Metal-ion Selectivity by Macrocyclic Ligands. Part 2.[1] The Interaction of Zn^{II}, Cd^{II} and Hg^{II} with Pyridinyl-derived N_3O_2 Macrocycles; X-Ray Structures of One Zinc and Two Cadmium Endomacrocyclic Complexes and of One Zinc and One Mercury Exomacrocyclic Complex†

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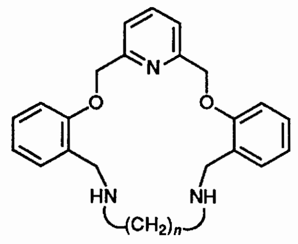
The interaction of Zn^{II}, Cd^{II} and Hg^{II} with the macrocycles L^1 and L^2, each containing an N_3O_2-donor set, has been investigated. Conductometric titration of the 1:1 complexes of Zn^{II} and Cd^{II} with chloride in each case indicated the sequential formation of a 1:1 electrolyte of the type $[ML(Cl)]^+$ and a 2:1 electrolyte of the type $[MLCl_2]$ in each case. Proton NMR titration of the ligands with $M(O_2CMe)_2$ in CD_3OD gave evidence for the formation of 1:1 and 1:2 (metal:ligand) species. The stability constants of the complexes have been determined in 95% methanol. The X-ray crystal structures of the 1:1 complexes $[ZnL^1I_2]\cdot H_2O$, $[ZnL^1(NO_3)]NO_3$, $[CdL^1(NO_3)(MeOH)]NO_3$, $[CdL^2(ClO_4)(MeCN)]ClO_4$ and $[HgL^1I_2]$ have been determined. The metal atoms in $[ZnL^1I_2]\cdot H_2O$ and $[HgL^1I_2]$ are four-co-ordinated in a tetrahedral geometry and lie outside the macrocyclic cavity. The donor set in each molecule comprises the two secondary amine nitrogen atoms from the macrocycle and the two iodide anions. The complex $[ZnL^1(NO_3)]NO_3$ has all donors of the macrocycle co-ordinated with one oxygen from a nitrate anion occupying the sixth site to yield an approximately trigonal-prismatic geometry. The structure of $[CdL^1(NO_3)(MeOH)]NO_3$ shows that the metal is seven-co-ordinated in an approximately pentagonal-bipyramidal environment consisting of the full donor set of the macrocycle together with one oxygen each from a nitrate anion and a methanol of solvation. The structure of $[CdL^2(ClO_4)(MeCN)]ClO_4$ shows that the metal has a similar co-ordination environment consisting of the full donor set of the macrocycle together with an oxygen from a perchlorate anion and a nitrogen from acetonitrile of solvation.

Recent publications have documented a tendency for oxa-azamacrocyclic ligands to show a marked preference for Cd^{II} over Zn^{II} and it has been suggested that in some cases the observed difference in affinity for Cd^{II} over Zn^{II} reflects the presence of structural 'dislocations' between the respective complexes.[2-5] Structural 'dislocations' arise when the balance between metal co-ordination requirements and ligand flexibility lead to an abrupt change in co-ordination geometry between the complexes of interest. Macrocyclic ligands, because of the constraints inherent in their cyclic nature, are especially able to induce 'dislocation' behaviour. Ligands such as L^1 and L^2 have a mixed donor set and the presence of the more weakly donating ether donors may act to provide labile sites where 'dislocations' can be induced.[5]

We report here the reaction of Zn^{II}, Cd^{II} and Hg^{II} with L^1 and L^2 together with the solution properties of the resulting complexes. The X-ray crystal structures of $[ZnL^1I_2]\cdot H_2O$, $[ZnL^1(NO_3)]NO_3$, $[CdL^1(NO_3)(MeOH)]NO_3$, $[CdL^2(ClO_4)(MeCN)]ClO_4$ and $[HgL^1I_2]$ are also presented.

Experimental

The details of the physical measurements have been given previously, as have the syntheses of the macrocyclic ligands.[1] The general procedure for the preparation of the metal complexes was reported in ref. 1.



L^1 $n = 2$
L^2 $n = 3$

Crystallography.—Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ for $[ZnL^1I_2]\cdot H_2O$, $[ZnL^1(NO_3)]NO_3$ and $[CdL^2(ClO_4)(MeCN)]ClO_4$ on a Nicolet R3 four-circle diffractometer and in the range $6.5 < 2\theta < 50°$ for $[CdL^1(NO_3)(MeOH)]NO_3$ and $[HgL^1I_2]$ on a Stoe Stadi-2 two-circle diffractometer by the ω-scan method. The structures were solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Atom coordinates (× 10^4) for $[ZnL^1I_2]\cdot H_2O$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	3 945.1(11)	865.0(5)	5 681.1(10)	C(8)	−2 612(11)	488(5)	1 687(10)
I(1)	4 740.4(7)	1 725.1(3)	4 759.6(7)	C(9)	−2 532(13)	1(6)	968(11)
I(2)	5 667.4(8)	87.3(4)	7 089.6(7)	C(10)	−1 360(14)	−208(6)	991(12)
O(1)	−1 327(6)	1 261(3)	3 133(6)	C(11)	−148(11)	70(5)	1 756(10)
O(2)	1 053(6)	2 244(3)	7 375(6)	C(12)	−121(9)	555(4)	2 498(8)
O(3)	8 085(10)	812(4)	5 824(10)	C(13)	1 231(9)	847(4)	3 314(8)
N(1)	−1 484(7)	2 002(4)	5 039(7)	C(14)	1 255(10)	537(4)	5 369(9)
N(2)	1 990(7)	538(3)	4 551(7)	C(15)	1 563(9)	1 102(4)	6 152(9)
N(3)	3 066(7)	1 144(3)	6 900(7)	C(16)	3 503(9)	1 709(4)	7 605(9)
C(1)	−1 152(10)	2 486(5)	5 754(10)	C(17)	3 098(10)	1 761(4)	8 669(9)
C(2)	−1 559(11)	3 066(5)	5 281(12)	C(18)	3 960(10)	1 530(5)	9 852(9)
C(3)	−2 429(12)	3 117(5)	3 992(12)	C(19)	3 610(12)	1 540(5)	10 846(10)
C(4)	−2 759(11)	2 618(5)	3 277(11)	C(20)	2 405(11)	1 816(5)	10 720(10)
C(5)	−2 271(10)	2 069(5)	3 798(10)	C(21)	1 532(11)	2 055(5)	9 572(11)
C(6)	−2 598(10)	1 514(5)	3 037(10)	C(22)	1 871(10)	2 022(4)	8 548(9)
C(7)	−1 386(9)	770(4)	2 448(8)	C(23)	−328(11)	2 391(5)	7 147(11)

Atom O(3) is part of the water molecule of crystallisation.

Table 2 Atom coordinates (× 10^4) for $[ZnL^1(NO_3)]NO_3$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	2058.2(7)	761.7(8)	2500	C(6)	395(7)	1120(10)	3468(10)
O(1)	795(4)	1683(6)	2572(8)	C(7)	456(7)	1887(8)	1509(10)
O(2)	3191(4)	643(6)	3713(6)	C(8)	−262(8)	1490(10)	1177(11)
O(3)	1076(6)	−2168(7)	1739(10)	C(9)	−511(9)	1737(10)	90(14)
O(4)	1909(5)	−1476(9)	2931(8)	C(10)	−92(10)	2353(12)	−669(14)
O(5)	1244(5)	−420(7)	1914(9)	C(11)	613(9)	2760(9)	−340(11)
O(6)	3313(6)	3397(10)	2952(10)	C(12)	899(7)	2514(8)	773(10)
O(7)	2370(7)	3590(11)	4114(14)	C(13)	1649(8)	2985(8)	1224(11)
O(8)	3315(10)	4572(15)	4112(15)	C(14)	2598(7)	1745(10)	316(9)
N(1)	1695(5)	1013(6)	4230(7)	C(15)	3199(7)	917(10)	622(9)
N(2)	2265(6)	2143(7)	1445(7)	C(16)	3455(7)	−731(9)	1822(10)
N(3)	2862(5)	42(7)	1350(8)	C(17)	4103(6)	−185(8)	2467(14)
N(4)	1412(5)	−1394(8)	2146(9)	C(18)	4875(7)	−383(10)	2183(11)
N(5)	2943(9)	3888(10)	3677(9)	C(19)	5481(8)	95(12)	2785(13)
C(1)	2201(7)	1070(8)	5136(8)	C(20)	5304(8)	818(11)	3665(12)
C(2)	1972(9)	1131(10)	6277(10)	C(21)	4554(7)	1049(10)	4026(11)
C(3)	1184(10)	1194(11)	6518(11)	C(22)	3967(6)	508(8)	3408(10)
C(4)	673(8)	1180(10)	5617(11)	C(23)	3039(7)	1082(9)	4853(8)
C(5)	937(7)	1107(8)	4460(10)				

Atoms N(5), O(6)–O(8) comprise the unco-ordinated nitrate anion.

Table 3 Atom coordinates (× 10^4) for $[CdL^1(NO_3)(MeOH)]NO_3$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd	−2266.2(7)	1508.6(10)	1401.4(12)	C(6)	−1493(11)	3128(14)	−259(17)
O(1)	−1884(7)	2225(8)	−620(10)	C(7)	−1602(9)	1619(12)	−1471(14)
O(2)	−1716(6)	1330(9)	3752(10)	C(8)	−888(8)	1647(13)	−1808(15)
O(3)	−3749(8)	3973(10)	1170(14)	C(9)	−653(11)	960(16)	−2727(17)
O(4)	−2789(8)	3131(10)	1869(15)	C(10)	−1133(11)	237(15)	−3170(18)
O(5)	−3426(9)	2709(12)	174(16)	C(11)	−1836(11)	183(16)	−2837(8)
O(6)	306(9)	3624(20)	−1790(17)	C(12)	−2090(9)	856(15)	−1937(16)
O(7)	−720(11)	4158(13)	−2560(18)	C(13)	−2847(8)	823(14)	−1536(16)
O(8)	−29(10)	3464(18)	−3812(19)	C(14)	−3573(9)	287(16)	154(16)
O(9)	−1506(8)	6(10)	1550(14)	C(15)	−3506(10)	46(14)	1615(17)
N(1)	−1172(7)	2351(10)	1785(12)	C(16)	−3093(9)	590(13)	3776(16)
N(2)	−2829(7)	476(11)	−180(14)	C(17)	−2830(9)	1466(14)	4569(15)
N(3)	−3226(7)	866(11)	2400(12)	C(18)	−3317(10)	1932(13)	5315(16)
N(4)	−3333(8)	3270(10)	1087(15)	C(19)	−3060(13)	2716(15)	6113(19)
N(5)	−136(11)	3723(15)	−2730(21)	C(20)	−2349(13)	3032(15)	6123(22)
C(1)	−750(8)	2289(13)	2866(14)	C(21)	−1886(10)	2604(13)	5341(16)
C(2)	−106(10)	2791(16)	3126(16)	C(22)	−2124(8)	1822(12)	4559(15)
C(3)	94(9)	3502(16)	2232(18)	C(23)	−939(10)	1470(16)	3817(16)
C(4)	−348(9)	3565(15)	1095(16)	C(24)	−974(12)	−312(20)	790(21)
C(5)	−953(9)	2992(12)	961(15)				

Atoms N(5), O(6)–O(8) comprise the unco-ordinated nitrate anion.

Table 4 Atom coordinates (× 10^4) for $[CdL^2(ClO_4)(MeCN)]ClO_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd	799.2(5)	974.5(2)	2671.6(4)	C(16)	−2693(5)	1432(2)	3434(5)
O(1)	1747(4)	862(2)	1231(4)	C(17)	−1522(5)	1483(2)	3578(5)
O(2)	−1121(4)	1466(2)	2705(3)	C(18)	−2008(6)	1458(4)	1620(5)
N(1)	−337(5)	1420(2)	988(4)	C(19)	−1471(6)	1560(3)	765(5)
N(2)	1939(5)	54(2)	3203(4)	C(20)	−2209(7)	1789(3)	−270(6)
N(3)	1095(5)	1043(3)	4541(4)	C(21)	−1765(9)	1873(3)	−1079(6)
N(4)	1968(6)	1953(3)	2962(5)	C(22)	−586(6)	1726(3)	−855(5)
C(1)	2810(4)	569(2)	1375(4)	C(23)	100(6)	1509(3)	188(5)
C(2)	3622(4)	837(2)	988(4)	C(24)	1385(7)	1379(3)	444(5)
C(3)	4641(4)	500(2)	1116(4)	C(25)	2566(7)	2385(3)	3080(5)
C(4)	4848(4)	−106(2)	1631(4)	C(26)	3341(7)	2953(4)	3233(6)
C(5)	4037(4)	−374(2)	2019(4)	Cl(1)	−1152(1)	−334(1)	2451(1)
C(6)	3018(4)	−37(2)	1891(4)	O(3)	−1031(3)	−1006(1)	2229(3)
C(7)	2125(6)	−327(3)	2300(5)	O(4)	−497(2)	−204(2)	3590(1)
C(8)	3063(6)	139(3)	4170(5)	O(5)	−2351(1)	−187(1)	2208(2)
C(9)	2847(6)	310(3)	5221(5)	O(6)	−722(3)	59(1)	1780(2)
C(10)	2302(7)	966(3)	5244(6)	Cl(2)	5057(1)	−2760(1)	−1086(1)
C(11)	596(7)	1660(3)	4811(5)	O(7)	4456(3)	−2867(2)	−2240(1)
C(12)	−687(5)	1587(2)	4627(5)	O(8)	4482(3)	−2261(1)	−717(3)
C(13)	−1024(5)	1641(2)	5532(5)	O(9)	6229(1)	−2566(1)	−886(3)
C(14)	−2195(5)	1591(2)	5388(5)	O(10)	5067(2)	−3348(1)	−497(2)
C(15)	−3029(5)	1486(2)	4339(5)				

Atoms Cl(1), O(3)–O(6) and Cl(2), O(7)–O(10) comprise the perchlorate anions.

Table 5 Atom coordinates (× 10^4) for $[HgL^1I_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg	1244.6(10)	571.6(6)	1324.8(8)	C(9)	6991(30)	1929(16)	4811(23)
I(1)	−718.3(21)	1433.6(11)	554.0(16)	C(10)	5979(27)	1582(15)	5087(22)
I(2)	1506.5(19)	−520.0(12)	2662.9(15)	C(11)	4712(30)	1579(16)	4414(23)
O(1)	5402(16)	2539(9)	2273(14)	C(12)	4570(24)	1891(14)	3439(19)
O(2)	4268(16)	1547(8)	−1362(11)	C(13)	3295(24)	1780(13)	2695(19)
N(1)	5896(19)	2451(10)	109(14)	C(14)	4024(22)	1197(12)	1257(17)
N(2)	3347(18)	1128(10)	2026(15)	C(15)	3954(22)	526(13)	614(18)
N(3)	2596(18)	378(10)	114(15)	C(16)	2185(22)	747(12)	−885(16)
C(1)	5467(21)	2621(11)	−863(16)	C(17)	2904(21)	535(12)	−1713(16)
C(2)	5180(25)	3297(14)	−1207(21)	C(18)	2506(25)	−63(13)	−2317(19)
C(3)	5434(30)	3837(18)	−553(24)	C(19)	3127(29)	−259(17)	−3091(23)
C(4)	5875(27)	3710(15)	449(22)	C(20)	4090(24)	126(13)	−3324(19)
C(5)	6059(25)	2999(14)	784(20)	C(21)	4511(23)	751(12)	−2755(18)
C(6)	6542(27)	2785(16)	1864(21)	C(22)	3905(20)	951(11)	−1989(15)
C(7)	5642(22)	2227(12)	3204(18)	C(23)	5360(25)	1987(13)	−1598(19)
C(8)	6830(21)	2273(12)	3858(16)				

positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Complex scattering factors were taken from ref. 6 and from the program package SHELXTL[7] as implemented on a Data General Nova 3 computer. Unit weights were used throughout the refinements except where noted. Tables 1–5 list atomic positional parameters with estimated standard deviations (e.s.d.s).

Crystal data for $[ZnL^1I_2]\cdot H_2O$. $C_{23}H_{27}I_2N_3O_3Zn$, M = 712.66, crystallises from ethanol–methanol as colourless prisms, crystal dimensions 0.40 × 0.33 × 0.11 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 10.632(5), b = 22.427(12), c = 11.629(6) Å, β = 114.87(4)°, U = 2516(2) Å^3, D_c = 1.881 g cm^{-3}, Z = 4, graphite-monochromated Mo-Kα X-radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 34.56 cm^{-1}, $F(000)$ = 1383.80.

The 3346 independent reflections (of 4813 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.220 and 0.421). Refinement converged at a final R 0.0544 (289 parameters; mean and maximum final shift/e.s.d. 0.000 and 0.002 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of −0.75 and +0.73 e Å^{-3}.

Crystal data for $[ZnL^1(NO_3)]NO_3$. $C_{23}H_{25}N_5O_8Zn$, M = 564.85, crystallises from ethanol–acetonitrile as colourless prisms, crystal dimensions 0.80 × 0.35 × 0.25 mm, orthorhombic, space group $Pna2_1$ (C^9_{2v}, no. 33), a = 17.12(4), b = 12.13(7), c = 11.41(8) Å, U = 2369(21) Å^3, D_c = 1.584 g cm^{-3}, Z = 4, graphite-monochromated Mo-Kα X-radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 11.17 cm^{-1}, $F(000)$ = 1167.74.

The 1563 independent reflections (of 2395 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.283 and 0.335). The correct enantiomeric form of the chosen crystal was confirmed by the smaller final R (by 0.0025) at convergence. Refinement converged to a final R 0.0544 (333 parameters; mean and maximum final shift/e.s.d. 0.012 and 0.049 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis gave minimum and maximum values of −0.30 and +0.40 e Å^{-3}.

Crystal data for $[CdL^1(NO_3)(MeOH)]NO_3$. $C_{24}H_{29}CdN_5O_9$, M = 643.92, crystallises from methanol as colourless

Table 6 Microanalytical[a] and mass spectral data for the complexes of Zn^{II}, Cd^{II} and Hg^{II}

	Analysis (%)				
Complex[b]	C	H	N	Other	*m/z* for $[ML(X)]^+$
$[ZnL^1(NO_3)_2]$	49.1	4.5	12.1		501
	(48.9)	(4.5)	(12.4)		
$[ZnL^1(ClO_4)_2]$[c]	43.0	4.2	6.5	11.5 Cl	538
	(43.2)	(3.9)	(6.6)	(10.8)	
$[ZnL^1I_2]\cdot H_2O$[d]	38.6	4.0	5.8	35.3 I	566
	(38.8)	(3.8)	(5.9)	(35.6)	
$[ZnL^1Cl_2]\cdot 1.5H_2O$[c]	51.1	5.5	7.4	13.1 Cl	474
	(51.3)	(5.2)	(7.8)	(13.2)	
$[CdL^1(NO_3)_2]$[c]	45.3	4.3	11.4		551
	(45.2)	(4.1)	(11.4)		
$[CdL^1(ClO_4)_2]\cdot H_2O$	39.5	3.7	6.0	9.8 Cl	588
	(39.2)	(3.9)	(6.0)	(10.1)	
$[CdL^1Cl_2]\cdot 0.5H_2O$[c]	48.4	4.7	7.2	12.2 Cl	524
	(48.6)	(4.6)	(7.4)	(12.5)	
$[HgL^1I_2]$[e]	32.8	3.4	5.0	30.2 I	702
	(32.3)	(3.0)	(5.1)	(30.6)	
$[ZnL^2(ClO_4)_2]$[c]	43.8	4.1	6.2	10.7 Cl	552
	(44.1)	(4.2)	(6.4)	(10.8)	
$[CdL^2(NO_3)_2]\cdot H_2O$[e]	45.1	4.5	10.8		565
	(44.8)	(4.5)	(10.9)		
$[CdL^2(ClO_4)_2]\cdot MeCN$	42.0	3.8	7.4	9.7 Cl	602
	(42.1)	(4.1)	(7.6)	(9.6)	

[a] Calculated values in parentheses. [b] Recrystallised from EtOH–MeCN unless otherwise stated. [c] Recrystallised from MeOH. [d] Recrystallised from MeOH–EtOH. [e] Recrystallised from MeCN.

needles, crystal dimensions 0.47 × 0.13 × 0.12 mm, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$, C^5_{2h}, no. 14), $a = 18.10(10)$, $b = 13.44(8)$, $c = 10.64(4)$ Å, $\beta = 95.60(5)°$, $U = 2575(23)$ Å^3, $D_c = 1.661$ g cm^{-3}, $Z = 4$, graphite-monochromated Mo-Kα X-radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 9.03 cm^{-1}, $F(000) = 1311.78$.

The 2167 independent reflections (of 4744 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, for absorption by the Gaussian integration method (minimum and maximum transmission coefficients 0.839 and 0.897), and for 13% decay based on the monitoring of standard reflections. Refinement converged at a final R 0.0676 (345 parameters; mean and maximum final shift/e.s.d. 0.004 and 0.025 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of two carbon atoms of the macrocycle. A final difference electron-density synthesis showed minimum and maximum values of -0.75 and $+0.87$ e Å^{-3}.

Crystal data for $[CdL^2(ClO_4)(MeCN)]ClO_4$. $C_{26}H_{30}CdCl_2N_4O_{10}$, $M = 741.85$, crystallises from acetonitrile–ethanol as colourless blocks, crystal dimensions 0.65 × 0.40 × 0.35 mm, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 12.380(28)$, $b = 20.590(21)$, $c = 13.059(21)$ Å, $\beta = 111.65(16)°$, $U = 3094(10)$ Å^3, $D_c = 1.593$ g cm^{-3}, $Z = 4$, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 9.33 cm^{-1}, $F(000) = 1503.80$.

The 3223 independent reflections (of 5685 measured) for which $|F|/\sigma|F| > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of five azimuthal scans (minimum and maximum transmission coefficients 0.441 and 0.480 respectively). Geometrical constraints of T_d symmetry were imposed on the two perchlorate anions, and of D_{6h} symmetry (C–C 1.395 Å) on the two phenyl fragments. Refinement converged at a final R 0.0668 (R' 0.0569, 365 parameters, mean and maximum final shift/e.s.d. = 0.114 and 0.493 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. The final electron-density synthesis showed minima and maxima of -0.78 and $+0.67$ e Å^{-3}. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\,25(F)^2]$ was used in the latter stages of the refinement.

Crystal data for $[HgL^1I_2]$. $C_{23}H_{25}HgI_2N_3O_2$, $M = 829.87$, crystallises from acetonitrile as pale yellow, well formed diamonds, crystal dimensions 0.50 × 0.50 × 0.175 mm, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$, C^5_{2h}, no. 14), $a = 10.522(18)$, $b = 18.829(18)$, $c = 13.409(12)$ Å, $\beta = 101.14(11)°$, $U = 2607(6)$ Å^3, $D_c = 2.114$ g cm^{-3}, $Z = 4$, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 82.71 cm^{-1}, $F(000) = 1543.68$.

The 2616 independent reflections (of 5007 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.044 and 0.313). Refinement converged at a final R 0.0634 (165 parameters, maximum shift/e.s.d. 0.005), with allowance for the thermal anisotropy of mercury, iodine, oxygen and nitrogen atoms only. A final difference electron-density synthesis showed peaks of -1.57 and $+1.45$ e Å^{-3}.

Additional material available for all structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Zinc(II), *Cadmium*(II) *and Mercury*(II) *Complexes of Ligands* L^1 *and* L^2.—A number of zinc and cadmium complexes having 1:1 (metal:ligand) stoichiometries were isolated from alcoholic solutions and characterised (Table 6); no 1:2 complexes were isolated, as were obtained for Cu^{II} and Ni^{II}.[1] A 1:1 metal:ligand complex of L^1 with HgI_2 was also isolated. The IR spectra of the complexes show secondary amine stretches in the region 3100–3300 cm^{-1} which are split and/or shifted from their corresponding positions for the free macrocycle (3320, L^1; 3250 cm^{-1}, L^2); in several cases these peaks are split. Anion stretches were also generally split or broadened due to co-ordination or the effect of hydrogen bonding. Furthermore the spectra are consistent with the presence of water (or solvent) where it is suggested to be present from the microanalytical data. For each complex the fast atom bombardment (FAB) mass spectra contained peaks corresponding to $[ML(X)]^+$ ($L = L^1$ or L^2).

Conductometric titrations of the $ML(ClO_4)_2$ species (M = Cd or Zn) with NH_4Cl in dimethyl sulphoxide (dmso)[8] indicated that all these complexes were 1:2 electrolytes initially. Inflections were observed in the respective plots at 1 and 2 mole

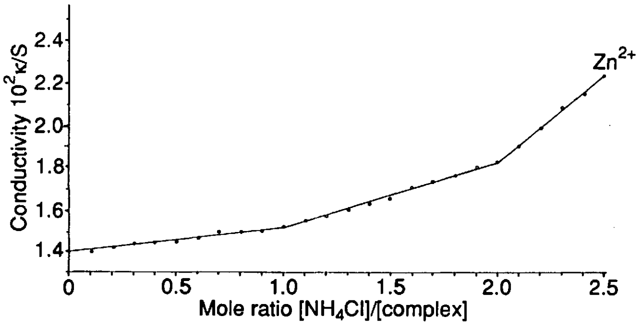
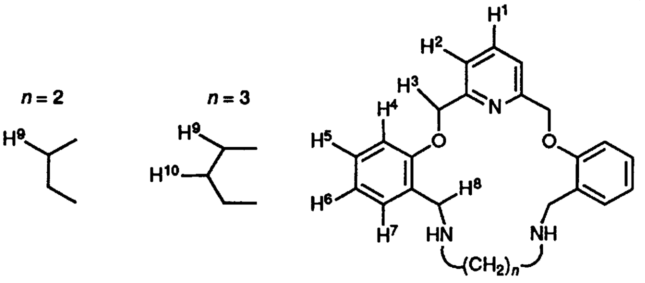


Fig. 1 Conductometric titration of ligand L^1 with Zn^{II}

Table 7 Proton NMR data: aliphatic signals for the 1:1 complexes ($\Delta = \delta_{complex} - \delta_{ligand}$)



(*i*) Zn^{II} and Cd^{II} in CD_3OD

	L^1	Zn^{2+}	$\Delta\delta$	Cd^{2+}	$\Delta\delta$
H^3	5.20	5.16	−0.04	5.48	0.28
H^8	3.74	4.00	0.25	4.16/3.86	0.42/0.12
H^9	2.59	2.71	0.12	3.07/2.89	0.48/0.30

	L^2	Zn^{2+}	$\Delta\delta$	Cd^{2+}	$\Delta\delta$
H^3	5.18	5.12	−0.06	5.40	0.22
H^8	3.66	4.31	0.65	4.16/3.80	0.50/0.14
H^9	2.50	2.70	0.20	2.90/2.82	0.40/0.32
H^{10}	1.58	1.67	0.09	1.93	0.35

(*ii*) Hg^{II} in $(CD_3)_2SO$

	L^1	Hg^{2+}	$\Delta\delta$
H^3	5.11	5.07	−0.04
H^8	3.59	3.7	0.19
H^9	2.48	2.57	0.09

Table 8 Thermodynamic stability constants

Cation	L^1	L^2	$\Delta \log K$
Zn^{2+}	5.91 (0.07)	5.75 (0.05)	0.16
Cd^{2+}	8.73 (0.06)	4.19 (0.05)	4.54
$\Delta \log K$	−2.82	1.56	

In 95% MeOH, 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C.

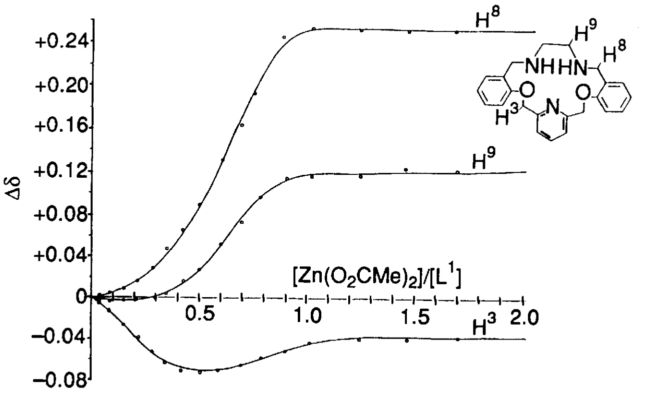
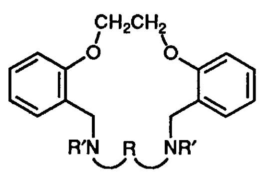


Fig. 2 Proton NMR titration of L^1 with Zn^{II} in CD_3OD



	R	R'
L^3	$(CH_2)_3$	Me
L^4	$(CH_2)_2NH(CH_2)_4$	H
L^5	$(CH_2)_2NH(CH_2)_2$	H
L^6	$(CH_2)_3NH(CH_2)_3$	H

ratios ([NH_4Cl]/[complex]) (Fig. 1) indicating the sequential formation of a 1:1 complex of the type [ML(Cl)]$^+$ and of a 2:1 complex of the type $MLCl_2$ in each case. This behaviour was not surprising in the case of Cd^{II} given the pentagonal-bipyramidal structure which has been previously observed for related complexes;[2,9] however, for Zn^{II} all the macrocyclic donor atoms may not co-ordinate with the metal to give a tetrahedral structure of the type observed previously with the ligand L^3.[10]

Proton NMR titrations of each macrocycle with $M(O_2CMe)_2 \cdot 2H_2O$ (M = Zn^{II} or Cd^{II}) were performed in CD_3OD. The aliphatic protons in each complex generally showed significantly large shifts (Table 7) whereas the aromatic proton signals shifted only slightly. All of the spectra broadened as the metal was added and all indicated the formation of 1:1 (metal:ligand) complexes. Interestingly, for Zn^{II}, the signals for the OCH_2 protons were shifted slightly downfield for both macrocycles on complexation. This suggested that the complex geometry might be different from that in the case of Cd^{II}. The formation of 1:2 species was again confirmed and a plot of changes in chemical shift ($\Delta\delta$) against mole ratio {[$Zn(O_2CMe)_2$]/[ligand]} for L^1 with Zn^{II}, particularly for proton H^3 (Fig. 2), indicates this clearly.

The proton NMR spectrum (Table 7) of [HgL^1I_2] in $(CD_3)_2SO$ was also broadened (presumably due to chemical exchange). The pattern of peak shifts in this case is again in accordance with co-ordination of each of the nitrogen donors, but gives little evidence for co-ordination of the ether donor groups.

Thermodynamic stability constants (log *K*) were determined in 95% MeOH (25 °C, I = 0.1 NEt_4ClO_4) (Table 8) using the potentiometric (pH) titration method.[11] The stability constants for Zn^{II} were found to be similar to those recorded for the related strained N_3O_2 macrocycle, L^4 (6.0),[2] but less than for the facially N_3-bonded L^5 (7.5). This again may indicate that only the aliphatic nitrogens are bound to Zn^{II} for both and comparison of the log *K* values for the last complexes indicates a small drop in stability on passing from the complex of L^1 to that of L^2 as expected for an increase in chelate ring size from five to six.[2,12]

For Cd^{II} a substantial drop in stability was observed on increasing the ring size from 17 to 18; this suggested that a significant change in co-ordination geometry and/or number had occurred.[2] The ligand L^1 was undoubtedy fully co-ordinated to Cd^{II} in an endomacrocyclic fashion accounting for the high stability constant and other solution data, but L^2 was not. The lower stability constant suggested that some donors of the macrocycle have become non-bonded to Cd^{II}, probably the pyridine and ether oxygen donors, although the metal was still retained inside the cavity. This was supported by comparing the shifts for the ^1H NMR signals of OCH_2 on complexation: for L^2 this was less indicating a greater separation from Cd^{II}; recently a structure of this type has been solved [$CdL^6(NO_3)_2$].[2]

Comparison of the stability constants of Zn^{II} and Cd^{II} show that for L^2 the 'natural' polyamine thermodynamic stability

Table 9 Bond lengths (Å) and angles (°) for [ZnL^{1}I$_2$]·H$_2$O

Zn–I(1)	2.519(2)	Zn–I(2)	2.560(2)	C(8)–C(9)	1.400(18)	C(9)–C(10)	1.321(22)
Zn–N(2)	2.071(7)	Zn–N(3)	2.095(9)	C(10)–C(11)	1.369(16)	C(11)–C(12)	1.381(16)
O(1)–C(6)	1.425(13)	O(1)–C(7)	1.346(12)	C(12)–C(13)	1.500(12)	C(14)–C(15)	1.513(14)
O(2)–C(22)	1.367(11)	O(2)–C(23)	1.417(13)	C(16)–C(17)	1.475(17)	C(17)–C(18)	1.393(12)
N(1)–C(1)	1.322(13)	N(1)–C(5)	1.338(12)	C(17)–C(22)	1.383(15)	C(18)–C(19)	1.355(19)
N(2)–C(13)	1.493(11)	N(2)–C(14)	1.463(16)	C(19)–C(20)	1.374(18)	C(20)–C(21)	1.375(14)
N(3)–C(15)	1.467(10)	N(3)–C(16)	1.475(12)	C(21)–C(22)	1.383(19)	N(2) ··· O(3)*	3.055
C(1)–C(2)	1.407(15)	C(1)–C(23)	1.499(14)	H(N2) ··· O(3)*	2.15	O(3) ··· I(1)	3.830
C(2)–C(3)	1.396(16)	C(3)–C(4)	1.350(16)	H(O3b) ··· I(1)	3.03	O(3) ··· I(2)	3.820
C(4)–C(5)	1.373(15)	C(5)–C(6)	1.481(16)	H(O3b) ··· I(2)	3.16		
C(7)–C(8)	1.383(13)	C(7)–C(12)	1.407(15)				
I(1)–Zn–I(2)	121.1(1)	I(1)–Zn–N(2)	115.4(2)	O(1)–C(7)–C(12)	116.8(8)	C(8)–C(7)–C(12)	119.8(10)
I(2)–Zn–N(2)	114.9(2)	I(1)–Zn–N(3)	112.6(2)	C(7)–C(8)–C(9)	117.4(11)	C(8)–C(9)–C(10)	124.0(11)
I(2)–Zn–N(3)	100.0(2)	N(2)–Zn–N(3)	85.4(3)	C(9)–C(10)–C(11)	118.3(12)	C(10)–C(11)–C(12)	122.0(12)
C(6)–O(1)–C(7)	118.2(7)	C(22)–O(2)–C(23)	116.5(9)	C(7)–C(12)–C(11)	118.5(8)	C(7)–C(12)–C(13)	121.4(9)
C(1)–N(1)–C(5)	117.8(8)	Zn–N(2)–C(13)	116.0(6)	C(11)–C(12)–C(13)	120.1(10)	N(2)–C(13)–C(12)	113.1(8)
Zn–N(2)–C(14)	104.8(5)	C(13)–N(2)–C(14)	114.0(7)	N(2)–C(14)–C(15)	110.6(8)	N(3)–C(15)–C(14)	108.5(8)
Zn–N(3)–C(15)	105.4(6)	Zn–N(3)–C(16)	120.5(7)	N(3)–C(16)–C(17)	113.5(9)	C(16)–C(17)–C(18)	119.8(9)
C(15)–N(3)–C(16)	113.2(7)	N(1)–C(1)–C(2)	123.8(9)	C(16)–C(17)–C(22)	123.0(8)	C(18)–C(17)–C(22)	117.2(11)
N(1)–C(1)–C(23)	116.3(9)	C(2)–C(1)–C(23)	119.8(10)	C(17)–C(18)–C(19)	122.3(10)	C(18)–C(19)–C(20)	119.6(10)
C(1)–C(2)–C(3)	116.7(10)	C(2)–C(3)–C(4)	118.5(11)	C(19)–C(20)–C(21)	119.8(13)	C(20)–C(21)–C(22)	120.1(11)
C(3)–C(4)–C(5)	121.2(10)	N(1)–C(5)–C(4)	121.7(10)	O(2)–C(22)–C(17)	115.7(10)	O(2)–C(22)–C(21)	123.6(9)
N(1)–C(5)–C(6)	115.7(9)	C(4)–C(5)–C(6)	122.6(9)	C(17)–C(22)–C(21)	120.8(9)	O(2)–C(23)–C(1)	108.9(10)
O(1)–C(6)–C(5)	108.1(8)	O(1)–C(7)–C(8)	123.3(10)				

* Symmetry operation: $1 - x, -y, 1 - z$.

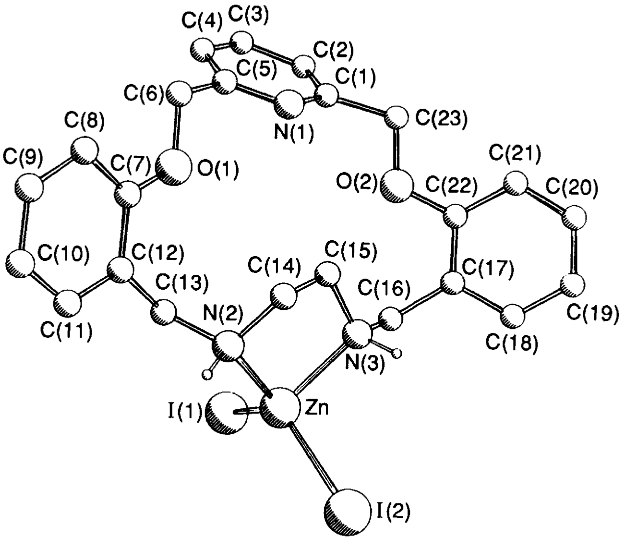


Fig. 3 The molecular structure, with atom labelling, of [ZnL^{1}I$_2$]

order[13] Zn^{II} > Cd^{II} was obeyed, whereas for L^1 this was reversed; this has been observed previously for the N$_2$O$_3$-donor set.[2] The nature of the 'dislocation' in this latter case was based on a hole size/ionic radii best fit, a mismatch occurring on moving from an 18- to a 19-membered ring system.

X-Ray Crystal Structures.—[ZnL^{1}I$_2$]·H$_2$O. The molecular structure, with atom labelling, is illustrated in Fig. 3, and bond lengths and angles with e.s.d.s are listed in Table 9. The zinc atom is co-ordinated exocyclically to the macrocycle *via* the two secondary amine nitrogen atoms: the co-ordination polyhedron of the metal is completed by the two iodine atoms. The structure strongly resembles that of the corresponding HgI$_2$ complex of the same macrocycle (see below). The zinc complex accommodates, in addition, a solvent water molecule; this is absent in the HgI$_2$ crystal structure. In both cases, the presence of the large, co-ordinating iodide favours a tetrahedral geometry at the metal; in view of the steric bulk, this can only be achieved by co-ordination outside the macrocycle cavity as has previously been observed for [ZnL^{3}I$_2$].[10]

The pyridyl and phenyl rings are each planar [root-mean-square (r.m.s.) deviations 0.014, 0.004 and 0.012 Å], and the whole macrocycle adopts a 'saddle' conformation, with the two phenyls bent 'up', and the pyridyl and zinc fragment bent 'down' from the mean macrocycle plane (the pyridyl is inclined at 64 and 64° to each of the two phenyl rings, which are mutually inclined at 64°). Consequently, both secondary amino hydrogens point 'upwards' relative to the mean macrocycle plane; the nitrogen configurations were found to be *R,S* (or *S,R*), the protons being mutually *cis*. The amino-nitrogen atom N(2) forms a hydrogen bond to a symmetry-related water molecule [N ··· O 3.055, H(N) ··· O 2.15 Å]: there is a possible further interaction involving this water molecule to the iodo ligands [O ··· I 3.83 and 3.82; H(O) ··· I 3.03 and 3.16 Å, involving the same hydrogen atom]. Comparison with other related systems showed that the Zn–N and Zn–I bond lengths were normal (2.04–2.13 and 2.53–2.56 Å respectively[10,14]).

[ZnL^1(NO$_3$)]NO$_3$. The structure of the cation is illustrated in Fig. 4: Table 10 gives bond lengths and angles with e.s.d.s. In contrast to the structure above, the zinc is co-ordinated in an endomacrocyclic fashion. The co-ordination geometry around the zinc cation is not very regular, but most closely approximates to a trigonal prism, comprising the full N$_3$O$_2$ donor set of the macrocycle and one oxygen atom of a very asymmetrically bidentate nitrato ligand; a second oxygen atom of that nitrate remotely 'caps' one of the rectangular faces of the prism. The pyridyl ring is planar (r.m.s. deviation 0.014 Å) and is inclined by 39 and 37° to the two phenyl rings (r.m.s. deviations 0.005 and 0.015 Å) which are mutually inclined at 65°. The configurations of the aliphatic nitrogens are *S,S* (or *R,R*), the protons being mutually *trans*. The three Zn–N distances are essentially identical at 2.09 Å; the two Zn–O(macrocycle) distances are much longer at 2.39 and 2.44 Å and the Zn–O(nitrate) distances are 2.11 and 2.77 Å. Two hydrogen-bonding interactions are formed between the amino-nitrogen atoms and unco-ordinated nitrate anions which serve to link molecules related by the *n*-glide plane [N ··· O 2.915 and 3.126 Å, H(N) ··· O 1.96 and 2.33 Å]. There are relatively few zinc(II) macrocyclic structures in the literature with which to make comparison, most being seven-[15] not six-co-ordinate.[16–18]

[CdL^1(NO$_3$)(MeOH)]NO$_3$. The structure of the cation is illustrated in Fig. 5; Table 11 gives bond lengths and angles with

Table 10 Bond lengths (Å) and angles (°) for $[ZnL^1(NO_3)]NO_3$

Zn–O(1)	2.436(14)	Zn–O(2)	2.387(14)	C(1)–C(23)	1.471(18)	C(2)–C(3)	1.380(23)
Zn–O(5)	2.109(14)	Zn ··· O(4)	2.771(15)	C(3)–C(4)	1.349(21)	C(4)–C(5)	1.397(19)
Zn–N(1)	2.091(13)	Zn–N(2)	2.093(13)	C(5)–C(6)	1.463(18)	C(7)–C(8)	1.375(19)
Zn–N(3)	2.091(13)	O(1)–C(6)	1.407(16)	C(7)–C(12)	1.363(17)	C(8)–C(9)	1.345(21)
O(1)–C(7)	1.366(16)	O(2)–C(22)	1.383(15)	C(9)–C(10)	1.350(22)	C(10)–C(11)	1.357(23)
O(2)–C(23)	1.428(14)	O(3)–N(4)	1.195(15)	C(11)–C(12)	1.392(19)	C(12)–C(13)	1.498(19)
O(4)–N(4)	1.238(15)	O(5)–N(4)	1.245(14)	C(14)–C(15)	1.480(18)	C(16)–C(17)	1.487(18)
O(6)–N(5)	1.199(18)	O(7)–N(5)	1.158(20)	C(17)–C(18)	1.382(18)	C(19)–C(20)	1.367(21)
O(8)–N(5)	1.158(23)	N(1)–C(1)	1.350(15)	C(20)–C(21)	1.378(20)	C(21)–C(22)	1.394(18)
N(1)–C(5)	1.329(16)	N(2)–C(13)	1.489(16)	N(2) ··· O(6)	2.915	H(N2) ··· O(6)	1.96
N(2)–C(14)	1.488(16)	N(3)–C(15)	1.466(16)	N(3) ··· O(7)*	3.126	H(N3) ··· O(7)*	2.33
N(3)–C(16)	1.485(16)	C(1)–C(2)	1.361(17)				
O(1)–Zn–O(2)	136.8(4)	O(1)–Zn–O(5)	74.7(4)	O(7)–N(5)–O(8)	120.3(15)	N(1)–C(1)–C(2)	123.4(11)
O(2)–Zn–O(5)	132.9(4)	O(1)–Zn–N(1)	68.7(4)	N(1)–C(1)–C(23)	117.3(9)	C(2)–C(1)–C(23)	119.3(11)
O(2)–Zn–N(1)	72.8(4)	O(5)–Zn–N(1)	101.6(4)	C(1)–C(2)–C(3)	118.3(12)	C(2)–C(3)–C(4)	118.8(12)
O(1)–Zn–N(2)	78.6(4)	O(2)–Zn–N(2)	104.2(4)	C(3)–C(4)–C(5)	120.7(13)	N(1)–C(5)–C(4)	120.5(11)
O(5)–Zn–N(2)	118.3(4)	N(1)–Zn–N(2)	118.4(4)	N(1)–C(5)–C(6)	117.8(10)	N(4)–C(5)–C(6)	121.7(11)
O(1)–Zn–N(3)	142.8(4)	O(2)–Zn–N(3)	78.7(4)	O(1)–C(6)–C(5)	105.0(10)	O(1)–C(7)–C(8)	124.1(11)
O(5)–Zn–N(3)	87.3(4)	N(1)–Zn–N(3)	148.0(4)	O(1)–C(7)–C(12)	114.3(10)	C(8)–C(7)–C(12)	121.5(11)
N(2)–Zn–N(3)	82.1(4)	Zn–O(1)–C(6)	103.5(7)	C(7)–C(8)–C(9)	117.3(12)	C(8)–C(9)–C(10)	123.1(14)
Zn–O(1)–C(7)	115.5(7)	C(6)–O(1)–C(7)	121.6(9)	C(9)–C(10)–C(11)	119.8(15)	C(10)–C(11)–C(12)	119.1(13)
Zn–O(2)–C(22)	129.9(7)	Zn–O(2)–C(23)	110.9(7)	C(7)–C(12)–C(11)	119.1(12)	C(7)–C(12)–C(13)	118.5(10)
C(22)–O(2)–C(23)	116.6(9)	Zn–O(5)–N(4)	115.1(8)	N(2)–C(13)–C(12)	113.8(9)	C(11)–C(12)–C(13)	122.2(11)
Zn–N(1)–C(1)	122.6(7)	Zn–N(1)–C(5)	119.3(8)	N(2)–C(14)–C(15)	106.5(9)	N(3)–C(15)–C(14)	110.6(10)
C(1)–N(1)–C(5)	118.1(9)	Zn–N(2)–C(13)	121.8(8)	N(3)–C(16)–C(17)	114.1(9)	C(16)–C(17)–C(18)	121.3(12)
Zn–N(2)–C(14)	107.6(7)	C(13)–N(2)–C(14)	110.4(9)	C(16)–C(17)–C(22)	121.9(10)	C(18)–C(17)–C(22)	116.7(11)
Zn–N(3)–C(15)	108.2(7)	Zn–N(3)–C(16)	119.1(7)	C(17)–C(18)–C(19)	122.1(13)	C(18)–C(19)–C(20)	118.2(13)
C(15)–N(3)–C(16)	113.2(9)	O(3)–N(4)–O(4)	123.2(11)	C(19)–C(20)–C(21)	123.8(13)	C(20)–C(21)–C(22)	115.2(11)
O(3)–N(4)–O(5)	123.5(11)	O(4)–N(4)–O(5)	112.9(10)	O(2)–C(22)–C(17)	115.5(10)	O(2)–C(22)–C(21)	120.7(10)
O(6)–N(5)–O(7)	126.1(14)	O(6)–N(5)–O(8)	111.2(16)	C(17)–C(22)–C(21)	123.8(11)	O(2)–C(23)–C(1)	111.9(9)

* Symmetry operation: 0.5 − *x*, −0.5 + *y*, −0.5 + *z*.

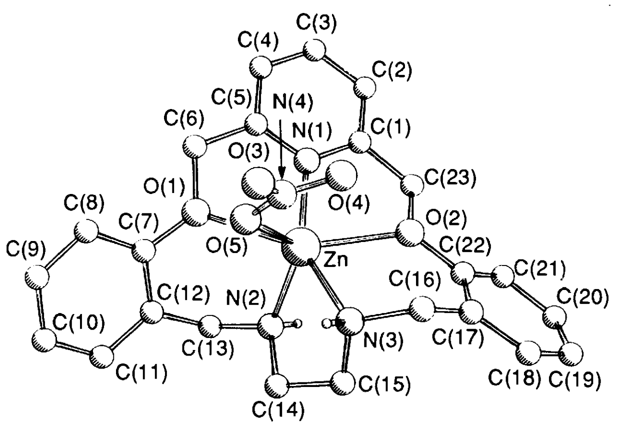


Fig. 4 The molecular structure, with atom labelling, of the cation $[ZnL^1(NO_3)]^+$

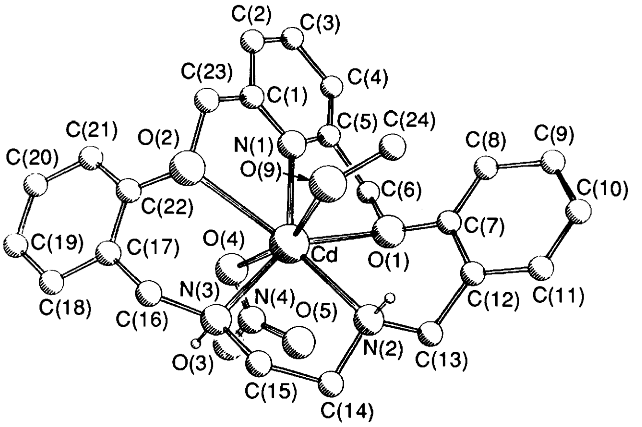


Fig. 5 The molecular structure, with atom labelling, of the cation $[CdL^1(NO_3)(MeOH)]^+$

e.s.d.s. The co-ordination geometry around the cadmium cation is approximately pentagonal bipyramidal, with the full N_3O_2 donor set of the macrocycle occupying the equatorial plane, which is puckered [deviations of the N_3O_2 donor set from their mean plane O(1) −0.33, O(2) +0.32, N(1) −0.00, N(2) +0.57, N(3) −0.56 Å; deviation of cadmium atom −0.17 Å]. The axial sites are occupied by a methanol of solvation and by an asymmetrically dihapto nitrate anion. This distorted pentagonal-bipyramidal geometry has been observed previously for other endomacrocyclic[2,19–21] and acyclic[9] cadmium complexes.

The pyridyl ring is planar (r.m.s. deviation 0.017 Å) and is inclined at 73 and 72° to the two phenyl rings (r.m.s. deviations 0.018 and 0.013 Å) which are themselves almost parallel at 3°: these three rings are inclined to the mean plane through the donor set of the macrocycle at 20, 53 and 52°. The three Cd–N distances are very similar (2.28–2.34 Å); the two Cd–O(macrocycle) distances are much longer at 2.51 and 2.61 Å. The Cd–O(methanol) distance is shorter at 2.44 Å, as is the shorter of the Cd–O(nitrate) distances at 2.45 Å; the longer contact is 2.86 Å. Two hydrogen-bonding interactions are formed, one between the amino-nitrogen atom N(3) and an unco-ordinated nitrate anion [N ··· O 2.954, H(N) ··· O 2.24 Å], the other linking screw-axis related molecules between the co-ordinated methanolic oxygen and the most remote of the oxygen atoms of the co-ordinated nitrato ligand [O ··· O 2.793, H(O) ··· O 1.83 Å]. The aliphatic nitrogen configurations are *R,R* (or *S,S*), the protons being mutually *trans*.

$[CdL^2(ClO_4)(MeCN)]ClO_4$. The structure of the cation is illustrated in Fig. 6; Table 12 gives bond lengths and angles with e.s.d.s. The co-ordination geometry around the cadmium cation is approximately pentagonal bipyramidal, with the full N_3O_2 donor set of the macrocycle occupying the equatorial plane, which is puckered [deviations of the N_3O_2 donor set from their mean plane O(1) +0.41, O(2) −0.32, N(1) −0.04, N(2) −0.63,

Table 11 Bond lengths (Å) and angles (°) for $[CdL^1(NO_3)(MeOH)]NO_3$

Cd–O(1)	2.513(17)	Cd–O(2)	2.610(17)	C(1)–C(23)	1.556(27)	C(2)–C(3)	1.420(29)
Cd–O(4)	2.447(19)	Cd ··· O(5)	2.860(20)	C(3)–C(4)	1.385(25)	C(4)–C(5)	1.335(25)
Cd–O(9)	2.440(18)	Cd–N(1)	2.283(17)	C(5)–C(6)	1.558(25)	C(7)–C(8)	1.377(23)
Cd–N(2)	2.335(18)	Cd–N(3)	2.292(18)	C(7)–C(12)	1.410(25)	C(8)–C(9)	1.437(27)
O(1)–C(6)	1.437(23)	O(1)–C(7)	1.354(21)	C(9)–C(10)	1.357(29)	C(10)–C(11)	1.356(30)
O(2)–C(22)	1.357(21)	O(2)–C(23)	1.414(21)	C(11)–C(12)	1.425(29)	C(12)–C(13)	1.476(25)
O(3)–N(4)	1.216(21)	O(4)–N(4)	1.240(21)	C(14)–C(15)	1.580(26)	C(16)–C(17)	1.498(26)
O(5)–N(4)	1.227(23)	O(6)–N(5)	1.224(27)	C(17)–C(18)	1.391(26)	C(17)–C(22)	1.366(24)
O(7)–N(5)	1.238(29)	O(8)–N(5)	1.236(31)	C(18)–C(19)	1.403(27)	C(19)–C(20)	1.354(33)
O(9)–C(24)	1.384(29)	N(1)–C(1)	1.318(20)	C(20)–C(21)	1.364(31)	C(21)–C(22)	1.383(24)
N(1)–C(5)	1.318(23)	N(2)–C(13)	1.513(23)	N(3) ··· O(6)[a]	2.954	H(N3) ··· O(6)[a]	2.24
N(2)–C(14)	1.449(23)	N(3)–C(15)	1.444(24)	O(9) ··· O(3)[b]	2.793	H(O9) ··· O(3)[b]	1.83
N(3)–C(16)	1.506(23)	C(1)–C(2)	1.352(24)				
O(1)–Cd–O(2)	138.0(5)	O(1)–Cd–O(4)	88.7(5)	O(3)–N(4)–O(4)	121.7(15)	O(3)–N(4)–O(5)	119.8(16)
O(2)–Cd–O(4)	90.3(5)	O(1)–Cd–O(9)	99.9(5)	O(4)–N(4)–O(5)	118.5(15)	O(6)–N(5)–O(7)	115.6(22)
O(2)–Cd–O(9)	72.7(5)	O(4)–Cd–O(9)	162.0(6)	O(6)–N(5)–O(8)	125.6(21)	O(7)–N(5)–O(8)	118.8(21)
O(1)–Cd–N(1)	69.9(5)	O(2)–Cd–N(1)	68.3(5)	N(1)–C(1)–C(2)	124.2(16)	N(1)–C(1)–C(23)	117.8(14)
O(4)–Cd–N(1)	82.4(6)	O(9)–Cd–N(1)	85.7(5)	C(2)–C(1)–C(23)	117.3(14)	C(1)–C(2)–C(3)	118.0(15)
O(1)–Cd–N(2)	75.5(5)	O(2)–Cd–N(2)	137.2(5)	C(2)–C(3)–C(4)	117.5(17)	C(3)–C(4)–C(5)	117.1(17)
O(4)–Cd–N(2)	121.7(6)	O(9)–Cd–N(2)	76.0(5)	O(1)–C(7)–C(8)	125.6(15)	O(1)–C(7)–C(12)	114.2(14)
N(1)–Cd–N(2)	137.2(6)	O(1)–Cd–N(3)	145.6(5)	C(8)–C(7)–C(12)	120.0(16)	C(7)–C(8)–C(9)	120.5(16)
O(2)–Cd–N(3)	76.0(5)	O(4)–Cd–N(3)	85.2(6)	C(8)–C(9)–C(10)	118.3(18)	C(9)–C(10)–C(11)	122.2(20)
O(9)–Cd–N(3)	96.1(6)	N(1)–Cd–N(3)	142.0(6)	C(10)–C(11)–C(12)	120.9(18)	C(7)–C(12)–C(11)	117.8(16)
N(2)–Cd–N(3)	79.2(6)	Cd–O(1)–C(6)	105.4(10)	C(7)–C(12)–C(13)	119.2(16)	C(11)–C(12)–C(13)	123.0(17)
Cd–O(1)–C(7)	119.6(10)	C(6)–O(1)–C(7)	118.6(14)	N(2)–C(13)–C(12)	110.5(13)	N(2)–C(14)–C(15)	107.0(13)
Cd–O(2)–C(22)	112.3(9)	Cd–O(2)–C(23)	108.6(10)	C(16)–C(17)–C(18)	119.4(15)	C(16)–C(17)–C(22)	121.1(16)
C(22)–O(2)–C(23)	120.3(13)	Cd–O(4)–N(4)	107.2(11)	C(18)–C(17)–C(22)	119.5(16)	C(17)–C(18)–C(19)	119.5(17)
Cd–O(9)–C(24)	129.6(14)	Cd–N(1)–C(1)	122.9(11)	C(18)–C(19)–C(20)	119.9(20)	C(19)–C(20)–C(21)	120.2(19)
Cd–N(1)–C(5)	121.2(10)	C(1)–N(1)–C(5)	115.7(14)	C(20)–C(21)–C(22)	120.9(17)	O(2)–C(22)–C(17)	113.7(14)
Cd–N(2)–C(13)	118.1(11)	Cd–N(2)–C(14)	106.2(11)	O(2)–C(22)–C(21)	126.4(15)	C(17)–C(22)–C(21)	119.9(16)
C(13)–N(2)–C(14)	110.7(12)	Cd–N(3)–C(15)	105.0(11)	O(2)–C(23)–C(1)	110.0(14)		
Cd–N(3)–C(16)	119.1(10)	C(15)–N(3)–C(16)	112.8(14)				

[a] Symmetry operation: $-0.5 + x, 0.5 - y, 0.5 + z$. [b] Symmetry operation: $-0.5 - x, -0.5 + y, 0.5 - z$.

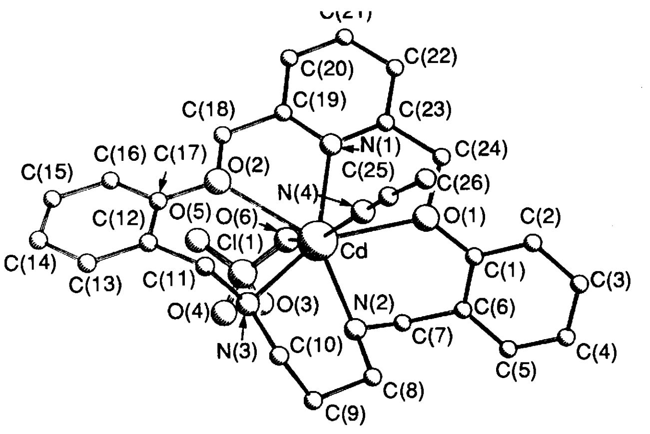


Fig. 6 The molecular structure, with atom labelling, of the cation $[CdL^2(ClO_4)(MeCN)]^+$

N(3) +0.58 Å; deviation of cadmium atom +0.11 Å]. The axial sites are occupied by an acetonitrile of solvation and by a monohapto perchlorate anion. The pyridyl ring is planar (r.m.s. deviation 0.004 Å) and is inclined at 45 and 29° to the two phenyl rings which are mutually inclined at 72°. The three Cd–N distances are very similar (2.31–2.34 Å) with the Cd–N-(acetonitrile) distance longer at 2.43 Å. The two Cd–O-(macrocycle) distances are much longer at 2.57 and 2.60 Å with the Cd–O(perchlorate) longest at 2.62 Å. The six-membered chelate ring involving the cadmium and amino-nitrogen atoms adopts a chair conformation, and both amino-hydrogen atoms are directed towards an oxygen atom [O(4)] of the co-ordinated perchlorate ligand and seem to each engage in weak (bifurcated) hydrogen-bond formation to that oxygen, thereby stabilising the co-ordination of the perchlorate. One of the amines perhaps interacts, even more remotely, with the same oxygen atom in an inversion symmetry-related perchlorate: in order to maintain separation of the two perchlorates, the hydrogen bonds are necessarily not very linear. There is no further capacity for hydrogen bonding. The amine protons are mutually *cis* and the nitrogen atoms have an *R,S* configuration; this is in contrast to that found for $[CdL^1(NO_3)(MeOH)]NO_3$.

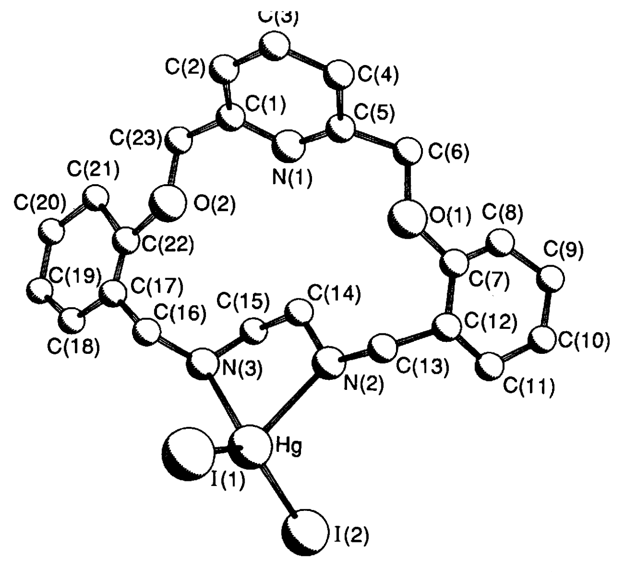


Fig. 7 The molecular structure, with atom labelling, of $[HgL^1I_2]$

The bond lengths are very similar to those in $[CdL^1(NO_3)(MeOH)]NO_3$ and the geometries of these two related systems are similar. A least-squares plane through O(1)–N(1)–O(2) showed that this meridional fragment defined a plane with the Cd^{II} sitting slightly above this. However the remaining nitrogens were markedly displaced from this plane with

Table 12 Bond lengths (Å) and angles (°) for $[CdL^2(ClO_4)(MeCN)]ClO_4$

Cd–O(1)	2.568(7)	Cd–O(2)	2.599(7)	C(18)–C(19)	1.510(12)	C(19)–C(20)	1.405(9)
Cd–N(1)	2.318(6)	Cd–N(2)	2.312(6)	C(20)–C(21)	1.370(14)	C(21)–C(22)	1.412(13)
Cd–N(3)	2.335(7)	Cd–N(4)	2.427(7)	C(22)–C(23)	1.387(8)	C(23)–C(24)	1.524(12)
Cd–O(6)	2.615(5)	O(1)–C(1)	1.397(7)	C(25)–C(26)	1.479(11)	C–C(phenyl)	1.395
O(1)–C(24)	1.433(8)	O(2)–C(17)	1.402(10)	Cl(1)–O(3)	1.432(3)	Cl(1)–O(4)	1.433(3)
O(2)–C(18)	1.436(7)	N(1)–C(19)	1.356(10)	Cl(1)–O(5)	1.431(3)	Cl(1)–O(6)	1.432(4)
N(1)–C(23)	1.355(10)	N(2)–C(7)	1.502(9)	Cl(2)–O(7)	1.431(3)	Cl(2)–O(8)	1.431(4)
N(2)–C(8)	1.505(8)	N(3)–C(10)	1.445(10)	Cl(2)–O(9)	1.432(3)	Cl(2)–O(10)	1.432(3)
N(3)–C(11)	1.509(10)	N(4)–C(25)	1.131(10)	N(2) ··· O(4)	3.280	H(N2) ··· O(4)	2.48
C(6)–C(7)	1.516(10)	C(8)–C(9)	1.533(11)	N(3) ··· O(4)	3.196	H(N3) ··· O(4)	2.44
C(9)–C(10)	1.516(11)	C(11)–C(12)	1.525(11)	N(3) ··· O(4)*	3.291	H(N3) ··· O(4)*	2.55
O(1)–Cd–O(2)	135.6(2)	O(1)–Cd–N(1)	67.8(2)	O(1)–C(1)–C(6)	116.6(3)	C(1)–C(6)–C(7)	119.6(3)
O(2)–Cd–N(1)	67.9(2)	O(1)–Cd–N(2)	75.7(2)	C(5)–C(6)–C(7)	120.4(3)	N(2)–C(7)–C(6)	114.5(5)
O(2)–Cd–N(2)	140.8(2)	N(1)–Cd–N(2)	134.3(2)	N(2)–C(8)–C(9)	111.5(6)	C(8)–C(9)–C(10)	116.6(6)
O(1)–Cd–N(3)	146.4(2)	O(2)–Cd–N(3)	75.6(2)	N(3)–C(10)–C(9)	116.7(5)	N(3)–C(11)–C(12)	111.9(5)
N(1)–Cd–N(3)	140.7(2)	N(2)–Cd–N(3)	83.9(2)	C(11)–C(12)–C(13)	118.6(4)	C(11)–C(12)–C(17)	121.4(4)
O(1)–Cd–N(4)	77.4(2)	O(2)–Cd–N(4)	99.8(2)	O(2)–C(17)–C(12)	116.6(3)	O(2)–C(17)–C(16)	123.4(3)
N(1)–Cd–N(4)	86.4(2)	N(2)–Cd–N(4)	111.8(2)	O(2)–C(18)–C(19)	110.1(6)	N(1)–C(19)–C(18)	121.0(5)
N(3)–Cd–N(4)	86.1(2)	O(1)–Cd–O(6)	93.3(1)	N(1)–C(19)–C(20)	122.2(8)	C(18)–C(19)–C(20)	116.8(7)
O(2)–Cd–O(6)	77.0(2)	N(1)–Cd–O(6)	77.2(2)	C(19)–C(20)–C(21)	118.8(8)	C(20)–C(21)–C(22)	119.4(6)
N(2)–Cd–O(6)	78.6(2)	N(3)–Cd–O(6)	108.6(2)	C(21)–C(22)–C(23)	119.0(7)	N(1)–C(23)–C(22)	121.8(7)
N(4)–Cd–O(6)	163.3(2)	Cd–O(1)–C(1)	127.1(3)	N(1)–C(23)–C(24)	119.3(5)	C(22)–C(23)–C(24)	118.9(7)
Cd–O(1)–C(24)	110.6(5)	C(1)–O(1)–C(24)	116.6(6)	O(1)–C(24)–C(23)	108.2(7)	N(4)–C(25)–C(26)	179.6(8)
Cd–O(2)–C(17)	128.5(3)	Cd–O(2)–C(18)	110.5(4)	C–C–C(phenyl)	120.0	Cd–O(6)–Cl(1)	120.3(2)
C(17)–O(2)–C(18)	115.6(5)	Cd–N(1)–C(19)	120.4(5)	O(3)–Cl(1)–O(4)	109.3(2)	O(3)–Cl(1)–O(5)	109.7(2)
Cd–N(1)–C(23)	120.7(4)	C(19)–N(1)–C(23)	118.8(5)	O(4)–Cl(1)–O(5)	109.6(2)	O(3)–Cl(1)–O(6)	109.3(2)
Cd–N(2)–C(7)	116.5(3)	Cd–N(2)–C(8)	115.4(4)	O(4)–Cl(1)–O(6)	109.5(2)	O(5)–Cl(1)–O(6)	109.5(2)
C(7)–N(2)–C(8)	110.9(5)	Cd–N(3)–C(10)	112.6(5)	O(7)–Cl(2)–O(8)	109.5(2)	O(7)–Cl(2)–O(9)	109.5(3)
Cd–N(3)–C(11)	112.0(4)	C(10)–N(3)–C(11)	111.1(5)	O(8)–Cl(2)–O(9)	109.5(2)	O(7)–Cl(2)–O(10)	109.5(2)
Cd–N(4)–C(25)	175.4(7)	O(1)–C(1)–C(2)	123.3(3)	O(8)–Cl(2)–O(10)	109.5(2)	O(9)–Cl(2)–O(10)	109.3(2)

* Symmetry operation: $-x$, $-y$, $1 - z$.

Table 13 Bond lengths (Å) and angles (°) for $[HgL^1I_2]$

Hg–I(1)	2.673(7)	Hg–I(2)	2.707(7)	C(4)–C(5)	1.414(39)	C(5)–C(6)	1.495(37)
Hg–N(2)	2.464(19)	Hg–N(3)	2.384(22)	C(7)–C(8)	1.384(30)	C(7)–C(12)	1.381(37)
O(1)–C(6)	1.487(36)	O(1)–C(7)	1.358(30)	C(8)–C(9)	1.413(38)	C(9)–C(10)	1.361(45)
O(2)–C(22)	1.411(26)	O(2)–C(23)	1.499(31)	C(10)–C(11)	1.458(39)	C(11)–C(12)	1.415(40)
N(1)–C(1)	1.333(27)	N(1)–C(5)	1.361(33)	C(12)–C(13)	1.524(33)	C(14)–C(15)	1.524(34)
N(2)–C(13)	1.529(32)	N(2)–C(14)	1.367(33)	C(16)–C(17)	1.514(34)	C(17)–C(18)	1.402(33)
N(3)–C(15)	1.483(28)	N(3)–C(16)	1.497(28)	C(17)–C(22)	1.418(32)	C(18)–C(19)	1.380(43)
C(1)–C(2)	1.368(33)	C(1)–C(23)	1.539(33)	C(19)–C(20)	1.332(41)	C(20)–C(21)	1.426(33)
C(2)–C(3)	1.335(42)	C(3)–C(4)	1.355(42)	C(21)–C(22)	1.363(34)		
I(1)–Hg–I(2)	133.6(2)	I(1)–Hg–N(2)	117.3(4)	O(1)–C(6)–C(5)	107.1(21)	O(1)–C(7)–C(8)	122.7(22)
I(2)–Hg–N(2)	95.8(5)	I(1)–Hg–N(3)	110.3(4)	O(1)–C(7)–C(12)	113.1(19)	C(8)–C(7)–C(12)	124.1(22)
I(2)–Hg–N(3)	109.7(5)	N(2)–Hg–N(3)	73.4(7)	C(7)–C(8)–C(9)	118.7(23)	C(8)–C(9)–C(10)	120.2(25)
C(6)–O(1)–C(7)	117.0(18)	C(22)–O(2)–C(23)	116.3(17)	C(9)–C(10)–C(11)	120.2(27)	C(10)–C(11)–C(12)	119.4(28)
C(1)–N(1)–C(5)	116.3(20)	Hg–N(2)–C(13)	115.7(14)	C(7)–C(12)–C(11)	117.2(22)	C(7)–C(12)–C(13)	124.5(23)
Hg–N(2)–C(14)	108.3(13)	C(13)–N(2)–C(14)	116.6(19)	C(11)–C(12)–C(13)	118.1(24)	N(2)–C(13)–C(12)	111.5(20)
Hg–N(3)–C(15)	108.3(14)	Hg–N(3)–C(16)	115.5(13)	N(2)–C(14)–C(15)	111.8(20)	N(3)–C(15)–C(14)	110.4(19)
C(15)–N(3)–C(16)	113.8(18)	N(1)–C(1)–C(2)	124.3(21)	N(3)–C(16)–C(17)	115.8(18)	C(16)–C(17)–C(18)	119.9(21)
N(1)–C(1)–C(23)	114.2(19)	C(2)–C(1)–C(23)	121.5(20)	C(16)–C(17)–C(22)	123.2(20)	C(18)–C(17)–C(22)	119.2(23)
C(1)–C(2)–C(3)	119.0(25)	C(2)–C(3)–C(4)	120.2(30)	O(2)–C(22)–C(17)	114.4(19)	O(2)–C(22)–C(21)	123.8(20)
C(3)–C(4)–C(5)	118.8(27)	N(1)–C(5)–C(4)	121.0(23)	C(17)–C(22)–C(21)	121.6(20)	O(2)–C(23)–C(1)	104.9(20)
N(1)–C(5)–C(6)	114.6(23)	C(4)–C(5)–C(6)	124.3(24)				

$[CdL^2(ClO_4)(MeCN)]ClO_4$ being less symmetrical than $[CdL^1(NO_3)(MeOH)]NO_3$. This may indicate the 'goodness of fit' of Cd^{II} into each macrocyclic cavity and is reflected in the stability constants for these systems. The gross conformations of the two complexes are different with $[CdL^1(NO_3)(MeOH)]^+$ having a 'stepped' shape, the two benzene rings being tilted to either side of the O(1)–N(1)–O(2) plane defining angles of 61 and 60°. The ion $[CdL^2(ClO_4)(MeCN)]^+$ has a 'crossed' shape, the benzene rings crossing the O(1)–N(1)–O(2) plane defining angles of 46 and 36°.

$[HgL^1I_2]$. The molecular structure, with atom labelling, is illustrated in Fig. 7; bond lengths and angles with e.s.d.s are listed in Table 13. The mercury atom is co-ordinated exocyclically to the macrocycle *via* the two secondary amine nitrogen atoms: the co-ordination polyhedron of the metal is completed by the two iodine atoms. The structure strongly resembles the corresponding ZnI_2 complex of the same macrocycle. Indeed, the general arrangement of the two molecules within the monoclinic unit cell (with 'the same' space group $P2_1/c$ or $P2_1/n$) is very similar, but the zinc complex accommodates, in addition, a solvent water molecule which is absent in the HgI_2 crystal structure. In both cases, the presence of the large, co-ordinating iodine favours a tetrahedral geometry at the metal; in view of the steric bulk, this can only be achieved by co-ordination outside the macrocycle cavity. The exomacrocyclic binding mode has been observed previously for other mercury(II) macrocyclic systems.[22–24]

The pyridyl and phenyl rings are each planar (r.m.s. deviations 0.025, 0.019 and 0.014 Å), and the whole macrocycle adopts a 'saddle' conformation, with the two phenyls bent 'down' and the pyridyl and mercury fragment bent 'up' from the mean macrocycle plane. Consequently, both secondary amino hydrogens point 'downwards' relative to the mean macrocycle plane. The nitrogen configurations are *R,S* with the two protons being mutually *cis*; this is emerging as a common feature of exomacrocyclic co-ordination. Neither of the two hydrogens is involved in hydrogen bonding.

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