Studies involving Nitrogen–Oxygen Donor Macrocyclic Ligands. Interaction of Copper(II) with New O_2N_3-Donor Macrocycles and the *X*-Ray Analysis of Aqua(1,12,16-triaza-3,4:9,10-dibenzo-5,8-dioxacyclo-octadecane)copper(II) Diperchlorate Hydrate †

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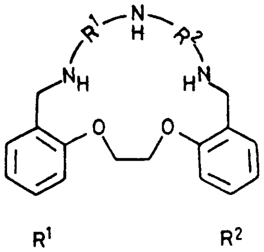
The interaction of Cu^{2+} with three new O_2N_3-donor macrocycles has been investigated. Complexes of the type $CuL(ClO_4)_2.nH_2O$ and $CuLX(ClO_4).nH_2O$ (where L = macrocycle, X = Cl or Br, and n = 0, 1, or 2) have been isolated. Conductance studies indicate that the halide ions in the latter complexes are co-ordinated in dimethyl sulphoxide. All complexes show the expected magnetic moments for Cu^{2+} with $S = \frac{1}{2}$. Potentiometric titration studies in 95% methanol (I = 0.1 mol dm^{-3}, $[NMe_4]Cl$) indicate that the following equilibria involving Cu^{2+} occur: $Cu^{2+} + L \rightleftharpoons CuL^{2+}$ and $Cu^{2+} + HL^+ \rightleftharpoons Cu(HL)^{3+}$ and the respective formation constants have been determined. The *X*-ray structure of $[CuL^3(OH_2)][ClO_4]_2{\cdot}H_2O$ indicates that this complex has a pseudo-square-planar co-ordination geometry with the co-ordination sphere consisting of the three nitrogen atoms of the macrocycle [Cu–N, 1.97(3)—2.07(2) Å] together with an oxygen from water [Cu–O, 1.96(2) Å]. The ether oxygen donors of the macrocycle do not co-ordinate. Crystals are monoclinic, with space group $P2_1/c$, a = 16.856(7), b = 10.717(4), c = 16.738(18) Å, β = 110.59(5)°, and Z = 4, R being 0.12 for 1 044 ' observed ' reflections.

THE interaction of crown polyethers with non-transition-metal ions has been studied extensively since the inherent selectivity of this ligand type has implications for a number of areas, including: the mechanisms of biological transport across membranes, the solubilisation of inorganic salts in non-polar solvents for use in organic reactions, the development of cation selective electrodes as well as a number of potential other analytical and therapeutic applications.[1-3] Although their interaction with transition metals has also received some attention, these macrocycles show general low affinity for such ions.[4] Incorporation of nitrogen-donor atoms in the macrocycle to produce rings containing mixed oxygen–nitrogen donor sets has been demonstrated to increase the affinity for transition-metal ions.[5-9]

As part of a continuing investigation of the co-ordination chemistry of mixed oxygen–nitrogen donor macrocycles and their potential for metal-ion recognition,[8-10] we now report a study of the interaction of copper(II) with the new macrocycles L^1—L^3.



	R^1	R^2
L^1	$-CH_2CH_2-$	$-CH_2CH_2-$
L^2	$-CH(CH_3)CH_2-$	$-CH_2CH(CH_3)-$
L^3	$-CH_2CH_2-$	$-CH_2CH_2CH_2-$

EXPERIMENTAL

The ligand protonation constants and complex stability constants were obtained by potentiometric titration under identical conditions to those described previously.[10] The apparatus was calibrated daily to yield E_0 and pK_w values for the system by titration of a solution containing HCl (4.00 × 10^{-3} mol dm^{-3}) and $[NMe_4]Cl$ (0.1 mol dm^{-3}; Fluka, puriss which had previously been recrystallised from a methanol–acetone mixture) with standardised $[NMe_4][OH]$ (0.1 mol dm^{-3}) in 95% methanol. The tetramethylammonium hydroxide was prepared by the literature procedure.[11] The free ligands or metal complexes were dissolved in 95% methanol which was 5.00 × 10^{-3} mol dm^{-3} in HCl (I = 0.1 mol dm^{-3}, $[NMe_4]Cl$) and were titrated with 0.1 mol dm^{-3} $[NMe_4][OH]$ under a stream of methanol-saturated nitrogen.

The ligand protonation titration data were treated using a locally written FORTRAN-IV version of the ALGOL program KONST.[12] The metal complex formation data were processed using a version [13] of the MINIQUAD program supplied by R. N. Sylva of the Australian Atomic Energy Commission (Sydney).

All other physical measurements were obtained as described previously.[9]

Preparation of L^1—L^3.—The mass spectrum of each macrocycle contained no peaks at higher *m/e* ratios than the corresponding parent ions. The i.r. spectra confirmed the absence of imine stretches at *ca.* 1 630 cm^{-1} and contained the expected secondary amine absorptions in the region 3 150—3 350 cm^{-1}. All products were dried over P_2O_5 *in vacuo.*

1,12,15-*Triaza*-3,4:9,10-*dibenzo*-5,8-*dioxacycloheptadecane*, L^1. 2,2′-Diaminodiethylamine (5.15 g) in methanol (20 cm^3) was added slowly to a stirred boiling solution of 1,4-bis(2′-formylphenyl)-1,4-dioxabutane [8] (13.5 g) in methanol (700 cm^3). The solution was allowed to boil for a further 0.25 h and was then filtered and allowed to cool. Sodium tetrahydroborate (8.0 g) (plus a small amount of borax) was added slowly and the volume was then reduced to 150 cm^3. The solution was cooled to room temperature. Water (400 cm^3) was slowly added and an oil separated. The oil was extracted with chloroform (3 × 100 cm^3). The chloroform extract was dried over anhydrous sodium sulphate and evaporated to 50 cm^3. Diethyl ether was slowly added to yield a white solid; yield 40%. The product was recrystallised from a chloroform–diethyl ether mixture.

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† Aqua(perhydrodibenzo[*e*,*q*][1,4,8,11,15]dioxatriazacyclo-octadecin)copper(II) diperchlorate hydrate.

Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.97 (s, N*H*), 2.5—2.8 (m, NCH_2CH_2N), 3.77 (s, arom-CH_2), 4.37 (s, OCH_2), 6.8—7.4 p.p.m. (m, C_6H_4). Carbon-13 (proton-decoupled) n.m.r. spectrum in $CDCl_3$: δ 48.68, 49.02 (NCH_2CH_2N), 50.73 (arom-CH_2), 67.05 (OCH_2), 110.91, 120.61, 128.31, 128.79, 130.99, 157.13 p.p.m. (C_6H_4).

1,12,15-*Triaza*-3,4 : 9,10-*dibenzo*-13,17-*dimethyl*-5,8-*dioxacycloheptadecane*, L^2. In a manner similar to the above 2,2′-diamino-2,2′-dimethyldiethylamine (6.55 g) yielded the product as a white solid; yield 50%. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.02 (3, CH_3), 2.0—2.9 [m, N*H*, $NCH(CH_3)CH_2N$], 3.73 (centre of AB quartet, $J \sim 12$ Hz, arom-CH_2), 4.33 (s, OCH_2), 6.8—7.4 p.p.m. (m, C_6H_4). Carbon-13 (off-resonance) n.m.r. spectrum in $CDCl_3$: δ 17.84 (q, CH_3), 47.56 [t, $NCH(CH_3)CH_2$], 51.65 (t, arom-CH_2), 56.82 [d, $CH(CH_3)$], 67.35 (t, OCH_2), 110.96, 120.56, 128.16, 130.93, 157.35 p.p.m. (C_6H_4).

1,12,16-*Triaza*-3,4 : 9,10-*dibenzo*-5,8-*dioxacyclo-octadecane*, L^3. In a manner similar to the above, *N*-(2-aminoethyl)-1,3-propanediamine (5.83 g) yielded the product as a white solid; yield 55%. Hydrogen-1 n.m.r. spectrum in $CDCl_3$: δ 1.45—1.75 (m, $CH_2CH_2CH_2$), 1.85 (s, N*H*), 2.5—2.8 (m, NCH_2CH_2N), 3.78, 3.81 (s, arom-CH_2), 4.52 (s, OCH_2), 6.8—7.4 (m, C_6H_4). Carbon-13 (proton-decoupled) n.m.r. spectrum in $CDCl_3$. δ 29.97 ($CH_2CH_2CH_2$), 47.81, 48.29 (NCH_2CH_2N), 49.85 (arom-CH_2), 67.49 (OCH_2), 111.69, 112.18, 120.80, 128.16, 129.57, 130.60, 157.01 p.p.m. (C_6H_4).

Preparation of Copper Complexes.—All complexes were dried over P_2O_5 *in vacuo*. Physical and analytical data are given in Tables 1—3.

TABLE 2

Values for the ligand protonation constants and complex stability constants [a]

	Free ligand [b,c]			Copper complexes [b,d]	
Macrocycle	log K_1	log K_2	log K_3	log K_{ML}	log β_{MLH}
L^1	9.47	8.27	2.35	14.41	17.32
L^2	9.32	8.09	1.97	14.31	17.29
L^3	10.07	8.16	4.34	14.00	17.97

[a] In 95% methanol (I = 0.1 mol dm^{-3}, $[NMe_4]Cl$); 25 °C. [b] Values are the mean of two or three separate determinations; in all cases individual titrations yielded standard deviations which were <0.02. [c] For the log K_1 and log K_2 values the respective mean deviations were approximately ±0.05 and for log K_3, ±0.2. [d] The mean deviation for each set of values was approximately ±0.1.

$[CuL^1(OH_2)][ClO_4]_2$. Ligand L^3 (0.17 g) in hot absolute ethanol (20 cm^3) was added to a stirred boiling solution of copper(II) perchlorate hexahydrate in absolute ethanol (20 cm^3). The volume was reduced to 15 cm^3 and, on standing for 6 h, dark blue crystals separated. The crystals were collected and washed with ethanol then diethyl ether; yield 30%.

$[CuL^1Cl][ClO_4]$. Lithium chloride (0.03 g) in hot dry methanol (20 cm^3) was added to a stirred boiling solution of L^1 (0.17 g) and copper(II) perchlorate hexa-hydrate (0.19 g) in butanol (30 cm^3). The volume was reduced to 25 cm^3 and allowed to stand for 12 h. The blue microcrystalline product which separated was collected and washed with ethanol then diethyl ether; yield 50%.

TABLE 1

Physical data for the complexes

Complex	μ [a]/B.M.	Λ [b]/ S cm^2 mol^{-1}	Visible (solid state) [c]/ nm	Selected i.r. absorptions/cm^{-1} H_2O	amine	ClO_4
$[CuL^1(OH_2)][ClO_4]_2$	1.80	61	625	3 500	3 240, 3 215	1 085
$[CuL^1Cl][ClO_4]$	1.79	29	650		3 295, 3 260, 3 175	1 090
$[CuL^1Br][ClO_4]$	1.82	43	570		3 285, 3 250, 3 170	1 090
$[CuL^2(OH_2)][ClO_4]_2\cdot H_2O$	1.88	66	590	3 490	3 230, 3 210	1 075
$[CuL^3(OH_2)][ClO_4]_2$	1.82	59	560	3 500	3 280, 3 240	1 080
$[CuL^3Cl][ClO_4]$	1.85	29	560		3 245, 3 200	1 080
$[CuL^3Br][ClO_4]\cdot H_2O$	1.86	42	580	3 500	3 240, 3 190	1 080

[a] At 296 K. 1 B.M. = 9.274 × 10^{-24} A m^2. [b] 10^{-3} mol dm^{-3} in dimethyl sulphoxide at 299 K. [c] Maximum of a broad envelope of bands.

$[CuL^1Br][ClO_4]$. In a manner similar to the above, LiBr (0.04 g) yielded the product as blue crystals; yield 25%.

$[CuL^2(OH_2)][ClO_4]_2\cdot H_2O$. In a manner similar to that used for $[CuL^1(OH_2)][ClO_4]_2$, L^2 (0.18 g) yielded blue crystals; yield 45%.

TABLE 3

Analytical data (%) for the compounds *

Compound	C	H	N	Cu
L^1	70.3 (70.3)	8.1 (7.9)	12.1 (12.3)	
L^2	71.1 (71.5)	8.5 (8.5)	11.1 (11.4)	
L^3	70.9 (70.9)	8.5 (8.2)	11.7 (11.8)	
$[CuL^1(OH_2)][ClO_4]_2$	38.4 (38.6)	5.2 (4.7)	6.2 (6.7)	9.8 (10.2)
$[CuL^1Cl][ClO_4]$	44.6 (44.5)	5.2 (5.1)	7.7 (7.8)	11.6 (11.8)
$[CuL^1Br][ClO_4]$	41.3 (41.1)	4.7 (4.7)	7.0 (7.2)	10.8 (10.9)
$[CuL^2(OH_2)][ClO_4]_2\cdot H_2O$	39.8 (39.6)	5.3 (5.3)	6.2 (6.3)	9.5 (9.5)
$[CuL^3(OH_2)][ClO_4]_2$	39.9 (39.7)	5.2 (4.9)	6.1 (6.5)	9.8 (10.0)
$[CuL^3Cl][ClO_4]$	45.4 (45.5)	5.3 (5.3)	7.8 (7.6)	11.3 (11.5)
$[CuL^3Br][ClO_4]\cdot H_2O$	41.0 (40.9)	5.1 (5.1)	6.5 (6.8)	10.4 (10.3)

* Calculated values are given in parentheses.

$[CuL^3(OH_2)][ClO_4]_2$. In a manner similar to that used for $[CuL^1(OH_2)][ClO_4]_2$, L^3 (0.18 g) yielded blue microcrystals; yield 70%.

$[CuL^3Cl][ClO_4]$. Ligand L^3 (0.18 g) in hot butanol (20 cm^3) was added to a stirred boiling mixture of copper(II) perchlorate hexahydrate (0.18 g) and LiCl (0.03 g) in methanol (30 cm^3). The volume was reduced to 20 cm^3 and allowed to stand. The blue microcrystalline product which formed was collected and washed with ethanol then diethyl ether; yield 60%.

$[CuL^3Br][ClO_4]\cdot H_2O$. In a manner similar to the above, lithium bromide (0.04 g) yielded blue crystals; yield 35%.

Crystallography.—Crystal data. $C_{21}H_{33}Cl_2CuN_3O_{12}$, M = 654.0, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 16.856(7), b = 10.717(4), c = 16.738(18) Å, β = 110.59(5)°, U = 2 831(4) Å^3, D_m = 1.53(1), Z = 4, D_c = 1.53 g cm^{-3}, $F(000)$ = 1 356, monochromatic Mo-K_α radiation (λ = 0.710 6$_9$ Å), μ = 10.1 cm^{-1}, specimen size 0.17 × 0.30 × 0.17 mm, T = 295(1) K.

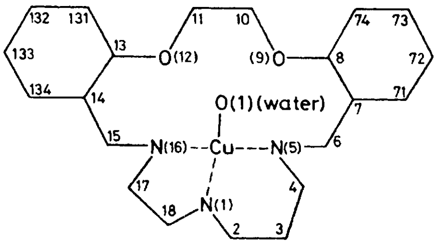
Structure determination. Deep blue crystals of $[CuL^3(OH_2)][ClO_4]_2\cdot H_2O$ were obtained on slow evaporation of the reaction solution after the initial crop of microcrystalline product had been removed by filtration. The blue crystals were air dried. A unique data set was gathered to $2\theta_{max.}$ 40° using a Syntex $P\bar{1}$ four-circle diffractometer in conventional θ—2θ scan mode. The data were weak and of poor quality, only 1 044 (out of a total of 2 638 independent reflections) with $I > 3\sigma(I)$ being considered ' observed ' and used in the solution and refinement after absorption correction. Refinement was by block-diagonal least squares, non-hydrogen atom thermal motion being refined anisotropically only for Cu and Cl. Hydrogen-atom positional and thermal parameters were included as constrained invariants. Final residuals (R,R',S) were 0.12, 0.13, 2.7; reflection weights were set at $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Neutral-atom scattering factors were employed, those for the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[14-16] Computation was carried out using the ' X-RAY '76 ' program system [17] implemented on a CYBER 73 computer. Material deposited in Supplementary Publication No. SUP 22905 (15 pp.) [*] comprises hydrogen-atom parameters, ligand geometry, all thermal parameters, and structure-factor amplitudes. The numbering system throughout the ligand is given below; hydrogen-atom numbers follow those of the parent carbon, suffixed A, B where necessary for distinguishing purposes. Non-hydrogen-atom fractional cell co-ordinates are listed in Table 4.

TABLE 4

Non-hydrogen-atom fractional cell co-ordinates

Atom	x	y	z
Cu	0.297 6(2)	0.184 3(3)	0.223 3(3)
Perchlorate groups			
Cl(1)	0.163 2(6)	0.025 2(8)	0.436 8(7)
O(101)	0.173(2)	0.144(4)	0.476(2)
O(102)	0.137(3)	−0.061(5)	0.469(3)
O(103)	0.244(2)	−0.006(3)	0.447(3)
O(104)	0.133(2)	0.037(3)	0.347(2)
Cl(2)	0.501 4(5)	0.146 2(9)	0.153 2(7)
O(201) *	0.432(3)	0.196(6)	0.154(4)
O(211) *	0.458(3)	0.166(4)	0.215(3)
O(202) *	0.513(7)	0.172(10)	0.076(6)
O(212) *	0.544(3)	0.222(5)	0.117(4)
O(203) *	0.521(3)	0.028(5)	0.154(4)
O(213) *	0.551(4)	0.051(7)	0.221(5)
O(204) *	0.567(3)	0.210(5)	0.223(3)
O(214) *	0.439(5)	0.104(8)	0.069(5)
Co-ordinated water			
O(1)	0.273(1)	0.327(2)	0.145(1)
Ligand			
N(1)	0.320(2)	0.034(2)	0.300(2)
C(2)	0.411(2)	0.020(3)	0.358(2)
C(3)	0.436(2)	0.130(3)	0.417(2)
C(4)	0.439(2)	0.254(3)	0.373(2)
N(5)	0.352(1)	0.299(2)	0.328(1)
C(6)	0.303(2)	0.336(3)	0.383(2)
C(7)	0.257(2)	0.453(3)	0.359(2)
C(71)	0.293(2)	0.559(3)	0.403(2)
C(72)	0.244(2)	0.675(3)	0.383(2)
C(73)	0.177(2)	0.681(3)	0.312(2)
C(74)	0.141(2)	0.577(3)	0.267(2)
C(8)	0.182(2)	0.469(3)	0.294(2)
O(9)	0.151(1)	0.354(2)	0.250(1)
C(10)	0.067(2)	0.353(3)	0.182(2)
C(11)	0.044(2)	0.214(3)	0.176(2)
O(12)	0.101(1)	0.150(2)	0.142(1)
C(13)	0.083(2)	0.027(3)	0.120(2)
C(131)	0.017(2)	−0.034(3)	0.135(2)
C(132)	0.001(2)	−0.161(3)	0.113(2)
C(133)	0.047(2)	−0.216(3)	0.068(2)
C(134)	0.112(2)	−0.155(3)	0.046(2)
C(14)	0.124(2)	−0.025(3)	0.072(2)
C(15)	0.196(2)	0.047(3)	0.054(2)
N(16)	0.276(1)	0.062(2)	0.130(2)
C(17)	0.307(2)	−0.060(3)	0.170(2)
C(18)	0.288(2)	−0.076(3)	0.243(2)
Lattice water			
O(301) *	0.689(5)	0.050(7)	0.332(5)
O(302) *	0.638(5)	−0.021(7)	0.366(5)

* Population set at 0.5.



The poor quality of the data and structure generally appears to result from the very high thermal motion throughout, notably on the perchlorates, one of which is disordered, and a lattice water molecule, also disordered. The disordered perchlorate was distributed over two sets of sites with populations estimated at 0.5 from difference maps.

RESULTS AND DISCUSSION

The Complexes.—Reaction of L^1, L^2, and L^3 with the corresponding appropriate copper salts has lead to isolation of the blue copper complexes listed in Table 1. All complexes have room-temperature magnetic moments in the range expected for copper(II) with $S = \frac{1}{2}$ and the i.r. spectrum of each complex contains absorptions in the range 3 150—3 350 cm^{-1} which are assigned to the ν(N–H) modes of the co-ordinated amines. For all complexes, the i.r. spectra show perchlorate absorptions in the range 1 075—1 090 cm^{-1} which are asymmetric in each case. Although such asymmetry could arise from the presence of co-ordinated perchlorate groups, the evidence is not sufficient to infer perchlorate co-ordination in all cases.

The solid-state visible spectrum of each complex consists of a broad envelope of bands in the region 500—800 nm ($\lambda_{max.}$ are listed in Table 1). The broadness of the bands makes spectral assignments difficult and none has been attempted here.

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

Conductivity measurements (Table 1) in dimethyl sulphoxide indicate that the diperchlorate complexes are 2 : 1 electrolytes and that all other complexes are 1 : 1 electrolytes in this solvent.[18] Conductometric titrations of the respective diperchlorate complexes with tetramethylammonium chloride (5×10^{-3} mol dm^{-3}) in dimethyl sulphoxide yielded distinct 1 : 1 end-points with no evidence for co-ordination of a second chloride ion in each case.

A spectrophotometric titration involving incremental addition of L^3 to copper(II) perchlorate in dimethyl sulphoxide has been carried out and an isosbestic point was observed during the initial portion of the titration (up to the addition of one mole ratio of ligand was complete). This initial part of the titration is assigned to the conversion of the solvated Cu^{2+} ion to a CuL^{2+} species and this is followed by the formation of a second species having a ligand to copper ratio greater than 1 : 1 (complex precipitation occurred before the formation of the second species was complete). If the copper ion is not to exceed its normal maximum co-ordination number of six then this implies that certain of the donor atoms do not co-ordinate in the second species. It seems likely that ether oxygens will remain unco-ordinated in this species since unco-ordinated ether groups have been documented in other related copper(II) complexes.[19-21]

Potentiometric Titration Studies.—Protonation constants for L^1—L^3 were determined by potentiometric titration of the ligand trihydrochloride in 95% methanol with tetramethylammonium hydroxide at 25 °C (Table 2). This solvent was employed because the ligands were found to be not sufficiently soluble in water. The successive constants are given below.

$$K_1 = [HL^+]/[L][H^+],\ K_2 = [H_2L^{2+}]/[HL^+][H^+],\ K_3 = [H_3L^{3+}]/[H_2L^{2+}][H^+]$$

Stability constants for the interaction of L^1—L^3 with Cu^{2+} in 95% methanol ($I = 0.1$ mol dm^{-3}, $[NMe_4]Cl$) have also been obtained potentiometrically. Initial attempts to fit the titration data solely to equilibria of the general type $Cu^{2+} + nL \rightleftharpoons CuL_n^{2+}$ using the program KONST[12] were unsuccessful. However a satisfactory fit to the data could be obtained (for the above equilibrium type with $n = 1$) in each case only if the points comprising the first portions of the respective curves were not used in the calculations. Using the more comprehensive program MINIQUAD[13] which can treat equilibria involving species of various stoicheiometries, all data refined satisfactorily when equilibria (1) and (2) involving copper were assumed. No improvement in the fit was obtained when equilibria involving other species were included. In each case, the titration was terminated by precipitation of either the complex or hydrolysis products. Complexation of the monoprotonated form of several related macrocyclic ligands to Cu^{2+} has been demonstrated to occur in a number of other recent studies.[7,22] The respective log K values are given in Table 2. The values for formation of the 1 : 1 complexes are all very similar; no significant ligand structural discrimination effects operate in this system.

$$Cu^{2+} + L \rightleftharpoons CuL^{2+} \qquad (1)$$

$$Cu^{2+} + HL^+ \rightleftharpoons Cu(HL)^{3+} \qquad (2)$$

X-Ray Studies.—To gain insight into the solid-state structures of the present complexes, an *X*-ray diffraction study of $[CuL^3(OH_2)][ClO_4]_2 \cdot H_2O$ has been undertaken. A view of the complex cation is shown in Figure 1 and bond lengths and bond angles about the copper atom are listed in Table 5. The packing arrangement is given in Figure

TABLE 5

The copper atom environment *

	r	N(1)	N(5)	N(16)	O(211)
O(1)	1.96(2)	178(2)	91(1)	93(1)	90(1)
N(1)	2.02(3)		90(1)	85(1)	90(1)
N(5)	2.07(2)			165(1)	86(1)
N(16)	1.97(3)				80(1)
O(211)	2.77(5)				

* r/Å is the copper–ligand distance. The other entries in the matrix are the angles in degrees subtended at the copper by the relevant atoms.

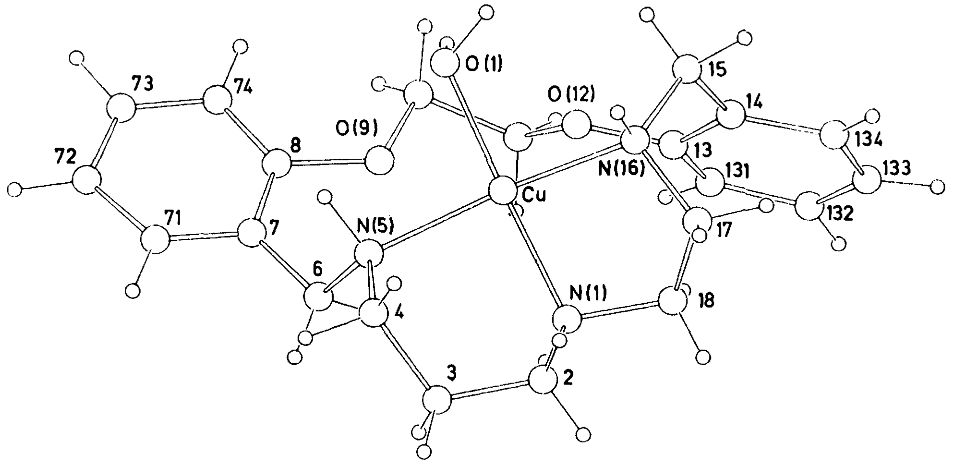

FIGURE 1 A projection of $[CuL^3(OH_2)]^{2+}$, showing ligand labelling. Carbon atoms are denoted by number only

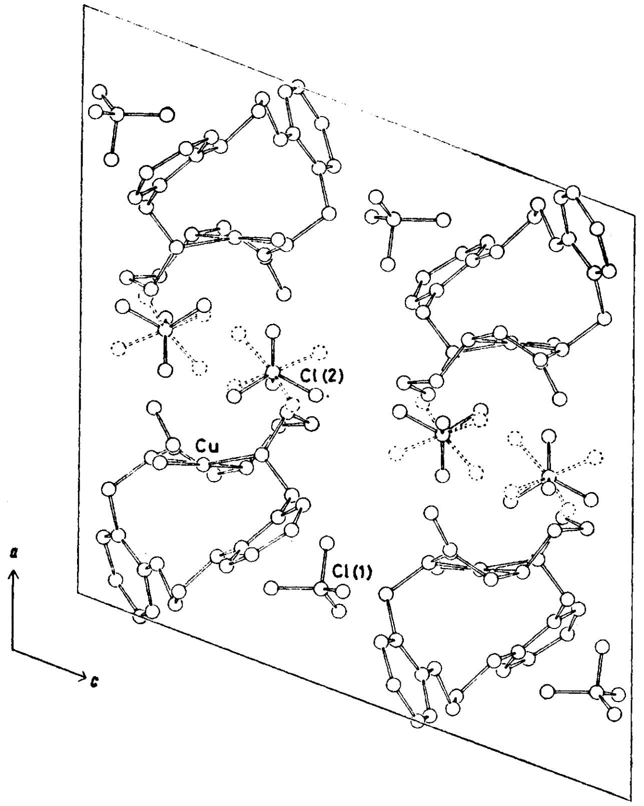

FIGURE 2 Unit-cell contents projected down *b*. Non-ligand labelling is shown

TABLE 6

Torsion angles in the macrocycle string

Atoms	Angle/°
Cu–N(1)–C(2)–C(3)	63
C(18)–N(1)–C(2)–C(3)	–176
N(1)–C(2)–C(3)–C(4)	–68
C(2)–C(3)–C(4)–N(5)	76
C(3)–C(4)–N(5)–C(6)	67
C(3)–C(4)–N(5)–Cu	–71
C(4)–N(5)–C(6)–C(7)	135
Cu–N(5)–C(6)–C(7)	–92
N(5)–C(6)–C(7)–C(8)	79
N(5)–C(6)–C(7)–C(71)	–98
C(6)–C(7)–C(8)–O(9)	1
C(6)–C(7)–C(8)–C(74)	–175
C(71)–C(7)–C(8)–O(9)	178
C(71)–C(7)–C(8)–C(74)	2
C(7)–C(8)–O(9)–C(10)	175
C(74)–C(8)–O(9)–C(10)	–9
C(8)–O(9)–C(10)–C(11)	–160
O(9)–C(10)–C(11)–O(12)	–68
C(10)–C(11)–O(12)–C(13)	–171
C(11)–O(12)–C(13)–C(131)	–4
C(11)–O(12)–C(13)–C(14)	167
O(12)–C(13)–C(14)–C(15)	7
O(12)–C(13)–C(14)–C(134)	179
C(131)–C(13)–C(14)–C(15)	178
C(131)–C(13)–C(14)–C(134)	–10
C(13)–C(14)–C(15)–N(16)	71
C(134)–C(14)–C(15)–N(16)	–101
C(14)–C(15)–N(16)–C(17)	54
C(14)–C(15)–N(16)–Cu	–80
C(15)–N(16)–C(17)–C(18)	–103
Cu–N(16)–C(17)–C(18)	40
N(16)–C(17)–C(18)–N(1)	–53
C(17)–C(18)–N(1)–Cu	39
C(17)–C(18)–N(1)–C(2)	–86

2, and torsion angles in Table 6. The structure of the complex cation indicates non-co-ordination of the ether oxygen atoms [O(9) and O(12)] which exhibit non-bonding distances of 3.22(2) and 3.14(1) Å from the copper, respectively. The copper is bound to the three secondary amines of the macrocycle and to the oxygen of the water molecule in a distorted square-planar arrangement; in addition, there is a very long [2.77(5) Å] contact between the copper ion and an oxygen of one of the perchlorate groups such that the overall geometry might alternatively be considered to be a distorted square pyramid. The structure provides further evidence for the low affinity of Cu^{2+} for ether oxygen-donor atoms; in addition, there are two other reports describing *X*-ray diffraction studies of copper complexes of oxygen–nitrogen donor macrocyclic ligands in which ether functions do not co-ordinate.[20,21] Such non-co-ordination of the ether functions of L^1—L^3 to copper in solution might also account for the absence of a definite macrocyclic ring-size effect in the potentiometric studies discussed above.

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