# Bi-copper(I) and Bi-copper(II) Complexes of a 30-Membered Macrocyclic Ligand: The Inclusion of Substrate Molecules and the Crystal and Molecular Structures of a μ-Hydroxo- and a μ-Imidazolato-complex

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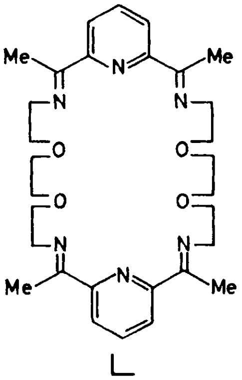
The preparation of the copper(II) complex $[CuL][ClO_4]_2\cdot H_2O$ of a 30-membered ' $N_6O_4$ ' macrocyclic Schiff-base ligand, L, in which the metal ion is octahedrally co-ordinated to the six nitrogen atoms, is described. In contrast to analogous complexes of the other first-row transition-metal ions, the macrocycle in $[CuL]^{2+}$ unfolds on treatment with excess of free metal ion to yield the binuclear complex $[Cu_2L][ClO_4]_4\cdot 2H_2O$. This complex is the starting point for the preparation of several derivatives containing small substrate ions [$OH^-$, imidazolate anion (im), $N_3^-$, $NCS^-$] intramolecularly bound between the metal centres. The structures of the μ-imidazolato- and μ-hydroxo-complexes have been determined. Crystals of $[Cu_2L(im)][ClO_4]_3$, (I), are triclinic, with $a$ = 12.89(1), $b$ = 13.64(1), $c$ = 16.51(1) Å, $\alpha$ = 89.9(1), $\beta$ = 114.1(1), $\gamma$ = 121.8(1)°, $Z$ = 2, and space group $P\bar{1}$. Crystals of $[Cu_2L(OH)][ClO_4]_3\cdot H_2O$, (II), are triclinic with $a$ = 12.634(9), $b$ = 14.103(8), $c$ = 14.689(8) Å, $\alpha$ = 88.3(1), $\beta$ = 118.4(1), $\gamma$ = 115.6(1)°, $Z$ = 2, and space group $P\bar{1}$. The two structures were solved by Patterson and Fourier methods from 1 567 and 2 786 above background reflections measured by a diffractometer and refined by full-matrix least squares to $R$ 0.081 and 0.084 respectively. In both (I) and (II) the two $Cu^{II}$ ions are each bonded to the three nitrogen atoms of the two planar trimethine groups (Cu–N 1.90—2.08 Å), the fourth position of the equatorial square plane being occupied by one nitrogen of a bridging imidazolate anion [Cu–N 1.92(2), 1.98(2) Å] or by the bridging hydroxo-oxygen atom [Cu–O 1.866(13), 1.912(10) Å]. Cu $\cdots$ Cu separations are 5.99 and 3.57 Å in (I) and (II) respectively. In (I), the plane of the imidazolate ring is inclined at 68.8, 79.1° to the two ' $N_4$ ' co-ordination planes. In (II), the Cu–O(H)–Cu angle is 141.7(7)°. In both structures the metal ions are weakly bonded to perchlorate or water oxygen atoms in axial positions. Magnetic susceptibility measurements as a function of temperature establish antiferromagnetic super-exchange in (I) and (II) with $J = -21.0$ and $-120$ cm$^{-1}$ respectively, where $2J$ is the singlet–triplet separation. Two heterobinuclear $Cu^{II}/Ni^{II}$ complexes have been prepared by reaction of mononuclear $[CuL]^{2+}$ with $Ni^{II}$ salts. A bi-copper(I) complex $[Cu_2L][ClO_4]_2\cdot H_2O$ has also been prepared by reduction of the bi-copper(II) complex with $BPh_4^-$ as well as by a metal-exchange method.

THE high-yield synthesis of a bi-lead(II) complex of the 30-membered (' $N_6O_4$ ' core) macrocyclic ligand, L, has been reported [1] as has the preparation of several mononuclear [2] and binuclear [3] complexes of transition metals by a transmetallation (metal-exchange) procedure. Among the latter are the complexes $[Cu_2L(N_3)_3][ClO_4]$ and $[Cu_2L(OH)][ClO_4]_3\cdot H_2O$ in which the two copper(II) ions are intramolecularly bridged by, respectively, single 1,3-azido- and hydroxo-groups. The structure of the former complex has been described while the occurrence of a μ-hydroxo-unit in the latter complex was inferred from its magnetic and other properties. This paper describes the crystal and molecular structures of the μ-hydroxo-complex and of a new μ-imidazolato-complex, along with the preparation and properties of other bi-copper(II) and bi-copper(I) complexes of this versatile macrocyclic ligand.

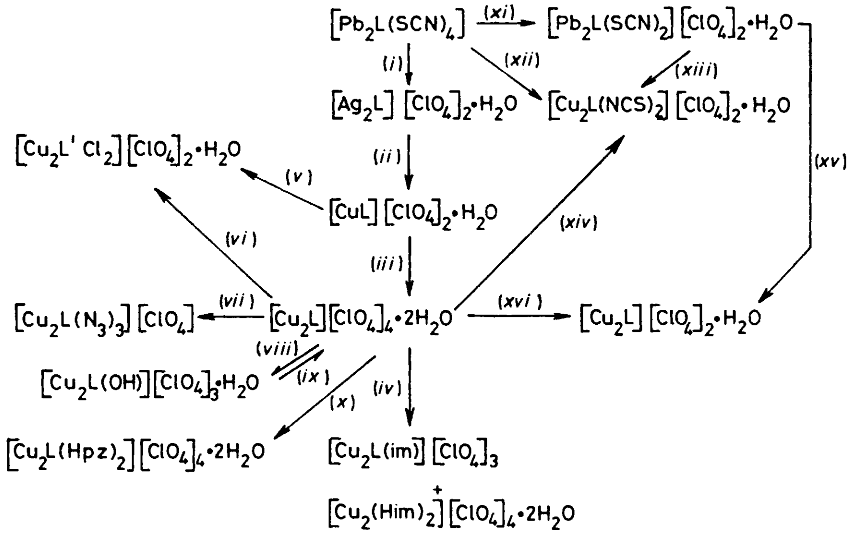


L

RESULTS AND DISCUSSION

*Preparation and Properties of the Copper*(II) *Complexes*.—The 30-membered macrocycle L was prepared from 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine *via* a cyclic (2 + 2) condensation using $Pb[SCN]_2$ as template. It was isolated as the complex $[Pb_2L(SCN)_4]$, as described earlier.[1] Attempts to isolate the metal-free macrocycle were unsuccessful, so complexes of L containing other metal ions were prepared by a transmetallation (ion-exchange) procedure. Thus, treatment of $[Pb_2L(SCN)_4]$ with $Ag[ClO_4]$ afforded the binuclear complex $[Ag_2L][ClO_4]_2\cdot H_2O$ which on treatment with not more than one equivalent of $Cu[ClO_4]_2\cdot 6H_2O$ gave the mononuclear complex $[CuL][ClO_4]_2\cdot H_2O$, believed to have a distorted octahedral ' $N_6$ ' structure in which the ether oxygen atoms are not co-ordinated, as shown [2] for the corresponding complexes of $Mn^{II}$, $Fe^{II}$, $Co^{II}$, and $Ni^{II}$. However, unlike those, $[CuL][ClO_4]_2\cdot H_2O$ yields a binuclear species $[Cu_2L][ClO_4]_4\cdot 2H_2O$ on treatment with a further equivalent of metal ion. This binuclear complex was the usual starting material for the preparation of a range of derivatives in all of which two copper atoms are encapsulated within the macrocycle (see Scheme).

Analytical and selected physical data for the complexes are collected in Tables 1 and 2. With one exception, the retention of the macrocycle intact in all the reactions is apparent from the i.r. spectra of the products. All exhibit a strong to medium intensity band at *ca.* 1 630 $cm^{-1}$ expected for the C=N group, as well as the various features characteristic of the pyridine ring. In the complex formulated in Tables 1 and 2 as $[Cu_2L'Cl_2][ClO_4]_2 \cdot H_2O$ elemental analysis requires the inclusion of a molecule of MeOH. Since the i.r. spectrum shows a well-defined ν(N–H) vibration at 3 300 $cm^{-1}$, we believe that the molecule of MeOH has added across one of the C=N bonds of L (to give L').



SCHEME (*i*) $Ag[ClO_4]$, (*ii*) $Cu[ClO_4]_2 \cdot 6H_2O$, (*iii*) excess of $Cu[ClO_4]_2 \cdot 6H_2O$, (*iv*) imidazole, (*v*) $CuCl_2$, (*vi*) LiCl, (*vii*) $Na[N_3]$, (*viii*) Na[OH] or Na[OMe], (*ix*) $HClO_4$, (*x*) pyrazole, (*xi*) $Na[ClO_4] \cdot H_2O$, (*xii*) $Cu[ClO_4]_2 \cdot 6H_2O$, (*xiii*) $Cu[ClO_4]_2 \cdot 6H_2O$, (*xiv*) Na[NCS], (*xv*) $[Cu(NCMe)_4][ClO_4]$, (*xvi*) $Na[BPh_4]$

TABLE 1

Analytical, magnetic, and electrical conductance data for the copper complexes

| Complex | Analysis/% Found C | H | N | Metal | Calc. C | H | N | Metal | $\mu_{eff.}$[a]/B.M. 293 K | 93 K | Λ [b]/ S $cm^2$ $mol^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $[CuL][ClO_4]_2 \cdot H_2O$ | 43.4 | 5.3 | 10.2 | | 43.4 | 5.3 | 10.1 | | 1.95 | | 320 |
| $[CuL][BPh_4]_2$ | 74.8 | 6.8 | 6.9 | | 74.7 | 6.8 | 6.7 | | 1.70 | | 264 |
| $[Cu_2L][ClO_4]_4 \cdot 2H_2O$ | 32.0 | 4.3 | 7.3 | | 32.4 | 4.2 | 7.5 | | 1.95 | 1.90 | 463 |
| $[Cu_2L(OH)][ClO_4]_3 \cdot H_2O$ | 35.2 | 4.6 | 8.2 | 13.2 | 35.6 | 4.5 | 8.3 | 12.7 | 1.62 | 0.62 | 386 |
| $[Cu_2L(im)][ClO_4]_3$ | 37.4 | 4.5 | 10.3 | | 38.0 | 4.3 | 10.7 | | 1.84 | 1.81 | 354 |
| $[Cu_2L(Him)_2][ClO_4]_4 \cdot 2H_2O$ | 35.0 | 4.5 | 11.2 | | 34.7 | 4.3 | 11.2 | | | | |
| $[Cu_2L(Hpz)_2][ClO_4]_4 \cdot 2H_2O$ | 34.4 | 4.3 | 11.1 | | 34.2 | 4.5 | 11.1 | | 1.96 | 1.97 | 423 |
| $[Cu_2L(N_3)_3][ClO_4]$ | 39.9 | 4.9 | 23.4 | | 39.9 | 4.7 | 23.3 | | 1.88 | 1.74 | 163 |
| $[Cu_2L'Cl_2][ClO_4]_2 \cdot H_2O$ | 37.4 | 4.9 | 8.4 | 13.1 | 37.3 | 4.9 | 8.4 | 13.1 | 1.84 | 1.93 | 300 |
| $[Cu_2L(NCS)_2][ClO_4]_2 \cdot H_2O$ | 37.9 | 4.3 | 11.2 | | 38.0 | 4.4 | 11.1 | | 1.95 | 1.82 | 334 |
| $[Cu_2L][ClO_4]_2 \cdot H_2O$ | 40.1 | 4.8 | 9.2 | | 40.3 | 5.0 | 9.2 | | Diamagnetic | | 152 |
| $[CuNiL'Cl_2][ClO_4]_2 \cdot H_2O$ | 37.4 | 4.9 | 8.5 | 7.4 [c]<br>6.0 [d] | 37.5 | 4.9 | 8.6 | 6.4 [c]<br>5.9 [d] | 2.50 | 2.42 | |
| $[CuNiL(NCS)_3][ClO_4] \cdot 2H_2O$ | 41.1 | 4.9 | 12.8 | 6.8 [c]<br>5.5 [d] | 40.3 | 4.7 | 12.8 | 6.5 [c]<br>6.0 [d] | | | |

[a] Per Cu atom; corrected for diamagnetism of ligands. [b] For $10^{-3}$ mol $dm^{-3}$ solutions at 25 °C. [c] Cu analysis. [d] Ni analysis.

Treatment of $[Cu_2L][ClO_4]_4 \cdot 2H_2O$ with one equivalent of Na[OH] or Na[OMe] affords the complex $[Cu_2L(OH)][ClO_4]_3 \cdot H_2O$. The reaction is reversible since the tetraperchlorate is regenerated on treatment of the triperchlorate with one equivalent of $HClO_4$. It will be shown below from the results of an *X*-ray crystallographic analysis that in $[Cu_2L(OH)][ClO_4]_3 \cdot H_2O$ the two $Cu^{II}$ ions are intramolecularly linked *via* a single $OH^-$ group. The occurrence of the $OH^-$ group is reflected in a strong temperature dependent magnetic moment in the 90—300 K range. Application of the Bleaney–Powers equation[4] for coupled pairs of $Cu^{(II)}$ ions gave good agreement between measured and calculated susceptibilities for the exchange integral $J = -120$ $cm^{-1}$ (where $2J$ = singlet–triplet separation), $g = 2.1$, and $\chi_m = 60 \times 10^{-6}$ c.g.s. Retention of the intramolecular hydroxy bridge in MeCN solution may be inferred from the 3 : 1 electrolyte behaviour (Table 1).

Although proof is lacking it seems likely that one of the water molecules of $[Cu_2L][ClO_4]_4 \cdot 2H_2O$ is also located as a bridge between the two $Cu^{II}$ ions. This view is

TABLE 2

Infrared and electronic spectral data for the copper complexes

| Complex | I.r./cm$^{-1}$ $\nu$(OH) | $\nu$(NH) | $\nu$(C=N) | $\nu_{asym}$[a] | Electronic[b]/ $10^3$ cm$^{-1}$ |
|---|---|---|---|---|---|
| $[CuL][ClO_4]_2 \cdot H_2O$ | 3 600, 3 550 | | 1 640 | | 14.4 (78), 6.4 (58) |
| $[CuL][BPh_4]_2$ | | | 1 630 | | |
| $[Cu_2L][ClO_4]_4 \cdot 2H_2O$ | 3 500 | | 1 625 | | 15.4 (225), 8.0 (sh) |
| $[Cu_2L(OH)][ClO_4]_3 \cdot H_2O$ | 3 580, 3 440 | | 1 630 | | 14.4 (175), 7.7 (sh) |
| $[Cu_2L(im)][ClO_4]_3$ | | | 1 630 | | 14.5 (365) |
| $[Cu_2L(Him)_2][ClO_4]_4 \cdot 2H_2O$ | 3 450 | 3 360 | 1 625 | | |
| $[Cu_2L(N_3)_3][ClO_4]$ | | | 1 630 | 2 060[c]<br>2 040[d]<br>1 342[e] | 13.8 (500), 9.3 (sh) |
| $[Cu_2L'Cl_2][ClO_4]_2 \cdot H_2O$ | 3 500 | 3 300 | 1 630 | | 14.2 (175) |
| $[Cu_2L(NCS)_2][ClO_4]_2 \cdot H_2O$ | 3 450 | | 1 630 | 2 090 | 14.8 (240) |
| $[Cu_2L][ClO_4]_2 \cdot H_2O$ | 3 550 | | 1 630 | | 23.0 (sh), 16.8 (sh)[f] |
| $[CuNiL'Cl_2][ClO_4]_2 \cdot H_2O$ | 3 420 | 3 300 | 1 630 | | |
| $[CuNiL(NCS)_3][ClO_4] \cdot 2H_2O$ | 3 430 | | 1 630 | 2 070 | |

[a] $NCS^-$ or $N_3^-$. [b] $\varepsilon$ ($dm^3$ $mol^{-1}$ $cm^{-1}$) in parentheses; sh = shoulder. [c] Assigned to terminally bonded $N_3^-$. [d] Assigned to bridging $N_3^-$. [e] $\nu_{sym}$ vibration of terminal $N_3^-$. [f] Nujol mull transmittance spectrum.

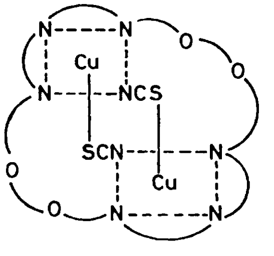
suggested not only by the matching stoicheiometry of the pair of complexes but also by the fact that the triperchlorate was often isolated from solutions of the tetraperchlorate containing no added base, an observation consistent with enhanced acidity of a water molecule as a result of co-ordination to two metal ions. When $[Cu_2L][ClO_4]_4 \cdot 2H_2O$ was treated with neutral imidazole (Him) in hot methanol, blue-green crystals of $[Cu_2L(im)][ClO_4]_3$ separated (im = imidazolate anion). Concentration of the filtrate subsequently yielded blue crystals of the complex $[Cu_2L(Him)_2][ClO_4]_4 \cdot 2H_2O$. A single-crystal *X*-ray diffraction analysis of the former complex (see below) shows that it contains an imidazolate bridge between the two Cu$^{II}$ ions. The complex is a 3 : 1 electrolyte in MeCN indicating that the imidazolate bridge is preserved on dissolution in this solvent. Magnetic susceptibility measurements provide no clear evidence for antiferromagnetic super-exchange, at least down to 93 K. The complex $[Cu_2L(Him)_2][ClO_4]_4 \cdot 2H_2O$ exhibits a $\nu$(N–H) vibration at 3 360 cm$^{-1}$ in the i.r. spectrum absent in the $\mu$-imidazolato-complex.

The use of neutral pyrazole (Hpz) in place of imidazole gave the complex $[Cu_2L(Hpz)_2][ClO_4]_4 \cdot 2H_2O$ which also showed a well defined N–H stretch in the i.r. at 3 300 cm$^{-1}$. Both this complex and $[Cu_2L(Him)_2][ClO_4]_4 \cdot 2H_2O$ presumably contain one neutral heterocyclic base bound to each Cu$^{II}$ ion in a terminal (non-bridging) mode. As is to be expected, $[Cu_2L(Hpz)_2][ClO_4]_4 \cdot 2H_2O$ is magnetically normal and is a 4 : 1 electrolyte in MeCN (Table 1). Attempts to prepare a $\mu$-pyrazolato-complex by treatment of $[Cu_2L(Hpz)_2][ClO_4]_4 \cdot 2H_2O$ with Na[OMe] gave only the mononuclear complex $[CuL][ClO_4]_2 \cdot H_2O$.

No pyrazine adducts were obtained on reaction of $[Cu_2L][ClO_4]_4 \cdot 2H_2O$ with pyrazine. Here the heterocyclic amine appears to function only as a non-co-ordinating base since the only product recovered was the $\mu$-hydroxo-complex. This behaviour contrasts with that of a bi-copper(II) complex of a closely related 24-membered macrocycle which does bind pyrazine intramolecularly.[5]

The structure of $[Cu_2L(N_3)_3][ClO_4]$ has been described in a preliminary communication.[3] Two of the three $N_3^-$ groups are terminally bonded, one to each of the two metal ions, to provide along with the two trimethine groups a square plane of nitrogen donors around each Cu$^{II}$ ion. The third $N_3^-$ group occurs as an axial bridge between the metal ions giving each an overall square-pyramidal co-ordination geometry. The oxygen atoms of the macrocycle are unco-ordinated. A small antiferromagnetic exchange interaction is suggested by magnetic susceptibility measurements in the temperature range 93—293 K. Once again, as judged by the 1 : 1 electrolyte behaviour, the 1,3-azido-bridge is preserved in MeCN solution.

In contrast to the single bridge in the azide the complex $[Cu_2L(NCS)_2][ClO_4]_2$ appears to contain two bridging $NCS^-$ groups. The $NCS^-$ asymmetric stretch occurs as a single band at 2 090 cm$^{-1}$, *i.e.* at a frequency associated with a bridging rather than a terminal mode. On the assumption that the bridges are intramolecular, a probable structure, shown by molecular models to be geometrically feasible, is as represented below. Slight splitting of the $\nu_4$ mode of $ClO_4^-$ at 625 cm$^{-1}$ in the i.r. spectrum suggests weak co-ordination of the $ClO_4^-$ groups. In MeCN the electrical conductance is at the high end of the range associated with 2 : 1 electrolytes. A slight temperature dependence of the magnetic moment was observed.



As mentioned above, the complex $[Cu_2L'Cl_2][ClO_4]_2 \cdot H_2O$ is thought to contain a modified macrocycle (L′) derived from L by addition of a molecule of MeOH across one C=N bond. The reason for the addition is unclear, and little can be said concerning the structure of this complex. A pair of bands at 365 cm$^{-1}$ and 350 cm$^{-1}$ in the i.r. may be due to the ν(Cu–Cl) vibrations. If this assignment is correct it would seem to rule out a di-μ-chloro-structure since this would be expected to absorb at a lower frequency.[6]

*Discussion of the Structures.*—In both (I) and (II) the two copper atoms are encapsulated within the 30-membered macrocycle and are bonded to the six nitrogen atoms. In (I), the copper ions are bridged by an imidazolate anion (Cu ··· Cu 5.99 Å) and in (II) by a single hydroxide ion (Cu ··· Cu 3.57 Å). The very different metal–metal separations clearly require very different conformations of the macrocycle. The high degree of flexibility of the macrocycle, apparent from the data in Table 3, can accommodate metal–metal distances ranging from 0.00 (in the mononuclear complexes [2] such as $[CuL]^{2+}$) to >6.0 Å. The macrocycle thus possesses a high potential versatility as a host for the insertion of bifunctional molecules and ions of varying size and shape.

TABLE 3

The different geometry of L in various metal complexes

| Cation | Distance between metal atoms/Å | Angle between trimethine units */° | Ref. |
|---|---|---|---|
| $[Pb_2L(SCN)_4]$ | 5.27 | 65.1 | 1 |
| $[Cu_2L(N_3)_3]^+$ | 6.02 | 40.6 | 2 |
| $[CoL]^{2+}$ |  | 81.1 | 4 |
| $[FeL]^{2+}$ |  | 80.0 | 4 |
| $[Cu_2L(im)]^{3+}$ | 5.99 | 40.0 | this work |
| $[Cu_2L(OH)]^{3+}$ | 3.57 | 79.1 | this work |

* In the binuclear complexes this angle represents the fold away from a planar macrocycle.

In Figure 1, the structure of the $[Cu_2L(im)]^{3+}$ cation is shown along with the macrocycle numbering scheme [(II) is numbered similarly]. The Cu–N(trimethine) bond lengths are 2.06(3), 1.90(2), 2.05(4) Å and 2.03(4), 2.01(2), 2.01(4) Å. These dimensions are unexceptional for this trimethine moiety bonded to Cu$^{II}$. Each Cu$^{II}$ ion is also strongly bonded to a nitrogen atom of the bridging imidazolate anion [1.92(2), 1.98(2) Å]. The geometry about each Cu$^{II}$ ion is thus square planar with the imidazolate nitrogen *trans* to the pyridine nitrogen. The metal ions are not displaced by any significant amount from the $N_4$ planes. The angles between the imidazolate anion plane and the $N_4$ planes containing the trimethine segments are 68.8, 79.1°. This is in contrast to the angles of *ca.* 90° found in the μ-imidazolato-bi-copper(II) complex of a closely related 24-membered macrocycle.[5]

In axial positions to the $N_4$ square planes lie the oxygen atoms of the perchlorate anions. There are two short bonds, Cu(1) ··· O(11) 2.46(3), Cu(2) ··· O(12*) 2.39(3) Å, and weaker bonds to the disordered perchlorate, Cu(2) ··· O(64**) 2.67(5), Cu(1) ··· O(61) 2.67(6), Cu(1) ··· O(65) 2.73(6), Cu(2) ··· O(67**) 2.52(5) Å. These contacts, particularly the former two, are quite short for axial Cu–O(perchlorate) bonds and lead to a polymeric chain along *y*, shown in Figure 2 where the macrocycle is omitted for clarity. In view of the relatively strongly bound perchlorate it is perhaps surprising that the perchlorate anion around Cl(6) is disordered. This chain formation may be the cause of the disorder in the third perchlorate ion, which occupies two sites each with 50% occupancy, in that it is unable to form even a weak (but stabilising) association with the metal ion as has been found in several structures. The conformation of the macrocycle in (I) is illustrated by the torsion angles in Table 4 which are similar to those found in the μ-azido-complex.

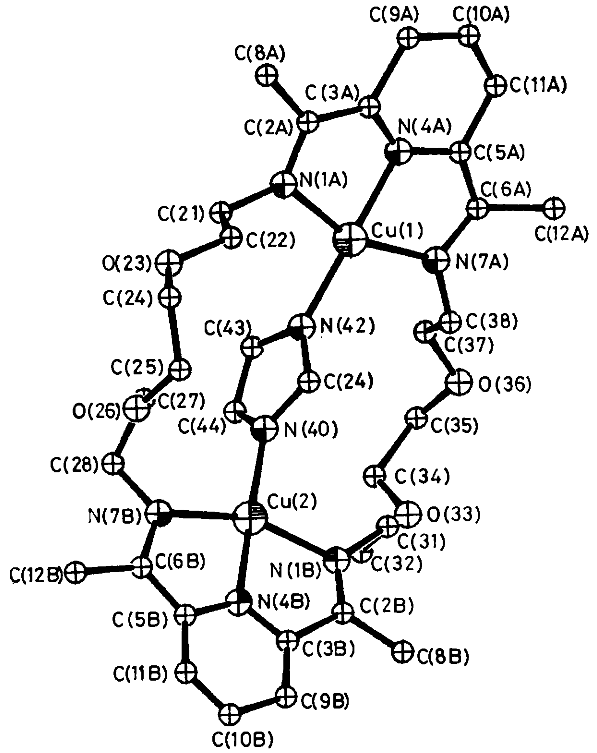


FIGURE 1 The $[Cu_2L(im)]^{3+}$ moiety in (I). Bridging perchlorates are omitted for clarity

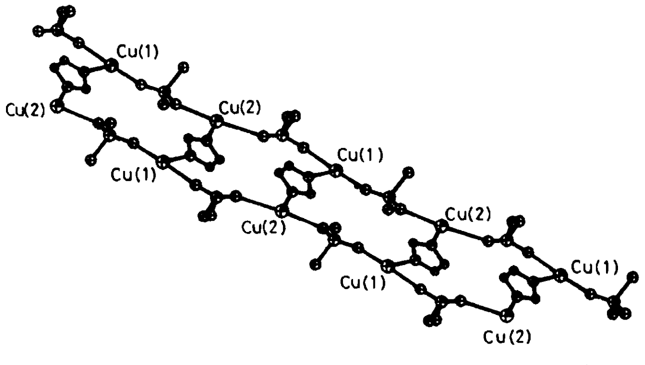


FIGURE 2 Polymeric chains of formula $[\{Cu_2L(im)(ClO_4)_2\}_n]^{n+}$ found in (I). Macrocycle atoms are omitted for clarity

Each metal atom in (II) is also bonded to the three

TABLE 4

Torsion angles(°) in (I) and (II)

| | (I) | | (II) | |
|---|---|---|---|---|
| | $n = 2$ | $n = 3$ | $n = 2$ | $n = 3$ |
| C(2)–N(1)–C($n$1)–C($n$2) | 114.1 | −94.7 | 92.0 | −94.6 |
| N(1)–C($n$1)–C($n$2)–O($n$3) | −70.6 | 157.7 | 76.4 | 78.7 |
| C($n$1)–C($n$2)–O($n$3)–C($n$4) | 158.4 | 149.5 | −166.2 | 85.6 |
| C($n$2)–O($n$3)–C($n$4)–C($n$5) | 80.2 | −95.0 | 84.3 | −177.0 |
| O($n$3)–C($n$4)–C($n$5)–O($n$6) | −62.2 | −29.0 | 79.7 | 60.6 |
| C($n$4)–C($n$5)–O($n$6)–C($n$7) | −89.8 | 148.6 | −77.7 | 161.2 |
| C($n$5)–O($n$6)–C($n$7)–C($n$8) | 172.0 | −123.7 | 131.2 | −177.2 |
| O($n$6)–C($n$7)–C($n$8)–N(7) | 178.1 | 171.0 | −59.3 | 81.2 |
| C($n$7)–C($n$8)–N(7)–C(6) | −81.8 | 96.0 | 102.3 | 107.3 |

nitrogens of the trimethine units at similar distances to those of (I), namely 2.039(11), 1.907(16), 2.060(9), and 2.076(14), 1.925(12), 2.059(14) Å. The oxygen atom of the hydroxide anion completes the square planes at 1.866(13), 1.912(10) Å. In view of the standard deviations we do not consider the difference in Cu–O bond length to be significant. The Cu–O–Cu angle is 141.7(7)°.

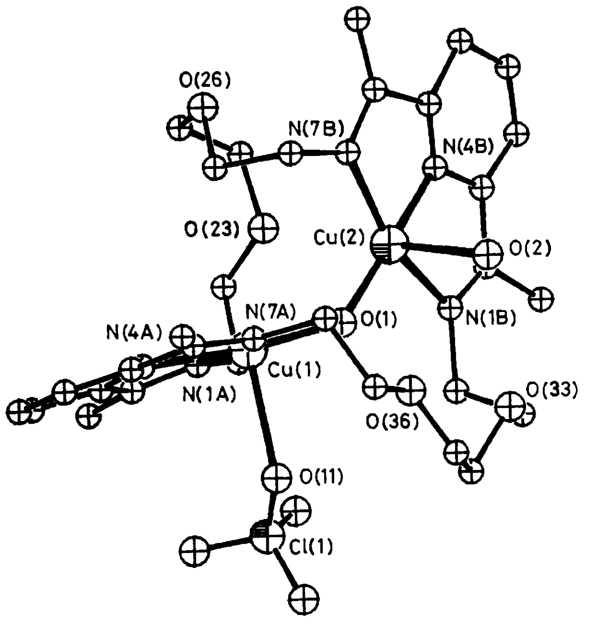


FIGURE 3 The structure of (II), $[Cu_2L(OH)(ClO_4)(OH_2)]^{2+}$. Carbon atoms are numbered in an equivalent manner to those of (I) in Figure 1

As shown in Figure 3, Cu(1) is axially bonded to a perchlorate oxygen O(11) at 2.48(2) Å while Cu(2) is axially bonded to a water molecule O(2) at 2.45(2) Å. The other axial positions are blocked by the polyether chain of the macrocycle. The short Cu ··· Cu distance in (II) causes the angle of fold (79.1°) to be much larger than in (I) where it is only 40.0° (Table 3). The large angle of fold in (II) ensures that the polyether chain will occupy space *trans* to the strongly bound oxygen on Cu(2). In fact, one of the ether oxygens O(23) lies 2.74 Å above Cu(2) and may be considered to be very weakly bonded. Despite the disparity in axial Cu–O bond lengths the metal atoms are not significantly displaced from the equatorial ' $N_3O$ ' plane towards the more strongly bound oxygen. There are two other perchlorate anions in the unit cell of (II) but neither are bonded to the anion. It is thus surprising that they are relatively ordered. There are no short contacts less than the sum of van der Waals radii in either structure.

It may be noted that in both (I) and (II) the bridging unit (im or $OH^-$) occupies an equatorial position, *trans* to the pyridine nitrogen, with respect to the co-ordination square planes. This contrasts with the situation in $[Cu_2L(N_3)_3][ClO_4]$ where the terminally bonded $N_3^-$ groups complete the square planes and the bridging $N_3^-$ group occupies the common axial position.[3] The reason for the variation in bridging position probably lies in the preference of the $Cu^{II}$ ion for tetragonal (five- or six-co-ordinate) geometries comprising four strongly bound equatorial ligands and one or two weakly bound axial ligands. Since in all the complexes under discussion three of the equatorial sites are always occupied by the powerfully co-ordinating trimethine group of the macrocycle, the fourth position will be taken up by the most strongly bonding ligand available. In (I) and (II) these are $im^-$ and $OH^-$ respectively, whereas in $[Cu_2L(N_3)_3][ClO_4]$ it is the terminal $N_3^-$ group, the more weakly bonding bridging $N_3^-$ group being forced into the axial position [compare the Cu–N(terminal) and Cu–N(bridging) bond lengths, 1.93(2), 1.94(3) *vs.* 2.25(2), 2.20(3) Å]. It may be that the availability of only one equatorial position is also the reason for the occurrence of a single $OH^-$ bridge.

While there are numerous examples of di-μ-hydroxo-bi-copper(II) complexes, which for the most part contain slightly longer (1.96—2.00 Å) Cu–O bonds,[7] copper(II) complexes containing a single hydroxy-bridge are rare.[8-10] Recent examples for which $X$-ray structures are available are $[(bipy)_2Cu\text{–}O(H)\text{–}Cu(bipy)_2][ClO_4]_3$ (III),[9] where bipy is 2,2′-bipyridine, and the complex $[Cu_2(em)(OH)][BF_4]_3$ (IV),[10] where em is the binucleating ' ear-muff ' ligand 1,4-bis(1-oxa-4,10-dithia-7-azacyclododecan-7-ylmethyl)benzene. In (III) the co-ordination geometry is approximately trigonal bipyramidal; the bridging $OH^-$ group is sited equatorially and the Cu–O–Cu bridge angle is 141.6(3)°, *i.e.* the same as in (II). In (IV) the co-ordination geometry is approximately square pyramidal with the bridging $OH^-$ group positioned in the basal plane, the Cu–O–Cu angle being 132.2(4)°.

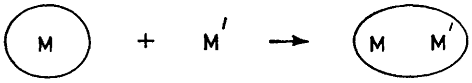
Since crystallographic details are now available for three monohydroxo-bridged bi-copper(II) complexes it is of interest to try to relate the extent of antiferromagnetic interaction to structure. Previous studies on dihydroxo-bridged complexes have indicated a linear relationship between the Cu–O–Cu bridge angle and the magnitude of the magnetic exchange parameter $J$ (in the spin Hamiltonian $\mathscr{H} = -2J\hat{S}_1 . \hat{S}_2$].[11] A moderately strong interaction ($J = -120$ cm$^{-1}$) between the copper(II) centres in (II) is observed in the present study. This compares to $J$ values of $-161$ for (III) [9] and $-410$ cm$^{-1}$ for (IV).[10] Since both (II) and (III) have the same Cu–O–Cu bridge angle, the reason for the difference in $J$ must lie elsewhere. The most obvious difference between the two complexes is in the electronic ground state, $d_{x^2-y^2}$ in (II) and $d_{z^2}$ in (III). However, on these considerations it might have been expected that (II) would exhibit the greater interaction since in (II), but not in (III), the singly occupied orbitals, one on each copper(II) centre, are more favourably positioned to overlap directly ($\sigma$ fashion) with orbitals of the bridging group.[9]

Comparing (II) and (IV) both of which have similar co-ordination geometries (distorted square pyramidal), and therefore $d_{x^2-y^2}$ ground states, there is again difficulty in accounting for the large difference in $J$. The difference (*ca.* 9°) in Cu–O–Cu bond angle is not large, and unlike the di-$\mu$-hydroxo-systems,[11] the results show that an increase in bridge angle is accompanied by a decreased interaction. It is clear that studies on a wider range of monohydroxo-bridged systems are needed. It may be that the spin–spin interaction is as sensitive to the nature of the non-bridging ligands as to geometrical factors.

The other internally bridged complexes described in the present study exhibit a much smaller temperature dependence of the magnetic moment in the range 93—293 K. For the im-bridged complex $[Cu_2L(im)][ClO_4]_3$ the magnetic susceptibility measurements have been extended down to 4.2 K by Professor Jan Reedijk of the State University Leiden to give $J = -21.0$ cm$^{-1}$. Almost exactly the same value ($J = -21.2$ cm$^{-1}$) was obtained for the analogous im-bridged bi-copper(II) complex of a closely related '$N_6S_2$' Schiff-base macrocycle. The two complexes have very similar structures, the only significant difference being that in the latter[5] the plane of the imidazolate ring and the $CuN_4$ co-ordination planes intersect at 90.4 compared to 68.8, 79.1° in (I). In other $Cu^{II}\cdots im\cdots Cu^{II}$ bridged complexes[12] (of non-macrocyclic ligands) in which the im ring is coplanar with the $CuN_4$ square plane, substantially larger coupling constants have been observed, and it has been speculated that there may be a dependence of the magnitude of $J$ on the orientation of the plane of the bridging imidazolate ring. However, the present results do not lend support to this idea.[13]

While an accurate determination of $J$ for the $\mu$-azido-complex $[Cu_2L(N_3)_3][ClO_4]$ must await measurements at lower temperatures it is clear that the coupling is relatively small (Table 1). It is of interest to compare the magnetic properties of this complex with the diamagnetism of a di-$\mu$-azido-derivative of a bi-copper(II) cryptand complex in which the bridging $N_3^-$ ions are strongly bonded [Cu-N 1.944(3), 2.013(3) Å] in equatorial positions of a tetragonally distorted octahedron.[14] Since in both cases the unpaired electron resides in the $d_{x^2-y^2}$ orbital, the strong coupling in the di-$\mu$-azido-complex can be related to the positioning of the bridging anions in the $xy$ planes (see discussion above).

*Attempts to prepare Heterobinuclear Complexes.*—It has been noted that the mononuclear complex ion $[CuL]^{2+}$ may be converted to binuclear complexes simply by treatment with an excess of free $Cu^{2+}$ ion in solution. This is in contrast to other mononuclear systems $[ML]^{2+}$ (M = low-spin $Fe^{II}$, low-spin $Co^{II}$, and $Ni^{II}$) for which there is substantial crystal-field stabilisation.[2] The facile 'unwrapping' of the macrocycle in $[CuL]^{2+}$ to accommodate a second $Cu^{2+}$ ion suggested experiments in which $[CuL]^{2+}$ is treated with a different metal ion with the aim of preparing heterobinuclear complexes (see below).



A heterobinuclear complex of interest would be one containing $Cu^{II}$ and $Zn^{II}$ bridged by the imidazolate anion, since this structural unit is believed to occur in superoxide dismutase.[15] However it was found, surprisingly, that the only product isolated from the reaction of $[CuL][ClO_4]_2\cdot H_2O$ with $ZnCl_2$ was the complex $[Cu_2L'Cl_2][ClO_4]_2\cdot H_2O$ referred to above. However, treatment of $[CuL][ClO_4]_2\cdot H_2O$ with a four-fold excess of $NiCl_2\cdot 6H_2O$ gave bottle green crystals in *ca.* 50% yield along with small amounts of $[NiL][ClO_4]_2\cdot H_2O$ and unreacted $[CuL][ClO_4]_2\cdot H_2O$. The i.r. spectrum of the green product was very similar (although not identical) to that of $[Cu_2L'Cl_2][ClO_4]_2\cdot H_2O$ and included a $\nu$(N–H) vibration at 3 300 cm$^{-1}$. Analytical data for Cu and Ni as well as C, H, and N (Table 1) are consistent with the formulation $[CuNiL'Cl_2][ClO_4]_2\cdot H_2O$. The observed average magnetic moments per metal assuming this formula are 2.50 and 2.42 B.M.* at 293 and 93 K respectively. The value at 293 K of 2.50 B.M. may be compared with the value of 2.52 B.M. calculated assuming equal numbers of $Cu^{II}$ and $Ni^{II}$ ions of moments 1.84 and 3.05 B.M., respectively. Although the possibility that the product is a mixture of the known complex $[Cu_2L'Cl_2][ClO_4]_2\cdot H_2O$ and a corresponding bi-nickel(II) complex cannot be excluded, we believe that it is a genuine heterobinuclear complex since treatment of $[NiL][ClO_4]_2\cdot H_2O$ with excess of $NiCl_2\cdot 6H_2O$ under the same reaction conditions led only to recovery of the unreacted mononuclear complex; and treatment of $[Cu_2L][ClO_4]_4\cdot 2H_2O$ with the same reagent gave only $[Cu_2L'Cl_2][ClO_4]_2\cdot H_2O$.

Similarly, treatment of $[CuL][ClO_4]_2\cdot H_2O$ with $Ni[NCS]_2\cdot 2H_2O$ gave green crystals of a product analysing (C, H, N, Cu, Ni) for $[CuNiL(NCS)_3][ClO_4]\cdot H_2O$. The i.r. spectrum is very similar to that of the complex $[Cu_2L(NCS)_2][ClO_4]_2\cdot H_2O$ although the $\nu_{asym}$(NCS) vibration now occurs at 2 070 cm$^{-1}$ rather than 2 090 cm$^{-1}$, suggesting that all three NCS groups may be terminally bonded. The $\nu_4$ vibration of the $ClO_4^-$ group is split. Insufficient information is available for a structure to be assigned. However, a difference electronic spectrum of the mixed-metal complex (0.008 mol dm$^{-3}$ in NCMe) measured against a reference solution 0.004 mol dm$^{-3}$ in $[Cu_2L(NCS)_2][ClO_4]_2\cdot H_2O$ showed a maximum at 11 800 cm$^{-1}$ of approximate absorption coefficient 50 dm$^3$ mol$^{-1}$ cm$^{-1}$, a result consistent with a six-co-ordinate geometry for the $Ni^{II}$ ion. As with the earlier case, support for the view that this product is a genuine hetero-binuclear

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* Throughout this paper: 1 B.M. = $9.274 \times 10^{-24}$ A m$^2$.

complex is found in the fact that no bi-nickel(II) species could be isolated from treatment of $[NiL][ClO_4]_2\cdot H_2O$ with $Ni[NCS]_2\cdot 2H_2O$.

*The Bi-copper*(I) *Complex.*—As indicated in the Scheme the dark brown bi-copper(I) complex $[Cu_2L][ClO_4]_2\cdot H_2O$ may be prepared either by direct transmetallation reaction of $[Pb_2L(SCN)_2][ClO_4]_2\cdot H_2O$ with $[Cu(NCMe)_4][ClO_4]$ or by the reduction of the bi-copper(II) complexes $[Cu_2L][ClO_4]_4\cdot 2H_2O$ or $[Cu_2L(OH)][ClO_4]_3\cdot H_2O$ using $Na[BPh_4]$. The latter method merits special note. Although often thought of as chemically inert to all but strong oxidising agents and strong protonic acids, a few cases are known where the $BPh_4^-$ ion is co-ordinated to,[16] weakly associated with,[17] or decomposed by [18] metal ions. We have recently reported [19] the reduction of a copper(II) complex of a macrocyclic '$N_3S_2$' Schiff-base ligand to the corresponding copper(I) complex by one equivalent of $Na[BPh_4]$ and the isolation of biphenyl as a reaction by-product. A mechanism involving nucleophilic attack of $Ph^-$ (or of $OMe^-$ generated from $Ph^-$ in methanol solution) at the imino-carbon, followed by electron transfer to the co-ordinated $Cu^{II}$ ion, was suggested. In the present case of the reduction of $[Cu_2L][ClO_4]_4\cdot 2H_2O$ by $Na[BPh_4]$, the stoicheiometry is also observed to be one $BPh_4^-$ to one $Cu^{II}$. When the reaction was carried out using one equivalent of $Na[BPh_4]$ per equivalent of bi-copper(II) complex, in an attempt to generate a mixed valence $Cu^I/Cu^{II}$ complex, a mixture of the bi-copper(I) complex and unreacted bi-copper(II) complex was obtained.

The complex $[Cu_2L][ClO_4]_2\cdot H_2O$ is diamagnetic and a mull electronic spectrum showed no absorption below *ca.* 16 000 cm$^{-1}$; strong bands at 23 000 and 16 800 cm$^{-1}$ may be due to copper(I)–trimethine charge-transfer transitions. The i.r. spectrum closely resembles those of the parent bi-copper(II) complexes. The broad $ClO_4^-$ $\nu_3$ band effectively masks the C–O–C stretching vibrations rendering it difficult to determine whether the macrocycle oxygen atoms are co-ordinated. The $ClO_4^-$ $\nu_4$ mode is considerably split suggesting the co-ordination of at least one of the perchlorate anions, perhaps in a bridging fashion. It may be significant in this regard that a $BPh_4^-$ salt could not be isolated and that the complex is a 1 : 1 electrolyte in MeCN.

Since we have shown that the macrocycle L [in its bi-copper(II) complexes] can bind both single-atom ($OH^-$) and three-atom ($N_3^-$, im) bridges between the metal centres, it should also accommodate to the insertion of (unhindered) diatomic bridges. The reaction of $[Cu_2L][ClO_4]_2\cdot H_2O$ with dioxygen was therefore briefly investigated. On exposure of an acetonitrile solution to air, the dark brown colour of the bi-copper(I) complex gradually turned to emerald green with separation of a small amount of an unidentified tan-coloured solid. Concentration of the green filtrate yielded crystals of the mononuclear copper(II) complex $[CuL][ClO_4]_2\cdot H_2O$. Thus it appears that one metal ion is rejected from the macrocycle cavity during the oxidation; the reason is not understood at this time. The behaviour of this complex with $O_2$ contrasts with that of the bi-copper(I) complex in its reduced (hydrogenated) derivative which reacts with $O_2$ *via* a series of $Cu^I_2/Cu^{II}_2$ cycles to generate dehydrogenated forms of the macrocycle along with water.[20] Attempts to isolate bi-copper(I) derivatives of L containing intramolecularly bridged species such as im, $NCS^-$, and 1,4-dithiane have not so far been successful.

## EXPERIMENTAL

*Preparation of the Complexes.*—$[CuL][ClO_4]_2\cdot H_2O$. To a solution of $[Ag_2L][ClO_4]_2\cdot H_2O$ (0.93 mmol) in MeOH (400 cm$^3$) was added a solution of $Cu[ClO_4]_2\cdot 6H_2O$ (1.3 mmol) in MeOH (20 cm$^3$). The emerald green solution so obtained was immediately concentrated to 30 cm$^3$ on a rotary evaporator. The product separated as emerald green crystals in 97% yield.

$[Cu_2L][ClO_4]_4\cdot 2H_2O$. Addition of solid $Cu[ClO_4]_2\cdot 6H_2O$ (2.9 mmol) to a refluxing methanolic solution of $[CuL][ClO_4]_2\cdot H_2O$ (9 mmol in 200 cm$^3$) followed by gentle reflux caused the colour to change gradually from green to blue-green. After 3 h, the solution was concentrated and cooled to give light blue crystals of product in 83% yield.

$[Cu_2L(OH)][ClO_4]_3\cdot H_2O$. A solution of $[Cu_2L][ClO_4]_4\cdot 2H_2O$ (0.18 mmol) in MeOH (350 cm$^3$) was slowly treated with a dilute solution of $Na[OH]$ or $Na[OMe]$ (0.2 mmol) in MeOH. An immediate blue to blue-green colour change was noted. The solution was refluxed for 10 min and then concentrated to *ca.* 90 cm$^3$ to give blue crystals of product in 55% yield. If a large excess of base is used a brown oily product is obtained.

$[Cu_2L(im)][ClO_4]_3$ and $[Cu_2L(Him)][ClO_4]_4\cdot 2H_2O$. To a solution of $[Cu_2L][ClO_4]_4\cdot 2H_2O$ (mmol) in hot MeOH (700 cm$^3$) was added solid imidazole (0.735 mmol). The solution quickly acquired a darker blue colour. After a 1 h reflux, the solution was rotary evaporated to *ca.* 100 cm$^3$ to give 0.22 g blue-green crystals of the $\mu$-imidazole complex. The dark blue filtrate was set aside to slowly concentrate. After 4 days, 0.07 g of royal blue crystals of the tetraperchlorate were recovered.

$[Cu_2L(Hpz)_2][ClO_4]_4\cdot 2H_2O$. Pyrazole (14.7 mmol) and $Cu[ClO_4]_2\cdot 6H_2O$ (8.1 mmol) were dissolved together in MeOH (20 cm$^3$). This solution was slowly added to a refluxing solution of $[Ag_2L][ClO_4]_2\cdot H_2O$ (0.61 mmol) in MeOH (400 cm$^3$). After gentle reflux for 30 min the solution was rotary evaporated to 100 cm$^3$ to give dark blue crystals of product in 65% yield.

$[Cu_2L(N_3)_3][ClO_4]$. A solution of $Na[N_3]$ (1.8 mmol) in MeOH (10 cm$^3$) was added to a solution of $[Cu_2L][ClO_4]_4\cdot 2H_2O$ (0.36 mmol) in MeOH (500 cm$^3$). An immediate colour change from light blue to dark green was observed. The mixture was refluxed for 10 min. Dark green crystals of product separated in 81% yield on cooling.

$[Cu_2L'Cl_2]][ClO_{42}\cdot H_2O$. This complex could be prepared either by treatment of a hot methanolic solution of $[CuL][ClO_4]_2\cdot H_2O$ with solid $CuCl_2$ or by addition of LiCl to a methanolic solution of $[Cu_2L][ClO_4]_4\cdot 2H_2O$. In each case the mixture was refluxed for *ca.* 1 h. On cooling, light blue crystals of product separated in *ca.* 70% yield.

$[Cu_2L(NCS)_2][ClO_4]_2\cdot H_2O$. This complex could be prepared by treatment of $[Pb_2L(SCN)_4]$ or $[Pb_2L(SCN)_2][ClO_4]_2\cdot H_2O$ with an excess of $Cu[ClO_4]_2\cdot 6H_2O$ in MeOH followed by 15 min reflux or by addition of $Na[NCS]$ (3.7 mmol) to a solution of $[Cu_2L][ClO_4]_4\cdot 3H_2O$ in MeOH (600

$cm^3$) followed by 20 min reflux. After removal of a small amount of tan-coloured material the product separated in *ca.* 80% yield on cooling.

$[CuNiL'Cl_2][ClO_4]_2\cdot H_2O$. To a solution of $[CuL][ClO_4]_2\cdot H_2O$ (0.72 mmol) in hot MeOH (300 $cm^3$) was added solid $NiCl_2\cdot 6H_2O$ (2.9 mmol). The mixture was heated to reflux for 5 h, then concentrated to 100 $cm^3$ by rotary evaporation. Bottle green crystalline rods of the mixed-metal product (0.33 g) separated. After removal of these crystals the filtrate was further concentrated to give small quantities of $[NiL][ClO_4]_2\cdot H_2O$ and $[CuL][ClO_4]_2\cdot H_2O$.

$[CuNiL(NCS)_3][ClO_4]\cdot 2H_2O$. To a solution of $[CuL][ClO_4]_2\cdot H_2O$ (0.6 g, 0.72 mmol) in hot MeOH (300 $cm^3$) was added solid $Ni[NCS]_2\cdot 2H_2O$ (0.3 g, 1.4 mmol). The mixture was refluxed for a few minutes before rotary evaporation to *ca.* 150 $cm^3$. A small amount of unreacted starting material was removed and the remaining dark green filtrate was set aside to give green crystals of the mixed-metal product.

$[Cu_2L][ClO_4]_2\cdot H_2O$. All operations were conducted in deoxygenated solvents under an atmosphere of $N_2$. To a solution of $[Pb_2L(SCN)_2][ClO_4]_2\cdot H_2O$ (1.2 mmol) in refluxing MeOH (950 $cm^3$) was added solid $[Cu(NCMe)_4][ClO_4]$ (6.1 mmol). The solution immediately changed to dark brown. A small amount of Cu[SCN] was filtered off and the brown solution rotary evaporated to 150 $cm^3$ to give the crystalline dark brown product in 50% yield. It was washed with oxygen-free methanol and dried *in vacuo*. An alternative method of preparation was to treat $[Cu_2L][ClO_4]_4\cdot 2H_2O$ or $[Cu_2L(OH)][ClO_4]_3\cdot H_2O$ (1.22 mmol) in refluxing MeOH (1 250 $cm^3$) with solid $Na[BPh_4]$ (2.6 mmol). The solution became dark brown within *ca.* 15 s. After refluxing for a further 30 s the solution was quickly rotary evaporated to *ca.* 120 $cm^3$ to give the product in 50% yield.

*Structures of* $[Cu_2L(im)][ClO_4]_3$ *and* $[Cu_2L(OH)][ClO_4]_3\cdot H_2O$.—*Crystal data.* $[Cu_2L(im)][ClO_4]_3$, (I). $C_{33}H_{45}Cl_3Cu_2N_8O_{16}$, $M = 1\ 042.8$, Triclinic, $a = 12.89(1)$, $b = 13.64(1)$, $c = 16.51(1)$ Å, $\alpha = 89.9(1)$, $\beta = 114.1(1)$, $\gamma = 121.8(1)^\circ$, $U = 2\ 167.1$ Å$^3$, $D_m = 1.60$, $Z = 2$, $D_c = 1.60$ g $cm^{-3}$, $\mu(\text{Mo-}K_\alpha) = 12.8$ $cm^{-1}$, $F(000) = 1\ 072$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å. Space group $P\bar{1}$ from the successful structure determination.

$[Cu_2L(OH)][ClO_4]_3\cdot H_2O$, (II). $C_{30}H_{45}Cl_3Cu_2N_6O_{18}$, $M = 1\ 018.8$, Triclinic, $a = 12.634(9)$, $b = 14.103(8)$, $c = 14.689(8)$ Å, $\alpha = 88.3(1)$, $\beta = 118.4(1)$, $\gamma = 115.6(1)^\circ$, $U = 2\ 009.2$ Å$^3$, $D_m = 1.63$, $Z = 2$, $D_c = 1.67$ g $cm^{-3}$, $F(000) = 1\ 040$, $\mu(\text{Mo-}K_\alpha) = 14.1$ $cm^{-1}$, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å. Space group $P\bar{1}$ from the successful structure determination.

Crystals of approximate size (0.1 × 0.9 × 0.5 mm) of (I) and (0.1 × 0.25 × 0.9 mm) of (II) were used. (I) was mounted with the (1 2 0) planes perpendicular to the instrument axis of a GE XRD 5 diffractometer which was used to measure reflections by the stationary-crystal–stationary-counter method and also to determine cell parameters by least-squares refinement of high-angle data. 2 843 Independent reflections were collected with $2\theta$ maximum of 35°; 1 567 reflections with $I > 2\sigma(I)$ were used in subsequent calculations. Crystals of (II) were mounted about the *b* axis on a Stoe STADI2 diffractometer and 5 219 reflections with $2\theta$ maximum of 45° were measured by $\omega$ scan with a scan speed of 0.033° $s^{-1}$ and a background count of 20 s. Of these, 2 786 with $I > 2\sigma(I)$ were used in subsequent calculations. Absorption and extinction corrections were not applied.

TABLE 5

Atomic co-ordinates (× $10^4$) for (I) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu(1) | 2 364(4) | 1 178(3) | 2 841(3) |
| Cu(2) | 7 141(4) | 3 538(3) | 6 688(3) |
| N(1A) | 559(26) | 320(22) | 2 935(18) |
| C(2A) | −520(38) | −626(32) | 2 225(24) |
| C(3A) | −232(33) | −780(27) | 1 521(21) |
| N(4A) | 1 027(28) | −11(22) | 1 689(17) |
| C(5A) | 1 492(32) | −45(27) | 1 139(22) |
| C(6A) | 2 972(40) | 941(34) | 1 474(28) |
| N(7A) | 3 560(28) | 1 629(24) | 2 202(19) |
| C(8A) | −1 887(39) | −1 388(34) | 2 154(27) |
| C(9A) | −1 176(36) | −1 740(29) | 732(22) |
| C(10A) | −759(34) | −1 800(28) | 162(22) |
| C(11A) | 593(36) | −959(29) | 334(23) |
| C(12A) | 3 606(38) | 964(32) | 930(25) |
| N(1B) | 8 713(30) | 4 470(24) | 6 374(21) |
| C(2B) | 9 989(46) | 4 920(35) | 7 086(30) |
| C(3B) | 9 980(36) | 4 607(28) | 7 890(23) |
| N(4B) | 8 806(27) | 4 052(21) | 7 908(16) |
| C(5B) | 8 504(33) | 3 601(26) | 8 557(21) |
| C(6B) | 7 075(35) | 2 947(28) | 8 317(24) |
| N(7B) | 6 222(29) | 2 839(23) | 7 468(19) |
| C(8B) | 11 330(55) | 5 470(45) | 7 033(34) |
| C(9B) | 11 206(44) | 4 878(34) | 8 795(28) |
| C(10B) | 10 946(49) | 4 475(38) | 9 432(32) |
| C(11B) | 9 755(39) | 3 877(31) | 9 452(26) |
| C(12B) | 6 618(47) | 2 509(40) | 9 003(27) |
| C(31) | 8 464(38) | 4 631(31) | 5 471(24) |
| C(32) | 8 574(49) | 5 680(40) | 5 378(31) |
| O(33) | 8 742(36) | 6 089(30) | 4 599(24) |
| C(34) | 7 840(64) | 6 309(51) | 4 087(41) |
| C(35) | 6 552(65) | 5 522(58) | 3 364(43) |
| O(36) | 6 417(42) | 4 780(37) | 2 812(28) |
| C(37) | 4 946(44) | 3 618(37) | 2 355(30) |
| C(38) | 4 981(39) | 2 612(32) | 2 616(26) |
| C(21) | 511(34) | 696(29) | 3 690(21) |
| C(22) | 1 300(35) | 453(28) | 4 551(22) |
| O(23) | 594(24) | −802(20) | 4 444(15) |
| C(24) | 1 477(41) | −1 122(35) | 4 967(26) |
| C(25) | 1 876(36) | −1 010(30) | 5 960(23) |
| O(26) | 2 666(23) | 193(20) | 6 448(15) |
| C(27) | 4 127(33) | 870(28) | 6 774(23) |
| C(28) | 4 740(36) | 2 102(31) | 7 137(25) |
| N(40) | 5 519(23) | 3 111(19) | 5 500(16) |
| C(41) | 4 771(34) | 2 298(30) | 4 731(23) |
| N(42) | 3 750(26) | 2 310(23) | 4 033(18) |
| C(43) | 3 886(31) | 3 238(27) | 4 381(21) |
| C(44) | 4 886(31) | 3 703(27) | 5 282(21) |
| Cl(6) | 1 468(15) | 3 517(12) | 2 092(8) |
| O(61) | 1 384(47) | 2 453(31) | 2 110(28) |
| O(62) | 2 323(53) | 4 251(44) | 1 689(38) |
| O(63) | 81(39) | 3 192(43) | 1 467(31) |
| O(64) | 1 993(44) | 4 172(35) | 2 954(22) |
| O(65) | 1 894(51) | 2 758(39) | 2 050(31) |
| O(66) | 695(57) | 3 612(49) | 1 307(28) |
| O(67) | 2 614(39) | 4 595(31) | 2 750(29) |
| O(68) | 570(59) | 2 910(53) | 2 559(43) |
| Cl(1) | 2 556(13) | −1 214(10) | 3 137(8) |
| O(11) | 2 984(20) | −139(19) | 3 577(13) |
| O(12) | 3 227(21) | −1 681(18) | 3 792(14) |
| O(13) | 1 031(36) | −2 014(29) | 2 826(22) |
| O(14) | 2 754(26) | −1 163(22) | 2 376(20) |
| Cl(4) | 6 533(52) | 832(44) | 981(37) |
| O(41) | 5 484(78) | 115(76) | 366(46) |
| O(42) | 7 760(94) | 835(75) | 1 083(58) |
| O(43) | 6 932(104) | 2 003(100) | 1 207(70) |
| O(44) | 6 696(109) | 706(95) | 1 656(80) |
| Cl(5) | 5 248(59) | 4 868(47) | −145(41) |
| O(51) | 4 031(66) | 4 538(54) | −612(44) |
| O(52) | 4 960(91) | 3 927(83) | 76(61) |
| O(53) | 5 417(111) | 4 448(98) | −831(75) |

*Structure determinations.* The positions of the copper atoms in (I) and (II) were obtained from the Patterson function and the positions of the remaining non-hydrogen

TABLE 6

Atomic co-ordinates (× $10^4$) for (II) with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Cu(1) | 513(2) | 1 713(1) | 2 743(1) |
| Cu(2) | −1 986(2) | 2 560(1) | 1 250(1) |
| O(1) | −898(9) | 2 054(7) | 2 344(7) |
| Cl(1) | 2 386(4) | 2 883(3) | 5 491(3) |
| O(11) | 1 274(10) | 1 910(8) | 4 652(8) |
| O(12) | 2 200(13) | 3 768(6) | 5 141(10) |
| O(13) | 2 364(12) | 2 762(9) | 6 444(8) |
| O(14) | 3 673(11) | 3 084(10) | 5 671(10) |
| Cl(4) | 7 543(5) | 3 047(3) | 6 437(3) |
| O(41) | 7 046(20) | 3 152(11) | 7 075(15) |
| O(42) | 7 306(16) | 3 664(10) | 5 659(10) |
| O(43) | 6 913(16) | 1 953(9) | 5 936(11) |
| O(44) | 8 943(18) | 3 472(17) | 7 042(14) |
| Cl(5) | 3 649(5) | 2 508(3) | 657(4) |
| O(51) | 4 047(21) | 1 953(15) | 177(16) |
| O(52) | 3 383(19) | 3 183(14) | −13(21) |
| O(53) | 2 473(17) | 1 800(15) | 650(19) |
| O(54) | 4 796(21) | 2 949(26) | 1 584(15) |
| N(1A) | 2 040(13) | 3 179(8) | 2 930(9) |
| C(2A) | 3 216(16) | 3 239(11) | 3 259(11) |
| C(3A) | 3 161(15) | 2 156(11) | 3 307(12) |
| N(4A) | 1 909(11) | 1 351(9) | 3 004(8) |
| C(5A) | 1 622(16) | 313(12) | 2 999(11) |
| C(6A) | 247(14) | −392(9) | 2 704(9) |
| N(7A) | −520(11) | 72(8) | 2 576(8) |
| C(8A) | 4 553(16) | 4 153(12) | 3 592(14) |
| C(9A) | 4 228(17) | 1 913(14) | 3 603(14) |
| C(10A) | 3 908(20) | 827(14) | 3 604(13) |
| C(11A) | 2 608(19) | 44(13) | 3 279(14) |
| C(12A) | −317(18) | −1 605(11) | 2 576(12) |
| C(21) | 1 893(17) | 4 140(11) | 2 833(12) |
| C(22) | 1 582(15) | 4 359(10) | 1 727(11) |
| O(23) | 206(10) | 3 665(7) | 976(7) |
| C(24) | −51(17) | 3 637(12) | −76(13) |
| C(25) | 221(18) | 2 866(13) | −521(15) |
| O(26) | −864(11) | 1 791(9) | −850(9) |
| C(27) | −787(20) | 1 281(13) | 41(15) |
| C(28) | −2 282(17) | 717(12) | −158(13) |
| N(1B) | −1 678(12) | 3 832(8) | 2 191(9) |
| C(2B) | −2 246(14) | 4 381(9) | 1 652(12) |
| C(3B) | −3 028(16) | 4 001(11) | 505(13) |
| N(4B) | −3 041(11) | 3 111(8) | 170(8) |
| C(5B) | −3 726(13) | 2 628(10) | −858(11) |
| C(6B) | −3 503(15) | 1 693(10) | −1 005(12) |
| N(7B) | −2 674(12) | 1 562(8) | −121(9) |
| C(8B) | −2 259(17) | 5 320(11) | 2 132(13) |
| C(9B) | −3 809(17) | 4 391(13) | −287(14) |
| C(10B) | −4 508(16) | 3 899(13) | −1 360(13) |
| C(11B) | −4 458(14) | 3 015(11) | −1 671(11) |
| C(12B) | −4 241(17) | 1 050(12) | −2 108(12) |
| C(31) | −996(16) | 4 085(11) | 3 355(11) |
| C(32) | −1 935(17) | 3 544(13) | 3 753(11) |
| O(33) | −2 378(11) | 2 424(9) | 3 666(8) |
| C(34) | −1 385(19) | 2 193(14) | 4 561(13) |
| C(35) | −1 919(19) | 1 018(13) | 4 355(13) |
| O(36) | −1 953(10) | 695(7) | 3 439(7) |
| C(37) | −2 005(16) | −336(11) | 3 349(12) |
| C(38) | −1 919(14) | −532(10) | 2 377(12) |
| O(2) | −3 914(11) | 1 322(8) | 1 449(9) |

atoms were obtained from Fourier maps. As usual, the perchlorate anions proved awkward. In (I), only one of the three perchlorates [that containing Cl(1)] was ordered. For the second perchlorate [containing Cl(2)] two tetrahedra were located in the difference-Fourier and each given an occupancy factor of 0.5 and refined as a rigid group. The third perchlorate could not at first be located at all but after all other atoms were refined, a difference-Fourier showed two regions of residual electron density. One [Cl(4) and environs] was considered to be a perchlorate of 50% occupancy and the other [Cl(5) and environs] to represent two perchlorates superimposed around the centre of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$ also with an occupancy of 0.5. In (II), the three independent anions had high thermal motion and were refined anisotropically but it did not prove necessary to postulate disorder.

In both (I) and (II), atoms in the macrocycle were refined anisotropically; hydrogen atoms were fixed in trigonal or tetrahedral positions at 1.08 Å from the carbon atoms. Their thermal parameters were set equivalent to those of the carbon atoms to which they were bonded. In (II), the hydroxide hydrogen atom could not be located. In both structures, refinement was carried out with parameters in two large blocks (one for the perchlorates, one for the cation). Final *R* values were 0.081, 0.084 respectively. Calculations were carried out using the 'SHELX-76' system [21] at the University of Manchester Computer Centre. Scatter-

TABLE 7

Molecular dimensions in (I) and (II), distances (Å) and angles (°)

(*a*) Geometry of the co-ordination sphere in (I)

| | | | |
|---|---|---|---|
| Cu(1)–O(11) | 2.461(29) | Cu(2)–N(1B) | 2.034(38) |
| Cu(1)–N(1A) | 2.057(34) | Cu(2)–N(4B) | 2.012(23) |
| Cu(1)–N(4A) | 1.900(22) | Cu(2)–N(7B) | 2.006(36) |
| Cu(1)–N(7A) | 2.049(40) | Cu(2)–N(40) | 1.984(22) |
| Cu(1)–N(42) | 1.919(22) | Cu(2)–O(12*) | 2.388(28) |
| Cu(1)–O(61) | 2.672(55) | Cu(2)–O(64**) | 2.673(48) |
| Cu(1)–O(65) | 2.727(60) | Cu(2)–O(67**) | 2.523(51) |
| O(11)–Cu(1)–N(1A) | 92.0(11) | N(1B)–Cu(2)–N(4B) | 78.7(12) |
| O(11)–Cu(1)–N(4A) | 93.0(11) | N(1B)–Cu(2)–N(7B) | 158.0(10) |
| N(1A)–Cu(1)–N(4A) | 77.2(13) | N(4B)–Cu(2)–N(7B) | 79.4(12) |
| O(11)–Cu(1)–N(7A) | 94.2(12) | N(1B)–Cu(2)–N(40) | 100.8(11) |
| N(1A)–Cu(1)–N(7A) | 156.5(9) | N(4B)–Cu(2)–N(40) | 177.1(12) |
| N(4A)–Cu(1)–N(7A) | 79.8(12) | N(7B)–Cu(2)–N(40) | 101.0(11) |
| O(11)–Cu(1)–N(42) | 83.3(11) | O(12*)–Cu(2)–N(40) | 89.5(10) |
| N(1A)–Cu(1)–N(42) | 103.4(13) | O(12*)–Cu(2)–N(1B) | 92.3(13) |
| N(4A)–Cu(1)–N(42) | 176.3(15) | O(12*)–Cu(2)–N(4B) | 93.3(11) |
| N(7A)–Cu(1)–N(42) | 99.9(12) | O(12*)–Cu(2)–N(7B) | 90.0(12) |

(*b*) Geometry of the co-ordination sphere in (II)

| | | | |
|---|---|---|---|
| Cu(1)–O(1) | 1.866(13) | Cu(2)–N(1B) | 2.076(14) |
| Cu(1)–N(1A) | 2.039(11) | Cu(2)–N(4B) | 1.925(12) |
| Cu(1)–N(4A) | 1.907(16) | Cu(2)–N(7B) | 2.059(14) |
| Cu(1)–N(7A) | 2.060(9) | Cu(2)–O(2) | 2.455(20) |
| Cu(1)–O(11) | 2.485(22) | Cu(2)–O(23) | 2.740(22) |
| Cu(2)–O(1) | 1.912(10) | | |
| O(1)–Cu(1)–N(1A) | 100.2(5) | O(1)–Cu(2)–N(1B) | 98.9(4) |
| O(1)–Cu(1)–N(4A) | 174.2(5) | O(1)–Cu(2)–N(4B) | 178.4(3) |
| N(1A)–Cu(1)–N(4A) | 79.1(5) | N(1B)–Cu(2)–N(4B) | 79.9(5) |
| O(1)–Cu(1)–N(7A) | 100.3(4) | O(1)–Cu(2)–N(7B) | 103.2(5) |
| N(1A)–Cu(1)–N(7A) | 158.9(6) | N(1B)–Cu(2)–N(7B) | 157.8(5) |
| N(4A)–Cu(1)–N(7A) | 80.0(5) | N(4B)–Cu(2)–N(7B) | 77.9(5) |
| N(7A)–Cu(1)–O(11) | 87.8(4) | O(1)–Cu(2)–O(2) | 87.2(4) |
| N(4A)–Cu(1)–O(11) | 89.3(5) | N(1B)–Cu(2)–O(2) | 90.1(5) |
| O(1)–Cu(1)–O(11) | 96.6(5) | N(4B)–Cu(2)–O(2) | 94.0(4) |
| N(1A)–Cu(1)–O(11) | 94.7(4) | N(7B)–Cu(2)–(O2) | 93.0(4) |

(*c*) Ligand dimensions in the two structures

| | (I) | (II) |
|---|---|---|
| N(1A)–C(2A) | 1.325(34) | 1.288(26) |
| N(1A)–C(21) | 1.38(5) | 1.439(23) |
| C(2A)–C(3A) | 1.40(6) | 1.500(24) |
| C(2A)–C(8A) | 1.45(6) | 1.457(20) |
| C(3A)–N(4A) | 1.286(44) | 1.341(18) |
| C(3A)–C(9A) | 1.388(40) | 1.40(3) |
| N(4A)–C(5A) | 1.29(6) | 1.346(20) |
| C(5A)–C(6A) | 1.481(46) | 1.419(22) |
| C(5A)–C(11A) | 1.375(41) | 1.33(3) |
| C(6A)–N(7A) | 1.19(5) | 1.329(24) |
| C(6A)–C(12A) | 1.43(8) | 1.519(18) |
| N(7A)–C(38) | 1.419(40) | 1.469(21) |
| C(9A)–C(10A) | 1.28(6) | 1.405(28) |
| C(10A)–C(11A) | 1.39(5) | 1.366(26) |
| N(1B)–C(2B) | 1.35(5) | 1.283(20) |
| N(1B)–C(31) | 1.43(5) | 1.467(18) |

Table 7 (*continued*)

| | (I) | (II) |
|---|---|---|
| C(2B)–C(3B) | 1.40(6) | 1.453(22) |
| C(2B)–C(8B) | 1.52(9) | 1.527(28) |
| C(3B)–N(4B) | 1.30(5) | 1.353(22) |
| C(3B)–C(9B) | 1.53(5) | 1.401(25) |
| N(4B)–C(5B) | 1.329(48) | 1.341(18) |
| C(5B)–C(6B) | 1.42(5) | 1.504(25) |
| C(5B)–C(11B) | 1.531(49) | 1.387(21) |
| C(6B)–N(7B) | 1.329(44) | 1.294(19) |
| C(6B)–C(12B) | 1.47(6) | 1.496(22) |
| N(7B)–C(28) | 1.444(49) | 1.485(27) |
| C(9B)–C(10B) | 1.24(7) | 1.399(27) |
| C(10B)–C(11B) | 1.32(7) | 1.376(29) |
| C(21)–C(22) | 1.53(5) | 1.536(23) |
| C(22)–O(23) | 1.421(42) | 1.402(14) |
| O(23)–C(24) | 1.40(6) | 1.418(23) |
| C(24)–C(25) | 1.49(5) | 1.52(3) |
| C(25)–O(26) | 1.398(41) | 1.425(17) |
| O(26)–C(27) | 1.426(44) | 1.458(25) |
| C(27)–C(28) | 1.42(5) | 1.57(3) |
| C(31)–C(32) | 1.38(7) | 1.508(29) |
| C(32)–O(33) | 1.45(6) | 1.417(21) |
| O(33)–C(34) | 1.31(9) | 1.471(22) |
| C(34)–C(35) | 1.36(3) | 1.471(22) |
| C(35)–O(36) | 1.25(10) | 1.408(27) |
| O(36)–C(37) | 1.532(47) | 1.433(21) |
| C(37)–C(38) | 1.46(7) | 1.525(29) |
| Cu(1)–N(1A)–C(2A) | 113.8(32) | 116.5(9) |
| Cu(1)–N(1A)–C(21) | 122.1(26) | 123.0(12) |
| C(2A)–N(1A)–C(21) | 124.1(35) | 120.1(11) |
| N(1A)–C(2A)–C(3A) | 113.4(35) | 112.1(11) |
| N(1A)–C(2A)–C(8A) | 123.6(45) | 131.8(16) |
| C(3A)–C(2A)–C(8A) | 122.9(28) | 116.1(17) |
| C(2A)–C(3A)–N(4A) | 114.9(26) | 113.3(16) |
| C(2A)–C(3A)–C(9A) | 123.9(33) | 127.8(13) |
| N(4A)–C(3A)–C(9A) | 121.0(42) | 118.9(15) |
| Cu(1)–N(4A)–C(3A) | 120.4(29) | 118.2(12) |
| Cu(1)–N(4A)–C(5A) | 115.9(19) | 117.8(11) |
| C(3A)–N(4A)–C(5A) | 123.5(26) | 123.6(16) |
| N(4A)–C(5A)–C(6A) | 113.8(30) | 113.9(17) |
| N(4A)–C(5A)–C(11A) | 118.1(31) | 119.6(14) |
| C(6A)–C(5A)–C(11A) | 128.1(44) | 126.5(15) |
| C(5A)–C(6A)–N(7A) | 116.7(48) | 116.1(12) |
| C(5A)–C(6A)–C(12A) | 118.4(33) | 122.5(17) |
| N(7A)–C(6A)–C(12A) | 124.9(35) | 121.4(14) |
| Cu(1)–N(7A)–C(6A) | 113.2(29) | 112.0(8) |
| Cu(1)–N(7A)–C(38) | 123.4(28) | 125.2(10) |
| C(6A)–N(7A)–C(38) | 123.2(44) | 122.8(10) |
| C(3A)–C(9A)–C(10A) | 117.5(33) | 116.5(18) |
| C(9A)–C(10A)–C(11A) | 121.6(29) | 121.7(23) |
| C(5A)–C(11A)–C(10A) | 118.3(43) | 119.7(18) |
| Cu(2)–N(1B)–C(2B) | 114.1(31) | 113.2(10) |
| Cu(2)–N(1B)–C(31) | 122.0(24) | 126.0(10) |
| C(2B)–N(1B)–C(31) | 123.9(39) | 120.7(15) |
| N(1B)–C(2B)–C(3B) | 114.1(43) | 116.0(15) |
| N(1B)–C(2B)–C(8B) | 126.4(45) | 124.6(14) |
| C(3B)–C(2B)–C(8B) | 118.1(41) | 119.1(14) |
| C(2B)–C(3B)–N(4B) | 118.0(35) | 114.2(14) |
| C(2B)–C(3B)–C(9B) | 128.2(41) | 129.6(18) |
| N(5B)–C(3B)–C(9B) | 113.7(36) | 116.1(14) |
| Cu(2)–N(4B)–C(3B) | 114.5(23) | 116.6(9) |
| Cu(2)–N(4B)–C(5B) | 114.6(21) | 120.3(11) |
| C(3B)–N(4B)–C(5B) | 129.8(30) | 123.1(13) |
| N(4B)–C(5B)–C(6B) | 115.1(29) | 111.7(13) |
| N(4B)–C(5B)–C(11B) | 114.8(33) | 122.7(15) |
| C(6B)–C(5B)–C(11B) | 130.1(35) | 125.4(14) |
| C(5B)–C(6B)–N(7B) | 115.9(37) | 113.0(13) |
| C(5B)–C(6B)–C(12B) | 120.7(32) | 117.9(13) |
| N(7B)–C(6B)–C(12B) | 123.3(38) | 129.0(16) |
| Cu(2)–N(7B)–C(6B) | 114.5(28) | 116.7(12) |
| Cu(2)–N(7B)–C(28) | 125.2(23) | 124.7(8) |
| C(6B)–N(7B)–C(28) | 119.6(34) | 118.6(13) |
| C(3B)–C(9B)–C(10B) | 117.3(45) | 120.9(19) |
| C(9B)–C(10B)–C(11B) | 129.7(46) | 121.1(16) |
| C(5B)–C(11B)–C(10B) | 114.3(39) | 115.9(15) |
| N(1A)–C(21)–C(22) | 111.5(41) | 109.5(15) |
| C(21)–C(22)–O(23) | 110.1(20) | 109.6(13) |
| C(22)–O(23)–C(24) | 113.0(24) | 111.8(13) |
| O(23)–C(24)–C(25) | 119.3(49) | 117.6(15) |

Table 7 (*continued*)

| | (I) | (II) |
|---|---|---|
| C(24)–C(25)–O(26) | 110.4(31) | 110.9(18) |
| C(25)–O(26)–C(27) | 116.9(37) | 112.4(11) |
| O(26)–C(27)–C(28) | 109.5(41) | 105.7(14) |
| N(7B)–C(28)–C(27) | 112.2(44) | 108.5(12) |
| N(1B)–C(31)–C(32) | 113.4(41) | 111.8(11) |
| C(31)–C(32)–O(33) | 117(5) | 113.6(18) |
| C(32)–O(33)–C(34) | 114(5) | 112.2(9) |
| O(33)–C(34)–C(35) | 127(6) | 107.2(11) |
| C(34)–C(35)–O(36) | 117(8) | 108.6(16) |
| C(35)–O(36)–C(37) | 112(5) | 113.9(12) |
| O(36)–C(37)–C(38) | 110.5(41) | 107.8(12) |
| N(7A)–C(38)–C(37) | 104.2(37) | 112.5(10) |

(*d*) Bridge dimensions in the two structures

In (I)

| | | | |
|---|---|---|---|
| N(40)–C(41) | 1.28(4) | N(42)–C(43) | 1.28(5) |
| N(40)–C(44) | 1.38(5) | C(43)–C(44) | 1.36(4) |
| C(41)–N(42) | 1.36(5) | | |
| Cu(2)–N(40)–C(41) | 134.4(31) | Cu(1)–N(42)–C(43) | 127.8(25) |
| Cu(2)–N(40)–C(44) | 126.3(19) | C(41)–N(42)–C(43) | 103.0(27) |
| C(41)–N(40)–C(44) | 99.3(28) | N(42)–C(43)–C(44) | 108.8(36) |
| N(40)–C(41)–N(42) | 118.0(42) | N(40)–C(44)–C(43) | 110.7(34) |
| Cu(1)–N(42)–C(41) | 129.1(29) | | |

In (II)

| | |
|---|---|
| Cu(1)–O(1)–Cu(2) | 141.7(7) |

(*e*) Perchlorate dimensions in the two structures

In (I)

| | | | |
|---|---|---|---|
| Cl(1)–O(11) | 1.34(1) | Cl(6)–O(67) | 1.39(3) |
| Cl(1)–O(12) | 1.46(2) | Cl(6)–O(68) | 1.53(8) |
| Cl(1)–O(13) | 1.49(2) | Cl(4)–O(41) | 1.14(6) |
| Cl(1)–O(14) | 1.37(2) | Cl(4)–O(42) | 1.52(15) |
| Cl(6)–O(61) | 1.40(5) | Cl(4)–O(43) | 1.39(15) |
| Cl(6)–O(62) | 1.45(6) | Cl(4)–O(44) | 1.08(14) |
| Cl(6)–O(63) | 1.46(5) | Cl(5)–O(51) | 1.24(9) |
| Cl(6)–O(64) | 1.37(4) | Cl(5)–O(52) | 1.24(13) |
| Cl(6)–O(65) | 1.42(7) | Cl(5)–O(53) | 1.41(18) |
| Cl(6)–O(66) | 1.33(5) | Cl(5)–O(51***) | 1.16(8) |
| O(61)–Cl(6)–O(62) | 111.3(42) | O(12)–Cl(1)–O(14) | 113.4(23) |
| O(61)–Cl(6)–O(63) | 107.4(29) | O(13)–Cl(1)–O(14) | 108.8(18) |
| O(62)–Cl(6)–O(63) | 105.1(32) | O(41)–Cl(4)–O(42) | 116(8) |
| O(61)–Cl(6)–O(64) | 111.8(29) | O(41)–Cl(4)–O(43) | 121(9) |
| O(62)–Cl(6)–O(64) | 108.8(27) | O(42)–Cl(4)–O(43) | 110(6) |
| O(63)–Cl(6)–O(64) | 112.2(38) | O(41)–Cl(4)–O(44) | 117(7) |
| O(65)–Cl(6)–O(66) | 118.8(39) | O(42)–Cl(4)–O(44) | 93(10) |
| O(65)–Cl(6)–O(67) | 108.1(29) | O(43)–Cl(4)–O(44) | 95(9) |
| O(66)–Cl(6)–O(67) | 115.5(31) | O(51)–Cl(5)–O(52) | 96(5) |
| O(65)–Cl(6)–O(68) | 101.5(40) | O(51)–Cl(5)–O(53) | 99(7) |
| O(66)–Cl(6)–O(68) | 107.4(40) | O(52)–Cl(5)–O(53) | 88(9) |
| O(67)–Cl(6)–O(68) | 103.6(31) | O(51)–Cl(5)–O(51***) | 124(10) |
| O(11)–Cl(1)–O(12) | 109.4(14) | O(52)–Cl(5)–O(51***) | 94(7) |
| O(11)–Cl(1)–O(13) | 105.2(25) | O(53)–Cl(5)–O(51***) | 136(9) |
| O(12)–Cl(1)–O(13) | 108.0(19) | Cu(1)–O(11)–Cl(1) | 125.4(12) |
| O(11)–Cl(1)–O(14) | 111.7(17) | Cu(2)–O(12*)–Cl(1*) | 125.4(12) |

In (II)

| | | | |
|---|---|---|---|
| Cl(1)–O(11) | 1.471(9) | Cl(4)–O(43) | 1.416(13) |
| Cl(1)–O(12) | 1.406(14) | Cl(4)–O(44) | 1.377(19) |
| Cl(1)–O(13) | 1.416(14) | Cl(5)–O(51) | 1.44(3) |
| Cl(1)–O(14) | 1.412(17) | Cl(5)–O(52) | 1.376(25) |
| Cl(4)–O(41) | 1.394(29) | Cl(5)–O(53) | 1.382(23) |
| Cl(4)–O(42) | 1.412(15) | Cl(5)–O(54) | 1.317(16) |
| O(11)–Cl(1)–O(12) | 108.0(6) | O(42)–Cl(4)–O(44) | 105.5(11) |
| O(11)–Cl(1)–O(13) | 109.7(6) | O(43)–Cl(4)–O(44) | 111.1(14) |
| O(12)–Cl(1)–O(13) | 111.4(10) | O(51)–Cl(5)–O(52) | 102.1(16) |
| O(11)–Cl(1)–O(14) | 111.3(9) | O(51)–Cl(5)–O(53) | 111.2(13) |
| O(12)–Cl(1)–O(14) | 106.9(9) | O(52)–Cl(5)–O(53) | 109.8(13) |
| O(13)–Cl(1)–O(14) | 109.6(8) | O(51)–Cl(5)–O(54) | 97.5(18) |
| O(41)–Cl(4)–O(42) | 110.4(12) | O(52)–Cl(5)–O(54) | 117.0(16) |
| O(41)–Cl(4)–O(43) | 110.6(10) | O(53)–Cl(5)–O(54) | 117.3(15) |
| O(42)–Cl(4)–O(43) | 109.5(8) | Cu(1)–O(11)–Cl(1) | 125.7(7) |
| O(41)–Cl(4)–O(44) | 109.6(12) | | |

Atoms marked with asterisks refer to the following equivalent positions relative to the $x$, $y$, $z$ set in Tables 1 and 2

| | |
|---|---|
| * | $1 - X, -Y, 1 - Z$ |
| ** | $1 - X, -Y, 1 - Z$ |
| *** | $1 - X, 1 - Y, 1 - Z$ |

ing factors and dispersion corrections were taken from international tables.[22]

The weighting schemes were chosen to give similar values of $w\Delta^2$ over ranges of $(\sin\theta)/\lambda$ and $F_o$. In (I) it was $w^{\frac{1}{2}} = 1$ for $F < 100$ and $w^{\frac{1}{2}} = 100/F$ for $F > 100$. In (II), $w = [\sigma^2(F) + 0.002I^2]$. The difference Fourier maps showed no significant peaks. Zero weighted reflections showed no serious discrepancies. Atomic co-ordinates for (I) and (II) are given in Tables 5 and 6; molecular dimensions in Table 7. Anisotropic thermal parameters, hydrogen-atom positions, and structure factor tables are given in the Supplementary Publication No. SUP 23075 (24 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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