Synthesis, Electrochemical and Magnetic Properties of New Acyclic 'Side-off' Binuclear Copper(II) Complexes†

Sambandhan Karunakaran and Muthuswamy Kandaswamy*
Department of Inorganic Chemistry, University of Madras, Guindy Campus, Madras-600 025, India

Binuclear copper(II) complexes $[Cu_2L][ClO_4]_2$ of acyclic 'side-off' ligands H_2L capable of providing two distinct co-ordination geometries to the metal centres have been synthesised. Cyclic voltammetric investigation of these complexes revealed that the reduction process involves two successive irreversible one-electron transfer steps at different potentials. Complexes $[Cu_2LX_2]$ (X = Cl or Br) containing halide as the counter ion were reduced relatively at more positive potentials than the corresponding perchlorate complexes. Cryomagnetic investigations reveal a weak antiferromagnetic spin exchange between the copper(II) ions within the complexes ($J = -35$ to -75 cm^{-1}). The redox and magnetic exchange properties of the complexes are found to be sensitive toward the structural variations of the ligand systems.

Continuing interest in the design and synthesis of various types of binucleating ligands is mainly due to their potential application as models for dinuclear metallobiosites.[1,2] In copper proteins the active sites effect a variety of reactions with dioxygen including reversible binding (haemocyanin),[3] activation (tyrosinase)[4] and reduction (laccase).[5] With few exceptions,[1,6,7] most ligand systems so far prepared for mimicking the properties of these bioactive sites have provided identical donor environments to the metal centres. However, in binuclear transition-metal biosites the metal ions are often found in chemically or geometrically distinct environments. For example, the unsymmetrical nature of the dicopper site in haemocyanin is demonstrated in the crystal structure of deoxyhaemocyanin[8] and sequence homology studies on tyrosinases have shown that whilst one of the copper sites has been highly conserved throughout evolution, the structure of the second copper site has been quite variable. For most of the tyrosinases, three histidines are suitably positioned to co-ordinate each of the copper ions, but for a few cases Cu_B is apparently only co-ordinated to two histidines and this latter observation led to the suggestion that for modelling studies, unsymmetrical binucleating 'end-off'[2a] and 'side-off'[2b] ligands should be viewed as desirable targets.

In our previous report[9a] we have indicated how the redox and magnetic exchange properties of the metal centres have been affected by the structural dissimilarity that arises due to the saturated and unsaturated sets of donor atoms of the co-ordination compartments in a single macrocyclic ligand system (Fig. 1, structure **I**). In this investigation our interest focusses on the differences in the properties of the complexes that may arise due to different constraints and accessibilities of the metal sites imposed by the ligand system. To serve this purpose, acyclic 'side-off' ligands have been synthesised (Fig. 1, structures **IIA** and **IIB**). These differ in that in **IIA** the imine nitrogen atoms are not linked to each other by an alkyl linkage, while the saturated nitrogens are linked to each other, whereas in structures **IIB** the situation is reversed. The consequence of these structural differences on the electrochemical and magnetic properties of the binuclear copper(II) complexes of these ligands are investigated herein.

† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Experimental

Physical Measurements.—Elemental analysis 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. The positive-ion fast atom bombardment (FAB) mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer. The matrix solvent used was 3-nitrobenzyl alcohol unless otherwise stated. IR spectra were recorded on a Schimadzu IR-408 spectrometer on KBr discs. Electronic spectra were recorded on a Hitachi-320 spectrophotometer. Magnetic susceptibilities of powder samples were measured in the temperature range 80–300 K on a PAR vibrating sample magnetometer model-155. The apparatus was calibrated by the use of Ni. The effective magnetic moment was calculated using the relation $\mu_{Cu} = 2.828\ (\chi_{Cu}T)^{\frac{1}{2}}$, where χ_{Cu} is the molar magnetic susceptibility per Cu corrected for diamagnetism. Cyclic voltammograms were recorded on an apparatus comprising of a PAR-175 Universal programmer, model-176 current to voltage convertor and model-179 Coulomb/amperehour meter (EG & G).

Materials.—Tetrabutylammonium perchlorate used as the supporting electrolyte in electrochemical measurements was purchased 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. 2-hydroxy-4-methylbenzaldehyde was synthesised by a literature method.[10] All other chemicals and solvents were of reagent grade and were used as received.

Synthesis of the Precursor Compounds.—The precursor compound **III** used for the synthesis of macrocyclic and acyclic 'side-off' (**IIA**) binuclear copper(II) complexes was prepared by a reported procedure.[9]

The precursor compound **IV** was synthesised by reaction of a mixture of piperidine (8.5 g, 0.1 mol), paraformaldehyde (3.3 g, 0.11 mol) and 2-hydroxy-4-methylbenzaldehyde (13.6 g, 0.1 mol) in ethanol–acetic acid (200 cm^3, 40:10 v/v). The reaction mixture was stirred for 6 h at 50 °C, and neutralised with solid sodium carbonate (9.25 g) after cooling to room temperature. Ethanol was removed by distillation under reduced pressure and the residue was extracted with chloroform (3 × 50 cm^3). The pale yellow solid was recovered after removing the solvent by distillation. Yield 18 g (78%), m.p. 165 °C (Found: C, 72.20;

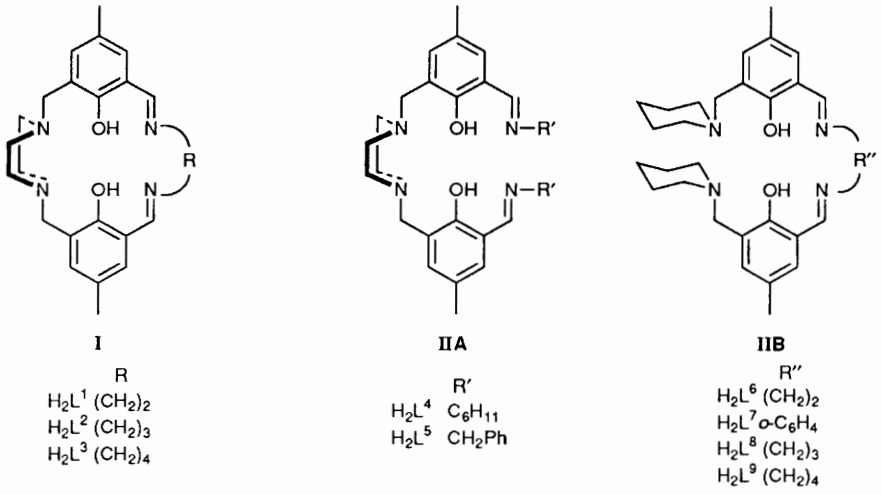
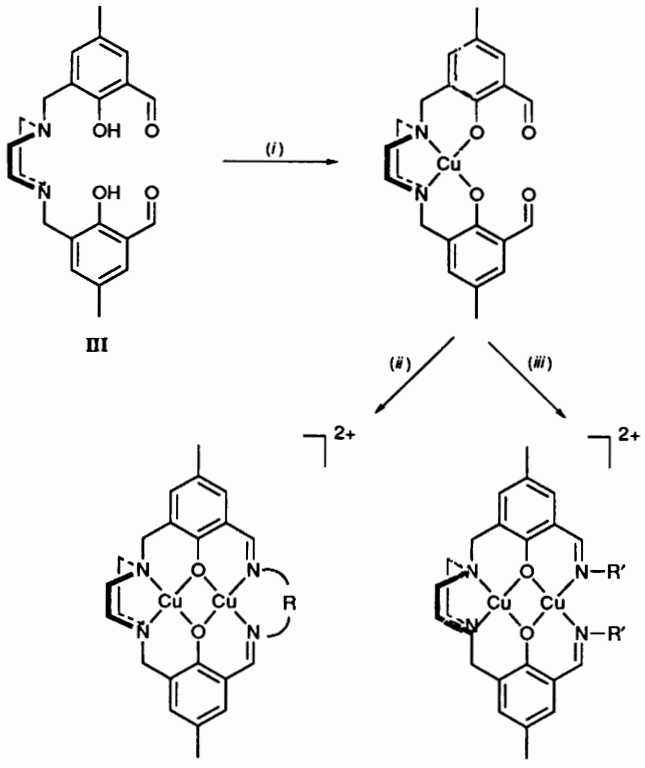


Fig. 1 Schematic diagrams of macrocyclic (**I**) and acyclic 'side-off' (**IIA** and **IIB**) binucleating ligands



Scheme 1 (*i*) $Cu(O_2CMe)_2$; (*ii*) H_2NRNH_2–Cu^{2+}; (*iii*) $2NH_2R'$–Cu^{2+}. R,R' as in Fig. 1

H, 8.20; N, 6.10. Calc. for $C_{14}H_{19}NO_2$: C, 72.10; H, 8.15; N, 6.00%); mass spectrum, *m/z* 234; ^{1}H NMR ($CDCl_3$), δ 1.6–2.1 (m, 6 H, piperidine CH_2), 2.35 (s, 3 H, CH_3), 3.3 (m, 4 H, piperidine NCH_2), 4.3 (s, 2 H, benzyl CH_2), 7.5, 8.1 (d, 2 H, aromatic CH) and 10.0 (s, H, CHO); IR (KBr disc) 2945–2840 (NCH_2), 1670–1655 (CHO) and 1450 cm^{-1} (aromatic skeleton).

Synthesis of the Complexes.—The binuclear copper(II) complexes of macrocyclic (H_2L^1–H_2L^3, **I**) and 'side-off' ligands (H_2L^4 and H_2L^5, **IIA**) were synthesised according to the reported procedure[9] by treating the precursor **III** with, respectively, the appropriate diamine or primary amines and copper(II) salts in stoichiometric amounts (Scheme 1).

$[Cu_2L^2Cl_2]$·2EtOH **3**. Compound **III** (3.82 g, 0.01 mol) was dissolved in boiling ethanol–chloroform (100 cm^3, 20:80, v/v) to which was added a solution of copper(II) acetate monohydrate (2 g, 0.01 mol) in ethanol (15 cm^3) and the mixture was refluxed for 30 min. The precipitate formed was subsequently treated with a mixture of 1,3-diaminopropane (0.74 g, 0.01 mol) and copper(II) chloride (1.70 g, 0.01 mol) in ethanol (30 cm^3) and refluxed for 2 h. The filtered solution was allowed to evaporate at room temperature, the precipitate formed was collected by filtration, washed with ethanol and dried *in vacuo* (Found: C, 49.20; H, 5.15; Cu, 18.00; N, 7.95. Calc. for $C_{25}H_{30}Cl_2Cu_2N_4O_2$·2EtOH: C, 49.15; H, 5.10, Cu, 17.95; N, 7.90%).

$[Cu_2L^4][ClO_4]_2$·2EtOH **5**. This complex was prepared by the reaction of compound **III** (3.82 g, 0.01 mol), copper acetate monohydrate (2 g, 0.01 mol), cyclohexylamine (2 g, 0.02 mol) and copper perchlorate hexahydrate (5.6 g, 0.015 mol) in chloroform–ethanol (200 cm^3, 30:70, v/v) (Found: C, 47.70; H, 6.20; Cu, 13.35; N, 5.85. Calc. for $C_{34}H_{46}Cl_2Cu_2N_4O_{10}$·2EtOH: C, 47.50; H, 6.05, Cu, 13.25; N, 5.85%).

$[Cu_2L^4Cl_2]$·$3H_2O$ **6**. This complex was prepared as for **5** using copper(II) chloride dihydrate (1.7 g, 0.01 mol) instead of $Cu(ClO_4)_2$ in methanol–chloroform (Found: C, 51.50; H, 6.60; Cu, 16.05; N, 7.15. Calc. for $C_{34}H_{46}Cl_2Cu_2N_4O_2$·$3H_2O$: C, 51.40; H, 6.55, Cu, 16.00; N, 7.05%).

$[Cu_2L^5Cl_2]$·$5H_2O$ **7**. This complex was prepared as for **6** using benzylamine (1.07 g, 0.01 mol) in the place of cyclohexylamine (Found: C, 51.15; H, 5.60; Cu, 15.15; N, 6.50. Calc. for $C_{36}H_{38}Cl_2Cu_2N_4O_2$·$5H_2O$: C, 51.05; H, 5.70, Cu, 15.00; N, 6.60%).

The 'side-off' ligands (H_2L^6–H_2L^9; **IIB**) were synthesised *in situ* by the Shiff-base condensation reaction of an appropriate diamine with the precursor compound **IV** in 1:2 molar ratio and subsequently used for complex preparations (Scheme 2).

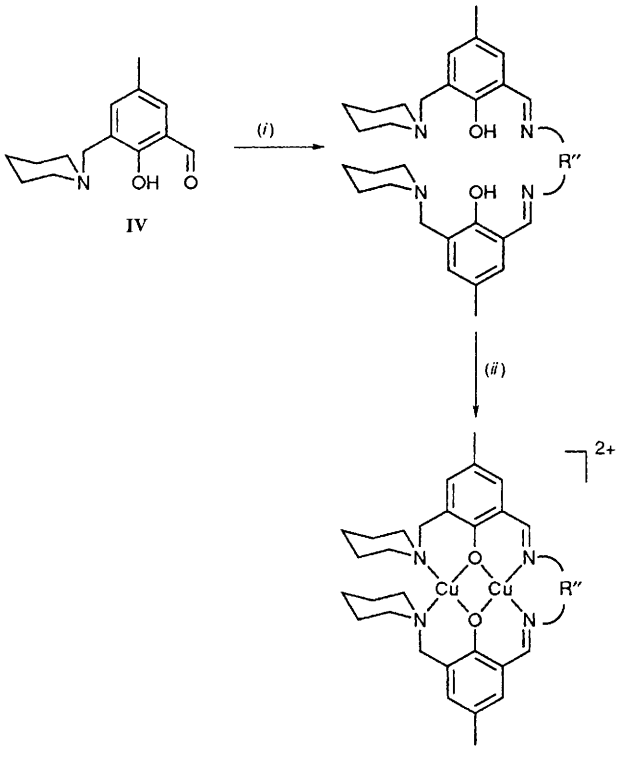
$[Cu_2L^6][ClO_4]_2$·$2H_2O$ **8**. To a boiling ethanolic solution (20 cm^3) of **IV** (2.33 g, 0.01 mol), ethylenediamine (0.3 g, 0.005 mol) dissolved in ethanol (10 cm^3) was added and refluxed for 3 h. The yellow solution was subsequently treated with copper(II) acetate (2 g, 0.01 mol) and copper(II) perchlorate (5.6 g, 0.015 mol) dissolved in ethanol (50 cm^3) and refluxed for 1 h. The filtered solution was slowly evaporated at room temperature and the precipitate was collected and recrystallised from ethanol and dried in vacuum (Found: C, 42.50; H, 5.25; Cu, 14.75; N, 6.50. Calc. for $C_{30}H_{40}Cl_2Cu_2N_4O_{10}$·$2H_2O$: C, 42.40; H, 5.20; Cu, 14.95; N, 6.60%).

$[Cu_2L^7][ClO_4]_2$·EtOH **9**. This complex was prepared by a procedure adopted for **8** except using *o*-phenylenediamine (0.54 g, 0.005 mol) in the place of ethylenediamine in ethanol (Found: C, 47.60; H, 5.40; Cu, 13.95; N, 6.20. Calc. for $C_{34}H_{42}Cl_2Cu_2N_4O_{10}$·EtOH: C, 47.50; H, 5.30, Cu, 14.00; N, 6.15%).

$[Cu_2L^8][ClO_4]_2$·MeOH **10**. This complex was prepared by

Table 1 Electronic spectral data of the complexes (in MeCN)

	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	
	c.t.	d–d
3 $[Cu_2L^2Cl_2]\cdot 2EtOH$	370 (6697), 273 (18 648), 240 (30 502), 232 (32 140)	625 (290)
5 $[Cu_2L^4][ClO_4]_2\cdot 2EtOH$	345 (6284), 270 (18 117), 238 (26 732)	605 (441)
6 $[Cu_2L^4Cl_2]\cdot 3H_2O$	345 (6319), 270 (18 741), 240 (33 573)	660 (407)
7 $[Cu_2L^5Cl_2]\cdot 5H_2O$	350 (5965), 275 (16 837)	660 (419)
8 $[Cu_2L^6][ClO_4]_2\cdot 2H_2O$	365 (6932), 268 (14 784), 248 (21 437), 230 (23 695)	575 (304)
9 $[Cu_2L^7][ClO_4]_2\cdot EtOH$	385 (9372), 270 (11 722), 245 (23 780)	600 (268)
10 $[Cu_2L^8][ClO_4]_2\cdot MeOH$	370 (7969), 275 (15 716), 243 (28 517), 228 (29 652)	605 (182)
11 $[Cu_2L^8Br_2]\cdot H_2O$	370 (10 566), 270 (19 256), 240 (37 996)	635 (162)
12 $[Cu_2L^9][ClO_4]_2\cdot 2H_2O$	370 (11 825), 275 (20 865), 245 (43 230), 228 (43 359)	615 (229)



Scheme 2 Synthesis of perchlorate salts **8**–**10** and **12**. (*i*) $H_2NR''NH_2$; (*ii*) $Cu(O_2CMe)_2$–Cu^{2+}. R″ as in Fig. 1

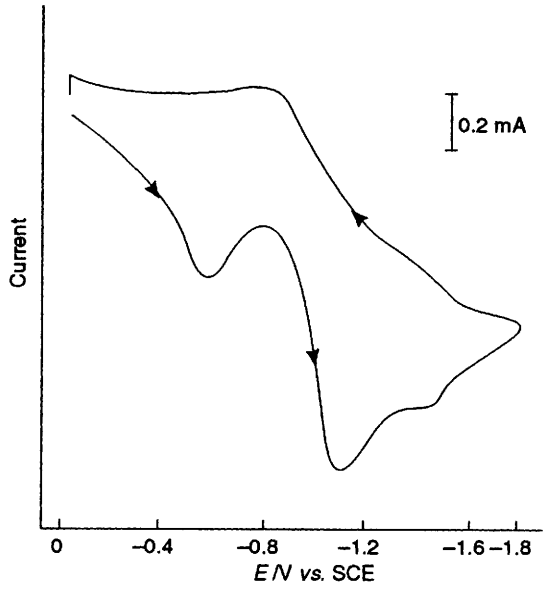


Fig. 2 Cyclic voltammogram of **12**: Pt electrodes, scan rate 100 mV s^{-1} in dmf

the method used for **8**, using 1,3-diaminopropane (0.37 g, 0.005 mol) in the place of ethylenediamine in methanol (Found: C, 44.75; H, 5.25; Cu, 14.85; N, 6.80. Calc. for $C_{31}H_{42}Cl_2Cu_2N_4O_{10}\cdot$MeOH: C, 44.65; H, 5.35, Cu, 14.90; N, 6.50%).

$[Cu_2L^8Br_2]\cdot H_2O$ **11**. This complex was prepared as for **10**, using copper(II) bromide (2.23 g, 0.01 mol) in the place of copper perchlorate in ethanol (Found: C, 46.15; H, 5.55; Cu, 15.60; N, 6.85. Calc. for $C_{31}H_{42}Br_2Cu_2N_4O_2\cdot H_2O$: C, 46.10; H, 5.45, Cu, 15.75; N, 6.95%).

$[Cu_2L^9][ClO_4]_2\cdot 2H_2O$ **12**. This complex was prepared by the method used for **8**, using 1,4-diaminobutane (0.44 g, 0.005 mol) in the place of ethylenediamine in ethanol (Found: C, 43.70; H, 5.55; Cu, 14.40; N, 6.35. Calc. for $C_{32}H_{44}Cl_2Cu_2N_4O_{10}\cdot 2H_2O$: C, 43.80; H, 5.50, Cu, 14.50; N, 6.40%).

Results and Discussion

The IR spectra of all the complexes exhibit a peak at 1630–1600 cm^{-1} corresponding to the C=N stretching vibration frequency which is lower than the C=O frequency of the respective precursor compounds (1670–1655 cm^{-1}). The perchlorate complexes exhibit a strong absorption band at 1100 cm^{-1} corresponding to the unco-ordinated perchlorate anion. A broad band around 3400 cm^{-1} suggests the presence of lattice water.

The electronic spectra of the complexes were measured in acetonitrile and the data are summarised in Table 1. The perchlorate complexes exhibit d–d transitions in the region 575–615 nm. Generally, the λ_{max} values for the 'side-off' complexes are observed at a relatively lower energy region than the macrocyclic complexes having the same alkyl linkage at the imine nitrogen-donor set suggesting a more distorted square-pyramidal geometry for the copper ions.[9,11–13] When compared to the perchlorate complexes the corresponding chloro or bromo complexes exhibit a maximum at an appreciably lower energy region. This is due to the enforced deviation of the metal ions from the square-basal co-ordination plane upon halide ion co-ordination.[14] The moderately intense band observed in the near-UV region is due to the overlap of the transition of the azomethine π–π^* transition with the charge-transfer band from bridging phenolate to the vacant d orbital of Cu^{II}.

The positive-ion FAB mass spectra of the complexes $[Cu_2L^5Cl_2]\cdot 5H_2O$ **7**, $[Cu_2L^6][ClO_4]_2\cdot 2H_2O$ **8**, $[Cu_2L^8Br_2]\cdot H_2O$ **11** and $[Cu_2L^9][ClO_4]_2\cdot 2H_2O$ **12** confirm the presence of a dipositive binuclear core $[Cu_2L]^{2+}$. Peaks at $M+1$ mass units corresponding to $[Cu_2L]^{2+}$ are assignable (Table 2).

The electrochemical behaviour of the complexes was investigated (in acetonitrile or dmf) by cyclic voltammetry. The cyclic voltammogram of **12** recorded in dmf is given in Fig. 2. The electrochemical data are summarised in Table 3.

Table 2 Positive-ion FAB mass spectra of the dinuclear complexes

Complex	[Fragment]	*m/z* (% intensity)*
7 $[Cu_2L^5Cl_2]\cdot 5H_2O$	$[Cu_2L^5]^{2+}$	686 (20)
8 $[Cu_2L^6][ClO_4]_2\cdot 2H_2O$	$[Cu_2L^6(H_2O)_2]^{2+}$	652 (40)
11 $[Cu_2L^8Br_2]\cdot H_2O$	$[Cu_2L^8(H_2O)]^{2+}$	648 (15)
12 $[Cu_2L^9][ClO_4]_2\cdot 2H_2O$	$[Cu_2L^9(H_2O)_2]^{2+}$	680 (50)

* Relative to base peak.

Table 3 Electrochemical data (*vs.* SCE) for the reduction of complexes **1**–**12**

	E^1_{pc}/V	E^2_{pc}/V	E_{pa}/V
1 $[Cu_2L^1][ClO_4]_2\cdot H_2O$*	−0.75	−1.02	−0.75
2 $[Cu_2L^2][ClO_4]_2\cdot 3H_2O$*	−0.70	−1.26	−0.73
3 $[Cu_2L^2Cl_2]\cdot 2EtOH$	−0.51	−0.90	−0.75
4 $[Cu_2L^3][ClO_4]_2\cdot 4H_2O$*	−0.38	−1.20	−0.74
5 $[Cu_2L^4][ClO_4]_2\cdot 2EtOH$	−0.83	−1.17	−0.71
6 $[Cu_2L^4Cl_2]\cdot 3H_2O$	−0.62	−0.87	−0.72
7 $[Cu_2L^5Cl_2]\cdot 5H_2O$	−0.65	−0.95	−0.69
8 $[Cu_2L^6][ClO_4]_2\cdot 2H_2O$	−0.67	−1.10	−0.73
9 $[Cu_2L^7][ClO_4]_2\cdot EtOH$	−0.61	−1.09	−0.75
10 $[Cu_2L^8][ClO_4]_2\cdot MeOH$	−0.53	−1.10	−0.72
11 $[Cu_2L^8Br_2]\cdot H_2O$	−0.48	−0.85	−0.62
12 $[Cu_2L^9][ClO_4]_2\cdot 2H_2O$	−0.56	−1.14	−0.78

* From ref. 9(*a*).

In the cathodic potential range (0 to −1.2 V), all the complexes exhibit two reduction waves at different potentials. Coulometric experiments conducted at potentials 100 mV more negative than the second reduction wave indicate the consumption of two electrons per molecule. Based on these observations, it is reasonable to suggest that the reduction process may involve the following steps [equation (1)].

$$Cu^{II}\text{–}Cu^{II} \overset{E^1_{pc}}{\rightleftharpoons} Cu^{I}\text{–}Cu^{II} \overset{E^2_{pc}}{\rightleftharpoons} Cu^{I}\text{–}Cu^{I} \quad (1)$$

The appearance of a reduction wave at a more negative potential region (> −1.4 V) is due to the reduction of Cu^I–Cu^I to Cu^0, and the reduced copper metal is deposited on the electrode surface. Coulometric experiments conducted at this potential region confirm the consumption of four electrons per molecule.

It is of interest to compare the redox properties of the macrocyclic (**1**, **2**) and side-off complexes (**8** and **10**). An anodic shift in the first reduction potential occurs in both types of complexes with increasing alkyl chain length of the imine nitrogen compartment, which is consistent with reported observations.[15] However, the first reduction of side-off complexes **8** and **10** is observed at a relatively more anodic potential than those of the macrocyclic analogues **1** and **2**. Although the macrocyclic and 'side-off' (**IIB**) complexes provide a similar set of donor atoms ($N_2O_2N_2$) to the two copper(II) ions, there is a structural difference in the arrangement of these atoms. Since the piperidine donor nitrogen atoms of side-off complexes (**8** and **10**) are not connected to each other, as in the case of macrocyclic complexes (**1** and **2**), they are more flexible than the piperazine ring nitrogens of the macrocyclic complexes. Hence, the enforced deviation of the metal ion from its co-ordination plane should be larger for the macrocyclic complexes so destabilising the Cu^{II} oxidation state.[16] Similar types of variations in the reduction potentials with respect to the geometrical changes have been reported previously.[12,16] The irreversible nature of the reductions observed for the side-off complexes may be attributed to the fact that, after reduction of $Cu^{II}Cu^{II}$ to Cu^ICu^I there may be a change in the co-ordination geometry and

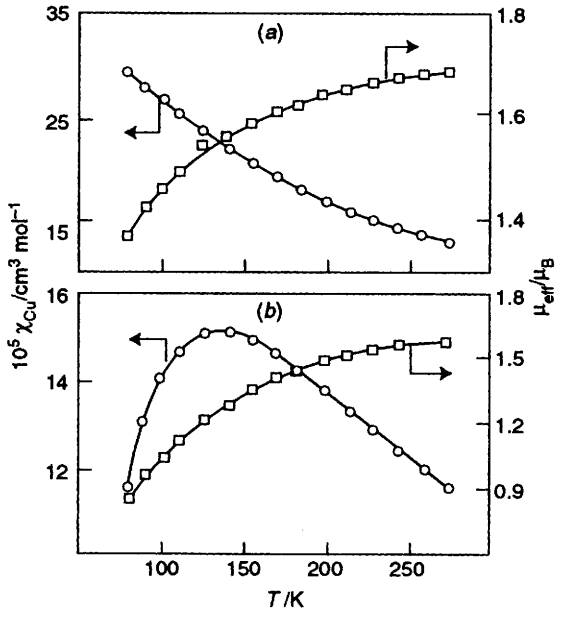


Fig. 3 Temperature dependence of magnetic susceptibility (χ_{Cu}) and effective magnetic moment (μ_{eff}) for (*a*) $[Cu_2L^6][ClO_4]_2\cdot 2H_2O$ **8** and (*b*) $[Cu_2L^4][ClO_4]_2\cdot 2EtOH$ **5**

number (due to solvent co-ordination) as well as expulsion of metal ions from the co-ordination sphere. It is apparent that the piperidine compartment may readily reorganise itself, after the first reduction step, to provide the required distorted geometry (preferably tetrahedral) to stabilise Cu^I. By contrast, for the macrocyclic complexes structural reorganisation is largely restricted owing to the rigid nature of piperazine ring system. It appears that the alkyl linkage of the imine nitrogen has appreciable control over the other compartment in determining its geometry and structure.[12,15] The replacement of perchlorate counter anion by halide considerably shifts both the first and second reduction potentials to more positive values. This may be attributed to the change in the nature and number of co-ordinating atoms.

Magnetic Properties.—The magnetic behaviour of the side-off complexes **5** and **8** was studied in the temperature range 80–300 K. Analyses were carried out using the Bleaney–Bowers equation[17] (2) where p is the fraction of monomeric impurity

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

and χ_{Cu} is the magnetic susceptibility per Cu. Fig. 3 shows plots of χ_{Cu} and μ_{Cu} *vs.* T for complexes **5** and **8**. Good magnetic simulation was obtained using $J = -75\ cm^{-1}$, $g = 2.046$, $p = 0.003$ for **5** and $J = -35\ cm^{-1}$, $g = 2.001$, $p = 0.001$ for **8**; and $N\alpha$ was fixed at $60 \times 10^{-6}\ cm^3\ mol^{-1}$ for both the magnetic simulations.

The J value observed for **8** is considerably lower than that for both the macrocyclic analogue **1** ($J = -85\ cm^{-1}$)[9a] and side-off complex **5** suggesting a weak antiferromagnetic interaction between the two copper(II) centres. Magnetostructural correlations in phenoxo-bridged dicopper(II) complexes reveals that the dominant pathway for superexchange through the two oxygen bridge atoms involves interaction of the two copper ($d_{x^2-y^2}$) orbitals and s and p orbitals on the oxygen with a predominantly σ overlap.[18] Thus the antiferromagnetic exchange interactions between the copper centres is likely to be influenced most significantly by the degree of planarity of the oxygen bridges and the phenoxide bridge angle.[18] Also, the exchange interaction is expected to be affected by out-of plane distortions at the copper centres.[19]

Therefore, it is reasonable to expect that in **8** the plane

constituted by the copper(II) ion and the more flexible piperidine nitrogen will be deviated significantly from that of the imine compartment, whereas in **5** the distortion around the piperazine compartment will be less due to the less flexible nature of the piperazine ring, hence leading to only a slight decrease in the *J* value.

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