In memory of S. M. Nelson

Complexes of Ligands providing Endogenous Bridges. Part 4.[1] Copper(II) Complexes of Macrocyclic Schiff Bases derived from 2,6-Diacetylpyridine and 1,*n*-Diamino-*n*′-hydroxyalkanes (*n*,*n*′ = 3,2; 4,2; and 5,3): Synthesis, Properties, and Structures†

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The synthesis, physicochemical properties, and *X*-ray crystal and molecular structures of three dinuclear copper(II) complexes of tetraimine Schiff-base macrocycles derived from 2,6-diacetylpyridine and 1,*n*-diamino-*n*′-hydroxyalkanes (*n*,*n*′ = 3,2; 4,2; and 5,3) are reported. The complex derived from a 20-membered macrocycle has present a single endogenous alkoxy bridge and so can serve as a speculative model for the dicopper(II) site in oxyhaemocyanin. As the ring size is increased this bridge is lost and is replaced by an unusually short hydrogen bond between the protonated and deprotonated hydroxyl groups.

Haemocyanin is the copper protein responsible for dioxygen transport in the haemolymph of several arthropods and molluscs.[2] Structural studies (EXAFS[3] and *X*-ray diffraction measurements[4]) have indicated that each copper atom of the strongly coupled binuclear site is co-ordinated to three histidine residues. Cumulative spectroscopic[5] and magnetic[6] measurements strongly suggest that in the oxy- and met-states of the protein the two copper atoms are bridged by an endogenous ligand. Although structural studies have so far failed to identify this bridging ligand it is generally accepted that it is an anionic oxygen donor (*i.e.* phenoxide, alkoxide, or hydroxide). A recent comparison of the resonance Raman spectra of several phenolate bridged binuclear copper(II) complexes with that of haemocyanin has led to the suggestion that the endogenous bridge cannot be a phenolate from a tyrosine residue.[7]

In recent years several studies have appeared which have tried to duplicate the basic structural properties of the haemocyanin active site.[8—10] In most cases a binucleating ligand involving two separate (N_3) donor sets linked by an endogenous phenol,[8] or alcohol[9] moiety was used as a building block; the hydroxide ion has also been used as a bridge.[10] The advent and exploitation of tetraimine Schiff-base macrocycles as binucleating ligands gave the opportunity to incorporate into these macrocycles aliphatic alcohols as lateral units, and hence make provision for the possibility of endogenous bridges.

We report here the syntheses and physicochemical properties of novel binuclear copper(II) complexes of macrocycles derived from 2,6-diacetylpyridine and 1,*n*-diamino-*n*′-hydroxyalkanes (*n*,*n*′ = 3,2; 4,2; and 5,3) together with the *X*-ray crystal structures of three complexes; $[Cu_2(HL^1)(CH_3CN)(H_2O)][ClO_4]_3$ (**1a**), $Cu_2(HL^2)(H_2O)_2(ClO_4)_3$ (**2**), and $Cu_2(HL^3)(H_2O)(ClO_4)_3$ (**3**).

Results and Discussion

It has been generally found that the synthesis of tetraimine Schiff-base macrocycles proceeds efficiently in the presence of alkaline-earth and main-group metal templating agents. The complexes formed are sufficiently kinetically labile that the template cation may be replaced by transition-metal cations in a transmetallation reaction to produce complexes not accessible by direct employment of the transition metal as a template.[11] The preparation of barium and lead complexes of the macrocycles H_2L^1, H_2L^2, and H_2L^3 has been described in Part 1 of this series.[12] The dinuclear copper(II) complexes $[Cu_2(HL^1)(H_2O)_2][ClO_4]_3$ (**1**), $Cu_2(HL^2)(H_2O)_2(ClO_4)_3$ (**2**), and $Cu_2(HL^3)(H_2O)(ClO_4)_3$ (**3**) are readily obtained *via* transmetallation of the appropriate precursor complex. In the case of (**1**) the dicopper(II) complex may be prepared either from $[Ba(H_2L^1)][ClO_4]_2\cdot 2H_2O$ or from the ring-contracted lead complex $[Pb(L^4)][ClO_4]_2\cdot H_2O$. In the latter case the transmetallation proceeds with concomitant ring expansion of the macrocycle.

The i.r. spectra show no bands at 1 690 cm^{-1} ($\nu_{C=O}$) or 3 100—3 300 cm^{-1} (ν_{NH_2}) indicating that the macrocyclic structure is retained; there are bands at *ca.* 1 650 cm^{-1} indicative of $\nu_{C=N}$. A broad band is noted at 3 450—3 475 cm^{-1} and is likely to be a superposition of bands from the ligand –OH and from the water molecules present. This information, and the elemental analyses, led to the proposition that the mono μ-alkoxo binuclear compounds (**1**)—(**3**) had been formed, two isomeric possibilities existing for (**3**). Crystals suitable for single-crystal *X*-ray structure determination were grown for all three complexes. For (**3**) transmetallation of $[Pb(H_2L^3)][ClO_4]_3OH$

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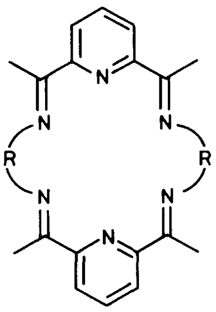
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

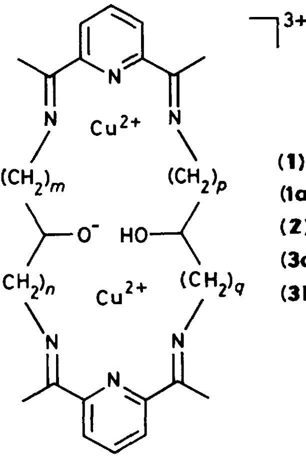
Table 1. Selected bond lengths and interatomic distances (Å) and bond angles (°) with estimated standard deviations for $[Cu_2(HL^1)(CH_3CN)(H_2O)][ClO_4]_3$ (**1**)*

Cu(1)–O(1)	1.971(9)	Cu(2)–O(1)	1.967(11)	N(2)–C(8)	1.453(16)	N(3)–C(10)	1.485(25)
Cu(1)–N(2)	1.975(10)	Cu(2)–N(3)	2.003(10)	N(2)–C(6)	1.260(17)	N(3)–C(11)	1.247(19)
Cu(1)–N(1)	1.925(10)	Cu(2)–N(4)	1.904(11)	N(6)–C(23)	1.275(16)	N(5)–C(18)	1.268(23)
Cu(1)–N(6)	2.003(9)	Cu(2)–N(5)	2.116(10)	N(6)–C(22)	1.461(19)	N(5)–C(20)	1.471(20)
Cu(1)–N(70)	2.276(7)	Cu(2)–O(80)	2.346(11)	N(70)–C(71)	1.110(11)	C(71)–C(72)	1.446(12)
O(1)–C(9)	1.467(17)	O(2)–C(21)	1.432(20)	Cu(1) ··· Cu(2)	3.638(8)	O(2) ··· O(2′)	2.59(1)
				Cu(1) ··· O(31″)	3.012(2)	Cu(2) ··· O(13)	2.77(1)
O(1)–Cu(1)–N(2)	82.1(4)	O(1)–Cu(2)–N(3)	81.9(5)	N(2)–Cu(1)–N(6)	158.3(4)	N(3)–Cu(2)–N(5)	156.0(5)
O(1)–Cu(1)–N(1)	159.4(4)	O(1)–Cu(2)–N(4)	158.9(3)	N(1)–Cu(1)–N(6)	80.1(4)	N(4)–Cu(2)–N(5)	77.6(4)
O(1)–Cu(1)–N(6)	117.6(4)	O(1)–Cu(2)–N(5)	121.8(4)	Cu(1)–O(1)–C(9)	106.6(9)	Cu(2)–O(1)–C(9)	112.1(9)
N(2)–Cu(1)–N(1)	79.0(4)	N(3)–Cu(2)–N(4)	78.3(5)	Cu(1)–N(70)–C(71)	168.6(12)	Cu(2)–O(1)–Cu(1)	135.0(4)

* (′) denotes −*x*, 1 − *y*, −*z*, (″) denotes −*x*, 1 − *y*, 1 − *z*.

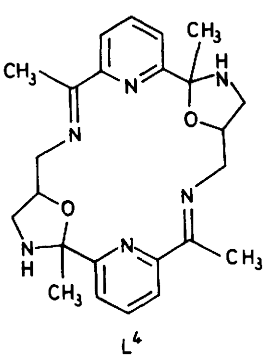


H_2L^1 ; R = $CH_2CH(OH)CH_2$
H_2L^2 ; R = $CH_2CH_2CH(OH)CH_2CH_2$
H_2L^3 ; R = $CH_2CH(OH)CH_2CH_2$



$Cu_2(HL)(H_2O)_x(ClO_4)_3$

(**1**) $m = n = p = q = 1$; $x = 2$
(**1a**) $m = n = p = q = 1$; $x = 1$; CH_3CN
(**2**) $m = n = p = q = 2$; $x = 2$
(**3a**) $m = q = 2$, $n = p = 1$; $x = 1$
(**3b**) $m = p = 2$, $n = q = 1$; $x = 1$



L^4

with $Cu[ClO_4]_2$ gave a dark blue solution from which, on slow evaporation, a mixture of two blue crystalline products were recovered. The crystals were separated by hand and although both forms were suitable for *X*-ray determination one form decomposed rapidly in the beam and so the structure of one component of the bulk sample was solved.

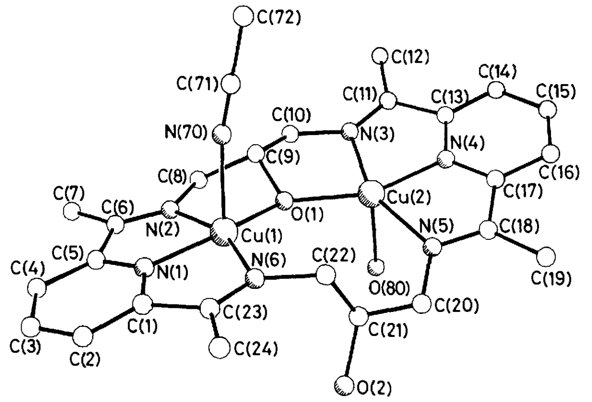


Figure 1. The molecular structure, with atom labelling, of the cation $[Cu_2(HL^1)(CH_3CN)(H_2O)]^{3+}$ of (**1a**)

The crystal structure of $[Cu_2(HL^1)(CH_3CN)(H_2O)][ClO_4]_3$ (**1a**) is illustrated in Figure 1, with, where appropriate, the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Table 1.

In the structure of $[Cu_2(HL^1)(CH_3CN)(H_2O)]^{3+}$, each copper(II) ion has approximately square-pyramidal geometry and is co-ordinated to two imino and one pyridyl nitrogen atoms. Deprotonation of the ligand is confirmed and the resulting alkoxide forms a symmetrical bridge between the metal centres. An axial solvent molecule [acetonitrile for Cu(1) and water for Cu(2)] completes the five-co-ordination. As expected, the axial bond lengths are considerably longer than those in the square plane. The second alcohol function remains protonated and is directed away from the macrocycle cavity, being intermolecularly hydrogen bonded to the equivalent group of a related molecule [O(2) ··· O(2′) 2.59(1) Å]. The angle between the mean copper co-ordination planes is 19.9°; the copper–copper separation is 3.64 Å and the Cu–O–Cu bridge angle is 135.0(4)°. The mean planes of the macrocycles are necessarily stacked parallel to each other in the unit cell. One of the perchlorate anions is weakly σ-bonded to Cu(2) [Cu(2)–O(13) 2.77(1) Å opposite to the water ligand] whereas the sixth site of Cu(1) is blocked at a greater distance by another perchlorate oxygen atom [Cu(1) ··· O(31″) 3.012(2) Å].

Binuclear copper(II) complexes involving single bridges are quite rare, and this is the first example of a mono μ-alkoxo species that has been structurally characterised.

Table 2. Selected bond lengths and interatomic distances (Å) and bond angles (°) with estimated standard deviations for $Cu_2(HL^2)(H_2O)_2(ClO_4)_3$ (**2**)*

Cu(1)–O(1)	1.871(8)	Cu(2)–O(2)	1.881(7)	N(3)–C(8)	1.273(16)	N(6)–C(22)	1.268(15)
Cu(1)–N(1)	1.997(9)	Cu(2)–N(4)	2.027(9)	N(3)–C(10)	1.454(17)	N(6)–C(24)	1.473(16)
Cu(1)–N(2)	1.895(9)	Cu(2)–N(5)	1.892(9)	Cu(1) ··· O(9)	2.982(10)	Cu(2) ··· O(8)	3.083(10)
Cu(1)–N(3)	1.999(10)	Cu(2)–N(6)	1.982(9)	Cu(1) ··· Cu(1′)	4.820(3)	Cu(2) ··· Cu(2′)	4.903(2)
Cu(1)–O(4)	2.401(9)	Cu(2)–O(3)	2.316(9)	O(1) ··· O(1′)	2.457	O(2) ··· O(2′)	2.466
O(1)–C(12)	1.433(14)	O(2)–C(26)	1.463(12)	Cu(1) ··· O(1′)	3.51	Cu(2) ··· O(2′)	3.56
N(1)–C(14′)	1.473(15)	N(4)–C(28′)	1.448(15)	O(3) ··· O(12′)	3.33(2)	O(12) ··· O(16″)	2.44(2)
N(1)–C(2)	1.236(16)	N(4)–C(16)	1.262(14)	O(3) ··· O(13′)	3.32(8)	O(16) ··· O(15‴)	2.87(3)
				O(3) ··· O(16′)	2.748(17)		
O(1)–Cu(1)–N(1)	99.8(4)	O(2)–Cu(2)–N(4)	99.0(3)	N(1)–Cu(1)–N(3)	159.5(4)	N(4)–Cu(2)–N(6)	159.0(4)
O(1)–Cu(1)–N(2)	171.1(4)	O(2)–Cu(2)–N(5)	166.3(4)	N(2)–Cu(1)–N(3)	80.2(4)	N(5)–Cu(2)–N(6)	79.7(4)
O(1)–Cu(1)–N(3)	100.3(4)	O(2)–Cu(2)–N(6)	100.0(3)	Cu(1)–O(1)–C(12)	122.4(7)	Cu(2)–O(2)–C(26)	120.7(6)
N(1)–Cu(1)–N(2)	79.3(4)	N(4)–Cu(2)–N(5)	79.7(4)	Cu(1)–O(4)–Cl(1)	127.1(5)		

* (′) denotes $-x, -y, z$, (″) denotes $1-x, -y, z$, (‴) denotes $x, y, z-1$.

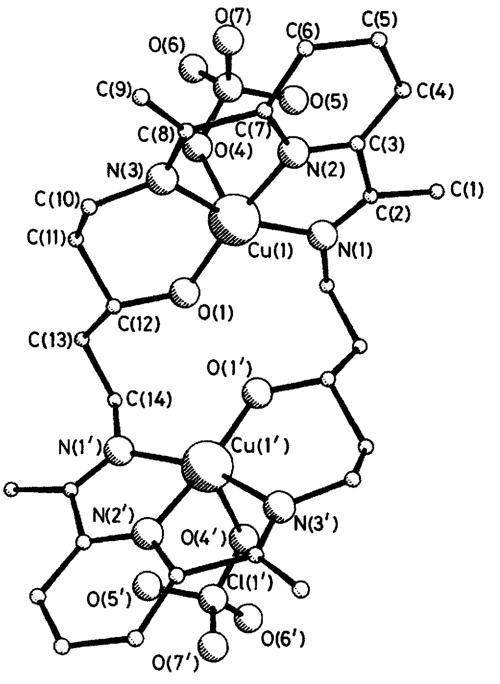


Figure 2. The molecular structure, with atom labelling, of the cation $[Cu_2(HL^2)(ClO_4)_2]^+$ of (**2**)

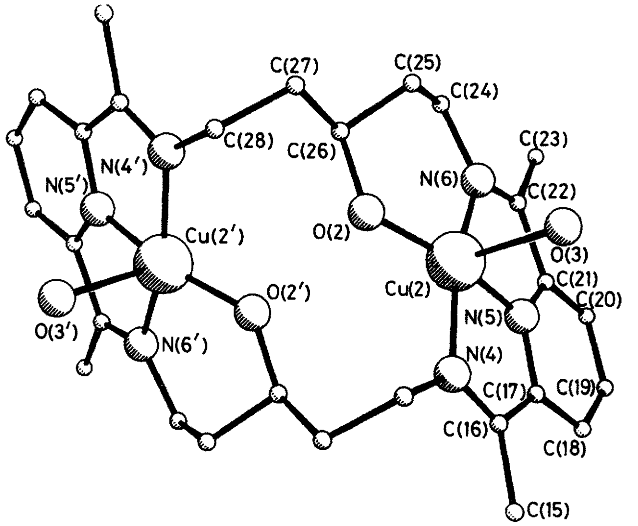


Figure 3. The molecular structure, with atom labelling, of the cation $[Cu_2(HL^2)(H_2O)_2]^{3+}$ of (**2**)

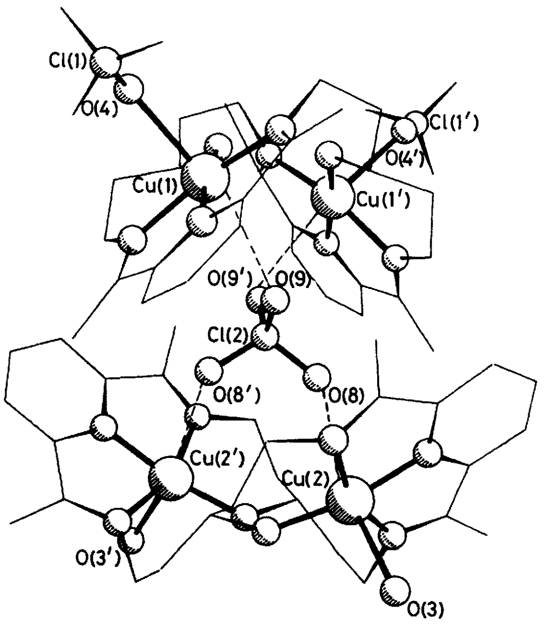


Figure 4. The encapsulated environment of the perchlorate showing the two cations in skeletal outline only in the structure of $Cu_2(HL^2)(H_2O)_2(ClO_4)_3$ (**2**)

The crystal structure of $Cu_2(HL^2)(H_2O)_2(ClO_4)_3$ (**2**) is illustrated in Figures 2—4, with, where appropriate, the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Table 2.

The crystal structure of the dicopper complex of HL^2 is rather complicated. It comprises two crystallographically independent, dicopper macrocyclic, cationic complexes, each possessing crystallographically imposed C_2 symmetry (Figures 2 and 3). In each, the well separated copper atoms (4.820 and 4.903 Å) are four-co-ordinated in approximately square-planar environments by a pyridyl and two imino nitrogen atoms and by the oxygen of one of the endogenous hydroxyl groups. One hydroxyl group in each macrocycle has been deprotonated and the two oxygens are mutually hydrogen bonded by the remaining hydroxyl hydrogen at short separations (O ··· O 2.457 and 2.466 Å respectively). One such hydrogen bond appears to be essentially ordered and symmetric (the hydrogen is located on the C_2 axis), whereas the other is disordered, asymmetric, and bent. The macrocycles are folded (95.8 and 94.7° between metal co-ordination planes) and face each other along the same C_2 axis (0, 0, z), with the planes of folding approximately perpendicular. Within the loose cavity so formed lies a perchlorate across the C_2 axis with each oxygen atom occupying an axial co-ordination site of one of the four copper metals. The opposite axial sites of the coppers are occupied, on one macrocycle, by two σ-perchlorate ligands, and, on the other macrocycle, by water ligands (Figure 4). The crystal structure is completed by two C_2-related perchlorate anions, one perchlorate anion lying across a second crystallographic C_2 axis (0.5, 0, z), and two C_2-related unco-ordinated solvent water molecules. The chemical units present are therefore $[Cu_2(HL^2)(ClO_4)_2]^+$, $[Cu_2(HL^2)(H_2O)_2]^{3+}$, 4 ClO_4^-, and $2H_2O$ occupying two equivalent positions. In both macrocycles, the pyridyl rings are planar and the imino nitrogen atoms are in essentially trigonal-planar environments with little pyramidalisation. The pentane chains only show significant deviations from antiperiplanar conformations in the regions of the hydroxy substituents. The oxygen-containing six-membered chelate rings have boat conformations with moderate out-of-plane deviations (0.12 and 0.17 Å respectively) of the copper atoms. The unco-ordinated water molecule forms hydrogen bonds to two ionic perchlorates and to a co-ordinated water ligand: there are two further long contacts between the co-ordinated water ligand and perchlorate anions.

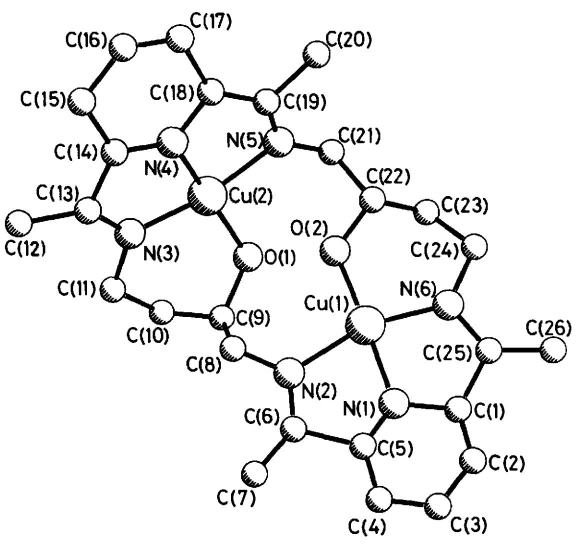


Figure 5. The molecular structure, with atom labelling, of the cation $[Cu_2(HL^3)]^{3+}$ of (3)

The crystal structure of $Cu_2(HL^3)(H_2O)(ClO_4)_3$ (3) is illustrated in Figures 5 and 6, with, where appropriate, the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Table 3.

The structure of the dicopper complex of HL^3 comprises two

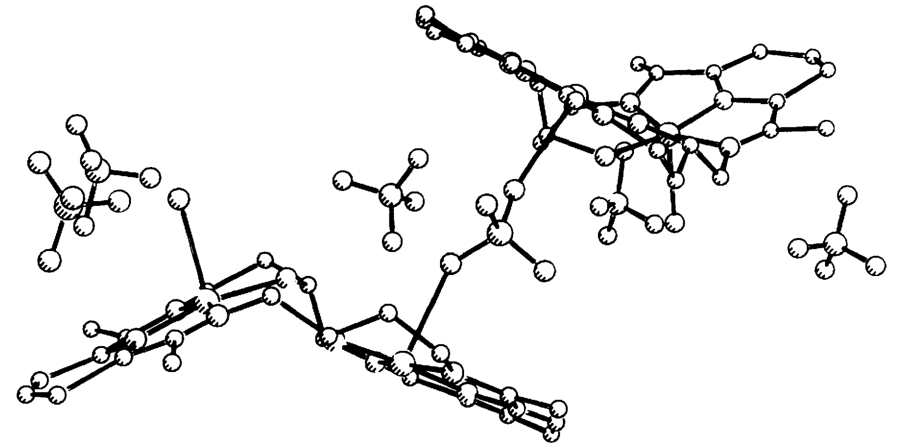


Figure 6. The dimeric association, *via* perchlorate bridging, of the aquated cations $[Cu_2(HL^3)(H_2O)]^{3+}$ of (3). The positions of the other perchlorates are also shown

Table 3. Selected bond lengths and interatomic distances (Å) and bond angles (°) with estimated standard deviations for $Cu_2(HL^3)(H_2O)(ClO_4)_3$ (3) *

Cu(1)–O(2)	1.850(23)	Cu(2)–O(1)	1.899(23)	N(2)–C(6)	1.306(37)	N(5)–C(19)	1.293(23)
Cu(1)–N(6)	1.998(20)	Cu(2)–N(3)	1.987(21)	N(2)–C(8)	1.506(33)	N(5)–C(21)	1.494(33)
Cu(1)–N(1)	1.853(17)	Cu(2)–N(4)	1.888(14)	Cu(1) ··· Cu(2)	4.706(7)	O(1) ··· O(2)	2.366(28)
Cu(1)–N(2)	2.040(19)	Cu(2)–N(5)	2.001(16)	Cu(1) ··· O(1)	3.42	Cu(2) ··· O(2)	3.22
Cu(1)–O(11)	2.693(22)	Cu(2)–O(15)	2.459(34)	O(3) ··· O(15)	2.85	Cu(1) ··· O(15′)	3.12
O(2)–C(22)	1.415(36)	O(1)–C(9)	1.416(27)	O(7) ··· O(15)	3.07	Cu(2) ··· O(5′)	3.74
N(6)–C(24)	1.499(38)	N(3)–C(11)	1.499(38)	O(16) ··· O(15)	2.74	Cu(2) ··· O(6′)	3.52
N(6)–C(25)	1.291(36)	N(3)–C(13)	1.284(29)				
O(2)–Cu(1)–N(6)	98.0(10)	O(1)–Cu(2)–N(3)	99.3(9)	N(6)–Cu(1)–N(2)	160.8(11)	N(3)–Cu(2)–N(5)	161.1(8)
O(2)–Cu(1)–N(1)	177.3(9)	O(1)–Cu(2)–N(4)	166.1(10)	N(1)–Cu(1)–N(2)	81.0(9)	N(4)–Cu(2)–N(5)	81.7(8)
O(2)–Cu(1)–N(2)	101.2(10)	O(1)–Cu(2)–N(5)	96.9(7)	Cu(1)–O(2)–C(22)	124.1(19)	Cu(2)–O(1)–C(9)	123.5(15)
N(6)–Cu(1)–N(1)	79.8(9)	N(3)–Cu(2)–N(4)	80.2(9)	Cu(1)–O(11)–Cl(3)	136.4(15)		

* (′) denotes x, $-y$, $z-\frac{1}{2}$.

C_2-symmetry related dicopper macrocyclic trications which are linked, between two coppers, *via* a bridging perchlorate situated on the C_2 axis. The second copper in each macrocycle carries a water ligand which forms hydrogen bonds (O $\cdots$ O 2.85, and 3.07 or 2.74 Å) to two ionic perchlorates (Figure 6). The remaining perchlorate is situated on the crystallographic C_2 axis and engages in no hydrogen bonding. The copper ions are four-co-ordinate and are separated by 4.71 Å: the basal sites are occupied by a pyridyl and two imino nitrogen atoms and one endogenous hydroxyl oxygen of the macrocycle. Cu(1) and the three nitrogen atoms are coplanar, with O(2) displaced 0.05 Å from the plane; Cu(2) is displaced 0.18 Å from the mean plane (r.m.s. deviation 0.05 Å) through the four ligating atoms. The macrocycle, which includes two asymmetric 1,4-di-iminobutan-2-ol fragments, exists exclusively as an isomer which provides equivalent environments for the two coppers. This again serves to bring into close proximity (2.37 Å) the two endogenous hydroxyl groups, one of which has again been deprotonated, which, at this separation, must be symmetrically hydrogen bonded. The distances from each copper to the hydroxyl oxygen to which it is not bonded (3.22 and 3.42 Å) are considerably shorter than those in the complex of HL^2 above (3.51 and 3.56 Å). However, these distances are still too great for the hydroxyl groups to be regarded as even semi-bridging, and the reduced distances are merely inevitable consequences of the reduction in chain length of the di-imino backbone, which is insufficient to permit hydroxy bridging. The macrocycle is bent by 42° between mean co-ordination planes: the axial sites of the copper ions are occupied, on the same side of the macrocycle, by, respectively, the bridging perchlorate and the water ligand. Neither copper atom carries a further ligand, the sixth sites being blocked by a *c*-glide related water ligand [3.12 Å from Cu(1)] and by two oxygen atoms of the ionic perchlorate based on Cl(1) [3.74 and 3.52 Å from Cu(2)]. Further discussion of the geometry of the molecule is not justified by the accuracy of the structure.

Discussion and Comparisons of Structures.—The three molecular structures, along with complexes of other metals with the same or similar macrocycles, illustrate the variations in molecular conformation and mode of bonding which may be used to match the cavity size of a macrocycle to the radii of the metal ions that are to be incorporated.

In the 20-membered macrocycle HL^1, there is little ring folding and one deprotonated endogenous hydroxy group symmetrically bridges the two coppers at a separation of 3.638(8) Å. The second hydroxy group remains protonated and conformational requirements oblige it to be directed away from the centre of the cavity and to take no direct part in the metal complexation. When the ring size is increased to 22 in HL^3, the two coppers are accommodated at a much increased separation [4.706(7) Å] and with markedly greater folding of the macrocycle. Both pendant hydroxy groups, one deprotonated, are now involved in bonding to, but not bridging, the copper atoms, and are mutually hydrogen bonded. In the 24-membered macrocycle HL^2, the two Cu^{2+} ions are slightly further separated [4.820(3) or 4.903(2) Å] but now with substantial macrocycle folding which serves to reduce the overall cavity size and bring the Cu–X (X = O or N) distances down to the optimum values for covalent bond formation to the metal. In all cases in the three molecules, axial sites of the coppers are occupied, or are blocked, by ions and/or solvents.

In comparison, a 24-membered macrocycle, *e.g.* HL^2 or an equivalent with furan head-units, can accommodate one barium and a solvent with little folding. It may be speculated that the dilead complex of the same macrocycle (HL^2) would be more closely planar than the dicopper complex, since the radius of the Pb^{2+} ion is intermediate between those of Cu^{2+} and Ba^{2+}.

Complex (**1a**) may be regarded as a putative structural model for the dicopper site in oxy- and met-haemocyanin. The intramolecular Cu–Cu separation of 3.64 Å is similar to the values determined by EXAFS studies for oxyhaemocyanin (3.8 Å) and methaemocyanin (3.5 Å).[3b] Moreover the geometry of the endogenous alkoxide bridge resembles that proposed for the biological system and reinforces the concept that the alkoxide from serine or threonine would be well suited to the role of an endogenous bridge.[9a] In metaquahaemocyanin the Cu–Cu separation is too long to permit double monoatomic bridging (exogenous and endogenous) of the copper(II) atoms.[3b] Consequently bridging by the exogenous water molecule can be ruled out in favour of a structure maintaining the endogenous bridge and with a water molecule co-ordinated to each copper. The structure of complex (**1a**) bears good resemblance to this proposition. We have also noted that in dinuclear copper(II) complexes derived from 2,6-bis[(salicylideneimino)methyl]-4-nitrophenol it is only with a 3.0 Å Cu–Cu separation that a double monoatomic bridge is supported.[13] If the separation is increased to 3.50 Å then the endogenous phenolic bridge is retained and the exogenous bridge is replaced by two monoligating groups.

Physicochemical Properties.—Owing to the presence of an uncharacterised component in the sample of (**3**) it was decided to confine the physicochemical studies to complexes (**1**) and (**2**).

An acetonitrile solution of (**1**) shows two electronic absorption bands at 15.38 × 10^3 (ε 357) and 30.3 × 10^3 cm^{-1} (ε 7 720 dm^3 mol^{-1} cm^{-1}). The spectrum is essentially the same as a solid-state diffuse-reflectance spectrum, indicating that the co-ordination geometry is unchanged in solution. The lower-energy band is assigned to metal *d–d* transitions whilst the high-energy band is attributed to a ligand-to-metal charge transfer,[14] providing evidence for the retention of the endogenous bridge in solution. The tetragonal geometry of each copper atom dictates a $d_{x^2-y^2}$ ground state which orientates the orbital lobes towards the bridging oxygen atom; this gives good opportunity for antiferromagnetic coupling between the metal centres. An acetonitrile solution of (**1**) at room temperature is e.s.r. silent as is a frozen solution at 4 K. This may suggest considerable spin exchange between the copper centres.

Electrochemical studies. The redox properties of (**1**) and (**2**) have been investigated in dimethyl sulphoxide solution at a platinum electrode using tetrabutylammonium tetrafluoroborate as the supporting electrode.

Figure 7 illustrates the cyclic voltammogram of (**2**) at a sweep rate of 6 V min^{-1}. It comprises two reduction peaks at $E_{pc}{}^1 = -0.51$ and $E_{pc}{}^2 = -0.67$ V and three oxidation peaks at $E_{pa}{}^1 = -0.43$, $E_{pa}{}^2 = -0.58$, and $E_{pa}{}^3 = -0.16$ [all *versus* saturated calomel electrode (s.c.e.)]. Cyclic voltammetric analysis showed that the first electron transfer ($E_{pc}{}^1$, $E_{pa}{}^1$) is quasi-reversible since the peak difference increases slightly with scan rate. In contrast the second electron transfer is electrochemically irreversible. Coulometric analyses at −0.42 and −0.65 V *vs.* s.c.e. indicate that both electron transfers are monoelectronic. Moreover reoxidations of the two-electron reduced solution at 0 and +0.75 V *vs.* s.c.e. also consume one Faraday per mole each and the overall process generates the initial solution.

The cyclic voltammogram of (**1**) at 3 V min^{-1} is also depicted in Figure 7. At first glance it is quite similar to that of (**2**) except for the values of the peak potentials: $E_{pc}{}^1 = -0.31$, $E_{pc}{}^2 = -0.58$, $E_{pa}{}^1 = -0.20$, $E_{pa}{}^2 = -0.50$, and $E_{pa}{}^3 = +0.18$ V *vs.* s.c.e. Both reductions are monoelectronic as is deduced from coulometric analyses at −0.36 and −0.60 V *vs.* s.c.e. However the two compounds differ in the reversibility of the electron transfers. When the one-electron reduced species for (**1**) is reoxidised, one Faraday per mole is consumed but the initial

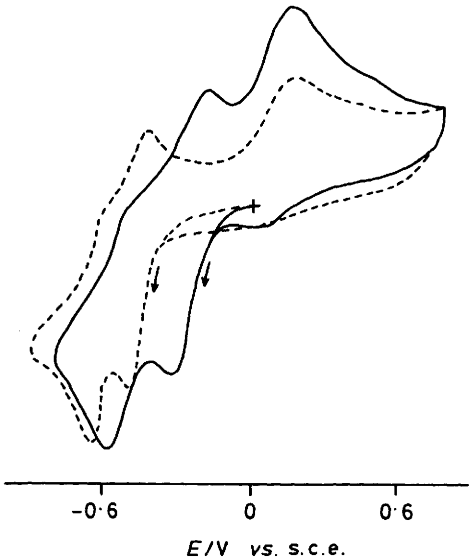
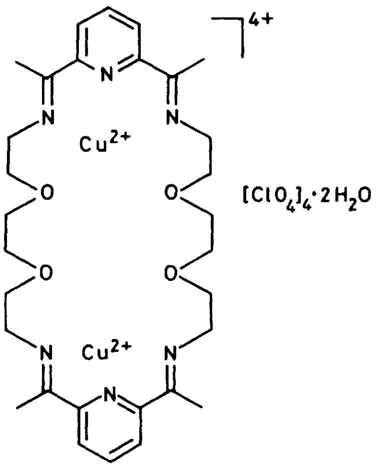


Figure 7. Cyclic voltammograms of (**1**) (——) and (**2**) (– – –) in dimethyl sulphoxide solution (10^{-1} mol dm^{-3} in tetrabutylammonium tetrafluoroborate) at 3 and 6 V min^{-1} respectively

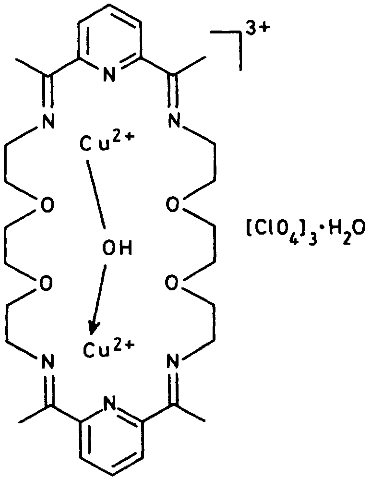
solution is only partly recovered. Reoxidation of the two-electron reduced solution still requires two electrons but it does not regenerate the starting solution. Moreover we observed that the reversibility of the first couple ($E_{pc}{}^1$, $E_{pa}{}^1$) depends on the solvent quality, *i.e.* its water content. This observation suggests that proton transfer may be associated to electron transfer. In order to prove this possibility we performed experiments using tetrafluoroboric acid as a proton source. Unfortunately although supportive to an extent these experiments have not given clear-cut results. Nevertheless it appears that the electrochemical behaviour of (**1**) is somewhat more complicated than that of (**2**).

It is well known that copper(II) exhibits a marked preference for tetragonal environments whereas copper(I) shows preference for tetrahedral environments. This implies that upon reduction of a copper(II) complex stereochemical changes are likely to intervene which may induce an electrochemically irreversible process. In this context it seems reasonable to infer that reversible electron transfers will be observed only when the ligand framework is able either freely to accommodate or totally to block any stereochemical change. These effects have been very recently observed and thoroughly studied by Mazurek *et al.*[15,16] for dinuclear copper complexes. Furthermore copper(I) generally has lower co-ordination numbers than copper(II) and so the loss of a ligand upon reduction is a likely event.[17]

In the case of (**2**) the above discussion and the fact that a reduction–oxidation cycle regenerates the starting solution strongly suggests that the process responsible for the electrochemical irreversibility is stereochemical. This irreversibility is noted only at the second electron transfer. It is thought likely that due to the long chain connecting the two –N=C(Me)–C_5H_3N–C(Me)=N– moieties the ligand can accommodate the stereochemical change associated with the first electron transfer but that the second electron transfer would introduce too much tension into the ligand system. Drew *et al.*[10a] have isolated a related compound, (**4**), with a longer bridging chain of eight atoms compared with five in (**2**) and the electrochemical behaviour has been studied.[10c] This complex presents two reversible electron transfers at $E_1 = -0.06$ and $E_2 = -0.44$ V *vs.* s.c.e. It therefore appears that the presence of the longer chain helps to accommodate the structural changes induced by the electron transfers.



(**4**)



(**5**)

The behaviour of (**1**) must be compared to that of μ-hydroxo complexes of similar ligands lacking the alcohol function.[10a,b] In the case of complex (**5**) the first transfer is monoelectronic and irreversible and corresponds to the reduction of one copper followed by its ejection with the hydroxide. The resulting product is the mononuclear copper(II) complex of the ligand.[10c]

The behaviour of complex (**6**) more closely resembles that of (**1**) as a first reversible one-electron transfer is observed at $E_{\frac{1}{2}} = -0.268$ V *vs.* s.c.e. followed by an irreversible process at $E_{pc} = -0.60$ V *vs.* s.c.e. 'with no discernible anodic counterpart.'[10c] The behaviour of the latter two compounds is most probably complicated by the loss of the exogenous hydroxide bridge which can induce the release of one copper ion when the ligand is flexible enough to wrap around a single metal ion. This is not the case with (**1**) and an involvement of the endogenous alkoxide is not unlikely. As noted above stereochemical changes alone, as in (**2**), cannot explain the experimental observations and proton transfers may accompany the reduction processes. The alkoxide is a most likely site for protonation and this reaction together with the steric tensions resulting from the stereochemical changes can probably lead to the cleavage of the bridge. Although these arguments are plausible they are still speculative and work is continuing in an attempt fully to support this hypothesis. The occurrence of changes at the bridging alkoxide upon reduction of dinuclear copper complexes is of special interest as it can provide clues as to

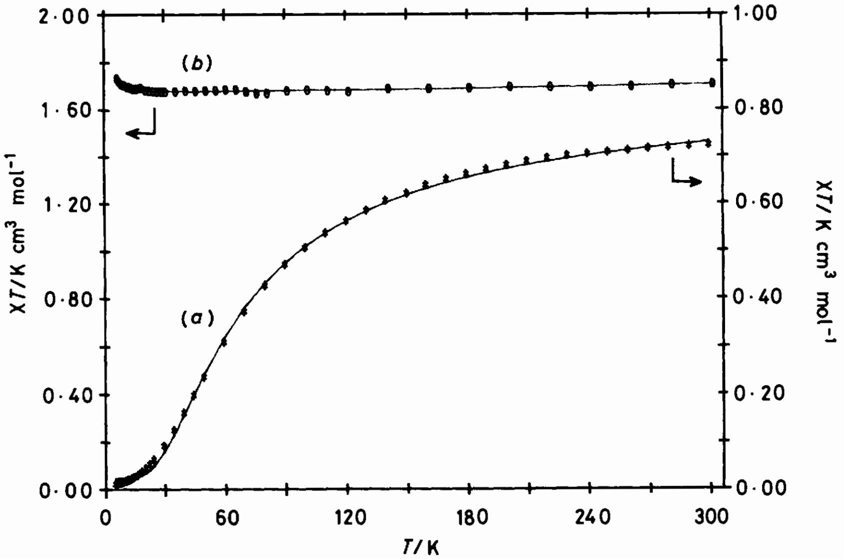
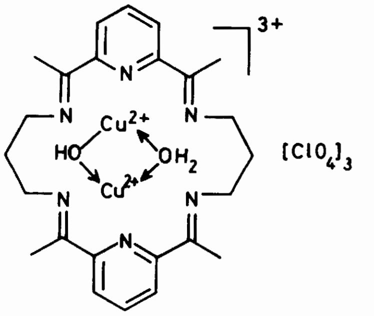


Figure 8. Temperature dependence of the product χT for (**1a**) (*a*) and (**2**) (*b*). The solid lines are the theoretical curves deduced from least-squares fitting as indicated in the text



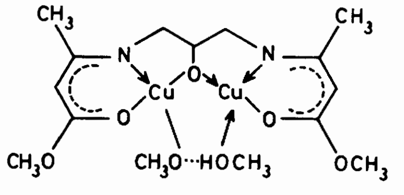
(**6**)

what happens at the active site in haemocyanin during oxygen transport.

Magnetic studies. Figure 8 depicts the temperature dependence of the molar magnetic susceptibility of (**2**) over the range 6–300 K in the form of a χT *vs.* T curve. χT slightly decreases from 1.71 K cm^3 mol^{-1} at 300 K to 1.67 K cm^3 mol^{-1} at 28 K and then increases at low temperatures to reach 1.73 K cm^3 mol^{-1} at 6 K. The experimental data have been fitted to the Curie–Weiss equation giving the following parameters: $g = 2.10$, $\theta = 0.26$ K, and temperature independent paramagnetism (t.i.p) = 1.82×10^{-4} cm^3 mol^{-1}. These results indicate that the four copper atoms behave in an essentially independent manner. This is not surprising since the only ligand bridging the coppers is a perchlorate anion which cannot transmit strong interactions. A small ferromagnetic interaction is apparent in the low-temperature region; this can equally arise from inter- or intra-molecular interactions.

The temperature dependence of the molar magnetic susceptibility of (**1a**) is also shown in Figure 8 as the product χT *vs.* T. The shape of the curve is characteristic of an antiferromagnetically coupled binuclear complex with a steady decrease of χT from 0.72 K cm^3 mol^{-1} at 300 K to 0.0015 K cm^3 mol^{-1} at 6 K. This behaviour can be accounted for by the usual Bleaney–Bowers equation, modified to include some monomeric impurity [equation (1)].

$$\chi = \frac{2Ng^2\beta^2}{kT}\left[3 + \exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1 - P) + \frac{Ng^2\beta^2P}{2kT} + \text{t.i.p.} \quad (1)$$



(**7**)

All the symbols have their usual meaning and P is the proportion of monomeric impurity. Fitting the experimental data with this equation gives the following results: $g = 2.03$, $2J = -84$ cm^{-1}, $P = +0.028$, t.i.p. = 1.2×10^{-4} cm^3 mol^{-1}.

In the very recent past several complexes have been described which possess a bridging alkoxide provided by a binucleating ligand.[9a,b,18–20] However in all but one case a second (exogenous) bridge is present: acetate, azide, or nitrite. The reported complex having a single alkoxide bridge between two copper atoms is that of a Schiff base derived from methyl acetoacetate and 1,3-diamino-2-hydroxypropanol, (**7**).[19b] To our knowledge the magnetic properties of this complex have not been studied extensively, nevertheless it is possible from the reported value of the room-temperature magnetic moment, $\mu_{eff.} = 0.74$, to estimate the singlet–triplet energy as *ca.* -650 cm^{-1} using the correlation defined by Thompson and Ramaswamy.[21] This is much larger than that found in the current work. In a very thorough study of copper aminoalkoxides Nieminen[22] has found several correlations between the singlet–triplet gap and various structural parameters such as the Cu–O–Cu bridging angle, the angle around the bridging alcoholate oxygen, and the distance to the Cu_2O plane of the carbon bound to this O atom. These correlations cannot explain the observed difference in the magnetic properties of the two complexes here which have rather similar structural features.

Conclusions

The evolution of binucleating ligands has led to a series of speculative models for the bimetallobiosite in haemocyanins.[23] Although there are no *X*-ray structural data for oxyhaemocyanin, EXAFS studies have indicated that an endogenous bridge, probably oxygen-derived, is present in this form.[3] *X*-Ray structural studies show that there is no endogenous bridge in deoxyhaemocyanin.[4] It is therefore likely that a bridge-making and -breaking process occurs upon interaction of the dicopper site with dioxygen notwithstanding the nature of the bridge (hydroxyl, seryl, threonyl, tyrosinyl, or carboxylate).

The complex (**1**)/(**1a**), involving an endogenous bridge may be viewed as a speculative model for oxyhaemocyanin; the electrochemical studies indicate structural changes during the reduction–oxidation reaction that are not incompatible with a bridge-breaking and -making process.

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. I.r. spectra were recorded as KBr discs using a Perkin-Elmer 297 i.r. spectrophotometer. Electronic spectra of solution samples were recorded using a Perkin-Elmer Lambda 3 u.v.–visible spectrophotometer and solid-state electronic spectra on a Unicam SP 735 diffuse-reflectance spectrophotometer. The barium and lead macrocyclic complexes were prepared according to the procedure described in ref. 12.

Preparation of the Dinuclear Copper(II) *Complexes*.—The macrocyclic dinuclear copper(II) complexes were prepared by employing the following general procedure.

The precursor barium or lead containing macrocyclic complex (2 mmol) was suspended in refluxing methanol (50 cm^3) and a methanolic solution of copper(II) perchlorate (4 mmol) was added dropwise over 5 min. The reaction mixture was refluxed for 3 h and allowed to cool to room temperature. The resulting blue solution was allowed to evaporate slowly at room temperature and the corresponding binuclear copper(II) complex was isolated as a crystalline material by filtration. Samples were dried *in vacuo* over silica gel.

$[Cu_2(HL^1)(H_2O)_2][ClO_4]_3$. Blue microcrystals (Found: C, 32.1; H, 3.6; Cl, 11.7; N, 9.6. $C_{24}H_{33}Cl_3Cu_2N_6O_{16}$ requires C, 32.2; H, 3.7; Cl, 11.9; N, 9.4%), yield 60%.

$Cu_2(HL^2)(H_2O)_2(ClO_4)_3$. Dark blue polyhedral crystals (Found: C, 35.2; H, 4.4; Cl, 11.1; N, 8.5. $C_{28}H_{41}Cl_3Cu_2N_6O_{16}$ requires C, 35.4; H, 4.3; Cl, 11.2; N, 8.8%), yield 30%.

$Cu_2(HL^3)(H_2O)_n(ClO_4)_3$. Dark blue needle-like crystals. The bulk sample contained more than one component and did not give reproducible analyses. One crystalline form was analysed crystallographically.

Magnetic Measurements.—Magnetic susceptibility measurements were performed with a variable-temperature superconducting SHE 900 magnetometer operating at 5.6 kG in the range 6–300 K. Diamagnetic corrections were evaluated by using Pascal's constants. Data for (**1a**) were corrected for a small amount of saturated ferromagnetic impurity. The data were least-squares fitted to the equations given in the text. $[T\chi_M(\text{obs.}) - T\chi_M(\text{calc.})]^2$ was the quantity minimised in the fitting process. The quality of the fit was estimated through the statistical indicator $R = \Sigma[T\chi_M(\text{obs.}) - T\chi_M(\text{calc.})]^2/N\Sigma[T\chi_M(\text{obs.})]^2$, where N is the number of measurements. R amounted to 4.7×10^{-6} for (**1a**) and 5.0×10^{-5} for (**2**) respectively.

Electrochemistry.—Electrochemical apparatus consisted of a PAR 173 potentiostat/galvanostat driven by a PAR 175 universal programmer, a PAR 179 coulometer, and a Sefram TGM XY recorder. Electrochemical studies were performed in dimethyl sulphoxide (dmso) (10^{-1} mol dm^{-3} in tetrabutylammonium tetrafluoroborate) using a conventional three-electrode cell with a saturated calomel reference electrode and a platinum working electrode. The reference electrode was

Table 4. Atomic positional parameters (× 10^4) with estimated standard deviations for $[Cu_2(HL^1)(CH_3CN)(H_2O)][ClO_4]_3$ (**1**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	1 049(1)	2 020(1)	1 862(1)	C(17)	4 486(11)	3 848(10)	3 138(8)
Cu(2)	2 741(1)	3 102(1)	3 215(1)	C(18)	3 980(13)	4 301(10)	2 158(9)
O(1)	1 654(7)	2 431(7)	3 065(6)	C(19)	4 509(16)	4 891(13)	1 392(10)
O(2)	922(11)	5 059(11)	211(11)	C(20)	2 588(16)	4 574(14)	1 028(13)
N(1)	13(7)	1 724(7)	1 083(7)	C(21)	1 827(13)	4 178(12)	781(16)
N(2)	166(7)	1 592(8)	3 012(7)	C(22)	2 327(10)	2 927(10)	283(9)
N(3)	2 924(9)	2 210(9)	4 575(8)	C(23)	919(9)	2 353(9)	−307(8)
N(4)	3 988(8)	3 270(8)	3 711(6)	C(24)	1 132(11)	2 537(11)	−1 461(9)
N(5)	3 146(9)	4 088(7)	1 996(7)	N(70)	2 643(8)	129(8)	1 577(7)
N(6)	1 437(8)	2 514(7)	423(7)	C(71)	3 518(9)	−694(10)	1 474(8)
C(1)	42(9)	1 930(10)	59(8)	C(72)	4 653(9)	−1 773(10)	1 355(9)
C(2)	−714(10)	1 782(13)	−512(11)	O(80)	1 264(13)	4 988(10)	3 978(13)
C(3)	−1 486(11)	1 432(12)	7(11)	Cl(1)	5 718(2)	823(2)	1 781(2)
C(4)	−1 530(9)	1 237(11)	1 098(11)	O(11)	5 636(7)	1 838(7)	1 158(7)
C(5)	−730(8)	1 399(10)	1 624(9)	O(12)	6 356(7)	749(8)	2 638(7)
C(6)	−604(8)	1 321(9)	2 779(9)	O(13)	4 580(6)	1 016(6)	2 194(6)
C(7)	−1 344(11)	953(13)	3 527(11)	O(14)	6 319(7)	−302(7)	1 162(7)
C(8)	474(11)	1 639(14)	4 068(9)	Cl(2)	1 954(4)	7 652(3)	3 320(3)
C(9)	1 691(13)	1 574(13)	3 901(10)	O(21)	2 372(10)	6 596(9)	3 920(8)
C(10)	2 006(14)	1 833(15)	4 884(12)	O(22)	2 506(10)	7 401(11)	2 257(8)
C(11)	3 696(11)	2 137(11)	5 113(9)	O(23)	802(14)	8 115(19)	3 268(11)
C(12)	3 993(13)	1 479(14)	6 130(10)	O(24)	2 113(23)	8 536(12)	3 798(11)
C(13)	4 359(10)	2 760(10)	4 626(8)	Cl(3)	2 096(3)	5 058(3)	7 353(3)
C(14)	5 266(11)	2 870(12)	5 014(9)	O(31)	1 103(6)	5 500(8)	8 006(7)
C(15)	5 753(13)	3 484(13)	4 433(11)	O(32)	2 216(9)	5 855(9)	6 693(9)
C(16)	5 391(14)	3 971(13)	3 497(11)	O(33)	2 978(11)	4 478(23)	7 916(14)
				O(34)	2 026(18)	4 203(13)	6 773(12)

* The perchlorate anions comprise the atoms: Cl(1), O(11)—O(14); Cl(2), O(21)—O(24); Cl(3), O(31)—O(34). Atom O(80) is the oxygen atom of the co-ordinated water ligand.

Table 5. Atomic positional parameters with estimated standard deviations for $Cu_2(HL^2)(H_2O)_2(ClO_4)_3$ (**2**)*

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	−0.009 61(12)	0.112 66(6)	0.513 72(11)	C(6)	−0.091 3(12)	0.249 8(6)	0.310 5(10)
Cu(2)	−0.182 20(9)	0.000 09(8)	0.010 94(9)	C(7)	−0.042 3(10)	0.202 0(6)	0.364 1(9)
Cl(1)	0.009 0(3)	0.245 3(1)	0.665 1(3)	C(8)	0.060 1(11)	0.179 2(5)	0.343 8(9)
Cl(2)	0.000 0(0)	0.000 0(0)	0.264 5(4)	C(9)	0.117 9(14)	0.198 6(7)	0.252 4(12)
Cl(4)	0.500 0(0)	0.000 0(0)	0.526 9(4)	C(10)	0.191 1(10)	0.113 8(6)	0.411 2(11)
O(1)	0.057 2(5)	0.044 8(3)	0.573 0(6)	C(11)	0.215 3(9)	0.086 3(5)	0.513 7(11)
O(2)	−0.069 3(5)	0.037 8(3)	−0.048 0(5)	C(12)	0.156 7(9)	0.028 2(5)	0.544 8(10)
O(3)	−0.298 8(7)	0.025 4(4)	−0.113 5(7)	C(13)	0.207 1(9)	−0.003 2(7)	0.633 7(9)
O(4)	0.049 7(7)	0.185 2(4)	0.640 8(7)	C(14)	0.155 1(9)	−0.061 3(5)	0.671 5(10)
O(5)	−0.091 9(7)	0.238 5(5)	0.693 8(10)	C(15)	−0.246 4(11)	−0.190 6(5)	−0.057 6(12)
O(6)	0.064 3(9)	0.271 1(5)	0.747 9(9)	C(16)	−0.232 2(8)	−0.125 2(5)	−0.019 8(10)
O(7)	0.017 1(12)	0.283 3(5)	0.578 1(8)	C(17)	−0.288 7(8)	−0.105 8(5)	0.071 0(10)
O(8)	−0.061 0(8)	−0.038 8(5)	0.201 9(7)	C(18)	−0.355 6(10)	−0.138 0(6)	0.133 9(11)
O(9)	−0.061 3(8)	0.038 2(4)	0.327 1(8)	C(19)	−0.398 8(10)	−0.108 7(6)	0.214 3(11)
O(14)	0.418 5(9)	−0.017 1(6)	0.472 7(9)	C(20)	−0.377 8(10)	−0.047 5(7)	0.239 4(11)
O(15)	0.475 1(16)	0.045 3(9)	0.590 6(13)	C(21)	−0.313 9(9)	−0.017 2(5)	0.174 6(9)
O(16)	0.380 6(10)	0.074 2(7)	−0.217 2(10)	C(22)	−0.279 4(9)	0.048 4(5)	0.182 6(9)
N(1)	−0.139 8(7)	0.106 0(4)	0.586 7(8)	C(23)	−0.312 7(12)	0.088 8(7)	0.271 1(11)
N(2)	−0.085 9(7)	0.172 0(4)	0.439 5(7)	C(24)	−0.173 4(10)	0.127 8(5)	0.109 5(10)
N(3)	0.091 5(8)	0.140 3(4)	0.410 6(8)	C(25)	−0.129 6(8)	0.139 9(5)	0.007 9(10)
N(4)	−0.171 5(7)	−0.085 6(4)	−0.055 2(7)	C(26)	−0.039 6(8)	0.101 2(4)	−0.018 8(9)
N(5)	−0.273 4(7)	−0.045 4(4)	0.092 9(7)	C(27)	0.014 8(9)	0.132 2(5)	−0.108 3(9)
N(6)	−0.218 8(7)	0.065 1(4)	0.113 0(7)	C(28)	0.108 3(9)	0.098 5(5)	−0.142 9(8)
C(1)	−0.306 8(11)	0.152 5(6)	0.603 4(13)	Cl(3)	0.436 7(3)	−0.166 1(2)	−0.055 9(3)
C(2)	−0.205 3(9)	0.143 7(6)	0.562 1(10)	O(10)	0.407 5(11)	−0.145 9(8)	0.042 1(6)
C(3)	−0.176 8(10)	0.185 2(5)	0.470 4(9)	O(11)	0.491 9(9)	−0.221 4(4)	−0.046 9(13)
C(4)	−0.230 5(11)	0.231 5(7)	0.423 7(12)	O(12)	0.495 0(9)	−0.119 9(5)	−0.102 6(12)
C(5)	−0.186 3(14)	0.264 0(7)	0.343 9(13)	O(13)	0.352 3(7)	−0.177 3(7)	−0.116 1(10)

* Atoms Cl(3), O(10), O(11), O(12), O(13) belong to the free, general position perchlorate anion; atoms Cl(4), O(14) and O(15) belong to the free perchlorate anion positioned on a C_2 axis; atom O(16) belongs to the free water molecule.

Table 6. Atomic positional parameters (× 10^4) with estimated standard deviations for $Cu_2(HL^3)(H_2O)(ClO_4)_3$ (**3**)*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	858(1)	1 002(5)	1 590(4)	C(3)	250(5)	1 140(13)	−932(10)
Cu(2)	1 524(1)	−1 043(5)	3 619(3)	C(4)	361(5)	35(13)	−609(10)
Cl(1)	2 009(4)	598(16)	6 379(10)	C(5)	533(5)	−5(13)	164(10)
O(3)	1 731(4)	497(16)	5 890(10)	N(4)	1 993(3)	−1 100(20)	3 732(14)
O(4)	2 276(4)	404(16)	5 887(10)	C(14)	2 157(3)	−2 205(20)	3 649(14)
O(5)	2 025(4)	1 724(16)	6 703(10)	C(15)	2 501(3)	−2 263(20)	3 752(14)
O(6)	2 002(4)	−239(16)	6 996(10)	C(16)	2 682(3)	−1 218(20)	3 938(14)
Cl(2)	1 437(6)	−4 913(22)	5 348(15)	C(17)	2 518(3)	−114(20)	4 021(14)
O(7)	1 224(6)	−4 099(22)	4 993(15)	C(18)	2 174(3)	−55(20)	3 918(14)
O(8)	1 636(6)	−5 315(22)	4 721(15)	N(2)	853(7)	−801(16)	1 298(16)
O(9)	1 616(6)	−4 334(22)	5 955(15)	N(3)	1 601(5)	−2 769(18)	3 316(18)
O(10)	1 272(6)	−5 841(22)	5 687(15)	N(5)	1 606(4)	720(12)	3 845(18)
Cl(5)	1 444(7)	−4 952(27)	5 301(18)	N(6)	768(7)	2 784(17)	1 523(15)
O(16)	1 418(7)	−3 756(27)	5 475(18)	C(6)	694(8)	−1 077(18)	593(17)
O(17)	1 707(7)	−5 133(27)	4 799(18)	C(7)	604(9)	−2 355(18)	303(22)
O(18)	1 483(7)	−5 577(27)	6 032(18)	C(8)	1 018(8)	−1 780(22)	1 823(11)
O(19)	1 163(7)	−5 324(27)	4 892(18)	C(9)	906(6)	−1 789(11)	2 750(13)
Cl(3)	0	1 477(10)	2 500	C(10)	982(7)	−3 068(11)	3 086(14)
Cl(4)	0	−3 824(9)	2 500	C(11)	1 333(6)	−3 612(30)	3 000(29)
O(1)	1 075(5)	−886(15)	3 230(15)	C(12)	2 031(11)	−4 384(19)	3 135(29)
O(2)	1 131(6)	1 014(19)	2 548(14)	C(13)	1 906(5)	−3 127(15)	3 356(27)
O(11)	263(5)	753(23)	2 336(17)	C(19)	1 919(4)	933(22)	3 975(24)
O(12)	66(6)	2 182(21)	3 182(13)	C(20)	2 050(10)	2 211(26)	4 119(29)
O(13)	206(6)	−3 124(26)	2 042(18)	C(21)	1 362(8)	1 744(26)	3 874(23)
O(14)	181(7)	−4 530(27)	3 030(18)	C(22)	1 236(10)	2 080(23)	2 976(22)
O(15)	1 342(8)	−1 352(32)	5 084(22)	C(23)	947(10)	2 991(38)	3 064(24)
N(1)	593(5)	1 059(13)	615(10)	C(24)	858(10)	3 643(30)	2 227(19)
C(1)	482(5)	2 163(13)	292(10)	C(25)	580(8)	3 150(10)	900(15)
C(2)	310(5)	2 204(13)	−482(10)	C(26)	447(12)	4 413(21)	707(33)

* Atoms Cl(1), O(3)—O(6) comprise the full-occupancy, perchlorate anion in a general position; atoms Cl(2), O(7)—O(10) comprise the 55% occupancy component of a disordered general perchlorate; atoms Cl(5), O(16)—O(19) comprise the 45% occupancy component of a disordered general perchlorate; atoms Cl(3), O(11), O(12) comprise a full occupancy perchlorate situated across the crystallographic C_2 axis; atoms Cl(4), O(13), O(14) comprise a second full-occupancy perchlorate situated across the crystallographic C_2 axis; and atom O(15) is the oxygen atom of the water ligand.

connected to the solution through a bridge of NBu_4BF_4 (10^{-1} mol dm^{-3}) in dmso. All potentials are referenced to the s.c.e electrode. In these conditions the oxidation potential of the ferrocene–ferrocenium couple, calculated as $E_{\frac{1}{2}} = \frac{1}{2}(E_{pc} + E_{pa})$, was 0.43 V *vs.* s.c.e.

Crystal Data.—$[Cu_2(HL^1)(CH_3CN)(H_2O)][ClO_4]_3$, $C_{26}H_{34}Cl_3Cu_2N_7O_{15}$, $M = 918.026$, crystallises from acetonitrile as blue needles, crystal dimensions 0.50 × 0.30 × 0.24 mm, triclinic, $a = 13.040(2)$, $b = 12.230(2)$, $c = 12.720(3)$ Å, $\alpha = 88.85(2)$, $\beta = 83.68(2)$, $\gamma = 62.17(1)°$, $U = 1\,782.0(6)$ Å^3 (by least-squares refinement of 25 accurately centred reflections with $2\theta > 20°$), $D_c = 1.711$ g cm^{-3}, $Z = 2$, space group $P\bar{1}$ (C_i, no. 2), graphite-monochromated Mo-K_α radiation, ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 14.99 cm^{-1}, and $F(000) = 935.81$.

Three-dimensional *X*-ray diffraction data were collected at -140 °C on a Nicolet *R3m* four-circle diffractometer by the ω-scan method (ω range = 1.6°) with variable scan rate (2.9 – 29.3° min^{-1}). 6 273 Unique reflections were collected in the range $4.0 < 2\theta < 50°$, and 3 504 having $I > 10\sigma(I)$ were used in the subsequent calculations. Crystal stability was monitored by recording three check reflections every 100 reflections: no significant variations were observed. The data were corrected for Lorentz-polarisation effects and an empirical absorption correction was applied, based on ψ-scan data.

The two copper atoms were located from a Patterson map; the remaining non-hydrogen atoms were located using difference Fourier calculations. Hydrogen atoms were included at calculated positions, using a riding model with thermal parameters equal to 1.2 times U_{eq} of their carrier atoms. All the non-hydrogen atoms were refined anisotropically and the refinement converged with $R = 0.0765$ and $R' = 0.0803$. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o)]^{-1}$. Geometric constraints were applied to the perchlorate anion based on Cl(3) (T_d symmetry, mean Cl–O 1.329 Å) which showed minor disorder, as did the macrocycle around C(20)—C(22): no attempts were made to model the disorder. A final difference map showed no significant features. Table 4 gives atomic positional parameters with estimated standard deviations. All programs used in data reduction and structure solution are contained in the SHELXTL (version 4.1) package.[24]

$Cu_2(HL^2)(H_2O)_2(ClO_4)_3$, $C_{28}H_{41}Cl_3Cu_2N_6O_{16}$, $M = 951.12$, crystallises from methanol as dark blue polyhedra, crystal dimensions 0.36 × 0.30 × 0.44 mm, orthorhombic, $a = 13.455(11)$, $b = 21.360(15)$, $c = 12.991(9)$ Å, $U = 3\,733(4)$ Å^3, $D_m = 1.67$, $D_c = 1.693$ g cm^{-3}, $Z = 4$, space group $P2_12_12$ (D_2^3, no. 18), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 14.34 cm^{-1}, and $F(000) = 1\,952$.

Three-dimensional *X*-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet *R3m* diffractometer by the ω-scan method. 2 167 Independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were detected and placed in calculated positions [C–H 0.95, O–H 1.00 Å, C–C–H(methyl) = 110°]; their contributions were included in structure factor calculations ($B = 10.0$ Å^2) but no refinement of positional parameters was permitted. The perchlorate anion centred on atom Cl(3) was refined with constrained geometry (T_d symmetry, Cl–O 1.40 Å). Refinement converged at R 0.0477 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of copper and chlorine, which very clearly indicated the absolute configuration of the chosen crystal. Table 5 lists the atomic positional parameters with estimated standard deviations.

$Cu_2(HL^3)(H_2O)(ClO_4)_3$, $C_{26}H_{35}Cl_3Cu_2N_6O_{15}$, $M = 905.03$, crystallises from methanol as dark blue elongated needles, crystal dimensions 0.208 × 0.07 × 0.576 mm, monoclinic, $a = 40.12(7)$, $b = 11.02(4)$, $c = 15.765(16)$ Å, $\beta = 91.07(12)°$, $U = 6\,970(30)$ Å^3, $D_m = 1.78$, $D_c = 1.725$ g cm^{-3}, $Z = 8$, space group $C2/c$ (C_{2h}^6, no. 15), Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 15.52 cm^{-1}, and $F(000) = 3\,696$.

The data were collected ($6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer) and processed [1 830 independent reflections with $I/\sigma(I) > 2.0$] as above. The structure was solved by image-seeking Patterson techniques. Hydrogen atoms were not detected or positioned. In view of the limited quality of the data, it was found necessary, during the refinement, to impose extensive restrictions on the molecular geometry such that chemically equivalent bond lengths were constrained to be approximately equal (within 0.02 Å), without the imposition of specific values. The geometries of the pyridyl fragments and of the general perchlorate anions were totally constrained (D_{6h} and T_d symmetries respectively). Refinement converged at $R = 0.165$ with allowance for anisotropic thermal motion of only copper and full occupancy chlorine atoms, and for the anomalous scattering of copper and all chlorine atoms. One perchlorate anion was clearly disordered and the populations of the two components were refined (0.55, 0.45) with coupled thermal vibrational parameters. Attempts to refine the structure in space group *Cc* did not lead to any improvement in the degree of convergence and the high value of *R* is attributed to the poor quality of the data set from a weak crystal (the best of many tried) and the further disorder of the remaining perchlorate anions. Table 6 lists atomic positions and estimated standard deviations.

For the structure of the complex of macrocycle HL^3, computer programs were part of the SHELXTL (version 4.1) package[24] from which the scattering factors were taken. For the structure of the complex of macrocycle HL^2, computer programs formed part of the Sheffield *X*-Ray System and scattering factors were taken from ref. 25. Unit weights were used throughout both these refinements.

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