

## Studies on Phenoxo-bridged Macrocyclic Dicopper Complexes. EPR Spectral Behaviour of Mixed-valence Systems $[\text{Cu(II)Cu(I)L}]^+$ and Magnetic Exchange Interaction in Complexes $[\text{Cu}_2\text{L}](\text{ClO}_4)_2$

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### Abstract

EPR spectra of two series of electrochemically generated macrocyclic mixed-valence copper complex species  $[\text{Cu(II)Cu(I)L}]^+$  have been investigated. Complexes belonging to series 1  $[\text{Cu}_2\text{L}](\text{ClO}_4)_2$  are derived from 6,12,18,24-substituted (H,H,H,H (a); Me,Me,Me,Me (b); Pr,Pr,Pr,Pr (c); Ph,Ph,Ph,Ph (d); H,H,Me,Me (e)) macrocycle 7,11,19,23-dimetheno-9,21-dimethyl-1,5,13,17-tetra-azacyclotetracos-5,7,9,12,17,19,21,14-octaene-25,26-diol ( $\text{H}_2\text{L}$ ). Complexes belonging to series 3,  $[\text{Cu}_2\text{L}](\text{ClO}_4)_2$ , are related to those of series 1 by replacement of two of the  $\text{CH}=\text{N}$  linkages by  $-\text{CH}_2-\text{NH}-$  groups of the segment containing two azomethine linkages having the 6,12-substituents H,H (a); Me,Me (b); Me,Ph (c). In the mixed-valence species derived from 1b–1e and 3a–3c in MeCN or  $\text{CH}_2\text{Cl}_2$  solutions the single unpaired electron is localized on one of the metal centres at room temperature on the EPR time scale. Only the species derived from 1a gives a seven-line EPR spectrum at room temperature indicating that the unpaired electron is delocalized over both metal centers. Variable temperature magnetic measurements on complexes 1b and 1c indicate strong antiferromagnetic exchange ( $-2J = 835 \pm 5 \text{ cm}^{-1}$  and  $806 \pm 9 \text{ cm}^{-1}$ , respectively) in both cases.

### Introduction

Intramolecular electron transfer in mixed-valence compounds is a subject of considerable interest [1–10]. The Robin and Day classification scheme [1] of mixed-valence systems aims at gauging the extent of electron delocalization between interacting metal centers. In  $\text{Cu(II)}-\text{Cu(I)}$  complexes the behaviour of the single unpaired electron can be

readily recognized on the EPR time scale. Thus, a seven-line EPR spectrum is expected in solution when the unpaired electron is delocalized over the two metal sites, as against a four-line spectrum for the electron localized on a single metal center. From variable temperature measurements and the temperature at which the seven-line spectrum coalesces to the four-line one it is possible to estimate the energy barrier for electron transfer [11].

The facile electrochemical generation of macrocyclic  $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}]^+$  species derived from 1–4 (Fig. 1), coupled with their thermodynamic stability with respect to disproportionation, makes them suitable systems for investigating the behaviour of the odd electron. Addison [12] has reported that the EPR spectrum of the mixed-valence species from 1b exhibits a four-line copper hyperfine pattern in MeCN at room temperature. In contrast, Gagné and co-workers [11] observed that the  $\text{Cu(II)}-\text{Cu(I)}$  species from 1a produces an isotropic seven-line spectrum in various solvents at room temperature, which changes to a four-line pattern at about 200 K. The seven-line spectrum also became four-line when the solutions were exposed to carbon monoxide. Long and Hendrickson [13] investigated variable temperature EPR spectra for acetone solutions of seven mixed-valence compounds belonging to the series 2, generated by dithionite reduction. At room temperature, four of these compounds (2a–2c, 2e) were found to be of the electron delocalized type on the EPR time scale.

In a recent study [14] we have shown that the EPR spectra of  $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}]^+$ , derived from 3a and 4 in solution by coulometric reduction at negative potential (*versus* SCE), are consistent with the interaction of the odd electron with just one copper centre. Similar four-line EPR spectra were also obtained for the species  $[\text{Cu}^{\text{II}}\text{Cu}^{\text{III}}\text{L}]^{3+}$ , derived from 3a and 4, which were generated coulometrically in solution at positive potentials (*versus* SCE) [14]. We report here that the EPR spectra of  $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}]^+$

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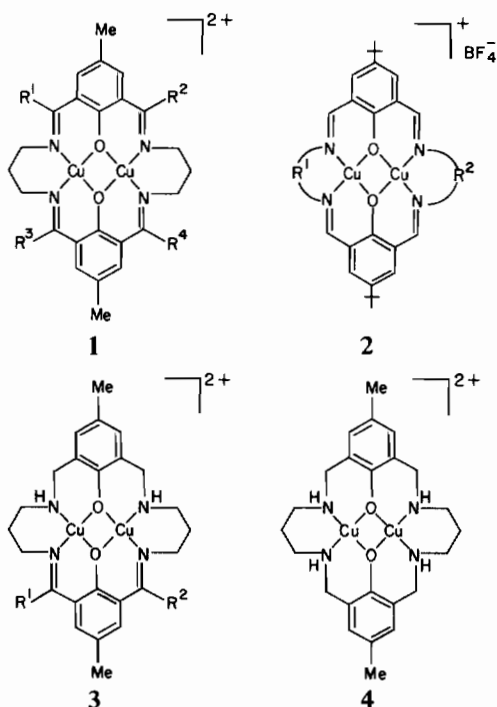


Fig. 1. Tetra-aza-macrocyclic dicopper complexes. **1**( $R^1, R^2, R^3, R^4$ ): **1a**(H,H,H,H); **1b**(Me,Me,Me,Me); **1c**(Pr<sup>n</sup>,Pr<sup>n</sup>,Pr<sup>n</sup>,Pr<sup>n</sup>); **1d**(Ph,Ph,Ph,Ph); **1e**(H,H,Me,Me). **2**( $R^1, R^2$ ): **2a**( $R^1 = R^2 =$  propylene); **2b**( $R^1 = R^2 =$  2,2-dimethylpropylene); **2c**( $R^1 = R^2 =$  butylene); **2d**( $R^1 = R^2 =$  biphenylene); **2e**(propylene, 2,2-dimethylpropylene); **2f**(propylene, 2,2-biphenylene); **2g**(propylene, butylene). **3**( $R^1, R^2$ ): **3a**(H,H); **3b**(Me,Me); **3c**(Me,Ph); **3d**(Ph,Ph). **4**[Cu<sub>2</sub>L(ClO<sub>4</sub>)<sub>2</sub>].

species generated by controlled potential electrolysis of **1b–1e** and **3a–3c** in MeCN and CH<sub>2</sub>Cl<sub>2</sub> all produce four-line hyperfine patterns for copper at room temperature.

The present study is also concerned with variable temperature magnetic measurements for the perchlorate salts of complexes **1b** and **1c**. Prior to this work Lambert and Hendrickson [15] determined the singlet–triplet separation energy ( $-2J$ ) to be 588 cm<sup>-1</sup> for the chloro derivative of **1a**, [Cu<sub>2</sub>LCl<sub>2</sub>]·6H<sub>2</sub>O, while in an earlier study we have shown that compound **4** exhibits much stronger exchange ( $-2J = 824$  cm<sup>-1</sup>) [16], comparable with the  $-2J$  values reported here for **1b** and **1c**.

## Experimental

The mixed-valence species were generated by controlled potential electrolysis of the corresponding [Cu<sub>2</sub>L](ClO<sub>4</sub>)<sub>2</sub> complexes in MeCN or CH<sub>2</sub>Cl<sub>2</sub> at room temperature using a potential 100 mV more negative than the redox potentials [17, 18] at which the first electron transfer occurs. Constant potential electrolyses were carried out with a PAR electro-

chemistry system using a platinum-mesh working electrode. Each electrolysis was carried out in an inert atmosphere dry box (Vacuum Atmosphere) and the reduced solutions transferred to EPR tubes. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) were used as the supporting electrolytes for MeCN and CH<sub>2</sub>Cl<sub>2</sub> solutions, respectively. X-band EPR spectra were recorded either at room temperature or liquid nitrogen temperature on a Varian E-4 spectrometer.

Variable temperature magnetic susceptibility data were obtained in the range 5–300 K using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. A main solenoid field of 1.5 T and a gradient field of 10 T m<sup>-1</sup> were employed.

## Results and Discussion

The room temperature EPR spectra of the electrochemically generated [Cu<sub>2</sub>L]<sup>+</sup> species derived from **1c** and **1d** in CH<sub>2</sub>Cl<sub>2</sub> and **1a**, **1e** and **3b** in MeCN are shown in Fig. 2 and EPR parameters for these and the other compounds (**1b**, **3a**, **3c**) are given in Table I. The seven-line copper hyperfine pattern for **1a** is a sharp contrast to the four-line patterns observed for the other compounds. The solid state spectra of these compounds at room temperature exhibit a featureless single symmetric line. However, in frozen solution, anisotropic spectra with axial symmetry having four  $A_{||}$  hyperfine lines are obtained for the two systems studied, as shown in Fig. 3 for the species obtained from **1c**. It may be noted that the spectrum in the frozen glass does not contain additional features that could be attributed to a triplet state dimer. The EPR parameters for the mixed-valence complexes (Table I) indicate that the solvent does not play a dominant role in deciding the nature of the interaction of the single unpaired electron with the copper atoms.

It may be expected that delocalization of the odd electron over both the copper centers will be maximized when the molecule is highly symmetric and the metal atoms are in square-planar configurations. However, attainment of this situation will be opposed by the strong reluctance of copper(I) to adopt a square-planar geometry. The X-ray crystal structure of [Cu<sup>II</sup>Cu<sup>I</sup>L](ClO<sub>4</sub>)·0.5MeOH [19], derived from **1a**, indicates that one copper centre is square-planar, while the other, which is disordered over two sites, exhibits significant distortion with the copper atom being displaced by 0.15 and 0.65 Å (two sites) from the O<sub>2</sub>N<sub>2</sub> basal plane. The square-planar site is assigned to the divalent copper ion and the distorted site to the monovalent copper ion [19]. One of the Cu(I) sites is considered to involve a weak axial interaction with the  $\pi$  system of an adjacent, macrocyclic ligand, leading effectively to a distorted square-

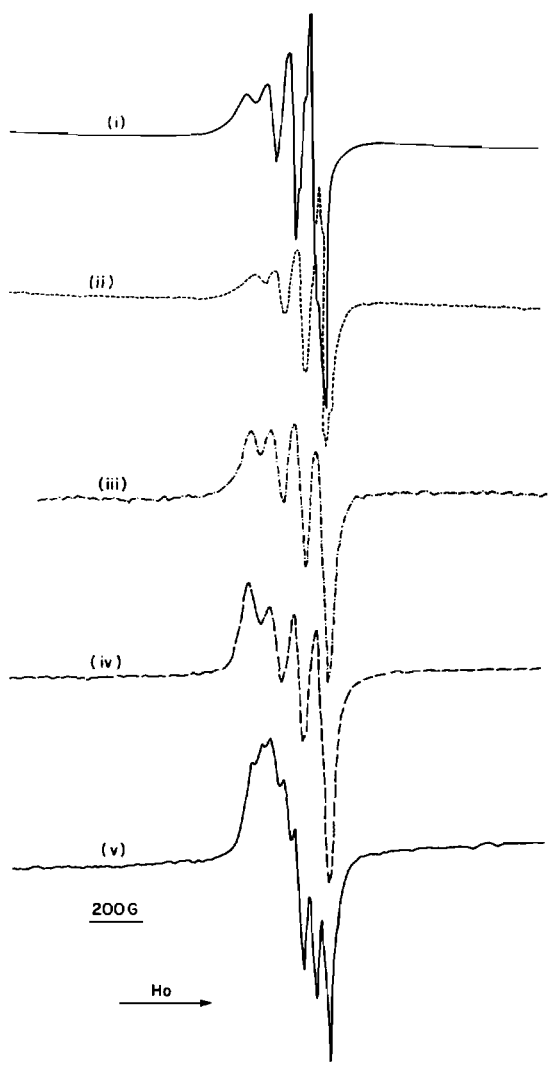


Fig. 2. Room temperature X-band EPR spectra for mixed-valence  $[\text{Cu}(\text{II})\text{Cu}(\text{I})\text{L}]^+$  species derived from one-electron reduction of dicopper(II) complexes: (i) **1d** in  $\text{CH}_2\text{Cl}_2$  ( $\nu = 9.55$  GHz); (ii) **1c** in  $\text{CH}_2\text{Cl}_2$  ( $\nu = 9.50$  GHz); (iii) **3b** in MeCN ( $\nu = 9.358$  GHz); (iv) **1e** in MeCN ( $\nu = 9.50$  GHz); (v) **1a** in MeCN ( $\nu = 9.51$  GHz).

pyramidal geometry. The presence of solution intramolecular electron transfer for the mixed valence species derived from **1a**, as indicated by the seven-line room temperature EPR spectrum [11], suggests that the stereochemical environment of the metal centres oscillates between two extremes to accommodate the valence changes. The rate of such conformational change ( $K_s$ ), from less symmetric to more symmetric states, and the rate of intramolecular thermal electron transfer ( $k_{\text{th}}$ ) both increase with increase of temperature. It should also be noted that delocalization of the single unpaired electron over two copper atoms can be detected on the EPR time scale when  $k_{\text{th}} \geq 5.5 \times 10^8 \text{ s}^{-1}$ , the EPR life-time.

TABLE I. EPR Data for Mixed-valence State Species Obtained from Electrochemical Reduction of Dicopper(II) Complexes

Complex	Solvent	$g_{\text{iso}}^{\text{a}}$	$g_{\parallel}^{\text{b}}$	$g_{\perp}^{\text{b}}$	$A_{\text{iso}}^{\text{a}}$ (G)	$A_{\parallel}^{\text{b}}$ (G)
<b>1a</b>	MeCN	2.111			42	
<b>1b</b>	MeCN	2.115			82	
<b>1c</b>	$\text{CH}_2\text{Cl}_2$	2.109	2.22	2.05	82	185
<b>1d</b>	$\text{CH}_2\text{Cl}_2$	2.125	2.23	2.06	78	180
<b>1e</b>	MeCN	2.111			85	
<b>3a</b>	MeCN	2.113			80	
<b>3b</b>	MeCN	2.115			82	
<b>3c</b>	$\text{CH}_2\text{Cl}_2$	2.121			85	
<b>4</b>	MeCN	2.109			80	

<sup>a</sup>Measured at 298 K.

<sup>b</sup>Measured at 77 K.

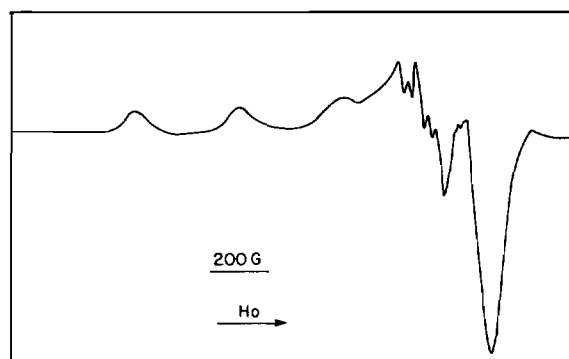


Fig. 3. Frozen (77 K)  $\text{CH}_2\text{Cl}_2$  glass X-band EPR spectrum for mixed-valence  $[\text{Cu}(\text{II})\text{Cu}(\text{I})\text{L}]^+$  obtained from one-electron reduction of complex **1c**.

Thus, observation of four-line copper hyperfine patterns in all the cases, except for the one obtained from **1a**, indicates that either  $k_s$  or  $k_{\text{th}}$ , or both, are less than  $5.5 \times 10^8 \text{ s}^{-1}$ . In the case of  $[\text{Cu}_2\text{L}]^+$ , generated from **1a**,  $k_{\text{th}}$  at 298 K was estimated [11] to be  $1.7 \times 10^{10} \text{ s}^{-1}$ , whereas for **2a–2c** and **2e**, which also exhibit seven-line spectra, this value ranged from  $1.6 \times 10^{10}$  to  $2.9 \times 10^9 \text{ s}^{-1}$  [13]. The mixed-valence complexes derived from **1b–1e** differ from the one derived from **1a** in that the hydrogen atoms of the azomethine linkages in **1a** are fully or partly replaced by alkyl or phenyl groups. These more bulky peripheral substituents could possibly hinder the conformational changes necessary for an EPR detectable exchange process. A coordinating solvent like MeCN may also reduce the intramolecular electron transfer rate by conferring a square-pyramidal geometry to the copper(I) site and also by stabilizing the lower oxidation state.

The square-planar stereochemical arrangement resulting from the presence of two unsaturated, azomethine nitrogen atoms at the copper(II) centre in the mixed-valence species  $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}](\text{ClO}_4) \cdot 0.5\text{MeOH}$  [19] contrasts sharply with the geometry

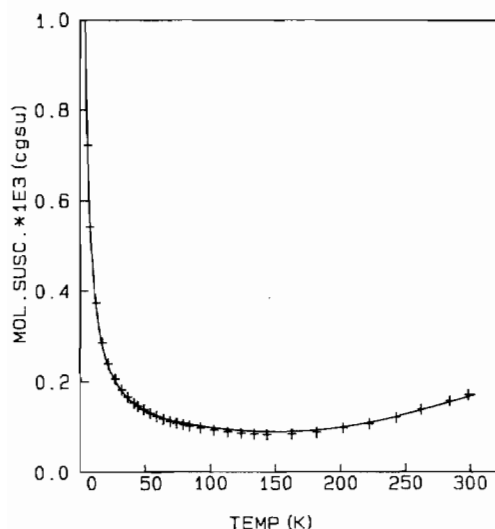


Fig. 4. Magnetic susceptibility data for complex **1b**,  $[\text{Cu}_2\text{L}](\text{ClO}_4)_2$  in the temperature range 5–300 K. The solid line was obtained from eqn. (1) with  $g = 2.121 \pm 0.004$ ,  $-2J = 835 \pm 5 \text{ cm}^{-1}$ ,  $\rho = 0.03$  and  $N\alpha = 60 \times 10^{-6} \text{ c.g.s. units (cm}^3 \text{ mol}^{-1})/\text{Cu}$ .

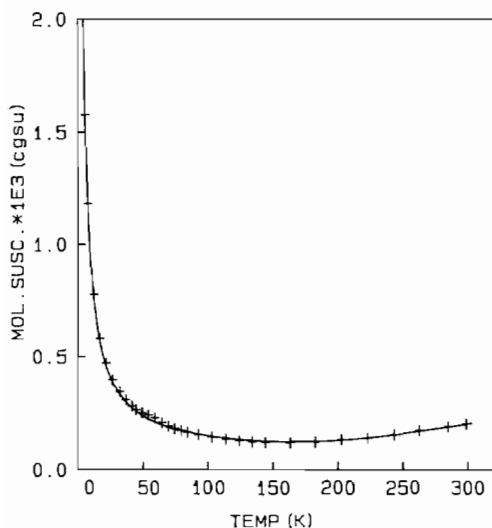


Fig. 5. Magnetic susceptibility data for complex **1c**,  $[\text{Cu}_2\text{L}](\text{ClO}_4)_2$  in the temperature range 5–300 K. The solid line was obtained from eqn. (1) with  $g = 2.154 \pm 0.004$ ,  $-2J = 806 \pm 9 \text{ cm}^{-1}$ ,  $\rho = 0.02$  and  $N\alpha = 60 \times 10^{-6} \text{ c.g.s. units (cm}^3 \text{ mol}^{-1})/\text{Cu}$ .

of the two copper(II) centres in **4** [14]. In this complex a pronounced tetrahedral twist is observed in the equatorial  $\text{CuN}_2\text{O}_2$  framework, which can be associated with the presence of two saturated ring nitrogen donors per metal. The presence of such groups shifts the first reduction potential cathodically (–0.43, –0.58, –0.76 V (Pt/CH<sub>3</sub>CN/TEAP/SCE) for **1a**, **3a**, **4** respectively) indicating a stabilizing effect of the  $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$  species with maximized ligand

unsaturation [14, 15]. Complex **4** exhibits a four-line room temperature ESR spectrum indicating that the tetrahedral distortion at the copper centres does not promote intramolecular electron transfer. Changing the substituent at the 4-position in the benzene ring has little effect on the odd electron exchange, while changing the identity of the bridge between the nitrogen donors (e.g.  $\text{R}^1$ ,  $\text{R}^2$  in **2**) has some effect [13]. In most symmetrically bridged compounds of this series, involving aliphatic bridge groups, seven-line spectra were observed, while with asymmetrically bridged species four-line spectra were observed in two cases out of three. The mixed-valence species derived from the half saturated macrocyclic systems **3a–3c** exhibit four-line spectra and at least in the case of **3a** would be expected to represent a structural intermediate between **1a** and **4**. The presence of one saturated nitrogen per copper is therefore sufficient to destroy the conditions required for room temperature electron delocalization.

Clearly little in the way of trends emerges from the limited examination of these odd electron species with respect to factors that control the delocalization process. It is clear that the degree of pyramidal distortion at an oxygen bridge can dramatically affect the spin-exchange between two Cu(II) centres [20, 21], and that trigonal planar oxygen bridges are the most efficient in terms of antiferromagnetic exchange; severe distortions can, in fact lead to an exchange situation dominated by a ferromagnetic component. Little attention has been paid to the bridge groups, especially the oxygen bridges, that undoubtedly communicate the spin delocalization between the copper(II) and copper(I) centres in the mixed-valence species and until more structural data are available it is clear that only part of this complicated situation is being examined.

Variable temperature magnetic susceptibility measurements were performed on powdered samples of the perchlorate salts of complexes **1b** and **1c** in the temperature range 5–300 K. The results are summarized in Figs. 4 and 5, respectively. The best-fit lines were calculated from the modified Van Vleck equation [22] for exchange-coupled pairs of copper(II) ions (eqn. (1))

$$\chi_{\text{M}} = \frac{N\beta^2 g^2}{3kT} \left[ 1 + \frac{1}{3} \exp(-2J/kT) \right]^{-1} \quad (1)$$

$$(1 - \rho) + \left[ \frac{N\beta^2 g^2}{4kT} \right] \rho + N\alpha$$

In this expression  $-2J$  (in the spin Hamiltonian  $\mathcal{H} = -2J\hat{s}_1\hat{s}_2$ ) is the singlet–triplet splitting or exchange integral and other symbols have their usual meaning.  $\rho$  gives the fraction of a possible magnetically dilute copper(II) impurity. The temperature

independent paramagnetism for a binuclear copper(II) complex,  $N\alpha$ , was taken as  $120 \times 10^{-6}$  c.g.s. units/mol. The parameters giving the best-fit were obtained by a non-linear regression analysis with  $\rho$  as a floating parameter. The singlet-triplet separation ( $-2J$ ) for **1b** was found to be  $835 \pm 5 \text{ cm}^{-1}$  ( $g = 2.121 \pm 0.004$ ,  $\rho = 0.03$ ) and for **1c** was found to be  $806 \pm 9 \text{ cm}^{-1}$  ( $g = 2.154 \pm 0.004$ ,  $\rho = 0.02$ ) indicating very strong exchange between the copper(II) centers in both cases.

Few variable temperature magnetic studies have been carried out on systems of this sort. The dichloro analogue of **1a**,  $[\text{Cu}_2\text{LCl}_2] \cdot 6\text{H}_2\text{O}$  is strongly antiferromagnetically coupled ( $-2J = 588 \text{ cm}^{-1}$ ) [16] and involves two square-pyramidal copper(II) centres with apically bound chlorine atoms [23]. The copper atoms are displaced by 0.21 Å from the  $\text{N}_2\text{O}_2$  basal plane, separated by 3.133 Å and involve a phenoxide bridge angle of  $104.5^\circ$ . Compound **4**, which involves the fully saturated macrocyclic ligand, is much more strongly coupled ( $-2J = 824 \pm 5 \text{ cm}^{-1}$ ). In this system the copper(II) atoms are in distorted six-coordinate environments with very long axial interactions with bidentate perchlorates and although there is a pronounced tetrahedral distortion in the equatorial  $\text{CuN}_2\text{O}_2$  plane the copper atom lies in the mean plane of the four donors [15]. A copper-copper separation of 2.993(2) Å and a Cu-O-Cu angle of  $102.8(2)^\circ$  are found in this case. Low room temperature magnetic moments ( $\mu_{\text{eff}}$ ) are observed for most complexes of this sort involving essentially planar copper(II) centres bridged by two phenoxide oxygen atoms. However few X-ray determinations have documented the structural features which are likely to influence magnetic exchange and so magneto-structural correlations, which have been successful with other oxygen bridged dicopper systems [24, 25] and show dominant magnetic trends based on oxygen bridge angles, cannot be made with the limited data available on the macrocyclic complexes.

Complexes **1a** and **3a** have room temperature magnetic moments (**1a**  $\mu_{\text{eff}} = 0.58 \text{ BM}$  [26],  $0.60 \text{ BM}$  [11]; **3a**  $\mu_{\text{eff}} = 0.60 \text{ BM}$  [18]) which are slightly larger than **4** ( $\mu_{\text{eff}} = 0.51 \text{ BM}$  [14]). It seems reasonable to assume, therefore, that the antiferromagnetic exchange in these systems is slightly weaker than in **4**, although variable temperature magnetic data are necessary to prove this point. The differences in magnetic moments for these systems has been discussed in terms of an influence of the unsaturated azomethine centres in **1a** and **3a** on the electron density in the copper magnetic orbitals [14]. However in view of the small differences in the magnetic moments, little can be said in this regard. Room temperature moments for **1b** and **1c** ( $0.51 \text{ BM}$  (298.1 K),  $0.58 \text{ BM}$  (289.6 K) respectively) are comparable with **1a**, **3a** and **4** and the exchange integrals for

these systems ( $-2J = 835 \pm 5 \text{ cm}^{-1}$ ,  $-2J = 806 \pm 9 \text{ cm}^{-1}$  respectively) are comparable with that observed for **4** indicating strong antiferromagnetic exchange in all cases.

The marked difference in exchange integral between  $[\text{Cu}_2\text{LCl}_2] \cdot 6\text{H}_2\text{O}$  (**1a** analogue) and compounds **1b**, **1c** and **4** cannot be rationalized in terms of major differences in the binuclear framework ( $\text{Cu}_2\text{N}_4\text{O}_2$ ) since this is likely to be similar in all cases. Pyramidal distortions at oxygen bridges have been shown to dramatically affect magnetic exchange interactions [20, 21], but in the case of  $[\text{Cu}_2\text{LCl}_2] \cdot 6\text{H}_2\text{O}$  (oxygen solid angle =  $357.4^\circ$  [23]) and **4** (oxygen solid angle =  $360.0^\circ$  [14]) this seems unlikely to be a factor. Out of plane distortion of the copper centres will lead to some reduction in  $\sigma$  overlap between the copper  $d_{x^2-y^2}$  magnetic orbitals and the oxygen bridge but the effect is likely to be small [27]. We are thus left with the alternative that the presence of transaxial chlorines in  $[\text{Cu}_2\text{LCl}_2] \cdot 6\text{H}_2\text{O}$  appears to exert an electron withdrawing effect on the electron density in the copper magnetic orbitals, thus effectively reducing exchange, an effect which has been observed in other strongly coupled systems involving orthogonally bound terminal halogens [25].

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