Complexes of Ligands providing Endogenous Bridges. Part 7.[1] The Concurrent Formation of 1 + 1 and 2 + 2 Oxa-azamacrocycles; The *X*-Ray Crystal Structure of an Exocyclic Dinuclear Copper(II) Complex†

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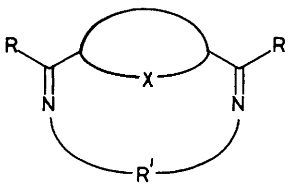
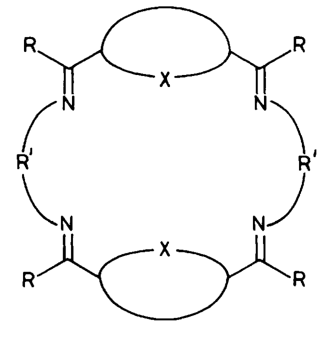
A series of oxa-azamacrocycles derived from the non-template condensation of 1,3-diamino-2-propanol and acyclic dialdehydes followed by *in situ* reduction with tetrahydroborate has been prepared. Fast atom bombardment mass spectrometry (f.a.b.m.s.) showed the presence of 1 + 1 and 2 + 2 condensates and these were separated using medium pressure liquid chromatography. Metal complexes of the 1 + 1 macrocycles (HL) were prepared and characterised. Mononuclear complexes, $M(HL)X_2$, were recovered for M = Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}, or Hg^{II} and X = Cl or Br and homo-dinuclear complexes, $Cu_2LCl_2(OH)\cdot nH_2O$, for $CuCl_2$. The salts $M(ClO_4)_2$ and $M(NO_3)_2$ (M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, or Cd^{II}) gave complexes [M(L)X] and f.a.b.m.s. provided evidence for oligomer formation. Mononuclear complexes were recovered from the reaction of one 2 + 2 macrocycle with $M(ClO_4)_2$ (M = Co^{II}, Ni^{II}, or Zn^{II}) and $CdCl_2$, whereas a homodinuclear complex was obtained for $Cu(ClO_4)_2$. The crystal structure of $[Cu_2(\mu\text{-}C_{19}H_{23}N_2O_3)(\mu\text{-}O_2CPh)(OH_2)Cl_2]\cdot 2PhCH_2OH$ reveals a dimeric structure in which the dinuclear units are linked by chloride bridges. The compound crystallises in monoclinic space group $P2_1/c$ (C^5_{2h}, no. 14) with unit-cell dimensions a = 13.460(15), b = 14.608(16), c = 17.096(8) Å, β = 96.227(9)°, and Z = 2; 3 678 independent reflections with $I/\sigma(I) > 3.0$ gave R = 0.0532.

Di-imine (1 + 1) and tetraimine (2 + 2) Schiff-base macrocycles have generally been prepared, *via* the condensation of polyfunctional 1,*n*-alkanediamines with heterocyclic dicarbonyls using metal template reactions, as the corresponding metal complex.[2] Employment of appropriate metal ions such as Mn^{II} or Pb^{II} as the template allows isolation of the reduced metal-free oxa-azamacrocycle on reduction of the Schiff-base complex with $NaBH_4$.[3] The reaction of the dialdehydes (**1**) with 1,*n*-alkanediamines therefore leads to di-imine Schiff-base macrocycles (**2**) which may be reduced *in situ* to the corresponding diaminomacrocycles. During the course of an investigation into the complexing properties of macrocyclic ligands bearing functional groups which could lead to the provision of endogenous bridges in dinuclear metal complexes[4] we have prepared a series of reduced 1 + 1 oxa-azamacrocycles (HL) derived from the condensation of (**1**) and 1,3-diamino-2-propanol without resort to template techniques.

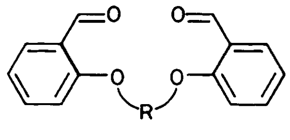
The synthesis and characterisation of the macrocycles and their complexes with halides, perchlorates, and nitrates of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, and Hg^{II} are discussed and provide a cautionary tale concerning the characterisation of macrocyclic ligands. The crystal structure of an exocyclic dinuclear copper(II) complex derived from HL (R = CH_2CH_2) is also described.



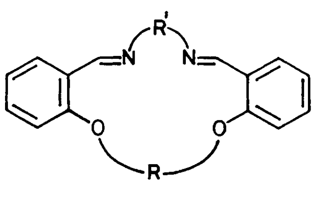
1 + 1



2 +2



(**1**)



(**2**)

Results and Discussion

The Oxa-azamacrocycles.—The macrocycles were prepared according to the pathway shown in the Scheme. The eight compounds were isolated as solids and characterised by elemental analysis, i.r., ^1H n.m.r. (220 MHz), and electron-impact mass spectrometry (e.i.m.s.). They were assigned as pure 1 + 1 oxa-azamacrocycles and complexation reactions were carried out with metal perchlorate salts. Due to the general insolubility of the products, fast atom bombardment mass spectrometry (f.a.b.m.s.) was used to help in their characterisation and revealed the presence of high-molecular-weight species with mass numbers well in excess of the anticipated molecular weights. Consequently it was necessary to reinvestigate the nature of the precursor macrocycles as, although these peaks may have been derived from associative processes, it was also possible that 2 + 2-derived products were present.

Analysis of the macrocycles using f.a.b.m.s. revealed that when R = $(CH_2)_3$, $(CH_2)_4$, and 2,6-C_5H_3N the peaks at highest mass corresponded to 2 + 2 macrocycle formation,

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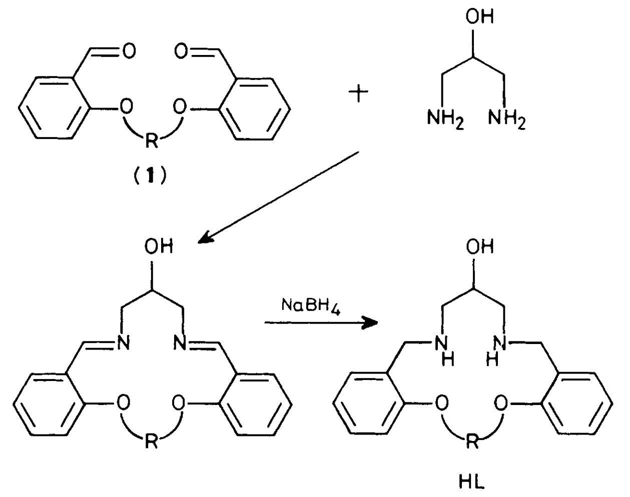
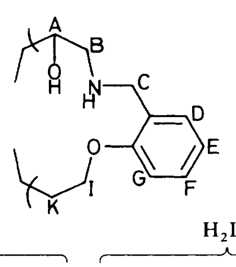
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme. HL: R = $(CH_2)_n$ where n = 2(HL^1), 3(HL^2), 4(HL^3), 5(HL^4), or 6(HL^5), $(CH_2)_2NH(CH_2)_2$(HL^6), 1,3-C_6H_4(HL^7), or 2,6- C_5H_3N-(HL^8)

Table 1. Proton chemical shifts for HL^2 and H_2L^9



HL^2			H_2L^9		
δ			δ		
7.24(t)	H_F	(2 H)	7.22t	H_F	(4 H)
7.19(d)	H_D	(2 H)	7.15d	H_D	(4 H)
6.95(d)	H_G	(2 H)	6.88t	H_E	(4 H)
6.94(t)	H_E	(2 H)	6.87d	H_G	(4 H)
4.27(m)	H_I	(4 H)	4.17m	H_I	(8 H)
3.76(m)	H_C	(4 H)	3.6	H_C	
3.71(t)	H_A	(1 H)	3.8m	H_A	(10 H)
2.66(m)	H_B	(4 H)	2.40m	H_B	(8 H)
2.30(q)	H_K	(2 H)	2.30m	H_K	(4 H)

Coupling constants (Hz) for HL^2: $J(H_AH_B)$ = 5.0, $J(H^AH^{B'})$ = 4.8, $J(H^BH^{B'})$ = 12.2, $J(H^CH^{C'})$ = 12.9, $J(H^DH^E)$ = 7.5, $J(H^DH^F)$ = 1.5, $J(H^EH^F)$ = 7.9, $J(H^EH^G)$ = 1.0, $J(H^FH^G)$ = 7.9, and $J(H^IH^K)$ = 5.7.

indicating that the original product was actually a mixture of 1 + 1 and 2 + 2 macrocycles. The 2 + 2 macrocycle was also found with R = $(CH_2)_6$ together with a highest mass peak (m/z 1 153) assigned to a 3 + 3 species; a related 3 + 3 Schiff-base macrocycle has been synthesised by employing lanthanum nitrate as the templating device in the reaction of 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane.[1]

No procedure is given in the literature for separating such a mixture and so a method was sought. A number of chromatographic techniques were assessed, ranging from silica gel gravity columns to gel permeation chromatography, and found to be ineffective, probably because of strong hydrogen-bonding interactions between the macrocycle and the binding sites available on the columns used. However, when a small amount of ammonia (0.1—0.5%) was added to the eluant (methanol) it was found possible to separate the macrocycles using medium-pressure liquid chromatography (m.p.l.c.) and a silica gel column. The 1 + 1:2 + 2 ratios detected were 8.5 for R = $(CH_2)_3$, 12 for $(CH_2)_4$ 4.4 for $(CH_2)_6$ and > 10 for 2,6-C_5H_3N and this allowed for separation of the pure macrocycles for R = $(CH_2)_n$ (n = 3, 4, and 6). In all cases tailing occurred; this was most acute for the 2,6-C_5H_3N system and together with a solubility problem eased somewhat by use of a mixed methanol–chloroform eluant, prevented isolation of the pure 2 + 2 species in this case.

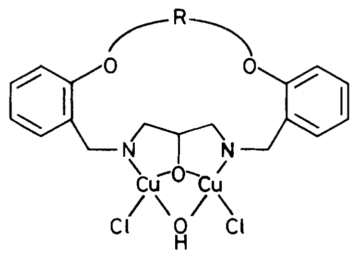
The ^1H n.m.r. spectra (400 MHz; $CDCl_3$) of the pure 1 + 1 and 2 + 2 compounds show very similar chemical shifts (Table 1); there is a greater complexity of splitting patterns in the 2 + 2 series due to the greater conformational freedom and the possible presence of diastereoisomers. Representative chemical shift data are given for the macrocycles derived from R = $(CH_2)_3$

An interesting observation in the f.a.b.m.s. reveals the potential of the macrocycles for metal-ion discrimination. The m.s. of the 2 + 2 macrocycles show peaks at M + 132 that are not detected with the 1 + 1 macrocycles. These are attributed to abstraction of Cs^+ from the CsI used as a calibrant (the matrix is 3-nitrobenzyl alcohol), the difference in behaviour being governed by the more compatible cation–ring cavity fit available with the 2 + 2 species. Furthermore peaks of mass M + 23 are detected for both series of macrocycles. These have probably arisen from retention of trace amounts of Na^+ used in the reduction step. In this case mononuclear complexes would be available for the smaller macrocycles and dinuclear complexes for the larger macrocycles.

Complexes of the 1 + 1 *Macrocycles with* MCl_2 *and* MBr_2.—The 1 + 1 macrocycles were treated with MCl_2 (M = Co, Ni, Cu, Cd, Zn, or Hg) and MBr_2 (M = Co, Ni, Cu, or Cd) to give precipitates which were generally found to be insoluble in common organic solvents. The complexes formed were characterised by elemental analysis, i.r. and f.a.b.m.s. spectra (Table 2). Mononuclear complexes were recovered for MX_2 (X = Cl or Br; M = Co, Ni, Zn, Cd, or Hg) and for the copper(II) complexes where R = $(CH_2)_2NH(CH_2)_2$ and 2,6-C_5H_3N whereas homodinuclear complexes of copper(II) were found using the remaining ligands. In the mononuclear complexes the stretching frequency of the ligand hydroxy-group is observed as a broad band in the region 3 400—3 500 cm^{-1}; this is associated with OH stretching bands from any water of crystallisation. In the homodinuclear complexes this band is replaced by a sharp medium-intensity absorption at *ca.* 3 600 cm^{-1} assigned to the OH stretch of an exogeneous bridging hydroxyl group.[5]

The f.a.b.m.s. of the majority of the complexes gave parent peaks corresponding to $[M(HL)X]^+$; the m.s. also commonly show peaks corresponding to $[ML]^+$ (L = the deprotonated ligand) and to $[HL]^+$. The exceptions to this statement are the homodinuclear complexes for which the highest peak corresponds to $[Cu_2(L)X]^+$ and the mercury complexes in which the parent peak corresponds to $[HL]^+$. A plausible explanation for the latter observation is that exocyclic complexation of the mercury(II) has occurred leading to an oligomeric linear array such has been found in the crystal structure of the HgI_2 complex of a related macrocyclic ligand.[6] This would lead to the facile recovery of free macrocycle on bombardment during the m.s. experiment.

The homodinuclear copper(II) complexes are proposed as having the structure (**I**). Attempts to grow crystals of these species were unsuccessful, however the complex $Cu_2L^1Cl_2(OH)$ was recovered from benzyl alcohol and the structure solved. This not only confirmed the exocyclic homodinuclear nature of the complex but also showed that the exogenous hydroxyl group had been replaced by a benzoate anion. At first it was thought that this had arisen from oxidation of the benzyl alcohol but a g.c. assay of the solvent revealed 0.27% benzoic acid in the solvent and so it is proposed that the dinuclear unit



(1)

of the complex scavenges this benzoic acid, the ligand being sufficiently flexible to allow replacement of the singly bridging hydroxyl group by the μ-1,3-benzoate.

The molecular structure of $[\{Cu_2L^1(\mu\text{-}O_2CPh)(OH_2)Cl_2\}_2]\cdot 2PhCH_2OH$ is shown in the Figure with atomic co-ordinates listed in Table 3 and bond lengths and angles in Tables 4 and 5. It comprises a centrosymmetric tetranuclear complex in which each of two pairs of copper atoms is co-ordinated exocyclically by a macrocyclic ligand *via* two amine nitrogen atoms (one to each copper), and by an oxygen of a deprotonated pendant hydroxyl group which bridges the two coppers; the pair of copper atoms is also bridged by a benzoate anion. The co-ordination sphere of the 'outer' copper of each pair is completed by a terminal chlorine and, more remotely, by a water ligand. The 'inner' two centrosymmetrically related copper atoms (one from each pair) are asymmetrically bridged by a pair of chlorine ligands. The Cu ••• Cu distances are 3.489 and 3.391 Å the latter being between symmetry-related, dichloride-bridged copper atoms.

Each of the independent copper atoms has a five-co-ordinate geometry. The co-ordination polyhedron of Cu(2) is closely square-based pyramidal with the copper displaced out of the plane towards a remote axial water ligand. The co-ordination geometry about Cu(1) is also square-based pyramidal, but here the basal plane is more 'tetrahedrally twisted,' and the axial site is occupied by the second bridging chlorine at a much greater distance than to the symmetry-related chlorine in the basal plane. Hence both co-ordination polyhedra illustrate the distorted geometries expected in Jahn-Teller distorted environments. Consequent on this molecular geometry, the four copper atoms lie in an approximate straight line, with a 43° bend at Cu(1) and alternate asymmetric bridges.

The conformation of the macrocycle is such that the diamine fragment is 'inverted' in order to provide exocyclic donor sets. The three six-membered rings of the macrocycle and of the bridging benzoate are each planar [root mean square (r.m.s.) deviations 0.005, 0.007, and 0.004 Å]; those of the two disorder components of the solvent benzyl alcohol were constrained to D_{6h} symmetry.

Table 2. Macrocyclic complexes of metal halides

			Analysis (%)*				I.r. bands (cm^{-1})	
Complex	M.p. (°C)	Mass spectral parent ion (*m/z*)	C	H	N	Cl or Br	Secondary amine N–H stretch	Aromatic and pyridine-ring stretches
$Ni(HL^1)Cl_2$	>280	421	49.7	5.3	6.2		3 255(sp)	1 605(sp), 1 585(sp)
(Light blue)		$[Ni(HL^1)Cl]^+$	(49.8)	(5.3)	(6.1)			
$Cd(HL^1)Cl_2\cdot H_2O$	270	457	42.5	5.3	5.4		3 310w, 3 290(sh),	1 605s(sp), 1 595(sp),
(White)	(decomp.)	$[Cd(HL^2)Cl]^+$	(43.1)	(5.0)	(5.3)		3 240(sh)	1 580(sh)
$Hg(HL^1)Cl_2$	179—180	329	38.5	4.0	4.3	12.1	3 270(sp)	1 600s(sp), 1 590(sp),
(White)		$[HL^1 + H]^+$	(38.0)	(4.0)	(4.7)	(11.8)		1 580w
$Cu_2L^1Cl_2(OH)$	189	489	42.4	4.7	5.4	12.9	3 280(sp), 3 250	1 600s(sp), 1 585w(sp)
(Turquoise)		$[Cu_2L^1Cl]^+$	(42.1)	(4.4)	(5.2)	(13.1)		
$Cd(HL^1)Br_2\cdot 2H_2O$	>270	466	39.1	4.9	4.9		3 240(br)	1 600(sp), 1 590(sh)
(Green)		$[Co(HL^1)Br]^+$	(39.1)	(4.8)	(4.8)			
$Cu_2(L^1)Br_2(OH)\cdot H_2O$	172—173	533	35.0	3.8	4.1	24.9	3 260(br)	1 600s(sp), 1 580w(sp)
(Black-green)		$[Cu_2L^1Br]^+$	(35.1)	(4.0)	(4.3)	(24.6)		
$Ni(HL^2)Cl_2\cdot 1.5H_2O$	>260	435	48.1	5.8	5.5	13.8	3 250(sp)	1 605(sp), 1 590(sp)
(Pale green)		$[Ni(HL^2)Cl]^+$	(48.1)	(5.8)	(5.6)	(14.2)		
$Co(HL^2)Cl_2\cdot MeOH$	246—248	436	50.4	6.1	5.5		3 280(sh)	1 605s(sp), 1 590(sp)
(Blue)		$[Co(HL^2)Cl]^+$	(50.0)	(6.0)	(5.5)			
$Cd(HL^2)Cl_2\cdot 2H_2O$	>280	489	43.0	5.5	5.0	14.2	3 300w, 3 280(sh)	1 600(sp), 1 590(sh)
(Off-white)		$[Cd(HL^2)Cl]^+$	(42.8)	(5.4)	(5.0)	(12.6)		
$Hg(HL^2)Cl_2\cdot H_2O$	107	343	38.2	5.0	4.5		3 280(br)	1 605s(sp), 1 595(sh)
(White)		$[HL^2 + H]^+$	(38.0)	(4.5)	(4.4)			
$Zn(HL^2)Cl_2$	184	441	50.1	5.4	5.8	14.0	3 275(sp)	1 600s(sp), 1 590w(sp)
(White)		$[Zn(HL^2)Cl]^+$	(50.2)	(5.8)	(5.9)	(14.8)		
$Cu_2L^2Br_2(OH)\cdot H_2O$	179—181	519	37.0	4.2	4.2	25.2	3 250(br)	1 600s(sp), 1 590(sh)
(Olive green)		$[Cu_2L^2Br]^+$	(37.3)	(4.4)	(4.3)	(24.8)		
$Co(HL^2)Br_2\cdot H_2O$	>270	400	41.8	4.9	5.0		3 300(sh)	1 600(sp), 1 590(sh)
(Grey-blue)		$[CoL^2]^+$	(41.5)	(4.9)	(4.8)			
$Ni(HL^2)Br_2\cdot H_2O$	>280	480	42.0	5.0	4.7	29.0	Obscured	1 600(sp), 1 595(sh)
(Greeny white)		$[Ni(HL^2)Br]^+$	(41.5)	(4.9)	(4.8)	(27.6)		
$Cd(HL^2)Br_2$	>280	443	38.7	4.0	4.4		3 280(br)	1 600s(sp), 1 590(sh)
(Off-white)		$[CdL^2]^+$	(39.1)	(4.3)	(4.6)			
$Co(HL^3)Cl_2\cdot H_2O$	230	450	49.9	5.7	5.2		3 290	1 605s(sp), 1 590w(sp)
(Pale Blue)		$[Co(HL^3)Cl]^+$	(50.0)	(6.0)	(5.5)			
$Cd(HL^3)Cl_2$	>280	503	46.6	5.0	5.0	14.3	3 310(sp), 3 265(sh)	1 600s(sp), 1 590w(sp)
(White)		$[Cd(HL^3)Cl]^+$	(46.7)	(5.2)	(5.2)	(13.1)		
$Hg(HL^3)Cl_2$	156—157	357	39.8	4.5	4.2		3 275(sp), 3 255(sp)	1 605s(sp), 1 585w (sp)
(White)		$[HL^3 + H]^+$	(40.2)	(4.5)	(4.5)			
$Zn(HL^3)Cl_2\cdot H_2O$	147—148	455	49.3	5.9	5.3	13.8	3 255(sp), 3 245(sh)	1 605s(sp), 1 590w(sp)
(White)		$[Zn(HL^3)Cl]^+$	(49.4)	(5.9)	(5.5)	(13.9)		

Table 2 (*continued*)

			Analysis (%)*				I.r. bands (cm^{-1})	
Complex	M.p. (°C)	Mass spectral parent ion (*m/z*)	C	H	N	Cl or Br	Secondary amine N–H stretch	Aromatic and pyridine-ring stretches
$Cu_2L^3Cl_2(OH)$	185—186	517	44.8	5.2	5.2	12.0	3 280w	1 605(sp), 1 590w(sp)
(Dark green)		$[Cu_2L^3Cl]^+$	(44.2)	(5.0)	(4.9)	(12.4)		
$Cd(HL^4)Cl_2·2H_2O$	>280	481	44.0	5.7	4.5	14.0	3 280(sh)	1 600s(sp)
(Off-white)		$[CdL^4]^+$	(44.8)	(5.8)	(4.7)	(12.0)		
$Hg(HL^4)Cl_2·H_2O$	94	371	39.4	4.8	3.9	12.5	3 260w(sh)	1 605s(sp), 1 595w(sp)
(Off-white)	(decomp.)	$[HL^4 + H]^+$	(40.0)	(4.9)	(4.2)	(10.7)		
$Co(HL^4)Br_2·H_2O$	>260	428	42.9	5.1	4.8		3 200(sh)	1 600s, 1 595(sh)
(Brown-green)		$[CoL^4]^+$	(43.5)	(5.3)	(4.6)			
$Hg(HL^5)Cl_2$	169—170	385	41.9	4.9	4.4		3 260(sp), 3 190(sh)	1 605s(sp), 1 590(sp), 1 580(sp)
(Off-white)		$[HL^5 + H]^+$	(42.1)	(4.9)	(4.3)			
$Cd(HL^7)Cl_2·2H_2O$	>280	533	49.9	5.9	4.0		3 250(sh)	1 600(sp), 1 590w(sh)
(Off-white)		$[CdL^7]^+$	(49.7)	(5.6)	(4.3)			
$Hg(HL^7)Cl_2$	192—193	433	46.2	4.6	3.9		3 285s(sp)	1 605s(sp), 1 590(sp)
(White)		$[HL^7 + H]^+$	(46.1)	(4.6)	(4.0)			
$Cu_2L^7Cl_2(OH)·H_2O$	173—174	593	49.2	5.2	4.4	11.0	3 280w	1 600s(sp), 1 590w(sp)
(Pale-green)		$[Cu_2L^7Cl]^+$	(48.9)	(5.0)	(4.2)	(10.7)		
$Ni(HL^6)Cl_2·2H_2O$	>260	465	47.0	5.9	5.3	13.0	3 290(sp)	1 600(sp), 1 595(sh)
(Olive green)		$[Ni(HL^6)Cl]^+$	(46.9)	(6.0)	(5.2)	(13.2)		
$Co(HL^6)Cl_2$	220—222	467	49.8	5.6	5.6	14.7	3 250(sp), 3 230sw	1 600s(sp), 1 595(sh)
(Blue-green)		$[Co(HL^6)Cl]^+$	(50.2)	(5.6)	(5.6)	(14.1)		
$Cd(HL^6)Cl_2$	>260	483	44.9	5.2	4.8		3 270(br)	1 600(sp), 1 590w(sp)
(White)		$[CdL^6]^+$	(45.4)	(5.1)	(5.0)			
$Hg(HL^6)Cl_2$	145—146	373	39.4	4.2	4.0	11.2	3 285(sp)	1 605(sp), 1 595(sp)
(White)		$[HL^6 + H]^+$	(39.2)	(4.4)	(4.3)	(11.0)		
$Zn(HL^6)Cl_2·H_2O$	168—169	471	48.0	5.8	5.1	13.6	3 255(sp), 3 245(sh)	1 605s(sp), 1 590w(sp)
(White)		$[ZnHL^6Cl]^+$	(47.9)	(5.7)	(5.3)	(13.5)		
$Cu(HL^6)Cl_2$	194—195	434	49.7	5.4	5.1	13.8	3 260	1 600(sp), 1 590w(sp)
(Pale green)		$[CuL^6]^+$	(49.8)	(5.6)	(5.5)	(14.0)		
$Co(HL^6)Br_2$	228—230	510	43.1	5.1	4.8		3 270(sp), 3 240w(sh)	1 600s(sp), 1 595w(sh)
(Lilac)		$[Co(HL^6)Br]^+$	(72.7)	(4.8)	(4.7)			
$Hg(HL^8)Cl_2$	224—226	406	43.0	3.8	5.8		3 300(sh)	1 600, 1 590(sh), 1 580(sh)
(White)		$[HL^8 + H]^+$	(42.6)	(4.0)	(6.2)			
$Zn(HL^8)Cl_2$	214	505	53.4	5.5	7.4	15.1	3 280(sp)	1 605(sh), 1 600, 1 590(sh), 1 580
(White)	(decomp.)	$[Zn(HL^8)Cl]^+$	(53.2)	(5.0)	(7.8)	(13.1)		
$Cu(HL^8)Cl_2$	162	503	52.9	5.2	8.0		3 240	1 605(sp), 1 590(sh), 1 580(sh)
(Lime green)		$[Cu(HL^8)Cl]^+$	(53.4)	(5.0)	(7.8)			

br = broad, v = very, s = strong; sp = sharp, sh = shoulder, and w = weak. * Calculated values given in parentheses.

The two halves of the tetranuclear complex are additionally held together by two, weak, symmetry-related hydrogen bonds between the secondary amine N(1) of the macrocycle and an oxygen of the bridging benzoate ligand $O(4^I)$ (O ··· N 3.267, O ··· H 2.39 Å). The other secondary amine N(2) engages in a weak intermolecular hydrogen bond to chlorine $Cl(2^{III})$ in an inversion-related molecule (through 0.5, 0, 0) (Cl ··· N 3.424, Cl ··· H 2.64 Å). The co-ordinated water O(7) also interacts weakly with the same inversion related $Cl(2^{III})$ at a distance of 3.142 Å. The lower-occupancy component of the solvent benzyl alcohol molecule lies close to Cu(1) at a distance Cu(1) ··· O(8) of 2.64 Å, *trans* to the more distant bringing chlorine, and the aromatic ring 'blocks' the sixth co-ordination site of Cu(2) at a range of about 3.6 Å. The higher-occupancy component of benzyl alcohol seems only to form a hydrogen-bonded interaction with a screw-related chlorine $Cl(2^{II})$ (operation $1 - x$, $0.5 + y$, $0.5 - z$) at a distance O(6) ··· $Cl(2^{II})$ of 3.264 Å.

Double bridging involving endogenous alkoxide groups and exogenous groups is a well known phenomenon in dinuclear copper(II) complexes of a range of acyclic ligands.[7] The exocyclic mode of co-ordination in the present case affords comparison with acyclic complexes in which the use of flexible ligands allows for the incorporation of single-atom, μ-1,2 and μ-1,3 exogenous bridges and the Cu ··· Cu separation lies in the range 2.90—3.20 Å for single-atom bridges and is greater than 3.30 Å for multiatom bridges.[8] The closest analogue μ-(benzoato-*O*:*O'*)-[*NN'*-(2-hydroxy-1,3-propanediyl)bis(salicylideneiminato)(3 −)(*NO*²*O*:*N'O*²*O'*]dicopper(II)[9] has a Cu ··· Cu separation of 3.482 Å and a Cu–benzoate–Cu angle of 132.7°.

The Cu ··· Cu separation for the dimer building chloro-bridged unit is 3.391 Å and the bridging Cu–Cl lengths are inequivalent (2.274 and 2.863 Å). The Cu–Cl–Cu angle is 81.6° and both this angle and the Cu ··· Cu separations are slightly smaller than the recorded range for comparable chloro-bridged environments.[10] The reference compounds for this comparison are $[\{Cu(Me_2NCH_2CH_2NHMe)Cl_2\}_2]$ having a Cu–Cl–Cu angle of 84.4°,[10] and $[\{Cu(pan)Cl_2\}_2]$ [pan = 1-(2-pyridylazo)-2-naphtholate] which has a Cu ··· Cu separation of 3.416 Å.[11]

The mononuclear complexes did not involve deprotonation of the ligand and gave in general broad bands in the diffuse reflectance spectra. Due to the sparing solubility it was only possible to obtain ^1H n.m.r. spectra in CD_3CN solution for two zinc complexes, $Zn(HL^3)Cl_2$ and $Zn(HL^6)Cl_2$. The parameters are given in Table 6 together with the changes in chemical shift between the free and complexed ligand. Large changes are observed in the chemical shifts of the methylene groups adjacent to the nitrogen donor atoms; this is in agreement with work carried out by Lindoy *et al.*[12] on related macrocyclic systems. It is suggested that the nitrogen atoms of the respective macrocycles are co-ordinated to the zinc. In the present study larger

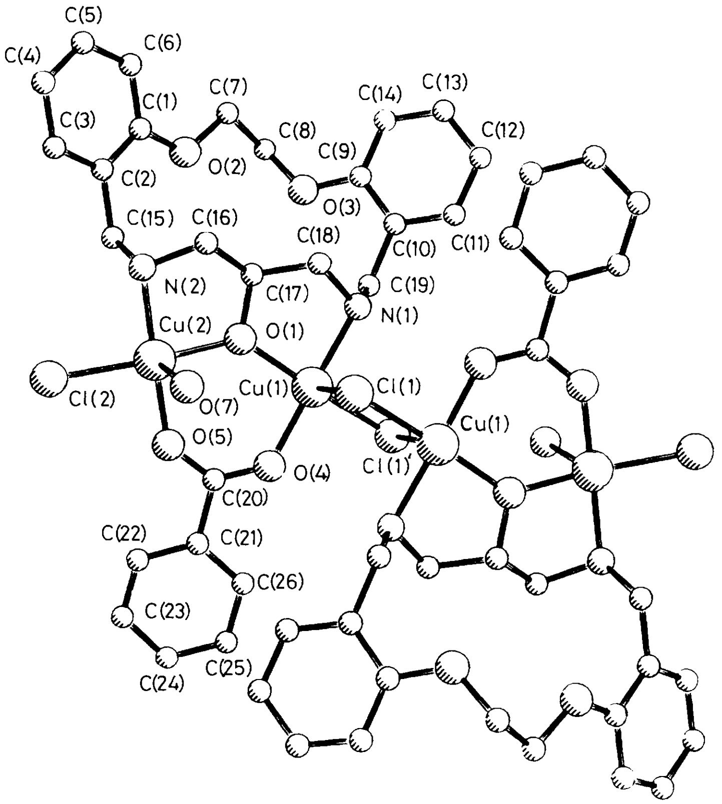


Figure. The molecular structure of the tetranuclear complex $[\{Cu_2L^1(\mu\text{-}O_2CPh)(OH_2)Cl_2\}_2]\cdot 2PhCH_2OH$

Table 3. Atomic co-ordinates ($\times 10^4$) for $[\{Cu_2L^1(\mu\text{-}O_2CPh)(OH_2)Cl_2\}_2]\cdot 2PhCH_2OH$

Atom	x	y	z
Cu(1)	906(1)	666(1)	474(1)
Cu(2)	3 509(1)	539(1)	693(1)
Cl(1)	−668(1)	552(1)	845(1)
Cl(2)	5 066(1)	175(2)	1 257(1)
O(1)	2 228(3)	1 028(3)	315(2)
O(2)	3 554(4)	3 903(4)	−134(3)
O(3)	1 440(4)	3 985(4)	−49(4)
O(4)	1 322(3)	−373(3)	1 167(3)
O(5)	2 964(4)	−244(4)	1 446(3)
O(6)	4 553(7)	3 900(6)	2 171(5)
O(7)	3 185(5)	−723(4)	−272(4)
O(8)	848(11)	1 622(12)	1 779(9)
N(1)	477(4)	1 652(4)	−324(3)
N(2)	4 039(4)	1 436(4)	−58(3)
C(1)	4 409(6)	3 726(6)	−455(5)
C(2)	4 902(6)	2 929(6)	−229(4)
C(3)	5 765(6)	2 722(7)	−539(5)
C(4)	6 159(7)	3 287(8)	−1 079(6)
C(5)	5 663(8)	4 082(7)	−1 289(6)
C(6)	4 802(7)	4 316(7)	−993(6)
C(7)	2 959(8)	4 674(6)	−408(6)
C(8)	2 128(8)	4 738(6)	72(6)
C(9)	620(6)	4 006(5)	−594(5)
C(10)	−42(6)	3 290(5)	−550(4)
C(11)	−883(7)	3 248(5)	−1 080(5)
C(12)	−1 069(9)	3 911(7)	−1 673(6)
C(13)	−393(8)	4 612(7)	−1 703(6)
C(14)	434(7)	4 673(5)	−1 167(5)
C(15)	4 494(6)	2 272(5)	342(4)
C(16)	3 181(5)	1 640(5)	−646(4)
C(17)	2 270(5)	1 766(4)	−221(4)
C(18)	1 331(5)	1 759(4)	−783(4)
C(19)	162(6)	2 526(5)	30(4)
C(20)	2 125(5)	−549(5)	1 556(4)
C(21)	2 115(5)	−1 166(4)	2 267(4)
C(22)	2 985(7)	−1 386(7)	2 694(5)
C(23)	2 987(8)	−1 927(8)	3 360(6)
C(24)	2 126(8)	−2 241(7)	3 582(5)
C(25)	1 262(7)	−2 035(6)	3 161(5)
C(26)	1 246(6)	−1 487(5)	2 500(4)
C(27)	2 569(5)	3 290(7)	2 109(6)
C(28)	1 579(5)	2 995(7)	2 071(6)
C(29)	1 367(5)	2 087(7)	2 242(6)
C(30)	2 145(5)	1 473(7)	2 451(6)
C(31)	3 134(5)	1 768(7)	2 489(6)
C(32)	3 347(5)	2 676(7)	2 318(6)
C(33)	4 434(7)	2 990(8)	2 429(9)
C(34)	2 186(11)	3 175(11)	2 171(11)
C(35)	2 947(11)	3 823(11)	2 166(11)
C(36)	3 944(11)	3 549(11)	2 289(11)
C(37)	4 181(11)	2 628(11)	2 417(11)
C(38)	3 420(11)	1 980(11)	2 421(11)
C(39)	2 423(11)	2 254(11)	2 298(11)
C(40)	1 627(14)	1 543(15)	2 413(12)

Atoms O(6), C(27)–C(33) comprise the benzyl alcohol with occupancy 0.64, O(8), C(34)–C(40) the benzyl alcohol with occupancy 0.36.

shifts are found for the protons adjacent to the ether and hydroxyl oxygen atoms than were found previously. This may indicate that the co-ordination sphere of the zinc ion may also include one, or more, of these oxygen atoms.

Complexes of the 1 + 1 *Macrocycles with* $M(ClO_4)_2$ *and* $M(NO_3)_2$.—The macrocycles form 1:1 complexes with the perchlorate salts of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} in which deprotonation of the macrocyclic ligand has occurred. The complexes

Table 4. Bond lengths (Å)

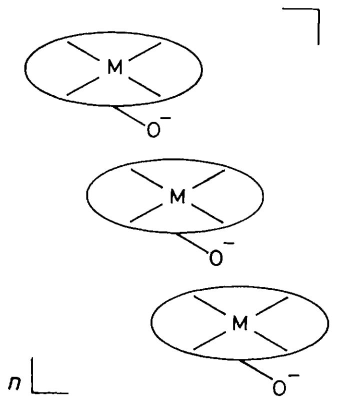
Cu(1)–Cl(1)	2.282(3)	Cu(1)–O(1)	1.904(5)
Cu(1)–O(4)	1.969(5)	Cu(1)–N(1)	2.024(5)
Cu(1)–Cl(1^{I})	2.863(3)	Cu(2)–Cl(2)	2.274(3)
Cu(2)–O(1)	1.912(4)	Cu(2)–O(5)	1.926(6)
Cu(2)–O(7)	2.481	Cu(2)–N(2)	2.018(6)
O(1)–C(17)	1.421(8)	O(2)–C(1)	1.351(11)
O(2)–C(7)	1.431(11)	O(3)–C(8)	1.439(11)
O(3)–C(9)	1.365(10)	O(4)–C(20)	1.233(8)
O(5)–C(20)	1.247(8)	O(6)–C(33)	1.415(15)
O(8)–C(40)	1.428(24)	N(1)–C(18)	1.469(8)
N(1)–C(19)	1.493(9)	N(2)–C(15)	1.498(9)
N(2)–C(16)	1.477(8)	C(1)–C(2)	1.374(12)
C(1)–C(6)	1.406(13)	C(2)–C(3)	1.361(12)
C(2)–C(15)	1.514(11)	C(3)–C(4)	1.387(14)
C(4)–C(5)	1.367(15)	C(5)–C(6)	1.358(15)
C(7)–C(8)	1.461(16)	C(9)–C(10)	1.381(11)
C(9)–C(14)	1.385(12)	C(10)–C(11)	1.373(11)
C(10)–C(19)	1.498(10)	C(11)–C(12)	1.406(13)
C(12)–C(13)	1.374(15)	C(13)–C(14)	1.365(14)
C(16)–C(17)	1.503(9)	C(17)–C(18)	1.503(8)
C(20)–C(21)	1.515(9)	C(21)–C(22)	1.350(11)
C(21)–C(26)	1.359(11)	C(22)–C(23)	1.386(15)
C(23)–C(24)	1.339(16)	C(24)–C(25)	1.333(14)
C(25)–C(26)	1.383(11)	C(32)–C(33)	1.525(12)
C(39)–C(40)	1.519(26)	C–C(phenyl)	1.395
Cu(1) · · · Cu(1^{I})	3.391	Cu(2) · · · Cu(1)	3.489
Cu(1) · · · O(8)	2.64	O(6) · · · Cl(2^{II})	3.264
O(4^{I}) · · · N(1)	3.267	O(4^{I}) · · · H(1)	2.39
Cl(2^{III}) · · · N(2)	3.424	Cl(2^{III}) · · · H(2)	2.64
Cl(2^{III}) · · · O(7)	3.142		

I Inversion related by the operation $-x$, $-y$, $-z$; II screw-related by $1 - x$, $0.5 + y$, $0.5 - z$; III inversion related by $1 - x$, $-y$, $-z$.

Table 5. Bond angles (°)

Cl(1)–Cu(1)–O(1)	165.9(2)	Cl(1)–Cu(1)–O(4)	89.3(2)
O(1)–Cu(1)–O(4)	95.2(2)	Cl(1)–Cu(1)–N(1)	92.0(2)
O(1)–Cu(1)–N(1)	84.8(2)	O(4)–Cu(1)–N(1)	174.7(2)
Cl(1)–Cu(1)–Cl(1^{I})	98.4(1)	O(1)–Cu(1)–Cl(1^{I})	95.0(1)
O(4)–Cu(1)–Cl(1^{I})	89.7(1)	N(1)–Cu(1)–Cl(1^{I})	85.0(2)
Cl(2)–Cu(2)–O(1)	170.6(2)	Cl(2)–Cu(2)–O(5)	88.7(2)
O(1)–Cu(2)–O(5)	93.0(2)	Cl(2)–Cu(2)–N(2)	92.8(2)
O(1)–Cu(2)–N(2)	84.9(2)	O(5)–Cu(2)–N(2)	175.9(2)
O(7)–Cu(2)–Cl(2)	101.3	O(7)–Cu(2)–O(1)	88.1
O(7)–Cu(2)–O(5)	87.2	O(7)–Cu(2)–N(2)	96.2
Cu(1)–Cl(1)–Cu(1^{I})	81.6(1)	Cu(1)–O(1)–Cu(2)	132.1(2)
Cu(1)–O(1)–C(17)	113.9(4)	Cu(2)–O(1)–C(17)	113.8(4)
C(1)–O(2)–C(7)	119.3(7)	C(8)–O(3)–C(9)	122.7(6)
Cu(1)–O(4)–C(20)	131.4(4)	Cu(2)–O(5)–C(20)	136.8(5)
Cu(1)–N(1)–C(18)	104.6(4)	Cu(1)–N(1)–C(19)	114.1(4)
C(18)–N(1)–C(19)	113.5(5)	Cu(2)–N(2)–C(15)	113.2(4)
Cu(2)–N(2)–C(16)	105.1(4)	C(15)–N(2)–C(16)	113.4(5)
O(2)–C(1)–C(2)	117.1(7)	O(2)–C(1)–C(6)	123.0(8)
C(2)–C(1)–C(6)	119.9(8)	C(1)–C(2)–C(3)	119.0(8)
C(1)–C(2)–C(15)	121.3(7)	C(3)–C(2)–C(15)	119.7(8)
C(2)–C(3)–C(4)	122.1(9)	C(3)–C(4)–C(5)	118.0(9)
C(4)–C(5)–C(6)	121.9(10)	C(1)–C(6)–C(5)	119.2(9)
O(2)–C(7)–C(8)	107.6(7)	O(3)–C(8)–C(7)	113.0(8)
O(3)–C(9)–C(10)	115.0(7)	O(3)–C(9)–C(14)	124.8(7)
C(10)–C(9)–C(14)	120.2(7)	C(9)–C(10)–C(11)	119.2(7)
C(9)–C(10)–C(19)	121.9(7)	C(11)–C(10)–C(19)	118.8(7)
C(10)–C(11)–C(12)	121.0(8)	C(11)–C(12)–C(13)	118.2(9)
C(12)–C(13)–C(14)	121.2(9)	C(9)–C(14)–C(13)	120.1(8)
N(2)–C(15)–C(2)	112.4(6)	N(2)–C(16)–C(17)	108.3(5)
O(1)–C(17)–C(16)	108.1(5)	O(1)–C(17)–C(18)	108.5(5)
C(16)–C(17)–C(18)	111.3(5)	N(1)–C(18)–C(17)	108.2(5)
N(1)–C(19)–C(10)	114.1(6)	O(4)–C(20)–O(5)	126.8(6)
O(4)–C(20)–C(21)	118.2(6)	O(5)–C(20)–C(21)	114.9(6)
C(20)–C(21)–C(22)	119.5(7)	C(20)–C(21)–C(26)	121.6(6)
C(22)–C(21)–C(26)	118.9(7)	C(21)–C(22)–C(23)	120.3(9)
C(22)–C(23)–C(24)	120.2(9)	C(23)–C(24)–C(25)	120.1(9)
C(24)–C(25)–C(26)	120.4(9)	C(21)–C(26)–C(25)	120.1(7)
C(27)–C(32)–C(33)	121.4(6)	C(31)–C(32)–C(33)	118.4(6)
O(6)–C(33)–C(32)	112.5(9)	O(8)–C(40)–C(39)	108.5(17)
C(34)–C(39)–C(40)	121.8(10)	C(38)–C(39)–C(40)	117.7(9)

I Inversion related atom by the operation $-x$, $-y$, $-z$.



(II)

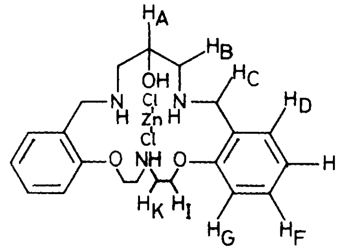
were characterised by elemental analysis, i.r. spectra and f.a.b. mass spectra (Tables 7 and 8). The i.r. spectra show NH stretching frequencies in the region 3 200—3 300 cm^{-1} and the free-ligand OH stretch is absent. The vibrations of the perchlorate group appear at *ca.* 1 100 and 625 cm^{-1}. For the majority of the complexes these are single absorptions characteristic of non-co-ordinated anions;[13] in a limited number of cases there is a discernible splitting of the bands which may reflect a lowered symmetry due to co-ordination of the anion to the metal or arise from crystal-packing or hydrogen-bonding effects.

The f.a.b. mass spectra all show peaks corresponding to $[ML]^+$. However, it is also possible to find $[ML(ClO_4)]^+$ suggesting that under the conditions of the experiment reprotonation of the ligand has occurred; the former peak is of greater abundance. Most interestingly, the f.a.b.m.s. of the perchlorate complexes gave peaks at high mass numbers corresponding to the presence of oligomeric species. As only g.c.-purified ligands were used in the complexation studies it is improbable that these species can be derived from 2 + 2 macrocycles and more likely that they arise from aggregation around the molecular ion in the matrix during the f.a.b.m.s. experiment, as has been observed for complexes such as $[Co\{H_2N(CH_2)_2NH(CH_2)_2NH_2\}_2][ClO_4]_3$.[14] Studies on complexes of cyclic polyethers have not revealed high-mass aggregates[15] and there has been no report of high-mass, oligomeric species derived from metal complexes of Schiff-base macrocycles. Therefore it is proposed that the aggregation here is linked to the presence of the deprotonated pendant hydroxy-function in the macrocycles and that the high-mass peaks are derived from the breakdown of oligomeric solid-state species.

The formation of a chain, or stack, involving two or more of the basic unit $ML(ClO_4)$ linked by a bridging group is possible. The i.r. spectra show that the anions are non-co-ordinating and so it is likely that the endogenous alkoxide is available for bridging to build up species such as **(II)**

The 1:1 complexes formed by the reaction of the 1 + 1 macrocycles and $M(NO_3)_2$ (M = Co, Ni, Cu, Zn, or Cd) follow the patterns exhibited by the perchlorate complexes (Tables 9 and 10). The i.r. spectra show NH stretching bands in the region

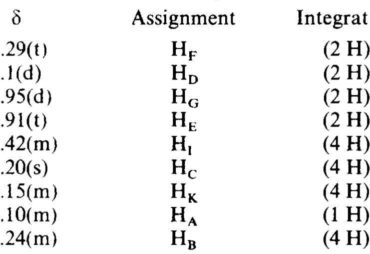
Table 6. Proton n.m.r. spectra (CD_3CN) of the zinc complexes



$Zn(HL^6)Cl_2$

δ	Assignment	Integration
7.29(t)	H_F	(2 H)
7.1(d)	H_D	(2 H)
6.95(d)	H_G	(2 H)
6.91(t)	H_E	(2 H)
4.42(m)	H_I	(4 H)
4.20(s)	H_C	(4 H)
4.15(m)	H_K	(4 H)
4.10(m)	H_A	(1 H)
3.24(m)	H_B	(4 H)

s = singlet, d = doublet, t = triplet, m = multiplet. Change in chemical shift as compared to free ligand (Δδ) (negative value indicates a shift to lower field): H_A, −0.14; H_B, −0.55; H_C, −0.37; H_D, +0.04; H_E, + 0.01; H_F, −0.05; H_G, −0.03; H_I, −0.22; and H_K, −0.17.



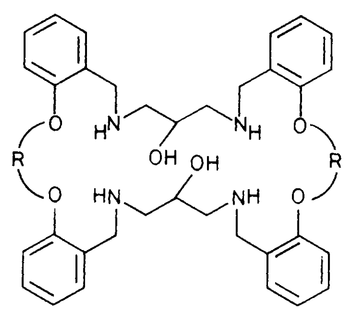
$Zn(HL^3)Cl_2$

δ	Assignment	Integration
7.28(t)	H_F	(2 H)
7.20(d)	H_D	(2 H)
6.92(t)	H_E	(2 H)
6.87(d)	H_G	(2 H)
4.41(m)	H_I	(4 H)
4.14(s)	H_C	(4 H)
4.11(m)	H_A	(1 H)
3.26(m)	H_B	(4 H)
2.13(m)	H_K	(4 H)

Change in chemical shift as compared to free ligand (Δδ): H_A, −0.16; H_B, −0.53; H_C, −0.34; H_D +0.03; H_E, −0.01; H_F, −0.04; H_G, −0.01; H_I, −0.34; and H_K, −0.06.

3 240—3 310 and a single band at 1 380 cm^{-1} due to the asymmetric N–O stretch of an ionic nitrate.[13] The reaction of HL^8 with $Ni(NO_3)_2$ gave two products, mauve $[NiL^8]NO_3\cdot0.5H_2O$ and green $[Ni(HL^8)(NO_3)]NO_3\cdot H_2O$ for which bands at 1 450, 1 380, and 1 295 cm^{-1} are found and attributed to the presence of both co-ordinated and non-co-ordinated nitrate.

The f.a.b.m.s. of the green complex shows a parent peak corresponding to $[Ni(HL)(NO_3)]^+$ whereas that for the mauve complex has peaks corresponding to $[NiL]^+$ and higher oligomeric species. The complexes of general formula $[ML]NO_3\cdot nH_2O$ all exhibit high-mass peaks and it is likely that oligomers of the form (**II**) are present.



	R
H_2L^9	$(CH_2)_3$
H_2L^{10}	$(CH_2)_4$
H_2L^{11}	$(CH_2)_6$

Complexes of a 2 + 2 *Macrocycle*.—Metal complexation studies were undertaken for one 2 + 2 macrocycle, HL^{10} where full reduction of the imine bonds and a double or 2 + 2 condensation has occurred. Mononuclear complexes with retention of the OH functions were recovered from reaction of the macrocycle with $M(ClO_4)_2$ (M = Co, Ni, or Zn) and $CdCl_2$ whereas a homodinuclear species in which the alcohol groups have been deprotonated is obtained from $Cu(ClO_4)_2$.

The analytical and m.s. data are presented in Table 11. The f.a.b.m.s. of the mononuclear complexes shows two major peaks attributable to the ions $[M(HL^{10})]^+$ and $[M(H_2L^{10})X]^+$ where X is an anion. The dinuclear copper(II) complex shows peaks corresponding to $[Cu(HL^{10})]^+$, $[Cu_2L^{10}]^{2+}$, and $[Cu_2L^{10}(ClO)_4]^+$. No higher-mass peaks were detected for these complexes.

The i.r. spectra show NH stretching frequencies in the region 3 250—3 300 cm^{-1} and, for the mononuclear complexes, the ligand OH stretching modes are at *ca.* 3 430 cm^{-1}. The single perchlorate stretch noted at *ca.* 1 100 cm^{-1} indicates the presence of non-co-ordinated anions. Comparison can be made with the potentially dinucleating octadentate macrocycle (**3**) for which only mononuclear complexes have been obtained.[16] This observation was assumed to reflect the preference of the transition-metal ions used for the N_4 donor set from the macrocycle and was confirmed with the crystal structure of the dithiocyanatonickel complex in which the nickel is octahedrally co-ordinated by the four N atoms of the macrocycle and two *cis*-thiocyanate anions. In the current study the complexes of Ni, Zn, and Cd are probably involved in a similar bonding pattern, there being no deprotonation of the endogenous alcohols. The dinuclear copper(II) complex is formed with double deprotonation of the ligand and in the absence of a crystal structure and with knowledge of the nature of (**I**) it is plausible to propose a doubly bridged species in which the endogenous alkoxy-groups are employed as the bridges (**III**).

Conclusions

The introduction of the hydroxyl group into the framework of the N_2O_2 Lindoy-type macrocycles has afforded interesting and novel features both in the formation of the macrocyclic ligands and of their transition-metal complexes. Detailed study of the complexes has however been hindered by solubility problems.

The involvement of the pendant hydroxyl group in complexation appears to be closely linked to the type of anion present. In the mononuclear halide complexes the hydroxyl remains protonated and is therefore unlikely to be involved in co-ordination because of the presence of strongly co-ordinating anions. For the complexes of the less strongly co-ordinating anions the hydroxyl is deprotonated and likely to be involved in complexation as it will readily displace the weak anion. These

Table 7. Macrocyclic complexes of metal perchlorates

	Analysis* (%)				I.r. bands (cm^{-1})	
Complex	C	H	N	Cl	Secondary amine N–H stretch	Perchlorate
$CuL^1(ClO_4)\cdot H_2O$	45.3	5.0	5.3	6.9	3 275	1 100(br), 625(sp)
	(44.9)	(5.0)	(5.5)	(7.0)		
$CoL^1(ClO_4)\cdot 0.5MeOH$	46.6	5.0	5.5	6.8	3 300(sh), 3 260(sp)	1 090(br), 625(sp)
	(46.7)	(5.0)	(5.6)	(7.1)		
$ZnL^1(ClO_4)\cdot H_2O$	44.0	5.0	5.4	5.8	3 290	1 115, 1 070, 625(sp)
	(44.7)	(4.9)	(5.5)	(7.0)		
$CuL^2(ClO_4)\cdot H_2O$	46.7	5.3	5.6		3 280	1 100(vbr), 620
	(46.0)	(5.4)	(5.4)			
$NiL^2(ClO_4)$	47.8	5.4	5.2	7.1	3 290, 3 260(sh)	1 090(br), 625(sp)
	(48.1)	(5.0)	(5.6)	(7.1)		
$ZnL^2(ClO_4)$	46.9	5.2	5.1		3 290	1 100(vbr), 620
	(47.4)	(5.0)	(5.5)			
$CuL^4(ClO_4)\cdot H_2O$	46.8	5.7	4.8	7.1	3 280	1 100(br), 620(sp)
	(47.0)	(5.5)	(5.2)	(6.6)		
$NiL^3(ClO_4)$	48.9	5.4	5.4		3 280	1 110(br), 620(sp)
	(49.1)	(5.3)	(5.5)			
$CoL^3(ClO_4)$	49.5	5.6	5.3	6.7	3 260(sp), 3 240(sh)	1 120, 1 090, 620(sp)
	(49.1)	(5.3)	(5.4)	(6.9)		
$ZnL^3(ClO_4)$	48.1	5.4	5.2	6.7	3 290	1 120, 1 100, 620(sp)
	(48.5)	(5.2)	(5.4)	(6.8)		
$CuL^4(ClO_4)\cdot H_2O$	47.9	5.9	5.2	6.9	3 270, 3 200(sh)	1 120, 1 085, 630(sh), 625
	(48.0)	(5.7)	(5.1)	(6.4)		
$ZnL^4(ClO_4)\cdot 2H_2O$	46.3	6.0	5.1	6.6	3 300(sh)	1 100(vbr), 625
	(46.3)	(5.8)	(4.9)	(6.2)		
$CuL^5(ClO_4)$	50.4	5.9	4.9		3 260(sp)	1 140, 1 090, 625(sp)
	(50.5)	(5.7)	(5.1)			
$ZnL^5(ClO_4)$	50.6	5.6	5.2		3 270(sh), 3 260	1 100(br), 620(sp)
	(50.3)	(5.7)	(5.1)			
$CuL^7(ClO_4)\cdot H_2O$	53.1	5.4	4.7		3 275	1 110(br), 620(sp)
	(52.9)	(5.4)	(4.6)			
$NiL^7(ClO_4)$	55.1	6.0	4.8	6.1	3 300(sp), 3 280(sh)	1 110, 1 060, 620(sp)
	(55.0)	(5.3)	(4.8)	(6.0)		
$CoL^7(ClO_4)\cdot MeOH$	54.4	6.1	4.6		3 295(sp)	1 120, 1 090, 625(sp)
	(54.0)	(5.8)	(4.5)			
$ZnL^7(ClO_4)$	54.4	5.8	4.6	5.9	3 280	1 100(br), 620(sp)
	(54.4)	(5.2)	(4.7)	(5.9)		
$L^6(ClO_4)$	46.9	5.2	5.1	6.9	3 280(sh), 3 260	1 110(br), 630(sp)
	(47.2)	(5.1)	(5.2)	(6.6)		
$NiL^6(ClO_4\cdot MeCN$	48.5	5.1	7.4	6.6	3 300(sp)	1 120, 1 070, 620(sp)
	(48.4)	(5.3)	(7.4)	(6.2)		
$CoL^6(ClO_4)\cdot 0.5BuOH$	49.2	5.8	5.5	6.3	3 295(sh)	1 120, 1 070, 630(sh), 625
	(48.7)	(5.7)	(4.9)	(6.3)		
$ZnL^6(ClO_4)\cdot 0.5BuOH$	48.2	5.8	4.8	6.0	3 280(br)	1 100(br), 625
	(48.2)	(5.6)	(4.9)	(6.2)		
$CuL^8(ClO_4)\cdot 0.5H_2O$	50.2	4.9	7.2	6.4	3 260(sp)	1 100(vbr), 625
	(50.0)	(4.7)	(7.3)	(6.1)		
$CoL^8(ClO_4)\cdot 0.5H_2O$	50.3	4.7	7.7	6.0	3 250(br)	1 120, 1 080, 620(sp)
	(50.4)	(4.8)	(7.4)	(6.2)		
$ZnL^8(ClO_4)\cdot H_2O$	48.9	4.9	6.7	8.3	3 290(sh), 3 250(sp)	1 090(br), 625(sp)
	(49.1)	(4.8)	(7.1)	(6.0)		

* Calculated values given in parentheses.

observations reinforce the view, advanced by Wang and Chung[17] in a discussion concerning changes in the dependence of the thermodynamic stability patterns of Lindoy-type macrocyclic complexes on the ring size when changing from chloride to nitrate anions, that the choice of the counter anion has a significant effect on the type of macrocyclic complex formed.

The usefulness of f.a.b.m.s. in this area has been demonstrated and the presence of intriguing oligomeric species has been established through application of this technique.

Experimental

Microanalyses were carried out by the University of Sheffield and the University of Leeds Microanalytical Services. I.r. spectra were recorded as KBr discs using a Perkin-Elmer 297 spectrophotometer. E.i. mass spectra were recorded using a Kratos MS 25 spectrometer and f.a.b.m.s. using a Kratos MS 80RF mass spectrometer (accelerating voltage 4 kV, resolution 1500) coupled to a DS55 data system. The atom gun was an adapted saddle-field source (Ion Tech Ltd.) operated at *ca.* 6 eV and a tube current of *ca.* 2 mA. Xenon was used to provide the primary beam of atoms and the samples were mixed with a small amount of 3-nitrobenzyl alcohol matrix on a stainless-steel probe. Spectra were recorded in the positive-ion mode at a scan speed of 30-s per decade. N.m.r. spectra were run on Perkin-Elmer R34, Bruker WH250, and Bruker WH400 spectrometers.

Table 8. F.a.b. mass spectra of the metal perchlorate complexes

Complex	m/z, Assignment, relative intensity (%)
$CuL^1(ClO_4)\cdot H_2O$	391, $[CuL^1]^+$, 100; 1 269, $[Cu_3L^1_3(ClO_4)]^+$, 3; 1 370 $[Cu_3L^1_3(ClO_4)_2]^+$, 15
$CoL^1(ClO_4)\cdot$ 0.5MeOH	386, $[CoL^1]^+$, 100; 870 $[Co_2L^1_2(ClO_4)]^+$, 25; 1 197 $[Co_2L^1_3(ClO_4) + H]^+$, 15
$ZnL^1(ClO_4)\cdot H_2O$	391, $[ZnL^1]^+$, 100; 883, $[Zn_2L^1_2(ClO_4)]^+$, 12; 1 375, $[Zn_3L^1_3(ClO_4)_2]^+$, 9
$CuL^2(ClO_4)\cdot H_2O$	405, $[CuL^2]^+$, 100; 909, $[Cu_2L^2_2(ClO_4)]^+$, 10; 1 412, $[Cu_3L^2_3(ClO_4)_2]^+$, 15
$NiL^2(ClO_4)$	399, $[NiL^2]^+$, 100; 741, $[NiL^2_2 + H]^+$, 46; 843, $[NiL^2_2(ClO_4) + H_2]^+$, 30
$CoL^2(ClO_4)$	400, $[CoL^2]^+$, 100; 900, $[Co_2L^2_2(ClO_4)]^+$, 35
$ZnL^2(ClO_4)$	405, $[ZnL^2]^+$, 100; 909, $[Zn_2L^2_2(ClO_4)]^+$, 32; 1 413, $[Zn_3L^2_3(ClO_4)_2]^+$, 1
$CuL^3(ClO_4)\cdot H_2O$	419, $[CuL^3]^+$, 100; 938, $[Cu_2L^3_2(ClO_4)]^+$, 5; 1 002, $[Cu_3L^3_2(ClO_4)]^{3+}$, 15; 1 455, $[Cu_3L^3_3(ClO_4)_2]^+$, 15
$NiL^3(ClO_4)$	413, $[NiL^3]^+$, 100; 769, $[NiL^3_2 + H]^+$, 25; 871, $[NiL^3_2(ClO_4)^+, H_2]^+$, 25
$CoL^3(ClO_4)$	414, $[CoL^3]^+$, 100; 928, $[Co_2L^3_2(ClO_4)]^+$, 35; 1 283, $[Co_2L^3_3(ClO_4) + H]^+$, 8
$ZnL^3(ClO_4)$	420, $[ZnL^3]^+$, 100; 938, $[Zn_2L^3_2(ClO_4)]^+$, 10; 1 460, $[Zn_3L^3_3(ClO_4)_2]^+$, 8; 1 982, $[Zn_4L^3_4(ClO_4)_3]^+$, 4
$CuL^4(ClO_4)\cdot H_2O$	433, $[CuL^4]^+$, 100; 1 497, $[Cu_3L^4_3(ClO_4)_2]^+$, 8
$ZnL^4(ClO_4)\cdot 2H_2O$	434, $[ZnL^4]^+$, 100; 966, $[Zn_2L^4_2(ClO_4)]^+$, 15; 1 502, $[Zn_3L^4_3(ClO_4)_2]^+$, 6
$CuL^5(ClO_4)$	447, $[CuL^5]^+$, 100; 1 553, $[Cu_3L^5_3(ClO_4)_2]^+$, 10
$ZnL^5(ClO_4)$	447, $[ZnL^5]^+$, 100; 993, $[Zn_2L^5_2(ClO_4)]^+$, 10; 1 555, $[Zn_3L^5_3(ClO_4)_2]^+$, 5
$CuL^7(ClO_4)\cdot H_2O$	494, $[CuL^7]^+$, 100; 1 087, $[Cu_2L^7_2(ClO_4)]^+$, 5
$NiL^7(ClO_4)$	489, $[NiL^7]^+$, 100; 589, $[NiL^7(ClO_4) + H_2]^+$, 40
$CoL^7(ClO_4)\cdot$MeOH	490, $[CoL^7]^+$, 100; 590 $[CoL^7(ClO_4) + H]^+$, 25; 1 022, $[CoL^7_2(ClO_4) + H_2]^+$, 22; 1 671 $[Co_3L^7_3(ClO_4)_2]^+$, 4
$ZnL^7(ClO_4)$	495, $[ZnL^7]^+$, 100; 1 088, $[Zn_2L^7_2(ClO_4)]^+$, 11
$CuL^6(ClO_4)$	435, $[CuL^6]^+$, 100; 971, $[Cu_2L^6_2(ClO_4)]^+$, 10; 1 032, $[Cu_3L^6_2(ClO_4)]^{3+}$, 8; 1 502, $[Cu_3L^6_3(ClO_4)_2]^+$, 17
$NiL^6(ClO_4)\cdot$MeCN	429, $[NiL^6]^+$, 100; 529, $[NiL^6(ClO_4) + H]^+$, 42; 901, $[NiL^6_2(ClO_4) + H_2]^+$, 22; 1 432, $[Ni_2L^6_3(ClO_4)_2 + H_2]^+$, 2
$CoL^6(ClO_4)\cdot$ 0.5BuOH	431, $[CoL^6]^+$, 100; 530, $[CoL^6(ClO_4) + H]^+$, 15; 803, $[CoL^6_2 + H]^+$, 12; 902 $[CoL^6_2(ClO_4)]^+$, 18
$ZnL^6(ClO_4)\cdot$ 0.5BuOH	435, $[ZnL^6]^+$, 100; 973, $[Zn_2L^6_2(ClO_4)]^+$, 10; 1 507, $[Zn_3L^6_3(ClO_4)_2]^+$, 7
$CuL^8(ClO_4)\cdot 0.5H_2O$	468, $[CuL^8]^+$, 100; 1 037, $[Cu_2L^8_2(ClO_4)]^+$, 54; 1 604, $[Cu_3L^8_3(ClO_4)_2]^+$, 19
$CoL^8(ClO_4)\cdot 0.5H_2O$	464, $[CoL^8]^+$, 100; 564, $[CoL^8(ClO_4) + H]^+$, 12; 968, $[CoL^8_2(ClO_4) + H_2]^+$, 14
$ZnL^8(ClO_4)\cdot H_2O$	470, $[ZnL^8]^+$, 100; 1 039, $[Zn_2L^8_2(ClO_4)]^+$, 90

Table 9. Macrocyclic complexes of metal nitrates

	Analysis (%)			I.r. bands (cm^{-1})	
Complex	C	H	N	Secondary amine N–H stretch	Nitrate
$CuL^1(NO_3)\cdot H_2O$	48.5	5.4	8.6	3 260(sp)	1 390s
	(48.5)	(5.4)	(8.9)		
$NiL^1(NO_3)\cdot H_2O$	48.7	5.4	8.7	3 255(sp),	1 380s(br)
	(49.0)	(5.4)	(9.0)	3 230(sp)	
$CuL^2(NO_3)\cdot 1.5H_2O$	48.9	5.7	8.4	3 260(br)	1 390s(br)
	(48.6)	(5.7)	(8.5)		
$NiL^2(NO_3)\cdot H_2O$	49.7	5.6	8.7	3 280(br)	1 385s
	(50.0)	(5.6)	(8.8)		
$ZnL^2(NO_3)\cdot H_2O$	48.9	5.2	8.5	3 280(sh)	1 385s(br)
	(49.3)	(5.6)	(8.6)		
$CdL^2(NO_3)\cdot H_2O$	44.8	5.0	7.7	3 280(br)	1 380(vbr)
	(44.9)	(5.1)	(7.9)		
$CuL^3(NO_3)\cdot$MeOH	51.5	6.0	8.0	3 270(br),	1 385s
	(51.5)	(6.1)	(8.2)	3 220(sh)	
$NiL^3(NO_3)$	53.4	5.4	9.2	3 300(sp),	1 380s
	(53.0)	(5.7)	(8.8)	3 235(sp)	
$CoL^3(NO_3)\cdot 1.5H_2O$	49.7	6.0	8.4	3 270(sh)	1 380s
	(50.1)	(6.0)	(8.3)		
$ZnL^3(NO_3)$	51.9	5.7	8.9	3 260(br),	1 390s
	(52.2)	(5.6)	(8.7)	3 240(sh)	
$CdL^3(NO_3)$	47.4	4.9	7.9	3 290(sp)	1 390s
	(47.6)	(5.1)	(7.9)		
$CuL^4(NO_3)\cdot 0.5H_2O$	52.3	6.4	8.2	3 250(sh)	1 380s
	(52.3)	(6.0)	(8.3)		
$CdL^4(NO_3)$	49.0	5.6	7.3	3 290	1 380s
	(48.6)	(5.4)	(7.7)		
$CuL^5(NO_3)$	54.3	6.2	8.1	3 280,	1 380s
	(54.3)	(6.1)	(8.2)	3 260(sh)	
$CuL^7(NO_3)\cdot 2H_2O$	53.9	6.0	7.4	3 250(br)	1 380s
	(54.7)	(5.9)	(7.1)		
$NiL^7(NO_3)\cdot 0.5H_2O$	57.5	6.2	7.5	3 300(sp)	1 380s
	(57.8)	(5.8)	(7.5)		
$CoL^7(NO_3)$	58.7	5.2	7.4	3 260(sh)	1 380s
	(58.6)	(5.8)	(7.6)		
$ZnL^7(NO_3)$	57.8	5.9	7.6	3 230(sh)	1 380s(br)
	(58.0)	(5.6)	(7.5)		
$CuL^6(NO_3)$	49.9	5.5	8.6	3 250(br)	1 390s(br)
	(50.7)	(5.5)	(8.5)		
$NiL^6(NO_3)$	50.9	5.5	8.5	3 300(sp)	1 390
	(51.2)	(5.5)	(8.5)		
$CoL^6(NO_3)\cdot H_2O$	48.5	5.3	8.7	3 260(sp)	1 380s
	(49.4)	(5.7)	(8.2)		
$ZnL^6(NO_3)$	49.8	5.5	8.6	3 280(sh),	1 390s
	(50.6)	(5.5)	(8.4)	3 255(sp)	
$CdL^6(NO_3)\cdot H_2O$	43.9	5.3	7.5	3 280(br)	1 380
	(44.7)	(5.2)	(7.4)		
$Ni(HL^8)(NO_3)_2\cdot$ H_2O	49.2	4.8	12.0	3 250(sh)	1 380(br)
	(47.6)	(4.8)	(11.6)		
$NiL^8(NO_3)\cdot 0.5H_2O$	54.1	5.2	10.7	3 280(sh)	1 380s
	(53.9)	(5.1)	(10.5)		
$CoL^8(NO_3)\cdot H_2O$	52.4	5.1	10.7	3 250w(sh)	1 385s
	(53.0)	(5.2)	(10.3)		

* Calculated values are given in parentheses.

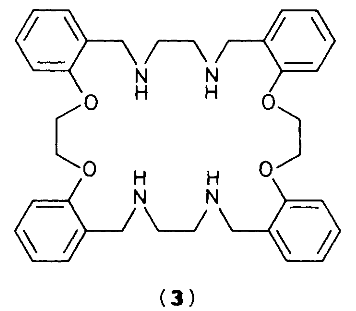
The organic ligands were prepared by literature methods or modifications thereof.[18–21] The preparation of HL^2 is described as a representative example.

(*i*) 1,3-Bis(2′-formylphenoxy)propane [**1**; R = $(CH_2)_3$] was prepared according to the method of Armstrong and Lindoy.[21]

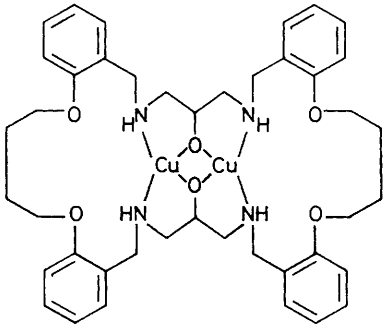
(*ii*) 1,3-Diamino-2-propanol (0.5 g, 5.5 mmol) in methanol (60 cm^3) was added slowly to a refluxing solution of the dialdehyde [**1**; R = $(CH_2)_3$] (1.42 g, 5 mmol) in methanol (60 cm^3). The solution was refluxed for 2 h and an excess of $NaBH_4$ (0.5 g) was added carefully. Reflux was continued for 15 min and then the solution was allowed to cool to ambient temperature and filtered. The filtrate was reduced under vacuum to a volume of 30 cm^3 and distilled water (100 cm^3) added. The solution was allowed to stand overnight in a refrigerator and a dark brown oil formed. This was extracted with $CHCl_3$, washed with water (2 × 50 cm^3), and dried over sodium sulphate. The $CHCl_3$ was removed under vacuum to give a brown viscous oil which was shown by f.a.b.m.s. to be a mixture of the 1 + 1 and 2 + 2 macrocycles. These were separated by m.p.l.c. using a silica gel column (40 cm × 30 mm). A typical run involved the injection of a sample of the product mixture (0.3—0.8 g) in methanol (8 cm^3) containing 0.3% ammonia. Under a pressure of 70 lbf in^{-2} separation was achieved in 3—8 h. Continuous monitoring of the column effluent with a u.v. detector (245 nm) ensured clean separation of the fractions. Both products were obtained as white powders on slow evaporation of the

Table 10. F.a.b. mass spectra of the metal nitrate complexes

Complex	m/z, Assignment, relative intensity (%)
$CuL^1(NO_3)\cdot H_2O$	390, $[CuL^1]^+$, 100; 453, $[CuL^1(NO_3) + H]^+$, 12; 842 $[Cu_2L^1{}_2(NO_3)]^+$, 3; 1 296, $[Cu_3L^1{}_3(NO_3)_2]^+$, 10
$NiL^1(NO_3)\cdot H_2O$	385, $[NiL^1]^+$, 60; 443 $[NiL^1(NO_3) + H]^+$, 100; 832, $[Ni_2L^1{}_2(NO_3)]^+$, 8
$CuL^2(NO_3)\cdot 1.5H_2O$	404, $[CuL^2]^+$, 100; 870, $[Cu_2L^2{}_2(NO_3)]^+$, 8
$NiL^2(NO_3)\cdot H_2O$	399, $[NiL^2]^+$, 100; 860, $[Ni_2L^2{}_2(NO_3)]^+$, 18
$ZnL^2(NO_3)\cdot H_2O$	405, $[ZnL^2]^+$, 100; 872, $[Zn_2L^2{}_2(NO_3)]^+$, 18; 1 340, $[Zn_3L^2{}_3(NO_3)_2]^+$, 7
$CdL^2(NO_3)\cdot H_2O$	453, $[CdL^2]^+$, 100; 968, $[Cd_2L^2{}_2(NO_3)]^+$, 4
$CuL^3(NO_3)\cdot MeOH$	419, $[CuL^3]^+$, 100; 901, $[Cu_2L^3{}_2(NO_3)]^+$, 10; 1 025, $[Cu_3L^3{}_2(NO_3)_2]^{2+}$, 10; 1 380, $[Cu_3L^3{}_3(NO_3)_2]^+$, 12
$NiL^3(NO_3)$	413, $[NiL^3]^+$, 100; 888, $[Ni_2L^3{}_2(NO_3)]^+$, 10; 1 072, $[Ni_3L^3{}_2(NO_3)_3]^+$, 18
$CoL^3(NO_3)\cdot 1.5H_2O$	414, $[CoL^3]^+$, 100; 890, $[Co_2L^3{}_2(NO_3)]^+$, 8
$ZnL^3(NO_3)$	419, $[ZnL^3]^+$, 100; 904, $[Zn_2L^3{}_2(NO_3)]^+$, 9; 1 383, $[Zn_3L^3{}_3(NO_3)_2]^+$, 8
$CdL^3(NO_3)$	467, $[CdL^3]^+$, 100; 996, $[Cd_2L^3{}_2(NO_3)]^+$, 11; 1 527, $[Cd_3L^3{}_3(NO_3)_2]^+$, 15; 1 772, $[Cd_2L^3{}_4(NO_3)_2 + H_3]^+$, 12
$CuL^4(NO_3)\cdot 0.5H_2O$	434, $[CuL^4]^+$, 100; 923, $[Cu_2L^4{}_2(NO_3)]^+$, 2; 1 055, $[Cu_3L^4{}_2(NO_3)_2]^{2+}$, 2; 1 424, $[Cu_3L^4{}_3(NO_3)_2]^+$, 6
$CdL^4(NO_3)$	482, $[CdL^4]^+$, 100; 1 024, $[Cd_2L^4{}_2(NO_3)]^+$, 4
$CuL^5(NO_3)$	447, $[CuL^5]^+$, 100; 954, $[Cu_2L^5{}_2(NO_3)]^+$, 81; 1 464, $[Cu_3L^5{}_3(NO_3)_2]^+$, 10
$CuL^7(NO_3)\cdot 2H_2O$	494, $[CuL^7]^+$, 100; 1 606, $[Cu_3L^7{}_3(NO_3)_2]^+$, 3
$NiL^7(NO_3)\cdot 0.5H_2O$	489, $[NiL^7]^+$, 100; 921, $[NiL^7{}_2 + H]^+$, 65; 984, $[NiL^7{}_2(NO_3) + H_2]^+$, 8; 1 040, $[Ni_2L^7{}_2(NO_3)]^+$, 6
$CoL^7(NO_3)$	490, $[CoL^7]^+$, 55; 922, $[CoL^7{}_2 + H]^+$, 100; 1 042, $[Co_2L^7{}_2(NO_3)]^+$, 82; 1 104, $[Co_2L^7{}_2(NO_3)_2 + H]^+$, 84
$ZnL^7(NO_3)$	495, $[ZnL^7]^+$, 100; 1 052, $[Zn_2L^7{}_2(NO_3)]^+$, 18; 1 609, $[Zn_3L^7{}_3(NO_3)_2]^+$, 10
$CuL^6(NO_3)$	435, $[CuL^6]^+$, 100; 497, $[CuL^6(NO_3) + H]^+$, 15; 932, $[Cu_2L^6{}_2(NO_3)]^+$, 3; 1 428, $[Cu_3L^6{}_3(NO_3)_2]^+$, 6
$NiL^6(NO_3)$	429, $[NiL^6]^+$, 100; 492, $[NiL^6(NO_3) + H]^+$, 12; 801, $[NiL^6{}_2 + H]^+$, 14; 864, $[NiL^6{}_2(NO_3) + H_2]^+$, 6
$CoL^6(NO_3)\cdot H_2O$	430, $[CoL^6]^+$, 100; 801, $[CoL^6{}_2 + H]^+$, 12; 922, $[Co_2L^6{}_2(NO_3)]^+$, 18; 985, $[Co_2L^6{}_2(NO_3)_2 + H]^+$, 38
$ZnL^6(NO_3)$	435, $[ZnL^6]^+$, 100; 932, $[Zn_2L^6{}_2(NO_3)]^+$, 4
$CdL^6(NO_3)\cdot H_2O$	483, $[CdL^6]^+$, 100; 1 029, $[Cd_2L^6{}_2(NO_3)]^+$, 6
$Ni(HL^8)(NO_3)_2\cdot H_2O$	462, $[NiL^8]^+$, 100; 525, $[NiL^8(NO_3) + H]^+$, 20
$NiL^8(NO_3)\cdot 0.5H_2O$	462, $[NiL^8]^+$, 100; 525, $[NiL^8(NO_3) + H]^+$, 18; 867, $[NiL^8{}_2 + H]^+$, 15; 986, $[Ni_2L^8{}_2(NO_3)]^+$, 24
$CoL^8(NO_3)\cdot H_2O$	463, $[CoL^8]^+$, 100; 868, $[CoL^8{}_2 + H]^+$, 10; 1 393, $[Co_2L^8{}_3(NO_3) + H]^+$, 3



(3)



(III)

solvent. HL^2: m.p. 54—56 °C (Found: C, 70.0; H, 7.4; N, 8.0. $C_{20}H_{26}N_2O_3$ requires C, 70.2; H, 7.7; N, 8.2%). M.s. has highest peak at m/z 343 $[HL^2 + H]^+$. H_2L^9: m.p. 50—52 °C (Found: C, 70.3; H, 7.4; N, 8.6. $C_{40}H_{52}N_4O_6$ requires C, 70.2; H, 7.7; N, 8.2%). M.s. has highest peak at m/z 685 $[H_2L^9 + H]^+$.

HL^1: m.p. 156—157 °C (lit.,[20] 156 °C).

HL^3: m.p. 130—132 °C (Found: C, 70.1; H, 7.8; N, 7.9. $C_{21}H_{28}N_2O_3$ requires C, 70.8; H, 7.9; N, 7.9%). M.s. has highest peak at m/z 357 $[HL^3 + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.24 (t, 2 H, aromatic), 7.22 (d, 2 H, aromatic), 6.91 (t, 2 H, aromatic), 6.86 (d, 2 H, aromatic), 4.07 (t, 4 H, OCH_2), 3.95 [m, 1 H, $C\mathit{H}(OH)$], 3.80 (m, 4 H, $C\mathit{H}_2C_6H_4$), 2.73 [m, 4 H, $NHC\mathit{H}_2CH(OH)$], and 2.07 (m, 4 H, $C\mathit{H}_2CH_2C_6H_4$); ^{13}C, δ 157.2, 130.8, 128.6, 128.3, 120.6, 110.9 (aromatic), 68.1 (HCOH), 67.1 (CH_2O), 52.8, 49.8 (CH_2NH), and 26.6 p.p.m. ($\mathit{C}H_2CH_2O$).

HL^4: m.p. 92—94 °C (Found: C, 71.4; H, 8.1; N, 7.6. $C_{22}H_{30}N_2O_3$ requires C, 71.3; H, 8.2; N, 7.6%). M.s. has highest peak at m/z 371 $[HL^4 + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.22 (t, 2 H, aromatic), 7.20 (d, 2 H, aromatic), 6.89 (t, 2 H, aromatic), 6.87 (d, 2 H, aromatic), 4.06 (t, 4 H, OCH_2), 3.85 [m, 1 H, $C\mathit{H}(OH)$], 3.80 (m, 4 H, $C\mathit{H}_2C_6H_4$), 2.71 [m, 4 H, $NHC\mathit{H}_2CH(OH)$], 1.90 (m, 4 H, $\mathit{C}H_2CH_2O$), and 1.80 (m, 2 H, $\mathit{C}H_2CH_2CH_2O$); ^{13}C, δ 157.3, 130.8, 128.7, 128.0, 121.1, 111.0 (aromatic), 68.0 (HCOH), 65.6 (CH_2O), 52.8, 49.0 (CH_2NH), 27.8 ($\mathit{C}H_2CH_2O$), and 21.8 p.p.m. ($\mathit{C}H_2CH_2CH_2O$).

HL^5: m.p. 62—63 °C (Found: C, 71,2; H, 8.4; N, 6.9. $C_{23}H_{32}N_2O_3$ requires C, 71.8; H, 8.4; N, 7.3%). M.s. has highest peak at m/z 385 $[HL^5 + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.22 (t, 2 H, aromatic), 7.20 (d, 2 H, aromatic), 6.89 (t, 2 H, aromatic), 6.86 (d, 2 H, aromatic), 4.02 (t, 4 H, OCH_2), 3.93 [m, 1 H, $C\mathit{H}(OH)$], 3.79 (m, 4 H, $C\mathit{H}_2C_6H_4$), 2.67 [m, 4 H, $NHC\mathit{H}_2CH(OH)$], 1.86 (m, 4 H, $\mathit{C}H_2CH_2O$), and 1.64 (m, 4 H, $\mathit{C}H_2CH_2CH_2O$); ^{13}C, δ 157.3, 130.5, 128.5, 128.2, 120.3, 111.2 (aromatic), 68.7 (HCOH), 67.6 (CH_2O), 53.1, 49.7 (CH_2NH), 29.4 ($\mathit{C}H_2CH_2O$), and 26.5 p.p.m. ($\mathit{C}H_2CH_2CH_2O$).

HL^6: m.p. 108 °C (Found: C, 67.6; H, 7.4; N, 7.2. $C_{21}H_{28}N_2O_4$ requires C, 67.7; H, 7.9; N, 7.5%). M.s. has highest peak at m/z 373 $[HL^6 + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.24 (t, 2 H, aromatic), 7.22 (d, 2 H, aromatic), 6.92 (t, 2 H, aromatic), 6.86 (d, 2 H, aromatic), 4.20 (t, 4 H, OCH_2), 3.98 (m, 4 H, $C\mathit{H}_2OCH_2$), 3.96 (m, 1 H, $\mathit{H}COH$), 3.83 (m, 4 H, $C\mathit{H}_2C_6H_4$), and 2.69 [m, 4 H, $NHC\mathit{H}_2(OH)$]; ^{13}C, δ 157.0, 130.8, 128.5, 128.4, 120.0, 111.2 (aromatic), 70.4, 67.6 ($O\mathit{C}H_2\mathit{C}H_2O$), 67.1 ($H\mathit{C}OH$), 52.4, and 49.4 p.p.m. (CH_2NH_2).

HL^7: m.p. 133—136 °C (Found: C, 74.8; H, 7.2; N, 6.3. $C_{27}H_{32}N_2O_3$ requires C, 75.0; H, 7.5; N, 6.5%). M.s. has highest peak at m/z 433 $[HL^7 + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.43 (s, 1 H, C_6H_4), 7.26 (t, 2 H, aromatic), 7.22 (d, 2 H, aromatic), 7.11 (s, 1 H, C_6H_4), 7.0—6.9 (m, 4 H, aromatic), 5.00 (m, 4 H, OCH_2), 3.76 (m, 4 H, $C\mathit{H}_2C_6H_4$), 3.62 [m, 1 H, $C\mathit{H}(OH)$], 2.50 [m, 4 H, $NHC\mathit{H}_2CH(OH)$], and 2.36 (s, 6 H, CH_3); ^{13}C, δ 157.4, 136.3, 132.8, 132.5, 130.7, 129.0, 128.9, 128.6, 112.0 (aromatic), 68.3 (CH_2O), 68.1 (CHOH), 52.6, 49.6 (CH_2NH), and 18.4 p.p.m. (CH_3).

Table 11. Metal complexes of a 2 + 2 macrocycle, H_2L^{10}

Complex	Analysis * (%)				F.a.b. mass spectral peaks (m/z)	I.r. bands (cm^{-1})	
	C	H	N	Cl		Secondary amine N–H stretch	Perchlorate
$Ni(H_2L^{10})(ClO_4)_2$	51.8	5.8	5.5	7.7	769, $[Ni(HL_{10})]^+$,	3 290	1 110s(br), 630(sp)
(Lilac)	(52.0)	(5.8)	(5.8)	(7.3)	869, $[Ni(H_2L^{10})(ClO_4)]^+$		
$Co(H_2L^{10})(ClO_4)_2$	52.2	6.0	5.7	7.4	770, $[Co(HL^{10})]^+$,	3 280	1 100s, 620(sp)
(Pink)	(52.0)	(5.8)	(5.8)	(7.3)	870, $[Co(H_2L^{10})(ClO_4)]^+$		
$Cd(H_2L^{10})Cl_2$	55.7	6.4	6.3	8.8	823, $[Cd(HL^{10})]^+$,	3 295(sp)	
(Off-white)	(56.3)	(6.3)	(6.2)	(7.9)	861, $[Cd(H_2L^{10})Cl]^+$		
$Zn(H_2L^{10})(ClO_4)_2$	51.2	5.5	5.5	7.2	775, $[Zn(HL^{10})]^+$,	3 250(sh)	1 100s(br), 620(sp)
(White)	(51.6)	(5.8)	(5.7)	(7.3)	875, $[Zn(H_2L^{10})(ClO_4)]^+$		
$Cu_2L^{10}(ClO_4)_2$	48.7	5.1	5.3	6.3	774, $[Cu(HL^{10})]^+$,	3 280(br)	1 100s(br), 625(sp)
(Pale blue)	(48.7)	(5.2)	(5.4)	(6.8)	837, $[Cu_2L^{10}]^+$,		
					937, $[Cu_2L^{10}(ClO_4)]^+$		

* Calculated values are given in parentheses.

HL^8: m.p. 180—181 °C (Found: C, 70.5; H, 6.5; N, 9.9. $C_{24}H_{27}N_3O_3$ requires C, 71.1; H, 6.7; N, 10.4%). M.s. has highest peak at m/z 406 $[HL^8 + H]^+$. N.m.r. ($CDCl_3$): ^1H δ 7.58 (t, 1 H, C_5H_3N), 7.41 (d, 2 H, C_5H_3N), 7.22 (t, 2 H, aromatic), 7.20 (d, 2 H, aromatic), 6.92 (t, 2 H, aromatic), 6.90 (d, 2 H, aromatic), 5.16 (d, 4 H, OCH_2), 3.9—3.8 (m, $CH_2C_6H_4/HCOH$), and 2.63 [m, 4 H, $NHCH_2CH(OH)$]; ^{13}C, δ 156.6, 156.5, 137.2, 130.3, 128.5, 128.3, 121.0, 120.2, 111.7 (aromatic C_5H_3N), 70.4 (CH_2O), 66.4 (CHOH), 53.0, and 49.6 p.p.m. (CH_2NH).

H_2L^{10}: m.p. 118—119 °C (Found: C, 70.4; H, 8.1; N, 8.1. $C_{42}H_{56}N_4O_6$ requires C, 70.8; H, 7.9; N, 7.9%). M.s. has highest peak at m/z 713 $[H_2L^{10} + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.22 (t, 4 H, aromatic), 7.12 (d, 4 H, aromatic), 6.87 (t, 4 H, aromatic), 6.84 (d, 4 H, aromatic), 4.05 (m, 8 H, OCH_2), 3.89 [m, 2 H, $CH(OH)$], 3.80 (m, 8 H, $CH_2C_6H_4$), 2.83 [m, 8 H, $NHCH_2CH(OH)$], and 2.04 (m, 8 H, $CH_2CH_2C_6H_4$).

H_2L^{11}: m.p. 131—133 °C (Found: C, 71.4; H, 8.4; N, 7.3. $C_{46}H_{64}N_4O_6$ requires C, 71.8; H, 8.4; N, 7.3%). M.s. has highest peak at m/z 769 $[H_2L^{11} + H]^+$. N.m.r. ($CDCl_3$): ^1H, δ 7.19 (t, 4 H, aromatic), 7.14 (d, 4 H, aromatic), 6.86 (t, 4 H, aromatic), 6.82 (d, 4 H, aromatic), 3.97 (t, 8 H, OCH_2), 3.8—3.7 [m, 1 H, $CH(OH)/CH_2C_6H_4$], 2.50 [m, 8 H, $NHCH_2CH(OH)$], 1.85 (m, 8 H, CH_2CH_2O), and 1.58 (m, 8 H, $CH_2CH_2CH_2O$).

Mononuclear Complexes of 1 + 1 *Macrocycles.*—The macrocycle (1 mmol) in hot methanol (10 cm^3) was added slowly to a stirred, boiling solution of the required metal salt (1 mmol) in methanol, n-butanol or methanol–acetonitrile (1:1) (20 cm^3). The complex that precipitated was filtered off (in some cases it was necessary to concentrate the solution first) washed with methanol, and dried under vacuum.

Homodinuclear Copper(II) *Complexes of* 1 + 1 *Macrocycles.*—The macrocycle (1 mmol) in hot methanol (10 cm^3) was added to a stirred boiling solution of the required copper(II) halide (2.2 mmol) in methanol (20 cm^3). The complex that precipitated out on cooling was filtered off, washed with methanol, and dried under vacuum.

Metal Complexes of 2 + 2 *Macrocycles.*—The macrocycle (0.5 mmol) in hot methanol (20 cm^3) was added slowly to a stirred boiling solution of the required metal salt (1 mmol) in methanol (20 cm^3). The complex that precipitated was filtered off (it was necessary to concentrate the solution first in some cases) washed with methanol, and dried under vacuum.

X-Ray Crystallography.—*Crystal data.* $C_{66}H_{76}Cl_4Cu_4N_4O_{14}$, M = 1 545.31, crystallises from benzyl alcohol as dark green prisms, crystal dimensions 0.31 × 0.23 × 0.23 mm, monoclinic, a = 13.460(15), b = 14.608(16), c = 17.096(8) Å, β = 96.227(9)°, U = 3 342(5) Å^3, D_c = 1.536 g cm^{-3}, Z = 2, space group $P2_1/c$ (C^5_{2h}, no. 14), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 14.85 cm^{-1}, F(000) = 1 591.72.

Three-dimensional, room-temperature X-ray data were collected in the range 6.5 < 2θ < 50° on a Stoe Stadi-2 diffractometer by the omega scan method. The 3 678 independent reflections for which $I/\sigma(I)$ > 3.0 were corrected for Lorentz and polarisation effects, and for absorption by Gaussian integration methods. The structure was solved by standard Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were placed in predicted positions with isotropic thermal parameters related to those of the supporting atoms, and refined in riding mode. A molecule of benzyl alcohol was found to be disordered in two interpenetrating sites and it was refined with occupancies of 0.64:0.36 with constrained geometry. The refinement converged at a final R of 0.0532 with allowance for the thermal anisotropy of all non-hydrogen atoms with the exception of those of the disordered benzyl alcohol. Unit weights were used throughout the refinement. Complex scattering factors were taken from the program package SHELXTL,[22] as implemented on the Data General Nova 3 computer, which was used throughout the refinement.

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