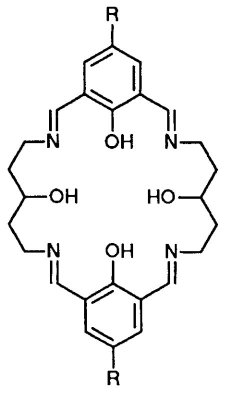
Synthesis and Characterisation of a Series of Tetra- and Octa-copper(II) Complexes with Macrocyclic Ligands†

Vickie McKee* and Santokh S. Tandon
Chemistry Department, University of Canterbury, Christchurch 1, New Zealand

A series of seven tetracopper(II) and three octacopper(II) complexes has been synthesised using the tetranucleating macrocyclic ligands H_4L^1 and H_4L^2 {13,26-dimethyl- and 13,26-di-*tert*-butyl-3,9,17,23-tetraazatetracyclo[23.3.1.1^{11,15}]triaconta-1(29),2,9,11,13,15(30),16,23,25,27-decaene-6,20,29,30-tetraol}. Four representative complexes have been structurally characterised by single-crystal X-ray diffraction studies: $[Cu_4(\mu_4\text{-}OH)L^2][NO_3]_3\cdot2H_2O$, **3**·$2H_2O$, monoclinic, $a = 10.384(2)$, $b = 18.515(5)$, $c = 11.264(2)$ Å, $\beta = 107.48(2)°$; $[\{Cu_4(\mu_5\text{-}O)L^1(ClO_4)\}_2][ClO_4]_2\cdot2H_2O$, **7**·$2H_2O$, triclinic, $a = 11.497(4)$, $b = 12.714(3)$, $c = 13.546(4)$ Å, $\alpha = 102.92(2)$, $\beta = 113.15(2)$, $\gamma = 100.36(3)°$; $[\{Cu_4(\mu_5\text{-}O)L^2(ClO_4)\}_2][ClO_4]_2\cdot CH_3OH$, **9**·$CH_3OH$, monoclinic, $a = 15.778(5)$, $b = 17.384(8)$, $c = 15.392(5)$ Å, $\beta = 109.54(3)°$; $[Cu_4(\mu\text{-}N_3)_2L^2(N_3)_2]\cdot2CH_3OH$, **10**·$2CH_3OH$, monoclinic, $a = 8.559(3)$, $b = 18.719(6)$, $c = 13.485(7)$ Å, $\beta = 97.29(4)°$. The tetranuclear complexes contain planar $Cu_4(\mu_4\text{-}OH)$ cores but the hydroxo donor can be replaced by two azido ligands to form **10**, in which the four copper(II) atoms are no longer coplanar. In non-protic solvents, or with added base, the tetracopper(II) complexes dimerise with loss of the hydroxo proton to form octacopper(II) complexes which contain two $Cu_4(\mu_5\text{-}O)$ units.

Since the first report by Pilkington and Robson[1] of a binucleating Schiff-base macrocycle derived from 2,6-diformyl-4-methylphenol, many examples of similar binuclear systems have been reported, both macrocyclic[2] and non-macrocyclic.[3] The binucleating ability of these ligands stems from the readiness of the phenol to deprotonate and bridge two metal ions. Recently we have investigated the co-ordination chemistry of a macrocyclic ligand derived from the condensation of 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane, which forms binuclear complexes with transition-metal ions in which the alcoholic groups may deprotonate and bridge the two metals.[4] We now report the synthesis and characterisation of tetra- and octa-nuclear copper(II) complexes of the (2 + 2) macrocyclic ligands H_4L^1 and H_4L^2, which incorporate the bridging abilities of both phenol and alcohol groups.

The macrocycles can be regarded as being constructed of two distinct sections; the rigid phenoldiimine, and the saturated side chains which carry the alcohol groups and impart some flexibility to the system. The latter feature permits some response to the co-ordination preferences of the metal ions. The length of the saturated chain is critical in determining the nuclearity of the final product. To date, only binuclear complexes have been characterised if 1,3-diamino-2-hydroxypropane is used,[5,6] however when 1,5-diamino-3-hydroxypentane (dahp) is used, tetranuclear products can readily be obtained. The ligand provides three donors for each metal ion in a tetranuclear complex and the co-ordination sphere is completed by exogenous ligands. In most cases a central oxygen donor, binding to all four metal ions, is incorporated. Preliminary reports of the structures of a tetracopper(II)[7] and a mixed-valence tetramanganese[8] complex have been published, as has a report of the dimerisation of a tetracopper(II) complex to an octacopper equivalent.[9] A somewhat similar tetranucleating ligand, which incorporates four phenolic groups, has been reported by Robson and co-workers.[10] This tetraphenolic ligand is rather less flexible than H_4L^1 or H_4L^2 and, in the tetranickel(II) and tetrazinc(II) complexes, the macrocycle adopts a domed configuration. Recently, the equivalent (3 + 3) hexaphenolic macrocycle has been shown to bind six copper atoms.[11] In contrast, H_4L^1 and H_4L^2 form planar tetrametallic complexes with copper and nickel[6,7,9] but are sufficiently flexible that they can adopt twisted or folded conformations with other metals, for example in the mixed-valence $Mn^{II}_2Mn^{III}_2$ complex the metal atoms adopt a distorted-tetrahedral arrangement about a central oxo ligand.[8] In this paper we report the synthesis and characterisation of ten tetracopper(II) or octacopper(II) complexes of the macrocyclic ligands H_4L^1 and H_4L^2 and single-crystal X-ray structure determinations of four representative examples.



H_4L^1 R = CH_3
H_4L^2 R = $C(CH_3)_3$

Results and Discussion

Synthesis.—The complexes synthesised are listed in Table 1. The tetranuclear complexes **1**–**6** were all prepared by refluxing the appropriate copper(II) salt with either 2,6-diformyl-4-methylphenol (dfmp) or 4-*tert*-butyl-2,6-diformylphenol (tdfp) and 1,5-diamino-3-hydroxypentane (dahp) in methanol solution. Compound **10**, the only complex which does not contain an oxo or hydroxo donor, was made by treatment of **3** with

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc. Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Physical properties of the complexes

Complex		Magnetic moment (μ_B per Cu^{2+}) 298	93 K	Electronic spectra in dmf, λ/nm (ε/dm^3 mol^{-1} cm^{-1})	Reflectance spectrum/nm
1	$[Cu_4(\mu_4\text{-}OH)L^1][NO_3]_3\cdot 2H_2O$	1.28	0.61	673 (305), 369 (12 350), 336 (10 250), 269 (51 850)	665
2	$[Cu_4(\mu_4\text{-}OH)L^1][ClO_4]_3$	1.20	0.48	647 (245), 375 (11 175), 327 (10 650), 268 (47 175)	648
3	$[Cu_4(\mu_4\text{-}OH)L^2][NO_3]_3\cdot H_2O$	1.32	0.74	672 (269), 360 (12 325), 320 (13 200), 268 (53 125)	670
4	$[Cu_4(\mu_4\text{-}OH)L^2][ClO_4]_3\cdot 2H_2O$	1.18	0.40	641 (273), 360 (11 750), 328 (11 925), 268 (51 950)	645
5	$[Cu_4(\mu_4\text{-}OH)L^1(CH_3CO_2)_3]\cdot 3H_2O$	1.57	1.16	674 (280), 376 (11 425), 344 (11 100), 269 (40 550)	675
6	$[Cu_4(\mu_4\text{-}OH)L^2(CH_3CO_2)_3]\cdot 2H_2O$	1.36	1.02	673 (279), 367 (12 250), 269 (30 825)	685
7.3 dmf	$[\{Cu_4(\mu_5\text{-}O)L^1(ClO_4)\}_2][ClO_4]_2\cdot 3dmf$	0.92	0.31	622 (548), 405 (sh), 378 (24 600) 336 (sh), 327 (23 450), 271 (83 400).	621
8	$[\{Cu_4(\mu_5\text{-}O)L^2(NO_3)\}_2][NO_3]_2\cdot 2H_2O$	0.83	0.25	627 (646), 430 (2525), 355 (25 825), 327 (29 450), 269 (76 675)	628
9	$[\{Cu_4(\mu_5\text{-}O)L^2(ClO_4)\}_2][ClO_4]_2$	0.76	0.14	624 (591), 410 (sh), 360 (23 325), 328 (25 025), 271 (77 625)	630
10$\cdot 2CH_3OH$	$[Cu_4(\mu\text{-}N_3)_2L^2(N_3)_2]\cdot 2CH_3OH$	1.61	0.81	Insoluble in dmf	685

NaN_3. The good yields obtained and the general absence of binuclear or polymeric side products is probably a consequence of the strong binucleating ability of the diformylphenol component. Formation of an initial binuclear diformylphenol complex would maintain the carbonyl groups in the correct orientation for macrocyclic formation and ensure that when the (2 + 2) macrocycle formed, it would contain four copper(II) ions. If these can be accommodated within the ring a tetranuclear complex is isolated; if, as is the case when 1,3-diamino-2-hydroxypropane is used in place of dahp, the macrocycle is too small to bind all four copper ions, a rearrangement to give the binuclear complex occurs.

The octacopper complexes **7**–**9** were prepared either by slow recrystallisation of the corresponding tetracopper complex from dimethylformamide (dmf)–methanol solutions or by treating the tetracopper compound with a base (such as 2,6-diaminopyridine) in dry methanol. These reactions are discussed below. The stoichiometries of the complexes were initially assigned on the basis of analytical data and were confirmed by spectroscopic studies and single-crystal X-ray structure determinations for complexes **3**, **7**, **9** and **10**.

Infrared Spectra.—The infrared spectra[12] of all of the complexes are broadly similar, except for those vibrations associated with the anions. The macrocyclic nature of the complexes was confirmed by the absence of the amine and carbonyl vibrations associated with the reactants and the presence of an imine stretch at 1625–1645 cm^{-1}. A band at 1550–1580 cm^{-1} is assigned to the C–O vibration of the phenol.[13] An envelope in the region 3400–3450 cm^{-1} was observed in the spectra of all the compounds (recorded as KBr discs) but no sharp O–H stretches could be distinguished. For the nitrate complexes **1** and **3** the $\nu_3(NO_3)$ vibrations appear as strong bands at 1375 cm^{-1}, suggesting that they are ionic (or weakly co-ordinated). The $\nu_3(ClO_4)$ vibrations in **2** and **4** appear at 1055 and 1080 cm^{-1} respectively, and are consistent with ionic perchlorate. In contrast, the same vibrations of the octacopper complexes **7** and **9** are split, suggesting perchlorate co-ordination. X-Ray crystallography (see below) revealed the presence of both ionic and co-ordinated perchlorate ions in these complexes. The third octanuclear complex **8** shows nitrate vibrations indicative of both co-ordinated (1330 and 1450 cm^{-1}) and free (1375 cm^{-1}) nitrate ions, suggesting a structure similar to those of **7** and **9**. The acetato complexes **5** and **6** show bands due to the asymmetric and symmetric stretches of co-ordinated carboxylate groups at 1540–1545 and 1395–1410 cm^{-1} respectively. The azido complex **10** exhibits two strong vibrations at 2070 and 2020 cm^{-1} which are assigned to bridging and terminal azide respectively. This assignment is supported by the crystallographic results (see below).

Table 2 Selected interatomic distances (Å) and angles (°) for $[Cu_4(\mu_4\text{-}OH)L^2][NO_3]_3\cdot 2H_2O$, (**3**$\cdot 2H_2O$)

Cu(1) ··· Cu(2)	3.000(1)	Cu(1)–Ox	2.082(1)
Cu(1)–O(1)	1.915(4)	Cu(1)–N(1)	1.940(6)
Cu(1)–O(2)	1.883(4)	Cu(1) ··· Cu(2′)	2.953(1)
Cu(2)–Ox	2.127(1)	Cu(2)–O(1)	1.916(5)
Cu(2)–N(2)	1.937(5)	Cu(2)–Ow(1)	2.249(5)
		Cu(2)–O(2′)	1.864(5)
Ox–Cu(1)–O(1)	83.5(1)	O(1)–Cu(1)–N(1)	94.5(2)
Ox–Cu(1)–N(1)	175.4(1)	Ox–Cu(1)–O(2)	83.8(2)
O(1)–Cu(1)–O(2)	167.1(2)	N(1)–Cu(1)–O(2)	98.4(2)
O(1)–Cu(2)–N(2)	94.4(2)	Ox–Cu(2)–O(1)	82.2(1)
Ox–Cu(2)–Ow(1)	89.9(1)	Ox–Cu(2)–N(2)	167.3(2)
N(2)–Cu(2)–Ow(1)	102.6(2)	Ox–Cu(2)–O(2′)	83.0(1)
O(1)–Cu(2)–O(2′)	163.6(2)	N(2)–Cu(2)–O(2′)	98.5(2)
Ow(1)–Cu(2)–O(2′)	93.5(2)	O(1)–Cu(2)–Ow(1)	93.5(2)
Cu(1)–Ox–Cu(2)	90.9(1)	Cu(1)–Ox–Cu(1′)	180.0
Cu(2)–Ox–Cu(1′)	89.1(1)	Cu(1)–Ox–Cu(2′)	89.1(1)
Cu(2)–Ox–Cu(2′)	180.0	Cu(1′)–Ox–Cu(2′)	90.9(1)
Cu(1)–O(1)–Cu(2)	103.1(2)		

Description of the Structures.—Single-crystal X-ray structural analyses have been carried out for the four representative complexes **3**, **7**, **9** and **10**.

The structure of **3**$\cdot 2H_2O$ had been communicated previously.[7] A perspective view of the cation $[Cu_4(\mu_4\text{-}OH)L^2]^{3+}$ is shown in Fig. 1, selected bond lengths and angles are given in Table 2, and atomic coordinates in Table 6. The cation is centrosymmetric, with the central oxygen atom Ox on a centre of symmetry. Within the macrocyclic ring, only the saturated carbon atoms show significant deviation from planarity and these are disordered, with 50% occupancy of equivalent sites on either side of the macrocyclic plane. This planar geometry is in marked contrast to the domed tetranickel(II) and tetrazinc(II) complexes reported by Robson and co-workers[10] for the tetraphenolic macrocycle and to the saddle-shaped conformation of the hexaphenolic system.[11]

Four copper(II) ions are bound within the L^2 macrocycle, each co-ordinated to one imine nitrogen, one phenoxide oxygen, one alkoxide oxygen, the central hydroxide ion (Ox), and to one axial donor (water or nitrate). The macrocyclic oxygen donors are all deprotonated and each bridges two copper atoms, so that the square plane about each copper shares two edges with the equivalent planes of the two neighbouring copper atoms. The Cu ··· Cu distances [3.000(1) and 2.953(1) Å for Cu(1) ··· Cu(2) and Cu(1) ··· Cu(2′) respectively] are quite short but are non-bonding.[14] Bond distances between the copper atoms and the macrocyclic donors are unremarkable; however the significantly longer Cu–Ox distances [2.082(1) and 2.127(1) Å], coupled with the

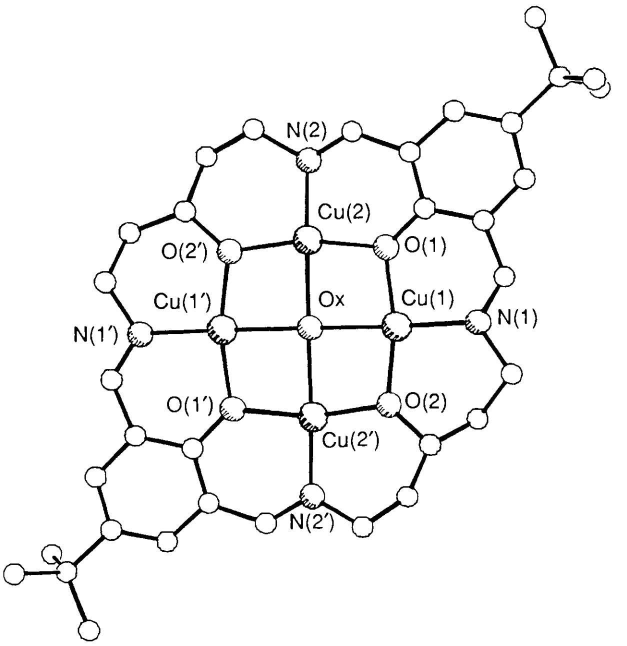


Fig. 1 Structure of the cation of complex **3**, $[Cu_4(\mu_4\text{-}OH)L^2]^{3+}$. The axial ligands have been omitted and the disordered atoms C(12), C(13) and C(15) are shown in one of the two possible configurations.

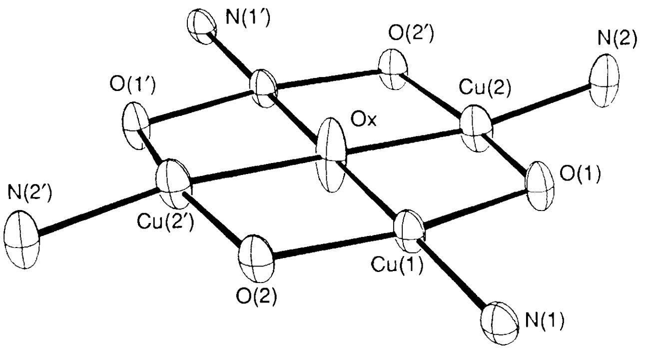


Fig. 2 The core of complex **3** showing 30% probability thermal ellipsoids

compressed O–Cu–Ox angles (82.2–83.8°), suggest that this bond is weaker than the other three. This may be partly a consequence of the unusual co-ordination about Ox, and also of the slight mismatch in size between the central cavity and the ideal Cu–Ox bond length. An extention of the latter effect is illustrated by a tetracopper(I) complex[15] in which the Cu ⋯ Cu distances are slightly longer and a central hydroxide, unable to bond to all four metal atoms simultaneously, is disordered between two sites adjacent to the centre of the cavity.

The slight geometrical diffences between Cu(1) and Cu(2) are accounted for by the differences in their axial co-ordination. Atom Cu(2) is bonded to a water molecule [Cu–Ow(1) 2.249(5) Å], while Cu(1) exhibits a longer interaction with either a 50% occupancy water or nitrate donor [Cu(1)–Ow(2) 2.48(1) Å or Cu(1)–O(22) 2.82(2) Å]. Individual macrocyclic units are linked by hydrogen bonds involving the nitrate anions and the co-ordinated water molecule Ow(1) [O(21) ⋯ Ow(1) 2.72(2) Å at $1 + x, y, z$ and O(12) ⋯ Ow(1) 2.86(2) Å at $-x, 1 - y, 1 - z$].

The central donor Ox is required by stoichiometry to have one negative charge and is therefore designated OH^-. Hence, Ox is five-co-ordinate and square pyramidal, with the hydrogen atom disordered above and below the plane of the macrocycle, as required by the centrosymmetric symmetry. Two pieces of evidence support this conclusion; the acid–base chemistry discussed below, and an examination of the thermal ellipsoids of the central part of the structure (Fig. 2). If Ox has square-pyramidal geometry it would be expected to be slightly displaced from the plane of the four copper atoms towards the proton. The centrosymmetric symmetry of the complex then requires that Ox be disordered between two positions slightly above and below the ring. This is reflected in the elongation of the Ox thermal ellipsoid in this direction relative to the other atoms of the core.

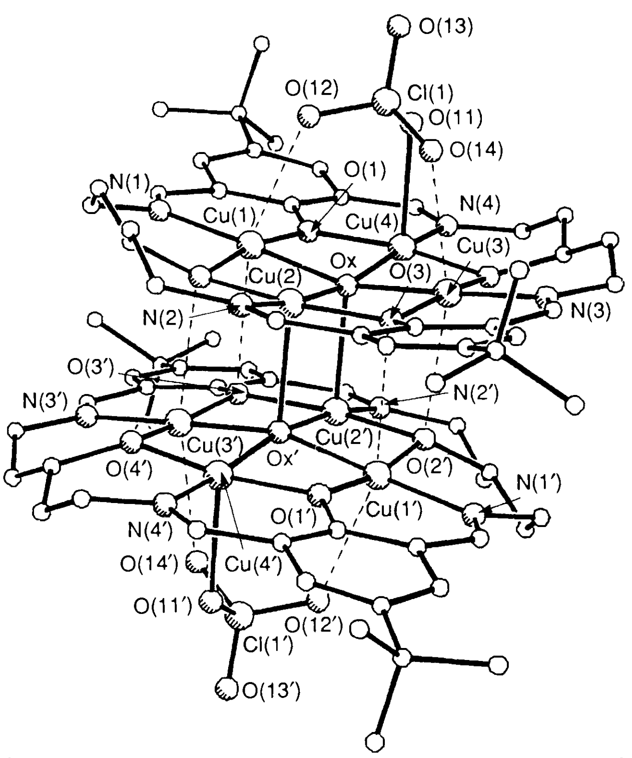


Fig. 3 Structure of the cation of complex **9**, $[\{Cu_4(\mu_5\text{-}O)L^2(ClO_4)\}_2]^{2+}$. Dotted lines represent long interactions.

Structural analyses of the acetato complexes **5** and **6** have not yet been obtained. Stochiometry requires that a hydroxide donor is present in each case and the infrared spectra suggest that the acetate groups are co-ordinated. We conclude, therefore, that the structures of **5** and **6** are similar to that of **3** but having acetate groups bonded axially to the metal ions. This proposed structure is similar to that determined[6] for $[Ni(\mu_4\text{-}OH)L^1(CH_3CO_2)_3]$, in which the acetate groups bridge adjacent metal ions.

The structures of complexes **7** and **9** are rather similar and that of **7** has been communicated previously. The cation of **9** is shown in Fig. 3, selected interatomic distances and angles for the complexes are listed in Tables 3 and 4, and the atomic coordinates are given in Table 6. Both structures are centrosymmetric dimers and, within each macrocycle, the arrangement is similar to that observed for **3**. In the dimers, however, the central oxygen donor is a five-co-ordinate oxo anion which is displaced from the mean plane of the four copper atoms by 0.29 and 0.27 Å for **7** and **9** respectively. The co-ordination sphere of Ox is completed by Cu(2′), a copper atom from the second macrocyclic unit of the dimer. This bond, and the symmetry-related Cu(2)–Ox′ linkage [2.372(7) and 2.38(1) Å for **7** and **9** respectively], hold the dimer together, along with weaker interactions involving Cu(1) and Cu(3) [for **7**, Cu(1)–O(3′) 2.84(1) and Cu(3)–O(2′) 2.72(1) Å; for **9**, Cu(1)–O(3′) 2.80(1) and Cu(3)–O(2′) 2.73(1) Å]. It is interesting that the *tert*-butyl groups of L^2 do not appear to present any steric barrier to the dimerisation.

The outer faces of the dimers are blocked by perchlorate ions which are bound, in tripod fashion, to the Cu_4 array. The geometry of perchlorate bonding is different in the two dimeric complexes, as illustrated in Fig. 4. These two configurations arise from the geometric mismatch between the square-planar

Table 3 Selected interatomic distances (Å) and angles (°) for $[\{Cu_4(\mu_5\text{-}O)L^1(ClO_4)\}_2][ClO_4]_2\cdot 2H_2O$, **7**·$2H_2O$

Cu(1) ··· Cu(2)	2.852(2)	Cu(1) ··· Cu(4)	2.876(1)
Cu(1)–Ox	2.032(6)	Cu(1)–O(1)	1.914(5)
Cu(1)–N(1)	1.969(8)	Cu(1)–O(2)	1.900(6)
Cu(2) ··· Cu(3)	2.918(1)	Cu(2)–Ox	2.066(5)
Cu(2)–O(2)	1.922(6)	Cu(2)–N(2)	1.974(7)
Cu(2)–O(3)	1.940(6)	Cu(2) ··· Cu(2′)	3.241(2)
Cu(2)–Ox′	2.372(7)	Cu(3) ··· Cu(4)	2.844(2)
Cu(3)–Ox	2.053(6)	Cu(3)–O(3)	1.914(6)
Cu(3)–N(3)	1.968(8)	Cu(3)–O(4)	1.887(6)
Cu(3)–O(12)	2.624(8)	Cu(4)–Ox	2.054(6)
Cu(4)–O(1)	1.894(6)	Cu(4)–O(4)	1.876(7)
Cu(4)–N(4)	1.976(8)	Cu(4)–O(11)	2.519(8)
Ox–Cu(2′)	2.372(7)		
Ox–Cu(1)–O(1)	85.2(2)	Ox–Cu(1)–N(1)	174.9(2)
O(1)–Cu(1)–N(1)	91.1(3)	Ox–Cu(1)–O(2)	87.7(2)
O(1)–Cu(1)–O(2)	171.1(3)	N(1)–Cu(1)–O(2)	95.6(3)
Ox–Cu(2)–O(2)	86.2(2)	Ox–Cu(2)–N(2)	171.0(3)
O(2)–Cu(2)–N(2)	96.5(3)	Ox–Cu(2)–O(3)	85.0(2)
O(2)–Cu(2)–O(3)	169.8(3)	N(2)–Cu(2)–O(3)	91.6(3)
Ox–Cu(2)–Ox′	86.4(3)	O(2)–Cu(2)–Ox′	90.6(3)
N(2)–Cu(2)–Ox′	102.1(3)	O(3)–Cu(2)–Ox′	93.8(2)
Ox–Cu(3)–N(3)	177.9(3)	Ox–Cu(3)–O(3)	86.0(2)
Ox–Cu(3)–O(4)	85.5(2)	O(3)–Cu(3)–N(3)	91.9(3)
N(3)–Cu(3)–O(4)	96.5(3)	O(3)–Cu(3)–O(4)	171.0(3)
O(3)–Cu(3)–O(12)	90.1(3)	Ox–Cu(3)–O(12)	86.7(2)
O(4)–Cu(3)–O(12)	92.5(3)	N(3)–Cu(3)–O(12)	93.4(3)
Ox–Cu(4)–O(4)	85.8(3)	Ox–Cu(4)–O(1)	85.1(3)
Ox–Cu(4)–N(4)	172.5(3)	O(1)–Cu(4)–O(4)	170.0(3)
O(4)–Cu(4)–N(4)	96.2(3)	O(1)–Cu(4)–N(4)	92.3(3)
O(1)–Cu(4)–O(11)	87.7(3)	Ox–Cu(4)–O(11)	91.4(2)
N(4)–Cu(4)–O(11)	95.5(3)	O(4)–Cu(4)–O(11)	96.8(3)
Cu(1)–Ox–Cu(3)	161.6(4)	Cu(1)–Ox–Cu(2)	88.2(2)
Cu(1)–Ox–Cu(4)	89.5(3)	Cu(2)–Ox–Cu(3)	90.2(2)
Cu(3)–Ox–Cu(4)	87.7(2)	Cu(2)–Ox–Cu(4)	166.2(4)
Cu(2)–Ox–Cu(2′)	93.6(3)	Cu(1)–Ox–Cu(2′)	99.5(3)
Cu(4)–Ox–Cu(2′)	100.2(2)	Cu(3)–Ox–Cu(2′)	98.9(3)

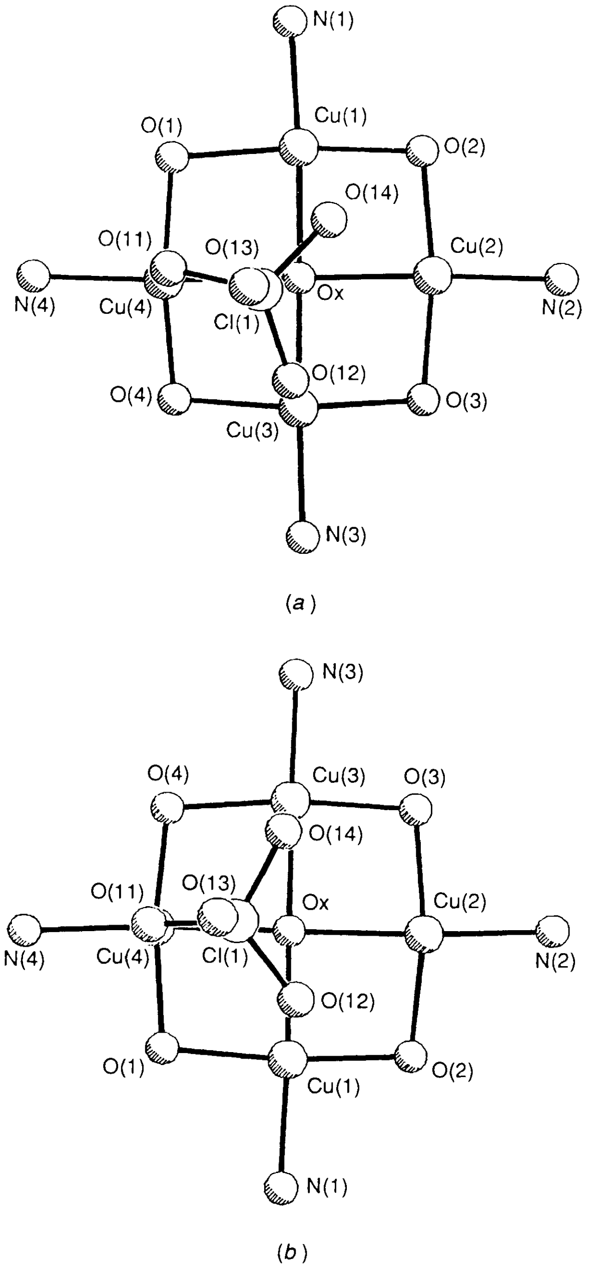


Fig. 4 View perpendicular to the mean plane of the copper atoms in one half of the dimers **7** (*a*) and **9** (*b*) showing the different orientations of the co-ordinated perchlorate ion

Cu_4 array and the tetrahedral perchlorate ion and represent two ways of maximising the bonding interaction. In **7** the anion has bonds to two of the copper atoms which are within the range observed[14,16] for Cu–O axial bonds [Cu(4)–O(11) 2.52(1), Cu(3)–O(12) 2.62(1) Å] and the third oxygen atom has rather longer interactions with the remaining copper atoms [Cu(1)–O(14) 2.87(1), Cu(2)–O(14) 3.22(2) Å]. In **9** the perchlorate interacts relatively strongly with three copper centres [Cu(4)–O(11) 2.41(1), Cu(3)–O(14) 2.59(1), Cu(1)–O(12) 2.89(2) Å] and only weakly with the fourth [Cu(2)–O(12) 3.55(2), Cu(2)–O(14) 3.69(2) Å]. It is significant that, in both complexes, the shortest Cu–$OClO_3$ bond involves Cu(4) which has no axial interaction on the opposite side of the macrocycle, while the longest Cu–$OClO_3$ distance is that to Cu(2) which has a strong axial bond to Ox′. These observations support the conclusion that distinct bonds between perchlorate and copper ions are present, rather than more generalised electrostatic or crystal-packing effects. To our knowledge, these complexes are the first crystallographically characterised examples of perchlorate as a tripod ligand; however, similar bonding has been described for a number of anhydrous metal perchlorate salts characterised by extended X-ray absorption fine structure (EXAFS) and spectroscopic techniques.[17] There are no significant interactions involving the second perchlorate anion or the solvate molecules in either structure.

The structure of the centrosymmetric azido complex **10** is shown in Fig. 5, selected interatomic distances and angles are given in Table 5 and the atomic coordinates are listed in Table 6. Complex **10** differs from the other compounds discussed in that it does not contain a central oxygen donor; the μ_4-hydroxo ligand of complex **3** has been replaced by two μ-azido ligands which lie on either side of the macrocyclic plane. The two independent copper atoms have very different co-ordination environments. Atom Cu(1) is four-co-ordinate, bonded to alkoxy, phenoxy, imine and μ-azido donors with somewhat irregular geometry (angles ranging from 78 to 98°, sum 365.8°). Atom Cu(2) is five-co-ordinate, having an additional terminal azido ligand. The geometry about Cu(2) is approximately square pyramidal but the axial donor is the phenoxy oxygen atom O(1) rather than the terminal azide. It is displaced by 0.2 Å from the mean plane of O(2′), N(2′), N(21) and N(11′). There is a marked difference between the singly and doubly bridged copper–copper distances [Cu(1) ··· Cu(2) 3.460(1), Cu(1) ··· Cu(2′) 3.045(1) Å] and also in the diagonal distances [Cu(1) ··· Cu(1′) 4.10(1), Cu(2) ··· Cu(2′) 5.05(1) Å]. There are no significant interactions involving the solvate methanol molecules and the macrocyclic ligand itself is close to planar. The structure of complex **10** demonstrates that the central oxygen donor is not required to maintain the tetracopper(II) structure and that the μ_4-OH can be replaced, opening up the possibility of activation of the central moiety.

Table 4 Selected interatomic distances (Å) and angles (°) for $[\{Cu_4(\mu_5\text{-}O)L^2(ClO_4)\}_2][ClO_4]_2\cdot CH_3OH$, **9**·$CH_3OH$

Cu(1)–Cu(2)	2.872(4)	Cu(1)–Cu(4)	2.882(3)
Cu(1)–Ox	2.032(11)	Cu(1)–O(1)	1.906(12)
Cu(1)–N(1)	1.972(15)	Cu(1)–O(2)	1.893(12)
Cu(2)–Cu(3)	2.911(3)	Cu(2)–Ox	2.079(11)
Cu(2)–O(2)	1.927(11)	Cu(2)–N(2)	1.962(18)
Cu(2)–O(3)	1.942(11)	Cu(2)–Cu(2′)	3.242(5)
Cu(2)–Ox′	2.381(12)	Cu(3)–Cu(4)	2.834(4)
Cu(3)–Ox	2.049(11)	Cu(3)–O(3)	1.921(12)
Cu(3)–N(3)	1.956(15)	Cu(3)–O(4)	1.869(13)
Cu(3)–O(14)	2.598(19)	Cu(4)–Ox	2.041(11)
Cu(4)–O(1)	1.915(11)	Cu(4)–O(4)	1.859(13)
Cu(4)–N(4)	1.983(15)	Cu(4)–O(11)	2.415(15)
Ox–Cu(2′)	2.381(12)		
Ox–Cu(1)–N(1)	176.3(6)	Ox–Cu(1)–O(1)	85.1(5)
Ox–Cu(1)–O(2)	87.4(5)	O(1)–Cu(1)–N(1)	92.5(6)
N(1)–Cu(1)–O(2)	94.6(6)	O(1)–Cu(1)–O(2)	169.3(5)
Ox–Cu(2)–O(2)	85.2(5)	Ox–Cu(2)–N(2)	170.7(6)
O(2)–Cu(2)–N(2)	97.3(6)	O(2)–Cu(2)–Ox′	91.4(4)
O(2)–Cu(2)–O(3)	169.7(5)	O(3)–Cu(2)–Ox′	91.7(5)
Ox–Cu(2)–Cu(2′)	47.2(3)	Ox–Cu(2)–O(3)	85.2(5)
N(2)–Cu(2)–Cu(2′)	141.6(6)	N(2)–Cu(2)–O(3)	91.6(6)
Ox–Cu(2)–Ox′	87.0(4)	Ox–Cu(3)–O(3)	86.6(5)
N(2)–Cu(2)–Ox′	101.9(6)	O(3)–Cu(3)–O(4)	169.7(6)
Ox–Cu(3)–N(3)	177.5(6)	O(3)–Cu(3)–N(3)	91.6(6)
Ox–Cu(3)–O(4)	85.1(5)	Ox–Cu(3)–O(14)	85.2(6)
N(3)–Cu(3)–O(4)	96.9(6)	N(3)–Cu(3)–O(14)	93.2(7)
Cu(4)–Cu(3)–O(14)	81.2(6)	Ox–Cu(4)–O(4)	85.6(5)
O(3)–Cu(3)–O(14)	91.7(6)	Ox–Cu(4)–N(4)	170.1(6)
O(4)–Cu(3)–O(14)	93.6(7)	O(4)–Cu(4)–N(4)	97.9(6)
Ox–Cu(4)–O(1)	84.6(5)	O(1)–Cu(4)–N(4)	91.0(6)
O(1)–Cu(4)–O(4)	169.1(6)	O(1)–Cu(4)–O(11)	92.6(6)
Ox–Cu(4)–O(11)	93.7(5)	N(4)–Cu(4)–O(11)	95.4(7)
O(4)–Cu(4)–O(11)	92.6(6)	Cu(1)–Ox–Cu(3)	161.8(7)
Cu(1)–Ox–Cu(2)	88.7(4)	Cu(1)–Ox–Cu(4)	90.1(5)
Cu(2)–Ox–Cu(3)	89.7(5)	Cu(3)–Ox–Cu(4)	87.7(4)
Cu(2)–Ox–Cu(4)	167.9(7)	Cu(2)–Ox–Cu(2′)	93.0(4)
Cu(1)–Ox–Cu(2′)	100.0(5)	Cu(4)–Ox–Cu(2′)	99.0(5)
Cu(3)–Ox–Cu(2′)	98.2(5)		

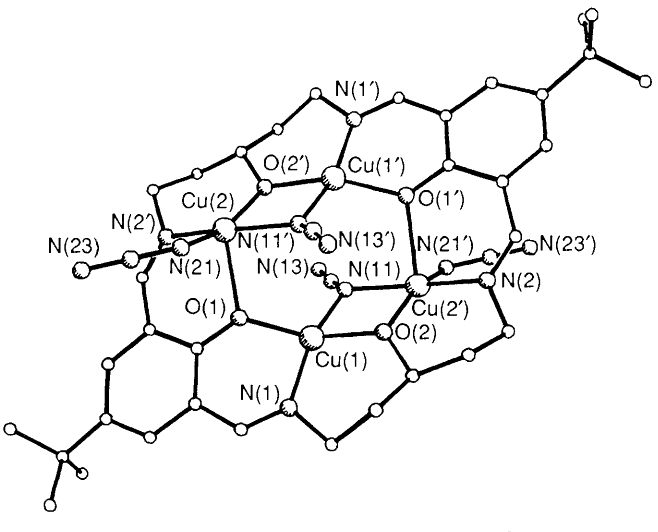


Fig. 5 Perspective view of complex **10**, $[Cu_4(\mu\text{-}N_3)_2L^2(N_3)_2]$

Electronic Spectra.—The electronic spectra of the complexes were recorded in dmf solution (800–200 nm) and as reflectance spectra of the solids (800–400 nm); the main features are listed in Table 1. The reflectance spectra correspond closely with the spectra of the respective freshly prepared dmf solutions, suggesting that the structures observed in the solids are maintained in solution.

Table 5 Selected interatomic distances (Å) and angles (°) for $[Cu_4(\mu\text{-}N_3)_2L^2(N_3)_2]\cdot 2CH_3OH$, **10**·$2CH_3OH$

Cu(1)–O(1)	1.916(4)	Cu(1)–N(1)	1.964(4)
Cu(1)–O(2)	1.921(4)	Cu(1)–N(11)	1.978(5)
Cu(1) ··· Cu(2′)	3.045(1)	Cu(2)–O(1)	2.341(4)
Cu(2)–N(21)	1.993(5)	Cu(2) ··· Cu(1)	3.460(1)
Cu(2)–O(2′)	1.957(4)	Cu(2)–N(2′)	1.977(5)
Cu(2)–N(11′)	1.978(5)		
O(1)–Cu(1)–N(1)	93.4(2)	O(1)–Cu(1)–O(2)	158.6(2)
N(1)–Cu(1)–O(2)	97.9(2)	O(1)–Cu(1)–N(11)	96.1(2)
N(1)–Cu(1)–N(11)	161.9(2)	O(2)–Cu(1)–N(11)	78.3(2)
O(1)–Cu(1)–Cu(2′)	132.9(1)	N(1)–Cu(1)–Cu(2′)	133.7(2)
O(1)–Cu(2)–N(21)	92.5(2)	O(1)–Cu(2)–Cu(1′)	104.3(1)
N(21)–Cu(2)–Cu(1′)	131.0(1)	O(1)–Cu(2)–O(2′)	109.5(1)
N(21)–Cu(2)–O(2′)	156.8(2)	N(21)–Cu(2)–N(2′)	97.8(2)
O(1)–Cu(2)–N(2′)	84.3(2)	O(2′)–Cu(2)–N(2′)	91.6(2)
Cu(1′)–Cu(2)–N(2′)	129.0(1)	N(21)–Cu(2)–N(11′)	95.6(2)
O(1)–Cu(2)–N(11′)	91.1(2)	O(2′)–Cu(2)–N(11′)	77.5(2)
N(2′)–Cu(2)–N(11′)	166.0(2)		

The tetracopper complexes exhibit four bands. The strong absorption at 268–269 nm (ε = 31 000–53 000 dm^3 mol^{-1} cm^{-1}) appears in almost the same position for the octacopper complexes (269–271 nm, ε = 76 000–83 000 dm^3 mol^{-1} cm^{-1}) and is probably a phenol-based σ–π* transition.[13] The two absorptions in the regions 320–340 and 360–376 nm are tentatively assigned to a combination of a ligand (C=N originated) π–π* transition and a phenolate-to-metal charge transfer.[18] Again, similar bands are found for the octacopper complexes, along with an extra transition at 405–430 nm, also attributed to mixed intraligand and charge-transfer transitions. The copper d–d transition is seen as a broad band in the region 641–685 nm (ε = 245–305 dm^3 mol^{-1} cm^{-1}) for the tetracopper complexes and 620–630 nm (ε = 550–650 dm^3 mol^{-1} cm^{-1}) for the octacopper cases.

The dimerisation of the tetranuclear complexes **2** and **4** to form the octacopper equivalents was followed by monitoring the d–d band in their electronic spectra. The reflectance spectra of the tetracopper complexes (λ_{max} 648 and 645 nm for **2** and **4** respectively) are similar to those of fresh dmf solutions. The solution spectra change slowly however, and after approximately 3 d are identical with those of **7** and **9** respectively. This is illustrated in Fig. 6 for the case of complex **2**. The same spectral change can be accomplished in a few seconds by addition of a non-co-ordinating base, such as triethylamine. Addition of a small amount of acid will readily reverse the process but excess of acid leads to other unidentified products, probably due to protonation of the alkoxy or phenoxy groups of the ligand. Provided the pH does not become too low, the tetra-, octa-, tetra-copper cycle can be repeated a number of times without any apparent decomposition.

This behaviour can be explained in terms of competition for the central oxygen donor between protons and macrocycle-bound copper atoms (Scheme 1). In more protic solvents such as ethanol the tetracopper monomer with hydroxide ion at the centre is favoured. In less protic media such as dmf the octacopper dimer is preferred but the rate of the conversion is slow. Addition of base deprotonates Ox, leading to rapid formation of the dimer.

Magnetic Properties.—Preliminary magnetic susceptibility measurements have been carried out on all the complexes in the range 93–300 K and the results are presented in Table 1. A nett antiferromagnetic interaction is observed for each of the complexes and, in general, the octacopper compounds show stronger coupling than their tetracopper equivalents. This may be a consequence of the deviation from tetragonal geometry in the tetracopper complexes which would reduce the orbital

Table 6 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*
(*a*) $[Cu_4(\mu_4\text{-}OH)L^2][NO_3]_3\cdot 2H_2O$, **3**·2H$_2$O			
Cu(1)	710(1)	5 138(1)	8 471(1)
Cu(2)	−1 068(1)	5 995(1)	9 610(1)
Ox	0	5 000	10 000
O(1)	−193(4)	6 049(2)	8 338(4)
C(1)	−118(6)	6 607(3)	7 609(5)
C(2)	−671(6)	7 285(3)	7 759(5)
C(3)	−571(6)	7 859(3)	6 977(6)
C(4)	28(6)	7 795(3)	6 042(5)
C(5)	172(6)	8 435(3)	5 213(6)
C(6)	−703(7)	9 076(3)	5 355(6)
C(7)	−272(7)	8 204(4)	3 841(6)
C(8)	1 644(7)	8 659(4)	5 612(6)
C(9)	534(6)	7 120(3)	5 891(5)
C(10)	478(6)	6 531(3)	6 654(5)
C(11)	1 056(6)	5 861(3)	6 363(6)
N(1)	1 221(5)	5 268(3)	6 964(5)
C(12a)	2 085(14)	4 722(6)	6 588(11)
C(12c)	1 610(15)	4 607(8)	6 371(13)
C(13a)	1 717(12)	3 966(6)	6 908(11)
C(13c)	2 589(15)	4 159(7)	7 350(13)
C(14)	2 123(7)	3 775(3)	8 248(6)
O(2)	1 496(4)	4 224(2)	8 937(4)
C(15a)	2 113(13)	3 008(6)	8 574(11)
C(15c)	2 870(14)	3 174(7)	9 044(12)
C(16)	2 444(11)	2 724(5)	9 780(8)
N(2)	−1 651(6)	6 994(3)	9 434(5)
C(17)	−1 392(7)	7 434(3)	8 658(6)
N(11)	1 455(5)	6 136(3)	2 526(6)
O(11)	1 349(5)	6 638(3)	3 220(5)
O(12)	1 470(5)	5 492(3)	2 879(5)
O(13)	1 522(6)	6 270(3)	1 450(5)
Ow(1)	−2 878(5)	5 411(3)	8 379(5)
Ow(2)	2 799(13)	5 805(7)	9 582(11)
N(21)	4 170(13)	5 467(7)	9 528(11)
O(21)	4 624(11)	5 630(6)	8 629(10)
O(22)	3 241(15)	5 765(8)	9 676(13)
O(23)	4 814(13)	4 998(7)	10 283(11)
(*b*) $[\{Cu_4(\mu_5\text{-}O)L^1(ClO_4)\}_2][ClO_4]_2\cdot 2H_2O$, **7**·2H$_2$O			
Cu(1)	2 231(1)	4 693(1)	9 992(1)
Cu(2)	926(1)	6 299(1)	10 480(1)
Cu(3)	−919(1)	5 531(1)	8 067(1)
Cu(4)	316(1)	3 854(1)	7 637(1)
Ox	471(6)	4 935(4)	9 089(4)
O(1)	1 772(6)	3 502(5)	8 633(4)
C(1)	2 277(9)	2 655(7)	8 444(7)
C(2)	1 716(9)	1 834(7)	7 363(7)
C(3)	2 270(10)	941(7)	7 236(8)
C(4)	3 306(10)	819(8)	8 081(8)
C(5)	3 865(11)	−174(8)	7 863(9)
C(6)	3 889(10)	1 643(7)	9 137(8)
C(7)	3 378(9)	2 559(7)	9 331(7)
C(8)	4 118(9)	3 409(7)	10 447(7)
N(1)	3 853(7)	4 314(6)	10 809(6)
C(9)	4 865(10)	5 109(8)	11 964(7)
C(10)	4 798(10)	6 268(8)	12 116(8)
C(11)	3 642(8)	6 499(7)	12 218(7)
O(2)	2 402(6)	5 804(4)	11 281(4)
C(12)	3 743(10)	7 758(8)	12 477(8)
C(13)	2 686(9)	8 061(8)	12 731(7)
N(2)	1 449(7)	7 748(6)	11 682(6)
C(14)	843(9)	8 502(7)	11 609(7)
C(15)	−279(9)	8 480(7)	10 659(7)
C(16)	−758(9)	9 438(7)	10 788(8)
C(17)	−1 793(9)	9 565(7)	9 913(7)
C(18)	−2 295(10)	10 568(8)	10 100(8)
C(19)	−2 351(10)	8 756(7)	8 858(8)
C(20)	−1 909(9)	7 779(7)	8 661(7)
C(21)	−904(9)	7 632(7)	9 575(7)
O(3)	−527(6)	6 680(4)	9 435(4)
C(22)	−2 513(9)	7 040(7)	7 506(7)
N(3)	−2 244(8)	6 144(6)	7 136(6)
C(23)	−2 953(11)	5 589(9)	5 900(8)
C(24)	−2 308(19)	5 032(15)	5 424(10)
C(25)	−1 781(10)	4 125(8)	5 686(7)
O(4)	−1 188(6)	4 271(5)	6 869(5)
C(26)	−1 265(21)	3 468(15)	5 067(10)
C(27)	−851(12)	2 564(9)	5 163(8)
N(4)	84(8)	2 652(6)	6 304(6)
C(28)	702(10)	1 889(7)	6 355(7)
Cl(1)	2 252(3)	6 500(2)	8 165(2)
O(11)	1 966(7)	5 356(5)	7 519(6)
O(12)	1 029(7)	6 774(5)	7 891(6)
O(13)	3 120(7)	7 217(6)	7 909(6)
O(14)	2 886(7)	6 633(7)	9 339(6)
Cl(2)	−2 366(4)	8 887(3)	5 549(2)
O(21)	−2 724(11)	7 851(7)	4 754(7)
O(22)	−2 852(15)	8 927(7)	6 317(10)
O(23)	−2 764(22)	9 603(11)	5 006(13)
O(24)	−1 082(12)	9 290(17)	6 088(13)
O(30)	5 371(26)	2 656(21)	3 279(21)
O(40)	5 394(26)	1 061(21)	4 345(22)
(*c*) $[\{Cu_4(\mu_5\text{-}O)L^2(ClO_4)\}_2][ClO_4]_2\cdot CH_3OH$, **9**·CH$_3$OH			
Cu(1)	−475(2)	966(1)	1 124(2)
Cu(2)	647(1)	727(1)	13(1)
Cu(3)	−977(2)	667(2)	−1 599(1)
Cu(4)	−2 068(2)	783(2)	−469(2)
Ox	−722(7)	633(7)	−204(7)
O(1)	−1 743(8)	878(8)	842(7)
C(1)	−2 318(13)	996(12)	1 356(12)
C(2)	−3 216(11)	934(11)	982(11)
C(3)	−3 731(13)	1 085(12)	1 562(13)
C(4)	−3 396(13)	1 271(12)	2 452(15)
C(5)	−3 996(13)	1 514(12)	2 982(13)
C(6)	−4 817(15)	1 032(14)	2 792(18)
C(7)	−3 514(14)	1 545(19)	4 032(14)
C(8)	−4 303(18)	2 283(13)	2 727(18)
C(9)	−2 455(13)	1 295(11)	2 849(12)
C(10)	−1 901(13)	1 136(11)	2 299(13)
C(11)	−914(15)	1 243(13)	2 757(15)
N(1)	−281(10)	1 231(10)	2 422(9)
C(12)	574(14)	1 401(14)	3 032(14)
C(13)	1 155(14)	1 751(15)	2 580(15)
C(14)	1 461(11)	1 322(13)	1 954(12)
O(2)	766(7)	876(7)	1 289(7)
C(15)	2 132(14)	1 637(14)	1 588(14)
C(16)	2 523(13)	1 211(13)	1 042(13)
N(2)	1 891(11)	981(11)	123(10)
C(17)	2 245(13)	994(12)	−555(11)
C(18)	1 728(14)	847(11)	−1 512(11)
C(19)	2 264(12)	949(10)	−2 106(11)
C(20)	1 893(12)	959(11)	−3 035(12)
C(21)	2 434(14)	1 138(11)	−3 637(13)
C(22)	2 093(19)	655(18)	−4 505(19)
C(23)	3 387(14)	1 006(14)	−3 240(13)
C(24)	2 295(22)	1 912(19)	−3 893(20)
C(25)	992(16)	897(11)	−3 335(13)
C(26)	393(13)	782(9)	−2 802(10)
C(27)	767(11)	751(11)	−1 861(11)
O(3)	304(8)	632(7)	−1 318(7)
C(28)	−568(11)	790(14)	−3 247(14)
N(3)	−1 178(9)	732(11)	−2 921(10)
C(29)	−2 064(15)	762(15)	−3 568(15)
C(30)	−2 728(18)	1 054(19)	−3 262(16)
C(31)	−2 977(12)	752(16)	−2 495(12)
O(4)	−2 185(8)	583(8)	−1 690(8)
C(32)	−3 783(16)	967(17)	−2 222(18)

Table 6 (*continued*)

Atom	x	y	z
C(33)	−3 976(20)	669(19)	−1 483(18)
N(4)	−3 363(9)	761(11)	−607(10)
C(34)	−3 687(12)	831(13)	15(13)
Cl(1)	−1 205(5)	2 536(3)	−651(5)
O(11)	−2 002(11)	2 157(9)	−676(10)
O(12)	−531(10)	2 426(8)	208(12)
O(13)	−1 331(16)	3 314(10)	−805(16)
O(14)	−950(15)	2 152(11)	−1 400(13)
Cl(2)	4 290(5)	2 296(5)	−299(5)
O(21)	4 322(10)	1 609(14)	158(13)
O(22)	4 009(34)	2 945(22)	−34(21)
O(23)	3 835(28)	2 230(19)	−1 140(19)
O(24)	5 056(28)	2 556(32)	−161(30)
O(50)	67(30)	4 169(26)	441(30)
C(50)	346(29)	5 037(32)	98(36)
(*d*) $[Cu_4(\mu\text{-}N_3)_2L^2(N_3)_2]\cdot 2CH_3OH$, **10**·$2CH_3OH$			
Cu(1)	884(1)	808(1)	933(1)
Cu(2)	−2 600(1)	−150(1)	689(1)
O(1)	−619(5)	437(2)	1 739(3)
C(1)	−1 073(7)	734(3)	2 541(4)
C(2)	−2 089(7)	359(3)	3 117(4)
C(3)	−2 363(7)	628(3)	4 041(4)
C(4)	−1 796(7)	1 284(3)	4 437(4)
C(5)	1 975(8)	1 529(3)	5 497(4)
C(6)	−579(8)	1 247(4)	6 191(5)
C(7)	−3 486(8)	1 236(3)	5 842(4)
C(8)	−2 013(9)	2 341(3)	5 590(4)
C(9)	−961(7)	1 683(3)	3 819(4)
C(10)	−574(7)	1 424(3)	2 900(4)
C(11)	314(7)	1 902(3)	2 342(4)
N(1)	856(6)	1 768(2)	1 520(4)
C(12)	1 723(7)	2 360(3)	1 104(4)
C(13)	1 627(9)	2 327(3)	−15(5)
C(14)	2 461(9)	1 739(3)	−422(5)
O(2)	1 789(5)	1 060(2)	−253(3)
C(15)	2 731(8)	1 835(3)	−1 490(4)
C(16)	3 843(7)	1 296(3)	−1 845(5)
N(2)	3 120(6)	584(2)	−1 944(4)
C(17)	2 855(7)	315(3)	−2 822(4)
N(11)	1 623(6)	−130(2)	506(3)
N(12)	1 883(6)	−669(2)	1 021(4)
N(13)	2 029(8)	−1 214(3)	1 440(5)
N(21)	−4 045(6)	687(2)	655(4)
N(22)	−4 882(6)	810(3)	1 290(4)
N(23)	−5 726(7)	954(3)	1 864(4)
O(20)	−6 470(6)	1 519(2)	3 683(3)
C(20)	−7 015(8)	867(3)	4 060(5)

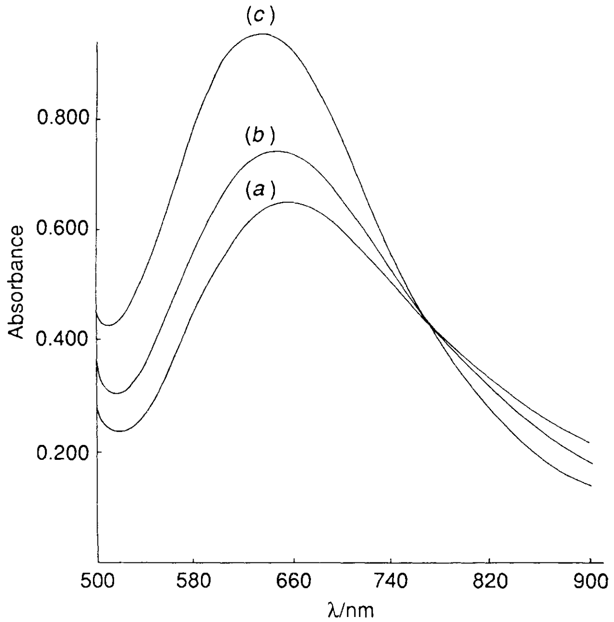
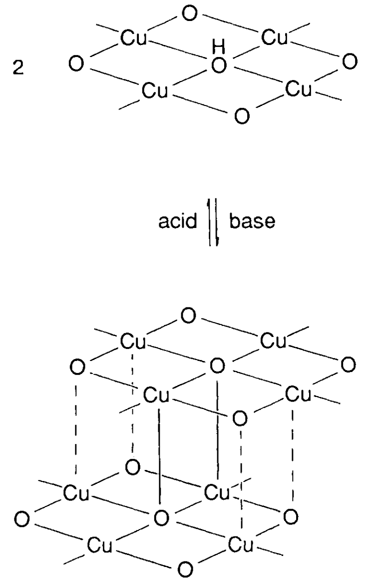


Fig. 6 Electronic spectrum of complex **2**, $[Cu_4(\mu_4\text{-}OH)L^1][ClO_4]_3$ in dmf: (*a*) fresh solution, (*b*) after 6 h and (*c*) after 3 d (identical to the spectrum of **7**)

overlap and hence the extent of antiferromagnetic coupling. The change in the nature of the central Ox donor is also likely to be significant. An extension of the magnetic studies to lower temperatures is underway and a detailed analysis of the coupling interactions will be presented elsewhere.[19]

Conclusion

A series of tetra- and octa-copper complexes with open, planar faces has been prepared. The exposed copper–oxygen array, with metal–metal distances of *ca.* 3 Å, is reminiscent of a metal oxide surface. Perchlorate anions are able to bind to this surface in the octacopper complex and there is evidence that the



Scheme 1

complex remains intact in solution. These observations suggest the interesting possibility of carrying out homogeneous metal-promoted reactions on the open faces by binding the substrates to the metal array. Investigations of the binding of substrates other than perchlorate are underway. Extension of the series to include more catalytically active metals would also be of interest. A planar tetranickel(II) complex[6] has been characterised and extension to the later transition series seems feasible.

Unusual co-ordination geometries are imposed on the central donor (Ox) in complexes **1–9** and this ligand can be displaced, as in the formation of complex **10**. Thus, it may be possible to vary the central species and to activate it to further reaction by placing it in an unusual geometric and electronic environment. The new structures described in this paper might be expected to give rise to unusual chemical properties. Further investigations of these properties, both for copper compounds and for complexes of other metals, are underway and will be reported in subsequent publications.

Experimental

Synthesis.—2,6-Diformyl-4-methylphenol (dfmp),[20] 4-*tert*-butyl-2,6-diformylphenol (tdfp),[20] and 1,5-diamino-3-hydroxypentane (dahp)[21] were prepared by literature methods. Other chemicals used were of Analar or reagent grade. Solvents were dried by the standard methods.

Preparation of the Complexes.—$[Cu_4(\mu_4\text{-}OH)L^1][NO_3]_3\cdot 2H_2O$ **1**. $Cu(NO_3)_2\cdot 6H_2O$ (1.2 g, 4 mmol) and dfmp (0.33 g, 2 mmol) were dissolved in hot, dry ethanol (40 cm^3) and the mixture refluxed on a steam-bath for 10 min. A solution of dahp (0.24 g, 2 mmol) in dry methanol–ethanol (1:1, 20 cm^3) was added dropwise with occasional stirring. (The dahp solution was obtained by neutralising a solution of the dihydrochloride salt with KOH.) A dark green solution resulted and, after *ca.* 30 min, a bright green solid began to separate. Refluxing was continued for 3 h, after which the solution was filtered hot. The green solid was washed with dry ethanol (3 × 5 cm^3) and dried *in vacuo* at 60 °C for 6 h. Yield 45% (Found: C, 34.0; H, 3.4; Cu, 26.6; N, 9.6. Calc. for $C_{28}H_{37}Cu_4N_7O_{16}$: C, 34.2; H, 3.7; Cu, 25.9; N, 10.0%).

$[Cu_4(\mu_4\text{-}OH)L^1][ClO_4]_3$ **2**. This complex was prepared in a similar way to **1**, using $Cu(ClO_4)_2\cdot 6H_2O$ (1.48 g, 4 mmol) in place of the nitrate salt. The mixture was refluxed for 24 h and product began to appear after 6 h. The green product was filtered off and washed as for **1**, then recrystallised from acetonitrile and dried *in vacuo* at room temperature (r.t.) for 24 h. Yield 55%. (Found: C, 31.8; H, 3.6; Cu, 23.6; N, 5.1. Calc. for $C_{28}H_{33}Cl_3Cu_4N_4O_{17}$: C, 31.8; H, 3.1; Cu, 24.0; N, 5.30%).

$[Cu_4(\mu_4\text{-}OH)L^2][NO_3]_3\cdot H_2O$ **3**. This complex was prepared in the same way as for **1** but using tdfp (0.41 g, 2 mmol) in place of dfmp. The reaction mixture was refluxed for 24 h, concentrated to *ca.* 10 cm^3, and refrigerated overnight. After filtration to remove a small amount of white solid (probably KCl), the filtrate was treated with diethyl ether which caused precipitation of a green powder. This product was collected, redissolved in the minimum amount of ethanol, refluxed for 1 h, and allowed to stand overnight at r.t. The dark green solid which separated was filtered off, washed with ethanol, and recrystallised from acetonitrile before being dried *in vacuo* at 60 °C for 6 h. Yield 76%. (Found: C, 38.8; H, 5.0; Cu, 23.8; N, 8.6. Calc. for $C_{34}H_{47}Cu_4N_7O_{15}$: C, 39.0; H, 4.5; Cu, 24.2; N, 9.3%). Crystals suitable for single-crystal X-ray studies were obtained by slow diffusion of diethyl ether into an acetonitrile solution of the complex. These crystals were not dried *in vacuo*, and were found to have stoichiometry **3**$\cdot 2H_2O$.

$[Cu_4(\mu_4\text{-}OH)L^2][ClO_4]_3\cdot 2H_2O$ **4**. The complex was prepared as for **1**, except that $Cu(ClO_4)_2\cdot 6H_2O$ (1.48 g, 4 mmol) and tdfp (0.41 g, 2 mmol) were used in place of $Cu(NO_3)_2\cdot 6H_2O$ and dfmp. The reaction mixture was refluxed for 20 h and the green solid which separated was filtered off, washed with dry ethanol (3 × 5 cm^3), and dried *in vacuo* at r.t. A second crop was obtained by concentration of the filtrate. Yield 57% (Found: C, 34.7; H, 4.6; Cu, 21.0; N, 4.6. Calc. for $C_{34}H_{49}Cl_3Cu_4N_4O_{19}$: C, 34.7; H, 4.2; Cu, 21.6; N, 4.2%).

$[Cu_4(\mu_4\text{-}OH)L^1(CH_3CO_2)_3]\cdot 3H_2O$ **5**. The salt $Cu(CH_3CO_2)_2\cdot H_2O$ (0.8 g, 4 mmol) and dfmp (0.33 g, 2 mmol) were dissolved in dry, boiling methanol (60 cm^3). A bright green solid separated and the suspension was refluxed for 30 min. The compound dahp (0.59 g, 2 mmol) in dry methanol (10 cm^3) was added dropwise with stirring and refluxing was continued. After 1 h the suspension had all dissolved and after 16 h of reflux the hot solution was filtered and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in dichloromethane, filtered, and evaporated to dryness to yield a dark green powder which was dried *in vacuo* at 60 °C for 6 h. Yield 73% (Found: C, 41.5; H, 4.8; Cu, 25.0; N, 5.4. Calc. for $C_{34}H_{48}Cu_4N_4O_{14}$: C, 41.2; H, 4.8; Cu, 25.6; N, 5.6%).

$[Cu_4(\mu_4\text{-}OH)L^2(CH_3CO_2)_3]\cdot 2H_2O$ **6**. This complex was prepared in the same way as for **5**, except that tdfp (0.40 g, 2 mmol) was used in place of dfmp. Yield 91% (Found: C, 45.9; H, 5.7; N, 4.8. Calc. for $C_{40}H_{58}Cu_4N_4O_{13}$: C, 45.4; H, 5.5; N, 5.3%).

$[\{Cu_4(\mu_5\text{-}O)L^1(ClO_4)\}_2][ClO_4]_2\cdot 3dmf$ **7**·3dmf. This octacopper complex was prepared from the corresponding tetracopper complex **2** by recrystallisation from methanol–dmf (1:1) by slow diffusion of diethyl ether. Yield 60% (Found: C, 36.6; H, 4.0; Cu, 23.8. Calc. for $C_{65}H_{85}Cl_4Cu_8N_{11}O_{29}$: C, 36.6; H, 4.0; Cu, 23.8%). Crystals suitable for single-crystal X-ray studies were found to have the stoichiometry **7**$\cdot 2H_2O$. The same product is obtained by treating a dmf solution of compound **2** with a base such as triethylamine or 2,6-diaminopyridine, or by treating a solution of **5** in dry methanol with excess of $NaClO_4$.

$[\{Cu_4(\mu_5\text{-}O)L^2(NO_3)\}_2][NO_3]_2\cdot 2H_2O$ **8**. This complex was prepared in the same way as the tetranuclear equivalent **3** except that the green solid obtained on addition of diethyl ether was refluxed for 10 h in carefully dried methanol. The resulting green solid was filtered off, washed with dry ethanol, and dried *in vacuo* at 60 °C for 6 h. Yield 74% (Found: C, 41.4; H, 5.4; Cu, 25.7; N, 8.3. Calc. for $C_{68}H_{92}Cu_8N_{12}O_{24}$: C, 41.4; H, 4.7; Cu, 25.8; N, 8.5%). The same complex was obtained by stirring a solution of **3** with triethylamine in dry methanol or dmf.

$[\{Cu_4(\mu_5\text{-}O)L^2(ClO_4)\}_2][ClO_4]_2$ **9**. Complex **4** (1.2 g, 1 mmol) was dissolved in boiling methanol (100 cm^3) to give a dark green solution. 2,6-Diaminopyridine (0.21 g, 2 mmol) was added dropwise with stirring and the mixture refluxed for 2 h, during which time a dark green solid separated. The suspension was cooled to r.t. and filtered. The solid product was washed with methanol (3 × 10 cm^3) and dried *in vacuo* at r.t. Yield 75% (Found: C, 39.5; H, 4.3; Cu, 24.1; N, 5.4. Calc. for $C_{68}H_{88}Cl_4Cu_8N_8O_{25}$: C, 39.2; H, 4.2; Cu, 24.4; N, 5.4%). Crystals suitable for single-crystal X-ray study were not dried *in vacuo* and were found to have stoichiometry **9**$\cdot CH_3OH$. The same product can be obtained by treating a dmf solution of compound **4** with triethylamine at r.t.

$[Cu_4L^2(N_3)_4]\cdot 2CH_3OH$ **10**$\cdot 2CH_3OH$. Complex **3** (1.05 g, 1 mmol) was dissolved in dry, boiling methanol (100 cm^3) and a solution of NaN_3 (0.26 g, 4 mmol) in hot, dry methanol was added dropwise with stirring. The mixture was refluxed for *ca.* 5 min and allowed to stand at r.t. overnight. The dark green, crystalline solid which separated was filtered off, washed with dry methanol (3 × 5 cm^3), and dried *in vacuo* at 60 °C for 6 h. Yield 60% (Found: C, 41.9; H, 4.7; Cu, 24.5; N, 21.0. Calc. for $C_{36}H_{52}Cu_4N_{16}O_6$: C, 40.8; H, 4.9; Cu, 24.0; N, 21.6%).

Crystallography.—The four data sets were collected at low temperature on a Nicolet *R*3*m* four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The unit-cell parameters were determined by least-squares refinement of 18–25 accurately centred reflections in the range $5 < 2\theta < 34°$. Crystal stability was monitored by recording three check reflections every 100 reflections and no significant variations were observed. The data sets were corrected for Lorentz and polarisation effects and empirical absorption corrections, based on φ-scan data, were applied. Each structure was refined using blocked-cascade least-squares techniques and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. All programs used in data processing and structure solution are contained in the SHELXTL (Version 4.0)[22] or SHELX 86[23] packages.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Crystal data for **3**$\cdot 2H_2O$. $C_{34}H_{49}Cu_4N_7O_{16}$, green, crystal dimensions 0.4 × 0.3 × 0.2 mm, monoclinic, space group $P2_1/a$, a = 10.384(2), b = 18.515(5), c = 11.264(2) Å, β = 107.48(2)°, U = 2665(1) Å^3, Z = 2, F(000) = 1112, μ = 2.12 mm^{-1}, T_{max} = 0.76, T_{min} = 0.67.

Using 1.8° ω scans at 3.91° min^{-1}, 3627 unique reflections were collected at 160 K in the range $4 < 2\theta < 50°$ and 2521 of these, with $I > 3\sigma(I)$, were used in the structure refinement. A Patterson calculation revealed the positions of the two independent copper atoms; the remaining non-hydrogen atoms were located from Fourier difference maps. Hydrogen atoms were inserted at calculated positions using a riding model with the thermal parameters equal to 1.2U of the carrier atoms. The necessarily disordered hydrogen bound to Ox was not located and has not been inserted. The non-hydrogen atoms were refined with anisotropic thermal parameters except for those exhibiting disorder [C(12a), C(12c), C(13a), C(13c), C(15a), C(15c), Ow(2), N(21), O(21), O(22) and O(23)], which were refined isotropically. The refinement converged with R = 0.047, R' = 0.066 and g = 0.0006. The final difference map showed no significant features.

Crystal data for **7**·2H$_2$O. $C_{56}H_{62}Cl_4Cu_8N_8O_{28}$, green, crystal dimensions 0.31 × 0.25 × 0.15 mm, triclinic, space group $P\bar{1}$, a = 11.497(4), b = 12.714(3), c = 13.546(4) Å, α = 102.92(2), β = 113.15(2), γ = 100.36(3)°, U = 1693(1) Å^3, Z = 1, F(000) = 980, μ = 2.69 mm^{-1}, T_{max} = 0.91, T_{min} = 0.78.

Using 2° ω scans at 5.86° min^{-1}, 4049 unique reflections were collected at 170 K in the range $4 < 2\theta < 45°$ and 2681 of these, with $I > 3\sigma(I)$, were used in the structure refinement. A Patterson calculation showed the positions of the four independent copper atoms and the remaining non-hydrogen atoms were located from Fourier difference maps. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters equal to 1.2U of the carrier atoms. Anisotropic thermal parameters were assigned to all non-hydrogen atoms except those in the unsaturated portion of the macrocycle and the solvate water molecules. The refinement converged with R = 0.050, R' = 0.064 and g = 0.0010. The final difference map showed no significant features.

Crystal data for **9**·CH$_3$OH. $C_{69}H_{48}Cl_4Cu_8N_8O_{27}$, green, crystal dimensions 0.52 × 0.52 × 0.20 mm, monoclinic, space group $P2_1/n$, a = 15.778(5), b = 17.384(4), c = 15.392(5) Å, β = 109.54(3)°, U = 3978(3) Å^3, Z = 2, F(000) = 2120, μ = 2.32 mm^{-1}, T_{max} = 0.95, T_{min} = 0.61. Using 0.6° peak top ω scans at 4.88° min^{-1}, 5188 unique reflections were collected at 160 K in the range $4 < 2\theta < 45°$ and 2276 of these, with $I > 3\sigma(I)$, were used in the structure refinement. The structure was solved by direct methods using the program TREF[22] which revealed most of the non-hydrogen atoms; the remainder were located from Fourier difference maps. Hydrogen atoms were inserted using a riding model with a common thermal parameter for all the atoms except those on the disordered methanol solvate molecule which were not included. Anisotropic thermal parameters were assigned to all the non-hydrogen atoms except C(12), C(16), C(24), C(33) and the methanol solvate [C(50) and O(50)]. The refinement converged with R = 0.081, R' = 0.112 and g = 0.0052. The final difference map showed no significant features.

Crystal data for **10**·2CH$_3$OH. $C_{36}H_{52}Cu_4N_{16}O_6$, green, crystal dimensions 0.65 × 0.20 × 0.06 mm, monoclinic, space group $P2_1/a$, a = 8.559(3), b = 18.719(6), c = 13.485(7) Å, β = 97.29(4)°, U = 2143(1) Å^3, Z = 2, F(000) = 1088, μ = 2.03 mm^{-1}, T_{max} = 0.97, T_{min} = 0.78. Using 2° ω scans at 4.88° min^{-1}, 2616 unique reflections were collected at 160 K in the range $4 < 2\theta < 45°$ and 1711 of these, with $I > 3\sigma(I)$, were used in the structure refinement. A Patterson calculation revealed the positions of the two independent copper atoms and the remaining non-hydrogen atoms were located from Fourier difference maps. Hydrogen atoms were inserted at calculated positions using a riding model with a common thermal parameter. All the non-hydrogen atoms were refined with anisotropic thermal parameters and the refinement converged with R = 0.041 and R' = 0.025 (unit weights). The final difference map showed no significant features.

Physical Measurements.—Infrared spectra of the solid samples were recorded as KBr discs on a Pye-Unicam SP3-300 spectrophotometer, electronic spectra of solids and dmf solutions using a Beckman DK-2A and a Varian DMS-100 spectrophotometer, respectively. Carbon, H and N analyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin. Copper was analysed by ethylenediaminetetraacetate titration.[24] Magnetic data were measured in the range 93–300 K using a Gouy balance supplied by Newport Instruments.

Acknowledgements

We thank the New Zealand University Grants Committee for the award of a postdoctoral Fellowship (to S. S. T.) and the Punjabi University, Patiala for granting him leave.

References

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

2 See, for example, P. Lacroix, O. Kahn, F. Theobald, J. Le Roy and C. Wakselman, *Inorg. Chim. Acta*, 1988, **142**, 129; N. A. Bailey, D. E. Fenton, P. B. Roberts and A. M. Walford, *J. Chem. Soc., Dalton Trans.*, 1987, 1865; S. K. Mandal, L. K. Thompson, K. Nag, J. P. Charland and E. J. Gabe, *Inorg. Chem.*, 1987, **26**, 1391; S. L. Lambert, C. L. Spiro, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1982, **21**, 68.

3 See, for example, D. Luneau, J.-M. Savariault and J.-P. Tuchagues, *Inorg. Chem.*, 1988, **27**, 3912; A. S. Borovic, V. Papaefthymiou, L. F. Taylor, O. P. Anderson and L. Que, jun., *J. Am. Chem. Soc.*, 1989, **111**, 6183; K. D. Karlin, R. W. Cruse, Y. Gultneh, A. Farooq, J. C. Hayes and J. Zubieta, *J. Am. Chem. Soc.*, 1987, **109**, 2668; R. M. Buchanan, M. S. Mashuta, K. J. Oberhausen, J. F. Richardson, Qiaoying Li and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1989, **111**, 4497; M. Suzuki, H. Oshio, A. Ueharu, K. Endo, M. Yanaga, S. Kida and K. Saito, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3907; N. A. Bailey, D. E. Fenton, R. Moody, P. J. Scrimshire, E. Beloritzky, P. H. Fries and J.-M. Latour, *J. Chem. Soc., Dalton Trans.*, 1988, 2817.

4 V. McKee and J. Smith, *J. Chem. Soc., Chem. Commun.*, 1983, 1465; N. A. Bailey, D. E. Fenton, R. Moody, C. O. Rodriguez de Barbarin, I. N. Sciambarella, J.-M. Latour, D. Limosin and V. McKee, *J. Chem. Soc. Dalton Trans.*, 1987, 2519; S. Brooker and V. McKee, *J. Chem. Soc., Chem. Commun.*, 1989, 619.

5 S. S. Tandon and V. McKee, *J. Chem. Soc., Dalton Trans.*, 1989, 19.

6 V. McKee and S. S. Tandon, unpublished work.

7 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 385.

8 V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 1334.

9 V. McKee and S. S. Tandon, *Inorg. Chem.*, 1989, **28**, 2901.

10 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1987, 1852; *Inorg. Chem.*, 1989, **111**, 3603.

11 B. F. Hoskins, R. Robson and P. Smith, *J. Chem. Soc., Chem. Commun.*, 1990, 488.

12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn., Wiley, New York, 1986.

13 S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1984, 2141.

14 A. F. Wells, *Structural Inorganic Chemistry*, 5th edn., Oxford University Press, Oxford, 1984, ch. 25.

15 K. P. McKillop, S. M. Nelson, J. Nelson and V. McKee, *J. Chem. Soc., Chem. Commun.*, 1988, 387.

16 J. E. Huheey, *Inorganic Chemistry*, 3rd edn., Harper and Row, New York, 1983, p. 401.

17 J. L. Pascal, J. Potier, D. J. Jones, J. Roziere and A. Michalowicz, *Inorg. Chem.*, 1985, **24**, 238; J. Potier, J. Roziere, A. Seigneurin, D. J. Jones and J. L. Pascal, *Nouv. J. Chim.*, 1987, **11**, 641.

18 S. K. Mandal, B. Adhikary and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1986, 1175; S. K. Mandal and K. Nag, *Inorg. Chem.*, 1983, **22**, 2567.

19 J.-M. Latour, V. McKee and S. S. Tandon, unpublished work.

20 R. R. Gagne, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073.

21 G. R. Owen and C. B. Reese, *J. Chem. Soc. C*, 1970, 2401; I. Murese, M. Hatano, M. Tanaka, S. Ueno, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2404.

22 G. M. Sheldrick, SHELXTL User Manual, Revision 4, Nicolet XRD Corporation, Madison, Wisconsin, 1984.

23 G. M. Sheldrick, SHELXS 86, A Program for Crystal Structure Solution, Göttingen University, 1986.

24 A. Vogel, *Textbook of Quantitative Inorganic Analysis*, 4th edn., Longman, London, 1978, ch. 10.

Received 12*th June* 1990; *Paper* 0/02633F