_3$), 2·23, (*s*, 3H, N-CH$_3$), 3·2–3·6 (*s*, 4H, benzylic CH$_2$), 4·2 (*m*, 2H Pro), 4·6 (*t*, N-CH Pro), 6·4–7·2 (*m*, 2H, ArH). IR (KBr disc): 1430 cm^{-1} (OCH$_3$), 3450 cm^{-1} (br, OH), 1690 cm^{-1} (COO), 1375 cm^{-1} (N-CH$_3$), 1620 cm^{-1} (aromatic).

2.5 *Preparation of the complexes*

2.5a *Preparation of hydroxo bridged complexes: $[Cu_2 L^1(OH)(H_2O)_2]ClO_4.H_2O$* **(1a)** – Sodium hydroxide (0·001 mol) was added to the methanolic solution of the ligand (0·001 mol), followed by a solution of copper (II) perchlorate hexahydrate (0·002) dissolved in methanol. The resulting greenish blue solution was refluxed for 4 h and then filtered. On evaporation of the solution at room temperature for several days a green precipitate was obtained. The complex was recrystallized from aqueous methanol. Anal: Calc. for $C_{24}H_{29}ClCu_2N_3O_4$: C, 39·38; H, 4·013; N, 4·92; and Cu, 14·88%. Found: C, 39·31; H, 3·97; N, 4·63 and Cu, 14·26%. Complexes **1b**, **1c**, and **1d** were synthesized by the same synthetic procedure as **1a** using L^2, L^3, and L^4 in place of L^1.

$[Cu_2\ L^2(OH)(H_2O)_2]ClO_4.H_2O$ **(1b)** – Anal: Calc. for $C_{25}H_{31}Cu_2N_3O_4$: C, 38·47; H, 4·13; N, 5·38; and Cu, 16·27%. Found: C, 38·38; H, 3·91; N, 5·24 and Cu, 16·15%.

$[Cu_2\ L^3(OH)(H_2O)_2]ClO_4.H_2O$ **(1c)** – Anal: Calc. for $C_{19}H_{26}ClCu_2N_3O_4$: C, 37·68; H, 4·33; N, 5·64 and Cu, 17·07%. Found: C, 37·60; H, 4·12; N, 5·74 and Cu, 16·86%.

$[Cu_2\ L^4(OH)(H_2O)_2]ClO_4.H_2O$ **(1d)** – Anal: Calc. for $C_{19}H_{27}Cu_2N_3O_5$: C, 34·20; H, 5·01; N, 5·69 and Cu, 17·22%. Found: C, 33·98; H, 5·12; N, 5·56 and Cu, 17·10%.

2.5b *Preparation of bis acetato bridged complexes: $[Cu_2L^1(OAc)_2]\ H_2O$* **(2a)** – Copper (II) acetate monohydrate (0·002 mol) was dissolved in warm aqueous methanol (75 ml). Addition of methanolic solution of the ligand (0.001 mol) to it led to the formation of a dark-green solution. The mixture was then refluxed for four h and filtered. Upon concentration, amorphous green powder was obtained. Anal: Calc. for $C_{28}H_{33}ClCu_2N_3O_7$: C, 42·75; H, 4·35; N, 5·34 and Cu, 16·34%. Found: C, 42·17; H, 4·65; N, 5·40 and Cu, 17·10%. Complexes **2b**, **2c**, and **2d** were prepared by the method used for **2a** using L^2, L^3 and L^4 in the place of L^1.

$[Cu_2L^2(OAc)_2]H_2O$ **(2b)** – Anal: Calc. for $C_{29}H_{36}Cu_2N_3O_7$: C, 43·72; H, 4·40; N, 5·27; and Cu, 15·95%. Found: C, 43·51; H, 4·18; N, 5·40; and Cu, 17·10%.

$[Cu_2L^3(OAc)_2]H_2O$ **(2c)** – Anal: Calc. for $C_{23}H_{31}Cu_2N_3O_7$: C, 33·67; H, 5·05; N, 6·19 and Cu, 14·74%. Found: C, 33·12 H, 4·96; N, 5·40 and Cu, 17·10%.

$[Cu_2L^4(OAc)_2]H_2O$ **(2d)** – Anal: Calc. for $C_{23}H_{32}Cu_2N_3O_8$: C, 38·87; H, 5·02; N, 5·66 and Cu, 17·12%. Found: C, 38·68; H, 4·85; N, 5·99 and Cu, 17·00%.

2.5c *Preparation of bis nitrito complexes: $[Cu_2\ L^1(NO_2)_2(H_2O)_2].H_2O$* **(3a)** – To a methanolic solution containing the ligand (0·001 mol) and copper (II) perchlorate hexahydrate (0·002 mol), a solution of sodium nitrite (0·003 mol) dissolved in methanol (75 ml) was added. The resulting bluish green solution was refluxed for 4 h and filtered. Concentration of this solution yielded a greenish black amorphous powder, which was recrystallized from aqueous methanol. Anal: Calc. for $C_{25}H_{27}ClCu_2N_5O_7$: C, 39·56; H, 4·03; N, 8·22; Cu, 14·90%. Found: C, 39·51; H, 3·88; N, 8·03 and Cu, 14·50%. Complexes **3b**, **3c** and **3d** were prepared by the same procedure as **3a** using L^2, L^3 and L^4 instead of L^1.

$[Cu_2L^2(NO_2)_2(H_2O)_2].H_2O$ **(3b)** – Anal: Calc. for $C_{30}H_{30}Cu_2N_5O_7$: C, 44·11; H, 4·67; N, 9·90 and Cu, 15·16%. Found: C, 44·00, H, 4·59, N, 9·86 and Cu, 15·01%.

$[Cu_2L^3(NO_2)_2(H_2O)_2].H_2O$ **(3c)** – Anal: Calc. for $C_{19}H_{25}Cu_2N_5O_7$: C, 32·30; H, 4·85; N, 9·91 and Cu, 17·97%. Found: C, 32·10; H, 4·55; N, 8·07 and Cu, 17·66%.

$[Cu_2L^4(NO_2)_2(H_2O)_2].H_2O$ **(3d)** – Anal: Calc. for $C_{19}H_{26}Cu_2N_5O_8$: C, 30·23; H, 4·38; N, 8·25 and Cu, 14·87%. Found: C, 30·10; H, 4·12; N, 7·32 and Cu, 15·04%.

3. Results and discussion

Complexes **1a**, **1b**, **1c** and **1d** are obtained by reaction of Cu(II) perchlorate and the respective ligand in a 2:1 molar ratio in the presence of NaOH. Complexes **2a**, **2b**, **2c** and **2d** are prepared by reaction of Cu (II) acetate and appropriate ligands in a 1:2 molar ratio. The dinitrito complex **3a**, **3b**, **3c** and **3d** were prepared using Cu (II) perchlorate in presence of sodium nitrite in aqueous ethanol. The growth of single crystals of these complexes for X-ray studies and EPR is very difficult owing to their amorphous nature and we were unsuccessful in our attempts to do so.

3.1 *IR studies*

Spectroscopic methods were used to elucidate the structure of these complexes. The hydroxo bridged complexes exhibit a sharp band each in the region 3480–3600 cm^{-1}, which is assigned to the OH stretch on the basis of previous reports [11,12]. The *bis* acetato bridged complexes [13] showed strong *g* (COO) bands around 1450 cm^{-1} and 1583 cm^{-1}. IR bands due to the nitrite groups in nitrito complexes were observed around 1450–1220 cm^{-1}, which by comparison with recently published structural correlations [14] would suggest a monodentate O-bonded mode for the nitrite groups. All complexes show bands around 480 cm^{-1} and 280 cm^{-1} indicating the presence of Cu–N and Cu–O groups respectively [15]. UV visible spectra of these complexes in acetonitrile show a *d-d* transition in the region 600–800 nm, indicative of pyramidal geometry [16], and a medium intensity band, occurring between 360 and 480 nm, assigned to the phenolato to Cu(II) charge transfer band [17].

3.2 *Cyclicvoltammetric studies*

3.2a *Hydroxo bridged complexes:* In the present study, all the complexes undergo two one-electron reduction and oxidation steps at different potentials. As seen in table 1, they are not truly reversible as evident from the larger ΔEp values. The reduction appears as two well-defined peaks in the range –0·2 to –1·63 V (V vs SCE). Two oxidation peaks are present in the range –0·12 to –1·7 V. The shape of the reduction peak changed after the first scan and a new redox couple was observed at lower negative potentials. The shape does not change after the second cycle. This electrochemical study reveals very complex redox behaviour whose analysis is complicated by the quasi reversibility of the electrode process. Nevertheless, the following indications can be derived from these results:

(1) Controlled potential electrolysis of the reduction process indicates that two electrons per mole are transferred which suggests the formation of two Cu(I) ions.
(2) Two peaks are obtained which may correspond to the sequential one-electron oxidation of the copper (I) species. Moreover the huge difference between Ep_c and Ep_a

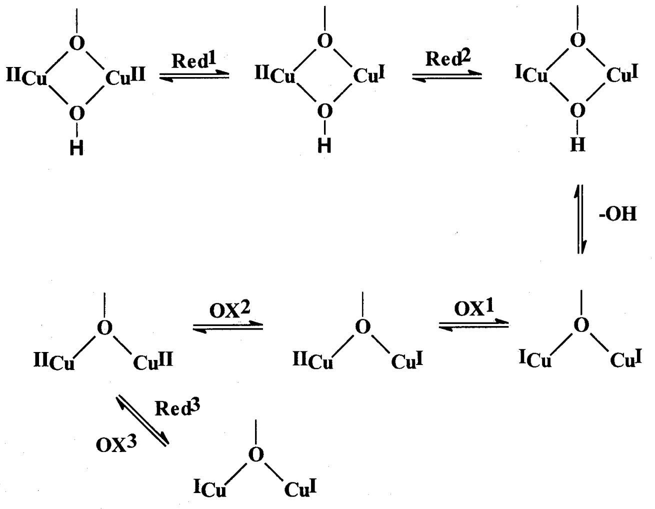
Table 1. Electrochemical data of the Cu(II) complexes and their conproportionation constants.

Complex	E_{Pa} (V)	E_{pc} (V)	ΔEp (V)	$E_{1/2}$ (V)	K_{con}
$[Cu_2L^1(OH)(OH)_2]ClO_4.H_2O$ (**1a**)	–1·56 –1·77	–1·27 –1·63	–0·29 –0·14	–1·41 –1·70	8·22 × 10^4
$[Cu_2L^2(OH)(OH)_2]ClO_4.H_2O$ (**1b**)	–0·64 –1·00	–0·24 –0·44	–0·40 –0·73	–0·44 –0·72	5·56 × 10^4
$[Cu_2L^4(OH)(OH)_2]ClO_4.H_2O$ (**1d**)	–0·12 –0·19	–0·19 –0·29	–0·07 –0·19	–0·15 –0·48	3·91 × 10^5
$[Cu_2L^1(OAc)_2].H_2O$ (**2a**)	–0·91 –1·30	–1·13 –1·24	–0·21 –0·05	–1·02 –1·27	1·698 × 10^4
$[Cu_2L^2(OAc)_2].H_2O$ (**2b**)	–0·89 –1·03	–0·76 –0·99	–0·21 –0·03	–0·82 –1·01	1·66 × 10^3
$[Cu_2L^4(OAc)_2].H_2O$ (**2d**)	–0·84 –1·42	–0·45 –0·80	–0·39 –0·62	–0·64 –1·11	9·24 × 10^7
$[Cu_2L^3(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3c**)	–1·04 –1·51	–0·25 –0·57	–0·78 –1·13	–0·65 –1·04	4·07 × 10^6

suggests that a chemical change occurs with the electron transfer. It may be due to the structural re-organization sphere.

(3) The formation of the new redox couple is associated with the copper structural forms. It is assumed that this form may be derived from some steric distortion of these copper environments, which may contain only an endogenous bridging unit.

These interpretations of the experimental data are based on a recent study of the occurrence of stereochemical changes[18] and the observation of ligand loss induced by electron transfer in related systems[19]. We thus speculate that the reduction of the complexes can be described by scheme 1.



Scheme 1.

Bis-acetato bridged complexes – The redox behaviour of the acetato-bridged complexes is shown in figure 1. The large Δ*Ep* values show that the complexes are not truly reversible systems. The value of the cathodic current is larger than the anodic current, showing that the complexes undergo a chemical charge after reduction. All the complexes undergo two one-electron reduction and oxidation at different potentials. The cyclic voltammogram consists of two reduction (Ep_c^1 = –0·10 to –1·13 V and Ep_c^2 = –0·2 to –1·24 V) and two oxidation (Ep_a^1 = –0·4 to –0·9 V and Ep_a^2 = –0·59 to –1·4 V) peaks.

Both reductions are mono electronic as is deduced from coulometric analysis. The shape of the main reduction peak is altered after the first cycle and a small reduction peak is observed around Ep_c^3 –0·04 V, apart from the main reduction peaks.

Thus, the systems show three redox complexes after the first complete cycle. The third redox couple may be due to the new species generated after the reduction of the original complex. Continuous scan shows that the peak current of the original complex decreases with increase in the peak currents of the generated species.

Thus, the following important conclusions can be drawn from the cyclic voltammetric studies.

(1) Controlled potential electrolysis of the reduction process indicates that two electrons per mole are transferred, suggesting the formation of two copper (I) ions and occurs in a two-step one-electron process.

(2) The huge Δ*Ep* values suggest that the system is quasi-reversible and that a chemical change occurs with electron transfer, resulting most probably from a structural re-organization of the copper co-ordination sphere, and the presence of the new redox couple can be attributed to the formation of a new complex, which may contain only endogenous bridging units.

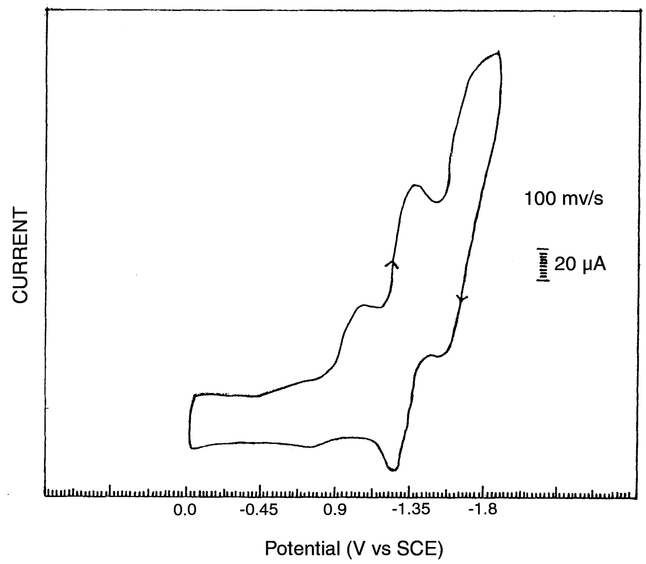
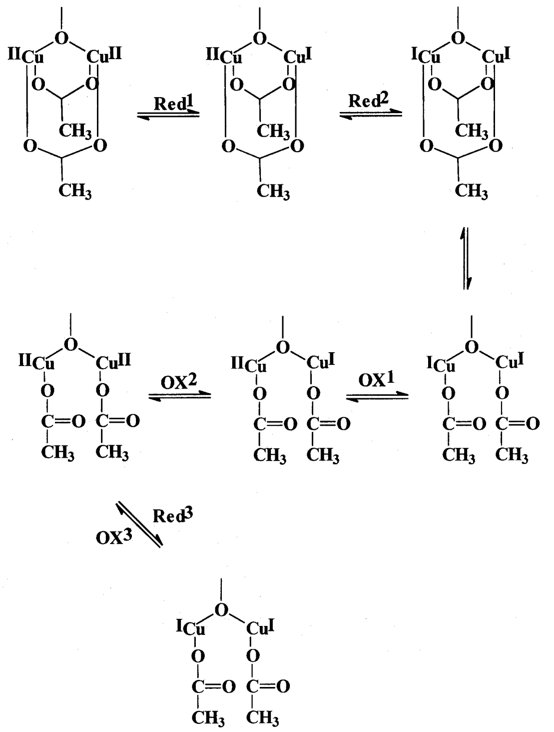


Figure 1. Cyclic voltammogram of $[Cu_2L^1(OAc)_2]H_2O$.

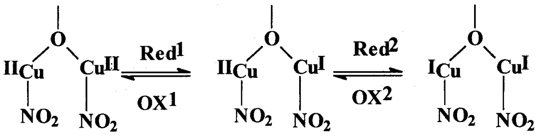


Scheme 2.

The redox mechanisms of the complexes proposed are described in scheme 2.

Bis-nitro complexes – Cyclic voltammograms for all the complexes in the current study are very similar and involve two quasi-reversible redox couples at negative potentials, $E_{1/2}{}^{1} = -0{\cdot}1$ to $-1{\cdot}0$ V and $E_{1/2}{}^{2} = 0{\cdot}5$ to $1{\cdot}2$ V corresponding to stepwise one-electron reduction through a Cu(II)–Cu(I) intermediate to the dinuclear Cu(I) species. Coulometric experiments carried out in acetonitrile medium show that in all cases each redox couple is associated with a one-electron transfer. The two redox couples are well-separated and the conproportionation constants K_{con} are calculated for these complexes.

The behaviour of the complexes is shown in scheme 3.



Scheme 3.

The coulometry experiments conducted at –1·8 V on the present complexes to confirm the consumption of 2 electrons per molecule indicated that each of the complexes is involved in a one-electron transfer process. The value of the cathodic current is greater than the anodic current. ΔEp greater than 60 mV indicates that the system is quasi-reversible. These molecules belong to K_{con} >4, which indicate that the second electron is more difficult to add than the first and the Cu(II)–Cu(I) mixed-valent species is stable with respect to disproportionation. The situation is most common and is observed in several binuclear systems.

Complexes containing exogenous bridging ligands allow different redox behaviour with respect to other complexes (after the first redox cycle). This is due to the loss of the exogenous bridging ligand and the stereochemical change in the systems. These are in good agreement with the results already reported by Fenton *et al*[20].

3.3 *EPR spectroscopic studies*

As we could not get well-shaped single crystals, EPR results are recorded only for powder and solution samples for all the copper complexes and the results are described below. All the powder samples were taken in quartz tubes to avoid Mn^{2+} or Fe^{3+} impurities and solution spectra were recorded in DMF solutions in capillary tubes. Solution spectra were recorded to confirm that the complexes do not undergo any structural change in solution.

Complex **1a** gave an axially symmetric EPR spectrum, with $g_{||}$ = 2·279, $g_{\perp}$ = 2·050, $A_{||}$ = 14·87 mT and $A_{\perp}$ = 2·66 mT. A solution spectrum in DMF solvent gave an isotropic EPR spectrum with g_{iso} = 2·129 and A_{iso} = 6·51 mT. A few typical EPR spectra are given in figures 2 and 3. We have also calculated the spin Hamiltonian parameters for all the four copper complexes having OH bridging, as solid and in solution. These values are given in table 2. A general look at these spin Hamiltonian parameters indicates that g values are close, whereas the A values differ. Complexes **1b** and **1d** have similar structures (except for a small change in the outside ring, where phenyl is replaced by methyl) and are confirmed by their g and A value in the powder spectra. On the other hand, complexes **1a** and **1c** behave similarly. The A_{iso} values indicate very weak coupling and the unpaired electrons are localized mainly on only one copper ion. We have recorded the EPR spectra for complexes **2a**, **2b**, **2c** and **2d** also in both solid and solution state. The spin Hamiltonian parameters thus obtained are also given in table 2. These results are similar to those of hydroxy-bridged complexes.

Complexes **3a**, **3b**, **3c** and **3d** have two NO_2 groups as compensating ions. We have recorded the EPR spectra for these 4 copper complexes also as solid and in solution form. The calculated spin Hamiltonian parameters are also included in table 2. Unlike hydroxy bridged complexes, which grouped into 2 sets, these four complexes have almost identical g and A values both in solution and solid state. In addition to this, the $A_{||}$ and $A_{\perp}$ values are much smaller than the previous four complexes (3·90 mT against 6·38 mT, see table 2) which is roughly half the value.

It has been mentioned earlier in the literature[21] that whenever an electron is shared by the two nearby interacting copper ions, the hyperfine coupling constant has been reduced to half the value compared to the situation when the electron is localized on a single nucleus. In the present case, the reduction is in the range of 40–50%. With the information available from powder EPR spectra, one can say that the NO_2 complexes have more interacting copper ions than the hydroxy complexes.

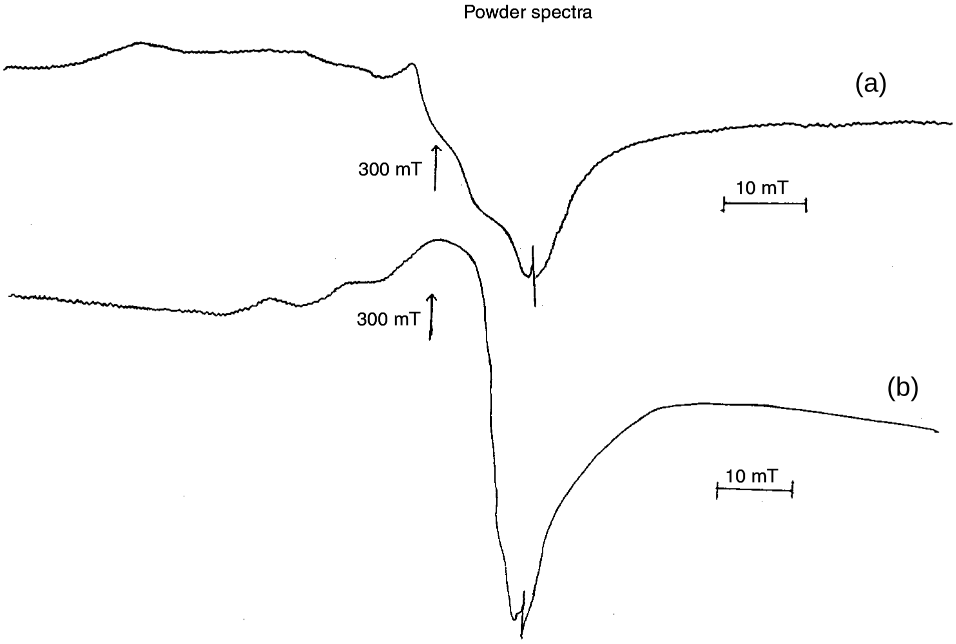


Figure 2. Powder EPR spectrum of hydroxo bridged complex $[Cu_2L^1(OH)_2(H_2O)_2]$-$ClO_4.H_2O$ (**a**) and nitrocomplex $[Cu_2L^1(NO_2)_2(OH)_2]ClO_4.H_2O$ (**b**).

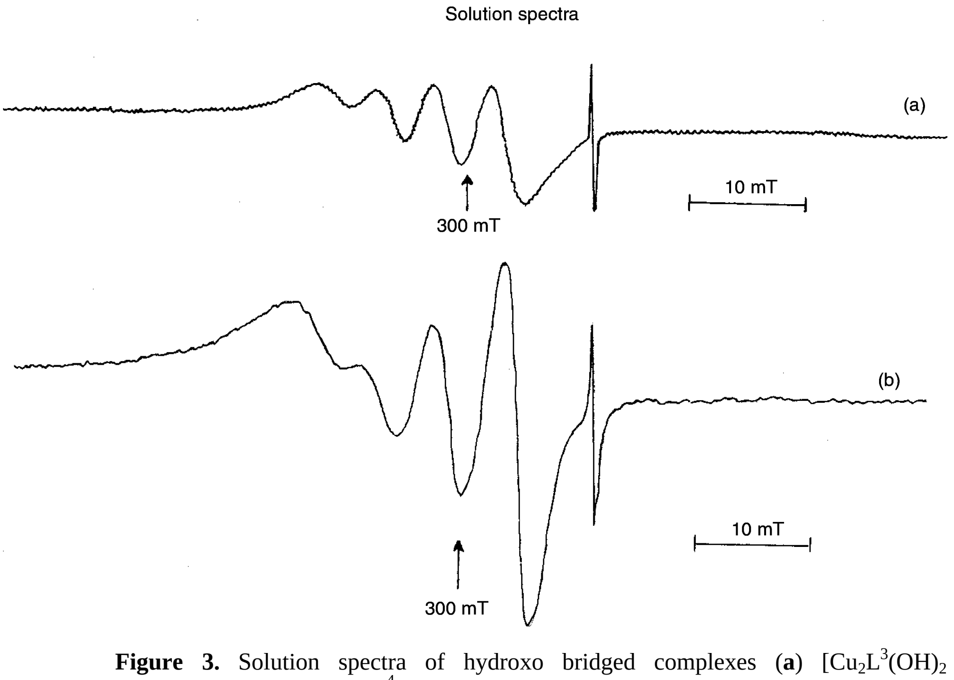


Figure 3. Solution spectra of hydroxo bridged complexes (**a**) $[Cu_2L^3(OH)_2(H_2O)_2]ClO_4.H_2O$ (**b**) $[Cu_2L^4(OH)_2(H_2O)_2]ClO_4.H_2O$.

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

					Solution data			
	Powder data				Expl.		Calc.	
Complex	$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$	$A_{\perp}$	g_{iso}	A_{iso}	g_{iso}	A_{iso}
$[Cu_2L^1(OH)(OH)_2]ClO_4.H_2O$ (**1a**)	2·279	2·05	14·87	2·66	2·129	6·51	2·134	6·34
$[Cu_2L^2(OH)(OH)_2]ClO_4.H_2O$ (**1b**)	2·149	2·042	8·38	6·66	2·078	7·23	2·123	7·89
$[Cu_2L^3(OH)(OH)_2]ClO_4.H_2O$ (**1c**)	2·120	2·075	16·38	1·70	2·090	6·59	2·116	6·3
$[Cu_2L^4(OH)(OH)_2]ClO_4.H_2O$ (**1d**)	2·15	2·04	8·805	5·56	2·076	6·64	2·1342	6·612
$[Cu_2L^1(OAc)_2].H_2O$ (**2a**)	2·2	2·05	16·5	3·72	2·100	7·98	2·1258	7·117
$[Cu_2L^2(OAc)_2].H_2O$ (**2b**)	2·15	2·032	9·23	7·33	2·0718	7·96	2·1242	8·33
$[Cu_2L^3(OAc)_2].H_2O$ (**2c**)	2·146	2·061	8·169	5·84	2·089	6·616	2·1216	6·98
$[Cu_2L^4(OAc)_2].H_2O$ (**2d**)	2·15	2·036	8·54	5·96	2·074	6·92	2·1239	7·24
$[Cu_2L^1(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3a**)	2·039	2·026	8·355	1·66	2·030	3·89	2·075	3·105
$[Cu_2L^2(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3b**)	2·0545	2·019	8·262	1·66	2·0718	3·86	2·0981	3.49
$[Cu_2L^3(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3c**)	2·0773	2·076	8·657	1·66	2·009	3·99	2·053	3·36
$[Cu_2L^4(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3d**)	2·137	2·035	7·573	2·00	2·049	3·85	2·057	3·013

*Values of *A* are in units of mT

The spin Hamiltonian parameters, covalency parameters (a^2, a', b_1^2) have been calculated using the standard formulae[22],

$$a^2 = (A_{||}/0{\cdot}036) + (g_{||} - 2{\cdot}0023) + 3/7\,(g_{\perp} - 2{\cdot}0023) + 0{\cdot}04,$$

$$a' = (1 - a^2)^{½} + aS,$$

$$g_{||} = 2{\cdot}0023 - 8r\,[ab_1 - \tfrac{1}{2}\,a'(1 - b_1^2)^{1/2}\,T(n),$$

where a denotes the in-plane s bonding, a' is the normalization condition on the ground state orbital, S is overlap integral between ground state orbital and normalized ligand orbital, b_1^2 is a direct measure of the covalency of the in-plane p bonding, $r = l_0 a b_1/\Delta E$ where l_0 is the spin orbit coupling constant for the free ion. We can assume $S = 0{\cdot}076$, $l_0 = -828$ cm^{-1} if the ligands are oxygen or nitrogen donors. $T(n)$ is a function involving metal–ligand distance, hybridization constant (n) and effective nuclear charges for the ligand 2*s*-, 2*p*-orbitals and the metal *d*-orbitals. This $T(n)$ value is assumed to be 0·220[23]. ΔE is the transition energy between $^2B_1$ and $^2B_2$ states. Using optical and EPR data, we have calculated the parameters a^2, a' and b_1^2 for all copper complexes and the results are given in table 3.

It is clear from table 3 that the admixture coefficients a^2, a' and b_1^2 form two groups, one consisting of acetate- and hydroxy-bridged complexes and the other of nitro complexes. Even though the values are calculated with a few approximations (such as constant values for S, l_0, $T(n)$ etc.), one can observe a general trend in these values. However, one complex in each set (complexes 3, 8 and 9, table 3) behaves differently. This complex has a slightly different spin Hamiltonian parameter in powder spectra,

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

Complex	$\Delta E\ ^2B_1 \rightarrow ^2B_2$ (cm^{-1})	a^2	a^1	b_1^2
$[Cu_2L^1(OH)(OH)_2]ClO_4.H_2O$ (**1a**)	15873	0·7502	0·5656	0·90
$[Cu_2L^2(OH)(OH)_2]ClO_4.H_2O$ (**1b**)	17241	0·4365	0·8008	0·90
$[Cu_2L^3(OH)(OH)_2]ClO_4.H_2O$ (**1c**)	15625	0·6338	0·6656	0·60
$[Cu_2L^4(OH)(OH)_2]ClO_4.H_2O$ (**1d**)	15552	0·4485	0·7935	0·90
$[Cu_2L^1(OAc)_2].H_2O$ (**2a**)	15576	0·7164	0·5968	0·78
$[Cu_2L^2(OAc)_2].H_2O$ (**2b**)	16638	0·4566	0·7885	0·93
$[Cu_2L^3(OAc)_2].H_2O$ (**2c**)	16000	0·4358	0·8013	0·93
$[Cu_2L^4(OAc)_2].H_2O$ (**2d**)	15197	0·4393	0·7990	0·91
$[Cu_2L^1(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3a**)	17241	0·3189	0·8681	0·63
$[Cu_2L^2(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3b**)	17513	0·3290	0·8627	0·73
$[Cu_2L^3(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3c**)	15243	0·3869	0·8302	0·72
$[Cu_2L^4(NO_2)_2(OH)_2]ClO_4.H_2O$ (**3d**)	15319	0·3991	0·8231	0·92

when compared to the other three members of the set. Further work is in progress to understand this peculiar behaviour. In a previous communication dealing with the binuclear copper complexes ions with acetate-, hydroxo- and nitro-bridges, magnetic moment measurements indicated that the coupling between the two copper ions follows the order $NO_2 > OAc \sim OH$[24]. From the present calculations also, we noticed that the complexes grouped into two sets, as mentioned above. From table 2, one can say that smaller the values of a^2 and b_1^2, the higher the ionic interactions of in-plane bonding, which in turn lead to higher interactions between metal and ligand atoms. We are in the process of confirming our results with magnetic susceptibility data at various temperatures, followed by single crystal EPR studies of the samples. Using available information, one can suggest that the interaction between the two copper ions is high in case of nitro-bridged complexes and very low in the other two cases. Roughly, one can suggest the order $NO_2 > OAc > OH$.

Further work is in progress to study these complexes at low temperatures and also as functions of temperature to confirm the above hypothesis. Also, single crystal work on nitrobridged complexes which may show half-field transition is worth attempting.

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