Metal Complexes of the New Tetra-aza Macrocyclic Ligand 1,5,9,13-Tetramethyl-1,5,9,13-tetra-azacyclohexadecane; Carbon-13 Nuclear Magnetic Resonance Study of the Complexes of Cd^{2+}, Hg^{2+}, and Pb^{2+} and *X*-Ray Crystal Structure of the Cadmium Complex †

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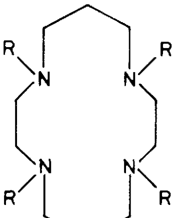
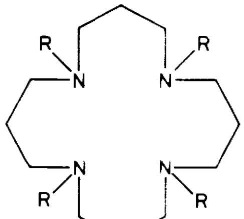
The new 16-membered tetra-aza macrocyclic ligand 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane (L^4) has been prepared, and the metal complexes of Cd^{2+} and Hg^{2+} isolated and characterised. The Pb^{2+} complex was also investigated by ^{13}C n.m.r. spectroscopy in nitromethane solution. Carbon-13 spectra of the Cd^{2+} and Hg^{2+} complexes revealed the presence of two isomers in methanol solution, including the complex with the unusual ' three up and one down ' set of nitrogen configurations, together with the more usual ' four up ' arrangement of the N-methyl groups. A crystal structure of the Cd^{2+} complex establishes the presence of these two structures in the solid phase. The crystals contain $[CdL^4(NO_3)]_2[Cd(NO_3)_4]$ and are monoclinic, space group *C*2/*c*, with a = 53.360(14), b = 10.248(6), c = 31.938(7) Å, β = 119.51(2)°; R = 0.063 for 4 920 diffractometer collected reflections with $I/\sigma(I) \geqslant 3.0$. The cations have pseudo-trigonal-bipyramidal geometry, with bidentate nitrate groups occupying one equatorial position. They show disordered ligand conformations comprising a ' three up and one down ' and two types of ' all four up ' arrangements of the N-methyl groups. The anions are dodecahedral, with bidentate nitrate groups. Cd–N (axial) is 2.41 Å (average) and Cd–N(equatorial) is 2.37 Å (average), while Cd–O is the range 2.27—2.60 Å, with the anions showing greater asymmetry.

We have previously investigated the co-ordination chemistry of the 14-membered tetra-aza macrocyclic ligands L^1 and L^2,[1,2] and the 16-membered tetra-aza macrocycle, L^3.[3] The new 16-membered tetra-aza macrocycle, L^4, has now been prepared, and we report here the synthesis of this ligand and the isolation of its complexes with cadmium(II) and mercury(II). These complexes were investigated in solution by ^{13}C n.m.r. spectroscopy, and a crystal structure of the Cd^{2+} complex undertaken to confirm the unusual solution behaviour. The Pb^{2+} complex was investigated by ^{13}C n.m.r. spectroscopy in nitromethane solution.



L^1 : R = H
L^2 : R = CH_3



L^3 : R = H
L^4 : R = CH_3

Experimental

Materials and Methods.—All chemicals used were of analytical grade. The ligand L^3 was prepared as described in the literature[4] and characterised by ^1H and ^{13}C n.m.r. and i.r. spectroscopy. Proton-decoupled, natural abundance ^{13}C n.m.r. spectra were recorded in the temperature range 203—323 K using either a Bruker WH400 or a WH90 Fourier-transform spectrometer. $[^2H_3]$Methanol or $[^2H_3]$nitromethane (both 99%) were used as solvent and lock signal, with *ca.* 5% dioxane as internal standard (δ 67.4). Hydrogen-1 n.m.r. spectra were recorded using a Perkin-Elmer (model R34) 220-MHz ^1H n.m.r. spectrometer with $CDCl_3$ as solvent and *ca.* 1% $SiMe_4$ as internal reference. The mass spectrum of the ligand was recorded using a Kratos instrument (MS80).

Preparation of L^4.—The ligand L^3 (2.0 g, 8.8 mmol) was dissolved in 98% formic acid (10 cm^3) and formaldehyde (10 cm^3 of a 40% aqueous solution) was added. After heating at 90 °C for 12 h, the reaction mixture was cooled in ice and basified (pH *ca.* 12) with 10% aqueous NaOH. Extraction with CH_2Cl_2 (5 × 30 cm^3), followed by drying of the combined extracts and removal of solvent in *vacuo* gave a pale yellow oil which distilled (b.p. 150 °C/0.1 mmHg, Kügelröhr apparatus) to a colourless oil. This oil rapidly crystallised to give 1,5,9,13-tetramethyl-1,5,9,13-tetra-azacyclohexadecane (L^4) (2.3 g, 8.1 mmol), m.p. 35—38 °C, in 92% yield. ^1H N.m.r. ($CDCl_3$): δ 1.60 (8 H, p), 2.20 (12 H, s), 2.57 p.p.m. (16 H, t). ^{13}C N.m.r. (CD_3NO_2): δ 25.80 (1), 43.02 (1), 55.63 p.p.m (2). I.r. (thin film): no N–H stretch. Mass spectrum: M^+, found 284.2944, expected 284.2940.

$[CdL^4][NO_3]_2$.—A solution of L^4 (0.5 g, 1.76 mmol) in methanol was added to a stirred solution of $Cd[NO_3]_2 \cdot 4H_2O$ (0.54 g, 1.76 mmol) in A.R. methanol at room temperature. The product was precipitated by addition of diethyl ether and the white crystals were filtered off, washed with ether, and dried *in vacuo* to give $[CdL^4][NO_3]_2$ (0.6 g, 1.15 mmol) in 65% yield. Combustion analysis (Found: C, 36.9; H, 6.95; N, 16.1. Calc. for $C_{16}H_{36}CdN_6O_6$: C, 36.9; H, 6.95; N, 16.15%).

$[HgL^4][NO_3]_2$.—This complex was prepared from equimolar amounts of L^4 and $Hg[NO_3]_2 \cdot 0.5H_2O$, as described above, to give $[HgL^4][NO_3]_2 \cdot H_2O$ (0.65 g, 1.05 mmol) in 59% yield. Combustion analysis (Found: C, 30.65; H, 6.10; N, 13.75. Calc. for $C_{16}H_{38}HgN_6O_7$: C, 30.65; H, 6.10; N, 13.4%).

Crystallographic Study.—Colourless chunky crystals suitable for *X*-ray determination were obtained by allowing a hot

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† *Supplementary data available* (No. SUP 23819, 86 pp.): full bond length listing, structure factors, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

concentrated methanolic solution of $[CdL^4][NO_3]_2$ to cool slowly at room temperature. Disproportionation occurs during this recrystallisation as shown in equation (i). The presence

$$3[CdL^4][NO_3]_2 \rightleftharpoons [CdL^4(NO_3)]_2[Cd(NO_3)_4] + L^4 \qquad \text{(i)}$$

of unco-ordinated L^4 was observed in the solution ^{13}C n.m.r. spectrum (see below).

Crystal data. $C_{32}H_{72}Cd_3N_{14}O_{18}$, $M = 1\ 278.2$, Monoclinic, space group $C2/c$, $a = 53.360(14)$, $b = 10.248(6)$, $c = 31.938(7)$ Å, $\beta = 119.51(2)°$, $U = 15\ 198(11)$ Å^3, $Z = 12$, $D_c = 1.68$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) $= 12.9$ cm^{-1}, $F(000) = 7\ 800$.

Data were collected with a Syntex $P2_1$ four-circle diffractometer. Maximum 2θ was 50°, with scan range $\pm$ 0.9° (2θ) around the $K_{\alpha1}$-$K_{\alpha2}$ angles, scan speed 3—29° min^{-1}, depending on the intensity of a 2-s pre-scan; backgrounds were measured at each end of the scan for one quarter of the scan

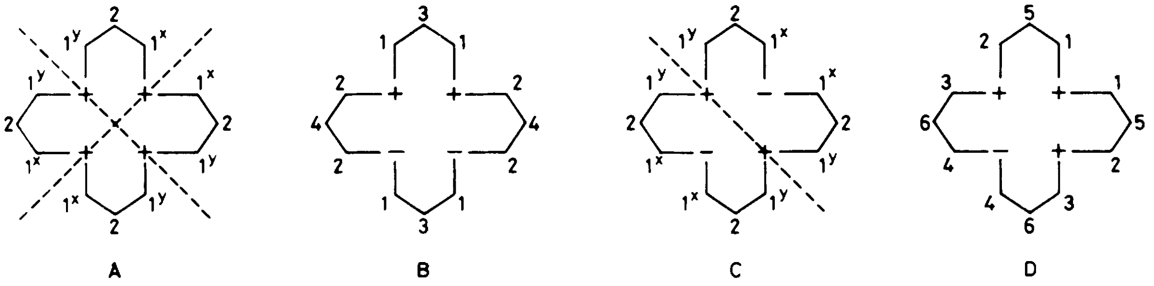
Table 1. Atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses *

Atom	*x*	*y*	*z*
Cd(1)	2 731.0(3)	2 080.0(13)	1 327.0(5)
Cd(2)	467.0(3)	2 780.0(12)	6 073.0(4)
Cd(3)	1 263.0(3)	2 536.0(13)	4 269.0(5)
Cd(4)	1 535.0(3)	1 911.0(16)	1 443.0(6)
Cd(5)	0	202(2)	7 500
N(101)	3 193(5)	2 356(22)	1 127(10)
N(11)	2 877(4)	−143(18)	1 559(6)
N(12)	2 294(4)	1 366(19)	658(7)
N(13)	2 601(5)	4 310(18)	1 083(9)
N(14)	2 788(3)	2 493(20)	2 097(6)
N(201)	405(5)	2 607(18)	5 138(8)
N(21)	281(4)	592(15)	5 978(6)
N(22)	63(3)	3 658(15)	6 094(6)
N(23)	663(3)	4 940(15)	6 142(6)
N(24)	901(3)	2 103(18)	6 751(5)
N(301)	1 861(4)	2 776(24)	4 575(7)
N(31)	1 197(5)	1 496(28)	3 553(7)
N(32)	962(4)	4 286(22)	3 843(10)
N(33)	1 353(5)	3 401(37)	5 053(10)
N(34)	1 109(4)	552(22)	4 463(8)
N(401)	1 025(5)	1 933(20)	554(8)
N(402)	1 728(5)	4 422(28)	1 439(8)
N(403)	1 846(6)	−322(23)	1 495(9)
N(404)	1 560(6)	1 641(18)	2 331(10)
O(11)	2 941(4)	2 003(15)	819(6)
O(12)	3 235(4)	2 548(19)	1 537(7)
O(13)	3 380(4)	2 427(21)	1 011(8)
O(21)	193(3)	3 016(14)	5 175(5)
O(22)	630(3)	2 297(16)	5 509(5)
O(23)	390(4)	2 556(19)	4 740(6)
O(31)	1 692(3)	3 665(16)	4 351(7)
O(32)	1 753(4)	1 783(20)	4 667(7)
O(33)	2 120(3)	2 845(18)	4 729(5)
O(411)	1 260(5)	2 228(20)	572(6)
O(412)	1 036(3)	1 621(16)	956(6)
O(413)	795(4)	1 983(19)	189(7)
O(421)	1 514(4)	4 247(19)	1 470(8)
O(422)	1 850(4)	3 481(21)	1 393(8)
O(423)	1 824(5)	5 514(20)	1 458(7)
O(431)	1 594(5)	−349(23)	1 355(9)
O(432)	1 963(4)	661(23)	1 660(10)
O(433)	2 002(4)	−1 245(19)	1 530(7)
C(101)	2 757(6)	−971(26)	1 118(10)
C(102)	2 435(6)	−1 057(27)	848(10)
C(1031)	2 342(6)	85(29)	483(11)
C(1032)	2 215(8)	47(38)	865(14)
C(1041)	2 187(7)	2 281(36)	244(12)
C(1042)	2 035(12)	2 224(60)	590(20)
C(105)	2 133(7)	3 669(30)	365(11)
C(106)	2 410(8)	4 426(34)	545(13)
C(107)	2 464(6)	5 013(26)	1 334(10)
C(108)	2 622(6)	4 930(28)	1 885(11)
C(109)	2 595(6)	3 612(30)	2 092(11)
C(110)	2 705(6)	1 419(29)	2 294(10)
C(111)	2 891(6)	96(29)	2 368(11)
C(112)	2 777(6)	−690(26)	1 898(10)
C(113)	3 200(6)	−263(26)	1 794(10)
C(1141)	2 088(7)	1 263(34)	840(13)
C(1142)	2 273(12)	846(57)	208(21)
C(115)	2 864(8)	5 006(35)	1 204(13)
C(116)	3 098(5)	2 919(26)	2 422(9)
C(201)	−50(5)	689(22)	5 715(8)
C(202)	−173(5)	1 400(23)	5 995(8)
C(2031)	−202(8)	2 939(41)	5 816(15)
C(2032)	−48(8)	2 662(37)	6 287(13)
C(2041)	−35(8)	4 973(39)	5 861(15)
C(2042)	173(9)	4 848(41)	6 446(15)
C(205)	242(6)	5 984(26)	6 154(10)
C(2061)	423(5)	5 877(21)	5 898(8)
C(2062)	612(12)	5 750(58)	6 495(21)
C(2071)	870(4)	5 385(19)	6 668(7)
C(2072)	969(14)	4 904(64)	6 342(25)
C(208)	1 123(5)	4 423(25)	6 925(9)
C(209)	1 029(5)	3 155(25)	7 118(9)
C(210)	860(5)	1 033(23)	7 031(9)
C(211)	708(5)	−214(22)	6 751(8)
C(212)	378(5)	−122(20)	6 443(8)
C(213)	359(5)	−148(25)	5 657(9)
C(2141)	151(9)	3 763(44)	6 619(16)
C(2142)	−186(7)	4 118(35)	5 591(13)
C(2151)	836(6)	4 983(26)	5 867(10)
C(2152)	472(11)	5 839(51)	5 697(20)
C(216)	1 109(5)	1 674(22)	6 590(8)
C(301)	1 166(10)	2 516(48)	3 200(17)
C(302)	837(7)	3 274(35)	3 031(13)
C(3031)	741(7)	3 791(31)	3 308(12)
C(3032)	1 023(14)	4 730(67)	3 390(26)
C(3041)	797(10)	4 714(48)	4 077(17)
C(3042)	1 045(17)	5 665(80)	4 212(29)
C(305)	1 029(7)	5 200(32)	4 653(12)
C(306)	1 373(10)	4 758(47)	4 995(18)
C(307)	1 171(7)	2 664(36)	5 230(12)
C(308)	1 160(8)	1 257(37)	5 207(14)
C(309)	931(8)	769(38)	4 678(14)
C(310)	892(8)	−217(35)	3 987(14)
C(311)	1 004(7)	−463(34)	3 647(13)
C(312)	938(9)	638(41)	3 276(14)
C(313)	1 460(7)	823(33)	3 617(12)
C(3141)	1 122(10)	5 412(47)	3 792(18)
C(3142)	670(13)	3 885(62)	3 654(23)
C(315)	1 654(9)	3 049(42)	5 401(15)
C(316)	1 354(7)	−419(34)	4 693(12)
O(4411)	1 799(6)	1 776(26)	2 292(10)
O(4412)	1 558(14)	2 501(66)	2 198(23)
O(443)	1 588(6)	1 442(26)	2 735(11)
O(4421)	1 325(8)	1 856(39)	1 956(15)
O(4422)	1 462(10)	868(51)	2 067(19)
N(501)	−62(5)	−1 724(22)	6 831(9)
N(502)	413(4)	2 192(21)	7 718(7)
O(511)	170(4)	−1 680(17)	7 181(7)
O(512)	−250(3)	−833(16)	6 780(6)
O(513)	9 841(4)	7 523(21)	6 481(8)
O(521)	311(3)	2 182(16)	7 986(6)
O(522)	352(3)	1 236(14)	7 427(5)
O(523)	581(4)	3 039(19)	7 729(7)

* Population ratios, atoms (*mnp*1) : atoms (*mnp*2); *m* = 1, 0.67(3) : 0.33; *m* = 2, 0.58(2) : 0.42; *m* = 3, 0.56(4) : 0.44; *m* = 4, 0.5 : 0.5.

time. All 8 030 reflections with $2\theta < 40°$ were recorded, but reflections with $2\theta > 40°$ were selected or rejected for measurement on the basis of an 8-s peak count (with only 1 100 being accepted). Three standard reflections were monitored every 300 reflections, and showed slight changes during data collection; the data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 high-angle reflections. 4 920 Observed reflections $[I/\sigma(I) > 3.0]$ were used in refinement, and corrected for Lorentz, polarisation, and absorption effects, the last with ABSCOR;[5] maximum and minimum transmission factors were 0.83 and 0.75. The crystal dimensions were 0.3 × 0.35 × 0.35 mm. Systematic absences hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$ indicated space groups $C2/c$ or Cc. The former was chosen on the evidence of intensity statistics, and shown to be correct by the successful refinement.

Initial structure solution was by MULTAN 80[6] starting from the three highest peaks on the most probable map. At this point, the composition of the crystal was uncertain, and only after some refinement was it discovered that the unit cell contained three $[CdL^4(NO_3)]^+$ and one $[Cd(NO_3)_4]^{2-}$ in general position $8f$, and one $[Cd(NO_3)_4]^{2-}$ in special position $4e$ (two-fold axis) giving the overall stoicheiometry stated above, and total unit-cell contents 24 cations + 12 anions. Refinement then proceeded smoothly, although slowly, to $R = 0.11$ when it appeared that each of the cations and one of the anions had some disordered atoms. With this accounted for, final refinement with Cd, N, and most O atoms anisotropic in large blocks gave $R = 0.063$. The refined populations of the disordered atoms in the cations were linked to keep their totals 1.0, but for the anion were set at 0.5. Hydrogen atoms were not included. Unit weights were used. Final refinement was with SHELX and further computing was with the X-RAY 76 system,[7] on a Burroughs B6700 computer. Scattering factors in the analytical form and anomalous dispersion factors were taken from ref. 8. Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.



Number of different ^{13}C n.m.r. resonances expected (relative populations)

Structure	A	B	C	D
N–CH_2	1 (8) (4x + 4y)	2 (4 + 4)	1 (8) (4x + 4y)	4 (2 + 2 + 2 + 2)
N–CH_3	1 (4) (2x + 2y)	1 (4)	1 (4) (2x + 2y)	3 (1 + 2 + 1)
C–CH_2–C	1 (4)	2 (2 + 2)	1 (4)	2 (2 + 2)
Total number of resonances	3	5	3	9

Figure 1. Schematic representation of the four possible ' planar ' isomers of metal complexes containing the ligand L^4, showing equivalent carbon atoms (numbered), and the number of ^{13}C resonances expected for each structure; (+) and (−) represent the positions of the Me–N– groups above or below the macrocycle plane respectively. For structures A and C, five resonances (areas 3 × 2 and 2 × 1) arise from folding about the dashed lines, causing splitting of the N–CH_2 and N–CH_3 resonances into pairs labelled x and y (superscripts)

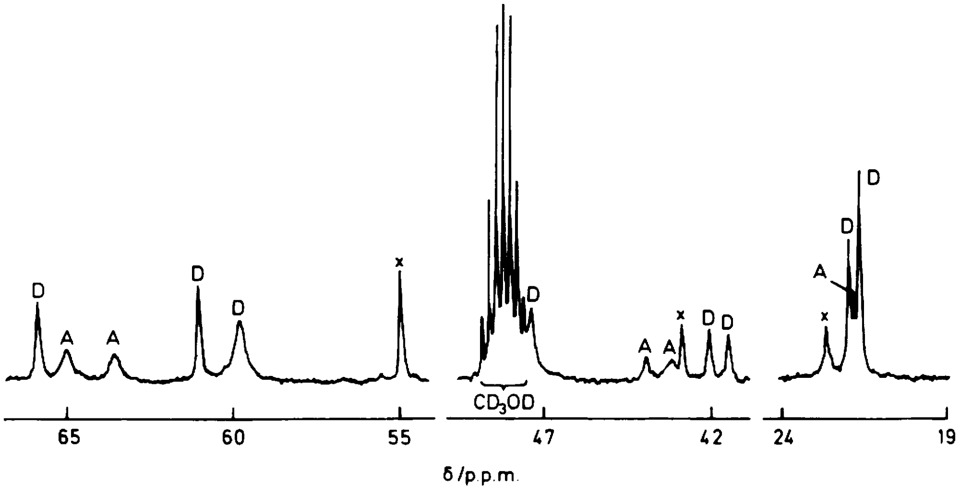


Figure 2. Carbon-13 n.m.r. spectrum (100.6 MHz) of $[CdL^4][NO_3]_2$ at 301 K (see Figure 1 for assignments)

Results and Discussion

The synthesis of the ligand L^4 in high yield from L^3 proceeds as described using formic acid–formaldehyde as the methylating agent,[9] even though this method failed to work in the case of two other tetra-aza macrocycles, producing products in which methylene bridges form across adjacent N atoms.[10] The ligand L^4 is the first fully saturated tetra-aza 16-membered macrocycle containing four tertiary amine donors to be reported.

Carbon-13 *N.M.R. Spectra.*—Both the Cd^{2+} and Hg^{2+} complexes of L^4 form readily in methanol and are very soluble in this solvent. Assuming that the four N atoms of L^4 are co-ordinated in a planar arrangement, four isomers (A—D) are possible, depending upon the relative positions of the N–Me groups either above (+) or below (−) the macrocycle plane as shown in Figure 1. The number of ^{13}C resonances expected for each of these symmetric ' planar ' structures and their relative populations are also shown in Figure 1. For example, structures A and C which are highly symmetric are expected to show three resonances of relative areas 2 : 1 : 1, whereas B should show a total of five (areas 3 × 2 and 2 × 1), with nine resonances (areas 7 × 2 and 2 × 1) for D. Identical backbone carbon atoms are assigned the same number in each of structures A—D of Figure 1. It is also known from previous studies that the highly symmetric structures A and C can readily fold about the diagonal axes shown by the dashed lines in Figure 1; this would cause a splitting of the $N-CH_2$ and $N-CH_3$ peaks into two equal-height resonances, giving a total of five resonances for each of the folded structures of A and C. This is shown by the superscripts x and y in Figure 1. In the case of structure A, five-co-ordinate trigonal-bipyramidal complexes of the type [M(L)X] (L = macrocycle, X = unidentate ligand) are expected to form by analogy with the known complexes of the ligand L^2.[1,11]

The ^{13}C n.m.r. spectrum of $[CdL^4][NO_3]_2$ in $[^2H_3]$methanol at 301 K is shown in Figure 2. Disproportionation occurs under such conditions as shown by equation (i), and the resonances associated with the unco-ordinated ligand are marked with a cross (×) in Figure 2. The spectrum obtained by mixing cadmium acetate with L^4 (1 : 1) in $[^2H_3]$methanol is very similar to that of the nitrate salt, but with free-ligand resonances absent, and further splitting of the resonance at δ 59.8 into two broad equal-height resonances. The relative areas of the resonances in Figure 2 indicate the presence of two species which are tentatively assigned to structures A (23%) and D (77%) respectively. Confirmation of the assignments comes from the *X*-ray analysis (see below), and a structure analogous to D has recently been detected for $[NiL^2]^{2+}$.[12] The $N-CH_2-C$, $N-CH_3$, and $C-CH_2-C$ resonances are found to lie in the ranges δ 55—67, 42—49, and 22—24 p.p.m. respectively. To species A are attributed the five resonances at δ 65.0, 63.5 ($N-CH_2$), 44.1 and 43.3 ($N-CH_3$), and 21.9 p.p.m. ($C-CH_2-C$) with relative areas 2 : 2 : 1 : 1 : 2 respectively. This is as expected for a folded trigonal-bipyramidal species. Analogous complexes of L^2 such as $[Zn(L^2)S]^{2+}$ (S = solvent) have been observed to be fluxional, with alternate folding about the two diagonal axes (analogous to the two dashed lines in Figure 1, A) causing averaging of the $N-CH_2$ and $N-CH_3$ resonances.[1] This would account for the pronounced broadening of the resonances associated with A (Figure 2), although the energy barrier to folding must be greater than in $[Zn(L^2)S]^{2+}$, because collapse to the expected three resonances does not occur at 323 K. The broad resonances (Figure 2) at δ 65.8, 61.0, 59.8 ($N-CH_2$), 47.5, 43.0, 42.3 ($N-CH_3$), and 22.0, 21.7 ($C-CH_2-C$) with relative areas 2 : 2 : 4 : 2 : 1 : 1 : 2 : 2 are assigned to structure D of Figure 1. The very broad resonance at δ 59.8 is assigned to four of the eight $N-CH_2$ groups, and in the corresponding cadmium acetate complex this resonance splits into two to give four $N-CH_2$ resonances and a total of nine resonances, as expected for structure D. In the acetate complex the $N-CH_3$ resonances of D are very broad and difficult to detect, and the $N-CH_2$ resonances are also broader than those found for the nitrato-complex. Again, folding of the macrocycle about a diagonal in Figure 1, D, would account for the observed line broadening. The ^{13}C n.m.r. spectrum of $[HgL^4(NO_3)_2]$ at 240 K in $[^2H_3]$methanol is similar to that of the cadmium nitrate complex, and corresponding assignments are made as shown in Table 3. At room temperature the Hg^{2+} spectrum is less well resolved. In $[^2H_3]$nitromethane as solvent, the nitrate and acetate complexes of Hg^{2+} and Pb^{2+} have relatively simple spectra with only three sharp resonances of areas 2 : 1 : 1 as expected for symmetric structures A or C. Comparison with previous studies would favour a square-pyramidal structure, A. Curiously for $[HgL^4Cl]Cl$, in nitromethane the $N-CH_2$ resonance at δ 56.9 is very broad indicat-

Table 2. Bond distances (Å) and angles (°)

(*a*) Distances *

(*i*) Cations	$n = 1$	$n = 2$	$n = 3$
Cd(*n*)–N(*n*1)	2.40(2)	2.41(2)	2.38(3)
Cd(*n*)–N(*n*2)	2.37(2)	2.37(2)	2.35(2)
Cd(*n*)–N(*n*3)	2.40(2)	2.41(2)	2.47(3)
Cd(*n*)–N(*n*4)	2.36(2)	2.37(1)	2.39(2)
Cd(*n*)–O(*n*1)	2.39(2)	2.51(1)	2.46(2)
Cd(*n*)–O(*n*2)	2.48(2)	2.41(2)	2.40(2)

(*ii*) Anions	$n = 4$	$n = 5$
Cd(*n*)–O(*n*11)	2.45(2)	2.55(2)
Cd(*n*)–O(*n*12)	2.35(1)	2.27(2)
Cd(*n*)–O(*n*21)	2.40(2)	2.60(2)
Cd(*n*)–O(*n*22)	2.39(2)	2.27(2)
Cd(*n*)–O(*n*31)	2.37(2)	
Cd(*n*)–O(*n*32)	2.40(2)	
Cd(*n*)–O(*n*411)	2.36(3)	
Cd(*n*)–O(*n*412)	2.43(8)	
Cd(*n*)–O(*n*421)	2.40(6)	
Cd(*n*)–O(*n*422)	2.45(7)	

(*b*) Angles

(*i*) Cations	$n = 1$	$n = 2$	$n = 3$
N(*n*1)–Cd(*n*)–N(*n*2)	90.6(6)	91.9(7)	92.9(10)
N(*n*1)–Cd(*n*)–N(*n*3)	177.3(10)	177.1(8)	174.2(10)
N(*n*1)–Cd(*n*)–N(*n*4)	89.7(7)	90.0(6)	87.8(9)
N(*n*2)–Cd(*n*)–N(*n*3)	90.1(7)	90.5(6)	92.7(10)
N(*n*2)–Cd(*n*)–N(*n*4)	124.0(8)	125.5(6)	125.1(8)
N(*n*3)–Cd(*n*)–N(*n*4)	92.1(9)	90.0(5)	87.8(10)
N(*n*1)–Cd(*n*)–O(*n*1)	89.3(7)	88.5(5)	90.3(8)
N(*n*1)–Cd(*n*)–O(*n*2)	87.5(7)	89.6(7)	88.5(8)
N(*n*2)–Cd(*n*)–O(*n*1)	87.6(7)	88.2(6)	92.2(7)
N(*n*3)–Cd(*n*)–O(*n*1)	88.1(9)	89.9(5)	91.1(8)
N(*n*3)–Cd(*n*)–O(*n*2)	90.3(8)	87.5(6)	87.9(8)
N(*n*4)–Cd(*n*)–O(*n*2)	96.8(6)	94.2(6)	90.8(7)
O(*n*1)–Cd(*n*)–O(*n*2)	51.6(6)	52.1(5)	51.9(6)

(*ii*) Anions	$n = 4$	$n = 5$
O(*n*11)–Cd(*n*)–O(*n*12)	54.1(8)	52.4(5)
O(*n*21)–Cd(*n*)–O(*n*22)	51.5(8)	51.5(6)
O(*n*31)–Cd(*n*)–O(*n*32)	49.5(8)	
O(*n*411)–Cd(*n*)–O(*n*421)	55.3(12)	
O(*n*412)–Cd(*n*)–O(*n*422)	41.8(22)	

* N–C, N–O, and C–C distances have standard values (σ 0.03—0.05 Å, apart from some distances involving disordered atoms which have σ up to 0.10 Å).

Table 3. Carbon-13 resonances [a] for $M(L^4)X_2$ and ligand L^4 in [$^2H_3$]methanol unless stated otherwise (for assignments refer to Figure 1)

M	X	*T*/K	N–*C*H$_2$–C	N–CH$_3$	C–*C*H$_2$–C	Assignment
Cd	NO_3^-	301	65.0, 63.5	44.1, 43.3	21.9	A
			65.8, 61.0, 59.8 [b]	47.5,[c] 43.0, 42.3	22.0, 21.7	D
Cd	O_2CMe^-	310	*ca.* 64.9 (vbr), *ca.* 62.9 (vbr)	*ca.* 45 (vbr)	(21.6) [d]	A
			65.6, *ca.* 61.4 (vbr), 60.2, *ca.* 58.8 (vbr)	47.8,[c] 43.1, 41.9	22.0, 21.8	D
Hg	NO_3^-	240	66.5 (vbr), *ca.* 63 (vbr)	49.9, 43.9	22.5	A
			67.1, 63.3, 62.1 [b]	46.5,[c] 44.2	22.9, 22.2	D
[e] Hg	NO_3^-	300	55.1	41.5	22.6	A
[e] Hg	O_2CMe^-	300	54.8	41.9	23.5 (22.9) [d]	A
[e] Hg	Cl^-	300	56.9 (vbr)	42.8	23.1	A
[e] Pb	NO_3^-	300	55.2	41.3	22.4	A
[e] Pb	O_2CMe^-	300	55.6	42.7	24.9 (25.7) [d]	A
L^4		300	54.98	42.96	24.24	
			55.63 [e]	43.02 [e]	25.80 [e]	

[a] δ/p.p.m., relative to 1,4-dioxane at δ 67.4; vbr = very broad. [b] *ca.* twice the area of the other N–CH$_2$ resonances. [c] *ca.* twice the area of the other N–CH$_3$ resonances. [d] Acetate methyl group. [e] Solvent [$^2H_3$]nitromethane.

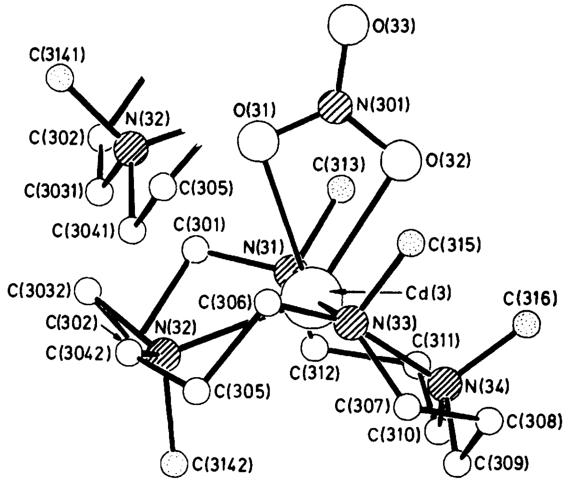


Figure 3. The $[CdL^4(NO_3)]^+$ ion, in the 'three-up, one-down' form, with an inset giving the alternative 'four-up' form. The atomic numbering for Cd(3) is given; for Cd(1) and Cd(2), the first digit should be amended appropriately

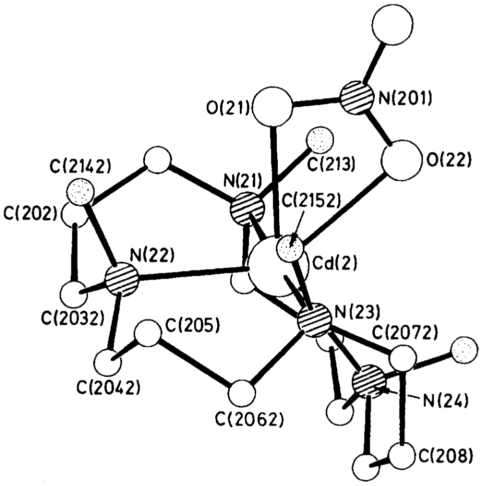


Figure 4. The $[CdL^4(NO_3)]^+$ ion in the 'four-up' form, with the twisted N(21)–N(23) axis

ing a greater energy barrier to folding than in the case of the nitrate and acetate complexes.

Crystal Structure of $[CdL^4(NO_3)]_2[Cd(NO_3)_4]$.—The overall cation geometry is trigonal bipyramidal (Figures 3 and 4), regarding the nitrate groups as occupying one position. This is a more satisfactory description than pseudo-octahedral, in view of the large N(2)–Cd–N(4) angles (124—125°). The nitrate group lies precisely in the equatorial plane [N(1)–Cd–O and N(2)–Cd–O are very close to 90°]. The presence of this group and the compact arrangement of the macrocyclic ligand leaving space for it, while still allowing alternative conformations, makes it likely that either nitrate groups or solvent molecules are also attached in solution. The anions (Figure 5) have the classic tetranitrato-arrangement with dodecahedral co-ordination geometry. It is apparently relatively uncrowded about Cd allowing some flexibility as one ion has regular Cd–O distances, but one of the nitrate groups is disordered, while the other ion has significant differences in Cd–O distances (four shorter and four longer, at 2.27 and 2.57 Å respectively). There is also some inequality of the Cd–O distance in the cations.

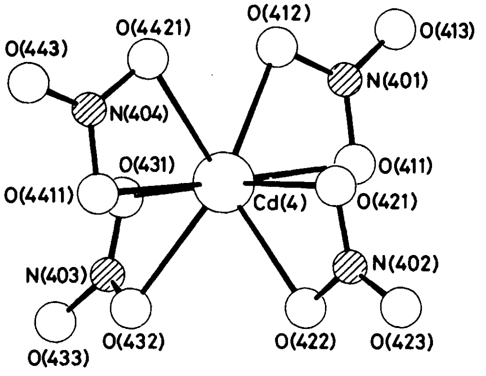


Figure 5. The $[Cd(NO_3)_4]^{2-}$ ion, with the atomic numbering for Cd(4)

The Cd–N distances show a very clear pattern, with average values for Cd–N(axial) of 2.41 Å and for Cd–N(equatorial) of 2.37 Å. The bond angles show the remarkable regularity of the trigonal bipyramids, with almost the only distortion being the N(*n*2)–Cd(*n*)–N(*n*4) angle, increased to 124.5° (average) from the idealised 120°. This increase gives N–Cd–O angles in the equatorial plane very close to 90°. These correspond almost exactly to the N(axial)–Cd–O angles, and therefore will equalise and minimise the non-bonded ligand–ligand repulsions.

The least expected result of the structure analysis is the occurrence of different ligand conformations, not independently in the three individual cations, but as disordered alternatives for each of them. All three cations show the methyl group conformation ' three up, one down ' (Figure 3); for Cd(1) and Cd(3), a simple inversion at N(*n*2) switches the positions of C(*n*03), C(*n*04), and C(*n*14), leading to the ' four-up ' conformation. The ' two-down, two-up ' arrangement might also be expected, but this probably leads to a too close approach between the ' down ' methyl groups on N(*n*2) and N(*n*4). However, Cd(2) does show another variant, still the ' four-up ' conformation, but with a twist in the C–C–C chain between N(23) and N(24), and a related shift to C(206). The effect of this is apparent on the methyl groups C(213) and C(215). The corresponding groups on Cd(1) and Cd(3) have their C–N directions exactly parallel with dihedral angles C(*n*13)–N(*n*1)–N(*n*3)–C(*n*15) of 2(3) and 0(2)° respectively. On Cd(2), they are by contrast substantially twisted [dihedral angle 79(3)° in the twisted form, 4(2)° in the other form].

The first two conformations come very close to having mirror symmetry though this is not crystallographically expressed. In solution, they might therefore be expected to contain three distinct methyl groups (1 : 2 : 1) (three-up, one-down) and two distinct groups (2 : 2) (four-up). The alternative ' four-up ' conformation of Cd(2) has a non-crystallographic two-fold axis and should therefore have two further types of methyl group, but as the interconversion of these two ' four-up ' varieties involves only flipping of the C–C–C ring, it is very unlikely that they would be distinguishable in solution.

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