Heavy-metal Macrocyclic Complexes: Crystal and Molecular Structures of Complexes of 1,5,9,13-Tetra-azacyclohexadecane with $Cd(NO_3)_2$, $HgCl_2$, $PbCl_2$, and $Pb(NO_3)_2$ †

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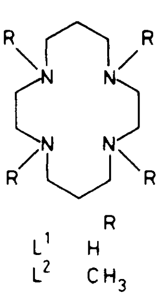
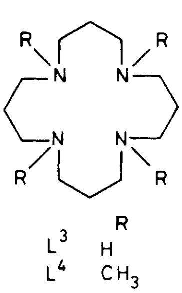
Heavy-metal complexes of the sixteen-membered macrocycle, 1,5,9,13-tetra-azacyclohexadecane (L^3), of formulae $[Cd(L^3)(NO_3)(H_2O)]NO_3{\cdot}H_2O$, $[Hg(L^3)Cl]_2[HgCl_4]$, $[Pb(L^3)Cl]Cl$, and $[Pb(L^3)][NO_3]_2$ have been prepared. Their structures were examined by ^{13}C and ^{15}N n.m.r. spectroscopy, and determined by *X*-ray crystallography which reveals a macrocycle cavity size which is most suitable for Hg^{2+} co-ordination. In each compound all four macrocyclic N–H groups point to the same side of the macrocyclic plane. The other ligands occupy *trans* positions for Cd^{2+} (NO_3^- and H_2O) and Hg^{2+} (Cl^-), but are in *cis* positions for the larger Pb^{2+}. In $[Pb(L^3)Cl]^+$ the chloride ligand and the lone pair occupy adjacent positions on one side of the Pb^{2+} ion. With $[Pb(L^3)][NO_3]_2$ the five independent molecules include one with two symmetrically bidentate NO_3^- groups, two with one bidentate and one unidentate, and two Pb atoms linked by two NO_3^- groups. Bond distance averages are Cd–N 2.334(6), Hg–N 2.38(3), Pb–N 2.54(1), Cd–O 2.413(8)—2.832(8), Hg–Cl 2.64(2)—2.83(2), Pb–Cl 2.98(1), and Pb–O 2.74(3)—3.17(4) Å.

We have previously reported the complexes formed by the 14-membered tetra-aza macrocyclic ligands (L^1) and (L^2) with Zn^{II},[1] Cd^{II}, and Hg^{II},[2] and with Pb^{II}.[3] Crystal structures were determined for $[Zn(L^2)Cl]ClO_4$, $[Hg(L^1)Cl]_2[HgCl_4]$, and *cis*-$[Pb(L^1)(NO_3)_2]$, and several other species were detected in solution by ^{13}C and ^{15}N n.m.r. spectroscopy. More recently we have prepared the 16-membered tetra-aza macrocycle (L^4) and studied complexes formed with Cd^{II}, Hg^{II}, and Pb^{II}, including a crystal structure of $[Cd(L^4)(NO_3)]_2[Cd(NO_3)_4]$.[4] The complexes of L^3 with $Cd(NO_3)_2$, $HgCl_2$, $PbCl_2$, and $Pb(NO_3)_2$ have now been prepared, and their structures determined by *X*-ray crystallography. We have established the conformations adopted by the macrocycle, and the effect of changing the ionic radius of the metal ion on the geometry of the complexes formed. We were particularly interested in establishing the ideal macrocycle cavity size for these toxic heavy-metal ions.





Experimental

Materials and Methods.—Ligand L^3 was prepared as described in the literature[5] and its purity confirmed by ^1H and ^{13}C n.m.r. spectroscopy. N.m.r. spectra were recorded with either a Bruker WH 90 or WH 400 spectrometer and deuteriated solvents (99% ^2H) were used for field-frequency locking; ^{13}C n.m.r. spectra were assigned with either *ca.* 5% dioxane as internal standard (δ 67.4) or from the solvent resonance as an intermediate reference, ^{15}N n.m.r. spectra with external nitromethane as a shift reference (δ 0). *X*-Ray crystallographic data were collected with a Syntex $P2_1$ four-circle diffractometer.

Synthesis of Complexes of L^3.—$[Cd(L^3)(NO_3)(H_2O)]NO_3{\cdot}H_2O$ (1). A solution of L^3 (0.46 g, 2.0 mmol) in methanol was added to a stirred solution of $Cd(NO_3)_2{\cdot}4H_2O$ (0.62 g, 2.0 mmol) in methanol with gentle heating. After *ca.* 20 min the solution turned pale yellow and on evaporation yielded a mass of yellow crystals. The solid was recrystallised from hot methanol–diethyl ether solution to give long needle crystals of $[Cd(L^3)(NO_3)(H_2O)]NO_3{\cdot}H_2O$ (0.7 g, 1.4 mmol) in 70% yield.

$[Hg(L^3)Cl]_2[HgCl_4]$ (2). This complex was prepared by mixing equimolar amounts of L^3 and $HgCl_2$ in methanol. A white precipitate immediately forms but redissolves on continued stirring to give a clear solution. The solvent was evaporated to give $[Hg(L^3)Cl]_2[HgCl_4]$ (0.89 g, 0.7 mmol) in 52% yield.

$[Pb(L^3)Cl]Cl$ (3). This complex was prepared by mixing equimolar amounts of $PbCl_2$ and L^3 in $[^2H_6]$dimethyl sulphoxide–$[^2H_4]$methanol (1 : 1) and was not isolated. The crystal for the *X*-ray diffraction study was obtained by very slow evaporation of the solvent.

$[Pb(L^3)][NO_3]_2$ (4). This complex was prepared by mixing $Pb(NO_3)_2$ (0.67 g, 2.0 mmol) with L^3 (0.57 g, 2.5 mmol) in dry methanol. Evaporation of the solvent left a white crystalline mass which was recrystallised as described for the cadmium complex to give $[Pb(L^3)][NO_3]_2$ (0.42 g, 0.7 mmol) in 37.5% yield.

Crystal Structure Analysis.—The crystal data and collection procedure are given in Table 1. Complexes (3) and (4) underwent decomposition at room temperature in the *X*-ray beam, and data were taken at −80 °C with the Syntex LT-1 attachment. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. Observed reflections $[I/\sigma(I) > 3.0]$ were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR.[6] In general, the heavy atoms were located by Patterson techniques and the light atoms then

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† *Supplementary data available* (No. SUP 56046, 7 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Crystal data [a]

Compound	$[Cd(L^3)(NO_3)(H_2O)]NO_3{\cdot}H_2O$	$[Hg(L^3)Cl]_2[HgCl_4]$	$[Pb(L^3)Cl]Cl$	$[Pb(L^3)][NO_3]_2$
Formula	$C_{12}H_{32}CdN_6O_8$ (1)	$C_{24}H_{56}Cl_6Hg_3N_4$ (2)	$C_{12}H_{28}Cl_2N_4Pb$ (3)	$C_{12}H_{28}N_6O_6Pb$ (4)
M	500.4	1 270.7	506.3	559.2
System	Monoclinic	Tetragonal	Orthorhombic	Triclinic
Absences	$h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$	$hk0$, $h + k \neq 2n$	hkl, h, k, l all even or all odd; $hk0$, $h + k = 4n$; $h0l$, $h + l = 4n$; $0kl$, $k + l = 4n$	—
Space group	$P2_1/c$	$P4/nmm$ [b]	$Fddd$ [b]	$P1$
a/Å	8.159(1)	13.426 5(14)	13.897(2)	8.139(2)
b/Å	15.092(3)	13.4265	18.631(3)	14.077(4)
c/Å	17.153(2)	10.973(3)	27.663(5)	20.729(5)
α/°	90	90	90	92.13(2)
β/°	96.97(1)	90	90	87.71(2)
γ/°	90	90	90	100.01(2)
U/Å^3	2 096.7(6)	1 978.1(7)	7 162.4	2 336(1)
Z	4	2	16	5
μ/cm^{-1}	10.8	120.4	97.9	91.3
D_c/g cm^{-3}	1.58	2.13	1.88	1.98
D_m/g cm^{-3}	—	2.11	—	—
Scan range (about $\alpha_1 - \alpha_2$ positions)	±0.75	±1.0	±1.0	±1.0
Reflections [$I \geqslant 3\sigma(I)$]	2 935	1 046	1 442	5 679
θ_c/°C	16	16	−80	−80
Transmission factor range	0.82—0.92	0.23—0.52	0.25—0.43	0.22—0.36
R(final)	0.033	0.040	0.044	0.068

[a] Details common to all compounds: radiation, Mo-K_α with graphite monochromator, $\lambda = 0.710\,69$ Å; scan θ—2θ at 1—29.3° min^{-1} depending on the intensity of a 2-s pre-scan, maximum $2\theta = 50°$; background measurements taken for $\frac{1}{4}$ of the scan time at each end of the scan; three standard reflections measured every 97 reflections. [b] Origin at $\bar{1}$.

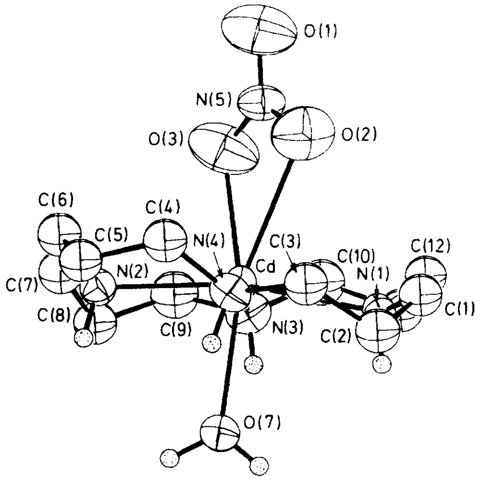

Figure 1. The $[Cd(L^3)(NO_3)(H_2O)]^+$ ion, showing the atomic numbering. Only hydrogen atoms (stippled) attached to nitrogen and oxygen are included

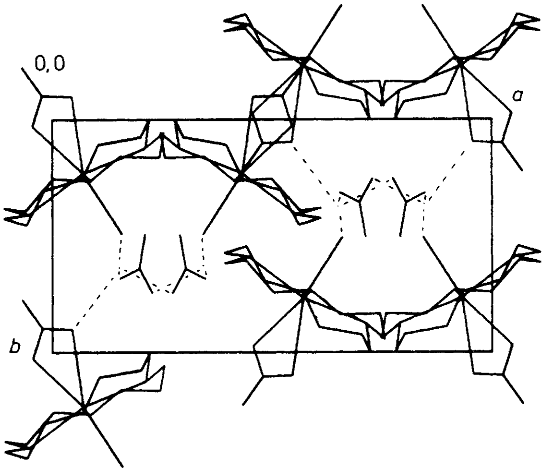

Figure 2. Packing diagram for complex (1), viewed down *c*. The hydrogen-bond network is dashed

found on successive Fourier syntheses. Final refinement was by least-squares methods, in large blocks, with analytical weighting schemes down-weighing reflections of low $(\sin\theta)/\lambda$ or large *F*. These were shown to be satisfactory by a weight analysis. Anisotropic thermal parameters were used for all non-hydrogen atoms for complexes (1)—(3), and for Pb only for (4). For final *R* values see Table 1. Computing was with the *X*-RAY 76 system,[7] on a Burroughs B6700. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 8. Final atomic co-ordinates are given in Table 2, bond lengths and angles in Table 3, and deviations from mean planes in Table 4.

Among the individual structures, the cadmium compound (1), Figure 1, has all atoms in general positions, and posed no problems in solution or refinement, apart from the discovery from Fourier difference maps of two water molecules, one co-ordinated to Cd and one free in the lattice (Figure 2). The mercury compound (2) was expected to be $Hg(L^3)Cl_2$, but the observed density suggested that it contained less ligand, and it was shown to be $[Hg(L^3)Cl]_2[HgCl_4]$. The Laue group and systematic absences defined the space group unambiguously as *P*4/*nmm*. With two molecules per cell, the tetrahedral anions could be placed unambiguously in position 2*a* (symmetry $\bar{4}2m$) with the chlorine atoms in 8*i*. The four cations would be expected in 4*d*—*e* (2/*m*) or 4*f* (*mm*), but the Patterson synthesis revealed two independent Hg atoms in 2*c* (4*mm*) (with the associated Cl atoms also in 2*c*). Refinement and Fourier dif-

Table 2. Atomic co-ordinates ($\times 10^4$), with standard deviations in parentheses

(*a*) $[Cd(L^3)(NO_3)(H_2O)]NO_3\cdot H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cd	2 320.1(6)	691.0(3)	2 307.0(3)	H(04)	2 131(86)	2 420(48)	2 573(43)
N(1)	2 652(8)	863(4)	990(3)	H(11)	1 900(136)	1 576(77)	18(67)
N(2)	2 563(7)	685(4)	3 676(3)	H(12)	531(104)	1 351(57)	525(50)
N(3)	4 090(8)	−532(4)	2 288(4)	H(21)	2 674(88)	2 516(48)	1 093(43)
N(4)	1 232(7)	2 116(4)	2 366(4)	H(22)	1 099(145)	2 846(83)	485(70)
N(5)	−1 024(8)	−229(4)	2 005(4)	H(31)	145(171)	3 193(99)	1 716(84)
N(6)	6 409(9)	1 974(5)	4 588(4)	H(32)	−378(99)	2 271(57)	1 477(48)
O(1)	−2 264(8)	−690(6)	1 988(6)	H(41)	−358(133)	2 817(77)	2 886(64)
O(2)	−972(10)	443(5)	1 608(6)	H(42)	−823(82)	1 826(46)	2 775(40)
O(3)	280(10)	−448(6)	2 405(6)	H(51)	1 736(101)	2 356(55)	3 905(49)
O(4)	7 461(8)	2 272(5)	5 097(4)	H(52)	−137(157)	2 188(89)	4 083(77)
O(5)	4 931(8)	2 107(5)	4 625(4)	H(61)	1 318(119)	906(67)	4 667(58)
O(6)	6 844(10)	1 527(5)	4 038(4)	H(62)	237(93)	750(54)	3 795(45)
O(7)	4 939(7)	1 581(4)	2 582(3)	H(71)	3 253(130)	−15(73)	4 665(64)
O(10)	6 249(8)	1 557(5)	1 179(4)	H(72)	2 134(78)	−480(43)	3 964(38)
C(1)	1 599(12)	1 538(7)	559(6)	H(81)	5 066(110)	−1 045(61)	4 198(54)
C(2)	1 645(12)	2 438(7)	967(6)	H(82)	5 370(125)	−245(70)	3 737(62)
C(3)	569(12)	2 538(7)	1 618(6)	H(91)	5 221(147)	−1 468(84)	2 954(70)
C(4)	31(12)	2 206(7)	2 948(6)	H(92)	3 348(84)	−1 295(47)	2 992(41)
C(5)	760(12)	2 012(7)	3 782(6)	H(101)	4 683(94)	−1 506(53)	1 690(45)
C(6)	1 082(12)	1 046(7)	3 996(6)	H(102)	2 705(87)	−1 283(48)	1 592(42)
C(7)	3 045(12)	−180(7)	4 051(6)	H(111)	4 032(110)	−1 029(61)	316(54)
C(8)	4 538(11)	−592(7)	3 767(5)	H(112)	4 818(76)	−348(42)	879(37)
C(9)	4 250(14)	−1 094(8)	3 001(7)	H(121)	2 597(94)	192(52)	−15(46)
C(10)	3 809(13)	−1 095(7)	1 577(7)	H(122)	1 431(107)	−258(61)	615(53)
C(11)	3 933(11)	−614(7)	822(6)	H(005)	5 597(127)	1 555(73)	3 084(63)
C(12)	2 550(11)	21(6)	543(5)	H(006)	5 486(109)	1 762(62)	2 226(54)
H(01)	3 646(93)	1 069(52)	994(45)	H(007)	7 143(111)	1 213(63)	1 237(54)
H(02)	3 378(77)	1 075(43)	3 838(37)	H(008)	6 481(110)	1 951(63)	874(53)
H(03)	5 006(80)	−257(44)	2 270(38)				

(*b*) $[Hg(L^3)Cl]_2[HgCl_4]$

Hg(1)	2 500	2 500	1 235(2)	C(12)	1 110(26)	381(20)	1 335(43)
Hg(2)	2 500	2 500	6 104(2)	C(21)	236(19)	3 404(19)	5 863(24)
Hg(3)	7 500	2 500	0	C(22)	649(17)	4 351	6 387(31)
Cl(1)	2 500	2 500	3 695(18)	H(221)	730(158)	4 270	7 309(246)
Cl(2)	2 500	2 500	8 685(18)	H(222)	122(307)	4 878	6 454(412)
Cl(3)	−2 500	966(6)	1 296(8)	H(211)	−478(280)	3 400(261)	6 137(287)
N(1)[a]	2 208(21)	763(25)	1 110(27)	H(212)	364(190)	3 378(187)	4 973(285)
N(2)	740(19)	2 500	6 325(24)	H(2)	666(212)	2 500	7 079(286)
C(11)[a]	1 991(32)	157(33)	1 629(41)				

(*c*) $[Pb(L^3)Cl]Cl$

Pb	3 211.6(4)	1 250.0	1 250.0	H(02)	4 742	1 783	1 917
Cl(1)	3 750	3 750	3 032(2)	H(11)	2 988	381	1 296
Cl(2)[b]	1 985(9)	2 561(8)	1 223(10)	H(12)	3 853	−15	2 430
Cl(3)[b]	1 265(24)	403(25)	940(15)	H(21)	3 521	997	2 861
N(1)	4 153(8)	384(6)	1 779(4)	H(22)	4 536	1 062	2 632
N(2)	4 094(8)	1 962(6)	1 893(4)	H(31)	2 912	1 795	2 284
C(1)	3 662(16)	402(8)	2 256(6)	H(32)	3 729	2 158	2 578
C(2)	3 857(15)	1 054(9)	2 560(5)	H(41)	3 480	2 917	1 770
C(3)	3 589(12)	1 792(9)	2 349(6)	H(42)	4 383	2 976	2 097
C(4)	4 125(12)	2 736(8)	1 814(6)	H(51)	4 957	3 418	1 404
C(5)	4 739(12)	2 925(7)	1 374(6)	H(52)	5 279	2 622	1 366
C(6)	4 228(12)	−358(7)	1 606(6)	H(61)	3 585	−551	1 571
H(01)	4 784	585	1 816	H(62)	4 553	−646	1 842

(*d*) $[Pb(L^3)][NO_3]_2$

Pb(1)	1 324.4(17)	7 608.7(10)	1 298.6(6)	N(34)	9 482(31)	7 746(18)	4 792(12)
Pb(2)	5 953.9(17)	3 554.2(9)	3 255.8(6)	N(35)	7 442(31)	9 617(18)	5 241(12)
Pb(3)	8 522.5(17)	8 645.0(9)	5 885.4(6)	N(36)	9 824(36)	10 430(20)	6 087(14)
Pb(4)	3 136.2(16)	4 586.4(9)	7 838.9(6)	C(31)	11 931(46)	7 655(26)	5 840(18)
Pb(5)	1 681.1(22)	1 606.4(12)	9 323.0(7)	C(32)	11 871(57)	7 163(32)	5 188(22)
O(11)	4 060(68)	9 336(40)	1 608(27)	C(33)	10 134(51)	6 880(29)	4 896(19)
O(12)	4 739(65)	10 392(37)	929(24)	C(34)	7 950(50)	7 384(29)	4 380(19)
O(13)	2 132(63)	9 693(33)	1 011(22)	C(35)	7 233(56)	8 287(32)	4 062(21)
O(14)	1 878(43)	8 278(24)	−34(16)	C(36)	6 139(55)	8 760(31)	4 657(21)
O(15)	3 784(32)	7 522(18)	246(12)	C(37)	6 418(40)	1 0278(23)	5 386(15)

Table 2 (*continued*)

(*d*) $[Pb(L^3)][NO_3]_2$

Atom	*x*	*y*	*z*
O(16)	4 388(33)	8 798(19)	−374(13)
N(11)	3 610(69)	9 855(37)	1 174(24)
N(12)	3 332(32)	8 197(18)	−49(12)
N(13)	177(40)	8 263(23)	2 397(15)
N(14)	2 690(28)	6 667(16)	2 198(11)
N(15)	503(32)	5 830(18)	947(12)
N(16)	−1 770(34)	7 492(19)	1 257(13)
C(11)	1 631(44)	8 509(31)	2 894(21)
C(12)	2 323(47)	7 615(27)	3 155(18)
C(13)	3 498(59)	7 191(34)	2 631(23)
C(14)	3 885(45)	6 134(26)	1 710(17)
C(15)	2 869(61)	5 163(35)	1 362(23)
C(16)	2 134(55)	5 366(31)	787(21)
C(17)	−645(43)	5 724(25)	364(17)
C(18)	−2 272(45)	5 982(25)	537(17)
C(19)	−2 294(45)	7 126(26)	618(17)
C(110)	−2 904(62)	8 055(36)	1 309(24)
C(111)	−2 235(63)	8 778(36)	1 938(24)
C(112)	−409(43)	9 095(25)	2 339(17)
O(21)	8 028(28)	3 105(16)	2 188(11)
O(22)	6 155(34)	3 899(19)	1 955(13)
O(23)	8 523(39)	3 989(22)	1 358(15)
O(24)	9 052(38)	5 367(22)	3 070(15)
O(25)	8 883(47)	6 101(26)	2 296(19)
O(26)	6 761(55)	5 762(31)	3 005(21)
N(21)	7 551(34)	3 655(19)	1 816(13)
N(22)	8 263(30)	5 846(17)	2 786(12)
N(23)	7 275(25)	2 696(14)	4 169(9)
N(24)	4 946(28)	1 784(16)	3 075(11)
N(25)	2 988(23)	3 473(13)	3 165(9)
N(26)	5 329(33)	4 431(19)	4 338(12)
C(21)	8 300	2 015	3 869
C(22)	7 081(61)	1 076(35)	3 553(23)
C(23)	6 120(58)	1 167(33)	2 873(22)
C(24)	3 641(53)	1 594(30)	2 534(20)
O(46)	546(65)	3 426(38)	9 542(25)
C(25)	2 106(41)	1 988(23)	2 666(16)
C(26)	2 153(44)	3 043(25)	2 636(17)
C(27)	2 546(53)	4 569(30)	3 223(20)
C(28)	2 630(41)	4 930(23)	3 970(16)
C(29)	4 358(38)	5 260(21)	4 199(14)
C(210)	6 707(46)	4 803(26)	4 728(17)
C(211)	7 458(52)	3 996(30)	4 978(20)
C(212)	8 304(45)	3 409(26)	4 572(17)
O(31)	6 683(64)	9 197(38)	6 975(25)
O(32)	8 390(62)	8 377(33)	7 298(22)
O(33)	6 373(45)	8 296(25)	7 853(18)
O(34)	6 120(44)	6 816(26)	5 851(18)
O(35)	7 693(64)	6 255(33)	6 184(22)
O(36)	5 961(104)	5 993(59)	6 743(41)
N(31)	7 048(60)	8 499(32)	7 367(23)
N(32)	6 327(62)	6 407(34)	6 304(24)
N(33)	12 039(39)	8 739(22)	5 856(15)
C(38)	7 339(41)	11 082(23)	5 558(15)
C(39)	8 302(43)	11 007(24)	6 143(16)
C(310)	10 824(47)	10 618(26)	6 643(18)
C(311)	12 549(48)	10 319(27)	6 487(18)
C(312)	12 467(63)	9 210(36)	6 528(24)
O(41)	1 468(39)	1 951(22)	5 240(15)
O(42)	2 276(62)	2 782(39)	4 630(24)
O(43)	3 612(64)	1 803(36)	5 175(25)
O(44)	605(48)	4 504(28)	8 877(19)
O(45)	2 864(54)	4 128(29)	9 222(19)
N(41)	2 670(74)	2 155(44)	4 819(28)
N(42)	1 233(85)	4 060(45)	9 240(31)
N(43)	4 018(34)	6 355(19)	8 214(13)
N(44)	6 259(50)	4 822(28)	7 905(19)
N(45)	4 209(34)	3 983(20)	6 684(13)
N(46)	2 017(34)	5 551(19)	7 178(13)
C(41)	4 974(52)	6 548(29)	8 791(20)
C(42)	6 818(58)	6 267(33)	8 668(22)
C(43)	6 918(64)	5 310(38)	8 611(25)
C(45)	6 794(50)	3 425(28)	7 046(19)
C(44)	6 701(40)	3 708(23)	7 849(15)
C(46)	5 220(56)	3 116(32)	6 879(21)
C(47)	3 099(54)	3 682(31)	6 223(21)
C(48)	2 263(58)	4 510(33)	6 033(22)
C(49)	1 067(43)	4 922(24)	6 481(16)
C(410)	862(47)	6 153(27)	7 381(18)
C(411)	1 618(45)	6 953(26)	7 714(17)
C(412)	2 662(41)	6 817(23)	8 369(15)
O(51)	2 237(30)	2 361(17)	8 022(11)
O(52)	−436(49)	1 666(28)	8 092(19)
O(53)	536(31)	2 963(18)	7 524(12)
O(54)	562(40)	290(23)	4 097(15)
O(55)	3 060(59)	100(34)	3 975(23)
O(56)	1 443(39)	−406(22)	4 772(15)
N(51)	793(40)	2 382(23)	7 840(15)
N(52)	1 781(24)	49(14)	4 223(9)
N(53)	2 673(41)	2 159(23)	10 431(15)
N(54)	−588(97)	303(53)	10 020(36)
N(55)	1 757(79)	−101(43)	8 808(30)
N(56)	4 876(43)	1 567(24)	9 209(16)
C(51)	1 424(69)	2 329(37)	10 854(25)
C(52)	−44(87)	1 949(48)	10 778(32)
C(53)	−1 184(84)	995(48)	10 504(32)
C(54)	−1 870(76)	171(42)	9 697(29)
C(55)	−1 166(62)	−676(36)	9 243(24)
C(56)	51(59)	−600(31)	8 684(21)
C(57)	3 001(120)	−80(63)	8 250(45)
C(58)	4 736(108)	483(60)	8 159(40)
C(59)	5 601(103)	1 037(58)	8 513(40)
C(510)	5 925(77)	2 482(45)	9 584(30)
C(511)	5 482(76)	2 539(43)	10 298(30)
C(512)	3 905(78)	2 878(42)	10 553(28)

[a] Occupancy 0.5. [b] Occupancies: Cl(2) 0.375, Cl(3) 0.125.

ference syntheses revealed the ligand molecule around Hg(2) (Figure 3), with N(2) lying on a mirror plane (position 8*i*), C(21) in a general position, and C(22) on the diagonal mirror plane (position 8*j*). Unexpectedly, the other molecule was disordered with N(1) occupying two alternative positions slightly off the mirror plane (Figure 4). Each half-occupancy nitrogen atom is linked to one half-occupancy carbon atom, C(11), and one full-occupancy atom which is also the central atom of the $(CH_2)_3$ chain, C(12); this is linked to 'itself,' C(12′), as the third atom of the chain. Hydrogen atoms were included and refined only for the ordered cation.

For the lead chloride complex (3) (Figure 5), with 16 molecules per cell, a Patterson synthesis showed the heavy atom in position 16*e*, with site symmetry 2. The ligand atoms are ordered, but the chlorine atoms show some disorder. One isolated Cl ion is in position 16*e*, while the second is weakly bound to Pb, in two alternative partially occupied positions. Although these were expected to have occupancy 0.5, their thermal parameters were rather high, and in final refinement the occupancy was reduced to 0.375, with a further isolated Cl^- ion included at occupancy 0.125. The alternative cannot be completely excluded, that Cl(2) is half occupied, despite the high thermal parameters, and the site labelled Cl(3) is a partly occupied lattice water molecule; however, this would

Table 3. Bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) $[Cd(L^3)(NO_3)(H_2O)]NO_3\cdot H_2O$ [a]

Cd–N(1)	2.325(6)	N(3)–C(10)	1.48(1)	N(5)–O(1)	1.23(1)
Cd–N(2)	2.330(6)	N(4)–C(3)	1.48(1)	N(5)–O(2)	1.22(1)
Cd–N(3)	2.347(7)	N(4)–C(4)	1.49(1)	N(5)–O(3)	1.24(1)
Cd–N(4)	2.333(6)	C(1)–C(2)	1.53(1)	N(6)–O(4)	1.23(1)
Cd–O(2)	2.832(8)	C(2)–C(3)	1.51(1)	N(6)–O(5)	1.23(1)
Cd–O(3)	2.413(8)	C(4)–C(5)	1.51(1)	N(6)–O(6)	1.25(1)
Cd–O(7)	2.519(6)	C(5)–C(6)	1.52(1)		
N(1)–C(1)	1.47(1)	C(7)–C(8)	1.50(1)	O(7) · · · O(6)	2.78(1)
N(1)–C(12)	1.48(1)	C(8)–C(9)	1.51(1)	O(7) · · · O(10)	2.75(1)
N(2)–C(6)	1.49(1)	C(10)–C(11)	1.51(1)	O(10) · · · O(2′)	2.85(1)
N(2)–C(7)	1.49(1)	C(11)–C(12)	1.51(1)	O(10) · · · O(4″)	2.83(2)
N(3)–C(9)	1.48(1)				

N(1)–Cd–N(3)	85.9(2)	C(6)–N(2)–C(7)	110.1(7)	C(2)–C(3)–N(4)	114.6(8)	O(1)–N(5)–O(2)	122.8(8)
N(1)–Cd–N(4)	91.6(2)	Cd–N(2)–C(6)	113.3(5)	N(4)–C(4)–C(5)	113.7(7)	O(1)–N(5)–O(3)	120.8(8)
N(1)–Cd–O(7)	85.7(2)	Cd–N(2)–C(7)	115.2(5)	C(4)–C(5)–C(6)	116.8(8)	O(2)–N(5)–O(3)	116.4(8)
N(2)–Cd–N(3)	92.0(2)	C(9)–N(3)–C(10)	109.9(7)	C(5)–C(6)–N(2)	112.7(8)	O(4)–N(6)–O(5)	120.4(8)
N(2)–Cd–N(4)	87.0(2)	Cd–N(3)–C(9)	115.5(6)	N(2)–C(7)–C(8)	113.9(8)	O(4)–N(6)–O(6)	119.7(8)
N(2)–Cd–O(7)	81.2(2)	Cd–N(3)–C(10)	115.4(5)	C(7)–C(8)–C(9)	116.3(8)	O(5)–N(6)–O(6)	119.9(7)
N(3)–Cd–O(7)	85.0(2)	C(3)–N(4)–C(4)	110.0(7)	C(8)–C(9)–N(3)	114.9(9)	O(6) · · · O(7) · · · O(10)	123.5(3)
N(4)–Cd–O(7)	79.6(2)	Cd–N(3)–C(3)	117.5(5)	N(3)–C(10)–C(11)	114.4(9)	O(7) · · · O(10) · · · O(2′)	99.4(3)
C(1)–N(1)–C(12)	110.0(6)	Cd–N(4)–C(4)	113.5(5)	C(10)–C(11)–C(12)	117.0(9)	O(7) · · · O(10) · · · O(4″)	140.4(3)
Cd–N(1)–C(1)	115.8(5)	N(1)–C(1)–C(2)	113.9(7)	C(11)–C(12)–N(1)	112.8(7)	O(2′) · · · O(10) · · · O(4″)	102.0(3)
Cd–N(1)–C(12)	113.7(5)	C(1)–C(2)–C(3)	116.3(9)				

(*b*) $[Hg(L^3)Cl]_2[HgCl_4]$ [b]

Ordered cation				Disordered cation			
Hg(2)–Cl(1)	2.64(2)	Cl(1)–Hg–Cl(2)	180.0	Hg(1)–Cl(1)	2.70(2)	Cl(1)–Hg–Cl(2)	180.0
Hg(2)–Cl(2)	2.83(2)	Cl(1)–Hg–N(2)	95.9(6)	Hg(1)–Cl(2)	2.80(2)	Cl(1)–Hg–N(1)	93.3(7)
Hg(2)–N(2)	2.38(3)	C(21)–N(2)–C(21′)	110(2)	Hg(1)–N(1)	2.37(3)	C(11′)–N(1)–C(12)	116(3)
N(2)–C(21)	1.48(3)	N(2)–C(21)–C(22)	113(2)	N(1)–C(11′)	1.46(5)	N(1)–C(12)–C(12′)	115(2)
C(21)–C(22)	1.50(3)	C(21)–C(22)–C(21′)	119(2)	N(1)–C(12)	1.58(4)	C(12)–C(12′)–C(11)	146(3)
				C(12)–C(12″)	1.39(4)		
				C(12′)–C(11)	1.26(6)		

Anion

Hg(3)–Cl(3)	2.503(9)	Cl(3)–Hg–Cl(3)	108.8(1), 108.8(3)

(*c*) $[Pb(L^3)Cl]Cl$ [c]

Pb–N(1)	2.54(1)	C(2)–C(3)	1.54(2)	N(1)–Pb–N(2)	71.3(4)	C(1)–C(2)–C(3)	118(1)
Pb–N(2)	2.53(1)	C(3)–N(2)	1.48(2)	N(1)–Ph–Cl(2)	76.1(4)	C(2)–C(3)–N(2)	114(1)
Pb–Cl(2)	2.98(1)	N(2)–C(4)	1.46(2)	N(1)–Pb–N(1′)	118.0(4)	C(3)–N(2)–C(4)	111(1)
N(1)–C(1)	1.49(2)	C(4)–C(5)	1.53(2)	N(1)–Pb–N(2′)	79.8(4)	N(2)–C(4)–C(5)	111(1)
N(1)–C(6)	1.47(2)	C(5)–C(6′)	1.51(2)	N(2)–Pb–N(2′)	122.1(4)	C(4)–C(5)–C(6′)	115(1)
C(1)–C(2)	1.50(2)			C(1)–N(1)–C(6)	110(1)	C(5′)–C(6)–N(1)	113(1)
				N(1)–C(1)–C(2)	115(1)		

(*d*) $[Pb(L^3)][NO_3]_2$ [d]

	Pb(1)	Pb(2)	Pb(3)	Pb(4)	Pb(5)
Pb(*n*)–N(*n*3)	2.64(3)	2.64(3)	2.73(3)	2.56(3)	2.51(3)
Pb(*n*)–N(*n*4)	2.72(2)	2.52(3)	2.70(3)	2.48(3)	2.69(5)
Pb(*n*)–N(*n*5)	2.57(2)	2.40(3)	2.25(3)	2.65(3)	2.59(5)
Pb(*n*)–N(*n*6)	2.56(3)	2.61(3)	2.55(3)	2.25(5)	2.60(3)
N(*n*3)–Pb(*n*)–N(*n*4)	76.1(9)	74.5(8)	71.8(8)	75.6(10)	83.5(12)
N(*n*4)–Pb(*n*)–N(*n*5)	76.9(7)	78.4(10)	84.9(9)	75.0(10)	71.0(15)
N(*n*5)–Pb(*n*)–N(*n*6)	80.1(9)	80.7(9)	70.1(10)	80.5(14)	79.0(13)
N(*n*6)–Pb(*n*)–N(*n*3)	71.4(9)	73.1(9)	72.8(10)	69.0(13)	78.0(9)
N(*n*3)–Pb(*n*)–N(*n*5)	120.4(8)	124.6(9)	117.7(9)	120.4(9)	125.4(13)
N(*n*4)–Pb(*n*)–N(*n*6)	122.1(8)	120.3(8)	119.0(8)	117.1(13)	125.3(14)

Pb(1)–O(11)	3.02(4)	Pb(2)–O(22)	2.74(3)	Pb(3)–O(34)	2.96(4)	Pb(4)–O(51)	3.16(2)
Pb(1)–O(13)	2.95(4)	Pb(2)–O(26)	3.01(4)	Pb(4)–O(44)	2.91(4)	Pb(5)–O(51)	2.91(2)
Pb(1)–O(14)	2.99(3)	Pb(3)–O(31)	2.80(4)	Pb(4)–O(45)	2.94(4)	Pb(5)–O(52)	3.17(4)
Pb(1)–O(15)	2.92(3)	Pb(3)–O(32)	2.94(5)	Pb(4)–O(53)	2.97(2)	Pb(5)–O(46)	2.89(6)
Pb(2)–O(21)	2.84(2)						

[a] O(2′) at $1 + x, y, z$; O(4″) at $x, \frac{1}{2} - y, z - \frac{1}{2}$. [b] Single primed atoms at $\frac{1}{2} - x, y, z$; double primed atoms at y, x, z. [c] Primed atoms at $x, \frac{1}{4} - y, \frac{1}{4} - z$. [d] The smallest of the numerous N–Pb–O angles are in the range 75—80°.

have negligible effect on refinement and on the resulting atomic positions. The lead nitrate complex (4) (Figures 6 and 7) is crystallographically very unusual both as an example of space group *P*1, and as containing five independent molecules. A search for a higher symmetry cell [9] was unsuccessful, and the lack of symmetry is confirmed by the five molecules all being chemically slightly different. Initially, structure solution was attempted in space group $P\bar{1}$, with two lead positions from a Patterson synthesis. This could be refined to $R = 0.28$, but not further. It was converted into *P*1, and a series of refinements with alternative lead positions eventually revealed the correct set of five heavy atoms. Refinement of the light atoms was very laborious, and in view of the large number of parameters only isotropic thermal parameters were used. The hand of the crystal examined was checked by a refinement of $\delta f''$ for Pb (together with the other lead parameters); it did not change in value significantly, indicating that the correct hand had been chosen.

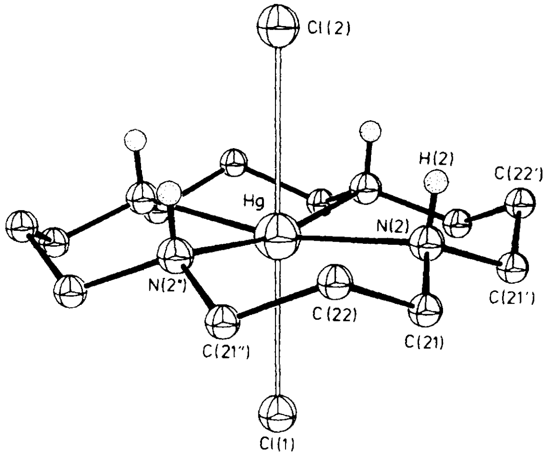

Figure 3. The $-Cl^{-}-[Hg(L^3)]^{2+}-Cl^{-}-$ chain, for the ordered ion of complex (2), showing the atomic numbering. Only hydrogen atoms (stippled) attached to nitrogen are included

A number of residual peaks on Fourier difference syntheses, and the fairly high thermal parameters of some atoms, suggest partial disorder in some rings and nitrate groups; it was felt that subdivision of these atoms was not justified in terms of the possible extra information to be obtained.

One carbon atom, C(21), proved unstable in refinement, and moved to a position 2.1 Å from C(22), and it was held fixed in a calculated position based on tetrahedral geometry for N(23); this behaviour is perhaps the result of interactions involving diffraction ripples around Pb(2). Hydrogen atoms were not included, and only the principal bond lengths and angles involving Pb are listed in Table 3(*d*).

Discussion

The four complexes studied show a remarkable range in their individual geometry and packing, but have a strong underlying similarity as far as the macrocycle is concerned (Figures 1, 2, and 4—6). In each, the nitrogen atoms are oriented so that all four N–H bonds point to one side of the macrocyclic plane.

The effect of metal atom size is very clear (Tables). The three cations have radii Cd^{2+} (0.97), Hg^{2+} (1.10), and Pb^{2+} (1.20 Å), and the 16-membered ligand L^3 appears to be large enough to take Cd^{2+} and Hg^{2+}, although both are slightly out-of-plane (0.29 Å for Cd, 0.14 and 0.24 Å for Hg). The Pb^{2+} ions are displaced by 1.2 Å in both complexes (3) and (4). In contrast, in the $[Hg(L^1)Cl]^+$ ion,[2] the metal atom is 0.8 Å out of plane. Although the structure of $[Cd(L^1)X]^+$ in the solid state has not been determined, n.m.r. evidence suggests that it contains two species in equilibrium, one with the Cd^{2+} in-plane and the other with it out-of-plane.[2] In both complexes (1) and (2) the co-ordination is sufficiently planar to allow extra ligands

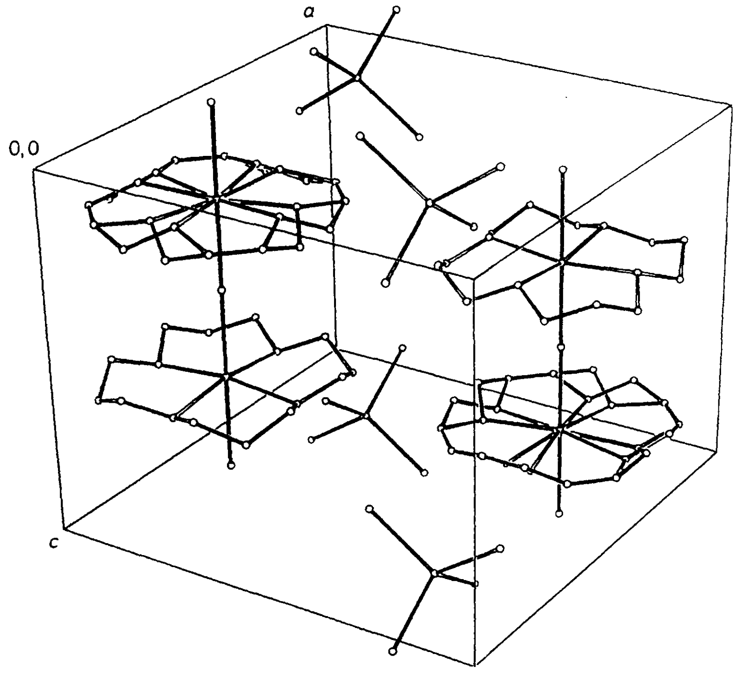

Figure 4. Packing diagram for $[Hg(L^3)Cl]_2[HgCl_4]$, showing the alternating ordered and disordered cations in the Cl–Hg–Cl–Hg–Cl chain

Table 4. Deviations (Å) from mean planes

Compound	Plane and deviations (defining atoms asterisked)
(1)	Cd, 0.29; N(1) *, −0.02; N(2) *, −0.02; N(3) *, 0.03; N(4) *, 0.03
(2)	Hg(1), 0.14; N(1) (four times) *, 0.00. Hg(2), 0.24; N(2) (four times)*, 0.00
(3)	Pb, 1.27; N(1) *, −0.04; N(2) *, 0.04; N(1′) *, −0.04; N(2′) *, 0.04
(4)	Pb(1), 1.28; N(13) *, −0.01; N(14) *, 0.01; N(15) *, −0.01; N(16) *, 0.01. Pb(2), 1.22; N(23) *, 0.05; N(24) *, −0.05; N(25) *, 0.05; N(26) *, −0.05. Pb(3), 1.29; N(33) *, 0.02; N(34) *, −0.02; N(35) *, 0.02; N(36) *, −0.03. Pb(4), 1.26; N(43) *, −0.04; N(44) *, 0.03; N(45) *, −0.03; N(46) *, 0.04. Pb(5), 1.19; N(53) *, 0.02; N(54) *, −0.02; N(55) *, 0.02; N(56) *, 0.02

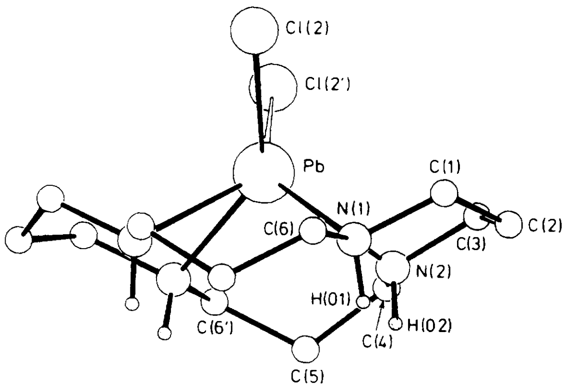

Figure 5. The $[Pb(L^3)Cl]^+$ ion, showing the atomic numbering. Only hydrogen atoms (stippled) attached to nitrogen are included. Both alternative positions for Cl(2) are drawn

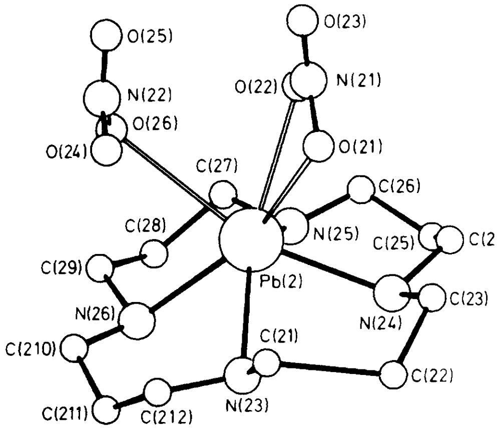

Figure 7. Structure of $[Pb(L^3)][NO_3]_2$, molecule 2, showing the atomic numbering

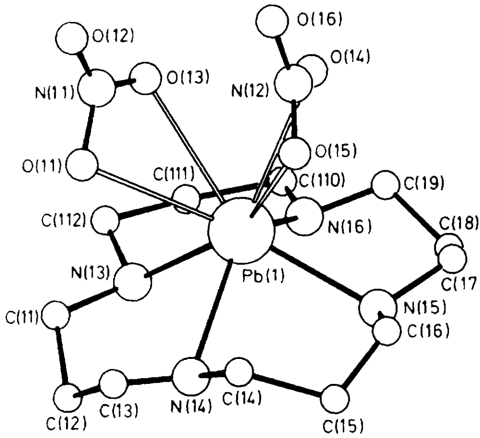

Figure 6. Structure of $[Pb(L^3)][NO_3]_2$, molecule 1, showing the atomic numbering

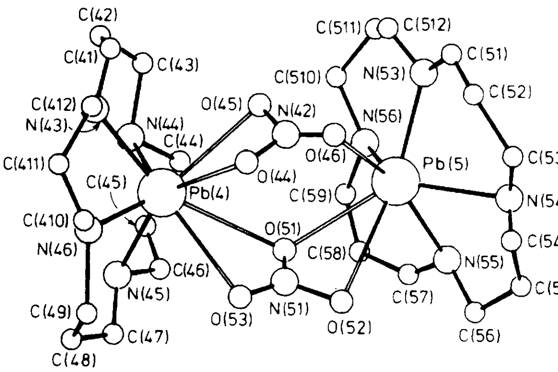

Figure 8. Structure of $[Pb(L^3)][NO_3]_2$, the $[Pb_2(L^3)_2(NO_3)_2]^{2+}$ unit containing Pb(4) and Pb(5), showing the atomic numbering

on both sides. In the cadmium complex (1) the N–H groups project towards the H_2O, no doubt because it is the less bulky of the two extra ligands (Figure 1). The NO_3^- is bidentate, but rather asymmetrical (Cd–O 2.41 and 2.83 Å). This contrasts with the most closely related structure,[4] that of $[Cd(L^4)(NO_3)]^+$ which has almost symmetrical nitrate groups [Cd–O 2.44 Å (av.)]. However, this has essentially a five-co-ordinate, trigonal bipyramidal geometry, rather than octahedral, a difference no doubt caused by the bulk of the methyl groups (considering the nitrate as occupying one co-ordination position in each case). It also has significantly longer Cd–N distances, with a differentiation between axial and equatorial positions [2.41 and 2.37 Å respectively, compared to 2.33 Å in (1)]. This difference may again be due to the methyl groups, although if so it is surprising that the nitrate group in complex (1) is less closely bound than in the tetramethyl derivative. The bidentate nitrate may have less space available in an octahedron [in (1)] than in an equatorial position of a trigonal bipyramid.

The packing in complex (1) (Figure 2) is probably dominated by electrostatic forces between the $[Cd(L^3)(NO_3)]^+$ and NO_3^- ions but hydrogen bonding is also significant, involving the co-ordinated and the free water molecules and both nitrate groups.

The Hg^{2+} complexes of L^3 and L^1 (ref. 5) show very little difference in Hg–N distance {2.37 Å both in (2) and in $[Hg(L^1)Cl]^+$}, despite the change in co-ordination number. However (2) has considerably longer Hg–Cl distances, 2.74 Å, as against 2.46, which is much closer to the distances in the $[HgCl_4]^{2-}$ ions (2.50 Å in both compounds). This is consistent with the long Cd–O bonds in the axial NO_3^- group of complex (1), but it may simply be caused by the Cl^- ions being shared between $[Hg(L^3)]^{2+}$ groups. The Hg–Cl distances show some variation, with those on the side to which the Hg atoms are out of plane being shorter (2.64, 2.70 Å, compared to 2.80, 2.83 Å). Both sets of N–H bonds project in the direction away from the shorter Hg–Cl bond. No firm explanation can be given for one cation being ordered and the other disordered (Figure 4), although this may be due to interactions between the cations and the $[HgCl_4]^{2-}$ ions. The shortest N ··· Cl distance to the anion is 3.47(3) Å, from the ordered cation, and the N(2) ··· Cl(3) distance from the disordered cation is not much longer [3.54(3) Å], but this would be significantly reduced if N(2) were on the mirror plane, perhaps to an unsatisfactorily small value.

The stereochemistry of the lead complexes (3) and (4) is complicated by a factor not present in (1) or (2), the lead lone pair, and this seems to have several alternative positions open to it. The structure of $[Pb(L^1)(NO_3)_2]$ provides a useful comparison, although it is significantly and surprisingly different in one respect. It can be described as distorted octahedral, with *cis*-nitrate groups, and with N–Pb–N angles across the ring of 83.3(4) and 134.7(6)° corresponding to *cis* and *trans* positions in the octahedron. The Pb is 1.39 Å out of the mean N_4 plane, although these atoms are themselves displaced by + and – 0.43 Å from the plane. The N–H bonds alternate up and down. In contrast, the complexes of L^3 have the ligand arranged symmetrically, with all N–H bonds pointing away from the metal, the nitrogen atoms virtually coplanar (Table 4), and all the *trans*-N–Pb–N angles close to 120° [overall average for (3) and (4), 121.0°]. The lead atom is displaced by 1.26 Å [av. for (3) and (4)] above the plane, and the space on its other side is taken up by one to four ligand atoms and the lone pair, whose stereochemical requirements can clearly be satisfied in many ways. The complex $[Pb(L^3)Cl]^+$ (Figure 5) shows the simplest pattern, with the chloride ion attached asymmetrically (in two alternative positions). The lone pair can be presumed to occupy the position not taken by the chloride ion.

The five independent molecules in the structure of $[Pb(L^3)][NO_3]_2$ show four distinct co-ordinations, although each lies within the broad pattern described above. The simplest is that of Pb(1) (Figure 6), with two symmetrical bidentate nitrate groups. The lone pair probably projects between O(13), O(14), and N(16), where the O–Pb–N angles are at their largest. For Pb(2) (Figure 7) and Pb(3) one nitrate group is bidentate (slightly asymmetric) with rather shorter Pb–O distances than for Pb(1), and the other is unidentate. Atoms Pb(4) and Pb(5) (Figure 8) are linked by two nitrate groups into a $[Pb_2(L^3)_2(NO_3)_2]^{2+}$ unit. One nitrate is asymmetrically bidentate to each Pb, and the other is symmetrically bidentate to Pb(4) and unidentate to Pb(5). Thus, Pb(4) resembles Pb(1) and Pb(5) resembles Pb(2) and Pb(3), although their links lead to some differences in detail. Finally, two nitrate groups are entirely isolated (Pb–O > 3.95 Å). The two lead complexes of L^3 have similar Pb–N distances [2.54 Å in (3) and 2.56 Å (av.) in (4)], although those in (4) are rather variable (for reasons noted above, this variation cannot be taken as very significant); they are both slightly longer than the average of the rather variable distances in $[Pb(L^1)]^{2+}$ (2.49 Å). The Pb–O distances in complex (4) are rather variable, with a minimum of 2.74(3) Å, somewhat lower than in the complex of L^1 (2.86—3.31 Å); as there, the variability is probably due in part to lone-pair repulsions. For neither (3) nor (4) does the packing show significant interactions between cations and anions, and the forces are presumably electrostatic.

Table 5. N.m.r. data

Complex	Solvent	^{13}C N.m.r. (δ/p.p.m.)	
(1) $[Cd(L^3)(NO_3)(H_2O)]NO_3 \cdot H_2O$ [a]	CD_3OD	55.1	29.8
(2) $[Hg(L^3)Cl]_2[HgCl_4]$	$(CD_3)_2SO$	54.0	28.0
(4) $[Pb(L^3)][NO_3]_2$	$CDCl_3$	52.9 [b]	29.5

[a] ^{15}N, δ –32.8; ^1J(Cd–N) = 116 Hz. [b] ^2J(Pb–C) = 20.6 Hz.

N.M.R. Spectra.—The chemical shifts and coupling constants, where measurable, are collected in Table 5.

In methanol the ligand L^3 gives a ^{15}N resonance at –345.7 p.p.m., and ^{13}C resonances at 47.55 and 28.24 p.p.m. The chemical shifts obtained for the complexes consistently show a small downfield shift for the $N-CH_2$ carbon and little, if any, change for $C-CH_2-C$. The shift in the ^{15}N resonance of the cadmium complex is also to low field of that for the free ligand and agrees with our earlier observations on a similar ligand of smaller ring size.[10]

The average ^1J(Cd–N), from the two isotopes of ^{111}Cd and ^{113}Cd, obtained for $[Cd(L^3)(NO_3)(H_2O)]^+$ is 116 Hz, and is close to the value of 110 Hz obtained for (1,4,8,11-tetra-azacyclotetradecane)cadmium(II) nitrate. These values are greater than for the Cd^{2+} complex of the *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate ion (82.4 Hz) which we have taken as a typical value for a normal octahedral complex, and this increase is a measure of the constrictive effect of the macrocycle on the Cd–N bond distance.

Acknowledgements

We thank the S.E.R.C. for support.

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Received 2nd March 1984; *Paper* 4/362