Macrocyclic Ligand Ring Size Effects. Part 1. Complexation of Tetra-aza Ligands containing Fused Dibenzo Substituents with Zn^{II} and Cd^{II}: a Solution Stability, *X*-Ray Crystal Structure, and Molecular Mechanics Study†

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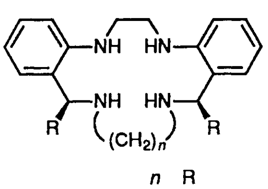
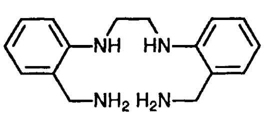
The interaction of Zn^{II} and Cd^{II} with an extensive series of dibenzo-substituted macrocyclic and open-chain tetra-amines has been investigated. All ligands form 1 : 1 (metal : ligand) complexes in solution with these metal ions; the thermodynamic stabilities of the complexes in 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4) have been determined. Along one series of 14- to 16-membered macrocyclic systems a dislocation in the stability pattern occurs for Zn^{II} at the 16-membered ring complex while, for Cd^{II}, the dislocation corresponded to the 15-membered ring species. As a consequence there is an enhanced stability difference ($Zn^{II} > Cd^{II}$) between the complexes of this latter ring. The observed discrimination shown by the 15-membered ring is largely maintained when bulky alkyl substituents are appended to carbons adjacent to two of the secondary amine donors; however, the absolute magnitudes of the respective stabilities are decreased because of steric effects. In an extension of this study it has been found that open-chain analogues show no unusual discrimination between Zn^{II} and Cd^{II}. Other macrocyclic and open-chain ligands containing only anilino nitrogen donors have been shown to form only very weak complexes with Zn^{II} and Cd^{II}. The *X*-ray structures and molecular mechanics investigation of two free ligands and three metal complexes are reported.

Metal-ion selectivity exhibited by a range of macrocyclic ligand types has now been well documented. For example, the factors influencing selective complex formation by a range of dibenzo-substituted, oxygen–nitrogen donor macrocycles have been investigated previously by us.[1–5] An aim of these latter studies has been the design of reagents for the recognition of particular transition- and post-transition-metal ions (in order that discrimination between such ions may be achieved). One discrimination mechanism little studied in the past[6] involves the occurrence of 'dislocation' co-ordination behaviour along a series of closely related macrocyclic ligands.[3–5] The presence of such a dislocation at one point along a series of ligands for one ion but not for a second will result in the adoption of different co-ordination geometries for the respective complexes. Behaviour of this type may form the basis for discrimination between ions since an enhanced stability difference or an unusual stability order may be a direct consequence of the structural changes associated with the dislocation. In previous studies variation of macrocyclic ring size has been the main parameter used to induce dislocation behaviour[3–5] although the degree of ring substitution present has also been employed.[3]

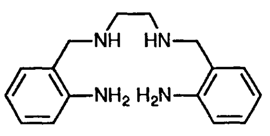
In the present investigation the interaction of Zn^{II} and Cd^{II} with the potentially quadridentate ligands L^1—L^{12} has been investigated. A structural feature of these ligand systems is the presence of fused benzo groups which serve to reduce the flexibility of the system; reduced ligand flexibility has been a factor in promoting dislocation behaviour in the previously studied systems.[5]



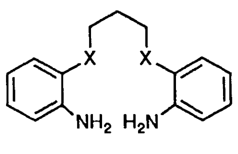
	n	R
L^1	2	H
L^2	3	H
L^3	4	H
L^4	3	Et
L^5	3	Pr^n
L^6	3	Bu^n



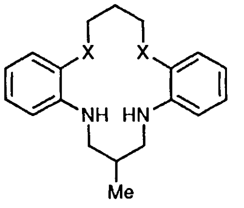
L^7



L^8



	X
L^9	NH
L^{10}	O



	X
L^{11}	NH
L^{12}	O

Experimental

Physical measurements were performed as described previously.[3,4] Stability constants were determined potentiometrically

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: dyn = 10^{-5} N.

in 95% methanol (I = 0.1 mol dm^{-3}, $\mathrm{NEt_4ClO_4}$) as described elsewhere [7] and the data processed using local versions of MINIQUAD [8] or SUPERQUAD.[9] Quoted log K values (Table 1) are the means of at least two (and up to five) individual determinations at different metal:ligand ratios.

Molecular mechanics calculations, based on Allinger's MM2 force field,[10] were performed using a suite of computer programs written at James Cook University. The minimisation of molecular geometry involves a quasi-Newton minimisation algorithm and BFGS update method with analytical first derivatives.

Macrocycles L^1—L^3 were obtained by reduction of the corresponding di-imine precursors with sodium tetrahydroborate under relatively forcing conditions (large excess of reagent in EtOH, 75 °C, 9 h).[11,12] The preparation and characterisation of L^7 and L^8 have been reported previously.[13] Ligands L^9, 1,3-bis(*o*-aminophenylamino)propane, and L^{10}, 1,3-bis(*o*-aminophenoxy)propane were also prepared as reported previously.[14,15]

Preparation of the meso-*Dialkyl-substituted Macrocycles* L^4—L^6.—The di-imine 8,9,16,17,18,19-hexahydro-7*H*-dibenzo[*e,n*][1,4,8,12]tetra-azacyclopentadecine [10] (2.30 g) was added in portions over 10 min to a freshly prepared solution of the appropriate Grignard reagent (150 mmol) in $\mathrm{Et_2O}$–benzene (1:1, 200 cm^3). The mixture was heated at reflux for 30 min, cooled, then treated with saturated ammonium chloride solution (200 cm^3) and extracted with dichloromethane (3 × 100 cm^3). The organic phase, after drying and evaporation, gave a pale yellow residue which on recrystallisation from methanol–light petroleum (b.p. 40–70 °C) (60:40) yielded L^4—L^6 as pale yellow needles in each case.

Compound L^4: yield 89%, m.p. 164 °C (Found: C, 75.3; H, 9.1; N, 15.2. $\mathrm{C_{23}H_{34}N_4}$ requires C, 75.4; H, 9.4; N, 15.3%); ^{1}H n.m.r. ($\mathrm{CDCl_3}$) δ 0.78 (t plus s, $\mathrm{CH_2C}H_3$ and NH), 1.25—2.29 (m, $\mathrm{C}H_2\mathrm{CH_3}$ and $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.53 (t, $\mathrm{NHC}H_2\mathrm{CH_2C}H_2\mathrm{NH}$), 3.17—3.77 (m, $\mathrm{CH_3CH_2C}H$ and $\mathrm{NHC}H_2\mathrm{C}H_2\mathrm{NH}$), and 6.34—7.32 (m, aromatic); parent ion at *m*/*z* 366. Compound L^5: yield 80%, m.p. 132—134 °C (Found: C, 76.0; H, 9.5; N, 14.3. $\mathrm{C_{25}H_{38}N_4}$ requires C, 76.1; H, 9.7; N, 14.2%); ^{13}C n.m.r. ($\mathrm{CDCl_3}$) δ 14.2 ($\mathrm{CH_3}$), 20.3 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 31.4 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 34.6 ($\mathrm{CH}C\mathrm{H_2CH_2}$), 41.8 ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 45.8 ($\mathrm{NH}C\mathrm{H_2}C\mathrm{H_2NH}$), 65.9 (NHCH), 109.6, 115.4, 125.4, 128.0, 129.5, and 147.4 (aromatic), parent ion at *m*/*z* 394. Compound L^6: yield 71%, m.p. 97—99 °C (Found: C, 76.5; H, 10.3; N, 13.3. $\mathrm{C_{27}H_{42}N_4}$ requires C, 76.7; H, 10.0; N, 13.3%); ^{13}C n.m.r. ($\mathrm{CDCl_3}$) δ 14.0 ($\mathrm{CH_3}$), 22.7 ($\mathrm{CH_2}C\mathrm{H_2CH_3}$), 29.2 ($C\mathrm{H_2CH_2CH_3}$), 31.4 ($\mathrm{NHCH_2}C\mathrm{H_2CH_2NH}$), 32.1 ($C\mathrm{H_2CH_2CH_2CH_3}$), 41.7 ($\mathrm{NH}C\mathrm{H_2CH_2}C\mathrm{H_2NH}$), 45.6 ($\mathrm{NH}C\mathrm{H_2}C\mathrm{H_2NH}$), 65.9 (NHCH), 109.4, 115.2, 125.3, 127.8, 129.3, and 147.3 (aromatic); parent ion at *m*/*z* 422. The spectroscopic and structural data for L^4—L^6 are consistent with the respective syntheses proceeding stereoselectively to yield *meso* isomers in each case.[13]

Preparation of Selected Zinc and Cadmium Complexes of L^2—L^6.—Crystalline metal nitrato complexes of these ligands were obtained from acetonitrile. The preparation of $\mathrm{[CdL^6(NO_3)]NO_3}$ is typical of the general procedure. Ligand L^6 (0.144 g) was added to a warm solution of $\mathrm{Cd(NO_3)_2\cdot 4H_2O}$ (0.128 g) in MeCN (50 cm^3). The solution was heated under reflux for 5 min, then water (15 cm^3) was added dropwise. The resulting solid which formed was then isolated. It was recrystallised by slow evaporation of a MeCN solution under reduced pressure to yield $\mathrm{[CdL^6(NO_3)]NO_3}$ as colourless needles (0.168 g). Yield 77%. A crystal from this product was used for the *X*-ray structure determination.

Preparation of L^{11} *and* L^{12}.—These macrocycles were obtained from L^9 or L^{10} in two steps *via* a condensation with 3-ethoxy-2-methylacryl aldehyde using a procedure developed for the unsaturated precursor of L^{11} by Breitmaier and Behr [15] and the corresponding precursor of L^{12} by Ansell *et al.*,[16] followed by hydrogenation.

15,16,17,18-*Tetrahydro-7-methyl-*9H,14H-*dibenzo*[b,i]-[1,4,8,11]*tetra-azacyclotetradecine.* This precursor was obtained in 40% yield using the procedure of Ansell *et al.*,[16] but performing the condensation reaction for 4 h in refluxing toluene under an atmosphere of nitrogen. M.p. 193.5—195 °C (lit.,[15] 192—194 °C). N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 2.00 (qnt.), *J* 5, $\mathrm{NHCH_2C}H_2$), 2.05 (s, $\mathrm{CCH_3}$), 3.41 (t, *J* 5, $\mathrm{NHC}H_2$), 4.72 (s, $\mathrm{CH_2}NH$), 6.50—7.40 (m, aromatic and $\mathrm{CHN}H$), and 7.93 (d, *J* 5 Hz, $\mathrm{NHC}H$); ^{13}C, δ 18.3 ($\mathrm{CH_3}$), 28.7 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 45.4 ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 103.1 ($C\mathrm{CH_3}$), 112.8, 113.6, 119.2, 124.1, 134.9, 139.8, and 146.5 [aromatic and $C\mathrm{HC(CH_3)}C\mathrm{H}$]. Parent ion at *m*/*z* 306.

5,6,7,8,15,16,17,18-*Octahydro-7-methyl-*9H,14H-*dibenzo*[b,i]-[1,4,8,11]*tetra-azacyclotetradecine* (L^{11}). The product (5.6 g) from the above preparation was suspended in toluene (600 cm^3) together with 5% palladium on activated carbon (3.24 g) in an autoclave (1 000 cm^3). Reduction was carried out at 30 °C under 50 atm (*ca.* 5 × 10^6 Pa) of hydrogen for 18 h with constant stirring. The filtered orange solution was evaporated to dryness, and ethyl acetate was then added. A yellow precipitate formed. Recrystallisation of this product from ethyl acetate yielded pale yellow crystals of L^{11} (3.24 g, 57%). M.p. 180—182 °C (Found: C, 73.2; H, 8.4; N, 17.9. $\mathrm{C_{19}H_{26}N_4}$ requires C, 73.5; H, 8.4; N, 18.0%). N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, δ 1.05 (d, *J* 6.7, $\mathrm{CH_3}$), 1.95—2.45 (m, $\mathrm{NHCH_2C}H_2$ and $\mathrm{CH_2C}H$), 2.94 (t, *J* 12 Hz, $\mathrm{NHC}H_2$), 3.10—3.26 (m, $\mathrm{NHC}H_2$), 3.36—3.60 (m, $\mathrm{NHC}H_2$), 4.35 (s, $\mathrm{CH_2N}H$), and 6.60—7.00 (m, aromatic); ^{13}C, δ 17.9 ($\mathrm{CH_3}$), 26.7 [$\mathrm{CH_2}C\mathrm{H(CH_3)CH_2}$], 31.5 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 45.7 ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 52.7 [$\mathrm{NH}C\mathrm{H_2CH(CH_3)}$], 111.1, 111.2, 119.3, 119.4, and 137.7 (aromatic). Parent ion at *m*/*z* 310.

16,17-*Dihydro-7-methyl-*9H,15H-*dibenzo*[b,i][1,11,4,8]*dioxadiazacyclotetradecine.* A solution of 3-ethoxy-2-methylacrylaldehyde (1.1 cm^3) and ^{10} (2.58 g) in toluene (90 cm^3) was refluxed with stirring under nitrogen for 4 h. After evaporating to dryness, methanol was added and yellow needles of the required compound (1.26 g, 41%) were obtained. Recrystallisation from methanol gave white needles of the product. M.p. 237—238 °C (lit.,[14] 237—238 °C).

5,6,7,8,16,17-*Hexahydro-7-methyl-*9H,15H-*dibenzo*[b,i]-[1,11,4,8]*dioxadiazacyclotetradecine* L^{12}. The product from the above preparation (9.34 g) together with 5% palladium on activated carbon (5.00 g) were added to toluene (1 000 cm^3) in an autoclave (2 000 cm^3). The reduction was performed under 50 atm of hydrogen with stirring for 18 h at 30 °C. The pale yellow solution obtained after filtration was evaporated to dryness and ethyl acetate was then added to yield white crystals of the product (0.96 g, 84%). Recrystallisation was from ethyl acetate. M.p. 153.5—155.0 °C (Found: C, 73.0; H, 7.8; N, 9.3. $\mathrm{C_{19}H_{24}N_2O_2}$ requires C, 73.0; H, 7.8; N, 9.0%). N.m.r. ($\mathrm{CDCl_3}$): ^{1}H, 1.05 (d, *J* 6.7, $\mathrm{CHC}H_3$), 2.00—2.50 (m, $\mathrm{OCH_2C}H_2$ and $\mathrm{CH_3C}H$), 3.03 (t, *J* 12 Hz, $\mathrm{NHC}H_2$), 3.35—3.54 (m, $\mathrm{NCH_2}$), 4.16—4.60 (m, $\mathrm{OCH_2}$), 5.05 (s, $\mathrm{CH_2N}H$), and 6.60—7.00 (m, aromatic); ^{13}C, δ 17.8, ($\mathrm{CH_3}$), 28.6 [$\mathrm{CH_2}C\mathrm{H(CH_3)CH_2}$], 31.4 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 51.5 [$\mathrm{NH}C\mathrm{H_2CH(CH_3)}$], 67.8 ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 109.7, 110.1, 116.4, 121.3, 138.1, and 146.5 (aromatic). Parent ion at *m*/*z* 312.

X-*Ray Structure Determinations.*—*Crystal data.* Ligand L^4, 5,11-diethyl-6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e,n*][1,4,8,12] tetra-azacyclopentadecine, $\mathrm{C_{23}H_{34}N_4}$, M = 366.55, orthorhombic, space group *Pbca*, a = 16.382(3), b = 16.502(3), c = 15.848(3) Å, U = 4 284.3 Å^3, Z = 8, D_c = 1.137 g cm^{-3}, F(000) = 1 600, μ(Mo-K_α) = 0.6 cm^{-1}.

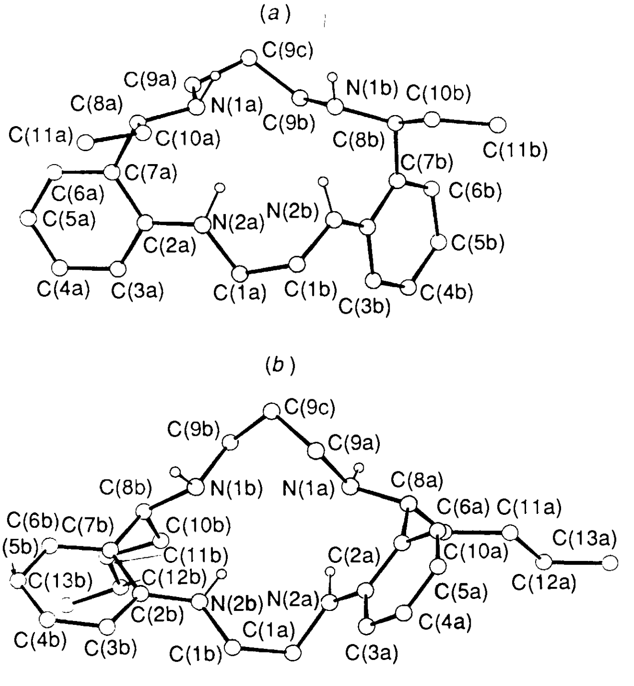

Figure 1. The structure of the 15-membered ring macrocycles (*a*) L^4 (*meso* isomer) and (*b*) L^6 (*meso* isomer)

Ligand L^6, 5,11-di-n-butyl-6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e*,*n*][1,4,8,12]tetra-azacyclopentadecine. $C_{27}H_{42}N_4$, $M = 422.67$, triclinic, space group $P\bar{1}$, $a = 11.305(3)$, $b = 11.031(3)$, $c = 10.947(2)$ Å, $\alpha = 109.44(2)$, $\beta = 84.66(2)$, $\gamma = 87.13(2)°$, $U = 1\,276.95$ Å^3, $Z = 2$, $D_c = 1.099$ g cm^{-3}, $F(000) = 464$, μ(Mo-K_α) = 0.6 cm^{-1}.

[ZnL^2(NO$_3$)(H$_2$O)]NO$_3$, aqua(6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e*,*n*][1,4,8,12]tetra-azacyclopentadecine)nitratozinc(II) nitrate. $C_{19}H_{28}N_6O_7Zn$, $M = 517.85$, monoclinic, space group $C2/c$, $a = 19.628(4)$, $b = 7.679(2)$, $c = 29.153(6)$ Å, $\alpha = 90$, $\beta = 99.28(2)$, $\gamma = 90°$, $U = 4\,336.5$ Å^3, $Z = 8$, $D_c = 1.586$ g cm^{-3}, $F(000) = 2\,160$, μ(Mo-K_α) = 2.8 cm^{-1}.

[CdL^2(NO$_3$)]NO$_3$, (6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e*,*n*][1,4,8,12]tetra-azacyclopentadecine)nitratocadmium(II) nitrate. $C_{19}H_{26}CdN_6O_6$, $M = 546.85$, monoclinic, space group $P2_1/c$, $a = 8.310(2)$, $b = 18.945(4)$, $c = 14.352(3)$ Å, $\alpha = 90$, $\beta = 100.09(2)$, $\gamma = 90°$, $U = 2\,224.5$ Å^3, $Z = 4$, $D_c = 1.633$ g cm^{-3}, $F(000) = 1\,112$, μ(Mo-K_α) = 10.23 cm^{-1}.

[CdL^6(NO$_3$)]NO$_3$,(5,11-di-n-butyl-6,7,8,9,10,11,16,17,18,19-decahydro-5*H*-dibenzo[*e*,*n*][1,4,8,12]tetra-azacyclopentadecine)nitratocadmium(II) nitrate. $C_{27}H_{42}CdN_6O_6$, $M = 659.1$, monoclinic, space group $P2_1/n$, $a = 16.487(3)$, $b = 23.196(4)$, $c = 7.905(2)$ Å, $\alpha = 90$, $\beta = 98.79(3)$, $\gamma = 90°$, $U = 2\,987.6$ Å^3, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $F(000) = 1\,368$, μ(Mo-K_α) = 7.74 cm^{-1}.

Data were collected in the range θ 3—25° for all structures and processed using methods which have been described previously.[17] No absorption corrections were applied. In both cadmium structures residual peaks of *ca.* 1.5 e Å^{-3} were located in the vicinities of the metal atoms. Equivalent reflections were averaged to give the following unique data with $I > 3\sigma(I)$; L^4, 1 140; L^6, 2 159; [ZnL^2(NO$_3$)(H$_2$O)]NO$_3$, 2 238; [CdL^2(NO$_3$)]NO$_3$, 2 013; [CdL^6(NO$_3$)]NO$_3$, 2 506.

Structure solution and refinement. The structures of the free ligands L^4 and L^6 were solved by direct methods using the automatic centrosymmetric routine of the SHELX program.[18] Most hydrogen atoms were located from Fourier-difference maps calculated using data with $\sin\theta < 0.35$. For consistency those attached to carbon atoms were included in calculated positions (C–H 1.08 Å) during refinement whereas amine hydrogens were included at the observed positions. All the non-hydrogen atoms, with the exception of those in the benzene rings of L^6, were assigned anisotropic thermal parameters in full-matrix refinement which converged at R and R' values of 0.065 and 0.060, respectively, for L^4 and 0.074 and 0.074, respectively, for L^6. Weighting schemes were as previously reported.[7]

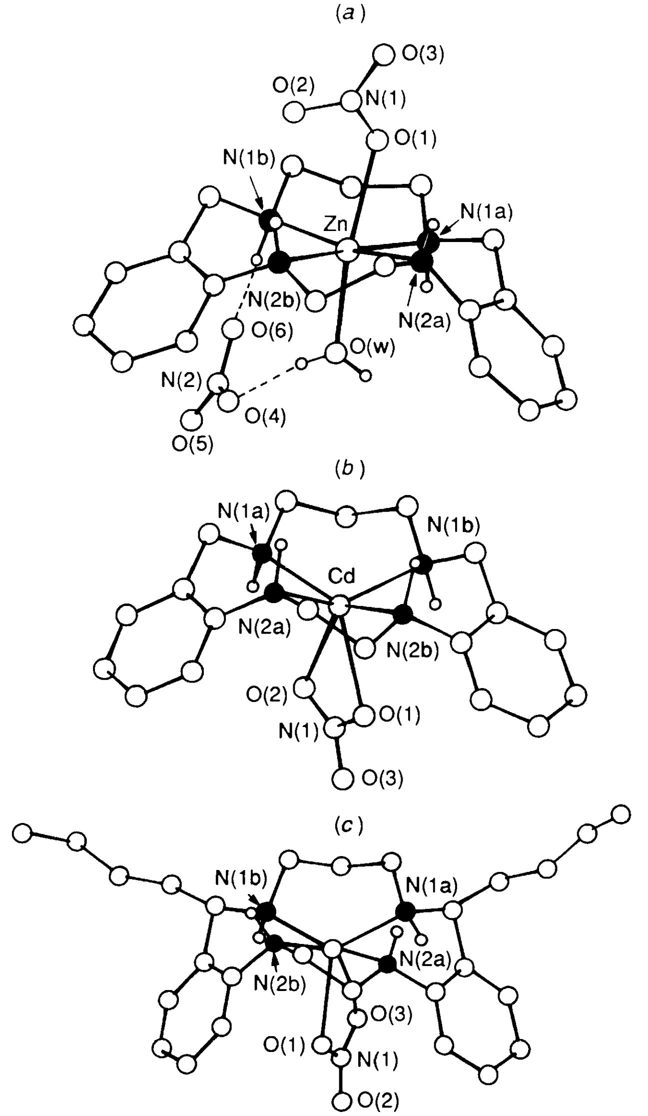

Figure 2. The structure of the cations (*a*) [ZnL^2(NO$_3$)(H$_2$O)]$^+$, (*b*) [CdL^2(NO$_3$)]$^+$, and (*c*) [CdL^6(NO$_3$)]$^+$. Atom labels in the macrocyclic ligands correspond to those used in Figure 1

For the complexes [ZnL^2(NO$_3$)(H$_2$O)]NO$_3$, [CdL^2(NO$_3$)]NO$_3$, and [CdL^6(NO$_3$)]NO$_3$ the metal atoms were located from Patterson syntheses. The remaining non-hydrogen atoms and the amine hydrogen atoms were found in Fourier-difference syntheses. Two carbon atoms, C(12a) and C(13a) in [CdL^6(NO$_3$)]NO$_3$, were disordered and each was assigned two sites at half occupancy during refinement. In the final stages of refinement for each complex, the nitrate atoms and the atoms occupying the respective co-ordination spheres of the metals were assigned anisotropic thermal parameters. Final values of R and R' were 0.043 and 0.045 for [ZnL^2(NO$_3$)(H$_2$O)]NO$_3$, 0.044 and 0.055 for [CdL^2(NO$_3$)]NO$_3$, and 0.048 and 0.048 for [CdL^6(NO$_3$)]NO$_3$. The final atomic co-ordinates are given in

Table 1. Ligand protonation constants and stability constants for the complexes of Zn^{II} and Cd^{II} with L^1–L^{12} [95% MeOH, I = 0.1 mol dm^{-3} (NEt_4ClO_4) at 25 °C]

	Free ligand[a]			log K_{ML}	
Ligand	log β_1	log β_2	log β_3	M = Zn	Cd
L^1	9.45	13.30	14.49	8.6	7.75
L^2	9.72	14.69	16.70	8.6	5.4
L^3	9.93	16.95	18.66[b]	6.4	6.2
L^4	9.69	16.88	18.76	6.3	4.0
L^5	9.51	16.52		6.0	3.9
L^6	9.43	16.53	18.17	5.9	4.1
L^7	9.75	18.55	20.87	8.6	8.1
L^8	9.05	14.36	16.96[c]	7.9	7.7
L^9	5.37	9.67		≈3.1	≈3.0
L^{10}	4.98	9.05		<3.0	<3.0
L^{11}	4.19	7.29		3.8	—
L^{12}	4.28	6.11		<3.0	<3.0

[a] In general, log β values beyond log β_3 (or for the systems indicated, log β_2) were not obtained. [b] Attempts to obtain the log β values for the next ligand in the series [that is, of similar structure to L^1—L^3 but with n = 5] was precluded by the presence of a persistent discontinuity (presumably reflecting precipitation) in the region of the titration curve corresponding to the highest ligand protonation constant. [c] log $\beta_4 \approx$ 18.24; literature values (D. W. Gruenwedel, *Inorg. Chem.*, 1968, **7**, 495) for water (I = 0.1 mol dm^{-3}) log β_1 = 9.00, log β_2 = 14.90, log β_3 = 19.28, log β_4 = 21.28; log K for zinc complex = 7.2.

Table 2 while details of the structures are shown in Figures 1 and 2.

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

Results and Discussion

Stability Constant Determinations.—Potentiometric (pH) titrations were used to determine the protonation constants for L^1—L^{12} as well as the stability constants for a range of the corresponding complexes of Zn^{II} and Cd^{II} (Table 1). The log K values correspond to the formation of the respective ML^{2+} species; equilibrium was attained quickly in each case.

The 14- and 15-membered rings L^1 and L^2 yield complexes with Zn^{II} whose stability constants are quite similar. In contrast, the stability of the corresponding complex of the 16-membered ring L^3 is considerably lower; the fall in stability appears greater than expected solely from the incorporation of a seven-membered chelate ring in this latter structure.[19] For Cd^{II} a similar drop in stability along the series is observed but in this case it is the 15-membered ring species which first has a lower stability than expected (there is a slight rise in stability on moving to the 16-membered ring complex).

The different stability patterns for the complexes of Zn^{II} and Cd^{II} are illustrated in Figure 3. Clearly, the occurrence of different dislocation points along the series for the above metal results in the 15-membered ring L^2 showing enhanced discrimination for Zn^{II} over Cu^{II}. The stability variations illustrated are consistent with the complexes of Zn^{II} and Cd^{II} with the 14-membered ring L^1 having similar structures in solution and with those of the 16-membered ring L^3 giving a different type of structure (but again similar in the respective complexes of Zn^{II} and Cd^{II}); the small additional stability of each zinc complex over the corresponding cadmium complex is typical of the situation found for simple polyamine ligands.[19] In contrast, the enhanced discrimination for Zn^{II} over Cd^{II} (Δ log K 3.2) found for the 15-membered ring L^2 very likely reflects the presence of complexes with significantly different structures in solution. Some support for this is provided by the results of X-ray determinations (see below) of the structures of the crystalline complexes of Zn^{II} and Cd^{II} with L^2 formed in the presence of the weakly co-ordinating nitrate anion. In the zinc complex two axial ligands are bonded to the metal in a pseudo-octahedral structure of type $[ZnL^2(NO_3)(H_2O)]^+$ whereas in $[CdL^2(NO_3)]^+$ the metal is five-co-ordinated and lies substantially out of the macrocyclic ligand-donor plane (towards the NO_3^- ligand). It seems probable that these same structures are not maintained in solution, but nevertheless it appears likely that different co-ordination geometries will persist leading to the observed enhanced stability difference.

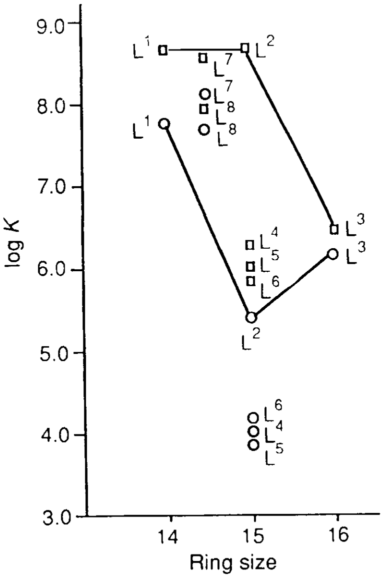

Figure 3. Log K values for the formation of 1:1 complexes with L^1—L^8 in 95% MeOH (I = 0.1 mol dm^{-3}, NEt_4ClO_4) at 25 °C: □, Zn^{II}; ○, Cd^{II}

One possibility is that the stability dislocation in solution, which is evident for the 15-membered ring, involves a change in the mode of co-ordination from one in which the metal interacts with all four donors of the macrocycle (in the case of Zn^{II}) to one in which, for Cd^{II}, a strong interaction with the more basic benzylamine nitrogen atoms is maintained while the much poorer donor anilino nitrogens are rejected in favour of solvent molecules. In a previous study, *exo* structures related to the type proposed are associated with structural dislocations involving complexes of Zn^{II} and Cd^{II} with O_2N_3-donor macrocyclic systems in which non-co-ordination of the ether functions occurs in one system but not the other.[4] In the present study, the similarity of the stabilities observed for the complexes of the 16-membered ring L^3 also fits the overall pattern; the data for both complexes are consistent with them having related structures in which non-co-ordination of the macrocyclic anilino nitrogens occurs.

In an extension to the present study, the poor donor properties of anilino nitrogen atoms towards Zn^{II} and Cd^{II} have been confirmed by determining the log K values for complexes of these metals with the related dibenzo ligands L^9 and L^{10} and L^{11} and L^{12}. These ligands, which contain only anilino-type nitrogen donors, form quite weak complexes with Zn^{II} and Cd^{II} (see Table 1). Inspection of the data suggests that the anilino nitrogen atoms have affinities towards Zn^{II} and Cd^{II} which are not greatly different from those of ether oxygen.

Additional support for the weak co-ordinating ability of anilino donors is provided by the previously published X-ray structure of $[CdL^8I_2]$.[12] The complex cation is five-co-ordinate in the solid state with both iodides bonded to the Cd^{II}, L^8 acts

Table 2. Fractional atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Ligand L^4							
C(1a)	0.116 2(5)	0.187 7(5)	0.154 0(5)	C(11b)	−0.295 3(5)	0.249 2(6)	0.112 2(6)
N(2a)	0.109 2(4)	0.107 8(4)	0.190 7(5)	C(10b)	−0.233 1(4)	0.191 8(5)	0.150 8(5)
C(2a)	0.169 7(5)	0.050 1(5)	0.183 5(5)	C(9b)	−0.103 2(5)	0.020 2(4)	0.065 3(5)
C(3a)	0.244 1(5)	0.065 7(5)	0.145 2(5)	N(1b)	−0.137 9(4)	0.079 2(4)	0.125 4(4)
C(4a)	0.306 3(5)	0.008 8(7)	0.143 2(6)	C(8b)	−0.129 5(5)	0.143 8(5)	0.084 3(5)
C(5a)	0.292 3(6)	−0.066 9(6)	0.177 9(6)	C(7b)	−0.129 5(5)	0.197 5(4)	0.032 2(5)
C(6a)	0.218 3(6)	−0.083 4(5)	0.216 0(5)	C(6b)	−0.152 5(5)	0.216 5(5)	−0.049 4(6)
C(7a)	0.155 7(5)	−0.027 9(5)	0.220 6(5)	C(5b)	−0.107 3(7)	0.269 5(5)	−0.099 4(6)
C(8a)	0.078 1(6)	−0.047 6(5)	0.269 4(6)	C(4b)	−0.036 0(6)	0.301 3(5)	−0.067 8(7)
C(9a)	−0.005 9(6)	−0.073 3(5)	0.147 7(5)	C(3b)	−0.010 4(5)	0.282 7(5)	0.012 7(6)
C(10a)	0.075 0(6)	−0.007 2(6)	0.355 3(7)	C(2b)	−0.056 6(5)	0.230 8(4)	0.064 5(6)
C(11a)	0.141 1(7)	−0.033 4(7)	0.414 0(6)	N(2b)	−0.033 9(4)	0.213 7(5)	0.146 6(5)
N(1a)	0.004 5(5)	−0.024 8(4)	0.221 1(5)	C(1b)	0.043 3(5)	0.238 3(4)	0.181 7(5)
C(9c)	−0.088 4(5)	−0.063 1(4)	0.102 8(5)				
(*b*) Ligand L^6							
N(1a)	1.080 5(3)	0.565 5(4)	−0.231 1(4)	C(11b)	0.575 1(4)	0.964 4(5)	0.186 7(5)
N(1b)	0.812 8(4)	0.713 6(4)	−0.041 4(4)	C(12b)	0.529 6(4)	1.097 3(5)	0.190 6(5)
N(2a)	1.200 6(4)	0.741 5(4)	−0.047 5(4)	C(13b)	0.417 7(5)	1.154 6(6)	0.286 5(6)
N(2b)	0.974 7(3)	0.874 0(4)	0.112 9(4)	C(2a)	1.298 4(4)	0.659 2(4)	−0.114 8(4)
C(1a)	1.196 2(4)	0.827 6(5)	0.086 3(4)	C(3a)	1.403 4(4)	0.649 5(5)	−0.057 9(5)
C(1b)	1.090 2(4)	0.926 0(4)	0.117 0(5)	C(4a)	1.502 3(4)	0.572 3(5)	−0.132 1(5)
C(9a)	0.967 0(4)	0.549 8(5)	−0.286 2(4)	C(5a)	1.501 2(5)	0.503 2(5)	−0.260 5(5)
C(9c)	0.878 7(4)	0.498 5(5)	−0.206 4(5)	C(6a)	1.397 0(4)	0.509 4(5)	−0.317 5(5)
C(9b)	0.853 6(4)	0.579 0(5)	−0.061 6(4)	C(7a)	1.294 6(4)	0.583 2(4)	−0.248 0(4)
C(8a)	1.183 2(4)	0.588 0(5)	−0.312 8(4)	C(2b)	0.981 9(4)	0.838 0(4)	0.212 4(4)
C(8b)	0.737 0(4)	0.778 4(5)	0.084 8(4)	C(3b)	0.972 2(4)	0.853 7(4)	0.327 7(5)
C(10a)	1.160 5(4)	0.713 0(5)	−0.342 3(5)	C(4b)	0.912 3(4)	0.819 8(5)	0.428 0(5)
C(11a)	1.256 5(5)	0.724 0(5)	−0.447 1(5)	C(5b)	0.803 5(4)	0.770 2(5)	0.416 0(5)
C(12a)	1.243 8(5)	0.846 7(6)	−0.475 5(6)	C(6b)	0.750 5(4)	0.755 1(5)	0.301 9(5)
C(13a)	1.338 1(6)	0.859 2(6)	−0.577 2(6)	C(7b)	0.806 8(4)	0.788 5(4)	0.200 1(4)
C(10b)	0.685 3(4)	0.909 9(5)	0.087 5(4)				
(*c*) $[ZnL^2(NO_3)(H_2O)]NO_3$							
Zn	0.097 59(3)	−0.125 14(9)	0.383 26(2)	C(6b)	0.280 3(3)	−0.042 2(9)	0.301 3(2)
C(1a)	0.145 4(3)	0.062 7(8)	0.474 4(2)	C(5b)	0.306 2(3)	0.125 3(11)	0.296 5(2)
N(2a)	0.080 3(2)	−0.021 7(6)	0.451 8(1)	C(4b)	0.292 7(3)	0.256 7(10)	0.327 2(2)
C(2a)	0.017 0(3)	0.076 0(7)	0.446 3(2)	C(3b)	0.257 0(3)	0.216 3(9)	0.363 2(2)
C(3a)	0.014 0(3)	0.249 8(8)	0.458 3(2)	C(2b)	0.232 9(3)	0.046 0(8)	0.368 3(2)
C(4a)	−0.049 8(3)	0.334 5(7)	0.453 5(2)	N(2b)	0.196 5(2)	−0.001 0(6)	0.406 0(1)
C(5a)	−0.109 7(3)	0.245 5(9)	0.434 9(2)	C(1b)	0.184 0(3)	0.141 5(8)	0.437 9(2)
C(6a)	0.105 9(3)	0.075 4(9)	0.421 1(2)	N(1)	0.177 4(2)	−0.416 1(6)	0.460 8(2)
C(7a)	−0.042 7(3)	−0.014 9(8)	0.427 0(2)	O(1)	0.121 6(2)	−0.369 3(6)	0.435 4(1)
C(8a)	−0.040 4(3)	−0.201 9(8)	0.412 0(2)	O(2)	0.232 7(2)	−0.366 0(9)	0.450 2(2)
N(1a)	−0.003 6(2)	−0.225 1(6)	0.371 3(2)	O(3)	0.175 3(2)	−0.511 5(6)	0.494 0(1)
C(9a)	−0.007 8(3)	−0.410 3(8)	0.355 4(2)	N(2)	0.086 4(3)	−0.923 6(7)	0.228 4(2)
C(9c)	0.027 5(3)	−0.438 5(9)	0.312 3(2)	O(4)	0.105 4(4)	−0.823 0(9)	0.261 0(2)
C(9b)	0.105 8(4)	−0.436 3(8)	0.322 1(2)	O(5)	0.074 6(3)	−0.875 4(9)	0.187 7(2)
N(1b)	0.135 3(3)	−0.258 9(6)	0.330 2(2)	O(6)	0.079 7(3)	−1.079 8(8)	0.236 3(2)
C(8b)	0.213 2(3)	−0.265 1(8)	0.338 3(2)	O(w)	0.067 4(2)	0.109 5(5)	0.344 9(1)
C(7b)	0.242 7(3)	−0.084 6(7)	0.336 1(2)				
(*d*) $[CdL^2(NO_3)]NO_3$							
Cd	0.010 06(8)	0.153 70(3)	0.129 96(4)	C(9c)	−0.357 7(11)	0.105 1(5)	0.028 8(6)
N(1)	0.181 4(9)	0.130 0(4)	−0.023 1(6)	C(9b)	−0.361 1(10)	0.183 7(5)	0.052 7(7)
O(1)	0.206 1(10)	0.178 1(4)	0.033 6(6)	N(1b)	−0.200 1(8)	0.218 6(3)	0.053 4(4)
O(2)	0.085 9(11)	0.085 5(4)	−0.008 8(5)	C(8b)	−0.198 7(11)	0.292 6(4)	0.090 2(6)
O(3)	0.246 9(9)	0.129 4(4)	−0.092 2(5)	C(7b)	−0.044 9(12)	0.330 7(4)	0.080 8(6)
C(1a)	0.251 2(11)	0.183 9(5)	0.329 1(6)	C(6b)	−0.050 2(13)	0.385 3(4)	0.014 2(6)
N(2a)	0.157 1(8)	0.122 5(3)	0.284 6(5)	C(5b)	0.090 1(16)	0.418 3(5)	0.000 7(7)
C(2a)	0.226 0(11)	0.054 8(4)	0.273 3(6)	C(4b)	0.236 6(15)	0.400 4(5)	0.052 0(8)
C(3a)	0.391 6(11)	0.044 1(5)	0.284 1(6)	C(3b)	0.248 9(12)	0.347 7(5)	0.119 8(6)
C(4a)	0.450 3(12)	−0.022 3(6)	0.266 9(7)	C(2b)	0.108 4(12)	0.314 8(4)	0.137 0(6)
C(5a)	0.345 3(13)	−0.077 9(5)	0.239 1(7)	N(2b)	0.115 6(8)	0.259 9(3)	0.207 0(5)
C(6a)	0.181 2(13)	−0.066 7(4)	0.228 1(6)	C(1b)	0.275 1(12)	0.239 3(5)	0.259 8(7)
C(7a)	0.115 8(11)	−0.001 3(4)	0.244 2(6)	N(2)	−0.226 5(10)	0.212 7(4)	0.327 2(5)
C(8a)	−0.066 9(11)	0.009 1(4)	0.225 3(6)	O(4)	−0.186 9(8)	0.165 6(3)	0.276 2(5)
N(1a)	−0.120 7(8)	0.048 7(3)	0.135 8(4)	O(5)	−0.128 8(10)	0.262 7(4)	0.348 5(5)
C(9a)	−0.299 3(10)	0.055 9(5)	0.111 7(7)	O(6)	−0.348 0(9)	0.210 4(5)	0.360 3(6)

Table 2 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*e*) $[CdL^6(NO_3)]NO_3$							
Cd	0.137 96(4)	0.227 12(3)	0.127 22(8)	C(5a)	0.328 3(6)	0.047 6(5)	0.182 6(14)
N(2a)	0.239 6(4)	0.203 1(3)	−0.031 6(8)	C(6a)	0.246 5(6)	0.051 5(4)	0.105 7(12)
N(2b)	0.176 4(4)	0.317 3(3)	0.008 0(9)	C(7a)	0.217 7(5)	0.102 8(4)	0.029 2(11)
N(1a)	0.082 4(4)	0.138 1(3)	0.072 6(9)	C(2b)	0.185 2(5)	0.350 4(4)	0.159 3(12)
N(1b)	0.028 1(4)	0.274 6(3)	0.194 0(8)	C(3b)	0.261 6(6)	0.368 9(4)	0.238 0(12)
C(1a)	0.293 4(5)	0.252 7(4)	−0.020 5(12)	C(4b)	0.269 1(6)	0.395 3(4)	0.396 5(13)
C(1b)	0.245 4(5)	0.306 1(4)	−0.086 3(12)	C(5b)	0.202 9(6)	0.402 3(4)	0.475 9(14)
C(9a)	−0.006 9(5)	0.141 4(4)	0.024 4(14)	C(6b)	0.127 0(5)	0.385 1(3)	0.399 7(12)
C(9c)	−0.046 9(5)	0.181 2(4)	0.140 2(14)	C(7b)	0.116 5(5)	0.358 8(3)	0.240 5(11)
C(9b)	−0.046 2(5)	0.245 7(4)	0.106 5(14)	C(12a)	0.096 3(13)	−0.022 7(9)	−0.350 2(30)
C(8a)	0.129 0(5)	0.107 9(4)	−0.049 6(12)	C(13a)	0.129 0(15)	−0.038 1(11)	−0.511 9(36)
C(8b)	0.033 1(5)	0.337 7(3)	0.158 2(12)	C(12c)	0.122 5(12)	0.046 0(8)	0.392 2(27)
C(10b)	−0.039 4(5)	0.370 2(4)	0.213 6(12)	C(13c)	0.143 7(14)	0.004 9(10)	−0.551 4(32)
C(11b)	−0.040 5(5)	0.434 3(4)	0.168 9(13)	O(1)	0.240 5(5)	0.234 9(3)	0.363 2(10)
C(12b)	−0.120 7(6)	0.463 2(4)	0.192 3(14)	O(3)	0.257 6(4)	0.194 2(4)	0.609 4(9)
C(13b)	−0.121 2(7)	0.528 5(4)	0.143 9(17)	O(2)	0.154 6(5)	0.174 4(4)	0.425 5(10)
C(10a)	0.090 3(6)	0.050 4(4)	−0.110 7(14)	N(1)	0.218 5(5)	0.201 8(4)	0.468 7(12)
C(11a)	0.131 8(7)	0.020 5(5)	−0.254 2(16)	O(2a)	0.069 6(5)	0.231 1(4)	−0.208 3(10)
C(2a)	0.270 9(5)	0.149 4(4)	0.035 0(11)	O(2b)	0.049 4(5)	0.317 7(5)	−0.289 4(13)
C(3a)	0.351 1(5)	0.144 9(4)	0.110 3(12)	O(2c)	−0.004 2(5)	0.249 7(5)	−0.450 5(11)
C(4a)	0.379 0(6)	0.093 7(4)	0.184 4(14)	N(2)	0.037 5(6)	0.263 0(6)	−0.321 8(15)

as a tridentate ligand with one of its anilino nitrogen donors unco-ordinated.

The influence of ring substitution on the discrimination for Zn^{II} shown by the 15-membered ring ligand L^2 was investigated by preparing the *meso*-dialkyl-substituted macrocycles L^4—L^6. As expected from steric considerations, the appending of bulky alkyl groups adjacent to the two 'aliphatic' amine donors of L^2 results in a drop in stability for each of the metal-containing species relative to the corresponding (unsubstituted) parent complexes. Indeed, in the case of the zinc complexes, there is a gradual drop in the log K value as the bulkiness of the alkyl substituent increases. However, even though the absolute values of the stabilities are decreased, a substantial stability difference still occurs between the respective pairs of zinc and cadmium complexes; that is, the discrimination observed for the parent 15-membered ring is largely maintained for its substituted derivatives.

In a further study, the interaction of the above ions with the open-chain ligands L^7 and L^8 was investigated. The dislocation behaviour shown by L^2 is no longer observed on complexation of the linear analogues L^7 and L^8. For the latter ligands the respective cadmium complexes are only slightly less stable than the corresponding zinc species. Thus, it seems likely that the dislocation behaviour discussed above is dependent on the presence of a macrocyclic ring in the ligand structure. Nevertheless, it is also clear that the observed behaviour does not simply reflect ring-size discrimination of the type which solely involves the match or otherwise of the metal ion for the macrocyclic cavity.[2,20] This is not unexpected for metal ions such as Zn^{II} and Cd^{II} which show considerable facility for variation of co-ordination number and interbond angles, making it relatively easy for them to achieve geometries in which the metal lies partly or wholely outside the macrocyclic cavity.

X-Ray Diffraction Studies.—In view of the discrimination observed within the ligand series L^1—L^6, the *X*-ray structures of a 'key' zinc complex, $[ZnL^2(NO_3)(H_2O)]^+$, and two cadmium complexes, $[CdL^2(NO_3)]^+$ and $[CdL^6(NO_3)]^+$, were determined. In addition, the structures of two (uncomplexed) ligands, L^4 and L^6, used in the investigation are also reported. Details of the structures are shown in Figures 1 and 2. The structure of L^1 has been reported previously.[21]

The complex $[ZnL^2(NO_3)(H_2O)]^+$ differs from the above cadmium complexes in having a six-co-ordinate structure with the metal atom lying fairly close to the best plane through the four nitrogen donors and with a monodentate nitrate and a water molecule defining apical sites in an approximately octahedral geometry. The displacement of the zinc from the N_4 plane (0.12 Å towards the co-ordinated water molecule) is comparable to that observed in the *trans* (six-co-ordinate) zinc thiocyanate complexes of the aliphatic ligands 1,4,8,11-tetra-azacyclotetradecane and 1,4,8,12-tetra-azacyclopentadecane which have the zinc located 0.18 and 0.19 Å from the respective N_4 planes.[22] The bond from zinc to the apical water molecule is significantly shorter than that to the nitrate group. The latter shows a bond length which falls outside the range observed[21] (2.04—2.05 Å) for monodentate ligands, but in these other complexes[21] the zinc has a lower co-ordination number. In contrast, the cadmium complexes $[CdL^2(NO_3)]^+$ and $[CdL^6(NO_3)]^+$ have only one ligand in addition to the macrocycle in the co-ordination sphere and have the metal much further displaced from the N_4 planes (0.61 and 0.49 Å, respectively) towards the co-ordinated nitrate ions. The nitrato groups adopt an unsymmetrical bidentate mode of co-ordination which is typical[20] of cadmium complexes. Bond lengths to the nitrate oxygen atoms fall centrally in the range 2.29—2.83 Å which has been observed[20] for such complexes. In all these complexes, and in the five-co-ordinate structure $[ZnL^2I]^+$ reported earlier,[23] the ligands adopt a folded conformation with the chelate rings incorporating the benzyl units being displaced to the same side of the N_4 plane as the metal ion is. This arrangement generates a pseudo-mirror-plane relationship between the two halves of the molecule and equivalent bonds in the inner great ring have torsion angles with similar values but opposite handedness (see Table 5). This pseudo-mirror-plane symmetry breaks down in the ethane linkage between the anilino nitrogen atoms, presumably because it would result in the high-energy eclipsed conformation of the chelate ring [with torsion angle N(2a)–C(1a)–C(1b)–N(2b) near 0°].

From the above discussion, it is unlikely that ligand cavity sizes make a major contribution to Zn^{II}/Cd^{II} selectivity in these

Table 3. Selected[a] bond lengths (Å)

	L^4		L^6	
	Part a	Part b	Part a	Part b
C(1)–N(2)	1.445(9)	1.441(8)	1.451(5)	1.450(6)
N(2)–C(2)	1.379(9)	1.382(9)	1.375(5)	1.388(9)
C(2)–C(3)	1.386(9)	1.406(9)	1.406(7)	1.412(7)
C(2)–C(7)	1.433(10)	1.410(9)	1.425(6)	1.405(6)
C(3)–C(4)	1.386(10)	1.377(10)	1.382(6)	1.402(8)
C(4)–C(5)	1.383(11)	1.374(10)	1.360(7)	1.371(7)
C(5)–C(6)	1.381(10)	1.393(10)	1.392(8)	1.400(8)
C(6)–C(7)	1.377(9)	1.382(9)	1.383(6)	1.395(7)
C(7)–C(8)	1.523(10)	1.511(9)	1.510(7)	1.526(7)
C(8)–C(10)	1.517(10)	1.540(9)	1.532(8)	1.526(7)
C(8)–N(1)	1.478(9)	1.465(8)	1.482(6)	1.489(5)
N(1)–C(9)	1.422(9)	1.477(8)	1.462(6)	1.470(7)
C(9)–C(9)	1.536(9)	1.517(9)	1.517(8)	1.529(6)
C(10)–C(11)	1.492(10)	1.521(9)	1.543(7)	1.527(6)
C(11)–C(12)	—	—	1.490(9)	1.514(8)
C(12)–C(13)	—	—	1.514(9)	1.528(7)
C(1)–C(1′)	1.522(9)	—	1.510(6)	—

	$[ZnL^2(NO_3)(H_2O)]NO_3$		$[CdL^2(NO_3)]NO_3$		$[CdL^6(NO_3)]NO_3$	
	Part a	Part b	Part a	Part b	Part a	Part b
C(1′)–C(1)	1.525(9)	—	1.483(14)	—	1.520(12)	—
C(1)–N(2)	1.488(7)	1.481(8)	1.483(11)	1.460(11)	1.446(11)	1.475(12)
N(2)–C(2)	1.438(7)	1.450(7)	1.426(11)	1.440(11)	1.418(11)	1.410(11)
C(2)–C(3)	1.381(8)	1.405(9)	1.372(13)	1.384(14)	1.368(12)	1.386(12)
C(2)–C(7)	1.402(7)	1.407(9)	1.417(12)	1.415(13)	1.390(12)	1.398(13)
C(3)–C(4)	1.396(9)	1.388(10)	1.387(14)	1.385(14)	1.373(14)	1.383(14)
C(4)–C(5)	1.391(8)	1.401(11)	1.381(14)	1.350(16)	1.355(15)	1.348(15)
C(5)–C(6)	1.371(9)	1.397(11)	1.362(15)	1.366(17)	1.395(13)	1.363(12)
C(6)–C(7)	1.406(8)	1.386(10)	1.387(12)	1.405(12)	1.386(13)	1.385(12)
C(7)–C(8)	1.502(9)	1.506(8)	1.507(13)	1.494(14)	1.505(11)	1.510(11)
C(8)–C(10)	—	—	—	—	1.524(13)	1.532(13)
C(8)–N(1)	1.496(8)	1.510(8)	1.487(10)	1.498(11)	1.497(12)	1.496(11)
N(1)–C(9)	1.492(7)	1.483(8)	1.470(10)	1.490(11)	1.465(10)	1.472(10)
C(9)–C(9c)	1.544(10)	1.518(10)	1.523(12)	1.529(13)	1.520(15)	1.520(13)
C(10)–C(11)	—	—	—	—	1.573(17)	1.526(13)
C(11)–C(12)[b]	—	—	—	—	1.337(25)	1.519(13)
C(12)–C(13)[b]	—	—	—	—	1.50(4)	1.561(15)
M–N(2)	2.227(5)	2.168(4)	2.412(6)	2.387(6)	2.310(7)	2.418(7)
M–N(1)	2.104(5)	2.089(5)	2.275(6)	2.257(6)	2.274(7)	2.251(7)
M–O(1)	2.410(5)	—	2.360(9)	—	2.325(7)	—
M–O(2)	—	—	2.544(8)	—	2.633(8)	—
M–O(w)	2.151(4)	—	—	—	—	—

[a] Primes denote atoms from the alternative part of the molecule; atom C(9c) is the central atom of the trimethylene bridge. [b] The carbon atoms C(12a) and C(13a) are disordered in the structure of $[CdL^6(NO_3)]NO_3$; bond lengths in the alternative location are C(11c)–C(12c) 1.23(3) and C(12c)–C(13c) 1.66(3) Å.

systems. Nevertheless, the availability of *X*-ray data has enabled the analysis by molecular mechanics of the geometries adopted by the respective species.

Molecular Mechanics Calculations.—Although the *X*-ray data discussed above are for related metal-free and metal-containing species, it appeared less than appropriate to compare the *X*-ray hole sizes of the free ligands L^4 and L^6 directly with those occurring in the corresponding metal complexes (Table 6) since the former adopt conformations which differ somewhat from those found in the respective complexes. However, using starting co-ordinates for L^2 derived from $[ZnL^2(NO_3)(H_2O)]^+$ by removal of the co-ordinates for the metal, nitrate, and water moieties, it was possible to use molecular mechanics to obtain a free-ligand structure showing a similar conformation to that found in its complex; a related strategy to this has been employed previously.[24] Minimisation of the structure generated in this way yielded a closely related structure in which the calculated macrocyclic hole size $(R_H)^2$ was 2.20 Å, that is, it lies intermediate between the hole size found in the zinc and cadmium complexes of this ligand by *X*-ray structure analysis. It should be noted that before the above calculation could be performed it was first necessary to obtain suitable force-field parameters for modelling anilino nitrogen groups in compounds such as the present one. No suitable values were available from the MM2 force field; there is uncertainty concerning whether the nitrogen in such groups should be treated as sp^2 and sp^3-hybridised. Using trial and error, it was found that an 'ideal' value for the C(aromatic)–N–C angle of 120° (sp^2 hybridisation) with a bending force constant of 0.5 mdyn Å rad^{-2} resulted in a close match to the respective *X*-ray structures of the free ligands L^4 and L^6 when calculations were performed on each of these species using the *X*-ray co-ordinates as the starting co-ordinates. The above parameters

Table 4. Interbond angles (°) in the co-ordination spheres of the complexes

	$[ZnL^2(NO_3)(H_2O)]NO_3$	$[CdL^2(NO_3)]NO_3$	$[CdL^6(NO_3)]NO_3$
N(2a)-M-N(2b)	80.1(2)	72.2(2)	75.0(2)
N(2a)-M-N(1a)	90.2(2)	85.4(2)	89.0(3)
N(2a)-M-N(1b)	164.4(2)	143.6(2)	157.2(2)
N(2a)-M-O(1)	75.7(2)	107.3(3)	87.5(3)
N(2a)-M-O(2)	—	116.1(2)	112.9(3)
N(2a)-M-O(w)	95.7(2)	—	—
N(2b)-M-N(1a)	170.1(2)	149.2(2)	146.5(2)
N(2b)-M-N(1b)	92.0(2)	87.5(2)	86.4(2)
N(2b)-M-O(1)	94.2(2)	82.6(3)	92.5(2)
N(2b)-M-O(2)	—	132.0(3)	138.9(2)
N(2b)-M-O(w)	87.1(2)	—	—
N(1a)-M-N(1b)	97.8(2)	99.2(2)	100.0(5)
N(1a)-M-O(1)	84.6(2)	125.2(3)	116.5(3)
N(1a)-M-O(2)	—	76.7(3)	74.4(3)
N(1a)-M-O(w)	92.6(2)	—	—
N(1b)-M-O(1)	91.7(2)	99.4(3)	106.7(3)
N(1b)-M-O(2)	—	99.9(2)	89.7(3)
N(1b)-M-O(w)	97.3(2)	—	—
O(1a)-M-O(2)	—	49.9(2)	49.8(3)
O(1)-M-O(w)	170.9(2)	—	—

Table 5. Torsion angles (°) in the inner great rings*

	L^4		L^6	
	Part a	Part b	Part a	Part b
N(2')-C(1')-C(1')-N(2')	−69	—	63	—
C(1')-C(1)-N(2)-C(2)	−174	−77	166	82
C(1)-N(2)-C(2)-C(7)	−179	174	−176	176
N(2)-C(2)-C(7)-C(8)	−2	0	−3	−5
C(2)-C(7)-C(8)-N(1)	50	−50	−52	50
C(7)-C(8)-N(1)-C(9)	67	−67	−174	64
C(8)-N(1)-C(9)-C(9c)	170	−154	166	154
N(1)-C(9)-C(9c)-C(9')	65	−86	60	54

	$[ZnL^2(NO_3)(H_2O)]NO_3$		$[CdL^2(NO_3)]NO_3$		$[CdL^6(NO_3)]NO_3$	
	Part a	Part b	Part a	Part b	Part a	Part b
N(2')-C(1')-C(1)-N(2)	−57	—	54	—	57	—
C(1')-C(1)-N(2)-C(2)	−4	180	109	179	−175	88
C(1)-N(2)-C(2)-C(7)	−177	−177	169	174	178	180
N(2)-C(2)-C(7)-C(8)	−1	4	−1	0	2	−6
C(2)-C(7)-C(8)-N(1)	−67	64	75	−73	−77	81
C(7)-C(8)-N(1)-C(9)	−175	168	176	−174	−174	−174
C(8)-N(1)-C(9)-C(9c)	178	−178	172	−171	−170	178
N(1)-C(9)-C(9c)-C(9')	74	−75	−87	88	81	−88

* Primes denote atoms from the alternative part of the molecule; atom C(9c) is the central atom of the trimethylene bridge.

Table 6. Macrocyclic hole sizes (R_H/Å)* in selected free ligands and complexes calculated from *X*-ray data

L^4	L^6	$[ZnL^2(NO_3)(H_2O)]NO_3$	$[CdL^2(NO_3)]NO_3$	$[CdL^6(NO_3)]NO_3$
2.10	2.14	2.14	2.24	2.25

* See text and ref. 2.

were used for each of the free-ligand calculations undertaken in the present investigation. In a series of further calculations, the starting co-ordinates used corresponded to L^2 in a conformation suitable for co-ordination but were modified such that R was made successively equal to Me, Et, Pr^n, and Bu^n (*meso* isomers). The corresponding hole sizes obtained initially increased as the bulk of R increased but then levelled out. The respective values are 2.20 (H), 2.32 (Me), 2.41 (Et), 2.41 (Pr^n), and 2.41 Å (Bu^n). These results are in accordance with a 'flattening' of the macrocyclic ring due to steric interactions as the bulk of the R substituents increases. This flattening reaches a maximum at R = Et; further lengthening of the alkyl chain no longer leads to an increase in steric interaction with the ring.

Calculations for the metal complexes $[ZnL^2(NO_3)(H_2O)]NO_3$ and $[CdL^2(NO_3)]NO_3$ were also carried out. Force-field parameters for those parts of the molecules involving the Zn^{II} and Cd^{II} were derived by a trial-and-error procedure in which the calculated structures were matched to those found by *X*-ray diffraction. An excellent match to the respective *X*-ray structures was achieved using the parameters listed in Table 7.

Table 7. Force-field parameters influenced by the metal

Bond stretching	r_0/Å	K_r/mdyn Å^{-1}	Bond stretching	r_0/Å	k_r/mdyn Å^{-1}
Zn–N(amine)	2.10	1.50	C–N(anilino)	1.45	5.1
Zn–N(anilino)	2.18	1.20	C[a]–(anilino)	1.43	5.1
Cd–N(amine)	2.29	2.0	H–N(anilino)	1.015	6.1
Cd–N(anilino)	2.40	1.5			

Angle bending	θ/°	k_θ/mdyn Å rad^{-2}	Angle bending	θ/°	k_θ/mdyn Å rad^{-2}
C–N–Zn	109.50	0.20	N(anilino)–Cd–N(amine)	90.0	0.01
C–N(anilino)–Zn	109.50	0.50	N(anilino)–Cd–N(anilino)	90.0	0.01
N(amine)–Zn–N(anilino)	90.0	0.10	C[a]–N(anilino)–C	117.0	0.5
N(anilino)–Zn–N(anilino)	90.0	0.05	C[a]–N(anilino)–H	109.5	0.5
C–N(amine)–Cd	114.0	0.7	C–N(anilino)–H	109.5	0.5
C–N(anilino)–Cd	109.5	0.7	C–C–N(anilino)	109.5	0.57
C[a]–N(anilino)–Cd	109.5	0.7	C[a]–C[a]–N(anilino)	120.0	0.45
N(amine)–Cd–N(amine)	90.0	0.01			

Torsional terms	V_1/kJ mol^{-1}	V_2/kJ mol^{-1}	V_3/kJ mol^{-1}	Torsional terms	V_1/kJ mol^{-1}	V_2/kJ mol^{-1}	V_3/kJ mol^{-1}
M[b]–N(amine)–C–C	0.00	0.00	4.18	C–N(anilino)–C[a]–C[a]	0.00	1.00	0.25
M–N(amine)–C–C[a]	−2.09	0.00	2.09	C[a]–N(anilino)–C–C	1.13	1.13	−0.39
M–N(anilino)–C–C	−1.26	0.00	2.51	N–C–C[a]–C[a]	0.00	1.00	0.25
M–N(anilino)–C–H	0.00	0.00	2.18	N(anilino)–C–C–N(anilino)	−1.67	−4.60	5.02
M–N(amine)–C–H	0.00	0.00	4.18				

[a] Aryl carbon. [b] M = Zn or Cd.

In part, the initial selection of parameters for $[CuL^2(NO_3)]NO_3$ was influenced by the force field used previously for the modelling of a related cadmium nitrate complex of a mixed-donor sexadentate ligand.[25]

All (corresponding) calculated and found bond distances and angles in the zinc structue agreed within 0.05 Å (and usually less than 0.035 Å) and 5°, respectively. For the cadmium structure, with one exception, the bond lengths were all within 0.04 Å; the exception was the C–C distance in the bridge between the anilino nitrogens which was calculated to be 0.053 Å longer than found in the crystal structure. Ignoring the axial ligands, all angles agreed within 5° with only one showing a deviation of greater than 4°.

It is noted that the Allinger (organic) force field does not deal directly with non-bonded interactions between atoms in 1,3 positions but rather the effect of such interactions are accounted for indirectly in the respective bending and torsional parameters associated with the atoms in question. Both metals in the present complexes have 'non-directional' d^{10} configurations and, apart from the need to allow for 1,3 interactions, there should be no requirement for bending or torsional terms for those angles or bonds which directly involve the central metal ion. However, for the present calculations, the incorporations of *small* torsional or bending terms associated with particular donor atom–metal bonds (in an attempt to compensate for 1,3 interactions in the immediate co-ordination spheres of the respective metals) resulted in improved 'fits' of the metal-containing regions of each complex.

The *X*-ray structure of $[ZnL^2(NO_3)(H_2O)]NO_3$ [Figure 2(*a*)] shows that the macrocyclic ligand adopts an arrangement in which both aromatic groups are orientated to one side of the co-ordination plane of this ligand with both anilino H atoms directed towards the opposite side while the 'aliphatic' amine hydrogens point to the same side as the aromatic rings. Starting from this structure, several new sets of co-ordinates were generated by 'manual' manipulation of the *X*-ray co-ordinates and then the structures were minimised using the force field employed to match the *X*-ray structure of $[ZnL^2(NO_3)(H_2O)]NO_3$. For the first calculation the co-ordinates corresponded to a modification of the *X*-ray co-ordinates in which the aromatic rings were orientated approximately in the donor-atom plane of the macrocyclic ring with no change in the relative orientations of the NH groups. Minimisation of this arrangement regenerated the geometry found in the crystal structure. Calculations based on five further starting geometries were performed (all of which were selected as approximating feasible structures following inspection of Drieding models). In all cases the minimised structures were appreciably higher in energy (24—70 kJ mol^{-1}) than that found for the minimised crystal structure (the structure closest in energy to the reference structure had the aromatic rings orientated on either side of the macrocyclic donor plane).

Related calculations to those outlined above were also performed for $[CdL^2(NO_3)]NO_3$. The *X*-ray structure of this complex shows that the anilino hydrogens are both on the same side of the macrocyclic donor plane [Figure 2(*b*)]. Corresponding to this, the aromatic rings are both directed to the other side of the plane. Four possible alternative structures incorporating different relative positions of the amine hydrogens (and also for the aromatic rings) were investigated in a similar manner to that described above. However, in accordance with the situation observed experimentally, all of these (minimised) alternative structures were found to be less stable (by 3, 18, 31, and 48 kJ mol^{-1}) than the reference structure. Given the somewhat approximate parameterisation for the parts of the force field involving the metal it is not clear that the 3 kJ mol^{-1} difference between the energy of the reference structure and that of the closest alternative structure is significant. In any case, as discussed previously,[25] the energy differences just quoted are only approximate as the parts of the force field involving the metal ion have not been calibrated with respect to energy but only with respect to geometry. Nevertheless, the results indicate that, of the several structures investigated, only one appears to be of comparable energy to that observed experimentally in the solid state. This corresponds to an isomer in which the aromatic rings are directed to opposite sides of the co-ordination plane with the anilino hydrogens also orientated to opposite sides of the plane while the 'aliphatic' amine hydrogens lie on the same side of the plane as the co-ordinated nitrato ligand.

Conclusion

Although the *X*-ray structure analysis of the complexes of Zn^{II} and Cd^{II} with L^2 show different structures in the solid state these provide little insight into the likely origins of the solution behaviour illustrated in Figure 3. Nevertheless, as discussed previously, it is probable that major structural differences are associated with the observed dislocation behaviour; likely involving the displacement of anilino donor atoms from the co-ordination sphere in particular complexes.

Overall, the present study documents a further example of dislocation discrimination. Although it has received little study in the past, such a discrimination mechanism is of potential relevance to a range of other metal-containing chemical and biochemical systems.

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