Proton Transfer in a Phenol-based Compartmental Cryptate; Solution and Solid-state Structural Studies†

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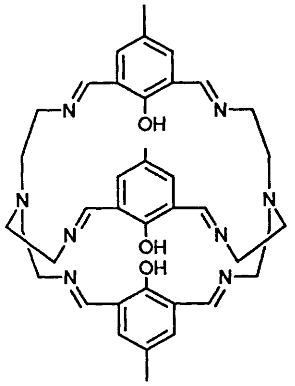
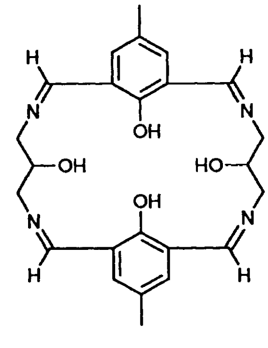
Under pH-neutral conditions, a potentially dinucleating azacryptand $N[(CH_2)_2N{=}CH{-}R{-}CH{=}N(CH_2)_2]_3N$ L^1(R = m-C_6H_2OH-2-Me-5) was found to accommodate just one metal cation; ^1H NMR spectra showed that the second site is occupied by three protons transferred from phenol to imino N. Under basic conditions, the protons can be displaced by a second cation forming a dinuclear cryptate. X-Ray crystallographic structure determinations have been made for the complexes $[PbL^1][BPh_4]_2$, two forms of $[CdL^1][ClO_4]_2$, **a** and **b** and $[Cd_2(L^1 - 3H)][ClO_4]_2$. In the first three complexes one metal ion is encapsulated within the macrocycle. However in all three cases the position is disordered over two equivalent sites; in the lead compound in the ratio 0.87:0.13 and in the cadmium compound **a** 0.66:0.34. In **b** the disorder is over two equivalent crystallographic positions so the ratio is 0.50:0.50. In the last complex two cadmium cations occupy the macrocycle. In all four structures the metal atoms are bonded to all three oxygen atoms and three imine atoms. In addition there is an interaction with a bridgehead nitrogen atom so that the metal co-ordination spheres can best be considered as seven-co-ordinate capped octahedra.

The polyether cryptands developed and successfully exploited by Lehn and co-workers[1] have found many valuable applications, especially in selectivity and transport of Group 1 and 2 cations, but are less effective hosts for softer transition- or main-group cations where nitrogen[2–5] or nitrogen/sulfur[6] donors are to be preferred. However, for borderline hard/soft guests such as cations from Groups 12–18 or transition ions in oxidation state > 3, there is a need for an O-donor contribution to the co-ordination sphere; in many circumstances anionic oxygen donors are ideal.

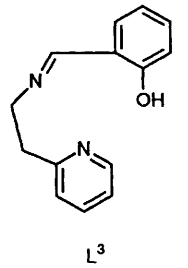
The diiminophenol head unit has been successfully exploited in macrocyclic chemistry where ready deprotonation of the phenol in the presence of M^{2+} ions generates μ-phenolate complexes of di- (or higher) nuclearity.[7,8] Another potential advantage of using ionisable cryptands as hosts for Lewis acids is that ionisation of the RO(H) donor to RO^- diminishes the Lewis acidity of the guest cation. Such Lewis acidity is known[2,4,5,9] to facilitate hydrolytic attack at the C=N imine function, leading to opening of the cryptand cage. Hence our interest in incoporating the phenol function within a macrobicycle, where the combination of strong oxygen and nitrogen donors together with the expected kinetic stability can make the cryptand an effective host for Group 12–18 or lanthanide cations of possible biomedical or environmental significance.



L^1



L^2



L^3

Hexa Schiff-base cryptands of general formula $N(CH_2CH_2N{=}CH{-}R{-}HC{=}NCH_2CH_2)_3N$ may be obtained by [2 + 3] condensation of tris(2-aminoethyl)amine (tren) with dialdehydes OHC–R–CHO, in some cases[10] without the aid of a template ion. In this case, we were unable to obtain the free cryptand, L^1, by metal-free [2 + 3] Schiff-base condensation of tren with 2,5-diformyl-4-methylphenol, but in the presence of a suitable Group 1 or 2 cation as template the appropriate cryptate (as shown by the appearance of $[ML^1]^+$ as parent ion in the FAB mass spectrum) was obtained in high yield. The Group 2 cryptates are poorly soluble, so the sodium cryptates $[NaL^1]X$ (X = BPh_4 **1a** or ClO_4 **1b**) were preferred as starting materials, for transmetallation. On transmetallation with a Group 12 or 14 salt under pH-neutral conditions, mononuclear cryptates **2–4** (Table 1) were obtained. Our general experience with mononuclear cryptates[11] has been that guest cations are unsymmetrically sited within the host ligand, and even at first

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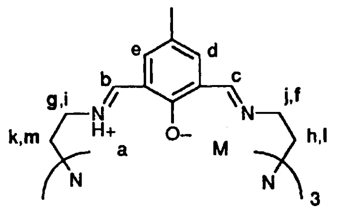
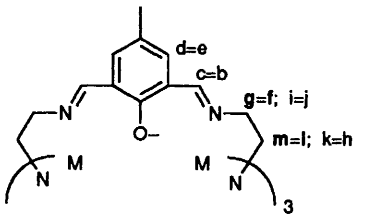
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Proton ^{1}H NMR spectra of L^1 cryptates^a



1–4



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Compound	T/K	NH$^+$ a	Imino CH b	c	CH (aromatic) d	e	CH$_2$^{b} j	**f**	**g**	i	h	**l**	k	**m**	Me^c
1 [NaL^1][BPh$_4$]	295	14.73	7.34 (d)	8.14 (s)	7.16 (s)	6.96 (s)	≈3.8^d		≈2.9^d		≈2.7^d		≈2.4 (s)^d		
	213	14.65 (br s)^e	7.55 (br s)^e	8.13 (s)^f	7.15 (s)^f	6.84 (s)^e	2.95 (m)	3.81 (t)^f	2.92 (m)	2.66 (d)	2.78 (d)^f	2.48 (t)	2.66 (d)^e	2.00 (t)	2.20 (s)
2 [PbL^1][BPh$_4$]$_2$	295	13.58 (m)^e	8.61 (d)^e	8.34 (s)^g	7.51^{f,h}	7.32^{e,f}	3.73 (br t)^{d,f,i}		3.30 (br s)^{d,e,i}		2.99 (br s)^{d,i}		2.86 (br s)^{d,e,i}		2.22 (s)
3 [ZnL^1][ClO$_4$]$_2$	295	13.86 (br s)^e	8.36 (d)^e	8.30 (s)^f	7.51^{f,h}	7.34^{e,h}	3.00 (d)^f	3.56 (t)^f	3.43 (t)^e	3.04 (m)^e	3.24 (d)^f	2.75 (t)^i	2.86 (d)^e	2.63 (t)^e	2.27 (s)
4 [CdL^1][ClO$_4$]$_2$	298	13.89 (br s)^e	8.34 (d)^e	8.34 (s)^{f,j}	7.51^{f,h}	7.32^{e,h}	3.12 (d)^{f,k}	3.65 (t)^f	3.41 (t)^e	2.97 (m)^{e,l}	2.97 (m)^l	2.66 (t)^f	2.97 (m)^{e,l}	2.66 (m)^e	2.26 (s)
5 [Cd$_2$(L^1 − 3H)]-[ClO$_4$]	295	—	8.33 (s)^{j,m}		7.20 (s)^m		3.06 (d)^m	3.65 (t)^m	3.65 (t)^m	3.06 (d)^m	2.90 (d)^m	2.65 (t)^m	2.90 (d)^m	2.65 (t)^m	2.22 (s)

^{a} δ in ppm from SiMe$_4$; intensity = 1H per cryptand strand unless otherwise stated; CD$_3$CN solution except complex **1** in CDCl$_3$. ^{b} Bold labelling denotes axial protons. ^{c} Intensity = 3H per cryptand strand. ^{d} Axial/equatorial signals undifferentiated. ^{e} Signals related *via* NOE experiments: protonated end of cryptand. ^{f} Signal related *via* NOE experiments: metal cation end of cryptand. ^{g} ^3J(HCNPb) ≈ 10 Hz. ^{h} Small four-bond coupling to the other aromatic H. ^{i} Related by decoupling experiments. ^{j} ^{111,113}Cd satellites: ^3J(CdNCH) ≈ 36 Hz. ^{k} ^{111,113}Cd satellites: ^3J(CdNCH) ≈ 22 Hz. ^{l} Signals i, h and k overlapped. ^{m} Both ends of the cryptand identical, so one signal of intensity = 2 H.

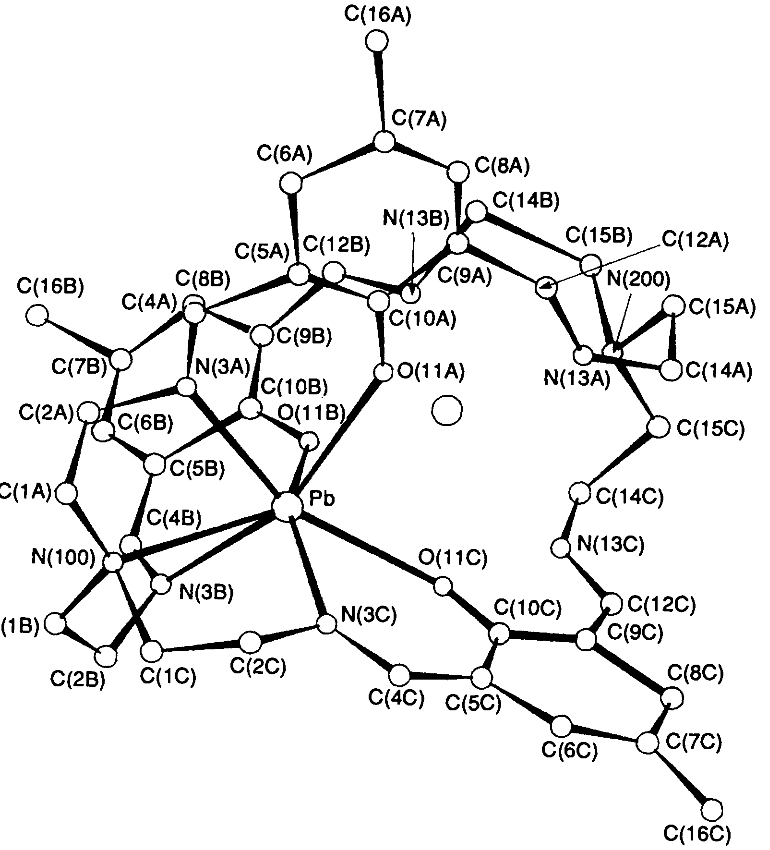

Fig. 1 Structure of the monolead cryptate **2**. The minor position of the lead atom is indicated as a circle but no bonds are attached

sight the complexity of the ^1H NMR spectra of **2**–**4** suggests that the L^1 system is no exception. Further investigation of the ^1H NMR spectrum was most informative, resulting in a complete assignment and a good description of the ligand conformation.

Results and Discussion

Mononuclear Cryptates: ^1H NMR Spectrum of the Lead Cryptate **2**.—Proton NMR spectra of all the mononuclear cryptates show a similar pattern of peaks at least at low temperature, consisting of two pairs of imine and aromatic resonances, together with an overlapped and complex methylene pattern. Where the methylene protons are fluxional, as in the room-temperature spectra of the lead and sodium cryptates, the pattern is of course simplifed.

The spectrum of $[PbL^1][BPh_4]_2$ **2**, for example, shows just four broad singlets in the range δ 2.8–3.3, corresponding to each type of methylene proton. The spectrum at high δ is much better resolved, and consists (in addition to the BPh_4^- spectrum) of two aromatic CH resonances close to δ 7.5 and a pair of HC(=N) imino signals around δ 8.5, the less-shielded component of which is coupled to a resonance at δ 13.6. Nuclear Overhauser effect (NOE) experiments show that each imine proton lies close in space to *one* of the protons responsible for the broad methylene signals, clearly demonstrating that the two ends of the cryptand host are different. The reason for the difference is revealed by inspection of the imino CH coupling pattern; while the signal at δ ≈ 8.4 shows the presence of poorly resolved satellites corresponding to $^3J(^{207}PbNCH)$, that at δ 8.6 has a relatively large and sharply resolved ^1H–^1H coupling of ≈ 15 Hz, which can only be explained on the basis of *trans* coupling to a proton on the imino nitrogen. The signal at δ 13.6 likewise exhibits a 15 Hz coupling, together with smaller coupling to one of the α-methylene resonances. It is thus clear that, under the influence of co-ordinated cation, proton transfer from phenol to imine N has occurred. The cryptand then presents two different sites: one end functioning as host for Pb^{2+} and the other as host for three protons. This conclusion is borne out by the single-crystal X-ray diffraction structure determination, described below.

X-Ray Crystallographic Structure Determination of Complex **2**.—The structure contains discrete cations PbL^{2+}, and two independent BPh_4^- anions. As stated in the Experimental section, there are two positions for the lead atom with occupancies of 0.87(1) and 0.13(1) respectively. The major position is found to one side of the cryptand and is bonded to the three phenoxy oxygen atoms [2.53(2), 2.50(2), 2.52(2) Å], the three imine nitrogen atoms [2.62(2), 2.65(3), 2.80(3) Å] and a bridgehead nitrogen atom [2.74(3) Å]. The minor position is very similar at the other end of the macrobicycle and also forms close contacts to seven donor atoms. These distances are listed in Table 2. There is no possibility that this minor position could be occupied by atoms other than lead as, though the electron density is acceptable for a water molecule, the distances from the donor atoms in the macrobicycle are too short. (The possibility that Na^+ had been retained upon transmetallation was ruled out by atomic absorption spectroscopy.) We therefore conclude that the cryptand can accommodate one Pb atom without notable distortion from two-fold symmetry and this leaves two possible positions for the metal atom with the other site occupied by three protons. Note that the two positions cannot be occupied simultaneously by lead cations as the Pb ··· Pb distance is only 2.959(7) Å. This assignment of two disordered positions for the lead cation is consistent with evidence provided by the two cadmium structures **4a** and **4b** (see later).

The structure is illustrated in Fig. 1 together with the atomic numbering scheme. The co-ordination geometry of the metal atom is best considered as an irregular capped octahedron with the bridgehead nitrogen in the capping position, the three imine

Table 2 Dimensions (distances in Å, angles in °) of the metal co-ordination spheres

Complex **2**

Pb(1)–O(11C)	2.52(2)	Pb(1) ··· Pb(2)	2.959(7)
Pb(1)–O(11B)	2.50(2)	Pb(2)–O(11A)	2.28(2)
Pb(1)–O(11A)	2.53(2)	Pb(2)–N(13A)	2.34(3)
Pb(1)–N(3B)	2.62(2)	Pb(2)–O(11C)	2.42(2)
Pb(1)–N(3C)	2.65(3)	Pb(2)–O(11B)	2.67(2)
Pb(1)–N(3A)	2.80(3)	Pb(2)–N(200)	2.76(3)
Pb(1)–N(100)	2.74(3)	Pb(2)–N(13B)	2.79(2)
		Pb(2)–N(13C)	2.78(2)
O(11C)–Pb(1)–O(11B)	84.3(6)	O(11B)–Pb(1)–N(100)	133.1(8)
O(11C)–Pb(1)–O(11A)	89.1(6)	O(11A)–Pb(1)–N(100)	125.2(7)
O(11B)–Pb(1)–O(11A)	86.5(6)	N(3B)–Pb(1)–N(100)	71.5(8)
O(11C)–Pb(1)–N(3B)	96.4(6)	N(3C)–Pb(1)–N(100)	62.9(8)
O(11B)–Pb(1)–N(3B)	68.9(7)	N(3A)–Pb(1)–N(100)	67.0(8)
O(11A)–Pb(1)–N(3B)	154.0(6)	O(11C)–Pb(1)–N(3A)	149.7(7)
O(11C)–Pb(1)–N(3C)	65.8(7)	O(11B)–Pb(1)–N(3A)	105.9(8)
O(11B)–Pb(1)–N(3C)	146.2(7)	O(11A)–Pb(1)–N(3A)	66.2(7)
O(11A)–Pb(1)–N(3C)	107.6(7)	N(3B)–Pb(1)–N(3A)	112.5(8)
N(3B)–Pb(1)–N(3C)	97.8(7)	N(3C)–Pb(1)–N(3A)	106.4(8)
O(11C)–Pb(1)–N(100)	124.5(5)		

Complex **4a**

Cd(1)–O(11C)	2.215(9)	Cd(1) ··· Cd(2)	2.865(3)
Cd(1)–O(11B)	2.229(8)	Cd(2)–O(11A)	2.077(8)
Cd(1)–O(11A)	2.281(8)	Cd(2)–O(11C)	2.195(9)
Cd(1)–N(3B)	2.340(10)	Cd(2)–O(11B)	2.248(9)
Cd(1)–N(3A)	2.338(9)	Cd(2)–N(13A)	2.403(11)
Cd(1)–N(3C)	2.376(10)	Cd(2)–N(13B)	2.405(11)
Cd(1)–N(100)	2.645(11)	Cd(2)–N(13C)	2.430(11)
		Cd(2)–N(200)	2.676(11)
O(11C)–Cd(1)–O(11B)	82.9(3)	O(11B)–Cd(1)–N(3C)	156.9(3)
O(11C)–Cd(1)–O(11A)	81.1(3)	O(11A)–Cd(1)–N(3C)	99.7(4)
O(11B)–Cd(1)–O(11A)	78.6(3)	N(3B)–Cd(1)–N(3C)	105.4(4)
O(11C)–Cd(1)–N(3B)	95.8(4)	N(3A)–Cd(1)–N(3C)	104.0(3)
O(11B)–Cd(1)–N(3B)	74.2(3)	O(11C)–Cd(1)–N(100)	132.9(4)
O(11A)–Cd(1)–N(3B)	152.8(3)	O(11B)–Cd(1)–N(100)	129.2(4)
O(11C)–Cd(1)–N(3A)	151.9(4)	O(11A)–Cd(1)–N(100)	132.2(3)
O(11B)–Cd(1)–N(3A)	97.3(3)	N(3B)–Cd(1)–N(100)	68.4(4)
O(11A)–Cd(1)–N(3A)	71.4(3)	N(3A)–Cd(1)–N(100)	67.4(3)
N(3B)–Cd(1)–N(3A)	111.4(4)	N(3C)–Cd(1)–N(100)	68.7(4)
O(11C)–Cd(1)–N(3C)	74.2(3)		

Complex **4b**

Cd(1)–O(11A*)	2.190(7)	Cd(1)–N(3A)	2.385(9)
Cd(1)–O(11B)	2.218(6)	Cd(1)–N(3B)	2.386(7)
Cd(1)–O(11A)	2.271(6)	Cd(1) ··· Cd(1*)	2.991(3)
Cd(1)–N(13A*)	2.364(7)	Cd(1)–N(100)	2.710(7)
O(11A*)–Cd(1)–O(11B)	80.3(2)	O(11A)–Cd(1)–N(3A)	71.1(3)
O(11A*)–Cd(1)–O(11A)	80.6(3)	N(13A*)–Cd(1)–N(3A)	106.1(3)
O(11A)–Cd(1)–O(11B)	78.6(2)	O(11A*)–Cd(1)–N(3B)	100.4(3)
O(11A*)–Cd(1)–N(13A*)	72.8(2)	O(11B)–Cd(1)–N(3B)	72.6(2)
O(11B)–Cd(1)–N(13A*)	152.5(2)	O(11A)–Cd(1)–N(3B)	150.5(2)
O(11A)–Cd(1)–N(13A*)	102.2(2)	N(13A*)–Cd(1)–N(3B)	106.3(2)
O(11A*)–Cd(1)–N(3A)	150.8(3)	N(3B)–Cd(1)–N(3A)	107.6(3)
O(11B)–Cd(1)–N(3A)	100.1(2)		

Complex **5**

Cd(1)–N(3B)	2.332(23)	Cd(1)–N(13A*)	2.291(20)
Cd(1)–O(11B)	2.250(19)	Cd(1)–O(11B*)	2.416(20)
Cd(1)–N(3A)	2.367(23)	Cd(1) ··· Cd(1*)	3.436(5)
Cd(1)–O(11A)	2.290(21)	Cd(1)–N(100)	2.787(28)
N(3B)–Cd(1)–O(11B)	78.8(8)	O(11A)–Cd(1)–O(11B*)	69.7(7)
N(3B)–Cd(1)–N(3A)	111.8(8)	N(3B)–Cd(1)–N(13A*)	95.3(8)
O(11B)–Cd(1)–N(3A)	103.5(7)	O(11B)–Cd(1)–N(13A*)	142.0(8)
N(3B)–Cd(1)–O(11A)	151.3(3)	N(3A)–Cd(1)–N(13A*)	113.4(8)
O(11B)–Cd(1)–O(11A)	72.6(6)	O(11A)–Cd(1)–N(13A*)	105.6(7)
N(3A)–Cd(1)–O(11A)	77.9(7)	O(11B)–Cd(1)–N(13A*)	72.8(6)
N(3B)–Cd(1)–O(11B*)	99.0(8)	Cd(1)–O(11A)–Cd(1*)	97.2(11)
O(11B)–Cd(1)–O(11B*)	71.1(6)	Cd(1)–O(11B)–Cd(1*)	94.8(6)
N(3A)–Cd(1)–O(11B*)	147.3(8)		

* Symmetry operation: $-x,y,\frac{1}{2}-z$.

nitrogen atoms in the capped face and the three phenoxy oxygen atoms in the uncapped face. The five relatively similar Pb–N,O donor distances, combined with the two longer (2.7–2.8 Å) contacts, indicate strong bonding for Pb^{2+} within the cryptand. These Pb–N distances are shorter by ≈0.05 Å than in a recently characterised aminocryptate,[12] and both Pb–N and Pb–O contacts are considerably shorter (by around 0.2–0.3 Å) than in the only other N,O cryptate of lead to be structurally characterised.[13] In an analogous macrocyclic structure $[PbL^2]^{2+}$,[14] Pb–O(phenolate) distances of ≈2.35 Å together with Pb–N (imino) distance of 2.5 Å are revealed, shorter than in the present case but relating to five- rather than seven-co-ordination.

Monosodium Cryptate, $[NaL^1][BPh_4]$ **1a**.—At ambient temperatures the ^1H NMR spectrum of complex **1a** demonstrates more conformational mobility than that of the lead analogue, presenting three (or maybe four) very broad overlapped resonances covering the range δ 2.3–3.6. However, its greater solubility in *e.g.* $CDCl_3$ allows for a low-temperature study. On cooling to 213 K the spectrum freezes out into broad but recognisable triplets and doublets, with some overlapping. As for the lead cryptate **2**, NOE and correlation spectroscopy (COSY) experiments relate two separate spin sets; imino and aromatic protons c and d with methylene signals f, h, l and j, and imino and aromatic protons a, b and e with k, g, i and m (Table 1), once more confirming the existence of different sites in an otherwise symmetric host for the metal cation and the set of three protons transferred from phenol oxygen to imino nitrogen. One difference between the lead and sodium cryptates lies in the extent of $NH^+ \cdots O^-$ hydrogen bonding; this appears more significant in **1a**, on the evidence of the greater chemical shift of the NH^+ resonance and its greater broadening. The coupled imino CH signal may provide indirect evidence of stronger hydrogen bonding in **1a**, based on the argument that the smaller three-bond *trans* coupling NH^+=CH (≈5 Hz in **1a** *vs.* ≈15 Hz in **2**) indicates a weaker N^+–H and therefore stronger $H^+ \cdots O^-$ bond. Presumably stronger hydrogen bonding in **1a** would reflect a greater charge density on O^- arising from co-ordination to a monopositive as against a dipositive cation. The broad nature of the CH resonance b (seen as a doublet only above 250 K) may in addition suggest the existence of some further conformational process, too fast to give more than a slight broadening to peaks other than NH.

Zinc and Cadmium Cryptates **3** *and* **4**.—As Pb^{2+} and Na^+ have similar ionic radii, it is not surprising that they should form mononuclear cryptates of similar conformation. However, the similarity in the stoichiometry and in the ^1H NMR spectra for lead and zinc cryptates **2** and **3** was unanticipated, before the effect of pH on the transmetallation equilibrium was realised. The major difference between the NMR spectra of the lead and zinc cryptates is in the rate of conformational change: at 298 K the zinc cryptate **3** shows a sharply resolved spectrum similar to the low-temperature spectrum of the sodium complex, indicating a slower rate of conformational change than for sodium or lead cryptates. Only the low-field NH^+ signal is broadened, again presumably on account of some conformational process involving this proton; hydrogen-bond exchange cannot be invoked, because the imino CH resonance to which it is coupled is well resolved, as a sharp doublet with 14 Hz splitting, not much less than in the case of **2**. The chemical shifts of the imino and aromatic protons in **3** are very similar to those of **2** although at slightly higher δ. The average of each pair of axial/equatorial methylene chemical shifts likewise compares reasonably well with that of the analogous undifferentiated resonance of **2**, the greatest difference evident referring to the methylene protons α to the imino N which may be affected by differing anisotropy of Pb^{2+} *versus* Zn^{2+} guest cations.

The monocadmium cryptate **4**, like the zinc analogue **3**, shows a sharply resolved spectrum at ambient temperature. Once again only the NH^+ signal around δ 13.9 is broadened. Cadmium-111,113 satellites are evident on the imino CH (c) resonance, which coincidentally has the same chemical shift as that of the imino CH (b) signal, giving overall the appearance of a quintet of irregular intensity.

The COSY and NOE experiments once more reveal two proton-spin sets corresponding to the different ends of the cryptand, with chemical shifts very similar to those of complex **3**. The coupling of imino CH (b) to NH^+ (^3J = 13.6 Hz) is also very similar to that in **2** and **3**, suggesting a hydrogen bond of similar strength, as indeed does the position of the NH^+ resonance.

The ^{13}C NMR resonance of the phenol *ipso*-carbon may be expected to respond to co-ordination/protonation equilibria, although it is not easy, when these effects are in competition, to predict the nature of the response. For the related macrocyclic system L^2, where the dilead *de*protonated (at phenol) and the *di*protonated form have been structurally characterised[14] together with a monolead 'neutral' form, a 14 ppm downfield shift of the ^{13}C NMR signal of the *ipso*-carbon accompanies the deprotonation ⟶ diprotonation trend. For the L^1 cryptates, a 5 ppm downfield shift is observed on going from $[Cd_2(L^1 - 3H)][ClO_4]$ **5** to $[CdL^1][ClO_4]_2$ **4**, consistent with higher shielding of the deprotonated form. It may be noted that the *ipso*-carbon resonance of the monozinc cryptate **3** is slightly more shielded than in **4**, perhaps reflecting a somewhat weaker hydrogen bond. The ^{13}C NMR spectra could not be obtained for cryptates **1** or **2**.

The position of the ^{13}C resonances, apart from that of the phenol *ipso*-carbon, barely alter from complex **4** to **5**, and this similarity, mirroring that evident in the ^1H NMR spectrum, emphasises the near-identical siting of Pb^{2+}, Zn^{2+} and Cd^{2+} in the cryptand cavity in the three mononuclear cryptates, a conclusion borne out by comparison of the X-ray crystallographic results for **2** and **4a** and **4b**.

Dicadmium Cryptate **5**.—Transmetallation of complex **1** under basic conditions, using cadmium acetate followed by sodium perchlorate, results in the isolation of a crystalline compound with a much simpler ^1H NMR spectrum than those of **1**–**4**. The compound was identified as the dicadmium salt of the triply deprotonated ligand, $[Cd_2(L^1 - 3H)][ClO_4]$ **5**. The simple spectrum now argues for equivalence of the two ends as well as the three strands of the cryptand. The triplet, doublet, doublet, triplet chemical shift sequence of the methylene signals seen is well established as the signature of a symmetric convergent conformation in our azacryptand series.[4,9,12] Just a single $^{111,113}Cd$-coupled imino-CH and one aromatic CH signal are seen, and no low-field resonance attributable to NH^+. As well as the expected coupling of cadmium to imino CH, cadmium satellites are seen on the doublet corresponding to H_{eq} adjacent to the imino N, with slightly lower coupling constant [*i.e.* $^3J(^{111,113}Cd-^1H)$ ≈ 24 *vs.* 36 Hz for the imine signal]. The three-bond couplings $^{111,113}Cd-^1H$(imino) are equal, within experimental error, in **4** and **5**, and considerably larger than the analogous $^{207}Pb-^1H$(imino) couplings in **2**. X-Ray crystallography, described below, confirms the spectroscopic findings.

X-Ray Crystallographic Structure Determinations of Complexes **4a**, **4b** *and* **5**.—Two different solid-state forms **4a** and **4b** of the monocadmium complex were isolated under slightly different synthetic conditions (see Experimental section). Complex **4a** has a similar structure (Fig. 2) to that of the monolead complex **2**, but here the two relative sites have occupancy factors of 0.66(1) and 0.34(1) respectively. The bond lengths between the metal atom and ligands in the co-ordination sphere are shorter, reflecting the smaller size of the cadmium relative to the lead atom: 2.215(9), 2.229(8), 2.281(8) Å to the three oxygen atoms and 2.340(10), 2.338(9), 2.376(10) Å to the three N atoms. A survey of the Cambridge Database shows that these are relatively short distances for both Cd–O

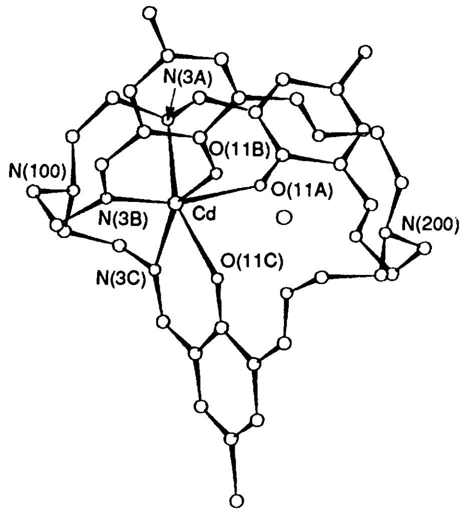

Fig. 2 Structure of the monocadmium cryptate **4a**. The minor position of the cadmium atom is indicated as a circle but no bonds are attached

and Cd–N, testifying to strong bonding for cadmium within the crypt. The cadmium is less strongly bound to the bridgehead nitrogen atom [2.645(11) Å]. Apart from shortening of cation–donor contacts, the general features of the molecule remain the same as in **2**. The lesser populated site at the other end of the macrocycle has a similar environment. The distance between the two disordered cadmium positions is 2.865(3) Å.

It is naturally difficult to sort out the geometry of the triprotonated sites in complexes **2** and **4a** because of the presence of the minor metal atom. However in **2** the $N^+ \cdots O^-$ distances (between N and O in the same linkage) are 2.62, 2.68 and 2.92 Å. The C–N···O angles, although not ideal for hydrogen bonding (at 84, 81, 64°), are typical of those found in other intramolecularly hydrogen-bonded systems. In **4a** comparable distances are 2.59, 2.62, 2.62 and angles 82, 84, 86°. In the protonated form of the macrocyclic ligand L^2 mentioned earlier,[14] PhO···N (imino) hydrogen-bond distances of around 2.5 Å have been noted. (Electrostatic interaction will of course contribute to the reduction of the $N^+ \cdots O^-$ distance in both cases.) The structure **4b** exhibits crystallographic C_2 symmetry with one cadmium in the macrocycle disordered over two sites (Fig. 3). In general, though, the essential features of the mononuclear complex apparent in **4a** are maintained.

The structure **5**, however, contains two cadmium atoms together in the macrocycle with one perchlorate. This indicates that it must comprise $[Cd_2(L - 3H)]^+$ cations together with ClO_4^- anions and the cation is shown in Fig. 4. The cation also has crystallographic C_2 symmetry (passing through one of the phenyl rings and OH and CH_3 groups). The metal environment can be considered to be six- or seven-co-ordinate. In addition to the bonds to three imine nitrogen atoms [2.332(23), 2.291(20) and 2.367(23) Å] and to three oxygen atoms [2.250(19), 2.290(21), 2.416(20) Å], there is a weak interaction to the bridgehead amine nitrogen at 2.787(28) Å. These distances are as expected. The cadmium–imino N distances are slightly shorter than in other[15] macrocyclic six- and seven-co-ordinate complexes of cadmium by around 0.05–0.1 Å, but of the same order as those seen[16] in the analogous acyclic six-co-ordinate complex $[CdL^3{}_2]$, which should correspond to 'normal' unstrained bond distances. The Cd–μ-OPh⁻ distances are also very similar at 2.22–2.28 Å in the acyclic complex. The position of the bridgehead nitrogen atoms in the co-ordination sphere in **5** is that of a capping atom in a seven-co-ordinate capped octahedron.

The structure of complex **5** can be compared to that of **4a** and **4b** in which only one Cd (albeit disordered) is found. Clearly replacement of the three protons from the second site of the mononuclear cryptates by a second divalent cation has little effect on the conformation of the ligand. This is indicated by the significant disorder in both mononuclear structures. There seems very little difference in the metal environments in **4a**, **4b** and **5** apart from a slight lengthening of the macrocycle in the presence of two metal atoms. Thus the distance between the two metal sites (one occupied) in **4a** and **4b** is 2.865(3), 2.991(3) compared to 3.436(5) Å in **5** and the distance between the bridgehead nitrogen atoms is 8.20 Å in **4a** and 8.41 Å in **4b** compared to 9.01 Å in **5**. In **5** the perchlorate anion is disordered. The Cl atom sits on the C_2 axis but there are four disordered positions for the oxygen atoms each with half occupancy.

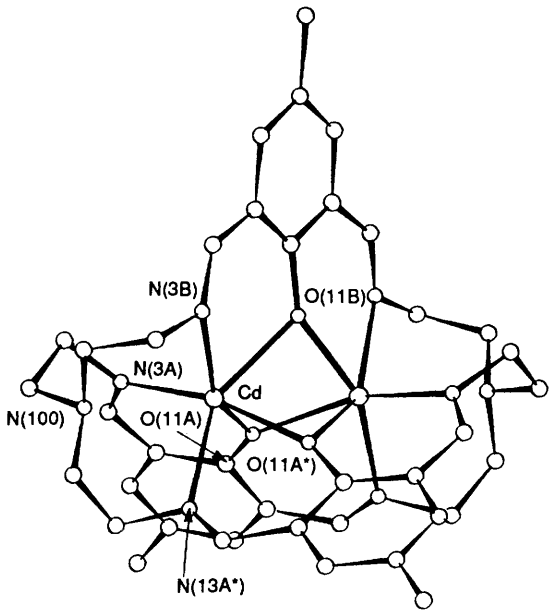

Fig. 3 Structure of the monocadmium cryptate **4b**. Both sites are shown in the cation which contains crystallographic C_2 symmetry

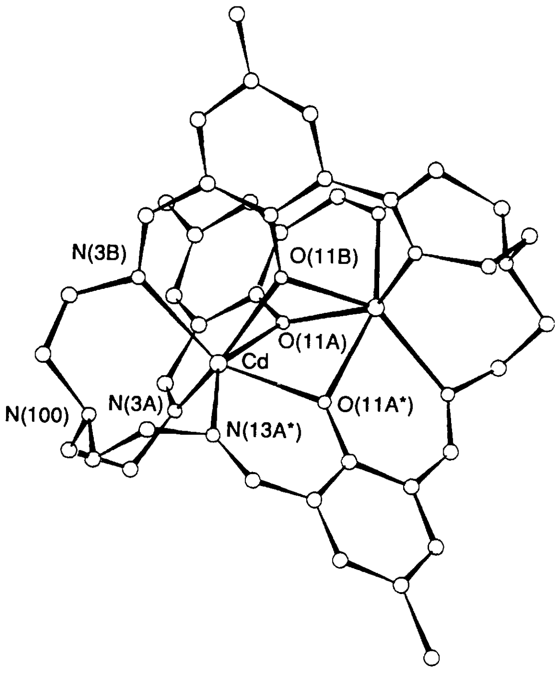

Fig. 4 Structure of the dicadmium cryptate **5**

In summary, we have established that under neutral conditions the phenol-derived cryptand L^1 acts as host for *one* Group 12 or 14 cation, co-ordination of which facilitates proton

Table 3 Crystal data and structure refinement for complexes **2**, **4a**, **4b** and **5***

Compound	**2**	**4a**	**4b**	**5**
Formula	$[PbL^1][BPh_4]_2$	$[CdL][ClO_4]_2\cdot 0.5MeCN\cdot 0.5EtOH$	$[CdL][ClO_4]_2\cdot 2MeCN$	$[Cd_2(L^1 - 3H)]$-$[ClO_4]$
Empirical formula	$C_{87}H_{88}B_2N_8O_3Pb$	$C_{41}H_{52.5}CdCl_2N_{8.5}O_{11.5}$	$C_{43}H_{54}CdCl_2N_{10}O_{11}$	$C_{39}H_{45}Cd_2ClN_8O_7$
M	1522.4	1031.7	1070.2	998.1
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$I2/c$
a/Å	18.913(15)	12.050(7)	22.492(7)	12.886(12)
b/Å	15.271(13)	12.566(7)	11.550(7)	23.690(22)
c/Å	15.466(13)	16.465(7)	19.638(7)	13.877(16)
α/°	117.0(1)	93.10(7)	90	90
β/°	106.9(1)	107.71(7)	111.56(7)	109.5(1)
γ/°	73.8(1)	102.64(7)	90	90
U/Å^3	3752.5	2297.8	4744.6	3993.2
Z	2	2	4	4
D_c/Mg m^{-3}	1.35	1.491	1.498	1.66
μ/cm^{-1}	23.0	0.660	0.642	11.9
F(000)	1564	1064	2208	2016
Crystal size/mm	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.2	0.3 × 0.15 × 0.20	0.2 × 0.25 × 0.25
θ/° range for data collection	25	2.15–25.15	2.12–25.90	25
hkl Index ranges	0–22, −18 to 19, −16 to 17	0–12, −14 to 14, −19 to 18	0–27, 0–14, −22 to 22	0–14, 0–28, −16 to 15
Independent reflections	11 499	6986	4285	3388
Independent reflections $[I > 2\sigma(I)]$	4027	5174	3480	1468
Goodness of fit on F^2	1.151	0.855	0.923	0.93
Final R $[I > 2\sigma(I)]$ $R1$	0.076	0.082	0.072	0.089
$wR2$	—	0.308	0.234	—
(all data) $R1$	—	0.134	0.144	—
$wR2$	—	0.372	0.432	—
Largest difference peak and hole/e Å^{-3}	2.437, −1.868	0.705, −1.026	0.484, −0.604	0.92, −0.87

* Details in common: 293(2) K; Mo-Kα radiation (λ 0.710 70 Å).

transfer to imino N. The cryptate is kinetically stable towards decomplexation, as shown by the appearance, at ambient temperatures, of three-bond coupling to lead or cadmium. The relatively short metal–donor distances and relatively large M ··· H couplings suggest that the cryptand N- and O-donor atoms form strong bonds with lead or cadmium. Dissociation is in any case kinetically disfavoured. These observations encourage experiments designed to introduce a second metal cation into the cavity.

The second (triprotonated) site is potentially available to a *second* identical or non-identical metal cation, merely upon adjustment of pH. Such pH control represents a valuable route to heterobinuclear iminocryptates, particularly given a system such as L^1 which is hydrolytically stable. Absence of Lewis-acid-assisted hydrolysis means that a wide range of transition- and non-transition-metal cations may safely be accommodated at the second site, which should permit the synthesis of a range of heterobinuclear cryptates of potential catalytic importance.

Experimental

Tris(2-aminoethyl)amine was obtained from Aldrich and used without further purification. 2,6-Diformyl-4-methylphenol was prepared by the literature methods.[17]

$[NaL^1]X$ ($X = BPh_4$ **1a** *or* ClO_4 **1b**).—The sodium salt (0.003 mol) and 2,6-diformyl-4-methylphenol (0.009 mol) were dissolved in methanol (50 cm^3), filtered and stirred at room temperature. Tris(2-aminoethyl)amine (0.006 mol) in methanol (30 cm^3) was added dropwise over 30 min. The resulting yellow precipitate was filtered off and recrystallised from ethanol–acetonitrile (60:40). Yields: 74 **1a** and 59% **1b** [Found (Calc.): **1a**, C, 74.20 (74.25); H, 6.70 (6.75); N, 10.70 (11.00). **1b**, C, 52.35 (58.60); H, 5.90 (6.05); N, 6.00 (4.00%)]. Despite unsatisfactory analysis, the sample of **1b** could be successfully used in transmetallation reactions to generate complexes **3** and **4**.

$[PbL^1][BPh_4]_2$ **2**.—Lead thiocyanate (0.0001 mol) was suspended in acetonitrile (40 cm^3) and a solution of $[NaL^1][BPh_4]$ (0.0001 mol) in acetonitrile–methylene chloride (50:50 v/v, 40 cm^3) was added dropwise at 30 °C. The mixture was stirred for 1 h by which time most of the lead thiocyanate had dissolved. Ethanol (40 cm^3) was added and the solvent volume was reduced by rotary evaporation. A small amount of lead thiocyanate was filtered off after standing overnight, before golden crystals were recovered on leaving the solution at −20 °C for 2 d. Yield 66%. FAB mass spectrometric isotopic cluster centred around m/z = 883 corresponding to $[PbL^1]^+$. (10% base peak) [Found (Calc.): C, 68.35 (68.65); H, 5.85 (5.85); N, 7.30 (7.30%)].

$[ZnL^1][ClO_4]_2$ **3**.—A solution of $[NaL^1][ClO_4]$ (0.0001 mol) in acetonitrile–methylene chloride (50:50 v/v, 40 cm^3) was added dropwise over 20 min to a solution of zinc perchlorate (0.0001 mol) in ethanol (40 cm^3) with stirring at 30 °C. The solvent volume was reduced and the zinc complex recovered as yellow microcrystals upon slow evaporation. Yield 42%. FAB mass spectrometric isotopic cluster centred around m/z = 739 (27% base peak) corresponding to $[ZnL^1]^{2+}$ and 837 (38% base peak) corresponding to $[Zn(L^1 - 3H)][ClO_4]$ (Found (Calc.): C, 49.55 (49.75); H, 5.30 (5.15); N, 12.20 (11.90%)].

$[CdL^1][ClO_4]_2$ **4a**.—This was the product obtained upon transmetallating $[NaL^1][ClO_4]$ with just less than 1 equivalent of cadmium perchlorate in the presence of mild acid, to prevent deprotonation and aid formation of the mononuclear product. A solution of cadmium perchlorate (0.0005 mol) in ethanol (100 cm^3) was added dropwise at room temperature over 30 min to a stirred solution of $[NaL^1][ClO_4]$ (0.0006 mol) in acetonitrile–methylene chloride (50:50 v/v, 40 cm^3) to which three drops of acetic acid had been added. A small amount of fluffy yellow material was removed and orange cubes formed on slow evaporation. Yield 40%. FAB mass spectroscopic isotopic

Table 4 Atomic coordinates ($\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **2**							
Pb(1)	1727(1)	574(1)	4548(1)	C(16C)	5383(18)	−1936(27)	2102(26)
Pb(2)	2642(4)	−776(5)	5511(5)	B(1)	8148(22)	2746(31)	1010(30)
N(100)	876(15)	1496(21)	3332(21)	C(101)	8479(12)	3200(17)	352(16)
N(200)	3540(13)	−1678(19)	6745(19)	C(102)	8321(14)	4136(19)	439(19)
C(1A)	28(11)	1573(16)	3271(16)	C(103)	8582(16)	4435(23)	−70(22)
C(2A)	−162(10)	1430(14)	4028(14)	C(104)	9023(15)	3736(22)	−781(21)
N(3A)	198(13)	498(19)	4136(18)	C(105)	9177(20)	2760(29)	−883(27)
C(4A)	−85(13)	−273(19)	3779(18)	C(106)	8905(19)	2497(27)	−283(26)
C(5A)	204(20)	−1264(27)	3636(26)	C(111)	8537(11)	3321(16)	2225(16)
C(6A)	−253(14)	−2018(21)	3114(19)	C(112)	8943(15)	4084(21)	2595(21)
C(7A)	−43(15)	−2943(21)	2943(20)	C(113)	9154(13)	4634(19)	3626(19)
C(8A)	719(14)	−3236(20)	3226(20)	C(114)	8988(17)	4356(23)	4256(23)
C(9A)	1175(16)	−2597(23)	3821(22)	C(115)	8550(14)	3623(20)	3904(20)
C(10A)	1021(12)	−1654(17)	4060(17)	C(116)	8371(16)	3110(22)	2925(22)
O(11A)	1454(10)	−921(14)	4613(14)	C(121)	7183(14)	3429(19)	968(20)
C(12A)	1942(21)	−3037(28)	4079(27)	C(122)	6770(16)	3273(22)	5(22)
N(13A)	2497(16)	−2452(21)	4679(21)	C(123)	6011(21)	3587(27)	−160(28)
C(14A)	3240(21)	−3060(29)	4859(29)	C(124)	5651(16)	4090(22)	573(22)
C(15A)	3470(30)	−2779(40)	6089(39)	C(125)	6019(18)	4344(23)	1545(24)
C(16A)	−596(21)	−3782(28)	2115(27)	C(126)	6781(21)	3979(27)	1679(28)
C(1B)	936(14)	2680(19)	3999(19)	C(131)	8216(19)	1642(25)	769(24)
C(2B)	1749(14)	2903(19)	4674(19)	C(132)	7613(16)	1082(24)	235(23)
N(3B)	1985(11)	2405(16)	5321(16)	C(133)	7812(23)	4(31)	−40(30)
C(4B)	2240(13)	2985(18)	6208(18)	C(134)	8539(22)	−416(28)	174(28)
C(5B)	2485(11)	2749(16)	7031(15)	C(135)	9090(22)	77(32)	627(29)
C(6B)	2866(9)	3428(13)	7979(13)	C(136)	8937(23)	1116(32)	937(29)
C(7B)	3050(13)	3323(19)	8855(19)	B(2)	3297(21)	3519(28)	2538(29)
C(8B)	3035(13)	2456(18)	8923(18)	C(201)	3794(12)	2676(16)	1638(16)
C(9B)	2679(13)	1715(18)	7973(17)	C(202)	4398(14)	2868(19)	1417(18)
C(10B)	2454(12)	1919(17)	7107(17)	C(203)	4770(17)	2124(24)	704(23)
O(11B)	2151(11)	1182(15)	6380(15)	C(204)	4593(16)	1184(22)	230(22)
C(12B)	2638(13)	902(18)	8136(17)	C(205)	4003(12)	959(16)	447(16)
N(13B)	2412(11)	85(16)	7449(15)	C(206)	3611(12)	1748(17)	1160(16)
C(14B)	2420(15)	−872(21)	7478(21)	C(211)	3473(12)	4705(16)	2684(16)
C(15B)	3250(14)	−1333(19)	7666(19)	C(212)	2946(21)	5255(29)	2240(27)
C(16B)	3355(21)	4188(31)	9732(29)	C(213)	3077(23)	6089(30)	2203(29)
C(1C)	1209(13)	1275(19)	2359(18)	C(214)	3749(20)	6393(27)	2678(26)
C(2C)	1418(16)	195(22)	2139(21)	C(215)	4288(14)	5884(20)	3121(19)
N(3C)	2119(15)	−28(20)	2827(19)	C(216)	4161(18)	5035(24)	3147(23)
C(4C)	2644(17)	−480(22)	2408(22)	C(221)	2368(11)	3544(15)	2071(15)
C(5C)	3409(14)	−681(19)	2993(19)	C(222)	1879(16)	3820(21)	2687(21)
C(6C)	2986(16)	−1129(22)	2361(22)	C(223)	1093(21)	3871(27)	2365(28)
C(7C)	4743(15)	−1388(21)	2807(22)	C(224)	777(21)	3680(27)	1403(28)
C(8C)	4889(16)	−1289(22)	3727(23)	C(225)	1252(24)	3443(30)	755(32)
C(9C)	4350(11)	−947(15)	4271(15)	C(226)	2054(17)	3374(22)	1112(23)
C(10C)	3546(14)	−583(19)	3876(20)	C(231)	3458(13)	3396(20)	3545(19)
O(11C)	3075(11)	−277(15)	4501(15)	C(232)	3530(30)	4086(43)	4434(43)
C(12C)	4579(8)	−671(12)	5318(12)	C(233)	3585(20)	3987(29)	5322(28)
N(13C)	4138(11)	−546(16)	6170(16)	C(234)	3633(18)	3047(27)	5202(26)
C(14C)	4424(14)	−624(19)	7019(19)	C(235)	3614(18)	2272(26)	4322(26)
C(15C)	4375(16)	−1571(23)	6859(22)	C(236)	3557(18)	2442(26)	3551(26)
Complex **4a**							
Cd(1)	3081(1)	5576(1)	3125(1)	C(14B)	2419(13)	1183(10)	3429(8)
Cd(2)	1773(3)	3313(2)	2719(2)	C(15B)	1408(13)	537(10)	2691(9)
N(100)	4324(11)	7651(9)	3565(7)	C(1C)	3451(12)	8355(9)	3466(9)
N(200)	596(11)	1187(9)	2324(7)	C(2C)	2351(12)	7712(10)	3633(9)
C(1A)	5098(12)	7788(10)	4440(8)	N(3C)	1791(9)	6789(8)	2976(6)
C(2A)	5356(9)	6744(10)	4637(7)	C(4C)	889(12)	6800(10)	2390(8)
N(3A)	4261(8)	5954(7)	4576(6)	C(5C)	203(11)	5983(9)	1695(7)
C(4A)	3935(11)	5877(10)	5233(7)	C(6C)	−795(11)	6210(12)	1118(7)
C(5A)	2855(9)	5240(8)	5265(7)	C(7C)	−1508(13)	5450(13)	455(8)
C(6A)	2585(12)	5333(11)	6016(9)	C(16C)	−2623(17)	5759(16)	−164(10)
C(7A)	1580(12)	4785(11)	6117(8)	C(8C)	−1263(12)	4531(13)	342(7)
C(16A)	1336(16)	4931(14)	6953(10)	C(9C)	−259(11)	4232(9)	870(7)
C(8A)	767(12)	4095(11)	5459(9)	C(10C)	512(11)	5008(11)	1580(8)
C(9A)	927(12)	3948(9)	4671(8)	O(11C)	1409(8)	4743(8)	2075(6)
C(10A)	2030(11)	4492(9)	4559(7)	C(12C)	−51(13)	3222(11)	710(8)
O(11A)	2240(8)	4337(7)	3866(5)	N(13C)	742(11)	2797(9)	1185(7)
C(12A)	36(12)	3190(10)	4018(9)	C(14C)	833(16)	1739(11)	992(9)
N(13A)	133(10)	2930(8)	3288(7)	C(15C)	115(15)	943(13)	1408(9)
C(14A)	−795(13)	2124(11)	2718(10)	Cl(8)	2564(4)	9191(3)	875(2)
C(15A)	−347(14)	1050(11)	2699(10)	O(81)	2764(19)	8552(15)	279(13)

Table 4 (*contd.*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **4a**							
C(1B)	4970(14)	7916(9)	2989(9)	O(82)	3549(15)	9676(11)	1570(10)
C(2B)	4300(14)	7235(9)	2131(9)	O(83)	1994(23)	9941(18)	527(15)
N(3B)	4231(10)	6104(8)	2231(7)	O(84)	1746(14)	8470(15)	1186(9)
C(4B)	4851(11)	5623(9)	1929(7)	Cl(9)	3118(4)	8985(3)	5945(3)
C(5B)	4945(11)	4514(9)	1969(7)	O(91)	2732(23)	7924(10)	5788(15)
C(6B)	5624(12)	4151(11)	1568(8)	O(92)	3052(24)	9455(16)	6674(13)
C(7B)	5746(12)	3116(12)	1523(9)	O(93)	2727(28)	9561(19)	5230(16)
C(16B)	6557(20)	2744(20)	1071(16)	O(94)	4303(21)	9230(23)	5963(16)
C(8B)	5198(13)	2427(12)	1924(9)	N(60)	6275(42)	9363(39)	1083(29)
C(9B)	4444(11)	2723(9)	2365(8)	C(61)	6690(35)	8578(32)	1072(24)
C(10B)	4310(10)	3801(9)	2412(7)	C(62)	7263(62)	7818(55)	1432(43)
O(11B)	3677(8)	4096(7)	2803(6)	C(63)	1417(87)	1317(73)	5349(61)
C(12B)	3810(13)	1932(10)	2767(8)	C(64)	643(56)	1154(47)	5792(39)
N(13B)	3065(10)	2083(8)	3123(6)	O(65)	1345(48)	1787(44)	6505(35)
Complex **4b**							
Cd(1)	715(1)	557(1)	2827(1)	C(1B)	2243(4)	1518(8)	3129(5)
N(100)	2015(4)	604(7)	3469(5)	C(2B)	1771(4)	1717(8)	2355(5)
C(1A)	2186(4)	783(9)	4242(5)	N(3B)	1172(3)	2115(6)	2389(4)
C(2A)	1660(4)	1404(9)	4379(6)	C(4B)	1049(3)	3184(7)	2356(5)
N(3A)	1076(4)	723(7)	4127(5)	C(5B)	506(3)	3709(6)	2421(4)
C(4A)	957(4)	104(8)	4601(5)	C(10B)	0	3072(8)	2500
C(5A)	429(4)	−671(8)	4440(5)	O(11B)	0	1975(6)	2500
C(6A)	395(4)	−1314(8)	5029(5)	C(6B)	481(4)	4915(7)	2422(5)
C(7A)	−107(5)	−2065(8)	4956(6)	C(7B)	0	5495(11)	2500
C(8A)	−577(4)	−2128(8)	4291(5)	C(16B)	0	−3192(14)	2500
C(9A)	−578(4)	−1492(7)	3683(5)	Cl(1)	2609(1)	83(2)	1314(1)
C(10A)	−64(4)	−736(7)	3758(5)	O(11)	2998(4)	−630(8)	1075(5)
C(16A)	−113(6)	−2757(11)	5598(6)	O(12)	2092(4)	−595(8)	1368(6)
O(11A)	−52(3)	−146(6)	3210(4)	O(13)	2957(3)	550(7)	2011(4)
C(11A)	−1094(4)	−1657(7)	3016(5)	O(14)	2334(5)	966(9)	811(6)
N(13A)	−1179(3)	−1157(6)	2411(4)	N(60)	−1096(10)	4936(18)	4334(12)
C(14A)	−1740(4)	−1412(8)	1782(5)	C(61)	−1073(11)	4519(19)	4881(15)
C(15A)	−2230(4)	−522(7)	1692(6)	C(62)	−971(13)	4058(25)	5542(17)
Complex **5**							
Cd(1)	257(2)	1607(1)	1362(2)	C(15A)	546(31)	1675(15)	6321(28)
N(100)	556(17)	1636(10)	−536(19)	C(1B)	1300(26)	2141(16)	−510(34)
C(1A)	1107(24)	1080(13)	−626(25)	C(2B)	2069(28)	2210(14)	599(28)
C(2A)	695(26)	618(12)	−81(24)	N(3B)	1400(20)	2364(10)	1228(17)
N(3A)	903(16)	742(10)	991(22)	C(4B)	1315(26)	2862(12)	1485(27)
C(4A)	1484(28)	364(15)	1611(30)	C(5B)	668(26)	3125(14)	2011(26)
C(16A)	3890(34)	−572(14)	4647(31)	C(10B)	0	2820(19)	2500
C(5A)	1936(22)	383(9)	2724(31)	O(11B)	0	2246(13)	2500
C(6A)	2523(31)	−66(13)	3131(29)	C(7B)	0	4006(17)	2500
C(7A)	3153(24)	−95(14)	4240(35)	C(6B)	658(33)	3703(14)	2023(26)
C(8A)	3008(29)	356(13)	4811(33)	C(16B)	0	4696(27)	2500
C(9A)	2254(19)	802(14)	4425(26)	Cl	0	3467(8)	7500
C(10A)	1783(22)	833(12)	3348(26)	O(11)	−887(47)	3378(26)	7770(56)
O(11A)	1113(12)	1266(9)	2943(14)	O(12)	574(46)	3968(20)	7723(52)
C(12A)	2162(20)	1185(14)	5164(27)	O(13)	−379(60)	3435(27)	6349(29)
N(13A)	1383(18)	1571(11)	4959(18)	O(14)	759(47)	3009(22)	7727(52)
C(14A)	1307(30)	1913(15)	5843(28)				

cluster at *m*/*z* = 788 (32% base peak) corresponding to $[CdL^1]^+$ and 888 (19% base peak) corresponding to $[CdL^1][ClO_4]$ [Found (Calc.): C, 47.25 (47.40); H, 5.25 (4.90); N, 11.50 (11.35%)].

Complex **4b** was the product of an earlier attempt to obtain the dinuclear cryptate in the absence of acetate, using 2 equivalents of cadmium perchlorate [and a MeCN–MeOH–CH_2Cl_2 (2 : 1 : 1) solvent mixture] in the transmetallation.

$[Cd_2(L^1 - 3H)][ClO_4]$ **5**.—The salt $[NaL^1][BPh_4]$ (0.0001 mol) and cadmium acetate (0.0002 mol) were gently refluxed together for 1 h in acetonitrile–methylene chloride (50:50 v/v, 50 cm^3). A solution of sodium perchlorate (0.0002 mol) in ethanol (30 cm^3) was added before solvent volume was reduced and the solution left to stand overnight. The resulting fluffy yellow powder contained tetraphenylborate impurity, but recrystallisation in the presence of silver perchlorate, after filtering off silver tetraphenylborate, afforded long yellow lathes of the perchlorate salt of the dinuclear cryptate. Yield 68%. FAB mass spectrometric cluster at *m*/*z* = 899 (92% base peak) corresponding to $[Cd_2(L - H)]$ [Found (Calc.): C, 47.10 (46.95); H, 4.90 (4.55); N, 11.00 (11.20%)].

Attempts to generate the monocadmium cryptate under basic conditions yielded the dicadmium cryptate, irrespective of stoichiometry.

The NMR spectral data were obtained using standard methods, on a Bruker ACP400 spectrometer.

Crystallography.—The structures of compounds **2**, **4a**, **4b** and **5** were determined. Data for **2** and **5** were measured on a STOE-2 diffractometer and details are given in Table 3. Both crystals were mounted to rotate around the *a* axis and data were measured *via* ω scan with a 2θ maximum of 50°. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of [1.5 + (sin μ/tan θ)]. Data for **4a** and **4b** were collected using the MARresearch Image plate system and details are provided in Table 3. The crystals were positioned 75 mm from the image plate. Ninety frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[18] All four structures were solved using direct methods with the SHELX 86 program.[19] For the mononuclear species **2**, **4a** and **4b** there was disorder in the metal positions. With **2**, after location of all the non-hydrogen atoms, a residual peak of *ca.* 10e was observed in the macrobicycle. Owing to its location, it was decided that this represented a disordered lead atom and in subsequent refinement the two lead positions were given refineable occupancy factors which summed to 1.0 and common thermal parameters. Hydrogen atoms on the cations and anions were placed in calculated positions. The lead atom was refined anisotropically and all other atoms isotropically. With **4a** the same disorder pattern was observed but here the two positions had relative electron densities of 2:1. The two atoms were also refined with population parameters summing to 1. All non-hydrogen atoms in the cation and anion were given anisotropic thermal parameters. Two solvent molecules were observed and identified as ethanol and acetonitrile and each were given 50% occupancy. Hydrogen atoms were included on the cation in calculated positions. The cation of **4b** exhibited crystallographic C_2 symmetry. The cadmium atom was given 50% occupancy but no other disorder was observed. All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically in fixed positions. The cation of **5** also exhibited C_2 symmetry. All hydrogen atoms were placed in calculated positions and the two independent methyl groups were included as rigid groups but the one located on the two-fold axis could not be refined successfully and was not included in the final refinement cycles. The perchlorate anion was disordered. The chlorine atom was located on the two-fold axis. Four oxygen atoms were found and each given 50% occupancy. In this refinement the Cl–O and O···O distances were constrained to be equivalent and the oxygen atoms were given a common refinable thermal parameter. All non-hydrogen atoms (except for the perchlorate oxygens) were refined anisotropically and hydrogen atoms isotropically. Structures **2** and **5** were refined with full-matrix least squares on *F*, using the SHELX 76 program.[20] Calculations were carried out on the Amdahl 5870 computer at the University of Reading. Structures **4a** and **4b** were refined with full-matrix least squares on F^2 using SHELXL[21] and calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. The final coordinates are given in Table 4. The macrobicycle is numbered identically in all four structures.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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