Dicopper(II,II) and Dicopper(I,II) Complexes of a Series of Dinucleating Macrocycles

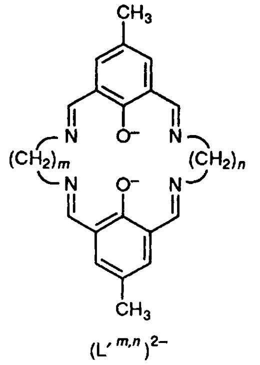
Hisashi Ōkawa,[*,a] Makoto Tadokoro,[a] Yuichiro Aratake,[a] Masaaki Ohba,[a] Kenji Shindo,[a] Minoru Mitsumi,[a] Masayuki Koikawa,[b] Mie Tomono[a] and David E. Fenton[c]
[a] *Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan*
[b] *Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan*
[c] *Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK*

The dinucleating macrocycles $H_2L^{m,n}$ containing two 2,6-di(aminomethyl)-4-methylphenol entities combined through two alkane chains, $(CH_2)_m$ and $(CH_2)_n$, at the amine nitrogens have been prepared for the (*m*,*n*) sets (2,3), (2,4), (2,5), (3,3) and (3,4). The dinuclear copper(II) complexes having general formula $[Cu_2L^{m,n}][ClO_4]_2$ have been prepared. Cryomagnetic investigations (80–300 K) reveal a strong antiferromagnetic spin-exchange between the copper(II) ions within each complex (*J* based on $\mathcal{H} = -2JS_1S_2$ in the range −345 to −255 cm^{-1}). The cyclic voltammograms show two reduction couples, $Cu^{II}Cu^{II}$–$Cu^{I}Cu^{II}$ and $Cu^{I}Cu^{II}$–$Cu^{I}Cu^{I}$. The comproportionation constants K_{com} for the mixed-valence $Cu^{I}Cu^{II}$ complexes have been determined electrochemically. The K_{com} value increase in the order of the macrocycles $(L^{2,3})^{2-} < (L^{2,4})^{2-} < (L^{2,5})^{2-}$ and $(L^{3,3})^{2-} < (L^{3,4})^{2-}$. The $Cu^{I}Cu^{II}$ mixed-valence state is shown to be 'spin-trapped' (Class I) for all the complexes based on ESR spectra.

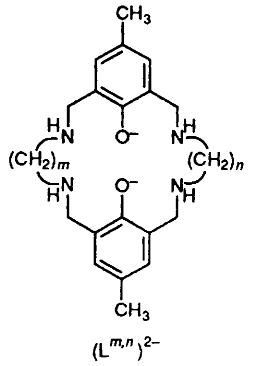
Studies on dinuclear metal complexes have been stimulated by interest in their unique physicochemical properties[1] arising from metal–metal interactions and unprecedented reactivities[2] associated with co-operative effects of metal ions. They are also studied as models of the active centre of some biological metalloenzymes such as haemocyanin (Cu_2),[3] Mn catalase (Mn_2)[4] or cytochrome c oxidase (CuFe).[5] The use of macrocyclic ligands in studies on polynuclear metal complexes has great advantages because macrocyclic complexes are thermodynamically stabilized and kinetically retarded toward metal dissociation or substitution relative to complexes of the corresponding non-cyclic ligands (macrocyclic effect).[6] Further, macrocyclic ligands can provide a well-defined environment for the bound metal ions and thence influence the physicochemical properties and reactivities of polynuclear metal complexes.[7]

Dinucleating macrocycles of type $(L'^{m,n})^{2-}$ have been obtained for a fairly wide range of (*m*,*n*) sets[8–10] and extensively used for studies on homo- and hetero-dinuclear complexes and mixed-valence complexes.[8–15] Recently a macrocyclic analogue $H_2L^{m,n}$ with fully saturated azomethine linkages was obtained for $m = n = 3$ and its dinuclear copper- and nickel-(II) complexes were reported.[16,17] It is suggested that the saturation of the azomethine linkages induces significant effects in the stereochemistry and redox chemistry of the dinuclear copper complexes. However, fully saturated macrocycles of type $H_2L^{m,n}$, except for that with $m = n = 3$, have not been previously studied.

In this study we have prepared the fully saturated macrocycles $H_2L^{m,n}$ with (*m*,*n*) sets of (2,3), (2,4), (2,5), (3,3) and (3,4), by the reduction of the unsaturated macrocycles $(L'^{m,n})^{2-}$ in their Cu_2Pb complexes.[10] For the macrocycles superscripts *m* and *n* denote the number of methylene groups on the lateral chains. Dinuclear copper(II) complexes having general formula $[Cu_2L^{m,n}][ClO_4]_2$ have been synthesized and their physicochemical properties were examined in comparison with the complexes of $(L'^{m,n})^{2-}$. In particular the electrochemical properties of $[Cu_2L^{m,n}][ClO_4]_2$, the generation of mixed-valence $Cu^{I}Cu^{II}$ complexes and the stability and electronic properties of the latter are reported.



$(L'^{m,n})^{2-}$



$(L^{m,n})^{2-}$

Experimental

Physical Measurements.—Elemental analyses for carbon, hydrogen and nitrogen were obtained from the Elemental Analysis Service Centre of Kyushu University. Analyses for copper were made on a Shimadzu AA-660 atomic absorption/flame emission spectrophotometer. Infrared (IR) spectra were recorded on a JASCO IR-810 spectrometer on KBr discs or Nujol mulls. Electronic spectra were recorded on a Shimadzu UV-210 spectrophotometer. Absorption spectra in the near-IR region were recorded on a model MSP-5000 Shimadzu multipurpose spectrophotometer. The 400 MHz H NMR spectra were measured with a JEOL JNM-GX 400 spectrometer in $CDCl_3$, using tetramethylsilane as the internal standard. Mass spectra were recorded on a Hitachi M-60 mass spectrometer. Magnetic susceptibilities of powder samples were measured in the temperature range 80–300 K on a Faraday balance. The apparatus was calibrated by the use of

$[Ni(en)_3][S_2O_3]$ (en = ethane-1,2-diamine).[18] The effective magnetic moment was calculated using, $\mu_{eff} = 2.828(\chi_A T)^{\frac{1}{2}}$, where χ_A is the molar magnetic susceptibility per Cu corrected for diamagnetism. Cyclic voltammograms were recorded on an apparatus comprising a HA-501 potentiostat/galvanostat, a HB-104 function generator, and a HF-201 Coulomb/Amperehour meter of Hokuto Denko Ltd. Measurements were carried out in acetonitrile, dimethylformamide (dmf) or dimethyl sulfoxide (dmso), using a three-electrode cell equipped with a glassy carbon working electrode, a platinum coil as the auxiliary electrode and a saturated calomel electrode as the reference. Tetrabutylammonium perchlorate was used as the supporting electrolyte. Controlled-potential electrolyses were performed on the same instrument using a platinum net as the working electrode.

Materials.—Tetrabutylammonium perchlorate used as the supporting electrolyte in electrochemical measurements was purchased from Nakarai Chemicals and recrystallized twice from hot water. Dimethylformamide and dimethyl sulfoxide for electrochemical measurements were dried by distillation from CaH_2 and stored over molecular sieves. All other chemicals and solvents were of reagent grade and were used as received. The synthesis of $[Pb(CuL'^{m,n})_2][ClO_4]_2$ was described in our previous paper.[10]

Preparation of Ligands $H_2L^{m,n}$.—$H_2L^{2,3}$. Powdered $[Pb(CuL'^{2,3})_2][ClO_4]_2$ (2.0 g, 1.1 mmol) was suspended in a mixture of dmf (60 cm^3) and methanol (40 cm^3). A portion of $NaBH_4$ (1.5 g) was added to the suspension and the mixture was stirred for 15 min at room temperature. The operation of the addition of $NaBH_4$ (1.0 g) and stirring for 30 min at room temperature was repeated twice. The reaction mixture was then diluted with water (50 cm^3), made weakly acidic (pH 4) with dilute sulfuric acid and evaporated to dryness. The residue was dissolved in methanol (200 cm^3), any insoluble materials were separated by filtration, and the filtrate was concentrated to a small volume to give a colourless oily substance. This was dissolved in water (200 cm^3) and the solution made weakly alkaline (pH 8.5) with aqueous ammonia and extracted with three 60 cm^3 portions of chloroform. The combined extract was dried with anhydrous Na_2SO_4 and evaporated to dryness. From the residue the macrocycle $H_2L^{2,3}$ was extracted with light petroleum by means of a Soxhlet apparatus. It formed colourless crystals melting at 145 °C, yield 0.42 g (47%) (Found: C, 69.60; H, 8.40; N, 13.90. Calc. for $C_{23}H_{34}N_4O_2$: C, 69.30; H, 8.60; N, 14.05%); mass spectrum m/z 399.

$H_2L^{2,4}$. This was obtained as colourless microcrystals by the reduction of $[Pb(CuL'^{2,4})_2][ClO_4]_2$ with $NaBH_4$ in a similar manner to that for $H_2L^{2,3}$, yield 56%, m.p. 98 °C (Found: C, 69.95; H, 8.55; N, 13.75. Calc. for $C_{24}H_{36}N_4O_2$: C, 69.85; H, 8.80; N, 13.60%); mass spectrum m/z 413.

$H_2L^{2,5}$. This was obtained as colourless microcrystals by the reduction of $[Pb(CuL'^{2,5})_2][ClO_4]_2$ with $NaBH_4$, yield 50%, m.p. 99 °C (Found: C, 69.95; H, 8.90; N, 13.00. Calc. for $C_{25}H_{38}N_4O_2$: C, 70.40; H, 9.00; N, 13.15%); mass spectrum m/z 427.

$H_2L^{3,3}$. This was obtained as colourless microcrystals by the reduction of $[Pb(CuL'^{3,3})_2][ClO_4]_2$ with $NaBH_4$, yield 69%, m.p. 149 °C (Found: C, 69.65; H, 8.85; N, 13.30. Calc. for $C_{24}H_{36}N_4O_2$: C, 69.85; H, 8.80; N, 13.60%); mass spectrum m/z 413.

$H_2L^{3,4}$. This was obtained as colourless microcrystals by the reduction of $[Pb(CuL'^{3,4})_2][ClO_4]_2$ with $NaBH_4$, yield 62%, m.p. 113 °C (Found: C, 69.85; H, 8.45; N, 13.55. Calc. for $C_{25}H_{38}N_4O_2$: C, 70.40; H, 9.00; N, 13.15%); mass spectrum m/z 427.

Preparation of Complexes $[Cu_2L^{m,n}][ClO_4]_2$.—$[Cu_2L^{2,3}][ClO_4]_2$ **1**. A solution of $H_2L^{2,3}$ (0.40 g, 1.0 mmol), triethylamine (0.3 g) and copper(II) perchlorate hexahydrate (0.78 g, 2.0 mmol) in methanol (20 cm^3) was heated for 30 min. The mixture was concentrated to *ca.* 10 cm^3, diluted with water (10 cm^3), and allowed to stand in a refrigerator to give green microcrystals. They were separated, washed successively with small amounts of water and methanol, and dried *in vacuo*, yield 0.58 g (76%) (Found: C, 38.05; H, 4.55; Cu, 17.4; N, 7.60. Calc. for $C_{23}H_{32}Cl_2Cu_2N_4O_{10}$: C, 38.25; H, 4.45; Cu, 17.6; N, 7.75%).

$[Cu_2L^{2,4}][ClO_4]_2\cdot H_2O$ **2**. This was obtained as green crystals by the reaction of $H_2L^{2,4}$ (0.42 g, 1.0 mmol) and copper(II) perchlorate hexahydrate (0.78 g, 2.0 mmol) in a similar manner to that used for the preparation of complex **1**, yield 0.69 g (91%) (Found: C, 38.35; H, 4.80; Cu, 16.6; N, 7.35. Calc. for $C_{24}H_{36}Cl_2Cu_2N_4O_{11}$: C, 38.20; H, 4.80; Cu, 16.8; N, 7.40%).

$[Cu_2L^{2,5}][ClO_4]_2\cdot H_2O$ **3**. This was obtained as green crystals by the reaction of $H_2L^{2,5}$ (0.43 g, 1.0 mmol) and copper(II) perchlorate hexahydrate (0.78 g, 2.0 mmol) in methanol, yield 0.66 g (86%) (Found: C, 38.95; H, 4.90; Cu, 16.2; N, 7.20. Calc. for $C_{25}H_{38}Cl_2Cu_2N_4O_{11}$: C, 39.05; H, 5.00; Cu, 16.5; N, 7.30%).

$[Cu_2L^{3,3}][ClO_4]_2$ **4**. This was obtained as deep blue crystals by the reaction of $H_2L^{3,3}$ (0.42 g, 1.0 mmol) and copper(II) perchlorate hexahydrate (0.78 g, 2.0 mmol) in methanol, yield 0.66 g (90%) (Found: C, 39.20; H, 4.65; Cu, 17.0; N, 7.60. Calc. for $C_{24}H_{34}Cl_2Cu_2N_4O_{10}$: C, 39.15; H, 4.65; Cu, 17.3; N, 7.60%).

$[Cu_2L^{3,4}][ClO_4]_2\cdot H_2O$ **5**. This was obtained as green crystals by the reaction of $H_2L^{3,4}$ (0.43 g, 1.0 mmol) and copper(II) perchlorate hexahydrate (0.78 g, 2.0 mmol) in methanol, yield 0.47 g (61%) (Found: C, 39.20; H, 4.80; Cu, 16.1; N, 7.00. Calc. for $C_{25}H_{38}Cl_2Cu_2N_4O_{11}$: C, 39.05; H, 5.00; Cu, 16.5; N, 7.30%).

Results and Discussion

Synthesis and Characterization of $H_2L^{m,n}$.—The macrocycles $H_2L^{m,n}$ [(m,n) = (2,3), (2,4), (2,5), (3,3) or (3,4)] were obtained in moderate yields by the reduction of the trinuclear Cu_2Pb complexes $[Pb(CuL'^{m,n})_2][ClO_4]_2$ with $NaBH_4$. In this reduction the metal ions were deposited as metallic Cu and Pb and the liberated ligands were extracted with chloroform. The formation of the macrocycles was established from mass spectra (see Experimental section) and 400 MHz ^1H NMR spectra.

The ^1H NMR spectral data of macrocycles $H_2L^{m,n}$ are summarized in Table 1. Each macrocycle shows signals due to the methyl protons (a) at δ 2.2, the ring protons (b and b′) at δ 6.7–6.8, and the benzyl protons (c and c′) at δ 3.8. The methylene proton signals on the lateral chains appear at higher field (δ 2.83–1.45). All the macrocycles, except for $H_2L^{3,3}$, are unsymmetrical with respect to the lateral chains and the spectra generally show two ring protons (b and b′) and two benzyl protons (c and c′). However, the ring protons of $H_2L^{3,4}$ are not resolved in its ^1H NMR spectrum.

The IR spectra of $H_2L^{m,n}$ are characterized by a ν(N–H) vibration near 3300 cm^{-1} which is absent in the precursor complexes $[Pb(CuL'^{m,n})_2][ClO_4]_2$. The ν(C=N) stretching mode at ≈1640 cm^{-1} found for $[Pb(CuL'^{m,n})_2][ClO_4]_2$[10] disappears in the saturated macrocycles $H_2L^{m,n}$.

Spectral and Magnetic Properties of Complexes $[Cu_2L^{m,n}][ClO_4]_2$ **1**–**5**.—The dinuclear copper(II) complexes **1**–**5** each show a ν(N–H) vibration at 3250–3270 cm^{-1} which is slightly shifted to lower frequency relative to that of the free macrocycles $H_2L^{m,n}$. The ν_3 vibration of the perchlorate ion appears as a single band around 1100 cm^{-1}, implying that the ion is not co-ordinated to the copper(II) ion. The presence of lattice water in **2**, **3** and **5** is suggested by a broad band around 3400 cm^{-1} when measured as Nujol mulls.

The electronic spectra of complexes **1**–**5** were measured in dmf or dmso and the spectral data are summarized in Table 2. The spectrum of **1** in dmso is given in Fig. 1 (trace a). Each complex shows a moderately intense band in the near-

Table 1 400 MHz H NMR spectral data (δ) for $H_2L^{m,n}$ *

$H_2L^{2,3}$	a	2.20 (s, 6 H)	en	2.81 (s, 4 H)
	b,b′	6.87 (s, 2 H), 6.77 (s, 2 H)	tn-α	2.71 (t, 4 H)
	c,c′	3.83 (s, 4 H), 3.80 (s, 4 H)	tn-β	1.75 (q, 2 H)
$H_2L^{2,4}$	a	2.20 (s, 6 H)	en	2.83 (s, 4 H)
	b,b′	6.80 (s, 2 H), 6.76 (s, 2 H)	bn-α	2.64 (br, 4 H)
	c,c′	3.82 (s, 4 H), 3.80 (s, 4 H)	bn-β	1.58 (br, 2 H)
$H_2L^{2,5}$	a	2.20 (s, 6 H)	en	2.80 (s, 4 H)
	b,b′	6.80 (s, 2 H), 6.77 (s, 2 H)	pm-α	2.65 (t, 4 H)
	c,c′	3.82 (s, 4 H), 3.80 (s, 4 H)	pm-β	1.52 (br, 4 H)
			pm-γ	1.45 (br, 2 H)
$H_2L^{3,3}$	a	2.18 (s, 6 H)	tn-α	2.55 (t, 8 H)
	b	6.72 (s, 4 H)	tn-β	1.70 (q, 4 H)
	c	3.83 (s, 8 H)		
$H_2L^{3,4}$	a	2.20 (s, 6 H)	tn-α	2.66 (t, 4 H)
	b,b′	6.76 (s, 4 H)	tn-β	1.72 (q, 2 H)
	c,c′	3.83 (s, 4 H), 3.81 (s, 4 H)	bn-α	2.58 (br, 4 H)
			bn-β	1.51 (br, 4 H)

* Abbreviations: a, methyl proton; b and b′, ring protons; c and c′, benzyl protons; en, $-CH_2CH_2-$; tn, $-CH_2CH_2CH_2-$; bn, $-CH_2CH_2CH_2CH_2-$; pm, $-CH_2CH_2CH_2CH_2CH_2-$; s, singlet; t, triplet; q, quintet; br, broad. α, β and γ denote the carbons on the lateral chain $N-C^{\alpha}-C^{\beta}-C^{\gamma}-C^{\beta}-C^{\alpha}-N$.

Table 2 Electronic spectral data for complexes **1**–**5**

	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})		
	c.t.	d–d	Solvent
1 $[Cu_2L^{2,3}][ClO_4]_2$	344 (2340) 372 (2470)	603 (190)	dmso
	342 (2310) 361 (2330)	603 (190)	dmf
2 $[Cu_2L^{2,4}][ClO_4]_2{\cdot}H_2O$	344 (2210) 361 (2210)	590 (190)	dmso
	344 (2280) 364 (2310)	596 (200)	dmf
3 $[Cu_2L^{2,5}][ClO_4]_2{\cdot}H_2O$	344 (2090) 375 (2310)	600 (200)	dmso
	344 (2050) 371 (2220)	603 (200)	dmf
4 $[Cu_2L^{3,3}][ClO_4]_2$	352 (3150)	599 (210)	dmso
	344 (3050)	598 (220)	dmf
5 $[Cu_2L^{3,4}][ClO_4]_2{\cdot}H_2O$	348 (3120)	608 (210)	dmso
	345 (3210)	609 (220)	dmf

Table 3 Magnetic data for **1**–**5** and related complexes[a]

	μ_{eff} per Cu			
Complex	290 K	80 K	J/cm^{-1}	p
1	0.75	0.24	−335	0.003
2	1.02	0.34	−285	0
3	0.78	0.20	−320	0
4	0.74	0.25	−345	0.001
5	1.06	0.51	−255	0.015
$[Cu_2L'^{2,3}][ClO_4]_2$			−395	0.002
$[Cu_2L'^{3,3}][ClO_4]_2$[b]			−450 ± 20	

[a] Value of g is fixed at 2.1 and $N\alpha$ at 60 × 10^{-6} cm^3 mol^{-1} for all the magnetic simulations. [b] Magnetic simulation was made using the literature data (ref. 8).

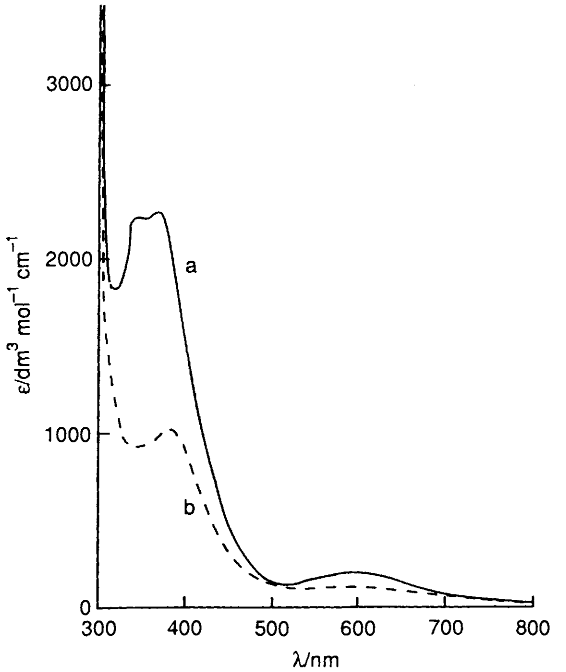


Fig. 1 Electronic spectra of $[Cu_2L^{2,3}][ClO_4]_2$ **1** (trace a) and its Cu^{I}Cu^{II} mixed-valence species (trace b) in dmso

ultraviolet region and a weak band in the visible region. A similar near-ultraviolet band has been observed for alkoxo-bridged dinuclear copper(II) complexes[19,20] and has been assigned to the charge-transfer (c.t.) band from the bridging phenolic oxygen to the vacant d orbital of the copper(II) ion. The visible band near 590 nm is assigned to the superposed band from the d–d transitions of the copper(II) ions. It is to be noted that in complexes **1**–**3** the c.t. band splits into two. This suggests that the two copper(II) ions in these complexes assume different geometries owing to the different lateral chains of the macrocycles and that there is a significant energy gap between the vacant d orbitals of the two metal ions. In **5**, however, such a splitting of the ligand to metal charge transfer (l.m.c.t.) band is not seen despite the different lateral chains in the macrocycle $(L^{3,4})^{2-}$, and so it appears that the two copper(II) ions in this complex assume similar geometries due to the flexibility of the macrocycle.

The electronic spectral features of complexes **1**–**5** resemble those of $[Cu_2L'^{3,3}]^{2+}$ and related complexes[10,13b,15b] except that the near-ultraviolet band is much weakened in the former: the absorption coefficient per complex molecule is *ca.* 3000 dm^3 mol^{-1} cm^{-1} in the former (see Table 2) but *ca.* 10 000 dm^3 mol^{-1} cm^{-1} or higher in the latter. This is because in the complexes of the unreduced macrocycles $L'^{m,n}$ the intense azomethine π–π* transition band[21,22] is superposed on the c.t. band.

The magnetic susceptibilities of complexes **1**–**5** were measured in the temperature range 80–300 K. Each complex shows a subnormal magnetic moment at room temperature which decreases on lowering of temperature. This is presumed to be due to antiferromagnetic spin-exchange between the pairs of copper(II) ions. Fig. 2 shows the χ_A *vs.* T and μ_{eff} *vs.* T plots for **1**. The magnetic analyses were carried using the Bleaney–Bowers equation[23] based on the isotropic Heisenberg model $\mathcal{H} = -2JS_1S_2$ [equation (1)] where p is the fraction of

$$\chi_A = (Ng^2\beta^2/kT)[3 + \exp(-2J/kT)]^{-1}(1 - p) + 0.45p/T + N\alpha \quad (1)$$

monomeric impurity and other symbols have their usual meanings. As shown by the solid lines in Fig. 2 the magnetism of this complex can be well reproduced by the Bleaney–Bowers equation using the magnetic parameters g = 2.10, J = −335 cm^{-1}, $N\alpha$ = 60 × 10^{-6} cm^3 mol^{-1} and p = 0.003. Similarly good magnetic simulations have been obtained for the other complexes and the magnetic parameters are summarized in Table 3.

Pilkington and Robson[8] reported the magnetic susceptibility

Table 4 Electrochemical data on the reduction of complexes **1–5** and their comproportionation constants

	In dmso			In dmf		
Complex	$E^1_{\frac{1}{2}}(\Delta E_p)$	$E^2_{\frac{1}{2}}(\Delta E_p)$	K_{com}	$E^1_{\frac{1}{2}}(\Delta E_p)$	$E^2_{\frac{1}{2}}(\Delta E_p)$	K_{com}
1	−0.69 (68)	−0.98 (95)	8.1×10^4	−0.81 (69)	−0.91 (71)	1.1×10^2
2	−0.64 (67)	−0.96 (100)	2.6×10^5	−0.63 (89)	−0.92 (115)	8.1×10^4
3	−0.51 (68)	−0.97 (123)	6.1×10^7	−0.51 (89)	−0.94 (105)	2.8×10^7
4	−0.77 (77)	−0.91 (88)	2.3×10^2	−0.81 (81)	−0.81 (81)	—
5	−0.74 (82)	−0.92 (100)	1.1×10^3	−0.70 (86)	−0.89 (100)	1.1×10^3

Potentials are given in V *vs.* SCE; $\Delta E_p = E_{pc} - E_{pa}$ in mV

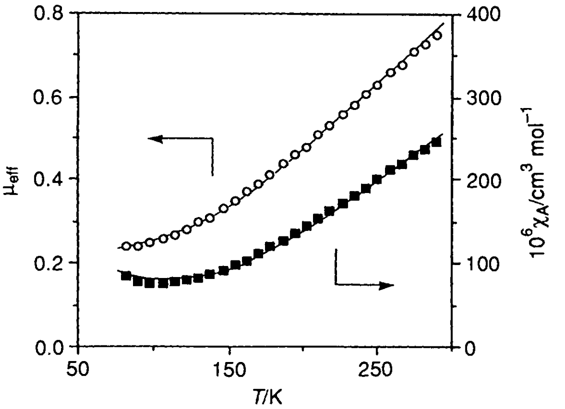


Fig. 2 χ_A *vs.* T and μ_{eff} *vs.* T plots of $[Cu_2L^{2,3}][ClO_4]_2$ **1**. Solid lines are drawn based on the modified Bleaney–Bowers equation given in the text, using $J = -335$ cm^{-1}, $g = 2.10$, $N\alpha = 60 \times 10^{-6}$ cm^3 mol^{-1} and $p = 0.003$

of $[Cu_2L'^{3,3}][ClO_4]_2$ in the range 90–300 K. The $-J$ value evaluated for this complex using the literature data is 450 ± 20 cm^{-1} which is significantly larger, in its absolute value, than the value of 345 cm^{-1} found for $[Cu_2L^{3,3}][ClO_4]_2$ **4**. The complex $[Cu_2L'^{2,3}]^{2+}$ was first obtained in our laboratory as the chloride salt[9] but its cryomagnetic properties were not studied. In this study we prepared the perchlorate salt $[Cu_2L'^{2,3}][ClO_4]_2$* and examined its cryomagnetic properties. The $-J$ value evaluated for this complex was 395 cm^{-1}, again larger than the value of 335 cm^{-1} found for $[Cu_2L^{2,3}][ClO_4]_2$ **1**. Despite the lack of detailed structural information on the complexes it appears that antiferromagnetic spin-exchange is stronger in $[Cu_2L'^{m,n}][ClO_4]_2$ than $[Cu_2L^{m,n}][ClO_4]_2$. Recent studies on magneto-structural correlations in dinuclear metal complexes have revealed some factors contributing to antiferromagnetic spin-exchange.[1,24] One significant factor is the coplanarity of two equatorial planes of the interacting metal ions. It is plausible that the macrocycles $(L'^{m,n})^{2-}$ with C=N linkages form a nearly coplanar $Cu^{II}Cu^{II}$ skeleton in which the magnetic orbitals of the copper(II) ions can overlap through the filled orbital of the bridging phenolic oxygen. On the other hand, the macrocycles $(L^{m,n})^{2-}$ which are fully reduced at the C=N linkages are sufficiently flexible to afford a non-coplanar $Cu^{II}Cu^{II}$ skeleton.

Cyclic Voltammetry.—The electrochemical properties of complexes **1–5** were studied by cyclic voltammetry. The cyclic voltammograms on reduction in dmso and dmf are given in Fig. 3 and the electrochemical data are summarized in Table 4.

The electrochemical behaviour in the negative potential range is sensitive to both the macrocycle structure and the solvent used. In dmso each complex shows two quasi-reversible or reversible couples. Coulometric experiments on **1** indicated that each of the couples involves a one-electron transfer, allowing us to assign the two waves to successive reductions at the metal centres, $Cu^{II}Cu^{II}$–$Cu^{I}Cu^{II}$ and $Cu^{I}Cu^{II}$–$Cu^{I}Cu^{I}$. The cyclic voltammogram of **4** in dmso was previously reported by Mandal *et al.*[16a] Our measurements for this complex gave the essentially same result. In dmf complexes **1–3** and **5** each shows two reductions at separate potentials whereas in the case of **4** the two reductions occur at the same potential.

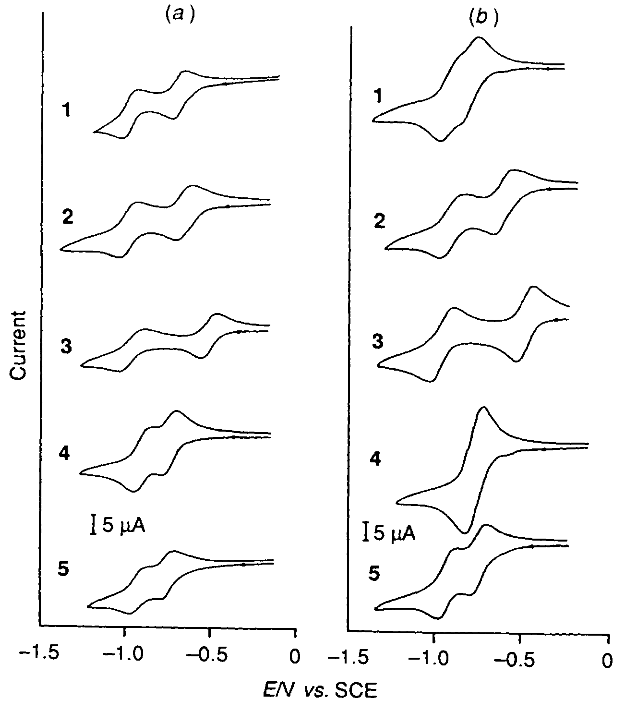


Fig. 3 Cyclic voltammograms of complexes **1–5** in dmso (*a*) and dmf (*b*)

It is seen that in both dmf and dmso the potential of the first reduction, $E^1_{\frac{1}{2}}$, varies significantly depending upon the macrocycle structure and shifts anodically on going from **1** to **3** $[(L^{2,3})^{2-} \longrightarrow (L^{2,5})^{2-}]$ and from **4** to **5** $[(L^{3,3})^{2-} \longrightarrow (L^{3,4})^{2-}]$. On the other hand, the second reduction potential, $E^2_{\frac{1}{2}}$, is practically invariant among **1–3** and **4** and **5**, respectively, except for the potential of **4** in dmf. Thus, the separation between the first and second reduction potentials, $E^1_{\frac{1}{2}} - E^2_{\frac{1}{2}}$, increases generally on going from **1** to **3** and from **4** to **5**. It is presumed that in the mixed-valence $Cu^{I}Cu^{II}$ complexes that the Cu^{II} ion assumes a similar configuration among **1–3** and **4** and **5**, respectively.

In the oxidation of complex **4** in acetonitrile on a Pt electrode, Mandal *et al.*[16] observed two quasi-reversible couples at +1.19 and +1.41 V *vs.* SCE and assigned them to the $Cu^{II}Cu^{II}$–$Cu^{II}Cu^{III}$ and $Cu^{II}Cu^{III}$–$Cu^{III}Cu^{III}$ processes, respectively. In our

---

* Found: C, 38.95; H, 3.50; Cu, 17.7; N, 7.75. $[Cu_2L'^{2,3}][ClO_4]_2$ requires C, 38.65; H, 3.40; Cu, 17.8; N, 7.85%; μ_{eff} per Cu = 0.63 at 290 K.

measurements in acetonitrile on a glassy carbon working electrode this complex showed two quasi-reversible couples at +1.18 and +1.38 V *vs.* SCE. Similarly, **1** showed two quasi-reversible couples at +1.19 and +1.38 V. For the other complexes the first oxidation near +1.2 V was quasi-reversible but the second oxidation near +1.4 V was irreversible.

It is valuable to compare the electrochemical properties of $[Cu_2L^{m,n}][ClO_4]_2$ and $[Cu_2L'^{3,3}][ClO_4]_2$. The latter complex shows two reductions at −0.43 and −0.90 V *vs.* SCE in dmso[16] but no oxidation in the available potential range. Evidently the saturated macrocycles $(L^{m,n})^{2-}$ stabilize the higher oxidation state Cu^{III} but destabilize the lower oxidation state Cu^{I} relative to the unsaturated macrocycle $(L'^{3,3})^{2-}$. The unsaturated macrocycle can accept electrons from copper(I) through the antibonding orbital of the C=N linkages whereas the saturated macrocycles act solely as electron donors.

Mixed-valence $Cu^{I}Cu^{II}$ *Complexes.*—The stability of the mixed-valence $Cu^{I}Cu^{II}$ complexes is expressed by the comproportionation constant K_{com} for the equilibrium (2).

$$[Cu^{II}Cu^{II}] + [Cu^{I}Cu^{I}] \xrightleftharpoons{K_{com}} 2[Cu^{I}Cu^{II}] \qquad (2)$$

The K_{com} values of **1**–**5** have been determined electrochemically using the equation $\log K_{com} = \Delta E_{\frac{1}{2}}/0.0591$ (at 25 °C), where $\Delta E_{\frac{1}{2}} = E^{1}_{\frac{1}{2}} - E^{2}_{\frac{1}{2}}$.[15a] The results are included in Table 4. The K_{com} value for the complex of $(L^{3,3})^{2-}$ in dmso was previously reported.[16] Our measurements for this complex gave exactly the same result. In both dmf and dmso K_{com} increases in the order of the macrocycles $(L^{2,3})^{2-} < (L^{2,4})^{2-} < (L^{2,5})^{2-}$ and $(L^{3,3})^{2-} < (L^{3,4})^{2-}$.

For the $Cu^{I}Cu^{II}$ complexes of $(L'^{3,3})^{2-}$ and related unsaturated macrocycles larger comproportionation constants (10^{6}–10^{13}) are reported.[14–16] Thus, the mixed-valence $Cu^{I}Cu^{II}$ state is destabilized on saturation of the C=N linkages of $(L'^{m,n})^{2-}$. This reaffirms that the unsaturated macrocycles can accept electrons from the filled d orbitals of Cu^{I} through the antibonding orbital of the C=N linkages.

The mixed-valence $Cu^{I}Cu^{II}$ complexes were generated electrochemically and subjected to ESR and visible spectral studies in order to observe the electronic properties of the mixed-valence state. The ESR spectrum of the $Cu^{I}Cu^{II}$ complex of $(L^{2,3})^{2-}$, generated *in situ* in dmso and measured at room temperature, shows an isotropic signal of four hyperfine structures due to one copper nucleus ($A_{iso} = 76.5 \times 10^{-4}$ cm^{-1}) at g_{iso} 2.10 (see Fig. 4). Such a spectrum is typical of planar CuN_2O_2 complexes[25] and clearly demonstrates that the unpaired electron is localized on one copper within the time-scale of ESR spectroscopy, probably on the copper at the sterically more favoured site formed with the ethylene lateral chain.

The electronic spectrum of the mixed-valence $Cu^{I}Cu^{II}$ complex in dmso (Fig. 1, trace b) resembles that of the corresponding $Cu^{II}Cu^{II}$ complex (trace a), but one of the split components of the c.t. band of the $Cu^{II}Cu^{II}$ complex is lacking and the intensity of the d–d transition band at 600 nm is significantly reduced in the $Cu^{I}Cu^{II}$ complex. In our spectral studies in the region 800–2000 nm any absorption band attributable to the intervalance transition band was not found. Thus, the $Cu^{I}Cu^{II}$ complex of $(L^{2,3})^{2-}$ is 'spin-trapped' and belongs to Class I of Robin and Day's classification.[26] Such a spin localization on one copper in the $Cu^{I}Cu^{II}$ state has also been verified for complexes **2**–**5**. Mandal *et al.*[16] have reported that the $Cu^{I}Cu^{II}$ complex of $(L^{3,3})^{2-}$ prepared in acetonitrile is also 'spin-trapped'. It is worth noting that the $Cu^{I}Cu^{II}$ complexes of $(L'^{3,3})^{2-}$ and related unsaturated macrocycles show seven hyperfine structures in their ESR spectra and an intervalance band in the near-IR spectra,[13b,14a] indicating the partial delocalization of one unpaired electron over the two copper nuclei (*i.e.* Class II).

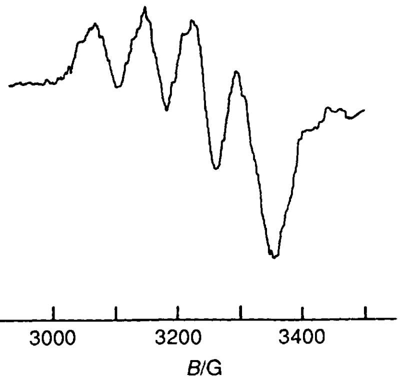


Fig. 4 Room-temperature ESR spectrum of the $Cu^{I}Cu^{II}$ complex of $(L^{2,3})^{2-}$ prepared *in situ* in dmso

Acknowledgements

The authors thank Professor Naohide Matsumoto and Dr. Masahito Kodera for fruitful discussions. This work was supported by a Grant-in-aid for Scientific Research on Priority Area (No. 03241105).

References

1 P. W. Ball, *Coord. Chem. Rev.*, 1969, **4**, 361; E. Sinn, *Coord. Chem. Rev.*, 1970, **5**, 313; M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259; C. J. Cairns and D. H. Busch, *Coord. Chem. Rev.*, 1986, **69**, 1; O. Kahn, *Struct. Bonding (Berlin)*, 1987, **68**, 89; P. Zanello, S. Tamburini, P. A. Vigato and G. A. Mazzocchin, *Coord. Chem. Rev.*, 1987, **77**, 165.

2 See, for example, F. Arena, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1986, **25**, 4589; Y. Aratake, H. Ōkawa, E. Asato, H. Sakiyama, M. Kodera, S. Kida and M. Sakamoto, *J. Chem. Soc., Dalton Trans.*, 1990, 2941; P. A. Vigato, S. Tamburini and D. E. Fenton, *Coord. Chem. Rev.*, 1990, **106**, 25.

3 E. I. Solomon, K. W. Penfield and D. E. Wilcox, *Struct. Bonding (Berlin)*, 1983, **53**, 1; E. I. Solomon, *Pure Appl. Chem.*, 1983, **55**, 1069.

4 S. V. Khangulov, V. V. Barynin, U. R. Melik-Adamyan, A. I. Grebenko, N. V. Voevedskaya, L. A. Blumenfeld, S. N. Dobryakov and V. B. Ilyasova, *Bioorg. Khim.*, 1986, **12**, 741; R. M. Fronko, J. E. Penner-Hahn and C. J. Bender, *J. Am. Chem. Soc.*, 1988, **110**, 7554; G. S. Allgood and J. J. Perry, *J. Bacteriol.*, 1986, **168**, 563.

5 G. Palmer, G. T. Babcock and L. E. Vickery, *Proc. Natl. Acad. Sci. USA*, 1976, **72**, 1349.

6 D. K. Cabbines and D. W. Margerum, *J. Am. Chem. Soc.*, 1969, **91**, 6450; J. D. Lamb, R. M. Izatt, J. J. Christensen and D. J. Eatough, *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979, p. 145.

7 J. F. Endicott and B. Durham, *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979, p. 393.

8 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.

9 H. Ōkawa and S. Kida, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 751; *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1749.

10 M. Tadokoro, H. Ōkawa, N. Matumoto, M. Koikawa and S. Kida, *J. Chem. Soc., Dalton Trans.*, 1991, 1657.

11 B. F. Hoskins, R. Robson and G. A. Williams, *Inorg. Chim. Acta*, 1976, **16**, 121; B. F. Hoskins and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2593; B. F. Hoskins and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2607.

12 A. W. Addison, *Inorg. Nucl. Chem. Lett.*, 1976, **12**, 899.

13 (*a*) R. R. Gagne, C. A. Koval and T. J. Smith, *J. Am. Chem. Soc.*, 1977, **99**, 8367; (*b*) R. R. Gagne, C. A. Koval, T. J. Smith and M. C. Cimolino, *J. Am. Chem. Soc.*, 1979, **101**, 4571; (*c*) R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; (*d*) C. L. Spiro, S. E. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.

14 (*a*) R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 1513; (*b*) S. L. Lambert and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.

15 (*a*) S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1983, 2429; (*b*) S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1984, 2141; (*c*) S. K. Mandal, B. Adhikary and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1986, 1175.

16 (*a*) S. K. Mandal, L. K. Thompson, K. Nag and J.-P. Charland, *Inorg. Chem.*, 1987, **26**, 1391; (*b*) S. K. Mandal, L. K. Thompson, K. Nag and J.-P. Charland, *Can. J. Chem.*, 1987, **65**, 2815.

17 R. Das, K. K. Nanda, K. Venkatsubramanian, P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1992, 1253.

18 N. F. Curtis, *J. Chem. Soc.*, 1961, 3147.

19 Y. Ishimura, Y. Nonaka, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3728; Y. Nishida and S. Kida, *Chem. Lett.*, 1974, 339.

20 M. Mikuriya, M. Nakamura, H. Ōkawa and S. Kida, *Chem. Lett.*, 1982, 839 and refs. therein.

21 B. Bosnich, *J. Am. Chem. Soc.*, 1968, **90**, 627.

22 R. S. Downing and F. L. Urbach, *J. Am. Chem. Soc.*, 1969, **91**, 5977.

23 B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

24 M. Handa, N. Koga and S. Kida, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3853.

25 B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

26 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

Received 16*th July* 1992; *Paper* 2/03808K