In memory of S. M. Nelson

Studies of Metal-ion Recognition. The Interaction of Co^{II}, Ni^{II}, and Cu^{II} with New Oxygen–Nitrogen Donor Macrocycles; *X*-Ray Structures of Complexes of Cu^{II} and Ni^{II} with a 15-Membered O_2N_3 Derivative‡

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Tetrahydroborate reduction of a range of Schiff-base di-imine macrocycles, prepared by template cyclization reactions on manganese(II) or lead(II), has afforded a series of structurally related metal-free macrocycles incorporating both oxygen and nitrogen donor atoms. In all, ten new rings are reported. Physical measurements indicate that many of these rings form 1:1 complexes with Co^{II} Ni^{II}, and/or Cu^{II}. The stabilities of selected complexes have been determined using the potentiometric (pH) titration technique. In all cases much greater stability for the complexes of Cu^{II} relative to those of Co^{II} or Ni^{II} was observed; the structural origin of this selectivity has been investigated by *X*-ray diffraction studies. These indicate that the complexes of Ni^{II} and Cu^{II} have markedly different structures for one of the O_2N_3 ligands. In the nickel(II) species the geometry is distorted octahedral with the macrocycle occupying four co-ordination positions with one ether oxygen not co-ordinated. The remaining (*cis*) co-ordination positions are filled by nitrate ions. In the copper(II) complex the macrocycle folds such that an unsymmetric but apparently favourable cavity is formed and all five donor atoms co-ordinate to the metal. A sixth co-ordination position is filled by a nitrate ion.

The interaction of metal ions with oxygen–nitrogen donor macrocycles has been the subject of a range of recent studies. A number of these investigations have involved synthetic, kinetic, thermodynamic, and/or structural aspects of complex formation with a range of heavy-metal ions.[1–3] A primary aim of much of this research has been to elucidate the factors governing metal-ion recognition by cyclic organic substrates: a phenomenon which has important consequences in diverse areas of both chemistry and biochemistry.

Apart from the usual parameters affecting the stabilities of metal complexes of acyclic ligands, for macrocyclic systems there is a further parameter, the cyclic cavity size, which is available to control thermodynamic stabilities. Such cavity-size variation has been extensively studied with respect to macrocyclic crown ethers and non-transition ions;[4] in many instances an observed discrimination has been interpreted in terms of the 'goodness-of-fit' between the macrocyclic cavity and the metal-cation radius.

A second approach for achievement of discrimination has involved 'dislocation' behaviour along a series of complexes of ligands which otherwise exhibit a systematic variation of their properties.[5,6] The accumulation of strain introduced into a complex by the gradual change in structural and/or electronic properties along the series reaches a 'critical' point, at which an abrupt change from one co-ordination arrangement to another occurs. When different geometries are induced by different metal ions for the same ligand, enhanced discrimination may result from the occurrence of a structural dislocation in one complex but not in the other.

The present study was undertaken in order to investigate further this approach to metal-ion discrimination. To serve as a basis for the study, the series of closely related ligands L^1—L^{10} were synthesized. The structures of these ligands reflect design strategies which were aimed to enhance the prospect that dislocation behaviour will occur for the corresponding metal complexes. First, the ligands all incorporate various combinations and sequences of nitrogen and oxygen donor atoms. Previous studies have well documented that incorporation of both weakly and strongly binding donors often aids the occurrence of dislocations.[2,5] Secondly, the partial rigidity inherent in the ligand backbones is such that co-ordination around the binding sites of an octahedral metal ion will be somewhat inhibited (provided all donor atoms remain co-ordinated). Thus for octahedral ions, the destabilization of the 'preferred' geometry will also increase the opportunity for dislocations to occur. In the present study, the interaction of Co^{II}, Ni^{II}, and Cu^{II} with L^1—L^{10} has been investigated.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer using either Nujol mulls or KBr discs. All spectra

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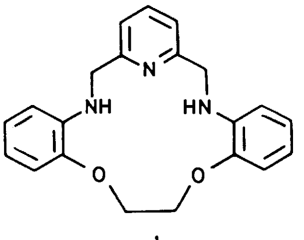
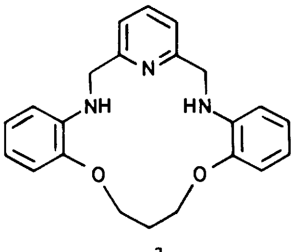
‡ (6,7-Dihydro-15,19-nitrilodibenzo[*j,p*][1,9,12,15]dioxadiazacycloheptadecine)(nitrato)copper(II) nitrate–methanol–hydrate (6/2/1) and (6,7-dihydro-15,19-nitrilodibenzo[*j,p*][1,9,12,15]dioxadiazacycloheptadecine-*O,N,N′,N″*)bis(nitrato)nickel(II) hydrate (2/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

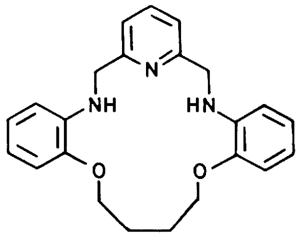
Non-S.I. unit employed: B.M. = 9.274×10^{-24} J T^{-1}.



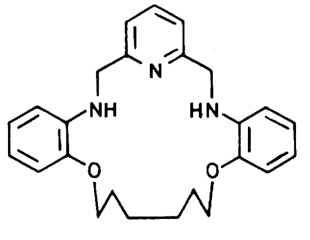
L^1



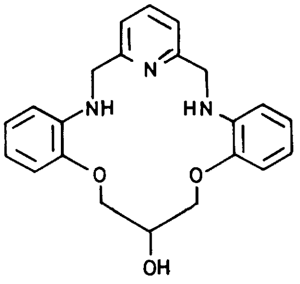
L^2



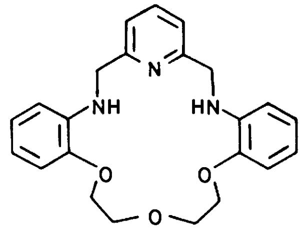
L^3



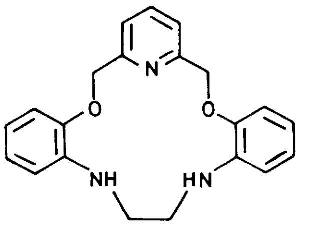
L^4



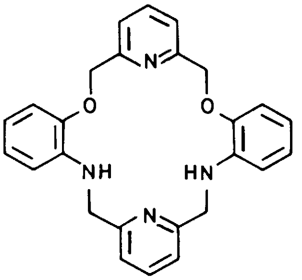
L^5



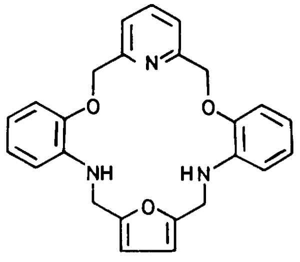
L^6



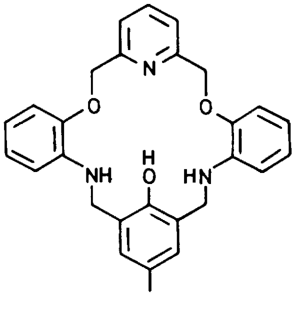
L^7



L^8



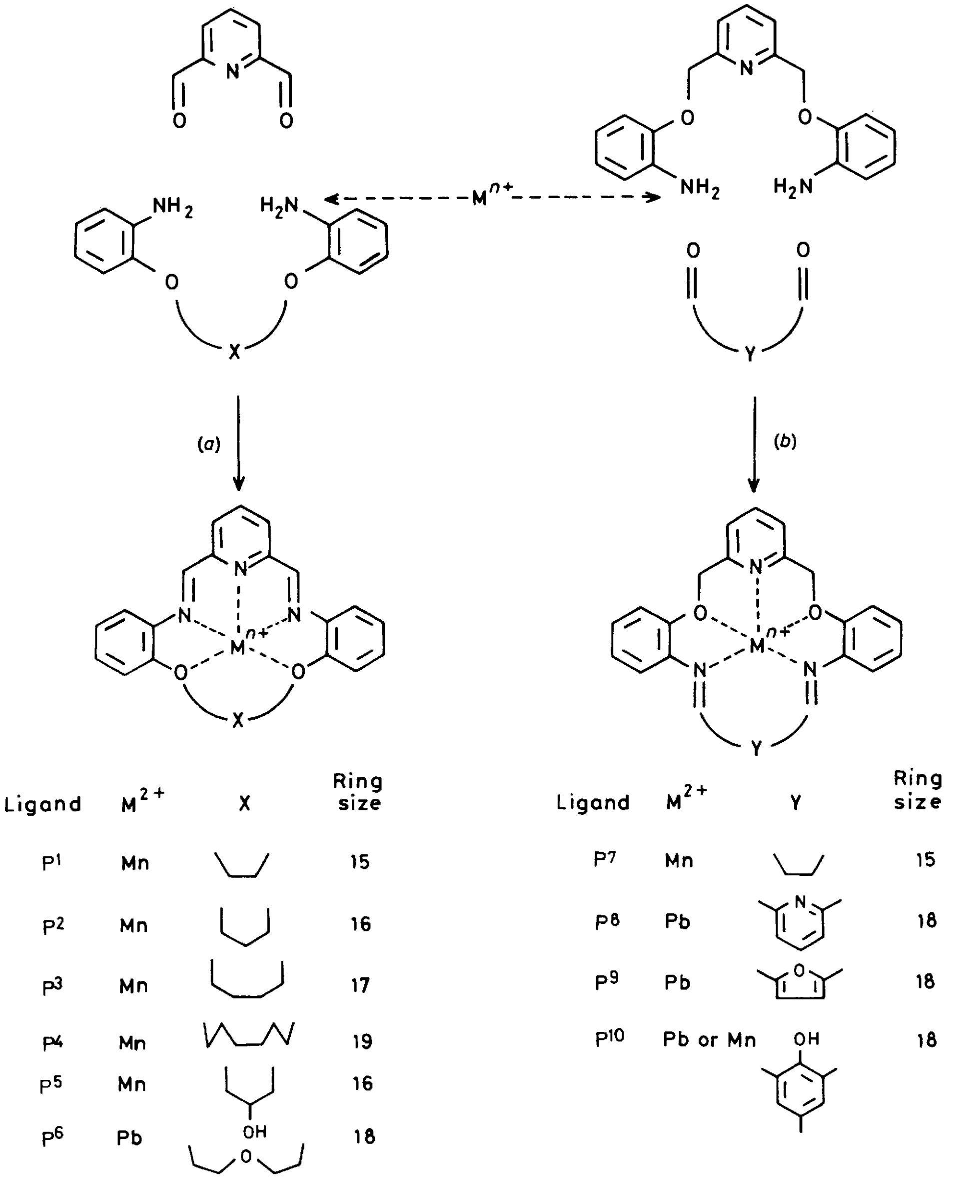
L^9



L^{10}

were calibrated using a polystyrene standard. U.v.–visible spectra of the complexes in methanol were obtained on a Beckman ACTA-IV spectrophotometer. Solid-state spectra were determined on the above spectrophotometer using Nujol mulls of the complex spread on filter paper. Spectrophotometric titrations were performed by direct incremental addition of known weights of the ligand to a 95% methanol solution of copper(II) perchlorate in the spectrophotometric cell. Magnetic moments were obtained on a Faraday balance calibrated against $Hg[Co(NCS)_4]$. Hydrogen-1 and ^{13}C n.m.r. spectra were determined using a Bruker WM250 instrument. Mass spectra [including fast atom bombardment (f.a.b.) source spectra] were recorded using a KRATOS MS80 spectrometer. A 3-nitrobenzyl alcohol matrix of the sample was used for the f.a.b. spectra. Microanalyses were determined by the microanalytical units at the Universities of Sheffield and Queensland.

log K *Determinations.*—The log *K* apparatus was identical to that described previously.[7] A microcomputer was used to control the operation of the automatic burette, to monitor the approach to equilibrium, and for data logging. Data were processed using local versions of MINIQUAD[8] or SUPERQUAD.[9] Duplicate calculations were also carried out on representative data sets using the program KONST;[10] in all cases the



Scheme. Synthetic route to the complexes of the precursor macrocyclic ligands P[1]—P[10]

values obtained were almost identical (well within experimental error) to the values obtained using the above programs. Measurements were made using 95% methanol (I = 0.1 mol dm^{-3} NEt_4ClO_4) at 25 °C. The log K values for the complexes were obtained by titration of a solution containing protonated macrocycle (*ca.* 10^{-3} mol dm^{-3}) and metal ion [(0.5—2) × 10^{-3} mol dm^{-3}] with tetraethylammonium hydroxide (0.1 mol dm^{-3}). Protonation constants were determined by a similar procedure using a solution of the macrocycle only.

The relatively low values for the protonation constants for the ligands together with the moderately high log K values for the corresponding copper(II) complexes necessitated recourse to competitive titration methods to obtain reliable estimates of the latter constants. For this purpose the previously studied[11] O_2N_3 macrocycle perhydrodibenzo[*e,p*][1,4,8,11,14]dioxatriazacycloheptadecine, whose protonation constants and log K value for Cu^{II} have been determined under similar conditions,[12] was employed as the competing ligand. The calculations were performed using SUPERQUAD with the above constants being 'fixed' in the equilibrium model used for the analysis.

Ligand Precursors.—2,6-Diformylpyridine,[13] 2,5-diformylfuran,[14] and 2,6-diformyl-*p*-cresol[15] were prepared using literature methods.

The series of diamines (see Scheme) were prepared by reduction of the corresponding dinitro precursors using a similar procedure to that described previously.[16,17] The alcohol derivative was synthesized by the general procedure starting from 1,3-dibromopropan-2-ol.

1,3-*Bis*(2-*nitrophenoxy*)*propan*-2-*ol*. Yellow crystals, yield 65% (Found: C, 53.70; H, 4.50; N, 8.60. Calc. for $C_{15}H_{14}N_2O_7$: C, 53.9; H, 4.20; N, 8.40%). Mass spectral parent ion: *m/z* 334. I.r. (KBr disc): ν(OH) 3 552, ν(NO_2) 1 520 and 1 350 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.89 (d, 2 H, C_6H_4), 7.58 (t, 2 H, C_6H_4), 7.19, 7.07 (d, t, 4 H, C_6H_4), 4.50—4.30 [m, 5 H, C*H*$_2$C*H*(OH)C*H*$_2$], and 3.08 [d, 1 H, CH(O*H*)].

1,3-*Bis*(2-*aminophenoxy*)*propan*-2-*ol*. White crystals, yield 65% (Found: C, 65.65; H, 6.80; N, 10.25. Calc. for $C_{15}H_{18}N_2O_3$: C, 65.7; H, 6.60; N, 10.2%). Mass spectral parent ion: *m/z* 274. I.r. (KBr disc): ν(OH) 3 357, ν(NH_2) 3 450, 3 350, and δ(NH_2) 1 625 cm^{-1}. N.m.r. ($CDCl_3$): ^{1}H, δ 6.90—6.63 (m, 8 H, C_6H_4),

Table 1. Fractional atomic co-ordinates for complexes (**1**) and (**2**), with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Cu(L^7)(NO_3)]NO_3{\cdot}0.33MeOH{\cdot}0.17H_2O$ (**1**)							
Cu	0.220 30(7)	0.047 87(9)	−0.033 87(9)	C(6a)	0.485 1(6)	0.058 5(8)	0.163 5(8)
N(1a)	0.310 5(4)	0.152 6(5)	−0.061 5(6)	C(5a)	0.550 4(7)	0.127 3(8)	0.150 6(9)
N(1b)	0.186 1(4)	0.046 4(6)	−0.211 7(6)	C(4a)	0.537 3(7)	0.206 5(8)	0.068 8(9)
O(1a)	0.341 0(4)	−0.002 4(5)	0.105 5(5)	C(3a)	0.458 5(6)	0.213 7(7)	−0.001 6(8)
O(1b)	0.101 5(4)	0.167 1(5)	−0.080 9(5)	C(2a)	0.392 9(5)	0.144 7(7)	0.011 7(7)
N(2c)	0.194 0(4)	0.109 6(6)	0.125 2(6)	C(7a)	0.406 3(6)	0.067 8(7)	0.094 4(8)
O(3a)	0.149 4(4)	−0.073 5(4)	−0.011 4(5)	C(1a)	0.318 5(6)	0.145 6(7)	−0.189 8(8)
O(3b)	0.136 1(5)	−0.237 8(5)	−0.053 5(7)	C(8b)	0.064 3(7)	0.189 5(9)	0.022 1(9)
O(3c)	0.248 0(4)	−0.155 1(5)	−0.090 1(6)	C(6b)	−0.037 3(6)	0.133 7(8)	−0.197 6(9)
N(3)	0.178 4(6)	−0.158 0(7)	−0.052 9(7)	C(5b)	−0.080 1(8)	0.078 0(9)	−0.291 9(10)
N(4)	0.234 1(8)	0.404 7(12)	−0.051 5(12)	C(4b)	−0.038 9(7)	0.011 4(9)	−0.355 6(10)
O(4a)	0.265 7(7)	0.375 1(8)	−0.132 7(10)	C(3b)	0.048 6(7)	0.001 0(8)	−0.329 6(9)
O(4b)	0.229 0(7)	0.351 0(9)	0.034 1(10)	C(2b)	0.094 1(5)	0.055 3(7)	−0.239 5(8)
O(4c)	0.190 0(8)	0.485 7(10)	−0.065 4(10)	C(7b)	0.051 8(6)	0.118 5(7)	−0.172 9(8)
C(10a)	0.241 7(7)	0.145 4(8)	0.324 0(9)	C(1b)	0.230 4(5)	0.140 4(7)	−0.256 4(8)
C(11c)	0.178 2(7)	0.214 7(8)	0.325 9(10)	O(5)	0.000 00	0.500 00	0.000 00
C(10b)	0.119 3(7)	0.232 7(8)	0.229 3(9)	O(6)	0.017 0(21)	0.448 9(28)	0.061 4(31)
C(9b)	0.129 4(6)	0.178 0(7)	0.126 5(8)	C(12)	0.027 5(33)	0.551 0(42)	0.024 1(48)
C(9a)	0.248 7(6)	0.090 0(8)	0.221 5(8)	H(N1a)	0.275 50	0.219 60	−0.049 70
C(8a)	0.310 2(7)	0.004 5(8)	0.216 5(9)	H(N1b)	0.221 60	−0.031 70	−0.244 00
(*b*) $[Ni(L^7)(NO_3)_2]{\cdot}0.5H_2O$ (**2**)							
Ni	−0.319 9(1)	−0.180 2(1)	−0.339 4(2)	C(7a)	−0.059 3(5)	−0.132 6(7)	−0.169 6(8)
N(1a)	−0.220 5(6)	−0.096 1(7)	−0.125 4(11)	C(2a)	−0.131 3(5)	−0.141 7(7)	−0.062 9(8)
N(1b)	−0.423 8(6)	−0.105 7(7)	−0.247 1(12)	C(8a)	−0.082 9(8)	−0.152 5(9)	−0.450 2(14)
O(1a)	−0.078 2(5)	−0.072 9(6)	−0.317 1(10)	C(1b)	−0.373 2(7)	−0.032 6(10)	−0.096 3(14)
O(1b)	−0.402 6(4)	−0.357 3(6)	−0.213 1(10)	C(3b)	−0.612 6(5)	−0.208 0(5)	−0.200 7(10)
N(2c)	−0.240 4(6)	−0.319 5(7)	−0.372 6(11)	C(4b)	−0.696 5(5)	−0.322 8(5)	−0.171 8(10)
O(3a)	−0.419 2(5)	−0.264 4(6)	−0.546 5(10)	C(5b)	−0.682 6(5)	−0.452 0(5)	−0.158 3(10)
O(3b)	−0.480 9(7)	−0.211 8(8)	−0.787 6(12)	C(6b)	−0.584 9(5)	−0.466 4(5)	−0.173 7(10)
O(3c)	−0.504 9(7)	−0.118 1(9)	−0.584 6(13)	C(7b)	−0.501 0(5)	−0.351 7(5)	−0.202 6(10)
N(3a)	−0.466 4(7)	−0.195 2(9)	−0.644 3(14)	C(2b)	−0.514 8(5)	−0.222 5(5)	−0.216 1(10)
O(4a)	−0.262 2(5)	−0.030 6(7)	−0.505 4(11)	C(8b)	−0.397 5(7)	−0.478 6(10)	−0.277 3(15)
O(4b)	−0.218 8(6)	0.138 1(7)	−0.344 2(12)	C(9a)	−0.147 1(7)	−0.297 5(9)	−0.425 2(14)
O(4c)	−0.167 4(6)	0.165 1(8)	−0.579 1(12)	C(10a)	−0.107 9(8)	−0.400 8(10)	−0.449 4(15)
N(4a)	−0.215 8(7)	0.093 7(9)	−0.473 9(15)	C(11c)	−0.168 2(8)	−0.534 6(11)	−0.423 1(16)
C(1a)	−0.290 3(8)	−0.092 9(10)	−0.007 5(15)	C(10b)	−0.262 1(8)	−0.559 4(10)	−0.365 2(14)
C(3a)	−0.117 2(5)	−0.200 1(7)	0.092 9(8)	C(9b)	−0.295 9(7)	−0.449 7(9)	−0.340 8(14)
C(4a)	−0.031 0(5)	−0.249 5(7)	0.142 0(8)	H(N1a)	−0.196 67	−0.012 31	−0.152 08
C(5a)	0.041 0(5)	−0.240 5(7)	0.035 3(8)	H(N1b)	−0.452 52	−0.061 97	−0.332 77
C(6a)	0.026 8(5)	−0.182 0(7)	−0.120 6(8)				

4.40 (qnt, 1 H, C*H*OH), 4.23—4.12 [m, 4 H, CH_2CH(OH)CH_2], and 3.50 (s, N*H*); ^{13}C, δ 146.3, 136.5, 122.1, 118.8, 115.7, 112.8 (C_6H_4), 70.2 and 69.0 [CH_2*C*H(OH)CH_2].

2,6-*Bis*(2-*aminophenoxymethyl*)*pyridine monohydrate*. The precursor dinitro compound was prepared using 2,6-bis(bromomethyl)pyridine[18] and potassium *o*-nitrophenolate by an analogous procedure to that just described. Recrystallization of the product from acetone gave beige crystals, yield 41% (Found: C, 60.1; H, 4.25; N, 11.0. Calc. for $C_{19}H_{15}N_3O_6$: C, 59.85; H, 3.95; N, 11.0%). Mass spectra parent ion: m/z 381. I.r. (KBr disc): ν(py) 1 580, ν(NO_2) 1 525 and 1 345 cm^{-1}. ^{1}H N.m.r. ($CDCl_3$): δ 7.92 (d, 2 H), 7.84 (t, 1 H), 7.64 (d, 2 H), 7.55 (t, 2 H), 7.16 (d, 2 H), 7.08 (t, 2 H), and 5.35 (s, 4 H). Reduction of the above dinitro intermediate to the corresponding diamine was effected by a modification of a previously published method.[19] The dinitro derivative (0.05 mol) and iron powder (0.5 mol) were suspended in ethanol–water (1:1, 1 l). The mixture was mechanically stirred and heated at reflux. Glacial acetic acid (15 cm^3) was then added dropwise and reflux was maintained for a further 18 h after which the mixture was filtered hot (using well packed filter aid). White crystals of product formed as the filtrate cooled. Further product was obtained by evaporation of the filtrate under vacuum. Recrystallization from ethanol–water gave the product in 72% yield (Found: C, 67.0; H, 6.45; N, 12.0. Calc. for $C_{19}H_{19}N_3O_2{\cdot}H_2O$: C, 67.25; H, 6.25; N, 12.4%). Mass spectral parent peak: m/z 321. I.r. (KBr disc): ν(OH) 3 450, ν(NH_2) 3 448, 3 375, δ(NH_2) 1 620, and ν[pyridine (py)] 1 580 cm^{-1}. N.m.r. ($CDCl_3$): ^{1}H, δ 7.74 (t, 1 H, py), 7.44 (d, 2 H, py), 6.89—6.65 (m, 8 H, C_6H_4), 5.26 (s, 4 H, CH_2O), and 3.04 (s, NH); ^{13}C, δ 156.7 (py), 146.0 (C_6H_4O), 137.6 ($C_6H_4NH_2$), 136.5 (py), 121.18, 120.1, 118.5, 115.4, 112.4 (C_6H_4, py), and 71.0 (CH_2O).

Di-imine Macrocyclic Complexes.—The synthesis of [Mn(P^1)(ClO_4)$_2$]·$x$$H_2O$ and [Pb(P^6)][ClO_4]$_2$·$x$$H_2O$ (x = 1—3) have been reported previously.[20,21] The remaining macrocycles were prepared by related procedures.

General Procedure for Mn(P^n)(ClO_4)$_2$·$x$$H_2O$ (n = 2—5, *or* 7).—2,6-Diformylpyridine or glyoxal (0.01 mol) was dissolved in methanol (300 cm^3) containing Mn(ClO_4)$_2$·6H_2O (0.01 mol). The solution was stirred vigorously and heated while a methanolic solution of 1,3-bis(2-aminophenoxy)propane, 1,4-bis(2-aminophenoxy)butane, 1,6-bis(2-aminophenoxy)hexane, or 2,6-bis(2-aminophenoxymethyl)pyridine monohydrate (0.01 mol) was added slowly. The resultant red solution was refluxed

Table 2. Bond lengths (Å) for complexes (**1**) and (**2**) with e.s.d.s in parentheses

(*a*) $[Cu(L^7)(NO_3)]NO_3{\cdot}0.33MeOH{\cdot}0.17H_2O$ (**1**)

Cu–N(1a)	2.002(7)	C(10a)–C(9a)	1.394(15)	Cu–N(1b)	2.046(6)	C(11c)–C(10b)	1.363(14)
Cu–O(1a)	2.393(6)	C(10b)–C(9b)	1.403(14)	Cu–O(1b)	2.407(6)	C(9b)–C(8b)	1.474(13)
Cu–N(2c)	2.088(8)	C(9a)–C(8a)	1.461(14)	Cu–O(3a)	1.944(6)	C(6a)–C(5a)	1.372(14)
N(1a)–C(2a)	1.446(10)	C(6a)–C(7a)	1.380(12)	N(1a)–C(1a)	1.503(11)	C(5a)–C(4a)	1.377(14)
N(1a)–H(N1a)	1.034	C(4a)–C(3a)	1.384(13)	N(1b)–C(2b)	1.437(11)	C(3a)–C(2a)	1.377(13)
N(1b)–C(1b)	1.511(12)	C(2a)–C(7a)	1.363(12)	N(1b)–H(N1b)	1.224	C(1a)–C(1b)	1.485(12)
O(1a)–C(8a)	1.432(13)	C(6b)–C(5b)	1.391(15)	O(1a)–C(7a)	1.380(11)	C(6b)–C(7b)	1.400(13)
O(1b)–C(8b)	1.422(12)	C(5b)–C(4b)	1.346(17)	O(1b)–C(7b)	1.374(10)	C(4b)–C(3b)	1.370(15)
N(2c)–C(9b)	1.339(12)	C(3b)–C(2b)	1.365(13)	N(2c)–C(9a)	1.329(11)	C(2b)–C(7b)	1.384(13)
O(3a)–N(3)	1.288(10)	N(4)–O(4a)	1.181(18)	O(3b)–N(3)	1.214(11)	N(4)–O(4b)	1.212(18)
O(3c)–N(3)	1.225(12)	N(4)–O(4c)	1.240(19)	C(10a)–C(11c)	1.333(15)	O(6)–C(12)	1.39(6)

(*b*) $[Ni(L^7)(NO_3)_2]{\cdot}0.5H_2O$ (**2**)

Ni–N(1a)	2.123(8)	N(2c)–C(a)	1.343(14)	Ni–N(1b)	2.061(10)	N(2c)–C(9b)	1.347(11)
Ni–O(1b)	2.116(6)	O(3a)–N(3a)	1.262(13)	Ni–N(2c)	2.098(9)	O(3b)–N(3a)	1.198(16)
Ni–O(3a)	2.078(7)	O(3c)–N(3a)	1.247(16)	Ni–O(4a)	2.035(8)	O(4a)–N(4a)	1.270(11)
N(1a)–C(1a)	1.474(16)	O(4b)–N(4a)	1.222(16)	N(1a)–C(2a)	1.428(11)	O(4c)–N(4a)	1.231(14)
N(1a)–H(N1a)	0.847	C(1a)–C(1b)	1.505(16)	N(1b)–C(1b)	1.478(14)	C(8a)–C(9a)	1.495(12)
N(1b)–C(2b)	1.468(9)	C(8b)–C(9b)	1.480(15)	N(1b)–H(N1b)	1.910	C(9a)–C(10a)	1.368(17)
O(1a)–C(7a)	1.350(10)	C(10a)–C(11c)	1.388(14)	O(1a)–C(8a)	1.418(14)	C(11c)–C(10b)	1.367(17)
O(1b)–C(7b)	1.359(10)	C(10b)–C(9b)	1.384(17)	O(1b)–C(8b)	1.428(13)		

for 2 h, cooled, then filtered. The volume of the filtrate was reduced to 50 cm^3. An equal volume of diethyl ether was slowly infused into the filtrate. In each case the product formed on standing as yellow crystals. The yields were 68, 65, 60, and 77%, respectively {(Found: C, 40.85; H, 3.65; N, 6.55. Calc. for $Mn(P^2)(ClO_4)_2{\cdot}2H_2O$: C, 40.8; H, 3.60; N, 6.50). (Found: C, 42.6; H, 4.05; N, 6.25. Calc. for $Mn(P^3)(ClO_4)_2{\cdot}H_2O$: C, 42.95; H, 3.60; N, 6.55). (Found: C, 40.25; H, 3.90; N, 5.20. Calc. for $Mn(P^5)(ClO_4)_2{\cdot}2H_2O$: C, 40.85; H, 3.50; N, 6.35). (Found: C, 41.2; H, 3.30; N, 6.60. Calc. for $[Mn(P^7)(ClO_4)_2]{\cdot}H_2O$: C, 41.0; H, 3.10; N, 6.85%)}. Analytically pure samples of $Mn(P^4)(ClO_4)_2$ were not obtained; however the crude product was allowed to react further to yield pure L^4 (see later).

$Pb(P^n)(ClO_4)_2{\cdot}xH_2O$ (*n* = 8 *or* 9).—2,6-Diformylpyridine or 2,5-diformylfuran (0.005 mol) and $Pb(ClO_4)_2{\cdot}3H_2O$ (0.005 mol) were dissolved in ethanol (500 cm^3). 2,6-Bis(2-aminophenoxymethyl)pyridine monohydrate (0.005 mol) dissolved in ethanol was slowly added. Stirring and heating of the solution was maintained during the addition and the solution was then refluxed for a further 2 h. Filtration followed by evaporation gave crystalline products (yellow and orange, respectively). Yields 70 and 90% respectively {Found: C, 38.0; H, 2.80; N, 6.60. Calc. for $[Pb(P^8)(ClO_4)_2]$: C, 37.8; H, 2.45; N, 6.75%}. ^1H N.m.r. (CD_3CN): δ 9.66 (s, 2 H, HC=N), 8.54 (t, 1 H, py), 8.27 (d, 2 H, py), 8.00 (t, 1 H, py), 7.68—7.20 (m, 10 H, C_6H_4, py), and 5.41 (s, 4 H, OCH_2). {Found: C, 36.80; H, 3.10; N, 4.90. $Pb(P^9)(ClO_4)_2{\cdot}EtOH{\cdot}H_2O$: C, 36.7; H, 3.10; N, 4.75%}. ^1H N.m.r. (CD_3CN): δ 9.00 (s, 2 H, HC=N), 8.21 (t, 1 H, py), 7.74 (d, 2 H, py), 7.60—7.22 (m, 10 H, C_6H_4 and furan), and 5.58 (s, 4 H, OCH_2).

$[Pb_2(P^{10}-H)_2P^{10}][ClO_4]_2{\cdot}3H_2O$.—2,6-Diformyl-*p*-cresol (0.005 mol) and $Pb(ClO_4)_2{\cdot}3H_2O$ (0.005 mol) were dissolved in ethanol (500 cm^3). 2,6-Bis(2-aminophenoxymethyl)pyridine monohydrate (0.005 mol) in ethanol was then added slowly. After a few minutes a bright orange precipitate formed. Recrystallization from acetonitrile–ethanol (1:1) gave large orange needles. Yield 75% {Found: C, 50.05; H, 3.70; N, 6.30. Calc. for $[Pb_2(P^{10}-H)_2P^{10}][ClO_4]_2{\cdot}3H_2O$: C, 50.05; H, 3.75; N, 6.25%}.

$[Mn_2(P^{10}-H)_2P^{10}][ClO_4]_2{\cdot}4H_2O$.—This red species was prepared from $Mn(ClO_4)_2{\cdot}6H_2O$ by an analogous procedure to that described for $[Pb_2(P^{10}-H)_2P^{10}][ClO_4]_2{\cdot}3H_2O$. Yield 70% {Found: C, 58.7; H, 4.40; N, 7.55. Calc. for $[Mn_2(P^{10}-H)_2P^{10}][ClO_4]_2{\cdot}4H_2O$: C, 58.45; H, 4.30; N, 7.30%}.

Metal-free Reduced Macrocycles.—The appropriate di-imine macrocyclic complex (0.01 mol) was slurried in ethanol (400 cm^3) and sodium tetrahydroborate (0.1 mol) was added, in several portions, to the cold stirred slurry. The reaction solution was then refluxed for 3 h, filtered while hot, and the filtrate concentrated to produce crude product. Recrystallization was from ethanol containing activated charcoal. The yields of L^8, L^9, and L^{10} were increased by Soxhlet extraction of the reaction residues; L^3 and L^4 were recrystallized from chloroform–ethanol. Yields 60—80%.

L^1 (Found: C, 72.3; H, 6.30; N, 12.4. Calc. for $C_{21}H_{21}N_3O_2$: C, 72.6; H, 6.10; N, 12.1%). Mass spectral parent ion: *m/z* 347. I.r. (KBr disc): ν(NH) 3 395 and 3 360 cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 7.65 (t, 1 H, py), 7.18 (d, 2 H, py), 7.03—6.65 (m, 8 H, C_6H_4), 5.89 (s, NH), 4.47 (s, 4 H, $NHCH_2$), and 4.43 (s, 4 H, OCH_2CH_2O); ^{13}C, δ 155.2 (py), 146.1 (C_6H_4O), 139.4 (C_6H_4NH), 136.7 (py), 122.4, 120.1, 116.4, 112.4, 110.7 (C_6H_4 + py), 67.8 (OCH_2), and 47.8 ($NHCH_2$).

L^2 (Found: C, 73.3; H, 6.80; N, 11.4. Calc. for $C_{22}H_{23}N_3O_2$: C, 73.1; H, 6.40; N, 11.60%). Mass spectral parent ion: *m/z* 361. I.r. (KBr disc): ν(NH) 3 400 cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 7.64 (t, 1 H, py), 7.17 (d, 2 H, py), 6.94—6.62 (m, 8 H, C_6H_4), 5.98 (s, NH), 4.46 (d, 4 H, $NHCH_2$), 4.27 (t, 4 H, OCH_2), and 2.42 (p, 2 H, OCH_2CH_2); ^{13}C, δ 156.5 (py), 147.0 (C_6H_4O), 138.4 (C_6H_4NH), 136.6 (py), 121.6, 120.5, 116.7, 111.3, 110.4 (C_6H_4 + py), 68.0 (OCH_2), 47.4 ($NHCH_2$), and 30.1 (OCH_2CH_2).

L^3 (Found: C, 73.6; H, 7.05; N, 10.90. Calc. for $C_{23}H_{25}N_3O_2$: C, 73.6; H, 6.70; N, 11.2%). Mass spectral parent ion: *m/z* 375. I.r. (KBr disc): ν(NH) 3 410 cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 7.64 (t, 1 H, py), 7.19 (d, 2 H, py), 6.97—6.63 (m, 8 H, C_6H_4), 5.89 (s, NH), 4.50 (s, 4 H, $NHCH_2$), 4.10 (m, 4 H, OCH_2CH_2), and 2.10 (q, 4 H, OCH_2CH_2); ^{13}C, δ 156.7 (py), 146.8 (C_6H_4O), 138.0 (C_6H_4NH), 136.6 (py), 121.1, 120.8, 116.6, 110.2, 110.1 (C_6H_4 + py), 67.3 (OCH_2), 48.5 ($NHCH_2$), and 27.0 (OCH_2CH_2).

L^4 (Found: C, 72.95; H, 7.30; N, 10.75. Calc. for $C_{25}H_{29}N_3O_2{\cdot}0.5H_2O$: C, 72.8; H, 7.35; N, 10.2%). Mass spectral parent ion: *m/z* 421 ($L^4{\cdot}H_2O$). I.r. (KBr disc) 3 420 and 3 380 cm^{-1}. N.m.r. ($CDCl_3$): ^1H, δ 7.53 (t, 1 H, py), 7.18 (d, 2 H, py), 6.87—6.53 (m, 8 H, C_6H_4), 5.36 (t, 2 H, NH), 4.45 (d, 4 H,

Table 3. Interbond angles (°) for (**1**) and (**2**) with e.s.d.s in parentheses

(*a*) $[\mathrm{Cu(L^7)(NO_3)]NO_3{\cdot}0.33MeOH{\cdot}0.17H_2O}$ (**1**)

N(1b)–Cu–N(1a)	86.5(3)	O(3c)–N(3)–O(3a)	118.8(8)	O(1a)–Cu–N(1a)	77.1(2)	O(3c)–N(3)–O(3b)	122.3(9)
O(1a)–Cu–N(1b)	138.0(3)	C(9a)–C(10a)–C(11c)	119.7(9)	O(1b)–Cu–N(1a)	94.8(2)	C(10b)–C(11c)–C(10a)	121(1)
O(1b)–Cu–N(1b)	72.1(2)	C(9b)–C(10b)–C(11c)	118(1)	O(1b)–Cu–O(1a)	146.7(2)	C(10b)–C(9b)–N(2c)	120.4(8)
N(2c)–Cu–N(1a)	96.7(3)	C(8b)–C(9b)–N(2c)	119.7(8)	N(2c)–Cu–N(1b)	145.8(3)	C(8b)–C(9b)–C(10b)	119.7(9)
N(2c)–Cu–O(1a)	75.2(2)	C(10a)–C(9a)–N(2c)	119.7(9)	N(2c)–Cu–O(1b)	73.7(2)	C(8a)–C(9a)–N(2c)	117.4(9)
O(3a)–Cu–N(1a)	169.1(3)	C(8a)–C(9a)–C(10a)	122.7(9)	O(3a)–Cu–N(1b)	92.9(3)	C(9a)–C(8a)–O(1a)	112.8(8)
O(3a)–Cu–O(1a)	96.3(2)	C(7a)–C(6a)–C(5a)	120.2(9)	O(3a)–Cu–O(1b)	95.5(2)	C(4a)–C(5a)–C(6a)	120.0(9)
O(3a)–Cu–N(2c)	89.9(3)	C(3a)–C(4a)–C(5a)	119(1)	C(2a)–N(1a)–Cu	117.0(5)	C(2a)–C(3a)–C(4a)	120.7(9)
C(1a)–N(1a)–Cu	105.9(5)	C(3a)–C(2a)–N(1a)	120.7(8)	C(1a)–N(1a)–C(2a)	112.4(7)	C(7a)–C(2a)–N(1a)	119.8(8)
H(N1a)–N(1a)–Cu	97.6(4)	C(7a)–C(2a)–C(3a)	119.5(8)	H(N1a)–N(1a)–C(2a)	115.3(6)	C(6a)–C(7a)–O(1a)	120.4(8)
H(N1a)–N(1a)–C(1a)	107.2(6)	C(2a)–C(7a)–O(1a)	119.2(7)	C(2b)–N(1b)–Cu	109.8(5)	C(2a)–C(7a)–C(6a)	120.4(9)
C(1b)–N(1b)–Cu	105.4(5)	C(1b)–C(1a)–N(1a)	108.3(7)	C(1b)–N(1b)–C(2b)	110.8(7)	C(9b)–C(8b)–O(1b)	110.1(8)
H(N1b)–N(1b)–Cu	104.2(4)	C(7b)–C(6b)–C(5b)	117(1)	H(N1b)–N(1b)–C(2b)	118.7(6)	C(4b)–C(5b)–C(6b)	122(1)
H(N1b)–N(1b)–C(1b)	107.0(6)	C(3b)–C(4b)–C(5b)	119(1)	C(8a)–O(1a)–Cu	104.5(5)	C(2b)–C(3b)–C(4b)	121(1)
C(7a)–O(1a)–Cu	106.9(5)	C(3b)–C(2b)–N(1b)	122.1(9)	C(7a)–O(1a)–C(8a)	112.8(7)	C(7b)–C(2b)–N(1b)	118.5(8)
C(8b)–O(1b)–Cu	109.4(5)	C(7b)–C(2b)–C(3b)	119.4(8)	C(7b)–O(1b)–Cu	103.1(5)	C(6b)–C(7b)–O(1b)	122.5(8)
C(7b)–O(1b)–C(8b)	118.8(7)	C(2b)–C(7a)–O(1b)	116.0(8)	C(9b)–N(2c)–Cu	119.7(6)	C(2b)–C(7b)–C(6b)	121.5(8)
C(9a)–N(2c)–Cu	118.7(6)	C(1a)–C(1b)–N(1b)	107.3(7)	C(9a)–N(2c)–C(9b)	121.0(8)	O(4b)–N(4)–O(4a)	123(1)
N(3)–O(3a)–Cu	112.3(6)	O(4c)–N(4)–O(4a)	117(1)	O(3b)–N(3)–O(3a)	118.9(9)	O(4c)–N(4)–O(4b)	119(1)

(*b*) $[\mathrm{Ni(L^7)(NO_3)_2]{\cdot}0.5H_2O}$ (**2**)

N(1b)–Ni–N(1a)	81.6(3)	C(9b)–N(2c)–Ni	112.8(7)	O(1b)–Ni–N(1a)	93.2(3)	C(9b)–N(2c)–C(9a)	117.5(9)
O(1b)–Ni–N(1b)	80.0(3)	N(3a)–O(3a)–Ni	121.3(6)	N(2c)–Ni–N(1a)	96.3(3)	O(3b)–N(3a)–O(3a)	121(1)
N(2c)–Ni–N(1b)	157.5(3)	O(3c)–N(3a)–O(3a)	117(1)	N(2c)–Ni–O(1b)	77.8(3)	O(3c)–N(3a)–O(3b)	121(1)
O(3a)–Ni–N(1a)	179.0(3)	N(4a)–O(4a)–Ni	125.0(8)	O(3a)–Ni–N(1b)	97.8(3)	O(4b)–N(4a)–O(4a)	121(1)
O(3a)–Ni–O(1b)	86.0(3)	O(4c)–N(4a)–O(4a)	117(1)	O(3a)–Ni–N(2c)	83.9(3)	O(4c)–N(4a)–O(4b)	122.4(9)
O(4a)–Ni–N(1a)	99.7(3)	C(1b)–C(1a)–N(1a)	106.9(9)	O(4a)–Ni–N(1b)	102.1(3)	C(6a)–C(7a)–O(1a)	124.0(7)
O(4a)–Ni–O(1b)	167.1(3)	C(3a)–C(2a)–N(1a)	123.3(7)	O(4a)–Ni–N(2c)	100.3(3)	C(7a)–C(2a)–N(1a)	116.6(7)
O(4a)–Ni–O(3a)	81.1(3)	C(9a)–C(8a)–O(1a)	111.6(9)	C(1a)–N(1a)–Ni	106.8(5)	C(1a)–C(1b)–N(1b)	110.2(9)
C(2a)–N(1a)–Ni	119.9(6)	C(2a)–C(7a)–O(1a)	116.0(7)	C(2a)–N(1a)–Ni	116.1(8)	C(2b)–C(7b)–O(1b)	116.6(5)
H(N1a)–N(1a)–Ni	103.2(7)	C(6b)–C(7b)–O(1b)	123.3(6)	H(N1a)–N(1a)–C(1a)	101.8(9)	C(7b)–C(2b)–N(1b)	117.5(7)
H(N1a)–N(1a)–C(2a)	106.8(7)	C(3b)–C(2b)–N(1b)	122.5(6)	C(1b)–N(1b)–Ni	111.0(6)	C(10a)–C(9a)–N(2c)	122.9(8)
C(2b)–N(1b)–Ni	107.3(5)	C(8a)–C(9a)–N(2c)	117(1)	C(2b)–N(1b)–C(1b)	110.8(8)	C(11c)–C(10a)–C(9a)	119(1)
H(N1b)–N(1b)–Ni	105.3	C(10a)–C(9a)–C(8a)	120(1)	H(N1b)–N(1b)–C(1b)	119.8	C(9b)–C(10b)–C(11c)	118.7(9)
H(N1b)–N(1b)–C(2b)	101.7(6)	C(10b)–C(11c)–C(10a)	119(1)	C(8a)–O(1a)–C(7a)	114.4(7)	C(10b)–C(9b)–N(2c)	123(1)
C(7b)–O(1b)–Ni	109.5(4)	C(8b)–C(9b)–N(2c)	119(1)	C(8b)–O(1b)–Ni	111.7(6)	C(9b)–C(8b)–O(1b)	109.2(7)
C(8b)–O(1b)–C(7b)	116.0(6)	C(10b)–C(9b)–C(8b)	117.9(8)	C(9a)–N(2c)–Ni	129.7(6)		

$\mathrm{NHC}H_2$), 3.95 (t, 4 H, $\mathrm{OCH_2}$), 1.87 (m, 4 H, $\mathrm{OCH_2C}H_2$), and 1.62 (m, 4 H, $\mathrm{OCH_2CH_2C}H_2$); ^{13}C, δ 158.0 (py), 146.3 ($\mathrm{C_6H_4O}$), 137.9 ($\mathrm{C_6H_4NH}$), 137.1 (py), 121.0, 119.6, 116.6, 110.2, 110.1 ($\mathrm{C_6H_4}$ + py), 67.9 ($\mathrm{OCH_2}$), 49.1 ($\mathrm{NHCH_2}$), 30.0 ($\mathrm{OCH_2}C\mathrm{H_2}$), and 26.3 ($\mathrm{OCH_2CH_2}C\mathrm{H_2}$).

$\mathrm{L^5}$ (Found: C, 69.5; H, 6.20; N, 11.3. Calc. for $\mathrm{C_{22}H_{23}N_3O_3}$: 70.0; H, 6.15; N, 11.15%). Mass spectral parent ion: *m/z* 377. I.r. (KBr disc): ν(NH) 3 400 and ν(OH) 3 400 cm^{-1}. N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 7.65 (t, 1 H, py), 7.18 (d, 2 H, py), 6.98—6.62 (m, 8 H, $\mathrm{C_6H_4}$), 4.45 (s, 4 H, $\mathrm{NHC}H_2$), and 4.40—4.18 [m, 5 H, $CH_2CH\mathrm{(OH)}CH_2$]; ^{13}C, δ 156.6 (py), 146.4 ($\mathrm{C_6H_4O}$), 139.1 ($\mathrm{C_6H_4NH}$), 136.7 (py), 123.0, 120.7, 116.9, 114.5, 110.8 ($\mathrm{C_6H_4}$ + py), 71.9 ($\mathrm{OCH_2}$), 69.2 (CHOH), and 47.9 ($\mathrm{NHCH_2}$).

$\mathrm{L^6}$ (Found: C, 71.65; H, 6.95; N, 10.95. Calc. for $\mathrm{C_{23}H_{25}N_3O_3}$: C, 70.55; H, 6.45; N, 10.75%). Mass spectral parent ion: *m/z* 391. I.r. (KBr disc): ν(NH) 3 410 cm^{-1}. N.m.r. ([$^2\mathrm{H_6}$]dimethyl sulphoxide): ^{1}H, δ 7.71 (t, 1 H, py), 7.39 (d, 2 H, py), 6.85—6.50 (m, 8 H, $\mathrm{C_6H_4}$), 5.42 (t, 2 H, NH), 4.36 (d, 4 H, $\mathrm{NHC}H_2$), 4.11 (m, 4 H, $\mathrm{C_6H_4OC}H_2$), and 3.85 (m, 4 H, $\mathrm{OCH_2C}H_2$); ^{13}C, δ 157.1 (py), 145.6 ($\mathrm{C_6H_4O}$), 137.5 ($\mathrm{C_6H_4NH}$), 137.1 (py) 121.4, 121.1, 116.1, 110.4, 109.9 ($\mathrm{C_6H_4}$ + py), 68.8 ($\mathrm{C_6H_4O}C\mathrm{H_2}$), 67.3 ($C\mathrm{H_2O}C\mathrm{H_2}$), and 47.6 ($\mathrm{NHCH_2}$).

$\mathrm{L^7}$ (Found: C, 72.45; H, 6.35; N, 12.3. Calc. for $\mathrm{C_{21}H_{21}N_3O_2}$: C, 72.6; H, 6.10; N, 12.1%). Mass spectral parent ion: *m/z* 347. I.r. (KBr disc): ν(NH) 3 420 and 3 370 cm^{-1}. N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 7.65 (t, 1 H, py), 7.24 (d, 2 H, py), 7.02—6.60 (m, 8 H, $\mathrm{C_6H_4}$), 5.16 (s, 4 H, $\mathrm{OCH_2}$), 5.06 (s, NH), and 3.42 (s, 4 H, $\mathrm{NHC}H_2$); ^{13}C, δ 156.7 (py), 146.7 ($\mathrm{C_6H_4O}$), 139.4 ($\mathrm{C_6H_4NH}$), 137.0, (py), 122.8, 122.3, 116.4, 114.5, 110.9 ($\mathrm{C_6H_4}$ + py), 73.0 ($\mathrm{OCH_2}$), and 42.0 ($\mathrm{NHCH_2}$).

$\mathrm{L^8}$ (Found: C, 73.15; H, 6.00; N, 13.35. Calc. for $\mathrm{C_{26}H_{24}N_4O_2}$: C, 73.55; H, 5.70; N, 13.2%). Mass spectral parent ion: *m/z* 424. I.r. (KBr disc): ν(NH) 3 400 and ν(py) 1 580 cm^{-1}. N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 7.71, 7.59 (t, 1 H, py), 7.34, 7.19 (d, 2 H, py), 7.00—6.69 (m, 8 H, $\mathrm{C_6H_4}$), 5.12 (s, 4 H, $\mathrm{OCH_2}$), and 4.31 (s, 4 H, $\mathrm{NHC}H_2$); ^{13}C, δ 157.7, 156.02 (py), 146.8 ($\mathrm{C_6H_4O}$), 138.6 ($\mathrm{C_6H_4NH}$), 137.3, 136.9 (py), 123.3, 121.8, 121.7, 116.9, 111.3, 110.8 ($\mathrm{C_6H_4}$ + py), 71.6 ($\mathrm{OCH_2}$), and 49.5 ($\mathrm{NHCH_2}$).

$\mathrm{L^9}$ (Found: C, 70.0; H, 6.50; N, 9.40. Calc. for $\mathrm{C_{25}H_{23}N_3O_3{\cdot}C_2H_5OH}$: C, 70.55; H, 6.35; N, 9.15%). Mass spectral parent ion: *m/z* 413. I.r. (KBr disc): ν(NH) 3 425 cm^{-1}. N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 7.78 (t, 1 H, py), 7.42 (d, 2 H, py), 7.00—6.65 (m, 8 H, $\mathrm{C_6H_4}$), 6.18 (s, 2 H, furan), 5.08 (s, 4 H, $\mathrm{OCH_2}$), 4.50 (s, NH), 4.18 (s, 4 H, $\mathrm{NHC}H_2$), 3.74 (q, 2 H, $\mathrm{CH_3C}H_2\mathrm{OH}$), and 1.26 (t, 3 H, $CH_3\mathrm{CH_2OH}$); ^{13}C, δ 155.7 (py), 151.3 (furan), 146.4 ($\mathrm{C_6H_4O}$), 137.9, 137.7 ($\mathrm{C_6H_4NH}$ + py), 124.0, 121.6, 117.1, 110.4, 110.2, 108.2 ($\mathrm{C_6H_4}$ + py), 71.3 ($\mathrm{OCH_2}$), and 41.4 ($\mathrm{NHCH_2}$).

$\mathrm{L^{10}}$ (Found: C, 73.95; H, 6.15; N, 9.45. Calc. for $\mathrm{C_{28}H_{27}N_3O_3}$: C, 74.3; H, 5.80; N, 9.30%). Mass spectral parent ion: *m/z* 453. I.r. (KBr disc): ν(NH) 3 400 and ν(OH) 3 400 cm^{-1}. ^{1}H N.m.r. ($\mathrm{CDCl_3}$): δ 8.58 (s, 1 H, OH), 7.74 (t, 1 H, py), 7.38 (d, 2 H, py), 7.00—6.77 (m, 10 H, $\mathrm{C_6H_4}$), 5.04 (s, 4 H, $\mathrm{NHC}H_2$), 4.55 (t, NH), 4.24 (d, 4 H, $\mathrm{O}CH_2\mathrm{C_6H_4}$), and 2.22 (s, 3 H, $\mathrm{CH_3}$).

Table 4. Infrared and f.a.b. mass spectral data for the Schiff-base macrocyclic complex precursors

	I.r./cm^{-1}			Mass spectrometry (f.a.b.)	
		ClO_4^-			
Complex	H_2O, C=N, and py	ν_3	ν_4	Peak (m/z)	Assignment
$[Mn(P^1)(ClO_4)_2]\cdot H_2O$	3 440(br), 1 615, 1 590, 1 583, 1 578 (sh)	1 125, 1 038, 920	622, 617	497	$[Mn(P^1)(ClO_4)]^+$
$Mn(P^2)(ClO_4)_2\cdot 2H_2O$	3 420(br), 1 620, 1 618, 1 595, 1 578 (sh)	1 110(br)	630	511	$[Mn(P^2)(ClO_4)]^+$
$Mn(P^3)(ClO_4)_2\cdot H_2O$	3 420(br), 1 628, 1 617, 1 592, 1 578 (sh)	1 110(br)	630	525	$[Mn(P^3)(ClO_4)]^+$
$Mn(P^4)(ClO_4)_2\cdot 2H_2O$	3 450(br), 1 630 (sh), 1 617, 1 590, 1 578 (sh)	1 090(br)	623		
$Mn(P^5)(ClO_4)_2\cdot 2H_2O$	3 420(br), 1 630, 1 617, 1 593, 1 578 (sh)	1 110(br)	630	527	$[Mn(P^5)(ClO_4)]^+$
$[Mn(P^7)(ClO_4)_2]\cdot H_2O$	3 430(br), 1 630 (sh), 1 618, 1 592, 1 578	1 128, 1 038, 922	628, 622	497	$[Mn(P^7)(ClO_4)]^+$
$[Pb(P^8)(ClO_4)_2]$	1 600, 1 588, 1 580	1 130, 1 035, 918	628, 618	729	$[Pb(P^8)(ClO_4)]^+$
$Pb(P^9)(ClO_4)_2\cdot EtOH\cdot H_2O$	3 430(br), 1 630 (sh), 1 609, 1 585, 1 578 (sh)	1 110(br)	623	716	$[Pb(P^9)(ClO_4)]^+$
$[Pb_2(P^{10}-H)_2P^{10}]$-$[ClO_4]_2\cdot 3H_2O$	3 450(br), 1 628 (sh), 1 625, 1 598, 1 578 (sh)	1 098(br)	623	655	$[Pb(P^{10})]^+$
				1 104	$[Pb(P^{10})_2]^+$
				1 205	$[Pb(P^{10})_2(ClO_4)]^+$
$[Mn_2(P^{10}-H)_2P^{10}]$-$[ClO_4]_2\cdot 4H_2O$	3 450(br), 1 642, 1 632, 1 618 (sh), 1 613 (sh), 1 598	1 110(br)	625	450	$P^{10} - 3H$

Reduced Macrocycle Complexes.—The following procedure was used in all cases. The ligand (0.001 mol) and appropriate hydrated metal salt (nitrate or perchlorate) (0.0015 mol) were mixed in warm methanol (150 cm^3); after 20 min the solutions were evaporated to one third of the original volume and chilled to produce crystals of the macrocyclic complexes. The latter were dried in air. Yields: 50—70%.

{Found: C, 47.05; H, 4.00; N, 12.9. Calc. for $[Cu(L^1)(NO_3)_2]$: C, 47.15; H, 3.95; N, 13.1. Found: C, 48.0; H, 4.50; N, 12.30. Calc. for $[Cu(L^2)(NO_3)_2]\cdot H_2O$: C, 48.15; H, 4.20; N, 12.75. Found: C, 49.65; H, 4.80; N, 12.15. Calc. for $[Cu(L^3)(NO_3)_2]$: C, 49.05; H, 4.50; N, 12.45. Found: C, 47.55; H, 4.90; N, 10.9. Calc. for $[Cu(L^4)(NO_3)_2]\cdot 2H_2O$: C, 47.9; H, 5.00; N, 11.15. Found: C, 41.45; H, 4.30; N, 5.90. Calc. for $[Cu(L^6)][ClO_4]_2\cdot H_2O$: C, 41.1; H, 4.05; N, 6.25. Found: C, 46.5; H, 4.15; N, 12.6. Calc. for $[Cu(L^7)(NO_3]NO_3\cdot 0.33MeOH\cdot 0.17H_2O$: C, 46.70; H, 4.15; N, 12.6. Found: C, 45.0; H, 3.5; N, 7.95. Calc. for $[Cu(L^8)][ClO_4]_2$: C, 45.5; H, 3.50; N, 8.15. Found: C, 46.6; H, 3.95; N, 12.85. Calc. for $[Ni(L^7)(NO_3)_2]\cdot 0.5H_2O$: C, 46.8; H, 4.10; N, 13.0. Found: C, 45.15; H, 3.55; N, 8.35. Calc. for $[Ni(L^8)(ClO_4)_2]$: C, 45.2; H, 3.65; N, 8.15. Found: C, 45.85; H, 4.10; N, 12.65. Calc. for $[Co(L^7)(NO_3)_2]\cdot H_2O$: C, 46.05; H, 4.25; N, 12.75%}. Complexes of macrocycle L^5 proved difficult to isolate because of their high solubility.

X-Ray Structure Analyses.—Single crystals of $[Cu(L^7)(NO_3)][NO_3]\cdot 0.33MeOH\cdot 0.17H_2O$ (**1**) and $[Ni(L^7)(NO_3)_2]\cdot 0.5H_2O$ (**2**) were obtained by slow evaporation of solutions in aqueous methanol.

Crystal data. (**1**). $C_{21}H_{21}CuN_5O_8\cdot C_{0.33}H_{1.67}O_{0.50}$, M = 548.62, monoclinic, space group $P2_1/n$ (alternative $P2_1/c$, no. 14), a = 15.665(3), b = 12.755(3), c = 11.527(2) Å, β = 97.93(2)°, U = 2 281.15 Å^3, Z = 4, D_c = 1.667 g cm^{-3}, F(000) = 1 118.7 (allowing for contribution from disordered solvents), μ(Mo-K_α) = 9.56 cm^{-1}.

(**2**). $C_{21}H_{21}N_5NiO_8\cdot 0.5H_2O$, M = 539.1, triclinic, space group $P\bar{1}$ (no. 2), a = 13.450(2), b = 10.320(2), c = 8.340(2) Å, α = 85.10(2), β = 99.24(2), γ = 108.01(2)°, U = 1 085.8 Å^3, Z = 2, D_c = 1.616 g cm^{-3}, F(000) = 546, μ(Mo-K_α) = 8.84 cm^{-1}.

Data collection. A Philips PW 1100 four-circle diffractometer was used for data collection in the range θ 3—25° by the method described previously,[22] using Mo-K_α radiation from a graphite crystal monochromator, with a constant scan speed of 0.05° s^{-1} and a scan width of 0.90° for both crystals, which were of dimensions 0.37 × 0.32 × 0.38 for (**1**) and 0.30 × 0.21 × 0.10 mm for (**2**). Three reference reflections were measured every 5 h in each case and showed no significant change in intensities. The data were corrected for Lorentz and polarization factors and equivalent reflections were merged to give a total of 2 418 [(**1**)] and 1 700 [(**2**)] unique data with $I > 3.0\sigma(I)$.

Structure solution and refinement.[23] For each structure the position of the metal atom was determined from a Patterson synthesis. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. From the elemental analysis and i.r. spectra both complexes had originally been formulated a demi-hydrates. In the difference Fourier syntheses of complex (**2**) no maxima attributable to the water molecule could be located indicating that it may be disordered over several sites in the solid state. For the copper compound (**1**) a triangle of peaks of *ca.* 2 e Å^{-3} were located on, and adjacent to, the inversion centre at 0.0, 0.5, 0.0. Two of these with a separation of *ca.* 1.5 Å were attributed to a methanol of crystallization and the third, on the symmetry site, to a water molecule. Impossibly short contacts between the two centrosymmetrically related methanols and the proximity of both these molecules to the oxygen of the water molecule indicated alternate occupation of this cavity throughout the crystal by one or other of the methanol molecules or by the water molecule, corresponding to a maximum solvent content of one half per molecule of complex. The three independent solvent atoms were therefore assigned fixed site occupancies of 0.333 for the two of the methanol and 0.167 for the water oxygen atom on the inversion centre, giving a total cavity occupation of one solvent molecule; the isotropic thermal parameters of these atoms refined to similar values (U 0.14—0.16 Å^2) which although relatively high are reasonable in view of the nature of the disorder. Due to the shortage of data, caused by poor diffraction by the crystal, the phenylene rings in the nickel compound (**2**) were treated as rigid hexagonal groups (C–C 1.395 Å) and for both structures the hydrogen atoms (apart from those bonded to the nitrogen donors, and the solvent molecules) were included at calculated positions 'riding' at a fixed distance of 1.08 Å from the carbon atom to which they were bonded. For each structure common isotropic thermal parameters were assigned to the hydrogen atoms of the phenylene, methylene, and pyridyl groups and these free variables refined to final values of 0.074, 0.068, and 0.094 respectively for (**1**) and 0.12, 0.062, and 0.14 Å^2 for (**2**). A difference Fourier synthesis using data with $(\sin\theta)/\lambda < 0.35$ revealed suitable maxima for the hydrogen atoms for the secondary amine donors in each structure and these were included in the structure-factor calculation with thermal parameters of 0.05 for (**1**) and 0.08 Å^2 for (**2**) but were not refined. In the final cycles of full-matrix refine-

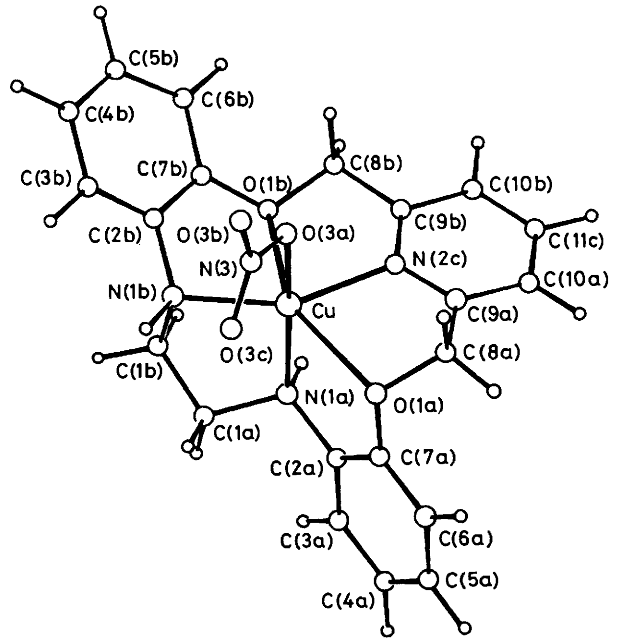


Figure 1. The configuration of the complex cation $[Cu(L^7)(NO_3)]^+$ showing how the donors of the quinquedentate ligand and monodentate nitrate anion occupy six of the vertices of a distorted pentagonal bipyramid. The closest intermolecular approach to the seventh site is the oxygen atom of the unco-ordinated nitrate ion (not shown) Cu $\cdots$ O(4b) 3.944 Å

ment of each structure the metal, nitrogen, and oxygen atoms (excluding those of the solvent) were assigned anisotropic thermal parameters. Neutral scattering factors,[24] corrected for the real and imaginary components of anomalous dispersion,[25] were used throughout. Individual weights of $1/\sigma^2(I)$ were assigned to each reflection and refinement converged at R 0.0762 and R' 0.0779 for complex (**1**) and R 0.0626 and R' 0.0590 for (**2**), where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$. The final atomic co-ordinates of (**1**) and (**2**) are listed in Table 1, selected bond lengths in Table 2, and selected angles in Table 3. The structures are shown in Figures 1 and 2 respectively.

Results and Discussion

Precursor Schiff-base Macrocycles.—The condensation of the appropriate dialdehyde and diamine in the presence of either Mn^{II} or Pb^{II}, using the conditions described in the Experimental section, results in isolation of the corresponding complexes of the di-imine ligands P^1—P^{10} (see Scheme) containing 15 to 19 members in their inner rings. Selected i.r. and f.a.b. source mass spectral data are listed in Table 4. Such template condensations are now well established for producing Schiff-base macrocyclic ligands (especially for systems incorporating pyridine moieties in the condensing fragments).[26—30] The i.r. data are consistent with the presence of imine linkages; each complex exhibiting at least one ν(C=N) mode between 1 638 and 1 600 cm^{-1}. The water present in the majority of the complexes is probably lattice and/or co-ordinated water. However the spectra do not rule out the possibility that water has added across an imine linkage in some of the complexes to yield corresponding carbinol-amine derivatives. Such hydrolysis (or solvolysis involving alcohol addition) has been demonstrated to occur for other imine macrocyclic systems containing rigid structures.[31]

In particular complexes, such as $[Mn(P^1)(ClO_4)_2]\cdot H_2O$ and $[Mn(P^7)(ClO_4)_2]\cdot H_2O$, clear splitting of the ν_3 and ν_4 modes of the perchlorate groups occur. This strongly indicates that the latter groups are co-ordinated in these complexes. Indeed, the *X*-ray crystal structure of the N_5 analogue of $[Mn(P^1)(ClO_4)_2]\cdot H_2O$ has been reported previously[20] and contains axial (C_{3v}) perchlorate co-ordination. The macrocycle forms an equatorial girdle.

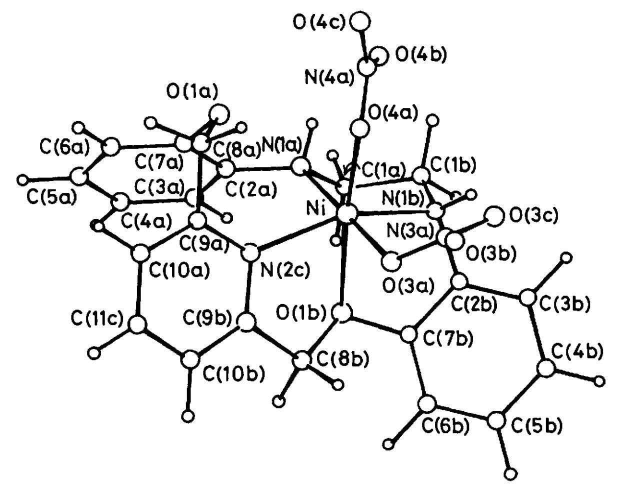


Figure 2. The conformation of the neutral complex molecule $[Ni(L^7)(NO_3)_2]$, showing that only four of the donor atoms of L^7 are bonded to the Ni^{II}, the slightly distorted octahedral geometry being completed by the two *cis* nitrate ions acting as monodentate ligands. The distance to the unco-ordinated ether oxygen atom O(1a) is 3.074 Å

Where soluble, the lead(II) complexes in CD_3CN show unremarkable ^1H n.m.r. spectra: all show singlets at δ *ca.* 9 corresponding to two co-ordinated imine methine groups.

The f.a.b. mass spectral results (Table 4) serve an important role in confirming the monomeric [1 + 1] (dicarbonyl and diamine) nature of the complexes. Formation of [2 + 2] macrocycles in such template Schiff-base condensations is not uncommon for other systems.[3,28]

The structures of the complexes of type $[Pb_2(P^{10}-H)_2P^{10}][ClO_4]_2\cdot 3H_2O$ and $[Mn_2(P^{10}-H)_2P^{10}][ClO_4]_2\cdot 4H_2O$ are unknown but may be of the 'triple-decker' sandwich type with the phenolic group on one macrocycle remaining protonated. F.a.b. mass spectroscopy of the lead(II) species is consistent with such a structure since the three major (positive-ion) peaks yield *m*/*z* values of 655, 1 104, and 1 205. These peaks are attributable to the ions $[Pb(P^{10})]^+$, $[Pb(P^{10})_2]^+$, and $[Pb(P^{10})_2(ClO_4)]^+$. A simulation of the isotope pattern for the 1 104 peak is shown in Figure 3; agreement with the observed pattern is excellent. For the manganese(II) complex, the parent ion (at *m*/*z* 453) corresponds to the free [1 + 1] macrocycle.

The routes to the macrocyclic complexes listed in the Scheme involve the template action of either Mn^{II} and/or Pb^{II}; Mn^{II} dominates route (*a*) while Pb^{II} dominates route (*b*). Lead(II) tends to be an effective template ion, not only for the larger (18-membered) rings, but also when X and Y contain additional ligating groups; thus the radius of the metal ion as well as its co-ordination preferences both appear to influence template behaviour although the relative importance of these factors is difficult to define for specific complexes.

Reduced Macrocycles.—The new macrocycles L^1—L^{10} were obtained by reduction of their complexed di-imine precursors using sodium tetrahydroborate. Although initially the intermediate complexes were isolated, it was also found possible to obtain the metal-free reduced macrocycles in one step by performing the reduction *in situ*. The i.r. spectra of L^1—L^{10} in all cases exhibit a ν(N–H) vibration in the 3 320—3 425 cm^{-1} region. The two isomeric macrocycles L^1 and L^7 each show splitting of this vibration; this most likely reflects different hydrogen-bonding patterns for each of the secondary anilino

Table 5. Magnetic susceptibility, electronic and selected i.r. spectral data for the complexes containing the reduced macrocyclic ligands

				I.r.[b]/cm^{-1}		
					ClO_4^-	
Complex	Colour	$\mu_{eff.}$/B.M.	Electronic spectra[a]	H_2O, NH_2	ν_3	ν_4
$[Cu(L^1)(NO_3)_2]$	Dark green	1.77	660 (204), 399 (1 369)	3 210 (sh), 3 160, 3 120		
$[Cu(L^2)(NO_3)_2]\cdot H_2O$	Dark green	1.86	662 (272), 402 (1 322)	3 400, 3 220, 3 165, 3 120 (sh)		
$[Cu(L^3)(NO_3)_2]$	Dark green	1.77	665 (320), 428 (1 440)	3 200 (sh), 3 155		
$[Cu(L^4)(NO_3)_2]\cdot 2H_2O$	Dark green	1.77	690 (291), 428 (1 535)	3 450, 3 225		
$[Cu(L^6)][ClO_4]_2\cdot H_2O$	Dark green	1.75	702 (464), 414 (2 070)	3 450, 3 225	1 098	625
$[Cu(L^7)(NO_3)]NO_3\cdot 0.33MeOH\cdot 0.17H_2O$ (**1**)	Emerald green	1.92	725 (150), 380 (sh)	3 430, 3 180, 3 100		
$[Cu(L^8)][ClO_4]_2$	Green	1.93	625 (106), 375 (sh)	3 200(br)	1 090	625
$[Ni(L^7)(NO_3)_2]\cdot 0.5H_2O$ (**2**)	Turquoise	3.06	*c*	3 400, 3 250, 3 195		
$[Ni(L^8)(ClO_4)_2]$	Lilac	3.16	*c*	3 235(br)	1 113	625
$[Co(L^7)(NO_3)_2]\cdot H_2O$	Lilac-pink	4.24	*c*	3 400, 3 235, 3 215, 3 175		

[a] Wavelength in nm. Absorption coefficients (dm^3 mol^{-1} dm^{-1}) in parentheses. [b] Nujol mull. [c] Insoluble.

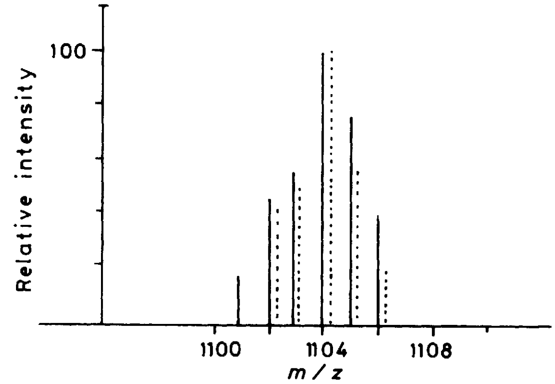


Figure 3. The isotope pattern in the f.a.b. mass spectrum of the lead complex of the precursor macrocyclic ligand P^{10}; observed (——) and calculated (· · · ·) for $[Pb(P^{10})_2]^+$

N–H groups in such rings. Hydrogen-1 and ^{13}C n.m.r. as well as mass spectral data are all consistent with the proposed structures.

Cobalt(II), *Nickel*(II), *and Copper*(II) *Complexes.*—Complexes with selected ligands from the range L^1—L^{10} have been isolated and characterized (Table 5). The procedure given in the Experimental section was used to obtain all the complexes listed in this Table. In general copper(II) species were found to be most readily isolated, perhaps reflecting their higher thermodynamic stabilities relative to the stabilities of the corresponding complexes of Co^{II} or Ni^{II} (see later). In a number of attempted syntheses, low stabilities and/or unfavourable solubility characteristics led to difficulty in isolating pure products using the general procedure.

The i.r. spectra of the complexes all contain secondary amine stretches in the region 3 100—3 300 cm^{-1} (Table 5). Further, the i.r. spectra are consistent with the presence of water where it is suggested to be present from microanalytical data. Comparison of the spectra of the three metal complexes of L^7 strongly indicates that the structure of $[Ni(L^7)(NO_3)_2]\cdot 0.5H_2O$ (**2**) differs markedly from that of its cobalt(II) and copper(II) analogues (both of which have similar spectra). A different conformation of the co-ordinated macrocycle was therefore expected in the case of (**2**), an observation in accord with subsequent *X*-ray diffraction studies of (**1**) and (**2**).

The room-temperature magnetic moments of the complexes are unexceptional (Table 5) although the moment of 4.24 B.M. for $[Co(L^7)(NO_3)_2]\cdot H_2O$ is somewhat below the usual range expected for high spin Co^{II} in an octahedral environment.[32]

The electronic spectra were recorded where solubility permitted, in methanol (Table 5). Each copper(II) complex displays a broad symmetrical envelope of bands in the region 500—900 nm; the broadness of the absorptions makes reliable stereochemical assignments difficult. All these complexes are intensely coloured owing to the presence of a strong charge-transfer band which extends into the visible region from the u.v. region. For the complexes of L^1—L^4 there is a gradual increase in $\lambda_{max.}$ for the envelope of bands in the visible region. This phenomenon appears to reflect the decrease in ligand-field strength as the O–Cu–O chelate-ring size increases from five to nine along the series; the concomitant increase in absorption coefficient is also qualitatively in accord with increased distortion of co-ordination geometry along the series. Examination of molecular models supports this view.

Spectrophotometric titrations of Cu^{II} in 95% methanol with L^2 and L^7 were carried out up to a ligand-to-metal ratio of 2.5. In both cases, a 1:1 end-point was observed with no evidence for formation of species with higher ligand-to-metal ratios. This result, which complements the synthetic and structural studies, contrasts with the behaviour of related O_2N_2 macrocycles which were also found to yield species having L:M ratios of other than 1:1.[33]

Stability Constant Studies.—Potentiometric (pH) titrations have been carried out to determine the protonation constants for the macrocyclic ligands and the stability constants for a range of 1:1 complexes of Co^{II}, Ni^{II}, and Cu^{II} (Table 6). In all cases equilibria were reached quickly (minutes) for these systems; such behaviour is commonly found for mixed O_nN_m-donor macrocycles[2,25] and contrasts with the long equilibration times (often months) sometimes associated with complex formation by tetra-aza macrocycles. Thus mixed-donor macrocycles tend to be ideal for studies of the present type. The log *K* values quoted correspond to equilibria of the type: $M^{2+} + L \rightleftharpoons ML^{2+}$, $K = [ML^{2+}]/[M^{2+}][L]$. The p$K_a$ values for the protonated ligands are low (all less than 4.6) as expected for compounds incorporating anilino- and pyridine-type nitrogens. Comparison of the values for the two isomeric macrocycles L^1 and L^7 indicates that the expected drop in acidity occurs as the anilino nitrogens are transferred from the immediate vicinity of the pyridine nitrogen in L^1 to the opposite side of the macrocyclic ring in L^7.

The highest stabilities occur for the complexes of the O_2N_4-donor ligand L^8 which, from molecular models, can encapsulate

Table 6. Macrocycle protonation constants and stability constant data for the corresponding complexes (95% MeOH, $I = 0.1$ mol dm^{-3}, $[NEt_4]ClO_4$ at 25 °C)[a]

Ligand	Donor set	Free ligand[b] log K_1		Copper complex[c,d] log K_1
		log K_1	log K_2	
L^1	O_2N_3	3.00 (0.06)	*ca.* 2.15	8.83 (0.2)[e]
L^2	O_2N_3	3.50 (0.02)	*ca.* 2.40	9.48 (0.2)[e]
L^3	O_2N_3	3.73 (0.05)	*ca.* 1.80	7.36 (0.2)[e]
L^4	O_2N_3	3.56 (0.10)	*ca.* 1.82	*ca.* 9.0 [e]
L^7	O_2N_3	4.41 (0.03)	2.18 (0.09)	6.84 (0.2)[e]
L^8	O_2N_4	4.53 (0.15)	2.64 (0.20)	11.08 (0.2)[f]

[a] All values are the mean (standard deviation in parentheses) of at least two, and up to ten, determinations. The values are the result of 172 individual titrations. Free ligands L^4, L^6, L^9, and L^{10} are either insoluble or precipitated during titration. [b] Protonation constants beyond log K_2 not obtained. [c] log K values were obtained at between two and four different metal-to-ligand ratios. [d] Values obtained from competitive titrations using perhydrodibenzo[*e,p*][1,4,8,11,14,]dioxatriazacycloheptadecine as the competing ligand. [e] log K for Co^{II} and Ni^{II} < 4.0. [f] log K for Ni^{II}, 4.56 (0.12); for Co^{II}, < 4.0.

a centrally co-ordinated transition metal in a near octahedral fashion. For the other ligands, all the cobalt(II) and nickel(II) complexes studied have values which were too low to measure reliably for these systems (log $K < 4$).

Results of stability constant measurements for the O_2N_3-donor series L^1—L^4 indicate a progressive reduction in thermodynamic stability as the macrocyclic ring size increases along the series L^1 to L^4. Although measurement of pK_a for L^4 was precluded by the extreme insolubility of the free ligand, an estimate of the log K value for its copper(II) complex (obtained using the pK_a for L^3) is consistent with the trend observed for ligands L^1—L^3 for which accurate log K values were obtained, Table 6. The log K values are highest for the first two members, L^1 and L^2, in which all chelate rings are either five- or six-membered. Preliminary results indicate that the dissociation in acid of these complexes is considerably slower than for the larger-ring members of the series. From these semi-quantitative observations it is clear that the log K values largely reflect complex dissociation rates, a situation well documented previously for the other macrocyclic ligand systems.[34,35]

For the two isomeric macrocycles L^1 and L^7 in which the donor atoms disposition varies, a marked difference in the thermodynamic stability occurs, Table 6. Similar observations on variation of donor atom sequence in otherwise identical macrocycles have been reported previously.[36]

Although molecular models show that the O_2N_4 ligand L^8, which gives the most stable complexes (see above) can present an octahedral donor set to a transition-metal ion, the potentially quinquedentate O_2N_3-donor systems L^1—L^4 and L^7 are unable to define five sites of a regular octahedron. The metals in the L^7 complexes studied by *X*-ray diffraction are known to have contrasting properties, Cu^{II} exhibiting 'plasticity' in its stereochemical requirements,[37] whereas Ni^{II} is much more rigid, preferring regular square-based geometries.

The *X*-ray structure analysis of $[Ni(L^7)(NO_3)_2]$ (**2**) shows that the metal is co-ordinated to only four atoms of the donor set which define vertices of a rather distorted octahedron (Figure 2) the remaining two co-ordination sites being occupied by *cis* monodentate nitrate ligands. In contrast, in the structure of $[Cu(L^7)(NO_3)]NO_3$ (**1**) the copper atom accommodates all five donors of the macrocycle in what may be described as a distorted *nido*-pentagonal bipyramidal geometry (Figure 1). The reduced macrocyclic effect in (**2**) relative to that in (**1**) resulting from the loss of two chelate rings would be an important contributing factor to the much higher thermodynamic stability of the copper(II) complex, (**1**), relative to the nickel(II) complex, (**2**), with the ligand L^7.

The distortions from regular octahedral geometry in the structure of $[Ni(L^7)(NO_3)_2]$ (**2**) can be seen in the range of *cis* angles at Ni^{II}, 77.8(3)—102.1(3)°, and of *trans* angles 157.5(3)—179.0(3)° (Table 3). The smallest angles O(1b)–Ni–N(1b) 80.0(3), N(2c)–Ni–O(1b) 77.8(3), and N(1a)–Ni–N(1b) 81.6(3)°, are associated with the five-membered chelate rings. The eight membered chelate ring is folded about the Ni $\cdots$ O(1a) vector and adopts a type of boat conformation, curving back towards the metal so that the ether oxygen atom O(1a) is at a distance of 3.074 Å from the nickel atom. However this distance is too long to represent any appreciable bonding interaction; the affinity of ether oxygen donors for Ni^{II} is known to be relatively low and non-co-ordination of such atoms in other macrocyclic complexes has been observed.[38]

In the six-co-ordinate structure of $[Cu(L^7)(NO_3)]^+$ the 'axial' sites are occupied by the anilino nitrogen atom N(1a) and an oxygen of the co-ordinated nitrate, O(3a), which present the only nearly linear arrangement of donors in the structure, N(1a)–Cu–O(3a) 169.1(3)°. The remaining four donor atoms may be regarded as occupying 'equatorial' sites of a distorted pentagonal-bipyramidal geometry, subtending angles at Cu in the range 72.1(2)—75.2(2)°, the angle across the missing fifth equatorial vertex, N(1b)–Cu–O(1a), being 138.0(3)°. The deviations from the plane of best fit through the equatorial donor atoms are N(1b) −0.075, O(1b) 0.117, N(2c) −0.122, and O(1a) 0.080 Å, and the axial Cu–N(1a) and Cu–O(3a) bonds are at angles of 77.62 and 89.49° to this plane respectively. The Cu atoms lies 0.161 Å above the equatorial donor plane toward the co-ordinated nitrate ligand. The only close interactions with the metal atom, in the vicinity of the gap in the co-ordination sphere, are intramolecular distances, to the co-ordinated nitrate ion Cu $\cdots$ O(3c) 2.719 Å, and to an anilino hydrogen atom Cu $\cdots$ H(N1b) 2.63 Å. This hydrogen atom is involved in a strong hydrogen bond to an unco-ordinated nitrate ion relative to the first by a screw axis ($0.5 - x$, $0.5 + y$, $-0.5 - z$), O(4a′) $\cdots$ H(1b) 1.88 Å.

The shortest bond from the copper atom is to the nitrate ligand Cu–O(3a) 1.944(6) Å, and the relatively longer bonds to the macrocyclic donors may be evidence of the steric strain involved in achieving co-ordination of all five donors to the metal; the second 'axial' bond Cu–N(1a) is also relatively short, 2.002(7) Å. The Cu–N distances (2.002—2.088 Å) are within the range observed previously for such donors, but the copper to ether oxygen distances are rather long, Cu–O(1a) 2.393(6) and Cu–O(1b) 2.407(6).

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