

Structure–function relationship in some macrocyclic dicopper complexes

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Abstract. A number of macrocyclic dicopper(II) complexes containing aza-, amino or amido nitrogen and phenolic oxygen donors are described, X-ray crystal structures of several of these compounds are discussed. An account of their electrochemical behaviour and magnetic properties is given. Factors that affect electron transfer behaviour with regard to stabilization of the iso- and mixed-valence species, intramolecular electron transfer, and spin-exchange interactions have been examined in terms of the structural features.

Keywords. Macrocyclic dicopper complexes; X-ray structure; electrochemistry; magnetic properties.

1. Introduction

The development of the chemistry of binuclear complexes has been stimulated by a desire to synthesize model systems that may “mimic” the active sites of metallobio-molecules, may bind and activate small molecules, and may be used to investigate the mutual influence of two metal centres in terms of cooperative effect on the electronic, magnetic and redox properties of such systems. Consequent to this, the design and synthesis of ligands that would bind two metal ions, either the same or different, in the iso-valent or hetero-valent states have been the focus of extensive studies (for reviews see: Groh 1976–77; Casellato *et al* 1979; Fenton 1983; Karlin and Gultneh 1987; Zanello *et al* 1987). Robson (1970) introduced 4-methyl-2,6-diformylphenol as the precursor for the synthesis of binucleating ligands and since then there has been a continuous growth of such ligands and related complexes. Of particular interest has been the generation of binuclear macrocyclic complexes through template condensation of 4-methyl-2,6-diformylphenol with 1,3-diaminopropane in presence of metal salts, whose structural, magnetic and electrochemical behaviour has received detailed consideration. In the past few years we have been interested in knowing how the stereochemistry, reactivity, redox and magnetic behaviour of macrocyclic binuclear copper(II) complexes of this kind are affected by peripheral substituents and by gradual reduction of $H_2L^1 \rightarrow H_2L^2 \rightarrow H_2L^3$ (figure 1). We have also been interested in knowing how the replacement of two azomethine nitrogens of H_2L^1 by two amido nitrogens (H_4L^4 , H_4L^5) affects the properties of binuclear copper complexes. Here we provide a brief account of our findings.

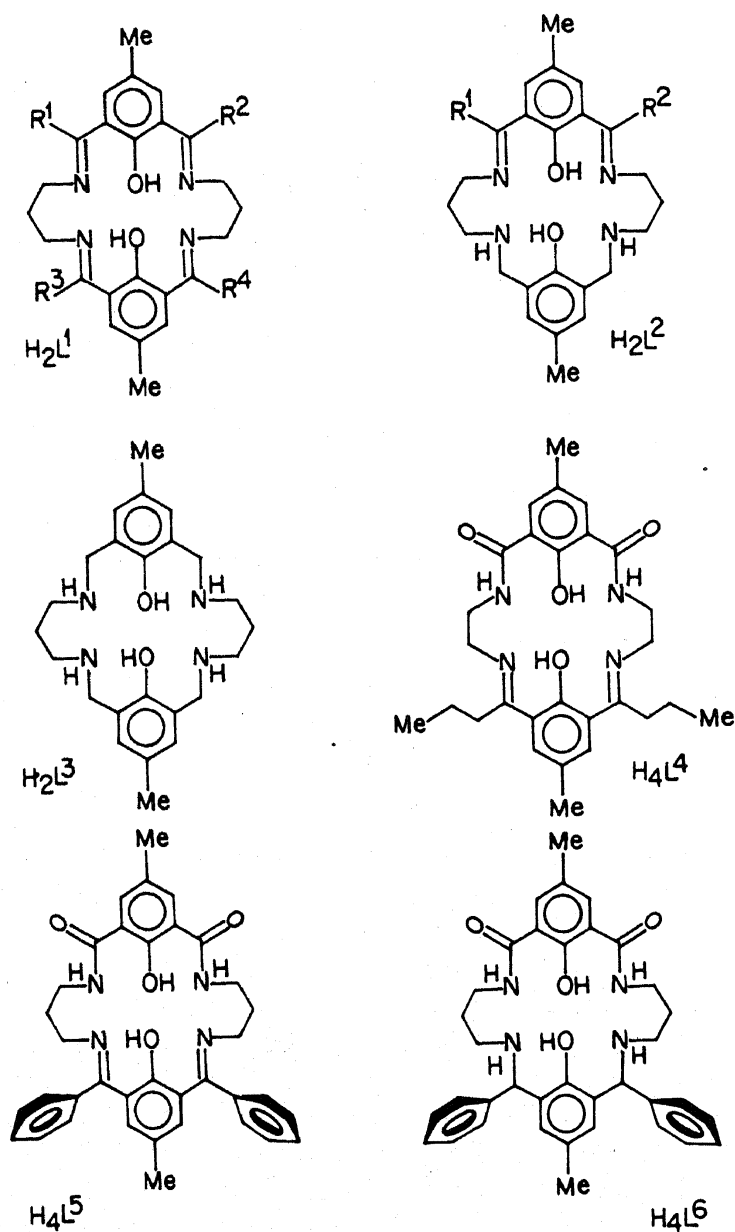
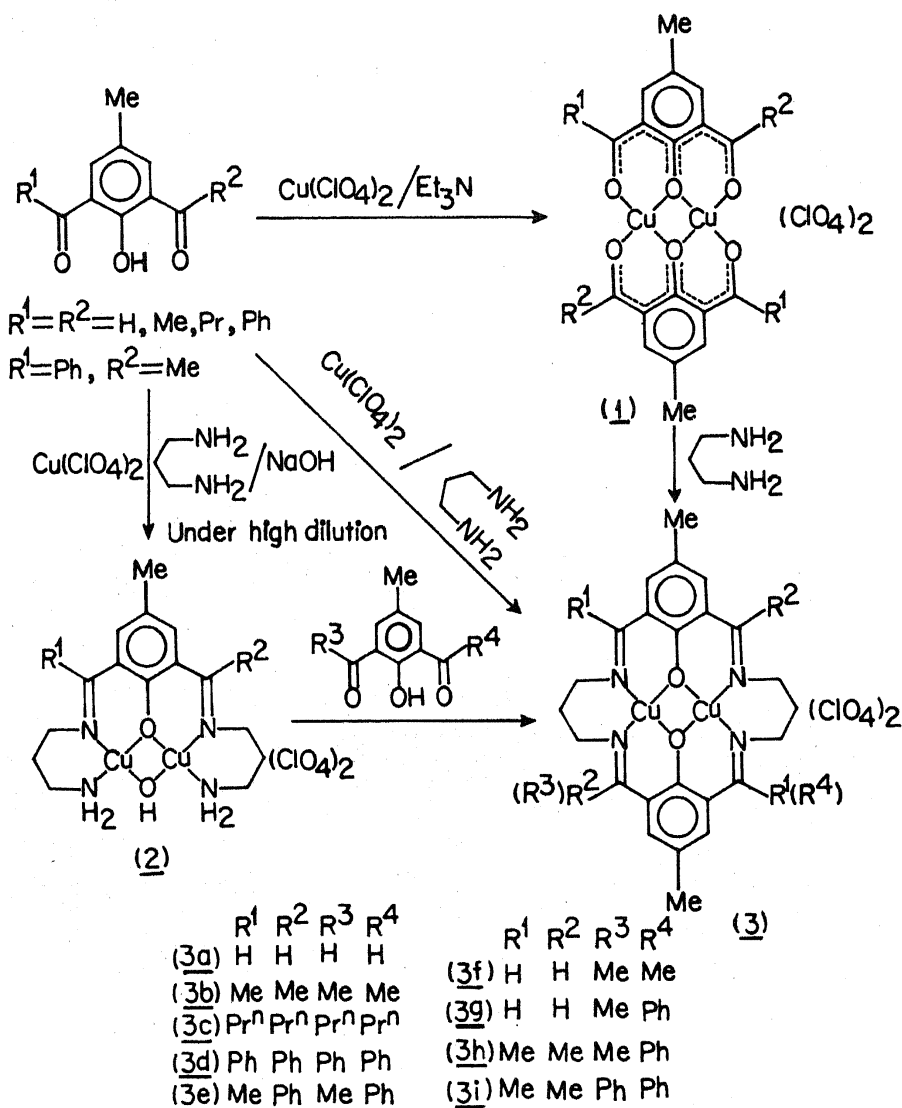


Figure 1. Structure of macrocyclic ligands.

2. Synthesis of the binuclear macrocyclic copper(II) complexes

The dicopper(II) perchlorate complexes (3) of variously tetrasubstituted macrocycles (H_2L^1) can be synthesized following three different routes (Mandal and Nag 1983; 1984) as delineated in scheme 1. Metathetical reactions involving complex (3a) and sodium halide or azide in aqueous solution lead to the formation of complexes $[Cu_2L^1Cl_2] \cdot 6H_2O$ (4), $[Cu_2L^1Br_2] \cdot 4H_2O$ (5), $[Cu_2L^1I_2] \cdot H_2O$ (6) and $[Cu_2L^1(N_3)_2] \cdot 3 \cdot 5H_2O$ (7) (Mandal *et al* 1989). On the basis of kinetic and preparative studies the mechanism for the formation of (3) from (2) has been proposed (Mandal and Nag 1984) to involve the pathways shown in scheme 2.

The synthesis of the dicopper(II) complexes (8a)–(8d) of the partially saturated

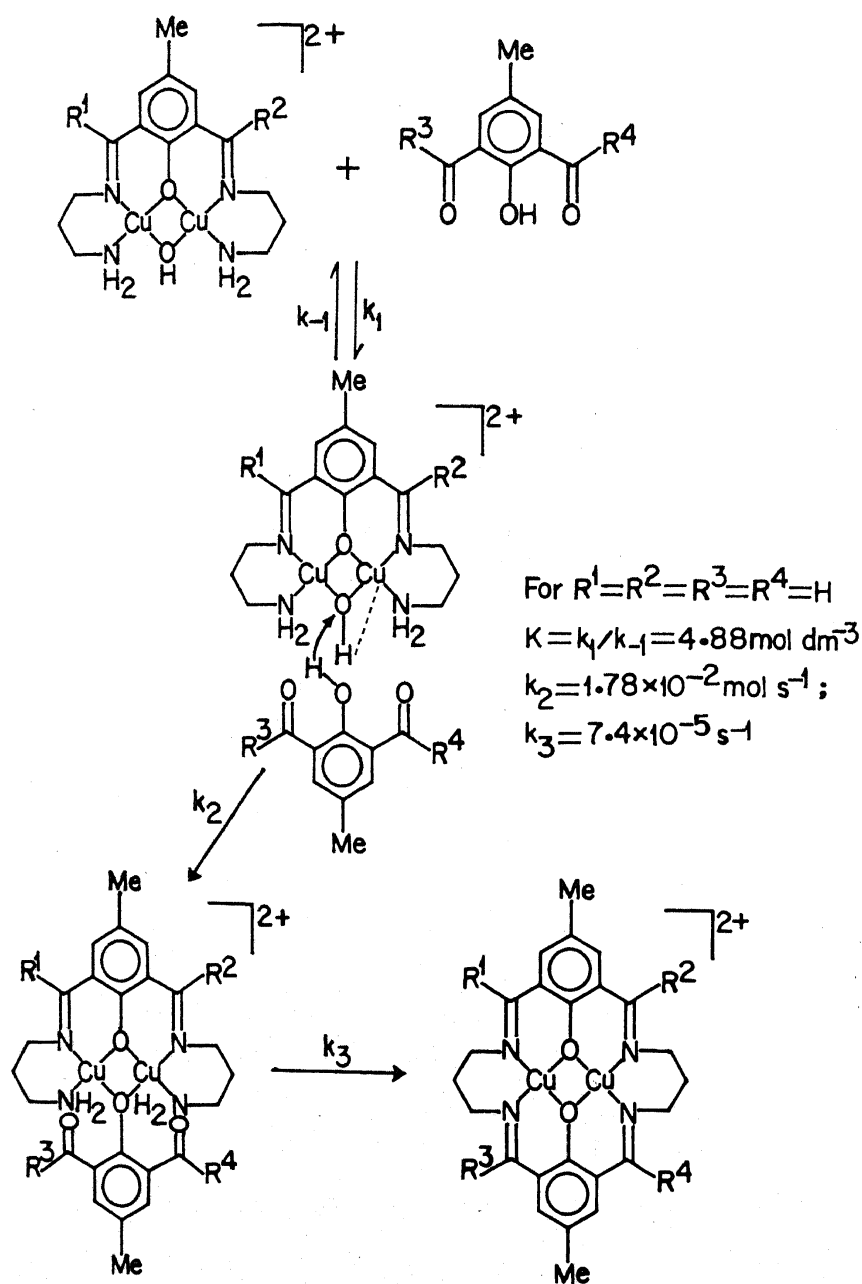


Scheme 1.

macrocycle (H_2L^2), in which two halves of the ring contain diamino and diaza moieties, is outlined in scheme 3.

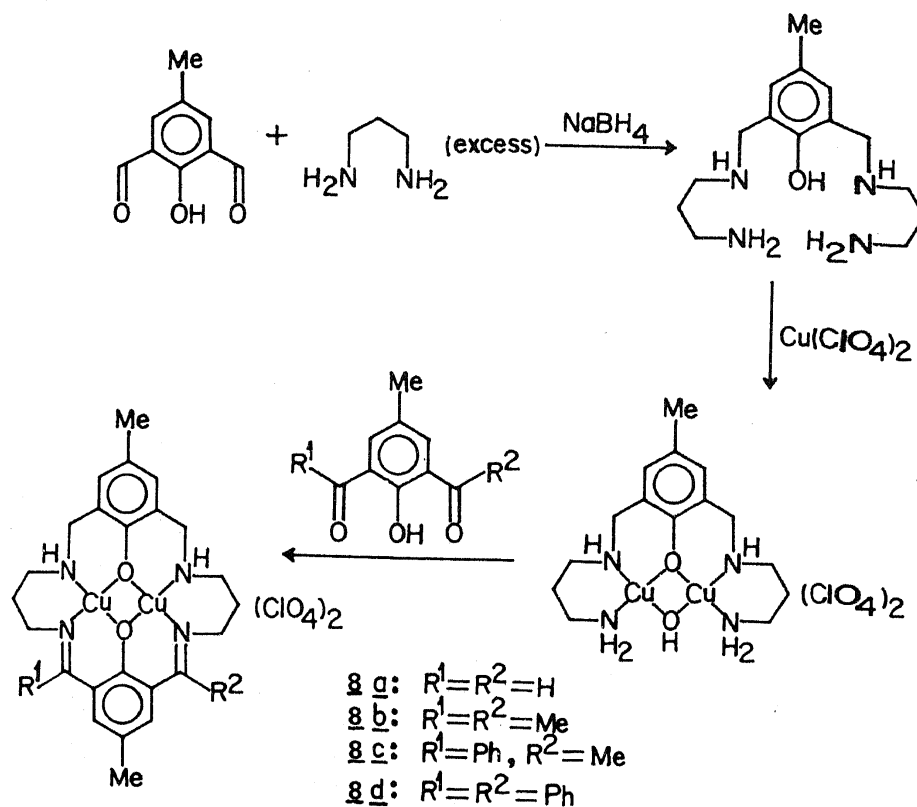
It may be mentioned that the macrocycles H_2L^1 or H_2L^2 are not available in the free state. Demetallation of their complexes leads to hydrolytic cleavage of the $CH=N$ groups. To synthesize H_2L^3 it was necessary to use a precursor complex analogous to (3a) in which the azomethine linkages can be reduced without reducing the metal centres. It was found that the lead complex $Pb_2L^1(NO_3)_2 \cdot 4H_2O$ can be smoothly reduced with $NaBH_4$. Removal of lead as $PbSO_4$ from the reduced species followed by extraction of the aqueous solution at $\approx pH 10$ with $CHCl_3$ affords H_2L^3 . In a similar way macrocycles of varying ring size related to H_2L^3 can be obtained (Mandal and Nag 1986). The formation of copper complexes of H_2L^3 is strongly affected by relatively subtle differences in reaction conditions. Thus, in the case of perchlorate derivatives four different compounds have been obtained (Mandal *et al* 1987). The formation of these and other complexes of H_2L^3 are summarized in scheme 4.

The synthetic routes involved in the generation of the copper complexes of the diaza-diamido macrocycles, H_4L^4 and H_4L^5 (Mandal *et al* 1989), are outlined in

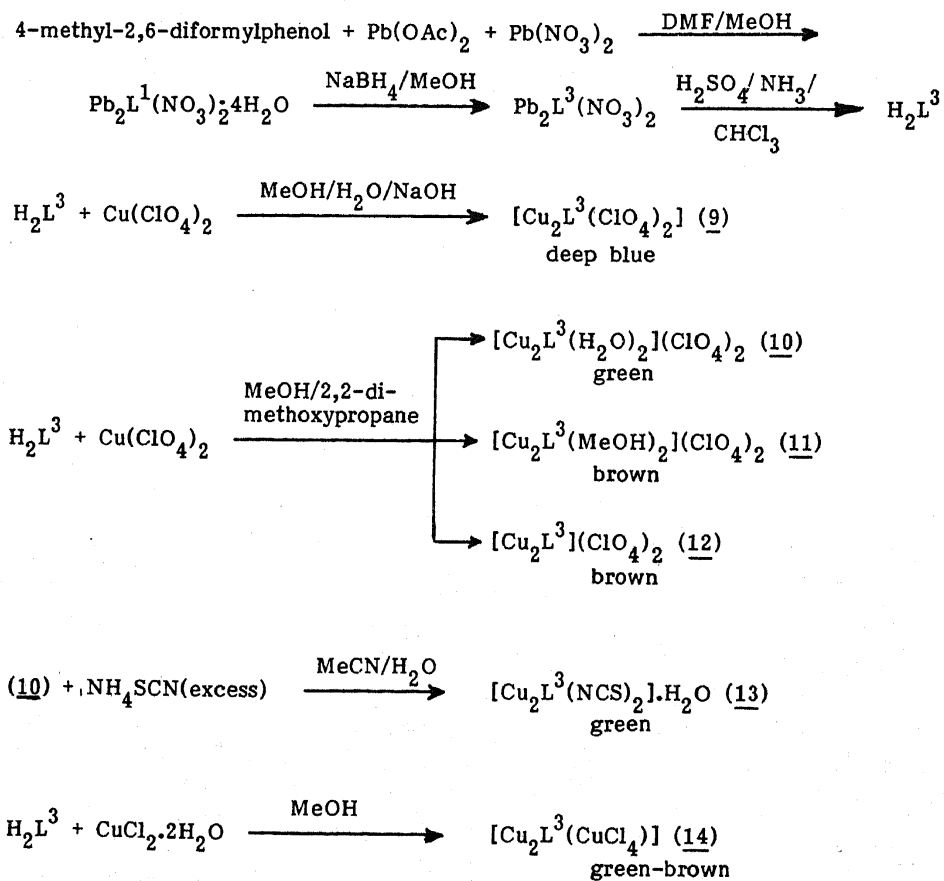


Scheme 2.

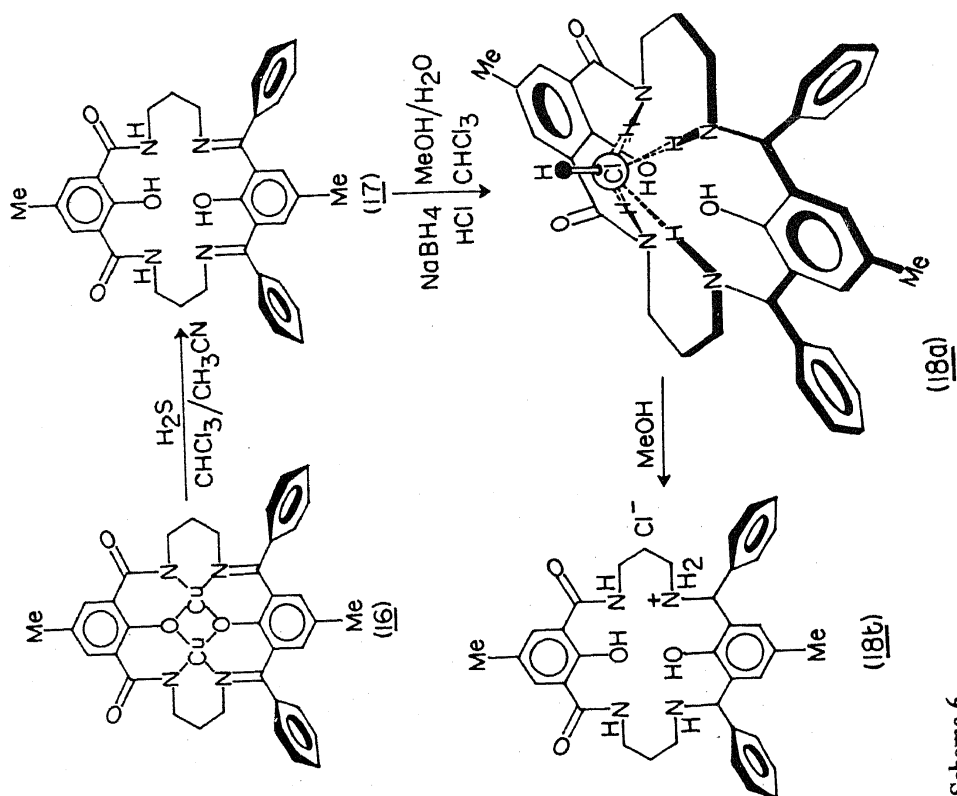
scheme 5. Complex $[\text{Cu}_2\text{L}^5]$ (16) can be best demetallated by treating a CHCl_3 -MeCN solution with a rapid stream of H_2S under dry conditions. H_4L^5 can be smoothly reduced with NaBH_4 and the reduced macrocycle gets precipitated when the pH of the aqueous solution is adjusted to 5.5 with HCl . The product isolated by extracting with CHCl_3 is found on analysis to have the composition $\text{H}_4\text{L}^6 \cdot \text{HCl}$. The composition of this compound remains unchanged on recrystallization from MeOH, however, it then becomes insoluble in CHCl_3 . The methanol-recrystallized product is a 1:1 electrolyte. The chloroform-soluble variety is also soluble in dichloromethane and benzene, but again becomes insoluble when recrystallized from MeCN. On the basis of these observations and their ^1H NMR spectra we conclude that the chloroform-soluble compound is a molecular complex of H_4L^6 and HCl (shown



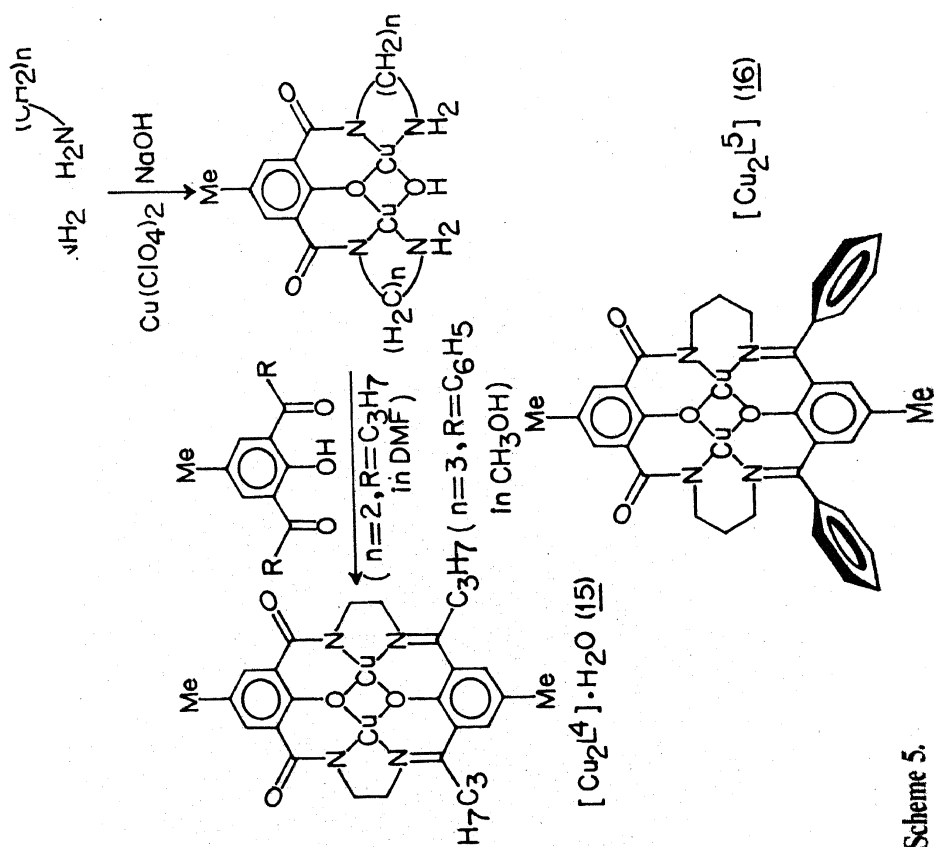
Scheme 3.



Scheme 4.



Scheme 6.



Scheme 5.

in scheme 6), where the chlorine atom of HCl is hydrogen-bonded to the amino and amido protons. In a polar solvent these hydrogen bonds break and the species becomes ionic.

3. Structure

For the sake of magneto-structural correlation we (Mandal *et al* 1989) have recently determined X-ray crystal structures of $[\text{Cu}_2\text{L}^1\text{Br}_2]\cdot\text{H}_2\text{O}$ (5) and $[\text{Cu}_2\text{L}^1\text{I}_2]\cdot\text{H}_2\text{O}$ (6) of the formyl derivative of the unsaturated macrocycle H_2L^1 . The structure of the corresponding chloro complex (4) was earlier determined by Hoskins *et al* (1976). All the three complexes have closely similar structures and consist of an almost flat macrocyclic ring enclosing two distorted square pyramidal copper(II) centres, bridged by phenoxide oxygen atoms and bound terminally in a *trans* arrangement to two halogen atoms; the copper centres are displaced from the N_2O_2 coordination plane towards the halogen atoms. Key structural parameters for these compounds are given below.

Complex	Cu–Cu (Å)	CuOCu (°)	Displacement of Cu (Å)	Cu–X (Å)
(4)	3.133	104.5	0.21	2.582
(5)	3.124	103.6	0.205	2.737
(6)	3.104	103.7	0.176	3.026

The structure of $[\text{Cu}_2\text{L}^3(\text{ClO}_4)_2]$ (9) (Mandal *et al* 1987) involving the fully saturated macrocycle consists of two copper(II) centres bridged by two phenoxide oxygen atoms with four secondary amine nitrogen donors completing the in-plane donor sets, and two axially bound perchlorates forming a distorted, axially elongated octahedron. The two copper atoms are separated by 2.993 Å, with a Cu–O–Cu bridge angle of 102.8°. The related structure for $[\text{Cu}_2\text{L}^3(\text{MeOH})_2](\text{ClO}_4)_2$ (11) (Mandal *et al* 1987) consists of a binuclear five-coordinated copper(II) species involving two weakly bound *trans*-axial methanol molecules (Cu–O = 2.413 Å). In this complex the Cu–Cu distance is 3.088 Å and the Cu–O–Cu bridge angle is 103.9°. Although crystal structures of $[\text{Cu}_2\text{L}^3(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (10) and $[\text{Cu}_2\text{L}^3](\text{ClO}_4)_2$ (12) have not been determined, it may be reasonably assumed that structurally (10) is very similar to (11), and in (12) the copper(II) centres attain square-planar configurations.

The molecular structures of the aza-amido macrocyclic complexes $[\text{Cu}_2\text{L}^4]\cdot\text{H}_2\text{O}$ (15) and $[\text{Cu}_2\text{L}^5]$ (16) have been determined recently (Mandal *et al* 1989). The structure of (15) consists of two essentially square-planar copper(II) centres bridged by two phenoxide oxygen atoms with one imino and one carboxamido nitrogen donor completing the CuN_2O_2 plane. However, one copper atom is displaced from the N_2O_2 mean plane by 0.137 Å towards a carboxamide oxygen of the neighbouring molecule forming a long Cu(1)–O(3) (2.808 Å) contact. In this complex the Cu–Cu distance is 2.898 Å, and the two bridge angles from the azomethine (99.0°) and carboxamide (100.6°) units are slightly different. The molecular structure of complex (16) is basically similar to that of (15) although both the copper(II) centres have distorted square-pyramidal geometry. The coordination of the apical site of each copper centre involves participation of an amide oxygen from a neighbouring molecule (Cu(1)–O(3) = 2.371 Å, Cu(2)–O(4) = 2.413 Å) that leads to a stacking of the molecules along the *b* axis in the crystal lattice. Compared to (15), the Cu–Cu distance in this complex is longer

(3.018 Å) and the bridge angle involving azomethine (98.18°) is quite different from that involving the amide moiety (104.91°).

4. Electrochemistry

The binuclear copper(II) complexes (1), which are precursors for the unsaturated macrocyclic complexes (3), exhibit uncommon electrochemical behaviour in that two-electron transfers ($\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} + 2e^- \rightleftharpoons \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$) occur reversibly at a single potential, $E_{1/2} \sim -0.05$ V vs SCE (Mandal and Nag 1983a). In contrast, heterodinuclear copper(II) complexes analogous to (1), undergo one-electron reduction in two steps and the voltammetric behaviour shows strong dependence on the nature of solvent (Adhikary *et al* 1987).

The redox chemistry of the macrocyclic systems (3) has been investigated in detail (Mandal and Nag 1983b; Mandal *et al* 1986). In all cases cyclic voltammograms show sequential reversible or quasi-reversible one-electron transfers at two different potentials (table 1), indicating that the mixed-valence $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ species is stable. The relative stability of the mixed-valence species in the equilibrium mixture of $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ and $\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ species, is given by the conproportionation constant, K_{con} , where



$$K_{\text{con}} = \exp(nF[E_{1/2}(1) - E_{1/2}(2)]/RT)$$

Thus, greater separation between the two redox potentials indicates greater stability of the mixed-valent species. Table 1 shows that throughout the series K_{con} varies between 10^6 and 10^{13} , it is minimum for (3a) and maximum for (3b) or (3c). A comparative electrochemical study involving some of these complex in MeCN and CH_2Cl_2 indicated that for a given complex K_{con} is greater in MeCN. The substituents in the macrocyclic ring show a more pronounced effect on $E_{1/2}$ (2) than on $E_{1/2}$ (1); the electron-releasing substituents shift the potential to a more negative value. In a recent study (Adhikary *et al* 1988) involving the dicopper(II) complexes of the Schiff bases obtained by condensing 4-methyl-2, 6-diformylphenol with different combina-

Table 1. Electrochemical data ($E_{1/2}$, V^a) for $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_2$ complexes in MeCN.

Complex	Substituents	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$	K_{con}
(3a)	H, H, H, H	-0.46 -0.43 ^b	-0.90 ^b	9.0×10^7
(3b)	Me, Me, Me, Me	-0.46 ^c	-1.23 ^c	1.1×10^{13}
(3c)	Pr, Pr, Pr, Pr	-0.47 ^c	-1.25 ^c	1.6×10^{13}
(3d)	Ph, Ph, Ph, Ph	-0.47	-1.01	1.4×10^9
(3e)	Ph, Me, Me, Ph	-0.48 ^c	-1.18 ^c	6.9×10^{11}
(3f)	H, H, Me, Me	-0.44	-0.98	1.4×10^9
(3g)	H, H, Me, Ph	-0.44	-0.97	9.3×10^8
(3h)	Me, Me, Me, Ph	-0.45	-1.06	2.1×10^{10}
(3i)	Me, Me, Ph, Ph	-0.46	-1.03	4.4×10^9

^aPotentials refer to standard calomel electrode (SCE); ^bin Me_2SO ; ^cpotentials refer to couples scanned separately between 0 and -0.6 V, and -1.0 and -1.4 V

tions of $p\text{-NH}_2\text{C}_6\text{H}_4\text{X}$ ($\text{X} = \text{H, Me, OMe, Cl, COMe}$ or NO_2), the effect of substituents on redox potentials has been convincingly demonstrated. The linear free energy relation obtained by plotting $E_{1/2}$ (1) or $E_{1/2}$ (2) vs $\sum\sigma_p$ (Hammett parameters) indicates that the electron-transfer reactions are governed by inductive and resonance effects.

One of our major objectives in studying the redox behaviour of complex systems (3) was to investigate intramolecular electron transfer in the mixed-valence species. In $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ complexes 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 centre. Gagné *et al* (1979) observed that the $\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$ species from (3a) produces an isotropic seven-line spectrum in solution, which changes to a four-line pattern at about 200K. Long and Hendrickson (1983) investigated variable temperature EPR spectra for several mixed-valence systems relating to the unsaturated macrocycles (3) obtained by template condensation of 4-*t*-butyl-2,6-diformylphenol with symmetric and asymmetric diamines. Both electron-delocalized and localized spectra were obtained in solution at room temperature.

We have examined (Mandal *et al* 1988) the room temperature EPR spectra of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}^1]^+$ complexes generated by controlled potential electrolysis of the corresponding $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_2$ complexes in MeCN or CH_2Cl_2 . Except for the one derived from (3a), for which a seven-line copper hyperfine pattern is observed, in all other cases the spectra belong to the four-line patterns. In frozen solution, anisotropic spectra with axial symmetry having four A_{11} hyperfine lines are obtained.

It may be expected that delocalization of the odd electron over both the copper centres will be maximized when the molecule is highly symmetric and the metal atoms are in square-planar configurations. Attainment of this situation, however, is opposed by the strong reluctance of copper(I) to adopt square-planar geometry.

The X-ray crystal structure of $[\text{Cu}^{\text{II}}\text{Cu}^{\text{I}}\text{L}^1](\text{ClO}_4)\cdot 0.5 \text{ MeOH}$ (Gagné *et al* 1980), derived from (3a), indicates that the Cu^{II} centre is square planar, while the Cu^{I} centre, which is disordered over two sites, is displaced by 0.15 and 0.65 Å from the O_2N_2 basal plane. Thus, a seven-line EPR spectrum of this species suggests that the stereochemical environment of the metal centres oscillates between $\text{Cu}^{\text{II}}(\text{planar})\text{Cu}^{\text{I}}(\text{planar})$ and $\text{Cu}^{\text{II}}(\text{planar})\text{Cu}^{\text{I}}$ (apically distorted planar), to accommodate the valence changes. The rate of such conformational changes (k_s), from less symmetric to more symmetric states, and the rate of intramolecular electron transfer (k_{th}) both increase with increase of temperature. The observation of four copper hyperfine patterns in all other cases indicates that either k_s or k_{th} or both are less than $5.5 \times 10^8 \text{ s}^{-1}$ (the limit of the EPR time scale). In the case of $[\text{Cu}_2\text{L}^1]^+$ from (3a), k_{th} at 298 K was estimated to be $1.7 \times 10^{10} \text{ s}^{-1}$, whereas for the species derived from 4-*t*-butyl-2,6-diformylphenol this value ranged from 1.6×10^{10} to $2.9 \times 10^9 \text{ s}^{-1}$. The mixed-valence species obtained from (3b)–(3i) differ from the one derived from (3a) in that the hydrogen atoms of the azomethine linkages in (3a) are fully or partly substituted with alkyl or phenyl groups. These bulkier peripheral substituents could possibly hinder the conformational changes that would be necessary to observe a EPR detectable exchange process. It is also possible that a coordinating solvent like MeCN may 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.

Table 2. Electrochemical data ($E_{1/2}$, V)^a for reduction and oxidation of complexes (3a), (8a), and (9).

Complex	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{I}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{I}} \rightleftharpoons \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$	$K_{\text{con}}^{\text{b}}$
$[\text{Cu}_2\text{L}^1](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (3a)	-0.43	-0.90	9.0×10^7
$[\text{Cu}_2\text{L}^2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (8a)	-0.58	-0.90	2.6×10^5
$[\text{Cu}_2\text{L}^3(\text{ClO}_4)_2]$ (9)	-0.76	-0.90	2.3×10^2
	$\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightleftharpoons \text{Cu}^{\text{II}}\text{Cu}^{\text{III}}$	$\text{Cu}^{\text{II}}\text{Cu}^{\text{III}} \rightleftharpoons \text{Cu}^{\text{III}}\text{Cu}^{\text{III}}$	$K_{\text{con}}^{\text{c}}$
$[\text{Cu}_2\text{L}^1](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (3a)	-	-	-
$[\text{Cu}_2\text{L}^2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (8a)	1.34	-	-
$[\text{Cu}_3\text{L}^3(\text{ClO}_4)_2]$ (9a)	1.19	1.41	5.2×10^3

^aPotentials (V) refer to standard calomel electrode (SCE); ^bin Me_2SO ; ^cin MeCN

As already stated we have been interested in knowing how the redox behaviour of copper(II) complexes is affected by gradual reduction of the azomethine linkages of H_2L^1 (H_2L^2 , H_2L^3 ; figure 1). A comparative study was therefore made (Mandal *et al* 1987) for the stepwise reduction of complexes (3a), (8a) and (9) in Me_2SO and oxidation of these compounds in MeCN. Electrochemical data for these systems are given in table 2. It may be noted that a dramatic negative shift in the first one-electron reduction potential,

$$E_{1/2}(1) = -0.43 \text{ V (3a)}, -0.58 \text{ V (8a)}, -0.76 \text{ V (9)},$$

occurs as a function of stepwise saturation of the azomethine linkages ($\text{H}_1\text{L}^1 \rightarrow \text{H}_2\text{L}^2 \rightarrow \text{H}_2\text{L}^3$), indicating enhanced stability of the copper(I) state with increased saturation. A second redox wave, associated with the reduction of the mixed-valence species is observed for all three compounds at the same potentials,

$$E_{1/2}(2) = -0.90 \text{ V},$$

independent of the degree of ligand saturation. A related trend is observed for the oxidation of these complexes. No redox waves are observed for complex (3a) in the range 0 to +1.7 V, while for (8a) a single reversible voltammogram,

$$E_{1/2} = 1.34 \text{ V},$$

is observed and for (9) two reversible waves,

$$E_{1/2} = 1.19 \text{ V}, 1.41 \text{ V},$$

are observed. Solution EPR spectra for the one-electron reduction (MeCN) and one-electron oxidation (Me_2SO) products of (9) exhibit four copper hyperfine lines, in accord with the interaction of the odd electron with just one copper centre. The EPR spectra for both one-electron reduction and oxidation products of (8a) are also consistent with the odd electron localized in one copper centre. The mixed-valence species derived from (8a) would be expected to represent a structural intermediate between (3a) and (9). The presence of one saturated nitrogen per copper is therefore sufficient to destroy the condition for room temperature delocalization. The electro-

chemical behaviour of (8b)–(8d) and the EPR spectral characteristics of their mixed-valence species are quite similar to that of (8a). Insofar as the electrochemical reduction of $[\text{Cu}_2\text{L}^3(\text{NCS})_2]\cdot\text{H}_2\text{O}$ (13) and $[\text{Cu}_2\text{L}^3(\text{CuCl}_4)]$ (14) is concerned, their behaviour is essentially identical to that of (9). The stepwise oxidation of the thiocyanato complex is preceded by a broad irreversible wave at (+0.51 V), which is implicated due to the oxidation of NCS^- ion. On the other hand, oxidation of complex (14) is dominated by a redox wave at +0.3 V associated with a mononuclear copper entity.

The dicopper(II) complex of the saturated macrocyclic ligand (H_2L^3), to our knowledge, represents the first example of a magnetically coupled binuclear copper(II) system that involves two successive one-electron oxidation steps to produce Cu(II)–Cu(III) and Cu(III)–Cu(III) as well as successive one-electron reduction steps to produce mixed-valence Cu(II)–Cu(I) and binuclear Cu(I) species.

Since complexes of deprotonated amide stabilize higher oxidation states, we expected that complexes (15) or (16) should undergo ready oxidation. However, the cyclic voltammogram of complex (16) in Me_2SO exhibits an irreversible anodic wave at about +0.45 V and no further electrochemical response up to +1.4 V (Adhikary *et al* 1990). Whether this irreversible electrode process involves the metal centres or not could not be ascertained. In the cathodic regime, complex (16) undergoes stepwise reduction at –1.0 and –1.46 V. Complex (15) behaves in almost the same way. A comparison between the aza-amido complexes and the previously described tetraaza/amino complexes shows that the former reduce at potentials significantly more negative than the latter. Clearly, amides stabilize the +2 oxidation state of copper to a greater extent. Moreover, the addition of electron to the neutral aza-amido complexes should be electrostatically more difficult than the cationic aza/amino complexes.

5. Magnetic properties

Magneto-structural correlation in the phenoxo-bridged macrocyclic dicopper(II) complexes has been the focus of our interest. 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 predominately σ -overlap. In other words, the antiferromagnetic exchange interaction between the copper centres is likely to be influenced most significantly by the planar arrangement of the oxygen bridges and the phenoxide bridge angle. It is well known that in a series of dihydroxo-bridged binuclear copper(II) complexes a linear relationship,

$$2J = -74.53Q + 7270 \text{ cm}^{-1},$$

exists between the singlet–triplet separation energy ($2J$) and the Cu–O–Cu angles (Q) involving the hydroxo group (Crawford *et al* 1976), and for a bridge angle of 104° , $-2J$ was found to be 509 cm^{-1} . In the binuclear complexes the exchange interaction is also expected to be affected by out-of-plane distortions at the copper centre, however, this effect is considered to be small (Kahn 1985a). In addition, the spin-exchange between oxo-bridged copper centres has been shown to depend on the geometry of the bridging ligand; distortion of oxygen from trigonal planar (sp^2) to pyramidal configuration (sp^3) leads to reduction of antiferromagnetic effect (Mazurek *et al* 1985).

The magnetic data given in table 3 are based on variable temperature magnetic

Table 3. Key structural data and magnetic data for macrocyclic dicopper(II) complexes.

Complex	CuOCu (°)	$\sum O$ (°)	Cu-Cu (Å)	Cu-O (Å)	Out-of-plane displacement (Å)	$-2J$ (cm^{-1})
$\text{Cu}_2\text{L}^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}^a$ (3a)	102.3	358.4	3.091	1.981	0.019	850
	103.6	359.1	3.096	1.989	0.083	
$[\text{Cu}_2\text{L}^1\text{Cl}_2] \cdot 6\text{H}_2\text{O}$ (4)	104.5	357.4	3.133	1.981	0.21	722
$[\text{Cu}_2\text{L}^1\text{Br}_2] \cdot \text{H}_2\text{O}$ (5)	103.6	360.0	3.124	1.989	0.205	771
$[\text{Cu}_2\text{L}^1\text{I}_2] \cdot \text{H}_2\text{O}$ (6)	103.7	359.1	3.104	1.974	0.176	852
				1.975		
$[\text{Cu}_2\text{L}^1(\text{N}_3)_2] \cdot \text{H}_2\text{O}$ (7)	-	-	-	-	-	780
$\text{Cu}_2\text{L}^1(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3b)	-	-	-	-	-	835
$\text{Cu}_2\text{L}^1(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (3c)	-	-	-	-	-	806
$[\text{Cu}_2\text{L}^3(\text{ClO}_4)_2]$ (9)	102.8	360.0	2.993	1.915	-	824
$[\text{Cu}_2\text{L}^3](\text{ClO}_4)_2$ (12)	-	-	-	-	-	827
$[\text{Cu}_2\text{L}^4] \cdot \text{H}_2\text{O}$ (15)	99.0	360.1	2.898	1.918	-	689
	100.6			1.885		
$[\text{Cu}_2\text{L}^5]$ (16)	98.18 ^b	354.3 ^b	3.018	1.986	-	816
	104.91 ^c	359.8 ^c		1.891		
				2.007		
				1.915		

^aL K Thompson (private communication); ^bfrom azomethine unit; ^cfrom amide unit.

susceptibility measurements in the temperature range 5–300 K. The best-fit lines were calculated from the modified Van Vleck equation for exchange coupled copper(II) pairs,

$$\chi_M = \frac{N\beta^2 g^2}{3kT} [1 + 1/3 \exp(-2J/kT)]^{-1} (1 - \rho) + \left[\frac{N\beta^2 g^2}{4kT} \right] \rho + N_\alpha.$$

In this expression $-2J$ is the singlet-triplet splitting and other terms have their usual meaning. ρ represents the fraction of a possible magnetically dilute, mononuclear copper(II) impurity. The temperature independent paramagnetism for a binuclear copper(II) complex, N_α , was taken as 120×10^{-6} c.g.s. units/mol.

A comparison of key structural parameters and exchange integrals for all the complexes in table 3 discloses several interesting features. In general, complexes belonging to all the macrocycles show very strong antiferromagnetic interaction and the magnitude of the exchange integrals are much greater than dihydroxo-bridged copper(II) complexes of similar CuOCu bridge angles, indicating that superexchange takes place more effectively through phenoxide bridges. In all the complexes, pyramidal distortion at the phenoxide bridge is not severe and therefore this factor is unlikely to affect exchange interaction significantly.

A comparison of structural parameters and exchange integrals for complexes $[\text{Cu}_2\text{L}^1\text{Cl}_2] \cdot 6\text{H}_2\text{O}$ (4), $[\text{Cu}_2\text{L}^1\text{Br}_2] \cdot \text{H}_2\text{O}$ (5) and $[\text{Cu}_2\text{L}^1\text{I}_2] \cdot \text{H}_2\text{O}$ (6) reveals that despite similar CuOCu bridge angles, Cu-O(phenoxide) separations, out-of-plane copper displacements and the solid angles at the phenoxide bridges, exchange integrals vary quite significantly with $\text{Cl}(722 \text{ cm}^{-1}) < \text{Br}(771 \text{ cm}^{-1}) < \text{I}(852 \text{ cm}^{-1})$. It is quite significant that although the CuOCu bridge angle for complex (4) is the maximum, the $-2J$ value is minimum. A comparison of the structural and magnetic features of (6) with the perchlorate complex $\text{Cu}_2\text{L}^1(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (3a) which involves two different molecules in the unit cell, one due to six-coordinate and the other to five-coordinate copper centres, reveals similar binuclear centre dimensions and identical singlet-triplet energy separations.

The marked difference in exchange between (4)–(6), which parallels the trend in electronegativity of the halogens, gives a clear indication that the axially bound halogens have a primary influence on exchange, though they are bound orthogonally to the copper magnetic orbital. The axially bound halogens polarize the electron density in the copper magnetic orbitals in the decreasing order $\text{Cl} > \text{Br} > \text{I}$. The electron-withdrawing effect of I is so small and the Cu–I distance (3.026 Å) is so large that axial perturbation practically vanishes. On the basis of the observed trend in $-2J$ we predict that for the fluoro-complex the exchange integral will be about 550 cm^{-1} . However, instead of electronegativities if we consider electron affinities of the halogens, $-2J$ for fluoro complex will be 770 cm^{-1} . The verification of this part has to wait till crystals of $[\text{Cu}_2 \text{L}^1 \text{F}_2]$ are available.

It may be noted that replacement of the azomethine hydrogen atoms of (3a) by methyl (3b) or propyl (3c) groups affect spin exchange only marginally [$850(3a)$, $835(3b)$, $806 \text{ cm}^{-1}(3c)$]. The saturation of the nitrogen donors of $\text{H}_2 \text{L}^1$ also does not have a major effect on spin exchange [$850(3a)$ vs. $827(9)$, $824 \text{ cm}^{-1}(12)$]. It appears that while reduction of the $\text{CH}=\text{N}$ moiety of (3a) to CH_2NH (9) contributes to decrease in delocalization of electrons (and hence exchange interaction), the shortening of the Cu–O(phenoxide) distance of (9) (1.91 Å) compared to that of (3a) (1.98 Å) acts in the reverse way; the CuOCu bridge angles for (3a) (average 102.9°) and (9) (102.8°) are identical.

It is of interest to compare the magnetism of complexes (15) and (16) in the light of their structural data. We note that in complex (15), for which $-2J = 690 \text{ cm}^{-1}$, the two phenoxo-bridge angles are 99.0° and 100.6° , and for (16), whose singlet-triplet energy separation is 815 cm^{-1} , the Cu–O–3u bridge angles are 98.18° and 104.91° . It may be also pointed out that some major differences exist between the two compounds in the bond distances within the $\text{N}_4\text{O}_2\text{Cu}_2$ framework (average Cu–N 1.875 Å, Cu–O 1.895 Å (15); average Cu–Cu–N 1.937 Å, Cu–O 1.950 Å (16)). On the basis of the shorter bond lengths within the magnetic framework (basal plane) in (15), an augmentation of spin exchange would be expected.

The large phenoxide bridge angle, Cu(1)–O(2)–Cu(2), 104.9° in (16) might be considered to dominate the exchange situation for this compound, but considering the magnitude of the exchange ($-2J = 815 \text{ cm}^{-1}$) it would be more reasonable to assume that both oxygen groups contribute significantly to spin exchange. The oxygen atom of the smaller CuOCu bridge angle of (16) has significant pyramidal character (solid angle 354.3°) which also contributes in reducing exchange in this compound. It is clear that the situation concerning these macrocyclic complexes, in which the two bridge angles are different, are very complicated because factors such as bridge angles, bond distances, pyramidal distortion of the oxygens, contribute to exchange in different ways and, until a larger selection of macrocyclic systems of this sort is examined, little can be said about magneto-structural trends.

6. Conclusion and outlook

We have tried to address certain basic issues related to redox behaviour and magnetic properties of phenoxo-bridged macrocyclic dicopper(II) complexes. Of particular interest is the dramatic effect of ligand saturation on both oxidation and reduction potentials. Our continuing interest in this area indicates that this phenomenon is not confined to copper alone, and in fact fascinating chemistry is emerging with other transition metals (R Das, S K Mandal and K Nag, unpublished results). We have

also demonstrated that a very different perturbation on the copper magnetic orbitals that does not involve a direct interaction with the magnetic orbitals can lead to fine tuning of the magnetic exchange in binuclear copper(II) complexes.

An unsolved problem concerning the copper binuclear systems is whether there exists a relation between the magnitude of magnetic interaction in a $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}$ species and its one-electron and two-electron reduction or oxidation potentials (Kahn 1985b). In the light of our findings we are in a position to say that although the redox potentials of structurally related dicopper(II) complexes can be varied widely, in particular through variation of donor capacity of the binding sites and by electronic effects, no effective variation takes place in singlet-triplet separation energies provided the geometry of the basal plane of the molecules remains unchanged.

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