Inorganica Chimica Acta, 62 (1982) 39–50

Binuclear Complexes of Macrocyclic Schiff Base Ligands as Hosts for Small Substrate Molecules

S. M. NELSON

Department of Chemistry, Queen's University, Belfast BT9 5AG, U.K.

Received February 23, 1982

Reaction of 2,6-diacetylpyridine or 2,5-diformylpyridine with a variety of diprimary amines in the presence of large alkaline earth metal ions acting as templates yields complexes of [2 + 2] macrocyclic Schiff bases in good yield. The single template ion may be replaced by Cu(II), and other transition metal ions, to afford binuclear complexes in most cases. The bi-Cu(II) complexes may act as receptors for one or two small bridging substrate molecules or ions including OH^-, OR^-, *halide,* N_3^-, NCS^-, $NCSe^-$, *pyrazolate, imidazolate, and pyrazine. Antiferromagnetic superexchange coupling has been recognized and measured by means of measurements of magnetic susceptibility and e.s.r. spectra. X-ray crystal structures of several of the complexes are described. The relationships between the macrocycle cavity size and the nature and mode of attachment of the bridging substrate are discussed. Some di-μ-hydroxo and alkoxo bi-Cu(II) complexes undergo ready reduction to bi-Cu(I) with accompanying oxidative coupling of available substrate molecules. The structure of a tetranuclear Cu(I) cluster containing phenylacetylide is described.*

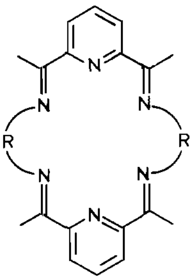
Introduction

Transition metal complexes of binucleating ligands are of interest because they provide the means to study (i) the intramolecular binding, and possible activation, of small substrate molecules and ions between the metal centres, (ii) multielectron redox reactions, and (iii) magnetic exchange interactions [1]. They may also serve as models in certain cases for some metalloproteins for which the biological function is associated with the occurrence of the metal centres in pairs. An example of the latter is bovine erythrocyte superoxide dismutase, known to contain an imidazolate bridged Cu(II)···Zn(II) active site [2]. Both imidazolate [3] and hydroxo [4] bridges have variously been proposed to link the Fe(III) and Cu(II) sites in cytochrome c oxidase, and antiferromagnetically coupled Cu(II) ions also occur in several other copper proteins including, for example, oxyhaemocyanin [5]. The investigation of synthetic binuclear complexes of known structure may contribute to the better understanding of the natural systems. Synthetic macrocyclic ligands having a cavity size large enough to encapsulate two metal ions provide a means whereby the interactions and structural relationships between the metal centres may be studied in the laboratory. This paper reviews the synthesis, structures and properties of some binuclear complexes, principally of copper, of a family of macrocyclic polyimine (Schiff base) ligands.

Synthesis of the Macrocyclic Ligands and their Bimetallic Transition Metal Complexes

The synthesis of the binucleating Schiff base macrocycles involves condensation of two molecules of a suitable dicarbonyl compound with two molecules of a diprimary amine. This type of reaction is termed a [2 + 2] condensation. Although such macrocycles may occasionally be prepared in reasonable yield in the absence [6] of a template it remains true that most such condensations are best carried out in the presence of a suitable metal ion which serves to direct the condensation preferentially towards cyclic rather than oligomeric/polymeric products (the kinetic template effect) and/or to stabilize the macrocycle once formed (the thermodynamic template effect). Particularly useful dicarbonyl precursors are 2,6-diformylpyridine, 2,6-diacetylpyridine, and 2,5-diformylfuran. A selection of the binucleating macrocycles derived from 2,6-diacetylpyridine are shown below [L^1–L^7).

0020-1693/82/0000-0000/$02.75



L^1, $R = (CH_2)_2$
L^2, $R = (CH_2)_3$
L^3, $R = (CH_2)_2–O–(CH_2)_2$
L^4, $R = (CH_2)_2–S–(CH_2)_2$
L^5, $R = (CH_2)_2–NH–(CH_2)_2$
L^6, $R = (CH_2)_3–NH–(CH_2)_3$
L^7, $R = (CH_2)_2–O–(CH_2)_2–$
$–O–(CH_2)_2$

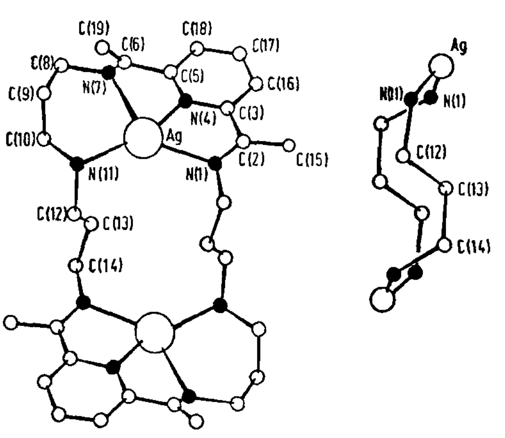
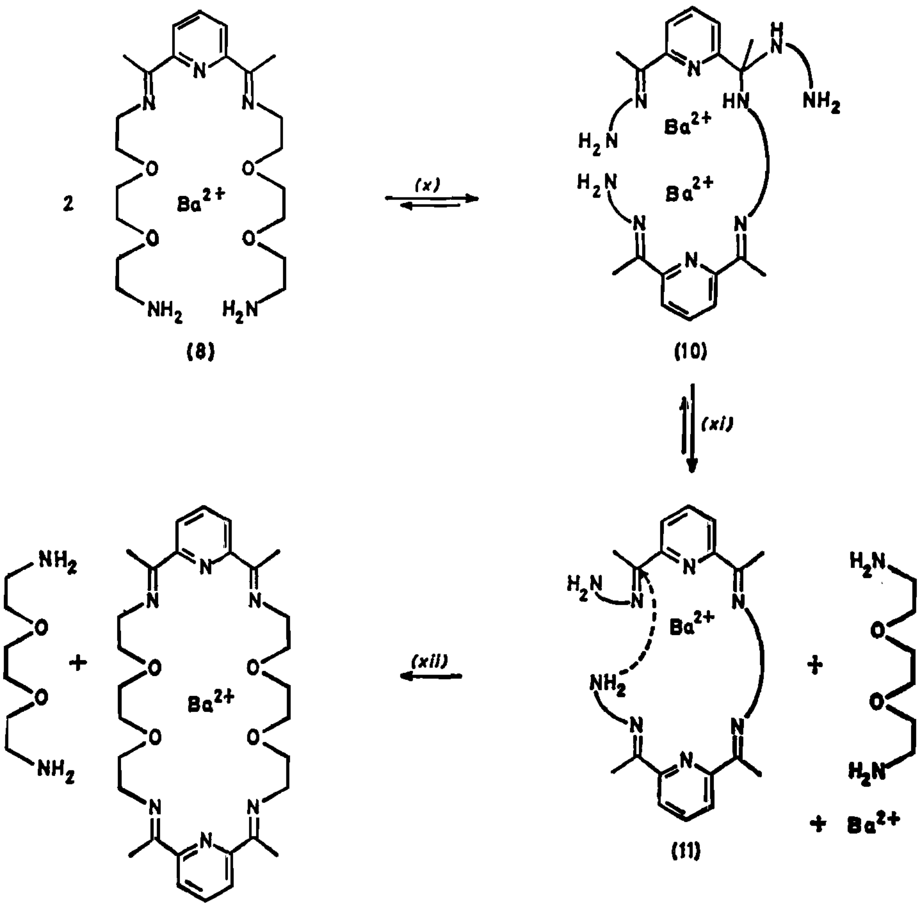
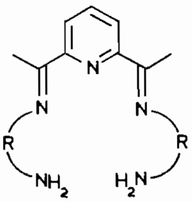


Fig. 1. The structure of the binuclear cation $[Ag_2L^3]^{2+}$ along with a view of the central 12-membered ring containing the two metal atoms.

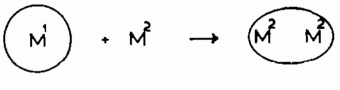


It has been found [7] that the most effective template ions for the synthesis of these [2 + 2] macrocycles are large non-transition metal ions, particularly Ca^{2+}, Sr^{2+} and Ba^{2+}, and, to a lesser extent, Pb^{2+} and Ag^{+}. In all these cases the macrocycles are isolated as the metal complexes, mononuclear in the case of the alkaline earth metal ions. Smaller metal ions such as the divalent ions of the first row transition series have generally been found to be ineffective as templates for [2 + 2] condensations. In some cases [1 + 1] condensations occur, however. Thus, for example, the use of Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) as templates for the condensation of 2,6-diacetylpyridine with 3,3′-diaminodipropylamine leads to complexes of the 14-membered [1 + 1] macrocycle [8] whereas when the reaction is carried out in the presence of Ag(I) the product is the bi-Ag(I) complex of the [2 + 2] macrocycle L^6 (Fig. 1) [9].

Insight into the mechanisms of the macrocycle formation reactions has been gained by the successful isolation, using mild reaction conditions, of open-chain species of type (1) [10]. That these species are intermediates in the formation of [2 + 2] macrocycles has been demonstrated by their subsequent ring closure reactions (a) in the presence of added dicarbonyl and (b) in the absence of dicarbonyl. In the latter cases the ring closure to [1 + 1] or [2 + 2] macrocyclic products, depending on the nature of the metal ion, occurs by a transamination mechanism involving inter and intra nucleophilic addition/elimination of NH_2 functions at coordinated imine centres as indicated in Scheme 1. Since nucleophilic attack by NH_2 groups requires that they are not coordinated, the special efficacy of the large alkaline earth metal ions can be understood in terms of the weak bonds which these 'hard' metal ions form with nitrogen donors in hydroxylic solvents such as methanol. For similar reasons it has generally been found possible to replace the alkaline earth metal ion by transition metal ions of interest [7, 11]. This transmetallation or metal ion exchange procedure is remarkably successful despite the apparent instability of the free (uncoordinated) macrocycle in most cases. It therefore seems likely that the transmetallation process involves a concerted mechanism in which the incoming transition metal ion becomes partially bound to the macrocycle before the outgoing template ion is fully released. An important feature of the transmetallation is that the single alkaline earth metal ion may be replaced by two transition metal ions. This is particularly true for the case of Cu(II) [reaction (1)]. In this way a range of binuclear Cu(II) complexes of L^1–L^7 have been prepared.



Scheme 1



(1)

M^1 = *e.g.* Ca^{2+}, Sr^{2+}, Ba^{2+}
M^2 = *e.g.* Cu^{2+}

Complexes of Macrocyclic Ligands containing two Pyridyl Moieties

The macrocycles L^1–L^7 all contain two rigid, planar and powerfully coordinating trimethine groups linked by two flexible chains containing other potential donor atoms in several cases. In all the bi-Cu(II) complexes each metal ion is strongly bound to one trimethine unit and, with the exception of L^5 and L^6, usually not ot any other macrocycle donor atom that may be present. The coordinatively unsaturated Cu(II) ions thus attain square-based five- (4 + 1) or six- (4 + 2) coordination geometries by complexation with available non-macrocyclic ligands. Where potentially bridging ligands are present these may be bound intramolecularly between the two metal centres. In the series of macrocyclic ligands L^1–L^7 the inner large ring varies in size from 18 to 30 member atoms and thus have appropriate cavity dimensions for the accommodation of bridging substrate molecules and ions of varying size. Examples of bridging ligands which may be incorporated by the different macrocycles are indicated in Table I; the structures of several of the complexes cited have been determined by single crystal X-ray diffraction. It will be noted that while the smaller rings L^1 and L^2 appear suitable for the accommodation of only single-atom bridges such as OH^-, OR^- or 1,1-N_3^-, the largest ring L^7 can adapt, by folding of the flexible carbon-oxygen chains, to the coordination of both three-atom bridges such as the imidazolate ion and to single atom bridges such as OH^-. Indeed, the 30-membered ring is sufficiently flexible to coordinate to a single metal ion giving mononuclear complexes of the type $[M(N_6)]^{n+}$ where (N_6) represents the two trimethine units disposed mutually at right angles [17]. These transition metal complexes are particularly stable and, except in the case of Cu(II), do not unfold to admit a second metal ion within the macrocycle 'hole' [11].

TABLE I. Bridging Substrate Molecules and Ions in bi-Copper(II) Complexes of Macrocyles L^1–L^7.

Macrocycle	Number of atoms in inner large ring	Bridging substrate	Cu···Cu separation (Å)	Ref.
L^1	18	OH^-		12
L^2	20	OH^-	3.145	13
		OMe		13
		1,1-N_3^-		13
L^3	24	imidazolate		14
L^4	24	1,2-N_3^-		15
		imidazolate	5.87	15
		pyrazine		15
L^7	30	OH^-	3.57	11
		1,1-N_3^-	6.02	16
		imidazolate	5.99	11

The occurrence of bridging substrate molecules within the binuclear macrocyclic complexes may be recognized from the stoichiometry of the complexes and from the results of a variety of physico-chemical studies, particularly measurements of magnetic susceptibility as a function of temperature and electron spin resonance spectra. In addition, the detailed structures of several of the complexes have been solved by X-ray diffraction studies carried out by Dr. M. G. B. Drew of the University of Reading.

Reference has already been made to the metalloprotein bovine erythrocyte superoxide dismutase, the enzyme responsible for destruction of the toxic superoxide ion *via* the disproportionation reaction

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$$

The structure has been determined by Richardson *et al.* [2] The active site comprises a bimetallic Cu(II)···Zn(II) unit bridged by an imidazolate group. The Zn(II) ion is believed to play a structural role, serving to position the Cu atom in the optimum way, this being the redox centre in the catalytic cycle. The Zn(II) ions may be replaced by Cu(II) ions with retention of enzymatic activity. Fee and Briggs [18] have demonstrated that pairs of Cu(II) ions in the tetra-Cu(II) derivative are antiferromagnetically coupled and a value of the coupling constant J of -26 cm^{-1} has been estimated from the temperature dependence of the e.s.r. spectrum. Here, J is the magnetic exchange parameter in the spin Hamiltonian $\mathcal{H} = 2\underline{J}\hat{S}_1\cdot\hat{S}_2$, $2\underline{J}$ being the energy separation between the singlet and triplet states. The observation of antiferromagnetic superexchange in the tetra-Cu(II) derivative of superoxide dismutase has stimulated efforts by several groups of workers [4b, 19–22] to synthesize and study model compounds containing imidazolate bridged Cu(II) ions.

The X-ray structures of two imidazolate bridged bi-Cu(II) complexes in the family of macrocycles under consideration have been determined [11, 15]. These are the complexes $Cu_2L^4(im)(ClO_4)_3JH_2O$ and $Cu_2L^7(im)(ClO_4)_3 \cdot H_2O$. The structures of the two complexes are very similar in that in each case each Cu(II) is strongly bonded in a square plane to three nitrogen atoms of the macrocycle and to one nitrogen atom of the bridging imidazolate group. In addition, in each case, the Cu(II) ions are weakly bonded to ClO_4^- or H_2O oxygen atoms in axial positions giving an overall tetragonal (4 + 2) six-coordinate environment. The structures differ, however, in the dihedral angles between the plane of the imidazolate ring and Cu(II) coordination square planes, being 88.6, 90.0° in the former complex and 68.8, 79.1° in the latter. The structure of $Cu_2L^4(im)(ClO_4)_3 \cdot H_2O$ is shown in Fig. 2.

Magnetic susceptibility measurements of both complexes in the temperature range 300–4 K established the occurrence of antiferromagnetic superexchange between the Cu(II) ions [23]. Figure 3 shows a plot of the magnetic susceptibility per Cu(II) ion for $Cu_2L^4(im)(ClO_4)_3 \cdot H_2O$ as a function of temperature in the range 100–4 K. Application of the Bleaney-Bowers equation [24] for coupled pairs of S = ½ spins gives $\underline{J} = -21.2$ cm^{-1}, for g = 2.11 (obtained from e.s.r. spectra), and the temperature independent paramagnetism, N(α) = 60 × 10^{-6} c.g.s.u. An equally satisfactory fit of the experimental and calculated χ_A/T curve was obtained for $Cu_2L^7(im)(ClO_4)_3 \cdot H_2O$ for $\underline{J} = -21.0$ cm^{-1} and the same values of g and N(α).

The occurrence of antiferromagnetic interaction in both imidazolate complexes is confirmed by the observation of a 'triplet' ΔM = 1 e.s.r. spectrum in frozen DMSO/MeOH solution at ~80 K [23]. Analysis of the spectra gave $g_\parallel = 2.18$, $g_\perp = 2.08$, D = 500 (±20) G and E = 100 (±20) G for both complexes. Well resolved seven-line spectra for the ΔM = 2 transi-

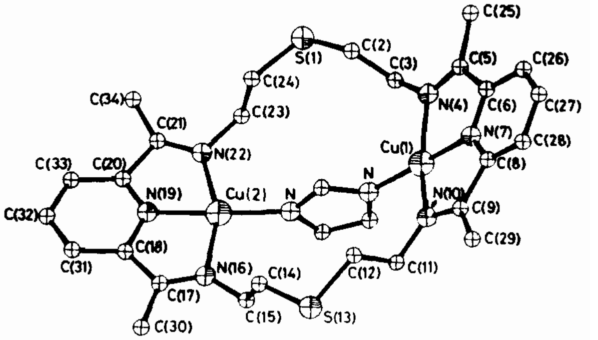


Fig. 2. The structure of the binuclear cation $[Cu_2L^4(im)]^{3+}$.

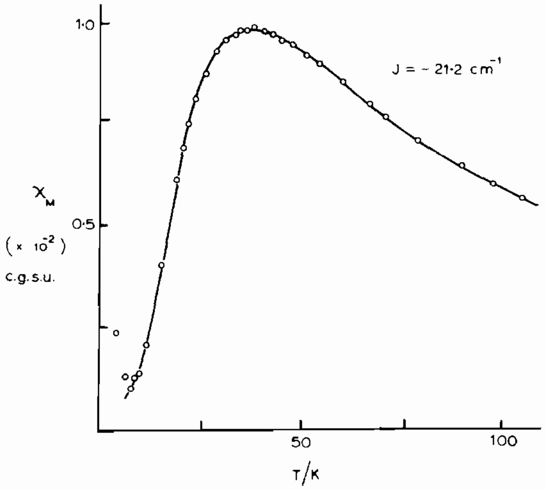


Fig. 3. The temperature dependence of the magnetic susceptibility, per Cu(II) ion, of $Cu_2L^4(im)(ClO_4)_3 \cdot H_2O$. The circles represent the experimental points while the solid line represents the theoretical curve calculated from the Bleaney-Bowers equation (see text).

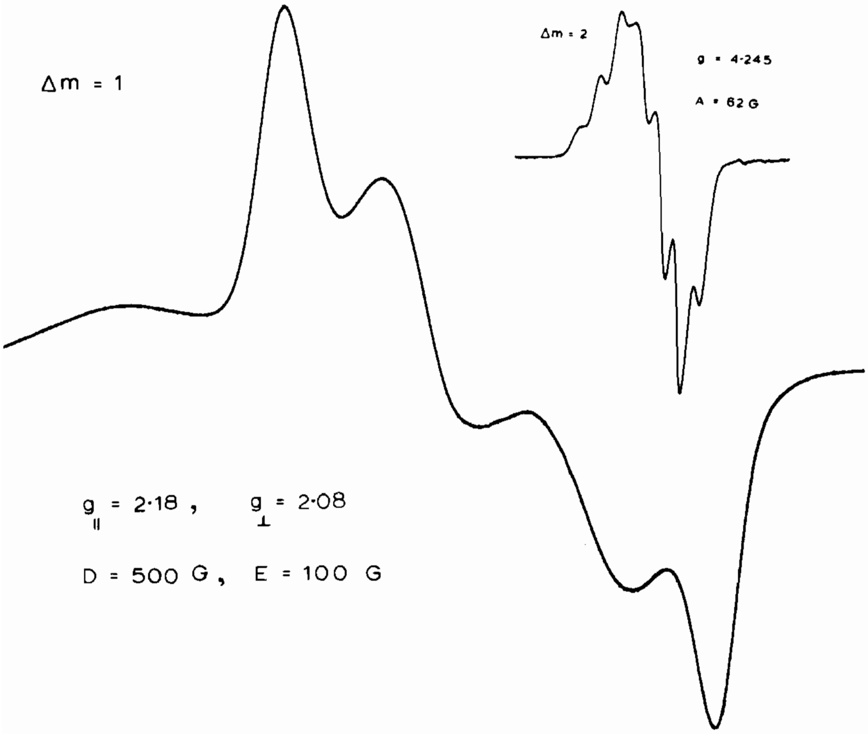


Fig. 4. The X-band e.s.r. spectra of $Cu_2L^7(im)(ClO_4)_3 \cdot H_2O$ in DMSO/MeOH glass at 77 K, in the g ~ 2 and g ~ 4 regions; the inset refers to the ΔM = 2 transition at g ~ 4.

tion were also observed at g = 4.24 with A = 62 G (Fig. 4). These results confirm the retention of the imidazole bridge in solution.

In recent years a rather wide variation in the coupling constant J (–10 to –90 cm^{-1}) has been found for synthetic imidazolate bridged bi-Cu(II) complexes [19–22]. It is of interest, therefore, to try to correlate the magnitude of J with the structures of the binuclear compounds. A number of facotrs would appear relevant including the stereochemistry of the Cu(II) coordination sphere (*e.g.* square pyramidal, tetragonal, or trigonal bipyramidal), the position (axial or equatorial) of the bridging imidazolate group, the nature of the associated ligands, the Cu–N(im) bond lengths, the Cu–N–C bond angle, the angle between the two Cu–N(im) vectors, the angle between the two 'CuN_4' square planes (in 'square' based complexes), and the dihedral angle between the plane of the imidazolate ring and the 'CuN_4' planes. The influence of these structural parameters has been discussed in the recent literature [4b, 19–22] and it now seems that the exchange is transmitted primarily by a sigma pathway and that the Cu–N–C bond angle is one of the more important factors determining its magnitude.

The flexibility of the 30-membered macrocycle has been mentioned. This ring can therefore fold to accommodate a single-atom bridge as well as the three-atom bridge (imidazolate) mentioned above. The structure of the μ-hydroxo complex $[Cu_2L^7(OH)(ClO_4)(H_2O)][ClO_4]_2$ has been determined [11]. As in the imidazolate complex the bridging unit (OH^- in this case) occupies an equatorial position *trans* to the pyridine nitrogen. The Cu···Cu distance is 3.57 Å compared to 5.99 Å in the μ-imidazolate complex. Again the ether oxygens of the macrocycle are not coordinated although one such oxygen atom lies 2.74 Å above one of the Cu(II) ions and may therefore be considered as weakly interacting. The two trimethine units are inclined at 79.1° to each other and the Cu–O(H)–Cu bond angle is 141.7(7)°.

Variable temperature magnetic susceptibility measurements in the range 90–300 K have shown that the metal ions are antiferromagnetically coupled. Not unexpectedly, the exchange constant J is appreciably larger at –120 cm^{-1} than in the μ-imidazolate complex. While there are many examples [25] of di-μ-hydroxobi-Cu(II) complexes, copper complexes containing a single hydroxo-bridge are rare. Recent examples for which X-ray structures are available are $[(bipy)_2Cu{-}O(H){-}Cu(bipy)_2][ClO_4]_3$ [26] and the complex $[Cu_2(em)(OH)][BF_4]_3$ [27] where bipy and em are 2,2′-bipyridine and the 'earmuff' ligand 1,4-bis(1-oxa-4,10-dithia-7-azacyclododecan-7-ylmethyl) benzene, respectively. In the former complex the coordination geometry is approximately trigonal bipyramidal, with the bridging group sited equatorially and the Cu–O(H)–Cu angle being 141.6(3)°. In the 'ear-muff' complex the coordination geometry is approximately square pyramidal, with the OH^- group in the basal plane and the Cu–O(H)–Cu angle 132.2(4)°. The coupling constants for these two complexes are, respectively, -161 cm^{-1} and -410 cm^{-1}.

Another binuclear Cu(II) complex [28] containing a single hydroxo bridge is $[Cu_2(mac)(OH)(ClO_4)][ClO_4]_2$ where mac is a 24-membered macrocycle similar to L^7 except that the trimethine segments of L^7 are replaced by saturated 'N_3' donor sets derived from diethylenetriamine. As in the L^7 complex the Cu(II) ions are in square pyramidal environments and the bridging hydroxo group occupies a position in the basal plane with a Cu–O(H)–Cu bond angle of 143.7°. Here, the coupling constant J is *ca.* -500 cm^{-1}.

Previous studies [25] on dihydroxo-bridged bi-Cu(II) complexes have indicated a linear relationship between the Cu–O(H)–Cu bridge angle and the magntidue of J. A similar relationship might be expected for systems containing single hydroxo bridges. However, if this is true factors other than geometrical ones must also be important. It would thus appear that the exchange is also dependent on the nature of the associated ligand(s), being appreciably smaller where this contains the unsaturated (potentially π-accepting) trimethine group as in L^7 than in the saturated diethylenetriamine derivative.

It is interesting to recall that an imidazolate-bridged Fe(III)···Cu(II) site has been proposed [3] for the enzyme cytochrome c with oxidase in which the Cu(II) ion is e.s.r. – silent. However, since this reflects a large coupling ($J > -200$ cm^{-1}) it seems unlikely that an imidazolate bridge is responsible. As discussed above mono-hydroxo bridges do lead to strong magnetic coupling and it may be that the enzyme contains a hydroxo (or alkoxo) bridge between the metal centres [4, 21].

When the ring size of the inner great ring is reduced to 18 or 20 member atoms as in L^1 and L^2 it is clear the bimetallic complexes can no longer act as receptors for other than small bridging substrates. Indeed molecular models suggest that for L^1 and L^2 only single-atom bridges can be accommodated, and only if the macrocycles are folded so that the two trimethine planes intersect at an angle appreciably less than 180°. This prediction is borne out by the results obtained [13]. Thus, transmetallation of the complex $[BaL_2(ClO_4)_2]$, for example, with $Cu(ClO_4)_2 \cdot 6H_2O$ in MeOH affords the binuclear complex $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$, believed from i.r. spectra to contain a μ-methoxo bridge. Recrystallization of the μ-methoxo complex from MeCN gives the μ-hydroxo complex $Cu_2L^2(OH)(ClO_4)_3 \cdot 2H_2O$. The X-ray structure of the hydroxo derivative has been determined [13]. Each copper atom is coordinated to three nitrogen atoms of a trimethine group of the macrocycle (Cu–N, 10916–2.061 Å) which occupy three corners of an approximate square plane. Completing the square plane about each copper atom is the bridging oxygen atom O(1) with Cu–O(1) of 1.916(9) Å. The two metal atoms are also linked in a shared axial position by a second oxygen atom O(2). This interaction is a much weaker one, however, since Cu–O(2) is 2.519(12) Å. The stoichiometry and properties of the complex require that one of the oxygen bridges is an OH^- ion and that the other is a H_2O molecule. While it was not possible to discern hydrogen atoms in a difference Fourier map there can be little doubt that it is the more basic ligand (OH^-) that occupies the strongly interacting equatorial site. As noted above the accommodation of the doubly bridged bi-Cu(II) unit within the relatively small macrocycle 'hole' requires that the planar $[Cu(OH)(H_2O)Cu]$ moiety is approximately perpendicular to the planes of the trimethine unit. It also requires that the macrocycle be severely folded (Fig. 5), the two symmetry related trimethine planes intersecting at 89.5°. The Cu–O(1)–Cu bond angle is 110.3(7)° while the Cu–O(2)–Cu bond angle is 77.3(4)°. The Cu···Cu distance is 3.145(4) Å.

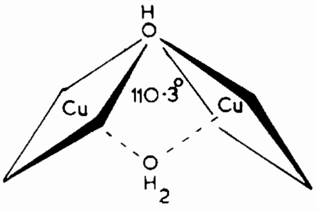


Fig. 5. Diagrammatic view of the μ-hydroxo-μ-aqua bi-Cu(II) moiety in $Cu_2L^2(OH)(ClO_4)_3 \cdot 2H_2O$.

Magnetic susceptibility measurements of both the μ-hydroxo and μ-methoxo complexes over the range 80–300 K reveal a distinct, but different, decrease in magnetic moment with decrease in temperature. Figure 6 compares the observed values of magnetic susceptibility (χ_A) and magnetic moment (μ_{eff}) per Cu(II) ion with those calculated from the Bleaney-Bowers equation [24] for interacting pairs of $S_1 = S_2 = ½$ spins in terms of the energy separation (2J) between the singlet and triplet states. The derived J values are -32 cm^{-1} and -53 cm^{-1} for the μ-hydroxo and μ-methoxo complexes, respectively.

On the assumption that the complex prepared in MeOH contains a methoxo bridge between the metal centres it is likely that the difference in antiferro-

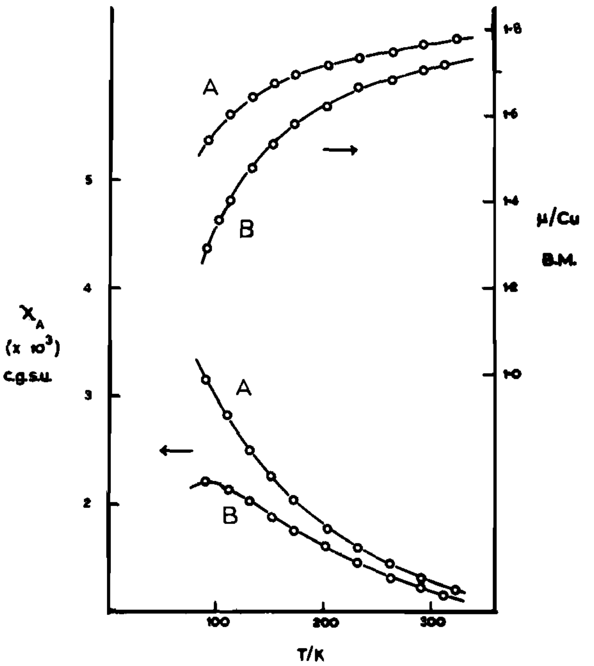
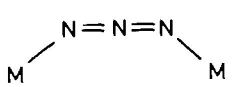


Fig. 6. The temperature dependence of the magnetic susceptibility (χ_A) and magnetic moment (μ_{eff}) per Cu(II) ion for (A) $Cu_2L^2(OH)(ClO_4)_3 \cdot 1H_2O$ and (B) $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$. The circles represent the experimental points while the solid line represents the theoretical curve calculated from the Bleaney-Bowers equation (see text).

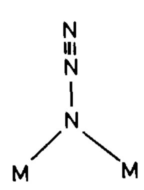
magnetic coupling is a consequence of the change in the nature of the bridge. Both theoretical [29] and experimental [30] studies indicate that an increase in the electron density on the bridging atom should enhance the superexchange interaction. The coupling (J = -32 cm^{-1}) found in $Cu_2L^2(OH)(ClO_4)_3 \cdot 2H_2O$ may be compared with that (J = -120 cm^{-1}) observed for $Cu_2L^7(OH)(ClO_4)_3 \cdot H_2O$, both complexes having the same type of (trimethine) ligand and coordination geometry but differing in the Cu–O(H)–Cu bond angle, this being 110.3° in the former and 141.7° in the latter. For the more common di-μ-hydroxo bi-Cu(II) systems it has been noted that the exchange parameter J is a function of the Cu–O(H)–Cu bond angle [25]. It therefore appears that a similar dependence of J on bond angle may be found in mono-μ-hydroxo complexes provided, as noted above, that comparisons are made between complexes of similar ligands and otherwise similar geometry.

The retention of the OH^- or OMe^- bridges in solution is evidenced by their 3:1 electrolyte behaviour in MeCN and by their e.s.r. spectra in frozen DMSO/MeOH solutions at ~80 K. Both complexes show 'triplet' type spectra in the g ~ 2 region and a half-band (ΔM = 2) spectrum in the g ~ 4 region shows a seven-line hyperfine pattern with average hyperfine spacing of 75 G.

As discussed above, the occurrence of small bridging substrate ions such as OH^- and OMe^-, but not larger substrates such as imidazolate, between the Cu^{II} centres in bi-Cu(II) complexes of L^2 can logically be related to the cavity size of L^2 being too small to accommodate other than a single-atom bridge. To test this conclusion some experiments involving the introduction of the azide ion between the Cu(II) ions were performed, since the azide ion is known [31] to occur in two different bridging modes, the end-to-end or μ-1,3-azide bridge [structure (A)] and the end-on or 1,1-azide bridge [structure (B)]. The 1,3-azido bridge (A) is the more common and has been observed in the complex $[Cu_2L^7(N_3)_3][ClO_4]$ [16] and in other binuclear complexes of macrocyclic ligands [32]. An interesting recent observation [33] is the occurrence of bridging mode (A) in a binuclear Cu(II) complex in which the metal atoms are only 3.615 Å apart. This may be compared to a Cu···Cu separation of 6.02 Å in $[Cu_2L^7(N_3)_3][ClO_4]$ [16].



(A)



(B)

Reaction of $Cu_2L^2(OMe)(ClO_4)_3 \cdot 2H_2O$ with one equivalent of NaN_3 in MeOH afforded the complex $Cu_2L^2(N_3)(ClO_4)_3$. The asymmetric stretch of the coordinated azide ion occurs at 2070 cm^{-1}, i.e. slightly higher than in complexes known to contain 1,3-azido bridges. A band at 1347 cm^{-1} absent in the spectra of L^2 complexes not containing the azide ion, is assigned to the symmetric stretch ν_s. The stoichiometry of the complex and the occurrence of ν_s as a moderately strong band is taken as evidence for an 'end-on' (μ-1,1) azide bridge (structure B). The ν_s vibration is expected to be inactive, or of low intensity, in symmetrically bridged 1,3-azido complexes.

The room temperature magnetic moment (1.95 B.M.) of $Cu_2L^2(N_3)(ClO_4)_3$ did not decrease appreciably on cooling to 93 K. However, evidence for a weak superexchange interaction was obtained from the e.s.r. spectra of frozen solutions in DMSO/MeOH at ~80 K. Both ΔM = 1 and ΔM = 2 transitions were seen, the former being of the 'triplet' type and the latter displaying the expected seven line hyperfine pattern of average spacing 75 G characteristic of coupled Cu(II) dimers (Fig. 7).

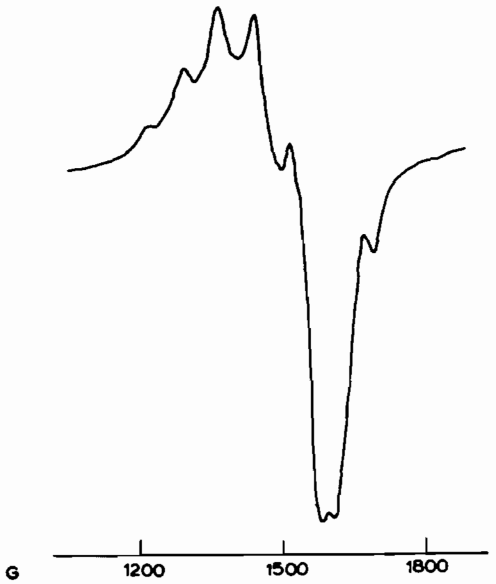
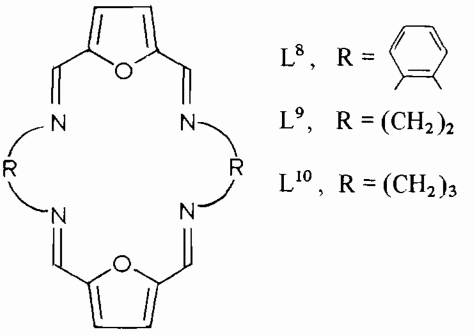


Fig. 7. the e.s.r. spectrum of $Cu_2L^2(N_3)(ClO_4)_3$ corresponding to the half-band $\Delta M = 2$ transition.

Complexes of a Macrocyclic Ligand containing two Furan Moieties

By analogous template methods to those described in the earlier section a second family of [2 + 2] macrocycles L^8–L^{10} containing two furan, in the place of the pyridyl, groups have been prepared. Experiment indicates that the 18-membered rings are too large to form stable mononuclear complexes with first row transition metal ions and too small to form binuclear complexes. However, the slightly larger 'hole' of the 20-membered ring L^{10} appears well suited to complexation with two transition metal ions, even though several larger, Main Group, metal ions form only mononuclear complexes. In fact, it appears that Ba^{2+} may be slightly too large to sit comfortably within the macrocycle cavity since complexes of both 1:1 and 2:1 Ba^{2+}:L^{10} stoichiometries may be prepared. An X-ray structure determination [34] of $[Ba(L^{10})_2(H_2O)_2][Co(NCS)_4]$ has shown that the Ba^{2+} ion is 11-coordinate being bonded to all six donor atoms of one ring, to two nitrogens and one furan oxygen atom of the second ring, and to two water molecules. The Ba^{2+} ion sits *ca.* 2 Å away from the plane of the first macrocycle and about 1 Å away from the bonded 'N_2O' plane of the second. In contrast to the Ba(II) complex, in the di-Cu(II) and di-Co(II) complexes of L^{10} the furan oxygen atoms are not coordinated (see later). This is not unexpected since furan is known to have a very low basicity. The bonding in the alkaline earth complexes is therefore presumed to be largely ion-dipolar in nature.



The non-coordination of the furan oxygens in the binuclear transition metal complexes means that, in contrast to the L^2 complexes, each metal ion is bound to the macrocycle via only two coordinate bonds. Thus, the binuclear system 'M_2L^{10}' has the potential to bind two bridging substrate molecules or ions in order to attain a coordination number of four, with higher coordination numbers being attained, if necessary, by the attachment of monodentate ligands. Since L^{10} has the same number of member atoms in the inner large ring as L^2, the size of the bridging substrate should similarly be restricted to those providing one-atom, or, at most, two-atom bridging units. The results are in good accord with these predictions [35].

As for L^2, the macrocycle L^{10} was prepared in 60% yield from 2,5-diformylfuran and 1,3-diaminopropane using Ba^{2+} as template ion. Transmetallation of $BaL^{10}(ClO_4)_2 \cdot EtOH$ with Cu(II) afforded $Cu_2L^{10}(OH)(ClO_4)_2 \cdot H_2O$ which was used as the starting material for a series of bi-copper complexes in both the +2 and +1 oxidation states. The Cu(II) ions in this complex are almost certainly bridged by two OH^- ions. As would be expected, the paramagnetic centres are antiferromagnetically coupled, the moment per Cu(II) ion falling from 1.37 B.M. at 293 K to 0.72 B.M. at 93 K. The susceptibility/temperature plot does not give a good fit to the Bleaney-Bowers equation, however, possibly because of the presence of some diamagnetic impurity. As will be seen, this complex is readily reduced to di-Cu(I) species. The electronic spectrum in the visible/near I.R. region consists of a broad band at 16,700 cm^{-1} in the solid state consistent with a square-based ('4 + 1' or '4 + 2') coordination geometry. Heating the complex in solution in the presence of NaX (X = Cl^-, Br^-, I^-, N_3^- or NCS^-) readily affords the red or brown diamagnetic complexes $[Cu_2L^{10}X_2]$. The structure of the di-thiocyanate has been determined [36]. As shown in Fig. 8, each Cu(I) ion is bonded to two nitrogen atoms of the macrocycle and to two sulphur atoms of the bridging

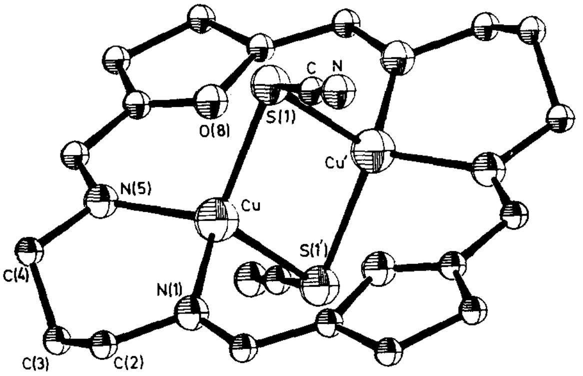


Fig. 8. The structure of $[Cu_2L^{10}(SCN)_2]$.

thiocyanate groups. The furan oxygen atoms are not coordinated. The macrocycle itself is approximately planar, the coordination about the Cu(I) ions is distorted tetrahedral and the Cu···Cu distance is 2.796 Å. This is the first example of sulphur atom-only bridging in thiocyanate complexes. Its unique occurrence here can readily be understood in terms of the structure of the macrocyclic complex which does not permit sufficient Cu···Cu separation for an end-to-end, three-atom NCS^- bridging mode as very commonly observed elsewhere [37]. The asymmetric stretch of the bridged NCS^- group occurs as a strong, fairly sharp band at 2105 cm^{-1} [36]. End-to-end NCS^- bridges also absorb in this region [37], so I.R. spectra are not diagnostic of this bridging mode. The corresponding selenocyanate $[Cu_2L^{10}(SeCN)_2]$ has been prepared and presumably contains single-atom selenium bridges.

When the reduction of $Cu_2L^{10}(OH)_2(ClO_4)_2H_2O$ is carried out in the absence of any potentially bridging substrate the complex $[Cu_2L^{10}(MeCN)_2][ClO_4]_2$ is isolated. An X-ray analysis [34] of this complex shows that each copper(I) atom is 3-coordinate being bonded to two nitrogen atoms of the macrocycle and to the nitrogen of one acetonitrile molecule. There is no bonding interaction between a copper atom and the triple bond of the second nitrile molecule. The coordination geometry is a distorted trigonal plane, the two copper atoms sitting somewhat out of the macrocycle plane, in opposite directions. The Cu···Cu separation is 3.35 Å. Exposure of solutions of this complex to carbon monoxide caused the colour to change from amber to yellow while replacement of the CO atmosphere by one of dinitrogen reversed the colour change. Presumably, a molecule of CO is bound to each coordinatively unsaturated metal atom. No CO-containing adducts could be isolated, however.

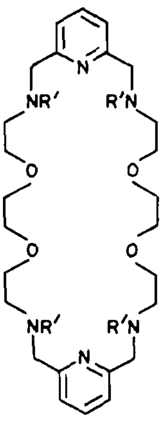
The facile di-Cu(II) to di-Cu(I) reduction can be traced to geometrical factors. Molecular models reveal that there exists a significant degree of steric interaction between the bridging ligands and the uncoordinated furan groups whenever the coordination about each metal ion is 'square'. The steric crowding is very severe if the two Cu(II) square planes are co-planar but may be partially relieved if the bridging groups are raised above the plane of the macrocycle so that the coordination planes, sharing a common edge, intersect at an angle. This is the arrangement believed to occur in $Cu_2L^{10}(OH)_2(ClO_4)_2 \cdot H_2O$ and in the di-μ-pyrazolato complex $Cu_2L^{10}(pz)_2(ClO_4)_2$. The steric crowding may alternatively be releved if the stereochemistry alters from 'square' to trigonal bipyramidal and this, as judged by electronic spectra, appears to be the arrangement in the strongly coupled di-μ-alkoxo complexes $Cu_2L^{10}(OR)_2(NCS)_2$ (R = Me, Et, ^nPr). However, some macrocycle bond angle strain is now involved in making these adjustments and it is apparent that the most strain-free arrangement is where the macrocycle remains approximately planar and the metal atoms are tetrahedrally coordinated, as found for $[Cu_2L^{10}(SCN)_2]$ [36]. It is this preference for tetrahedral coordination that is the thermodynamic driving force for the ready reduction of $Cu(II)_2$ to $Cu(I)_2$.

An example of the reduction of two trigonal bipyramidal Cu(II) ions to two tetrahedral Cu(I) ions is the conversion by heat (*ca.* 120 °C) of $Cu_2L^{10}(OR)_2(NCS)_2$ to $[Cu_2L^{10}(SCN)_2]$ with accompanying fomation of alcohol and aldehyde (gas phase i.r. and mass spectral analysis) derived from the disproportionation of alkoxide radicals. As noted above, and unlike macrocycle L^2, the bi-Cu(II) unit in macrocycle L^{10} can apparently adjust, though presumably with some cost in macrocycle bond angle strain, to the accommodation of two two-atom bridging species. This is evidenced by the preparation of the complex $Cu_2L^{10}(pz)_2(ClO_4)_2$ where pz = pyrozolate anion. The metal ions appear to have a square-based coordination geometry (electronic spectra) and they are strongly antiferromagnetically coupled ($J = -145$ cm^{-1}). This complex does not undergo reduction to a di-Cu(I) species probably because two-atom bridges cannot be accommodated between two tetrahedrally coordinated metal ions with the macrocycle in a planar conformation.

Activation of Bridging Substrates by Bi-Copper Complexes

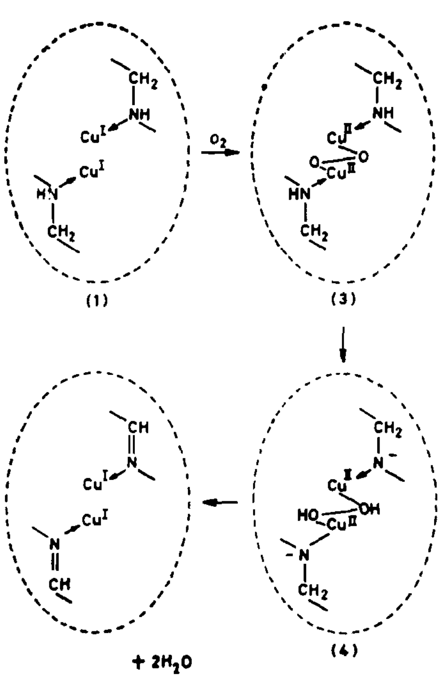
The coordination of a variety of bridging substrate molecules and ions to two copper ions held by the macrocyclic ligand, at separations which are subject to some control by appropriate ligand design, has been amply demonstrated by the results described. It would be of considerable interest to know whether the bridging substrate can be activated to chemical reaction. One type of reaction of potential biological and industrial relevance is the activation of dioxygen.

Since bi-Cu(II) complexes of the 30-membered ring L^7 have been shown [11, 16] to act as receptors for both three-atom and one-atom bridging ligands, they should also accommodate to the binding of (unhindered) diatomic bridges. The reaction of the bi-Cu(I) complex $[Cu_2L^7][ClO_4]_2 \cdot H_2O$ with O_2 was therefore investigated. However, no oxygen-containing complex could be isolated, the major product of reaction being the mononuclear Cu(II) complexes $[CuL^7][ClO_4]_2 \cdot H_2O$. More interesting behaviour [38] was observed for the reaction of the binuclear bi-Cu(I) complex $[Cu_2L^{11}][ClO_4]_2$ with O_2 in dry MeCN where L^{11} is the reduced (hydrogenated) derivative of a close relative of L^7. This yellow complex rapidly consumes one mol of O_2 per $Cu_2(I)$ unit [38]. This rapid uptake is then followed by a much slower consumption of O_2, the total uptake being in excess of three mol of O_2 per 2 Cu(I). The absorption of the first mol of O_2 is accompanied by the development of a green colour (ν_{max} 15,300 cm^{-1}) which did not intensify on further oxygenation. Interruption of the oxygenation by replacement of the O_2 atmosphere by one of argon caused the green colour to change to amber while re-admission of O_2 reversed the spectral changes with resumption of the O_2 uptake at an accelerated rate. On the basis of these observations and of a kinetic analysis of the rates of O_2 uptake the results are interpreted [38] in terms of a bi-Cu(I)/bi-Cu(II) redox cycle leading to dehydrogenated forms of the ligands (Scheme 2). The results are consistent with the first rapid step being the formation of a μ-peroxo-di-Cu(II) species, this being followed by proton transfer from the coordinated secondary amine groups to the coordinated peroxide. Elimination of H_2O regenerates the bi-Cu(I) species together with two C=N imine groups. The system is now set for further O_2 uptake leading to further oxidative dehydrogenation. Support for the mechanism is provided by the observation that when the secondary amine groups are methylated, as in L^{12}, the consumption of O_2 after the first rapid uptake of one mol is suppressed about 100 fold. However, attempts to isolate an O_2 adduct at this stage where unsuccessful. Notwithstanding, the results demonstrate the occurrence of a $Cu(I)_2/Cu(II)_2$ cycle in the reduction of O_2 to H_2O with concomitant oxidation of organic functional groups. Investigations of the possibility of directing the oxidation towards organic substrates other than the macrocycle itself are in progress.



L^{11}, R' = H

L^{12}, R' = Me



Scheme 2. Proposed mechanism for the first redox cycle in the oxidative dehydrogenation of the macrocycle L^{11} in $[Cu_2L^{11}]_2$.

The stabilization of the Cu(I) state in the bicopper complexes of the 20-membered macrocycle L^{10} derived from 2,5-diformylfuran has been mentioned. It would therefore seem that the Cu(II) → Cu(I) reduction in these systems might effect oxidation of a suitable organic substrate. When the bi-Cu(II) complex $Cu_2L^{10}(OH)_2(ClO_4)_2 \cdot 2H_2O$ was gently heated with phenylacetylene in MeOH/MeCN solution the solution rapidly changed from green to red. The red solution deposited red crystals of composition $Cu_4(L^{10})_2(C{\equiv}CPh)(ClO_4)_3 \cdot 0.5$ DPDA where DPDA = diphenyldiacetylene. An X-ray structure determination [34] shows that two binuclear $[Cu_2L]^{2+}$ cations are associated together in such a way that all four metal ions are interacting with a single phenylacetylide anion. As illustrated in Fig. 9 one copper atom is σ bonded to the acetylide carbon atom and the

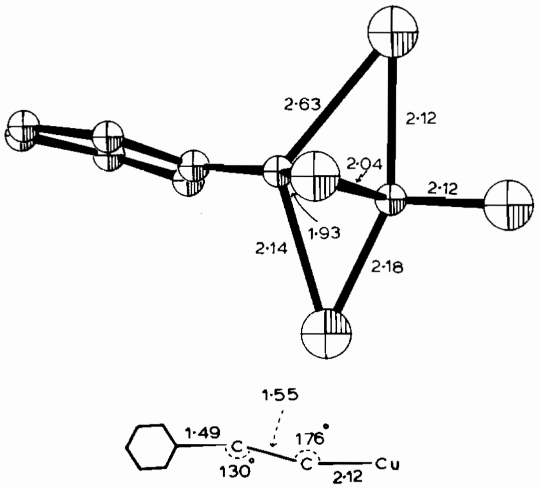


Fig. 9. The structure of the 'Cu_4 [C≡CPh)' cluster with selected bond distances and angles.

other three appear to be π-bonded to the acetylene triple bond. The $Cu_4(C\equiv CPh)$ cluster has a very irregular geometry as is apparent from the Cu–C bond distances given in the Figure. The metal-acetylene π-interaction is reflected in the lengthening of the C–C triple bond to 1.55 Å and in the non-linearity of C–C–C(Ph) bond. There is no interaction between any of the metal atoms and the diphenyldiacetylene in the lattice. The presence of this molecule in the crystal (and in the solution from which the complex was isolated) is a demonstration of oxidative coupling accompanying the Cu(II) → Cu(I) reduction.

$$[Cu_2^{II}(OH)_2] + 2RC\equiv CH \rightarrow [Cu_2^{I}] + RC\equiv C-C\equiv CR$$

Experiments designed to render the reaction catalytic by the re-oxidation of the bi-Cu(I) complex by atmospheric oxygen are in progress.

References

1 See, for example, U. Castellato, P. A. Vigato, D. E. Fenton and M. Vidali, *Chem. Soc. Rev.*, *8*, 199 (1979).
2 J. S. Richardson, K. A. Thomas, B. H. Rubin and D. C. Richardson, *Proc. Natl. Acad. Sci. U.S.A.*, *72*, 1349 (1975).
3 G. Palmer, G. T. Babcock and L. E. Vickery, *Proc. Natl. Acad. Sci. U.S.A.*, *73*, 2206 (1976).
4 (a) J. T. Landrum, C. A. Reed, K. Hatano and W. J. Scheidt, *J. Am. Chem. Soc.*, *100*, 3232 (1978);
(b) M. S. Haddad, E. N. Duesler and D. N. Hendrickson, *Inorg. Chem.*, *18*, 141 (1979).
5 D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, *75*, 3019 (1978).
6 N. A. Bailey, M. M. Eddy, D. E. Fenton, G. Jones, S. Moss and A. Mukhopadhyay, *J. Chem. Soc., Chem. Comm.*, 628 (1981).
7 S. M. Nelson, *Rev. Pure Appl. Chem.*, *52*, 2461 (1980) and references therein.
8 J. L. Karn and D. H. Busch, *Nature*, 211, 160 (1960); R. L. Rich and Stucky, *Inorg. Nucl. Chem. Lett.*, *1*, 61 (1965);
J. C. Dabrowiak, L. A. Nafie, P. C. Bryan and A. T. Torkelson, *Inorg. Chem.*, *16*, 540 (1977).
9 M. G. B. Drew, S. G. McFall, S. M. Nelson and C. P. Waters, *J. Chem. Research*, (S) 16-17 (M) 0360-0378 (1979).
10 S. M. Nelson, C. V Knox, M. McCann and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1981, 1669;
M. G. B. Drew, J. Nelso and S. M. Nelson, *ibid.*, 1678 (1981).
11 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc. Dalton Trans.*, 1868 (1981).
12 S. M. Nelson, F. S. Esho and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 409 (1982).
13 M. G. B. Drew, J. Nelson, F. S. Esho and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, in press.
14 C. V. Knox and S. M. Nelson, unpublished results.
15 C. Cairns, A. Lavery, S. M. Nelson and M. G. B. Drew, *J. Chem. Soc., Chem. Comm.*, 1122 (1980).
16 M. G. B. Drew, M. McCann and S. M. Nelson, *J. Chem. Soc., Chem. Comm.*, 481 (1979).
17 S. M. Nelson, M. McCann, C. Stevenson and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1477 (1979).
18 J. A. Fee and R. G. Briggs, *Biochem. Biophys. Acta*, *400*, 439 (1975).
19 See, for example, C-L. O'Young, J. C. Dewan, H. R. Lilienthal and S. J. Lippard, *J. Am. Chem. Soc.*, *100*, 7291 (1978).
P. K. Coughlin, J. Dewan, S. J. Lippard, E-I. Watanabe and J-M. Lehn, *ibid.*, *101*, 265 (1979).
P. K. Coughlin, S. J. Lippard, A. E. Martin and J. E. Bulkowski, *ibid.*, *102*, 7617 (1980).
20 M. S. Haddad and D. N. Hendrickson, *Inorg. Chem.*, *17*, 2622 (1978).
21 H. M. J Hendriks and J. Reedijk, *Inorg. Chim. Acta*, *37*, L509 (1979);
H. M. J. Hendriks, P. J. Birker, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, in press.
22 W. Mori, A. Nakahara and Y. Nakao, *Inorg. Chim. Acta*, *37*, L507 (1979).
23 M. G. B. Drew, S. M. Nelson and J. Reedijk, *Inorg. Chim. Acta*, *64*, L189 (1982).
24 B. Bleaney and K. D. Bowers, *Proc. Roy. Soc. Ser. A*, *214*, 451 (1952).
25 See, for example, D. G. Hodgson, *Progr. Inorg. Chem.*, *19*, 173 (1975);
M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul and J. Martin-Frere, *Inorg. Chem.*, *18*, 1675 (1979).
26 M. S. Haddad, S. R. Wilson, D. J. Hodgson and D. N. Hendrickson, *J. Am. Chem. Soc.*, *103*, 1273 (1981).
27 P. L. Burk, J. A. Osborn, M-T. Youinou, Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, *103*, 1273 (1981).
28 P. K. Coughlin and S. J. Lippard, *J. Am. Chem. Soc.*, *103*, 3228 (1981).
29 P. J. Hay, J. C. Thibeault and R. Hoffman, *J. Am. Chem. Soc.*, *97*, 4884 (1975).
30 H. E. LeMay, D. J. Hodgson, P. Pruettiangkura and L. J. Theriot, *J. Chem. Soc. Dalton Trans.*, 781 (1979).
31 Z. Dori and R. F. Ziolo, *Chem. Rev.*, *73*, 247 (1973); T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, *17*, 444 (1978).

32 Y. Agnus, R. Louis and R. Weiss, *J. Am. Chem. Soc.*, *101*, 3381 (1979).

33 V. McKee, J. V. Dagdigian, R. Bau and C. A. Reed, *J. Am. Chem. Soc.*, *103*, 7000 (1981).

34 M. G. B. Drew, unpublished results.

35 S. M. Nelson, F. S. Esho and M. G. B. Drew, unpublished results.

36 S. M. Nelson, F. S. Esho and M. G. B. Drew, *J. Chem. Soc., Chem. Comm.*, 388 (1981).

37 J. L. Burmeister, in 'The Chemistry and Biochemistry of Thiocyanic Acid and its Derivatives', ed. A. A. Newman, Academic Press, London, 1975.

38 M. G. Burnett, V. McKee and S. M. Nelson, *J. Chem. Soc., Chem. Comm.*, 829 (1980).