Complexes of Ligands providing Endogenous Bridges. Part 8.[1] Metal Complexes of Oxa-azamacrocycles derived from 1,5-Diamino-3-pentanol; The *X*-Ray Crystal Structure of a Free Macrocyclic Ligand†

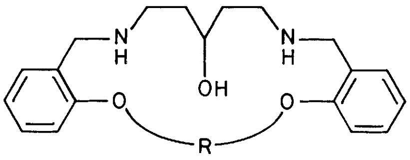
Neil A. Bailey, David E. Fenton, and Derek J. Winter
Department of Chemistry, The University, Sheffield S3 7HF

A series of oxa-azamacrocycles derived from 1,5-diamino-3-pentanol and acyclic dialdehydes have been prepared by non-template procedures and used to synthesise mononuclear complexes of Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. The crystal structure of the free macrocycle $C_{21}H_{28}N_2O_3$ is reported. The compound crystallises in the triclinic space group $P\bar{1}$ (C_i, no. 2) with unit-cell dimensions $a = 9.028(6)$, $b = 10.207(7)$, $c = 11.314(9)$ Å, $\alpha = 108.52(6)$, $\beta = 85.51(6)$, $\gamma = 100.09(6)°$, and $Z = 2$; 922 independent reflections with $|F|/\sigma(|F|) > 6.0$ gave $R = 0.0473$.

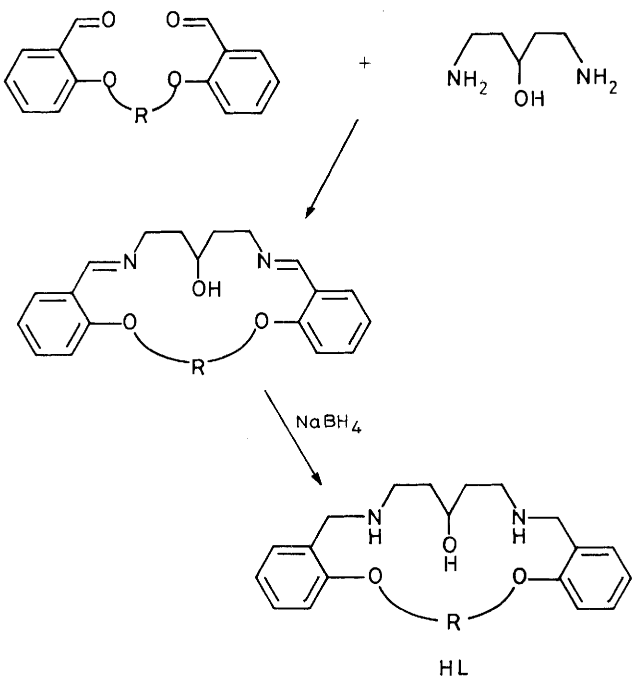
The metal-template cyclocondensation of a series of dialdehydes with a group of 1,*n*-diamines followed by reductive demetallation of the metal complex of the Schiff-base macrocycle formed has been shown to provide a facile route to metal-free oxa-azamacrocycles.[2] During the course of an investigation into the complexation of macrocyclic ligands bearing functional groups[1] we have prepared a series of reduced 1 + 1 oxa-azamacrocycles (HL) derived from 1,5-diamino-3-pentanol without resort to metal-template procedures. The synthesis and characterisation of the macrocycles and their complexes with Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} are discussed in this paper together with the crystal structure of the free macrocycle, HL^1.

Results and Discussion

The Macrocyclic Ligands.—The macrocycles HL^1, HL^2, and HL^3 were prepared by an *in situ* $NaBH_4$ reduction of the Schiff-base precursors (Scheme) and characterised by elemental analysis, i.r. and n.m.r. spectroscopy, and mass spectrometry. Fast atom bombardment mass spectrometry (f.a.b.m.s.) gave only peaks attributable to the monomeric macrocycle with the major peak being the parent macrocycle peak $[HL]^+$. There was no evidence for Na^+ or Cs^+ inclusion or ligand oligomerisation as had been detected in the f.a.b.m.s. of the related macrocycles derived from 1,3-diamino-2-propanol.[1] Electron-impact mass spectrometry (e.i.m.s.) showed standard breakdown patterns with initial loss of the hydroxyl group. The i.r. spectra show the NH stretch as a sharp peak at *ca.* 3 310 cm^{-1} and there is a broader peak in the region 3 120—3 250 cm^{-1} attributable to the OH stretch. The ^1H and ^{13}C n.m.r. data are reported in Table 1.



	R
HL^1	$(CH_2)_2$
HL^2	$(CH_2)_3$
HL^3	$(CH_2)_4$



Scheme. R = $(CH_2)_n$ where n = 2—4

The X*-Ray Crystal Structure of* HL^1.—During an attempted reaction of the macrocyclic ligand HL^1 with $NiCl_2$ in methanol excellent crystals of the free ligand were recovered. The structure was solved and is shown in Figure 1; bond lengths and angles are listed in Table 2. The macrocycle is not unduly twisted, with both ether oxygen atoms and both N–H groups directed into the cavity. However, the pendant hydroxy group is directed outwards and forms a hydrogen bond with N(1) of a centrosymmetrically related molecule, using the hydroxy hydrogen. Molecules are therefore hydrogen bonded in pairs with two symmetry-related hydrogen bonds (Figure 2). There appears to be a possible weak intramolecular interaction between the hydrogen atom of the same hydrogen bonded N–H group and one of the ether oxygen atoms (H • • • O 2.34 Å); the other such N–H • • • O intramolecular distance is much longer. The two phenyl rings are each planar [root mean square (r.m.s.)

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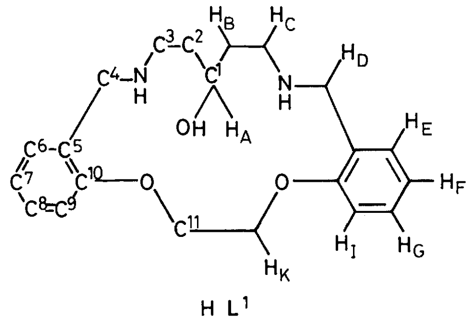
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

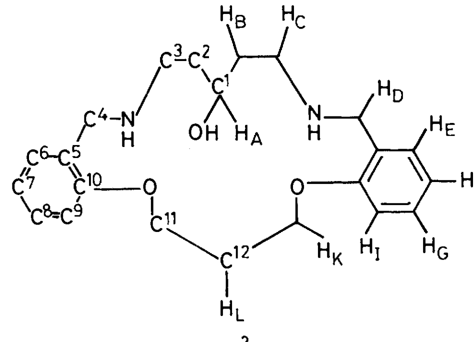
Table 1. Proton and ^{13}C n.m.r. data



H L^1

HL^1

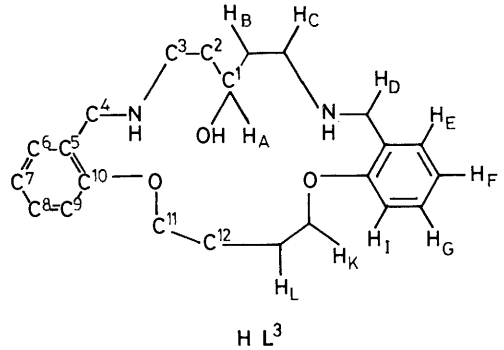
^{1}H			^{13}C	
δ	Assignment	Integration	δ (p.p.m.)	Assignment
7.24 (t)	H$_G$	2 H	157.1	C^{10}
7.20 (d)	H$_E$	2 H	130.8	C^8 or C^6
6.92 (t)	H$_F$	2 H	128.5	C^5
6.91 (d)	H$_I$	2 H	128.4	C^6 or C^8
4.42 (s)	H$_K$	4 H	120.8	C^7
3.93 (m)	H$_A$	1 H	111.5	C^9
3.78 (m)	H$_D$	4 H	70.8	C^1
2.79 (m)	H$_C$	4 H	67.3	C^{11}
1.59 (m)	H$_B$	4 H	49.7	C^3 or C^4
			46.0	C^4 or C^3
			34.6	C^2



HL^2

HL^2

^{1}H			^{13}C	
δ	Assignment	Integration	δ (p.p.m.)	Assignment
7.24 (t)	H$_G$	2 H	157.5	C^{10}
7.15 (d)	H$_E$	2 H	131.0	C^6 or C^8
6.89 (d)	H$_I$	2 H	128.7	C^8 or C^6
6.88 (t)	H$_F$	2 H	128.2	C^5
4.20 (m)	H$_K$	4 H	120.2	C^7
3.7—3.8 (m)	H$_A$ and H$_D$	5 H	111.5	C^9
2.7—2.9 (m)	H$_C$	4 H	74.6	C^1
2.49 (m)	H$_L$	2 H	64.5	C^{11}
1.46 (m)	H$_B$	4 H	51.0	C^3 or C^4
			48.3	C^4 or C^3
			35.6	C^2
			29.3	C^{12}



H L^3

HL^3

^{1}H			^{13}C	
δ	Assignment	Integration	δ (p.p.m.)	Assignment
7.14—7.22 (m)	H$_E$ and H$_G$	4 H	157.4	C^{10}
6.85 (t)	H$_F$	2 H	130.6	C^6 or C^8
6.83 (d)	H$_I$	2 H	128.6	C^8 or C^6
4.02 (m)	H$_K$	4 H	127.7	C^5
3.92 (m)	H$_A$	1 H	120.0	C^7
3.73 (s)	H$_D$	4 H	110.5	C^9
2.7—3.1 (m)	H$_C$	4 H	71.9	C^1
2.07 (m)	H$_L$	4 H	67.4	C^{11}
1.5 (m)	H$_B$	4 H	51.2	C^3 or C^4
			48.1	C^4 or C^3
			36.5	C^2
			26.2	C^{12}

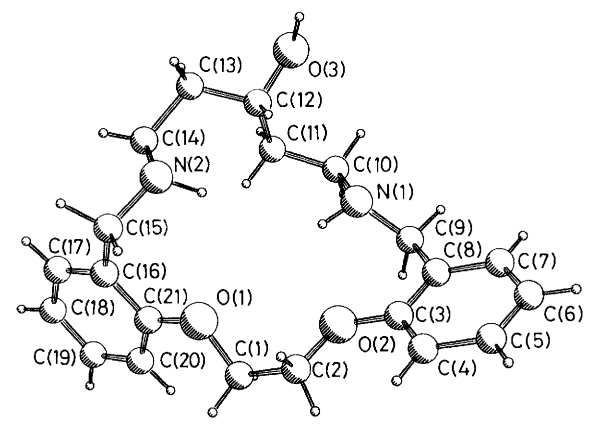


Figure 1. The molecular structure of the free macrocyclic ligand (HL^1)

deviations 0.011 and 0.015 Å]. The torsion angles of the macrocycle are given in Table 3.

Transition-metal Complexes of the Macrocycles.—Each of the three macrocycles was treated with a wide range of transition-metal salts; no complexes of Mn^{II} or Ag^{I} were isolable and no analytically pure products were recovered from reactions involving salts of Cd^{II} and Hg^{II}. Those complexes which were isolated and found to be analytically pure are listed in Table 4 together with the relevant analytical and spectroscopic data. The metal halide complexes do not have the hydroxyl group of the macrocycle deprotonated whereas the metal perchlorate and metal nitrate complexes do involve deprotonation of this group thus paralleling the trend reported for the equivalent complexes of the related macrocycles derived from 1,3-diamino-2-propanol.[1] The i.r. spectra of the complexes (run as KBr discs) all show peaks in the region *ca.* 3 180—3 280 cm^{-1} indicative of

Table 2. Bond lengths (Å) and angles (°) for HL^1

O(1)–C(1)	1.434(11)	O(1)–C(21)	1.385(9)
O(2)–C(2)	1.424(7)	O(2)–C(3)	1.383(8)
O(3)–H(O3)	1.13(6)	O(3)–C(12)	1.448(9)
N(1)–H(N1)	0.94(5)	N(1)–C(9)	1.464(10)
N(1)–C(10)	1.468(10)	N(2)–H(N2)	1.03(6)
N(2)–C(14)	1.458(11)	N(2)–C(15)	1.472(10)
C(1)–C(2)	1.510(10)	C(3)–C(4)	1.375(11)
C(3)–C(8)	1.393(10)	C(4)–C(5)	1.399(11)
C(5)–C(6)	1.370(11)	C(6)–C(7)	1.386(12)
C(7)–C(8)	1.382(10)	C(8)–C(9)	1.530(11)
C(10)–C(11)	1.506(15)	C(11)–C(12)	1.476(12)
C(12)–C(13)	1.518(13)	C(13)–C(14)	1.565(11)
C(15)–C(16)	1.514(12)	C(16)–C(17)	1.392(12)
C(16)–C(21)	1.390(13)	C(17)–C(18)	1.386(12)
C(18)–C(19)	1.360(15)	C(19)–C(20)	1.382(12)
C(20)–C(21)	1.381(11)	O(2) ··· H(N1)	2.34
N(1) ··· O(3^{I})	2.839	N(1) ··· H($O3^{I}$)	1.72
C(1)–O(1)–C(21)	116.4(6)	C(2)–O(2)–C(3)	118.0(5)
H(O3)–O(3)–C(12)	110(3)	H(N1)–N(1)–C(9)	113(4)
H(N1)–N(1)–C(10)	105(4)	C(9)–N(1)–C(10)	113.2(6)
H(N2)–N(2)–C(14)	102(3)	H(N2)–N(2)–C(15)	115(4)
C(14)–N(2)–C(15)	112.8(6)	O(1)–C(1)–C(2)	108.7(6)
O(2)–C(2)–C(1)	107.7(5)	O(2)–C(3)–C(4)	122.5(6)
O(2)–C(3)–C(8)	116.1(7)	C(4)–C(3)–C(8)	121.4(7)
C(3)–C(4)–C(5)	119.4(6)	C(4)–C(5)–C(6)	119.4(8)
C(5)–C(6)–C(7)	120.8(8)	C(6)–C(7)–C(8)	120.4(6)
C(3)–C(8)–C(7)	118.5(7)	C(3)–C(8)–C(9)	121.3(6)
C(7)–C(8)–C(9)	120.2(6)	N(1)–C(9)–C(8)	111.2(5)
N(1)–C(10)–C(11)	112.9(6)	C(10)–C(11)–C(12)	115.0(7)
O(3)–C(12)–C(11)	105.6(6)	O(3)–C(12)–C(13)	108.3(7)
C(11)–C(12)–C(13)	114.7(7)	C(12)–C(13)–C(14)	116.0(8)
N(2)–C(14)–C(13)	110.9(7)	N(2)–C(15)–C(16)	115.8(6)
C(15)–C(16)–C(17)	122.2(8)	C(15)–C(16)–C(21)	121.7(7)
C(17)–C(16)–C(21)	116.1(8)	C(16)–C(17)–C(18)	122.5(9)
C(17)–C(18)–C(19)	119.8(8)	C(18)–C(19)–C(20)	119.3(8)
C(19)–C(20)–C(21)	120.6(8)	O(1)–C(21)–C(16)	114.7(7)
O(1)–C(21)–C(20)	123.9(7)	C(16)–C(21)–C(20)	121.4(7)

Symmetry operation I is $-x, 1 - y, 1 - z$.

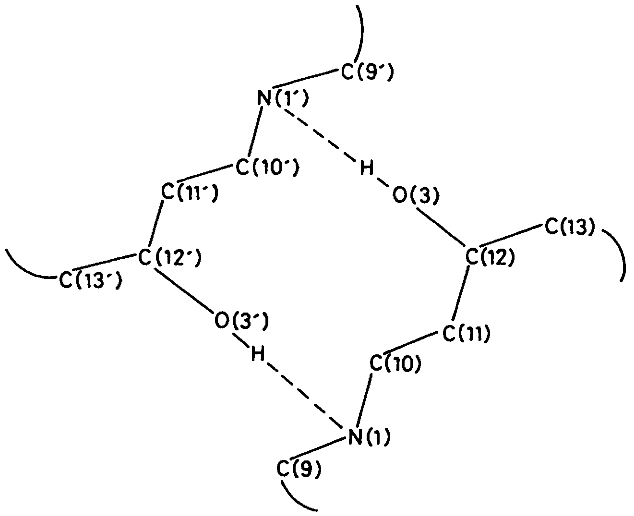


Figure 2. Intermolecular hydrogen-bonding between pairs of macrocycles

Table 3. Torsion angles (°) for HL^1

C(21)–O(1)–C(1)–C(2)	180	O(1)–C(1)–C(2)–O(2)	−77
C(1)–C(2)–O(2)–C(3)	−173	C(2)–O(2)–C(3)–C(8)	180
O(2)–C(3)–C(8)–C(9)	+1	C(3)–C(8)–C(9)–N(1)	+61
C(8)–C(9)–N(1)–C(10)	+176	C(9)–N(1)–C(10)–C(11)	+159
N(1)–C(10)–C(11)–C(12)	+64	C(10)–C(11)–C(12)–C(13)	−175
C(11)–C(12)–C(13)–C(14)	+54	C(12)–C(13)–C(14)–N(2)	+57
C(13)–C(14)–N(2)–C(15)	+175	C(14)–N(2)–C(15)–C(16)	+60
N(2)–C(15)–C(16)–C(21)	+79	C(15)–C(16)–C(21)–O(1)	−5
C(16)–C(21)–O(1)–C(1)	+169		

co-ordinated NH groups. In the spectra of the metal halide complexes there are also bands at *ca.* 3 400 cm^{-1} attributable to the OH group in the ligand. The i.r. bands detected for the perchlorate and nitrate anions are those found for free ionic anions;[3] the complex $Cu(L^3)ClO_4$ shows a split perchlorate band at 1 100 cm^{-1} but this may reflect hydrogen-bonded interactions of the anion rather than a co-ordinating anion. The reaction between $Co(NCS)_2$ and HL^3 gave two products; one, a pale lavender coloured solid, showed retention of the hydroxyl proton whilst the second, a dark green solid, involved deprotonation of the hydroxyl group. The i.r. spectra indicated the presence of bonded thiocyanate groups; for $Co(HL^3)(SCN)_2$ bands are noted at 2 090 and 2 070 cm^{-1}, whereas for the deprotonated complex $Co(L^3)(SCN)$ a single band is noted at 2 075 cm^{-1}. The higher band is likely to arise from an ionic anion but the lower bands occur at the border between N- and S-bonded thiocyanate[4] and so it is difficult to make an unambiguous assignment. The diffuse reflectance spectra of the complexes were broad and gave little help in assigning co-ordination geometries. Further spectroscopic investigation of the complexes was inhibited by their negligible solubility in appropriate organic solvents. The f.a.b.m.s. of the metal halide complexes show highest peaks corresponding to the ions $[ML]^+$ and $[MLX]^+$ whereas the spectra of the metal perchlorate and nitrate complexes show the presence of higher mass number peaks derived from the ions $[M_2L_2X]^+$ and $[M_3L_3X_2]^+$. Such oligomeric species have previously been noted for metal complexes of the related oxa-azamacrocycles derived from 1,3-diamino-2-propanol and are proposed to arise from intermolecular interactions between the deprotonated hydroxyl group and a metal ion in the adjacent metal complex.[1]

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Service. I.r. spectra were run as KBr discs using a Perkin-Elmer 297 spectrophotometer, n.m.r. spectra on Perkin-Elmer R34, Bruker WH250 and WH400 spectrometers, and mass spectra using Kratos MS25 and MS 80RF spectrometers.

The precursor dialdehydes were prepared by literature methods or by modifications thereof.[5–8] 1,5-Diamino-3-pentanol was prepared by the method of Murase *et al.*[9] The macrocycles were prepared by the following general procedure with the synthesis of HL^1 given here as an example.

To a refluxing solution of 1,2-bis(2-formylphenoxy)ethane (0.81 g, 3 mmol) in methanol (30 cm^3) was added slowly 1,5-diamino-3-pentanol (0.40 g, 3.5 mmol) in methanol (30 cm^3). The solution was refluxed for 1 h then an excess of $NaBH_4$ (0.4 g) was added carefully. The solution was allowed to cool to room temperature and water (100 cm^3) was added. The solution was left to stand overnight and a white solid precipitated. This was filtered off and the filtrate evaporated to near-dryness under reduced pressure. Water (60 cm^3) was added to the filtrate and a brown tar precipitated which was extracted into $CHCl_3$, dried over Na_2SO_4, and evaporated to dryness under reduced pressure to yield a brown oil. Addition of a large volume of ethyl acetate (300 cm^3) resulted in the slow formation of cream coloured crystals of HL^1 (yield 20%), m.p. 126—127 °C (Found: C, 70.7; H, 7.7; N, 7.6. $C_{21}H_{28}N_2O_3$ requires C, 70.8; H, 7.9; N, 7.9%). M.s.: P^+ at m/z 357 $[HL^1]^+$.

Table 4. Analytical and spectroscopic data for the metal complexes of the macrocycles

	Analysis (%)[a]					I.r. bands (cm^{-1})[b]	
Complex	C	H	N	Cl or S	m/z, Assignment	Secondary amine N–H stretch	Anion
$Ni(HL^1)Cl_2·3H_2O$	46.6	6.4	5.4	12.7	413, $[NiL^1]^+$;	3 280(sh), 3 220	
(Pale green)	(46.7)	(6.3)	(5.2)	(13.1)	448, $[Ni(HL^1)Cl]^+$		
$Zn(HL^1)I_2$	37.1	3.6	4.4		419, $[ZnL^1]^+$	3 260, 3 180	
(Off-white)	(37.3)	(4.1)	(4.1)				
$Ni(L^1)ClO_4$	49.1	5.3	5.7		413, $[NiL^1]^+$;	3 245(sp)	1 080s(br), 615s(sp)
(Pink)	(49.1)	(5.2)	(5.5)		927, $[Ni_2L^1{}_2(ClO_4)]^+$		
$Ni(HL^2)Cl_2$	52.1	5.6	5.2	13.8	427, $[NiL^2]^+$;	3 230(sh)	
(Yellow-green)	(52.8)	(6.0)	(5.6)	(14.2)	462, $[Ni(HL^2)Cl]^+$		
$Ni(L^2)ClO_4$	50.3	5.6	5.0		427, $[NiL^2]^+$;	3 260w	1 090s(br), 615
(Pale pink)	(50.1)	(5.5)	(5.3)		955, $[Ni_2L^2{}_2(ClO_4)]^+$		
$Cu(L^2)ClO_4·MeOH$	48.7	5.3	4.6		433, $[CuL^2]^+$;	3 250(br)	1 090s(br), 620s(sp)
(Green)	(48.9)	(5.9)	(5.0)		965, $[Cu_2L^2{}_2(ClO_4)]^+$		
$Ni(L^3)ClO_4·H_2O$	50.0	5.7	5.3		422, $[NiL^3]^+$;	3 260(sp)	1 090s(br), 620s(sp)
(Dark pink)	(49.4)	(6.0)	(5.0)		983, $[Ni_2L^3{}_2(ClO_4)]^+$		
$Cu(L^3)ClO_4$	50.8	6.1	4.9		447, $[CuL^3]^+$;	3 260(sh), 3 250	1 100s, 1 080s,
(Green)	(50.6)	(5.7)	(5.1)		993, $[Cu_2L^3{}_3(ClO_4)]^+$		625(sp)
$Cu(L^3)NO_3·H_2O$	52.8	6.6	8.2		447, $[CuL^3]^+$;	3 265w(sp), 3 240(sp)	1 385s
(Green)	(52.4)	(6.3)	(8.0)		1 465, $[Cu_3L^3{}_3(NO_3)_2]^+$		
$Co(HL^3)(SCN)_2$	52.9	5.8	10.3	10.4	442, $[CoL^3]^+$;	3 280(sp), 3 200(br)	2 090s, 2 070s
(Lavender)	(53.7)	(5.8)	(10.0)	(11.5)	501, $[Co(HL^3)(SCN)]^+$		
$Co(L^3)(SCN)$	54.5	6.1	8.5	6.4	442, $[CoL^3]^+$;	3 260w(sh)	2 075s
(Dark green)	(52.8)	(6.2)	(8.4)	(6.4)	942, $[Co_2L^3{}_2(SCN)]^+$		

[a] Calculated values are given in parentheses. [b] br = Broad, s = strong, sp = sharp, sh = shoulder, and w = weak.

Table 5. Atomic co-ordinates (× 10^4) for HL^1

Atom	x	y	z
O(1)	4 195(5)	1 109(5)	2 364(4)
O(2)	3 179(5)	1 188(4)	4 913(4)
O(3)	862(5)	6 460(5)	4 504(5)
N(1)	2 318(6)	3 959(6)	5 654(5)
N(2)	2 140(7)	2 859(6)	1 488(5)
C(1)	4 752(9)	432(8)	3 133(7)
C(2)	3 464(8)	−21(7)	3 925(6)
C(3)	2 159(7)	1 002(8)	5 846(6)
C(4)	1 419(7)	−295(7)	5 848(7)
C(5)	434(8)	−409(8)	6 840(8)
C(6)	222(8)	773(10)	7 794(8)
C(7)	938(8)	2 082(8)	7 767(7)
C(8)	1 906(7)	2 212(8)	6 788(7)
C(9)	2 700(8)	3 658(7)	6 765(6)
C(10)	2 971(8)	5 374(7)	5 633(9)
C(11)	3 065(9)	5 515(8)	4 343(9)
C(12)	1 601(9)	5 308(7)	3 758(7)
C(13)	1 706(9)	5 328(8)	2 418(8)
C(14)	2 681(10)	4 296(8)	1 500(8)
C(15)	2 937(10)	1 836(8)	555(8)
C(16)	4 622(9)	2 032(8)	702(7)
C(17)	5 643(10)	2 619(8)	−49(7)
C(18)	7 186(10)	2 704(9)	15(7)
C(19)	7 750(9)	2 224(9)	850(8)
C(20)	6 771(9)	1 654(8)	1 624(6)
C(21)	5 238(8)	1 605(7)	1 580(6)

HL^2: (yield 10%), m.p. 127—128 °C (Found: C, 71.2; H, 7.6; N, 7.2. $C_{22}H_{30}N_2O_3$ requires C, 71.3; H, 8.1; N, 7.6%). M.s.: P^+ at m/z 371 $[HL^2]^+$.

HL^3: (yield 20%), m.p. 138 °C (Found: C, 71.3; H, 8.4; N, 7.0. $C_{23}H_{32}N_2O_3$ requires C, 71.8; H, 8.4; N, 7.3%). M.s.: P^+ at m/z 385 $[HL^3]^+$.

Preparation of Metal Complexes.—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, butanol, or methanol–acetonitrile (20 cm^3). The complex that precipitated was washed with methanol or butanol and dried under vacuum. In some cases it was necessary to concentrate the solution in order to effect precipitation (yields 30—50%).

X-Ray Crystallography.—*Crystal data.* $C_{21}H_{28}N_2O_3$, M = 356.46, crystallises from methanol as pale yellow plates, crystal dimensions 0.40 × 0.28 × 0.11 mm, triclinic, a = 9.028(6), b = 10.207(7), c = 11.314(9) Å, α = 108.52(6), β = 85.51(6), γ = 100.09(6)°, U = 973.0(12) Å^3, D_c 1.217 g cm^{-3}, Z = 2, space group $P\bar{1}$ (C_i, no. 2), Mo-K_α radiation ($\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 0.76 cm^{-1}, F(000) = 383.94.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the omega scan method. The 922 independent reflections for which $|F|/\sigma(|F|) > 6.0$ were corrected for Lorentz and polarisation effects. The structure was solved by direct methods. Hydrogen atoms were detected and refined with isotropic thermal parameters initially related to those of the supporting atom, then frozen: the positions of hydrogen atoms on C(11), C(12), and C(15) were subject to some further constraints after unsatisfactory refinement. Refinement by blocked-cascade least-squares methods converged to a final R of 0.0473, with allowance for thermal anisotropy of all non-hydrogen atoms. Scattering factors were taken from the program package SHELXTL[10] which was used for the solution and refinement. Unit weights were used throughout the refinement. Atomic co-ordinates are given in Table 5.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

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