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Stability constants of the zinc(II), cadmium(II) and mercury(II) complexes of the mono-aza coronands 1,4,7,10-tetraoxa-13-azacyclopentadecane (L^1), 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) and 1,4,7-trioxa-10-azacyclododecane (L^3). Crystal and molecular structures of the cadmium complexes of L^1 and L^2

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Abstract

The stability constants for the 1:1 complexes of zinc, cadmium and mercury with 1,4,7,10-tetraoxa-13-azacyclopentadecane (L^1), 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) and 1,4,7-trioxa-10-azacyclododecane (L^3) have been determined potentiometrically (0.1 M NEt_4ClO_4, 95% methanol). Reaction between L^1 or L^2 and cadmium nitrate tetrahydrate in methanol results in the isolation of colourless crystalline solids. Crystals of $[Cd(L^1)(NO_3)_2]$ are monoclinic, space group $P2_1/c$ with $a=7.614(2)$, $b=28.566(2)$, $c=7.707(1)$ Å, $\beta=107.364(9)°$; $R=0.025$, $R_w=0.027$ for 2195 ($I>3\sigma(I)$) reflections. The structure of $[Cd(L^1)(NO_3)_2]$ consists of an almost planar macrocyclic ligand enclosing a cadmium ion in its cavity, with a monodentate and a bidentate nitrate ligand coordinating the cadmium ion on opposite sides of the macrocycle. Crystals of $[Cd(L^2)(NO_3)_2]$ are orthorhombic, space group $Pca2_1$ with $a=8.738(11)$, $b=14.140(9)$, $c=15.176(8)$ Å; $R=0.019$, $R_w=0.022$ for 3058 ($I>2.5\sigma(I)$) reflections. The structure of $[Cd(L^2)(NO_3)_2]$ consists of a cadmium atom enclosed in the cavity of the macrocycle, with a monodentate and a bidentate nitrate ligand on opposite sides of the macrocycle. Two of the oxygen atoms of L^2 in $[Cd(L^2)(NO_3)_2]$ do not coordinate the cadmium ion, but the remaining donor atoms of the macrocycle form an almost planar assembly around the cadmium.

Introduction

We have been investigating the interactions of the 15- and 18-membered ring oxaaza- and oxacoronands with Group 12 and 14 cations. Previously we have reported the interactions of 1,4,7,10-tetraoxa-13-azacyclopentadecane (L^1) and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) with Pb(II) [1] and Hg(II) [2], and we have now extended this study to the products formed from interaction of cadmium(II) with these ligands. We also report the stability constants for L^1, L^2 and 1,4,7-trioxa-10-azacyclododecane (L^3) with Group 12 cations.

Experimental

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Jeol GX400 spectrometer at 399.65 and 100.40 MHz, respectively. Elemental analyses were carried out by the University of Queensland Microanalytical Service and National Analytical Laboratories, Ferntree Gully, Vic., Australia. 1,4,7,10-Tetraoxa-13-azacyclopentadecane (L^1) ($^{13}C\{^1H\}$ NMR (dmso-D_6): 69.6, 69.4, 69.3, 69.2 (CH_2CH_2O), 48.5 (NCH_2CH_2O)) and 1,4,7,10,13-pentaoxa-16-azacyclooctadecane (L^2) ($^{13}C\{^1H\}$ NMR (dmso-D_6): 70.0, 69.9, 69.8, 69.73, 69.67 (CH_2CH_2O), 49.0 (NCH_2CH_2O)) were prepared by literature procedures [3].

Synthesis of $[Cd(L^1)(NO_3)_2]$

1,4,7,10-Tetraoxa-13-azacyclopentadecane (L^1) (0.36 g, 1.6 mmol) and cadmium nitrate tetrahydrate (0.50

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TABLE 1. Crystal data, data collection and refinement for $[Cd(L^1)(NO_3)_2]$ and $[Cd(L^2)(NO_3)_2]$

Compound	$[Cd(L^1)(NO_3)_2]$	$[Cd(L^2)(NO_3)_2]$
Formula	$C_{10}H_{21}CdN_3O_{10}$	$C_{12}H_{25}CdN_3O_{11}$
Formula weight	455.7	499.8
Crystal data		
Crystal size (mm)	0.35×0.23×0.14	0.50×0.50×0.30
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pca2_1$
a (Å)	7.614(2)	8.738(11)
b (Å)	28.566(2)	14.140(9)
c (Å)	7.707(1)	15.176(8)
β (°)	107.364(9)	
V (Å^3)	1599.7(5)	1875(3)
Z	4	4
D_{calc} (g/cm^3)	1.892	1.770
$F(000)$	920	1016
μ(Mo Kα) (cm^{-1})	14.1	12.2
Data collection and refinement		
Temperature (K)	296	298
Scan type	$2\theta/\omega$	$2\theta/\omega$
Scan range, in ω (°)	$0.45+0.34 \tan \theta$	$0.60+0.34 \tan \theta$
$2\theta_{max}$ (°)	50	50
Dataset (h, k, l)	0:9; 0:34; −9:9	0:10; 0:16; −18:18
Crystal decay (%)	4.2	3.2
Total no. reflections	3159	3806
No. unique reflections	3096	3251
No. observed reflections	2195	3058
Reflections observed if	$I>3\sigma(I)$	$I>2.5\sigma(I)$
No. variables	217	246
R	0.025	0.019
R_w	0.027	0.022
Weighting	$1.6/(\sigma^2(F_o)+0.0024F^2)$	$1.0/(\sigma^2(F_o)+0.0028F^2)$
GOF	2.01	0.60
Max Δ/σ (final cycle)	0.03	0.12
Residual density, (e/Å^3)	0.50	0.74

g, 1.6 mmol) were stirred in methanol (10 ml) for 30 min. The solution was evaporated to dryness under reduced pressure, and the white residue recrystallized from boiling methanol. Colourless crystals of $[Cd(L^1)(NO_3)_2]$ were isolated after decanting the solvent and drying the product under vacuum (0.51 g, 68%). $^{13}C\{^1H\}$ NMR (dmso-D$_6$): 69.4, 69.2, 69.1, 68.8 ($CH_2\mathit{C}H_2O$), 48.3 ($N\mathit{C}H_2CH_2O$). *Anal.* Calc. for $C_{10}H_{21}CdN_3O_{10}$: C, 26.4; H, 4.7; N, 9.2. Found: C, 26.7; H, 4.4; N, 9.1%.

Synthesis of $[Cd(L^2)(NO_3)_2]$

1,4,7,10,13-Pentaoxa-16-azacyclooctadecane (L^2) (0.49 g, 1.9 mmol) dissolved in methanol (2 ml) was added to a methanol solution (3 ml) of cadmium nitrate tetrahydrate (0.60 g, 1.9 mmol). A white precipitate formed immediately. The suspension was stirred for 10 min, the solution heated just to reflux, methanol (20 ml) added and the suspended solids removed by filtration. The clear filtrate was cooled slowly to 4 °C. Upon standing colourless crystals were deposited. The white product was isolated after decanting the mother liquor, washing with cold methanol and drying *in vacuo*. A second crop of crystalline product was obtained after concentration of the mother liquor and recrystallization of the product from hot methanol (0.55 g, 58%). $^{13}C\{^1H\}$ NMR (dmso-D$_6$): 69.7, 69.6, 68.8 ($CH_2\mathit{C}H_2O$), 48.4 ($N\mathit{C}H_2CH_2O$). *Anal.* Calc. for $C_{12}H_{25}CdN_3O_{11}$: C, 28.8; H, 5.0; N, 8.4. Found: C, 28.5; H, 5.0; N, 8.2%.

Potentiometric titrations and data evaluation

The potentiometric titrations were carried out under a solvent-saturated nitrogen atmosphere in a water jacketed vessel maintained at 298 K. Data were obtained from 10 ml aliquots of solutions containing 0.006 M $HClO_4$, 0.1 M NEt_4ClO_4 and approximately 1.0×10^{-3} M ligand titrated with 0.10 M NEt_4OH. All solutions were in 95% vol./vol. methanol/water. Complete experimental details have been reported previously [1].

Single crystal X-ray structure determinations

Crystal data

See Table 1.

TABLE 2. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $[Cd(L^1)(NO_3)_2]$

Atom	x	y	z	U_{eq}[a] (Å^2)
Cd(1)	1.19833(3)	0.13278(1)	1.18751(3)	0.0363(1)
O(4)	1.4276(3)	0.10978(7)	1.0525(3)	0.0380(7)
O(7)	1.1437(3)	0.16982(8)	0.9062(3)	0.0437(8)
O(10)	0.9534(3)	0.18558(8)	1.1560(3)	0.0424(7)
O(13)	1.0610(3)	0.11892(8)	1.4188(3)	0.0475(8)
O(1A)	0.9010(4)	0.09096(9)	0.9941(4)	0.0626(10)
O(2A)	1.0274(4)	0.04078(12)	0.8591(4)	0.0797(13)
O(3A)	0.7456(4)	0.05919(12)	0.7431(5)	0.0823(11)
O(1B)	1.3581(4)	0.20330(10)	1.3011(4)	0.0721(11)
O(2B)	1.4759(5)	0.14673(10)	1.4720(4)	0.0701(11)
O(3B)	1.5832(4)	0.21582(10)	1.5400(4)	0.0731(11)
N(1)	1.2584(4)	0.05664(9)	1.2598(4)	0.0387(9)
N(1A)	0.8921(4)	0.06379(10)	0.8638(4)	0.0439(10)
N(1B)	1.4742(4)	0.18896(10)	1.4415(4)	0.0433(10)
C(2)	1.4453(5)	0.04590(12)	1.2558(5)	0.0466(12)
C(3)	1.4665(5)	0.06052(12)	1.0753(5)	0.0464(11)
C(5)	1.3900(5)	0.12579(13)	0.8677(5)	0.0463(11)
C(6)	1.3125(5)	0.17435(14)	0.8596(5)	0.0485(11)
C(8)	1.0449(6)	0.21253(13)	0.9053(5)	0.0533(12)
C(9)	0.8839(5)	0.20163(13)	0.9695(5)	0.0511(12)
C(11)	0.8153(5)	0.16693(14)	1.2277(5)	0.0521(11)
C(12)	0.9077(5)	0.14917(15)	1.4147(6)	0.0584(14)
C(14)	1.0398(6)	0.06914(13)	1.4332(5)	0.0536(12)
C(15)	1.2199(5)	0.04711(12)	1.4337(5)	0.0486(11)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U.

Data collection and processing

Data sets were measured and corrected for absorption (ψ scans) using a CAD-4 diffractometer fitted with graphite monochromated Mo Kα radiation source ($\lambda = 0.71069$). The structures were solved using the Patterson-heavy atom technique (SHELXS86 [4]) and refined using full matrix least-squares (SHELX76 [5]). Residuals R, R_w and goodness of fit are quoted at convergence. Neutral complex scattering factors were used [6]. Hydrogen atoms were included at idealized positions as constrained estimates except for the hydrogen bonded to N(1) in $[Cd(L^2)(NO_3)_2]$, which was located from Fourier-difference maps. No disorder was found. Figures were drawn with PLATON [7]. Final atomic coordinates and equivalent isotropic thermal parameters for $[Cd(L^1)(NO_3)_2]$ and $[Cd(L^2)(NO_3)_2]$ are listed in Tables 2 and 3, respectively. See also 'Supplementary material'.

Results and discussion

TABLE 3. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for $[Cd(L^2)(NO_3)_2]$

Atom	x	y	z	U_{eq}[a] (Å^2)
Cd(1)	0.44826(2)	0.22816(1)	0.5[b]	0.0317(1)
O(4)	0.3452(2)	0.10373(12)	0.40584(13)	0.0427(6)
O(7)	0.5373(2)	0.07160(15)	0.54159(14)	0.0394(6)
O(10)	0.5504(2)	0.23117(13)	0.64891(18)	0.0395(9)
O(13)	0.5247(2)	0.42049(14)	0.57372(17)	0.0443(6)
O(16)	0.4191(3)	0.4896(2)	0.3972(2)	0.0684(9)
O(1A)	0.7052(3)	0.26069(14)	0.48585(16)	0.0467(8)
O(2A)	0.6686(2)	0.17398(16)	0.36972(15)	0.0542(7)
O(3A)	0.8953(3)	0.21902(16)	0.4033(2)	0.0628(9)
O(1B)	0.2311(3)	0.16011(15)	0.58396(18)	0.0611(8)
O(2B)	0.2232(3)	0.30824(17)	0.56432(17)	0.0583(8)
O(3B)	0.0332(3)	0.2380(3)	0.6280(3)	0.0677(11)
N(1)	0.3445(3)	0.30093(18)	0.37547(16)	0.0405(7)
N(1A)	0.7580(3)	0.21725(13)	0.41847(17)	0.0368(7)
N(1B)	0.1596(3)	0.23547(17)	0.59313(17)	0.0383(8)
C(2)	0.2425(4)	0.2332(2)	0.3293(3)	0.0507(11)
C(3)	0.3170(3)	0.1378(2)	0.31882(18)	0.0479(8)
C(5)	0.4282(4)	0.0167(2)	0.4078(3)	0.0509(10)
C(6)	0.4533(3)	−0.0058(2)	0.5047(4)	0.0485(9)
C(8)	0.5536(3)	0.0632(3)	0.6348(2)	0.0490(10)
C(9)	0.6404(3)	0.1479(2)	0.6667(2)	0.0483(9)
C(11)	0.6297(4)	0.3137(2)	0.6799(2)	0.0492(10)
C(12)	0.5315(4)	0.3988(3)	0.6646(3)	0.0552(11)
C(14)	0.4374(4)	0.5051(3)	0.5597(3)	0.0633(13)
C(15)	0.4739(5)	0.5463(3)	0.4685(3)	0.0694(13)
C(17)	0.5323(3)	0.4273(3)	0.3625(3)	0.0541(11)
C(18)	0.4481(3)	0.3510(3)	0.3145(2)	0.0500(10)

[a] U_{eq} = 1/3 of the trace of the orthogonalized U. [b] Fixed position (spacegroup $Pca2_1$, chirality confirmed).

Protonation constants of the oxaazacoronands L^1 and L^2 have been reported [1]. The formation constants of the complexes between the ions Zn(II), Cd(II) and Hg(II) with L^1, L^2, L^3 and a variety of oxaazacoronands and azacoronands are compared in Table 4. Comparison of the stability constants of the Zn(II) and Cd(II) complexes of the 15-membered ring coronands L^1, (21) and [15]aneN_4 illustrates the influence of the increasing number of N donors. The stability constants for Zn(II) with L^2 and Cd(II) with L^1 and L^3 could only have upper limits placed on their values due to competing formation of insoluble metal hydroxides. No formation of mercuric oxide was observed during the titration of L^1, L^2 or L^3 in the presence of Hg^{2+} above pH 3, consistent with the high stability of these mercury complexes. The relatively low formation constants for the complexes of L^1, L^2 and L^3 with Zn(II) and Cd(II) compared with their Hg(II) analogues is an indication of how strongly water competes with the macrocycles for the former two metals. The water ligands in the mercury complexes of L^1, L^2 and L^3 are quite strongly polarized by the Hg(II) ion, as the pK_as for $[Hg(L)(H_2O)_n]$ lie between 3 and 4 (Table 4). For each of the metals in this study, there is no evidence for any size selectivity between L^1, L^2 and L^3. Similarly, for any one of L^1, L^2 or L^3, Hg(II) forms the most stable complexes, even though Hg(II) does not sit in the cavity of the macrocycle L^1 [2], while Cd(II) does (see below). Luckay and Hancock [13] have proposed that the Cd(II) ion should best fit into the cavity of

TABLE 4. Complex formation constants for oxaaza- and azacoronands with Zn(II), Cd(II) and Hg(II)

Ligand	pK_a [a]	log β [b]			pK_a([Hg(L)(H_2O)$_n$])
		Zn	Cd	Hg	
L^3	9.35(2)[c] 9.05(1)[e]	3.7(1)[c]	< 4.5[c, d]	> 11[c]	3.7(1)[c]
L^1	9.17(3)[c, f] 8.69(1)[e, f]	4.1(1)[c]	< 3.7[c, d]	10.3(2)[c]	3.3(1)[c]
L^2	9.82(2)[c, f] 9.41(1)[e, f]	< 4.0[c, d]	3.7(1)[c]	> 12[c]	3.9(1)[c]
(21)		7.42[g]	8.72[h]		
(22)		4.84[g] 3.19[j]	7.83[h] 5.25[k]	 17.85[k]	
[13]aneN_4		15.74[l]	12.71[m]		
[14]aneN_4		15.34[l]	11.23[m]		
[15]aneN_4		15.35[l]	12.10[m]		
[16]aneN_4		13.05[l]	12.65[m]		

[a] The equilibrium constant K_a refers to the equation $LH^+ \leftrightharpoons L + H^+$, and p$K_a = -\log_{10} K_a$. [b] The formation constant β refers to the equation $M^{n+} + L \leftrightharpoons ML^{n+}$, and is defined as $\beta = [ML^{n+}]/([M^{n+}][L])$. [c] This work, 0.1 M NEt_4ClO_4, 95% vol./vol. methanol/water, 298 K. The apparent pK_w of water in 95% vol./vol. methanol/water was determined as 14.92(5) (neutrality at pH 7.46), $I = 0.1$ M NEt_4ClO_4 (compared with the experimentally determined value for aqueous 0.1 M NEt_4ClO_4 of 13.83(2)). [d] Values for these formation constants are of limited significance or could only have an upper limit defined because formation of metal hydroxides precluded use of some or all of the data points in the pH range of interest. [e] This work, 0.1 M aqueous NEt_4ClO_4, 298 K. [f] Ref. 1. [g] 0.05 M NEt_4ClO_4, anhydrous methanol, 298 K [8]. [h] 0.05 M NEt_4ClO_4, anhydrous methanol, 298 K [9]. [j] 0.1 M aqueous Et_4NClO_4, 298 K [10]. [k] 0.1 M ionic strength aqueous solution, 298 K [11]. [l] 0.5 M aqueous KNO_3, 298 K [12]. [m] 0.1 M aqueous $NaNO_3$, 298 K [13].

the [n]aneN_4 macrocycle in which the maximum number of larger chelate rings is formed, with a progressive change from octahedral to tetrahedral geometry for the [n]aneN_4 complexes with increasing macrocycle size. This proposal does not hold for the oxaazacoronands L^1 and L^2.

Reaction of L^1 with cadmium nitrate tetrahydrate in methanol and subsequent recrystallization from hot methanol results in the isolation of a colourless crystalline solid of empirical formula [Cd(L^1)(NO_3)$_2$]. The structure of [Cd(L^1)(NO_3)$_2$] consists of the cation and the two nitrate anions in discrete clusters in the crystal lattice (Fig. 1). Each of the four oxygen atoms, and the nitrogen atom, of the macrocycle are bound to the cadmium with Cd–O distances ranging from 2.336(2) to 2.376(2) Å and a Cd–N distance of 2.258(3) Å. Relevant bond lengths and bond angles are reported in Table 5. The cadmium atom lies in the plane of the approximately isosceles triangle formed by O(4)–O(10)–O(13) with O(4)–Cd–O(10) 142.65(8)°, O(4)–Cd–O(13) 146.68(8)° and O(10)–Cd–O(13), 70.65(8)°. The atoms N(1) and O(7) lie 0.943(11) and 0.396(10) Å, respectively, below this plane as defined by the orientation of the molecule in Fig. 1. The coordination sphere in the cadmium complex of L^1 is completed by the nitrate anions. Both nitrate groups lie in proximity to the cation with one coordinated to the cadmium above the O(4)–O(10)–O(13) plane as an asymmetric bidentate ligand with distances Cd(1)–O(1B) and Cd(1)–O(2B) of 2.381(3) and 2.582(3) Å, respectively. The second nitrate group is only weakly coordinated to the cadmium below this plane through a single oxygen donor, with Cd(1)–O(1A) 2.600(3) Å.

The structure of [Cd(L^2)(NO_3)$_2$] is quite unlike those of the complexes of L^1 and L^2 with Pb(II) [1] or Hg(II) [2], or indeed L^1 with Cd(II), in that it shows no symmetry or near-symmetry in the metal–macrocycle moiety. The structure of [Cd(L^2)(NO_3)$_2$] consists of a cadmium ion placed off-centre in the cavity of a 1,4,7,10,13-pentaoxa-16-azacyclooctadecane ligand, with one nitrate group either side of the macrocyclic cavity (Fig. 2). The macrocyclic nitrogen atom N(1) and the three oxygen atoms O(4), O(7) and O(10) coordinate the cadmium ion, the cadmium–nitrogen bond Cd(1)–N(1) being the shortest macrocyclic donor–cadmium distance, 2.335(4) Å. The location of the hydrogen atom attached to the macrocyclic nitrogen atom in the difference Fourier map made the assignment of this atom unequivocal. The macrocyclic cadmium oxygen distances are Cd(1)–O(4) 2.439(4); Cd(1)–O(7) 2.430(4); Cd(1)–O(10) 2.430(4); Cd(1)–O(13) 3.016(4) and Cd(1)–O(16) 4.021(6) Å. The atoms Cd(1), N(1), O(4), O(7) and O(10) almost lie in one plane: N(1) and O(7) lie 0.142(7) and 0.274(7) Å, respectively,

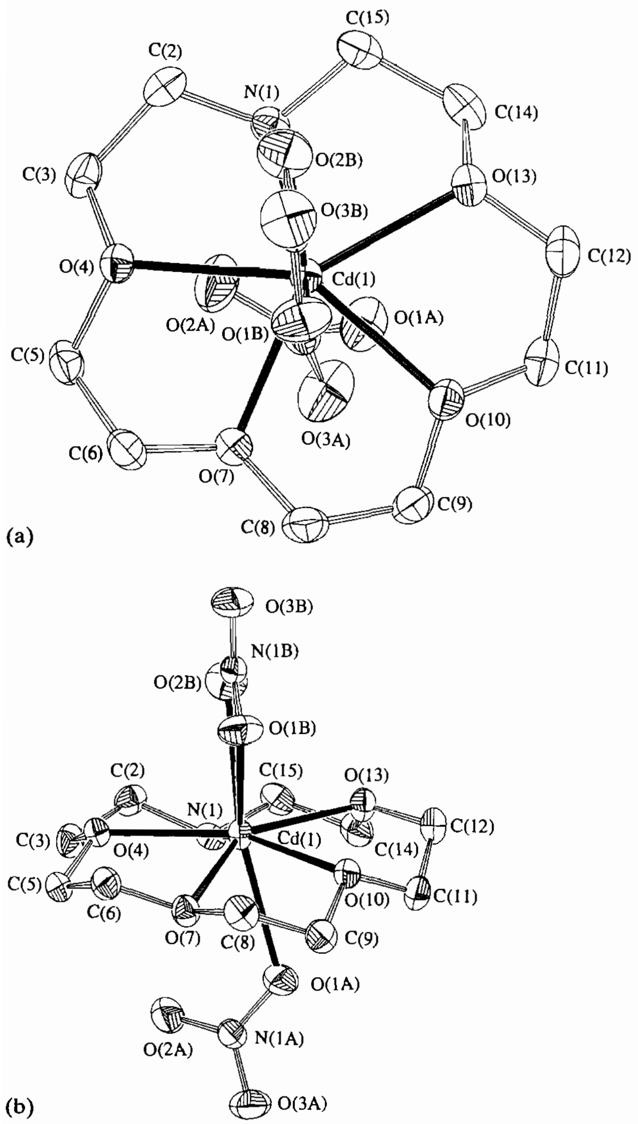

Fig. 1. PLATON plot of $[Cd(L^1)(NO_3)_2]$ showing (a) macrocyclic numbering scheme adopted, and (b) view of the nitrate coordination (30% ellipsoids).

above the calculated least-squares plane Cd(1) N(1) O(4) O(7) O(10), while O(4) and O(10) lie 0.274(6) and 0.171(8) Å below the plane. The atoms O(13) and O(16) lie somewhat further from this least-squares plane, 0.344(9) and 0.785(9) Å, respectively. The coordination sphere in the cadmium complex of L^2 is completed by the nitrate anions. Both nitrate groups lie in proximity to the cation with one coordinated to the cadmium above the macrocycle 'plane' as an symmetric bidentate ligand with distances Cd(1)–O(1B) Cd(1)–O(2B) of 2.480(4) and 2.470(4) Å, respectively. The second nitrate group is coordinated to the cadmium below this plane through a single oxygen donor, with Cd(1)–O(1A) 2.302(4) Å. Further bond distances and bond angles for $[Cd(L^2)(NO_3)_2]$ are listed in Table 6.

TABLE 5. Bond lengths (Å) and bond angles (°) for $[Cd(L^1)(NO_3)_2]$

Bond lengths (Å)			
Cd(1)–N(1)	2.258(3)	N(1)–C(2)	1.465(5)
Cd(1)–O(4)	2.376(2)	C(2)–C(3)	1.507(5)
Cd(1)–O(7)	2.336(2)	C(3)–O(4)	1.438(4)
Cd(1)–O(10)	2.354(2)	O(4)–C(5)	1.441(4)
Cd(1)–O(13)	2.354(2)	C(5)–C(6)	1.501(5)
Cd(1)–O(1A)	2.600(3)	C(6)–O(7)	1.440(5)
Cd(1)–O(1B)	2.381(3)	O(7)–C(8)	1.432(5)
Cd(1)–O(2B)	2.582(3)	C(8)–C(9)	1.485(6)
O(1A)–N(1A)	1.255(4)	C(9)–O(10)	1.450(4)
O(2A)–N(1A)	1.232(5)	O(10)–C(11)	1.429(5)
O(3A)–N(1A)	1.228(5)	C(11)–C(12)	1.491(6)
O(1B)–N(1B)	1.245(4)	C(12)–O(13)	1.445(5)
O(3B)–N(1B)	1.216(4)	O(13)–C(14)	1.439(4)
O(2B)–N(1B)	1.228(4)	C(14)–C(15)	1.508(6)
		C(15)–N(1)	1.480(5)
Bond angles (°)			
O(4)–Cd(1)–O(7)	70.69(8)	C(2)–N(1)–C(15)	115.9(3)
O(4)–Cd(1)–O(10)	142.65(8)	N(1)–C(2)–C(3)	109.5(3)
O(4)–Cd(1)–O(13)	146.68(8)	O(4)–C(3)–C(2)	108.0(3)
O(4)–Cd(1)–N(1)	73.77(9)	C(3)–O(4)–C(5)	113.8(3)
O(7)–Cd(1)–O(10)	72.41(8)	O(4)–C(5)–C(6)	107.1(3)
O(7)–Cd(1)–O(13)	141.53(8)	O(7)–C(6)–C(5)	106.0(3)
O(7)–Cd(1)–N(1)	129.22(10)	C(6)–O(7)–C(8)	115.4(3)
O(10)–Cd(1)–O(13)	70.65(8)	O(7)–C(8)–C(9)	107.7(3)
O(10)–Cd(1)–N(1)	137.61(10)	O(10)–C(9)–C(8)	107.6(3)
O(13)–Cd(1)–N(1)	75.77(10)	C(9)–O(10)–C(11)	114.1(3)
Cd(1)–O(4)–C(3)	111.6(2)	O(10)–C(11)–C(12)	108.1(3)
Cd(1)–O(4)–C(5)	112.9(2)	O(13)–C(12)–C(11)	111.7(3)
Cd(1)–O(7)–C(6)	110.32(19)	C(12)–O(13)–C(14)	119.0(3)
Cd(1)–O(7)–C(8)	109.77(19)	O(13)–C(14)–C(15)	106.8(3)
Cd(1)–O(10)–C(9)	110.4(2)	N(1)–C(15)–C(14)	110.3(3)
Cd(1)–O(10)–C(11)	111.9(2)	O(1A)–Cd(1)–O(1B)	149.48(10)
Cd(1)–O(13)–C(12)	114.9(2)	O(1A)–Cd(1)–O(2B)	155.47(9)
Cd(1)–O(13)–C(14)	108.1(2)	O(1B)–Cd(1)–O(2B)	50.08(10)
Cd(1)–N(1)–C(2)	108.8(2)	Cd(1)–O(1B)–N(1B)	101.2(2)
Cd(1)–N(1)–C(15)	108.7(2)	Cd(1)–O(2B)–N(1B)	91.7(2)
Cd(1)–O(1A)–N(1A)	124.9(2)	O(4)–Cd(1)–O(1B)	91.92(9)
O(1A)–Cd(1)–O(4)	104.46(9)	O(4)–Cd(1)–O(2B)	83.82(10)
O(1A)–Cd(1)–O(7)	78.03(9)	O(7)–Cd(1)–O(1B)	83.56(9)
O(1A)–Cd(1)–O(10)	73.01(8)	O(7)–Cd(1)–O(2B)	126.32(9)
O(1A)–Cd(1)–O(13)	81.33(9)	O(10)–Cd(1)–O(1B)	78.34(9)
O(1A)–Cd(1)–N(1)	77.08(10)	O(10)–Cd(1)–O(2B)	114.28(9)
O(13)–Cd(1)–O(1B)	99.07(9)	O(13)–Cd(1)–O(2B)	79.57(10)
O(1B)–Cd(1)–N(1)	132.90(11)	O(2B)–Cd(1)–N(1)	83.39(10)
O(3A)–N(1A)–O(1A)	119.5(3)	O(1B)–N(1B)–O(3B)	120.7(3)
O(3A)–N(1A)–O(2A)	120.0(3)	O(1B)–N(1B)–O(2B)	117.0(3)
O(1A)–N(1A)–O(2A)	120.5(3)	O(3B)–N(1B)–O(2B)	122.3(3)

The Cd–N bond length in $[Cd(L^2)(NO_3)_2]$ is similar to those observed in the cadmium complex of the oxaazacoronand 1,4,10-trioxa-7,13-diazacyclopentadecane (21) [14], 2.352 and 2.338 Å, and shorter than those observed for 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (22), where Cd–N distances of 2.482(22) Å has been reported [15]. In contrast, the Cd–N bond length in $[Cd(L^1)(NO_3)_2]$ is significantly shorter than these values. The range of Cd–O distances in $[Cd(L^1)(NO_3)_2]$, 2.336–2.376 Å, and the Cd–O bond lengths for O(4), O(7) and O(10) in $[Cd(L^2)(NO_3)_2]$,

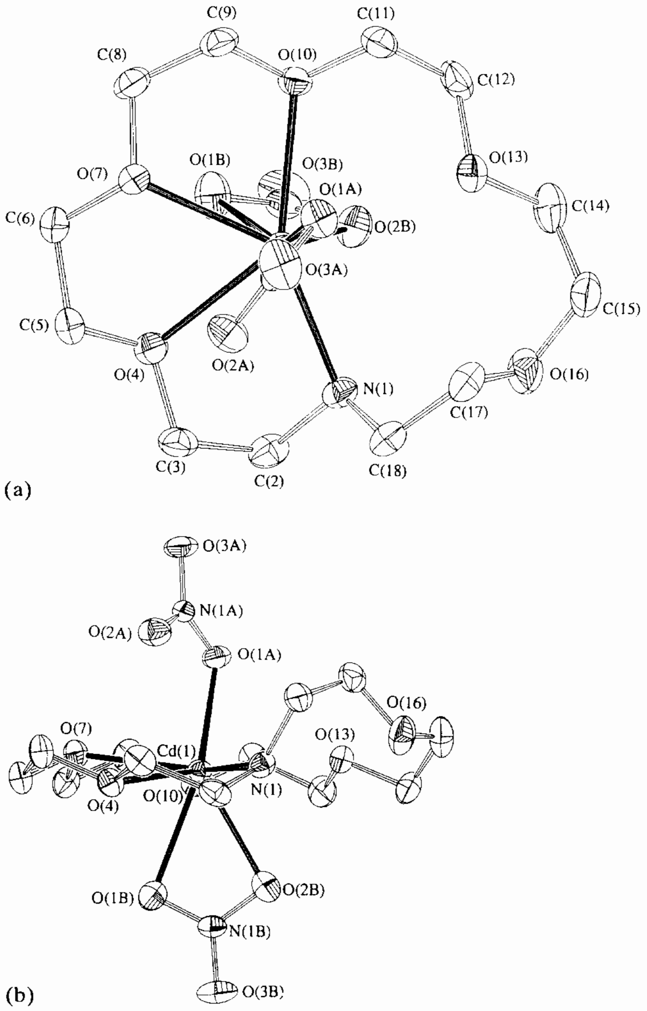

Fig. 2. PLATON plot of $[Cd(L^2)(NO_3)_2]$ showing (a) macrocyclic numbering scheme adopted, and (b) view of nitrate coordination and macrocyclic ring conformation (30% ellipsoids).

TABLE 6. Bond lengths (Å) and bond angles (°) for $[Cd(L^2)(NO_3)_2]$

Bond lengths (Å)			
Cd(1)–O(1A)	2.302(4)	N(1)–C(2)	1.484(5)
Cd(1)–O(4)	2.439(4)	C(2)–C(3)	1.506(5)
Cd(1)–O(7)	2.430(4)	C(3)–O(4)	1.427(4)
Cd(1)–O(10)	2.430(4)	O(4)–C(5)	1.429(4)
Cd(1)–O(1B)	2.480(4)	C(5)–C(6)	1.520(8)
Cd(1)–O(2B)	2.470(4)	C(6)–O(7)	1.432(4)
Cd(1)–N(1)	2.335(4)	O(7)–C(8)	1.427(4)
O(1A)–N(1A)	1.279(4)	C(8)–C(9)	1.498(5)
O(2A)–N(1A)	1.238(4)	C(9)–O(10)	1.441(4)
O(3A)–N(1A)	1.222(4)	O(10)–C(11)	1.436(4)
O(1B)–N(1B)	1.243(4)	C(11)–C(12)	1.496(5)
O(2B)–N(1B)	1.249(4)	C(12)–O(13)	1.414(6)
O(3B)–N(1B)	1.225(4)	O(13)–C(14)	1.435(5)
N(1)–H(1)	0.86(4)	C(14)–C(15)	1.535(7)
		C(15)–O(16)	1.429(6)
		O(16)–C(17)	1.425(5)
		C(17)–C(18)	1.495(6)
		C(18)–N(1)	1.475(4)
Bond angles (°)			
O(4)–Cd(1)–O(7)	67.24(6)	N(1)–C(2)–C(3)	111.6(3)
O(4)–Cd(1)–O(10)	133.88(6)	O(4)–C(3)–C(2)	106.2(3)
O(4)–Cd(1)–N(1)	72.56(8)	C(3)–O(4)–C(5)	113.4(2)
O(7)–Cd(1)–O(10)	69.93(7)	O(4)–C(5)–C(6)	105.9(3)
O(7)–Cd(1)–N(1)	137.39(8)	O(7)–C(6)–C(5)	107.0(3)
O(10)–Cd(1)–N(1)	152.57(8)	C(6)–O(7)–C(8)	112.0(3)
Cd(1)–O(4)–C(3)	111.25(14)	O(7)–C(8)–C(9)	107.7(3)
Cd(1)–O(4)–C(5)	114.94(19)	O(10)–C(9)–C(8)	108.4(2)
Cd(1)–O(7)–C(6)	115.51(18)	C(9)–O(10)–C(11)	109.8(2)
Cd(1)–O(7)–C(8)	111.4(2)	O(10)–C(11)–C(12)	109.0(3)
Cd(1)–O(10)–C(9)	111.12(17)	O(13)–C(12)–C(11)	110.5(3)
Cd(1)–O(10)–C(11)	119.73(18)	C(12)–O(13)–C(14)	110.4(3)
Cd(1)–N(1)–C(2)	109.3(2)	O(13)–C(14)–C(15)	109.9(3)
Cd(1)–N(1)–C(18)	118.74(18)	O(16)–C(15)–C(14)	113.6(3)
O(1A)–Cd(1)–O(4)	116.72(7)	C(15)–O(16)–C(17)	113.2(3)
O(1A)–Cd(1)–O(7)	83.91(7)	O(16)–C(17)–C(18)	106.5(2)
O(1A)–Cd(1)–O(10)	74.04(8)	N(1)–C(18)–C(17)	110.0(3)
O(1A)–Cd(1)–N(1)	102.42(9)	C(2)–N(1)–C(18)	112.5(3)
O(1B)–Cd(1)–N(1)	106.84(9)	O(2B)–Cd(1)–N(1)	78.97(9)
O(4)–Cd(1)–O(1B)	74.85(7)	O(4)–Cd(1)–O(2B)	105.56(7)
O(7)–Cd(1)–O(1B)	76.00(7)	O(7)–Cd(1)–O(2B)	124.74(7)
O(10)–Cd(1)–O(1B)	79.05(8)	O(10)–Cd(1)–O(2B)	85.23(7)
O(1A)–Cd(1)–O(1B)	150.67(8)	Cd(1)–O(1A)–N(1A)	109.30(18)
O(1A)–Cd(1)–O(2B)	136.20(8)	Cd(1)–O(1B)–N(1B)	96.29(17)
O(1B)–Cd(1)–O(2B)	50.63(8)	Cd(1)–O(2B)–N(1B)	96.60(18)
O(1A)–N(1A)–O(2A)	119.2(3)	O(1B)–N(1B)–O(2B)	116.3(3)
O(1A)–N(1A)–O(3A)	119.7(3)	O(1B)–N(1B)–O(3B)	121.8(3)
O(2A)–N(1A)–O(3A)	121.1(3)	O(2B)–N(1B)–O(3B)	121.9(3)

2.430–2.439 Å, are shorter than those observed in the oxaazacoronands (21) and (22), where the Cd–O distances range from 2.495–2.841 Å, the shorter distances associated with the smaller macrocyclic ring [14, 15]. In the case of the oxacoronands 1,4,7,10,13,16-hexaoxacyclooctadecane (18C6) and 1,4,7,10,13-pentaoxacyclopentadecane (15C5), the Cd–O distances range from 2.239–2.752 Å, again the shorter interactions associated with the 15-membered coronand [16–18]. For the complex $[Cd(L^2)(NO_3)_2]$, the interatomic distance Cd–O(13), 3.016(4) Å, is significantly longer than all of these bonding distances, being fractionally less than the sum of the van der Waals radii suggested for cadmium and oxygen [19], 1.58 and 1.52 Å, respectively. While this indicates that there is no formal bond between the cadmium ion and O(13), an electrostatic interaction of the type observed for the lead complexes $[Pb(22)(SCN)_2]$ [20] and $[Pb(222)(SCN)_2]$ (222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) [21] is possible.

The Cd–O(16) distance of 4.021(6) Å in $[Cd(L^2)(NO_3)_2]$ indicates that there is no interaction between the cadmium and O(16). Although O(16) lies 0.785 Å from the macrocyclic least-squares plane, it is not as far out of the macrocyclic plane as the N donor atom in $[Cd(L^1)(NO_3)_2]$. This may, however, be a requirement of the conformation the ring L^2 has adopted. The conformation of the macrocycle L^2 in $[Cd(L^2)(NO_3)_2]$ is not that of an idealised crown ether shown by two potassium complexes of N-alkylated de-

TABLE 7. Torsion angles for the macrocyclic rings of $[Cd(L^1)(NO_3)_2]$ and $[Cd(L^2)(NO_3)_2]$

	$[Cd(L^1)(NO_3]_2]$	$[Cd(L^2)(NO_3)_2]$
C(15)–N(1)–C(2)–C(3)	−176.1(3)	
C(18)–N(1)–C(2)–C(3)		87.2(3)
N(1)–C(2)–C(3)–O(4)	58.3(4)	61.5(3)
C(2)–C(3)–O(4)–C(5)	−162.9(3)	−174.9(2)
C(3)–O(4)–C(5)–C(6)	167.8(3)	177.5(2)
O(4)–C(5)–C(6)–O(7)	−62.3(3)	−59.3(2)
C(5)–C(6)–O(7)–C(8)	−179.5(3)	173.7(2)
C(6)–O(7)–C(8)–C(9)	−175.8(3)	−179.1(2)
O(7)–C(8)–C(9)–O(10)	63.7(3)	63.4(3)
C(8)–C(9)–O(10)–C(11)	−170.9(3)	179.2(2)
C(9)–O(10)–C(11)–C(12)	176.4(3)	−177.4(3)
O(10)–C(11)–C(12)–O(13)	−50.1(4)	−71.7(3)
C(11)–C(12)–O(13)–C(14)	−104.3(4)	−176.8(3)
C(12)–O(13)–C(14)–C(15)	179.8(3)	161.2(3)
O(13)–C(14)–C(15)–N(1)	−62.9(3)	
C(14)–C(15)–N(1)–C(2)	167.7(3)	
O(13)–C(14)–C(15)–O(16)		68.7(4)
C(14)–C(15)–O(16)–C(17)		−95.8(4)
C(15)–O(16)–C(17)–C(18)		159.7(3)
O(16)–C(17)–C(18)–N(1)		−59.4(4)
C(17)–C(18)–N(1)–C(2)		172.2(3)

rivatives of L^2 [22, 23], $(ag^+\ aag^-\ a)_3$, but has the sequence of torsion angles $g^+\ g^+\ aag^-\ aag^+\ aag^-\ aag^+\ g^-\ ag^-\ a$ (starting with the torsion angle C(18)–N(1)–C(2)–C(3); Table 7) [24]. The macrocycle in the 1,4,7,10,13,16-hexaoxacyclooctadecane complex $[Na(18C6)(H_2O)]SCN$ also shows significant deviation from the idealized crown conformation, possessing the conformation $ag^+\ aag^-\ aag^+\ g^+\ ag^+\ ag^+\ g^+\ ag^-\ g^-\ a$ [25]. This twist of the macrocycle in the sodium complex allows one of the ether oxygens to coordinate the sodium ion from an apical position in the distorted pentagonal bipyramid. Similarly, we propose that the buckling in the macrocycle of $[Cd(L^2)(NO_3)_2]$ allows O(13) to interact with the cadmium ion. The fold in the ring is not the result of crystal packing: there is only one short intermolecular contact in the folded region of the ring, between H(121) and H(182)′, of 2.47 Å. The resonances at δ 69.7 and 69.6 ppm in the $^{13}C\{^1H\}$ NMR spectrum of $[Cd(L^2)(NO_3)_2]$ in dmso-D_6 at 100 MHz each show a poorly resolved shoulder which could be due to slow exchange of coordinating and non-coordinating ether oxygens. Thus the structure observed in the solid state may be retained to some extent in solution. The macrocycle L^1 in $[Cd(L^1)(NO_3)_2]$ has a sequence of torsion angles $ag^+\ aag^-\ aag^+\ aag^-\ aag^-\ a$ (Table 7). This conformation has not yet been observed for complexes of L^1 or its N-alkylated derivatives. The macrocyclic ligands in $[Cd(L^4)]_4[CdCl_4]_2 \cdot 3H_2O$ (HL^4 = 13-carboxymethyl-1,4,7,10-tetraoxa-13-azacyclopentadecane) have quite a different conformation, $g^+\ g^+\ aag^-\ aag^-\ g^-\ ag^-\ aag^+\ a$ or its opposite, but in $[Cd(L^4)]_4[CdCl_4]_2 \cdot 3H_2O$, the cadmium ion sits above the macrocyclic cavity [26].

All of the nitrate oxygen–cadmium distances in $[Cd(L^1)(NO_3)_2]$ and $[Cd(L^2)(NO_3)_2]$ lie within the extremes observed in the literature for this interaction, 2.27–2.84 Å [27, 28]. The Cd–O bond lengths for the bidentate nitrate ligand in $[Cd(L^2)(NO_3)_2]$ are equal within error, and are equal to the average Cd–O distance for the bidentate nitrate ligand in $[Cd(L^1)(NO_3)_2]$, which is slightly longer than the average Cd–O distance of 2.44 Å for all cadmium nitrato complex structures in the Cambridge Data Base to July 1991. In contrast to the weakly bound unidentate nitrate in $[Cd(L^1)(NO_3)_2]$, the unidentate nitrate of $[Cd(L^2)(NO_3)_2]$ shows a short Cd–O bond length, 2.302(4).

On the basis of the structure of their cadmium complexes, the cavity of L^2 is too large to have a significant overlap between the Cd^{2+} ion and all of the ether oxygens, whereas the cavity of L^1 seems ideally suited for Cd^{2+}. This is further substantiated by the rather short unidentate nitrate oxygen–cadmium distance in $[Cd(L^2)(NO_3)_2]$ compared with that in $[Cd(L^1)(NO_3)_2]$, which is apparently an electronic compensation for a lower effective coordination number for the macrocycle L^2 in its cadmium complex. The apparent suitability of L^1 for Cd^{2+} is not reflected in the solution behaviour of L^1 and L^2, as neither ligand exhibits a strong affinity for Cd(II).

Supplementary material

Listings of atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factor amplitudes are available from the authors.

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