Synthesis, Electrochemical and Magnetic Properties of a Series of New Unsymmetrical Macrocyclic Binuclear Copper(II) Complexes

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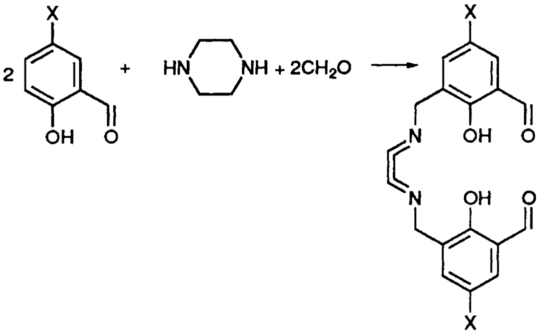
A series of binuclear macrocyclic copper(II) complexes $[Cu_2L][ClO_4]_2$ have been prepared in which the two copper(II) ions are placed in two geometrically distinct co-ordination environments, comprising saturated and unsaturated nitrogen-donor sets. Cyclic voltammetry has revealed two reduction couples, $Cu^{II}Cu^{II} \longrightarrow Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} \longrightarrow Cu^{I}Cu^{I}$. The first is sensitive to the macrocyclic structure as well as to electronic effects of the substituents at the aromatic ring of the ligand system, shifting to positive potentials as the macrocycle size increases. The comproportionation constants K_{com} for the mixed-valence $Cu^{I}Cu^{II}$ complexes have been determined electrochemically. Cryomagnetic investigations (80–300 K) reveal a weak antiferromagnetic spin exchange between the copper(II) ions within each complex ($J = -85$ to -195 cm^{-1}).

The chemistry of binucleating ligands having dissimilar co-ordination environments is of recent interest to bioinorganic chemists. Metal complexes derived from these ligands may serve as suitable models for the active sites of some biologically important metalloenzymes such as tyrosinase,[1] haemocyanin[2] and bovine erythrocyte superoxide dismutase,[3] and can be used to investigate the mutual influence of two metal centres in terms of their co-operative effect on the electronic, magnetic and redox properties of such enzymes. Since the pioneering work of Robson[4] on the synthesis of binucleating ligands, a number of symmetrical macrocyclic metal complexes have been synthesised and their properties studied.[5–11] The influence of the co-ordination geometry and the ring size of the binucleating ligands on the redox and magnetic properties of the interacting metal ions has been well investigated.[7,10b,12,13] Recent works on unsymmetrical binucleating ligands have dealt mainly with acyclic compounds having different exogenous bridging units.[14] However, studies on macrocyclic ligands having dissimilar co-ordination environments are sparse, being confined to (*i*) variations in the size of the co-ordination cavity and (*ii*) the nature of the C–N bond.[6,7,13a,15,16]

The desire to have two metal centres of different co-ordination geometries in a single molecule has prompted us to synthesise a macrocyclic ligand in which the saturated and unsaturated nitrogen-donor sets are available for co-ordination from two separate compartments. It is not unreasonable to expect that the compartments consisting of unsaturated and saturated nitrogen-donor atoms may provide, respectively, a nearly coplanar and a distorted geometry for the metal ions (depending on the flexible nature of the carbon–nitrogen bond). One more advantage of this ligand type is that the size of a particular co-ordination site can be varied, by choosing appropriate diamines, keeping the size of the other compartment fixed.

The precursor compound **I** was synthesised by the introduction of two molecules of 4-substituted 2-formylphenol at the 1 and 4 positions of a piperazine molecule by an acid-mediated Mannich reaction as outlined in Scheme 1. Binuclear copper(II) complexes were obtained by template condensation of appropriate diamines with **I** (Scheme 2).



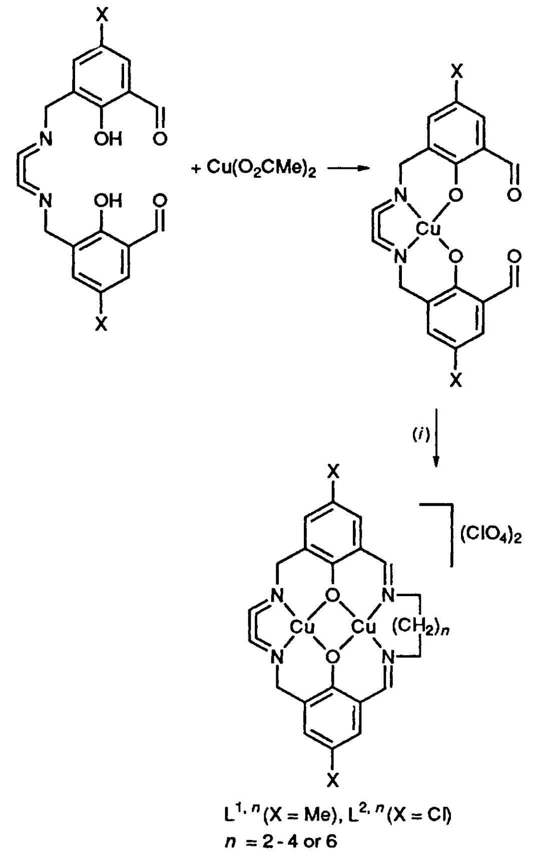
I X = Me
II X = Cl

Scheme 1

Experimental

Physical Measurements.—Elemental analyses for C, H, N and Cu and the ^1H NMR and mass spectra were obtained from the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras. Infrared spectra were recorded for KBr discs on a Shimadzu IR-408 spectrometer, electronic spectra on a Hitachi-320 spectrophotometer. Magnetic susceptibilities of powder samples were measured in the temperature range 80–300 K on a PAR model 155 vibrating-sample magnetometer. The apparatus was calibrated by the use of Ni. The effective magnetic moment was calculated from the expression $\mu_{Cu} = 2.828(\chi_{Cu}T)^{\frac{1}{2}}$, where χ_{Cu} is the molar magnetic susceptibility per Cu corrected for diamagnetism. Cyclic voltammograms were recorded on apparatus comprising a PARC-175 universal programmer, model 176 current-to-voltage converter and model 179 coulomb/ampere hour meter (EG&G Ltd.).

Materials.—Tetrabutylammonium perchlorate used as the supporting electrolyte in electrochemical measurements was obtained from Fluka and recrystallised from hot water. Acetonitrile (HPLC grade) was obtained from SD Fine Chemicals, and dimethylformamide (dmf) was dried by distillation from CaH_2 and stored over molecular sieves.



Scheme 2 (*i*) $Cu(ClO_4)_2$, $H_2N(CH_2)_nNH_2$

4-Substituted 2-formylphenols were synthesised by the literature method.[17] All other chemicals and solvents were of reagent grade and used as received.

Preparation of the Precursor Compounds **I** *and* **II**.—A mixture of piperazine (4.3 g, 0.05 mol), paraformaldehyde (3.2 g, 0.1 mol) and the 4-substituted 2-formylphenol (X = Me, 13.6 g, 0.1 mol; X = Cl, 15.65 g, 0.1 mol) in ethanol–acetic acid (40 : 10 v/v, 200 cm^3) was stirred for 6 h at 50 °C. It was then cooled to room temperature and neutralised with solid Na_2CO_3 (9.25 g). Ethanol was removed by distillation under reduced pressure and the residue was extracted with $CHCl_3$ (3 × 50 cm^3 portions). Removal of chloroform by distillation yielded a pale yellow crystalline solid, which was further purified by silica gel column chromatography using chloroform–light petroleum (b.p. 60–80 °C) (30 : 70 v/v) as the eluent. The pure compound was eluted by chloroform and the solvent evaporated. Compound **I**: yield 25 g (65%) (Found: C, 69.15; H, 6.75; N, 7.40. Calc. for $C_{22}H_{26}N_2O_4$: C, 69.10; H, 6.80; N, 7.30%); mass spectrum, *m*/*z* 383; ^1H NMR in $CDCl_3$, δ 2.2 (s, 6 H, CH_3), 2.45 (m, 8 H, piperazine CH_2), 3.5 (s, 4 H, benzyl CH_2), 6.85, 7.1 (d, 4 H, aromatic CH) and 9.85 (s, 2 H, CHO); IR (KBr disc) 2940–2840 (NCH_2), 1675–1650 (CHO) and 1450 cm^{-1} (aromatic skeleton); an X-ray crystallographic study has also been carried out.[17b] Compound **II**: yield 18 g (42%) (Found: C, 56.75; H, 4.75; N, 6.60. Calc. for $C_{20}H_{20}Cl_2N_2O_4$: C, 56.70; H, 4.75; N, 6.65); ^1H NMR in $CDCl_3$, δ 2.55 (m, 8 H, piperazine CH_2), 3.55 (s, 4 H, benzyl CH_2), 7.1, 7.3 (d, 4 H, aromatic CH) and 9.85 (s, 2 H, CHO); IR (KBr disc) 2940–2840 (NCH_2), 1675–1650 (CHO) and 1450 cm^{-1} (aromatic skeleton).

Preparation of the Complexes.—The binuclear copper complexes were prepared from the respective precursor compound **I** or **II** in a stepwise procedure. For example, **I** and copper acetate (1 : 1 molar ratio) in chloroform–methanol (30 : 70, v/v) were refluxed to obtain the mononuclear complex, and subsequently Schiff-base condensation of the formyl groups with a diamine in the presence of a copper(II) salt was effected (template condensation, Scheme 2).

$[Cu_2L^{1,2}][ClO_4]_2\cdot H_2O$ **1a**. To a boiling solution of compound **I** (3.82 g, 0.01 mol) in chloroform–methanol (30 : 70 v/v, 100 cm^3) was added copper(II) acetate monohydrate (2 g, 0.01 mol) dissolved in methanol (15 cm^3) and the mixture was refluxed for 30 min. The precipitate formed was subsequently treated with a mixture of ethylenediamine (0.6 g, 0.01 mol) and copper(II) perchlorate hexahydrate (5.6 g, 0.015 mol) in methanol (10 cm^3) and refluxed for 2 h. During the course of reflux all the solid mononuclear complex dissolved and a homogeneous solution resulted. After cooling to room temperature, the solution was filtered and the filtrate allowed to evaporate at room temperature. The dark brown precipitate formed was filtered off, washed with cold methanol and vacuum dried, yield 5.5 g (74%) (Found: C, 38.30; H, 4.00; Cu, 16.85; N, 7.35. Calc. for $C_{24}H_{28}Cl_2Cu_2N_4O_{10}\cdot H_2O$: C, 38.50; H, 4.00; Cu, 17.00; N, 7.50%).

$[Cu_2L^{2,2}][ClO_4]_2\cdot 1.5EtOH$ **1b**. This complex was prepared as for **1a** using compound **II** (4.23 g, 0.01 mol) instead of **I**. The reaction was carried out in chloroform–ethanol (30 : 70 v/v, 150 cm^3), yield 6.1 g (75%) (Found: C, 34.10; H, 3.45; Cu, 15.80; N, 7.00. Calc. for $C_{20}H_{18}Cl_4Cu_2N_4O_{10}\cdot 1.5C_2H_5OH$: C, 34.05; H, 3.35; Cu, 15.70; N, 6.90%).

$[Cu_2L^{1,3}][ClO_4]_2\cdot 3H_2O$ **2a**. This complex was prepared by the reaction of compound **I** (3.82 g, 0.01 mol), copper acetate monohydrate (2 g, 0.01 mol), 1,3-diaminopropane (0.74 g, 0.01 mol) and copper perchlorate hexahydrate (5.6 g, 0.015 mol) in chloroform–methanol (30:70 v/v, 200 cm^3), yield 6 g (75%) (Found: C, 37.10; H, 4.40; Cu, 16.00; N, 6.95. Calc. for $C_{25}H_{30}Cl_2Cu_2N_4O_{10}\cdot 3H_2O$: C, 37.60; H, 4.50; Cu, 15.90; N, 7.00%).

$[Cu_2L^{2,3}][ClO_4]_2\cdot EtOH$ **2b**. This complex was prepared by the method used for **2a**, using compound **II** (4.23 g, 0.01 mol) in place of **I**, dissolved in chloroform–ethanol (30:70 v/v, 150 cm^3), yield 6.3 g (86%) (Found: C, 34.55; H, 3.30; Cu, 15.95; N, 7.05. Calc. for $C_{21}H_{20}Cl_4Cu_2N_4O_{10}\cdot C_2H_5OH$: C, 34.45; H, 3.25; Cu, 15.85; N, 7.00%).

$[Cu_2L^{1,4}][ClO_4]_2\cdot 4H_2O$ **3a**. This complex was prepared by the reaction of compound **I** (3.82 g, 0.01 mol), copper acetate monohydrate (2 g, 0.01 mol), 1,4-diaminobutane (0.88 g, 0.01 mol) and copper perchlorate hexahydrate (5.6 g, 0.015 mol) in chloroform–methanol (30 : 70 v/v, 200 cm^3), yield 6.9 g (83%) (Found: C, 37.30; H, 4.55; Cu, 15.15; N, 6.75. Calc. for $C_{26}H_{32}Cl_2Cu_2N_4O_{10}\cdot 4H_2O$: C, 37.60; H, 4.80; Cu, 15.30; N, 6.75%).

$[Cu_2L^{2,4}][ClO_4]_2\cdot H_2O$ **3b**. This complex was prepared by the method used for **3a**, with compound **II** (4.23 g, 0.01 mol) in place of **I**, yield 6.5 g (82%) (Found: C, 33.60; H, 3.10; Cu, 16.25; N, 7.20. Calc. for $C_{22}H_{22}Cl_4Cu_2N_4O_{10}\cdot H_2O$: C, 33.55; H, 3.05; Cu, 16.15; N, 7.10%).

$[Cu_2L^{1,6}][ClO_4]_2\cdot 4H_2O$ **4a**. This complex was prepared by the reaction of compound **I** (3.82 g, 0.01 mol), copper acetate monohydrate (2 g, 0.01 mol), 1,6-diaminohexane (1.16 g, 0.01 mol) and copper perchlorate hexahydrate (5.6 g, 0.015 mol) in chloroform–methanol (30 : 70 v/v, 250 cm^3), yield 7.2 g (84%) (Found: C, 39.25; H, 5.20; Cu, 14.90; N, 6.60. Calc. for $C_{28}H_{36}Cl_2Cu_2N_4O_{10}\cdot 4H_2O$: C, 39.15; H, 5.15; Cu, 14.80; N, 6.55%).

Results and Discussion

Preparation of the Complexes.—The reaction of copper(II) acetate and **I** in 1 : 1 molar ratio leads to the precipitation of a monomeric neutral complex, in which the two formyl groups are at a favourable distance for further condensation with another mole of alkanediamine and a copper(II) salt. Since the incorporation of a second copper(II) ion leads to the formation of a soluble dicationic complex, a homogeneous solution of the binuclear complex was obtained on reflux.

Spectral and Magnetic Studies.—The Schiff-base formation was evident from the C=N stretching vibration frequency observed at 1610 cm^{-1} which is lower than the C=O frequency (at 1675–1650 cm^{-1}) observed for the precursor **I**. The ν_3 vibration of the unco-ordinated perchlorate anion appears as a single band around 1100 cm^{-1}. A broad band around 3400 cm^{-1} suggests the presence of lattice water.

The electronic spectra of complexes **1**–**4** were measured in methanol and the data are summarised in Table 1. All the complexes exhibit d–d transitions in the 580–610 nm region. It may be noted that these λ_{max} values are observed[6b,12,15b] at relatively lower energies compared to analogous symmetrical binuclear copper(II) complexes, in which the metal ions are in planar environments.[18] The moderately intense band observed in the near-UV region is due to the overlap of the transition of the azomethine with the charge-transfer band from bridging phenolic oxygen to the vacant d orbital of the Cu^{II}.[16b]

Cyclic Voltammetry.—The electrochemical properties of complexes **1**–**4** were studied by cyclic voltammetry. The cyclic voltammogram of **3a** recorded in dmf is given in Fig. 1. The electrochemical data are summarised in Table 2.

The electrochemical behaviour in the negative potential range is sensitive to the macrocyclic structure and the electron-inductive (+I or −I) nature of the substituents at the *para* positions of the benzene rings. For all the complexes two quasi-reversible waves were observed. Coulometric experiments indicated that each of the couples is involved in a one-electron transfer process. Therefore it is reasonable to assign the two waves to successive one-electron reductions at the metal centres, $Cu^{II}Cu^{II} \longrightarrow Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I} \longrightarrow Cu^{I}Cu^{I}$. From Table 2 it is seen that the first reduction potential shifts anodically as the size of the macrocycle increases ($L^{1,2}$ to $L^{1,6}$ and $L^{2,2}$ to $L^{2,4}$). This behaviour is consistent with a previously reported observation.[16b] It is important to note that the replacement of a relatively electron-releasing methyl group (**2a** and **3a**) by an electron-withdrawing chlorine atom (**2b** and **3b**) shifts the first reduction to more positive potentials. A similar trend has been reported by Lacroix *et al.*[19] For complexes **1**–**4** no oxidation wave was observed at positive potentials.

The stability of the mixed-valence $Cu^{I}Cu^{II}$ complexes is expressed by the comproportionation constant K_{com} for equilibrium (1). The K_{com} values of **2a**, **2b**, **3a** and **3b** have been

$$[Cu^{II}Cu^{II}] + [Cu^{I}Cu^{I}] \rightleftharpoons 2[Cu^{I}Cu^{II}] \qquad (1)$$

determined electrochemically using the equation $\log K_{com} = E_{\frac{1}{2}}/0.0591$ (at 25 °C), where $E_{\frac{1}{2}} = E^1_{\frac{1}{2}} - E^2_{\frac{1}{2}}$.[13c] From Table 2 it is evident that K_{com} increases with increasing macrocycle size $(L^{1,3})^{2-} < (L^{1,4})^{2-}$. Also that (on the basis of K_{com} values) an electron-withdrawing substituent at the aromatic ring of the ligand system relatively destabilises the mixed-valence $Cu^{I}Cu^{II}$ state (K_{com} of **2a** > **2b** and **3a** > **3b**). At negative potentials (−1.3 to −1.5 V) the $Cu^{I}Cu^{I}$ species undergoes further reduction and copper metal is deposited on the electrode; the corresponding stripping peak is observed at +0.15 V. Coulometric experiments conducted at −1.5 V confirm the consumption of four electrons per molecule. This demetallation process was not usually observed for the analogous unsaturated symmetrical macrocyclic complexes.[10b]

The magnetic susceptibilities of complexes **1a**, **1b** and **3a** were measured in the temperature range 80–300 K. Analyses were

Table 1 Electronic spectral data for complexes **1**–**4** (in methanol)

Complex		λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	
		c.t.	d–d
1a	$[Cu_2L^{1,2}][ClO_4]_2 \cdot H_2O$	342 (7200), 262 (22 200), 247 (32 066)	586 (412)
1b	$[Cu_2L^{2,2}][ClO_4]_2 \cdot 1.5EtOH$	345 (6676), 265 (21 812), 247 (32 422)	590 (430)
2a	$[Cu_2L^{1,3}][ClO_4]_2 \cdot 3H_2O$	340 (6792), 265 (18 812), 242 (27 285)	592 (267)
2b	$[Cu_2L^{2,3}][ClO_4]_2 \cdot EtOH$	345 (7012), 265 (19 157), 243 (27 044)	595 (230)
3a	$[Cu_2L^{1,4}][ClO_4]_2 \cdot 4H_2O$	342 (9383), 270 (26 102), 240 (36 414)	600 (376)
3b	$[Cu_2L^{2,4}][ClO_4]_2 \cdot H_2O$	345 (6980), 265 (28 345), 242 (35 286)	605 (368)
4a	$[Cu_2L^{1,6}][ClO_4]_2 \cdot 4H_2O$	350 (6385), 268 (24 534), 248 (33 567)	610 (395)

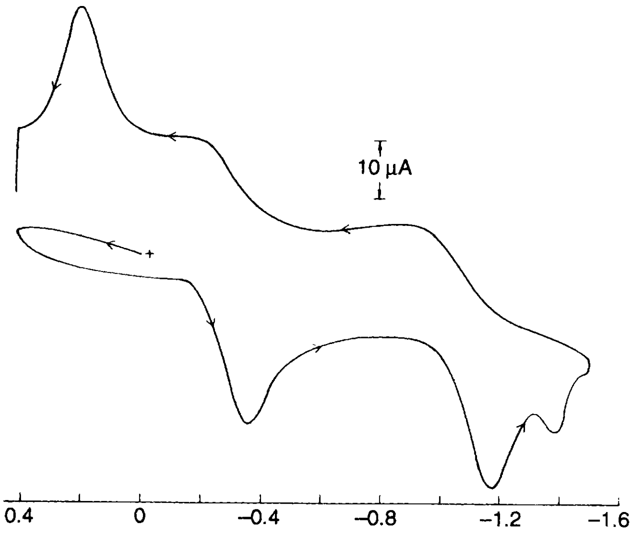


Fig. 1 Cyclic voltammogram of complex **3a**: platinum electrodes, scan rate 100 mV s^{-1}, in dmf

Table 2 Electrochemical data[a] on the reduction of complexes **1**–**4** and their comproportionation constants

Complex	E^1_{pc}	E^1_{pa}	$E^1_{\frac{1}{2}}(\Delta E_p)$	E^2_{pc}	E^2_{pa}	$E^2_{\frac{1}{2}}(\Delta E_p)$	K_{com}[b]
1a	−0.75	*c*	—	−1.05	*c*	—	. . .
1b	−0.65	*c*	—	−1.02	*c*	—	. . .
2a	−0.7	−0.55	−0.63 (150)	−1.26	−1.13	−1.2 (130)	4.4×10^9
2b	−0.53	−0.45	−0.49 (80)	−1.08	−0.97	−1.03 (110)	1.1×10^9
3a	−0.38	−0.18	−0.28 (200)	−1.2	−0.92	−1.1 (280)	7.5×10^{13}
3b	−0.21	−0.08	−0.15 (250)	−0.95	−0.7	−0.83 (250)	3.2×10^{11}
4a	−0.26	ir	—	−0.98	ir	—	. . .

[a] Potentials are given in V *vs.* saturated calomel electrode (SCE); $\Delta E_p = E_{pc} - E_{pa}$ in mV; ir = irreversible. [b] Ref. 13(*c*). [c] Only one anodic wave was observed, at −0.75 V.

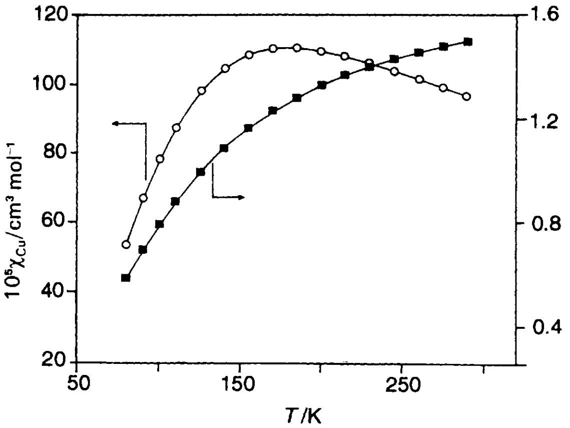


Fig. 2 Plots of χ_{Cu} *vs.* T and μ_{Cu} *vs.* T for $[Cu_2L^{1,4}][ClO_4]_2$ **3a**. Solid lines are based on the Bleaney–Bowers equation given in the text, with $J = -100$ cm^{-1}, $g = 2.003$, $N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} and $p = 0.1$

Table 3 Magnetic data

Complex	μ_{eff} per Cu/μ_B 80 K	μ_{eff} per Cu/μ_B 290 K	J/cm^{-1}	g	p
1a	0.74	1.58	−85	2.042	0
1b	0.73	1.55	−85	2.006	0
2a	0.58	1.49	−195	2.08	0
3a	0.59	1.50	−100	2.003	0.1

Value of N_α was fixed at 60×10^{-6} cm^3 mol^{-1} for all magnetic simulations.

carried out using the Bleaney–Bowers equation[20] (2) where p is

$$\chi_{Cu} = (Ng^2\beta^2/kT)\,[3 + \exp(-2J/kT)]^{-1}\,(1 - p) + N_\alpha \quad (2)$$

the fraction of monomeric impurity and χ_{Cu} is the magnetic susceptibility per Cu. Fig. 2 shows plots of χ_{Cu} *vs.* T and μ_{Cu} *vs.* T for **3a**. Good magnetic simulation was obtained using $J = -100$ cm^{-1}, $g = 2.003$, and $N_\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1}. The magnetic parameters are summarised in Table 3. The value of the observed magnetic exchange integral, $-J$, is considerably lower compared to those of analogous symmetrical macrocyclic complexes.[16b] Owing to the lack of complete structural information (because of the amorphous nature of the complexes, attempts to grow an X-ray-quality crystal were unsuccessful) it is reasonable that the lowering of J is due to the geometrical distortion around the Cu^{II} co-ordinated to the piperazine nitrogen when compared to the Cu^{II} co-ordinated to the unsaturated imine nitrogen, which will otherwise favour coplanar geometry. An increase in the alkyl chain length of one compartment effects a change in the dihedral angle of the alkyl linkage at the other compartment,[12] and hence alters the geometry of the piperazine-co-ordinated copper(II) ion. Recent studies[5,16b,21–23] on magnetostructural correlations in binuclear metal complexes have revealed that the deviation from coplanarity of each metal co-ordination environment reduces the effective overlap of the metal orbitals with those of the bridging ligand, and hence reduces the antiferromagnetic spin exchange between the metal centres. Low J values have been reported for complexes[5,15b] in which the metal co-ordination environment is distorted. It is interesting that for complexes **1a** and **1b**, which have comparable macrocyclic structures, the magnetic properties are essentially the same ($J = -85$ cm^{-1}) indicating that the electron-withdrawing chlorine atom does not influence magnetic exchange significantly, despite the fact that the metal-centred electrochemical reductions are shifted to more positive potentials for the chloroderivative (see Table 2). A very similar behaviour has been reported.[19,24]

Acknowledgements

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