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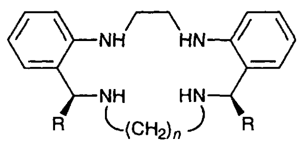
Complexation of lop-sided 16- and 17-membered tetraaza macrocycles containing fused dibenzo substituents with zinc(II) and cadmium(II) †

Philip J. Baillie,*[a] **Nick Choi**,[a] **Leonard F. Lindoy**,[b] **Mary McPartlin**,[a] **Harold R. Powell**[a] and **Peter A. Tasker***[c]

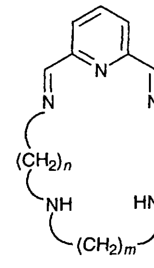
[a] *Department of Molecular Sciences, James Cook University, Queensland 4811, Australia*
[b] *School of Applied Chemistry, University of North London, London N7 8DB, UK*
[c] *Zeneca Specialties, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, UK*

A series of previously reported dibenzo-substituted tetraaza macrocycles has been extended by increasing the length of the bridge between one pair of nitrogen atoms. The new 'lop-sided' 16- and 17-membered macrocycles as well as a range of their zinc(II) and cadmium(II) complexes have been prepared and characterized. Crystal structures of both new macrocycles and of their respective cadmium(II) complexes have been determined. The 16-membered macrocycle yields a pseudo-square-pyramidal cadmium(II) complex whereas the 17-membered one forms a distorted-octahedral complex. Comparison of these structures with those for the cadmium(II) complexes of corresponding 15-membered ring ligands shows that, as the ring size increases, the ligand is generally better able to accommodate the cadmium(II) in the centre of the cavity, thus aiding the formation of a six- rather than five-co-ordinate geometry in the complex of the 17-membered ring.

As an extension of our studies of the effect of variation of ligand ring size on metal-ion complexation behaviour,[1-4] we have expanded the series of dibenzo-substituted tetraaza macrocycles, typified by L^1, to include new members having 16- and 17-membered inner rings, L^3 and L^4. The ring expansion has been achieved by lengthening the polymethylene bridge between the two benzylamino nitrogen atoms. In this way it was intended not only to increase the available macrocycle cavity size, but also to introduce increased 'lop-sidedness' into the larger members of this homologous series. The influence of these changes on the formation of complexes of zinc(II) and cadmium(II), two metals exhibiting 'flexible' co-ordination spheres,[2,3,5] is considered.



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



	n	m
L^7	2	3
L^8	3	2

Experimental

Infrared spectra were recorded as potassium bromide microdiscs on a Bio-Rad FTS-40 spectrophotometer linked to a 3240-SPC data station, with internal He-Ne laser calibration. The NMR spectra of the macrocycles were recorded using a Bruker AM 250 spectrometer with the ^{1}H and ^{13}C referenced to tetramethylsilane at δ 0, ^{15}N NMR spectra with external referencing to nitromethane as a 1 : 1 (v/v) mixture with CDCl$_3$ containing tris(pentane-2,4-dionato)chromium(III) (0.033 mol dm^{-3}).[6] The ^{15}N chemical shifts are quoted with respect to ammonia at δ 0.

Preparation of the macrocycles

The syntheses of L^1 and L^2 have been reported previously.[7,8] The ^{15}N NMR spectrum of L^2 is reported here. The atom labelling scheme in the NMR assignments corresponds to that in the X-ray diffraction studies (see Fig. 1).

L^2. ^{15}N NMR {CDCl$_3$-MeNO$_2$ 1 : 1, [Cr(pd)$_3$] (0.033 mol dm^{-3}), 25.346 MHz}: δ 38.0 [N(1)] and 60.4 [N(2)].

L^3. 7,8,9,10,17,18,19,20-Octahydrodibenzo[*e*,*o*][1,4,8,13]-tetraazacyclohexadecine (4.0 g, 12 mmol) was added to a stirred suspension of lithium tetrahydridoaluminate (5.0 g) in dry diethyl ether (200 cm^3) under nitrogen and heated at reflux for 4 h. After cooling, the mixture was carefully treated with successive additions of water (4 cm^3), sodium hydroxide (15% aqueous, 4 cm^3) and water (12 cm^3) followed by reflux for 0.5 h. The solid residue was filtered off and extracted with boiling dichloromethane (4 × 25 cm^3). The solution was dried with magnesium sulfate and the solvents removed to give a colourless oil which slowly solidified. Recrystallisation from methanol-water (10 : 1 v/v, 110 cm^3) gave L^3 (2.7 g, 8.3 mmol, 68%), m.p. 117–118 °C [Found: C, 73.3; H, 8.4; N, 17.6%; *m*/*z* 324 (M^+). $C_{20}H_{28}N_4$ requires C, 74.0, H, 8.7; N, 17.3%; *M* 324.5]. IR: $\tilde{\nu}$(N–H)/cm^{-1} 3320, 3243 and 3171. NMR (CDCl$_3$): ^{1}H (250.13 MHz), δ 1.2 [2 H, br, N(1)H], 1.56 [4 H, c, H(10)], 2.63 [4 H, c, H(9)], 3.44 [4 H, s, H(1)], 3.77 [4 H, s, H(8)], 6.6 [2 H, b, N(2)H], 6.61 [2 H, c, H(5)], 6.67 [2 H, c, H(3)], 7.00 [2 H, c, H(6)] and 7.16 [2 H, c, H(4)]; ^{13}C (62.896 MHz), δ 27.40 [C(10)], 42.94 [C(1)], 47.81 [C(8)], 53.52 [C(9)], 110.02 [C(3)], 115.96 [C(5)], 123.86 [C(7)], 128.36 [C(4)], 129.65 [C(6)] and 148.36 [C(2)].

L^4. A similar reduction procedure to that used in the preparation of L^3 was performed using the homologous diimine 8,9,10,11,18,19,20,21-octahydro-7*H*-dibenzo[*e*,*p*][1,4,8,14]-tetraazacycloheptadecine to give L^4 as colourless crystals (from

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† Macrocyclic Ligand Ring Size Effects. Part 3.[1]

acetonitrile) (93% yield), m.p. 93.5–94.5 °C [Found: C, 74.5; H, 9.0; N, 16.6%; *m/z* 338 (*M*$^+$). $C_{21}H_{30}N_4$ requires C, 74.5; H, 8.9; N, 16.6%; *M* 338.5]. IR: $\tilde{\nu}$(N–H)/cm^{-1} 3327, 3269 and 3228. NMR: ^{1}H (CDCl$_3$, 250.13 MHz), δ 1.1 [2 H, br, N(1)H], 1.46 [4 H, c, H(10)], 1.60 [2 H, c, H(11)], 2.70 [4 H, t, H(9)], 3.46 [4 H, s, H(1)], 3.75 [4 H, s, H(8)], 6.61 [2 H, c, H(5)], 6.66 [2 H, c, H(3)], 6.8 [2 H, br, N(2)H], 7.01 [2 H, c, H(6)] and 7.17 [2 H, c, H(4)]; ^{13}C (CDCl$_3$, 62.896 MHz), δ 24.15 [C(11)], 27.40 [C(10)], 43.47 [C(1)], 48.42 [C(8)], 53.59 [C(9)], 109.99 [C(3)], 116.06 [C(5)], 124.32 [C(7)], 128.40 [C(4)], 129.62 [C(6)] and 148.60 [C(2)]; ^{15}N {CDCl$_3$–NO$_2$ 1:1, [Cr(pd)$_3$] (0.033 mol dm^{-3}), 25.346 MHz}, δ 35.8 [N(1)] and 63.7 [N(2)].

Preparation of complexes

[CdL^{3}Br]$_2$[CdBr$_4$]·MeOH. Solutions of compound L^3 (0.056 g, 0.17 mmol) in acetonitrile (7 cm^3) and cadmium(II) bromide tetrahydrate (0.110 g, 0.32 mmol) in methanol (5 cm^3) were mixed and the resulting solution was filtered. After 48 h at room temperature colourless crystals were filtered off and washed with a small amount of cold methanol. A few crystals were removed for X-ray diffraction study and the remainder dried *in vacuo* to give [CdL^{3}Br]$_2$[CdBr$_4$] (0.042 g, 0.028 mmol, 34%) (Found: C, 33.3; H, 3.9; N, 8.2. $C_{40}H_{56}Br_6Cd_3N_8$ requires C, 32.8; H, 3.9; N, 7.7%). IR: $\tilde{\nu}$(N–H)/cm^1 3513, 3470, 3298, 3268, 3234, 3200 and 3186.

[CdL^{4}Br$_2$]. Similar treatment of compound L^4 and cadmium(II) bromide tetrahydrate gave [CdL^{4}Br$_2$] (0.022 g, 0.036 mmol, 62%) (Found: C, 41.5; H, 4.9; N, 9.1. $C_{21}H_{30}Br_2CdN_4$ requires C, 41.3; H, 4.9; N, 9.2%). IR: $\tilde{\nu}$(N–H)/cm^{-1} 3253 and 3158. The infrared spectrum of the crystals obtained from acetonitrile, and used for the X-ray diffraction study, was identical to the above except for an extra band at 2249 cm^{-1} due to the presence of acetonitrile.

[CdL^{3}I$_2$]. The compound L^3 (0.32 g, 1.0 mmol) in dichloromethane (5 cm^3) was added to a solution of cadmium(II) iodide (0.37 g, 1.0 mmol) in dichloromethane (40 cm^3) and methanol (20 cm^3) at reflux. After 0.5 h the mixture was evaporated to 5 cm^3 to yield a white solid which was filtered off, washed with methanol, and recrystallised from acetonitrile to give white microcrystals (0.56 g, 0.81 mmol, 81%) (Found: C, 34.8; H, 4.1; N, 8.1. $C_{20}H_{28}CdI_2N_4$ requires C, 34.8; H, 4.1; N, 8.1%). IR: $\tilde{\nu}$(N–H)/cm^{-1} 3232 and 3196.

[ZnL^{3}I$_2$]. A similar procedure to that above using zinc(II) in place of cadmium(II) iodide gave white needles of [ZnL^{3}I$_2$] (85%) (Found: C, 37.4; H, 4.4; N, 8.7. $C_{20}H_{28}I_2N_4Zn$ requires C, 37.3; H, 4.4; N, 8.7%). IR: $\tilde{\nu}$(N–H)/cm^{-1} 3217 and 3193.

[ZnL^{4}I$_2$]. A similar procedure to the above using compound L^4 and zinc(II) iodide gave white microcrystals of [ZnL^{4}I$_2$] (61%) (Found: C, 38.3; H, 4.7; N, 8.5. $C_{21}H_{30}I_2N_4Zn$ requires C, 38.4; H, 4.6; N, 8.5%). IR: $\tilde{\nu}$(N–H)/cm^{-1} 3271, 3228, 3210 and 3176.

[ZnL^{3}Br$_2$]·0.5H$_2$O. A mixture of zinc(II) bromide (0.15 g, 0.67 mmol) and compound L^3 (0.11 g, 0.34 mmol) in acetonitrile (40 cm^3) was heated at reflux for 0.5 h and the resulting white powder was filtered off, washed with acetonitrile, and dried *in vacuo* for 18 h, yield 0.13 g (0.24 mmol, 70%) (Found: C, 43.1; H, 5.9; N, 9.9. $C_{20}H_{29}Br_2N_4O_{0.5}Zn$ requires C, 43.0; H, 5.2; N, 10.0%). IR: $\tilde{\nu}$(N–H)/cm^{-1} 3225 and 3172.

[ZnL^{4}Br$_2$]. A procedure similar to that above gave the required product in 69% yield (Found: C, 44.9; H, 5.4; N, 9.9. $C_{21}H_{30}Br_2N_4Zn$ requires C, 44.8; H, 5.4; N, 9.9%). IR: $\tilde{\nu}$(N–H)/cm^{-1} 3280, 3239, 3229 and 3172.

Crystallography

Crystal data. L^3, $C_{20}H_{28}N_4$, $M = 324.5$, monoclinic, space group $P2_1/n$, $a = 19.374(4)$, $b = 8.403(2)$, $c = 11.225(3)$ Å, $\beta = 94.18(2)°$, $U = 1822.57$ Å^3, $Z = 4$, $D_c = 1.182$ g cm^{-3}, $F(000) = 704$, μ(Mo-Kα) = 0.39 cm^{-1}.

L^4, $C_{21}H_{30}N_4$, $M = 338.5$, triclinic, space group $P\bar{1}$, $a = 11.437(3)$, $b = 9.592(3)$, $c = 9.024(3)$ Å, $\alpha = 96.72(2)$, $\beta = 102.60(2)$, $\gamma = 88.64(2)°$, $U = 959.50$ Å^3, $Z = 2$, $D_c = 1.171$ g cm^{-3}, $F(000) = 368$, μ(Mo-Kα) = 0.38 cm^{-1}.

[CdL^{3}Br]$_2$[CdBr$_4$]·MeOH, $C_{41}H_{60}Br_6Cd_3N_8O$, $M = 1497.6$, triclinic, space group $P\bar{1}$, $a = 13.135(3)$, $b = 19.633(4)$, $c = 10.993(3)$ Å, $\alpha = 100.25(2)$, $\beta = 103.53(2)$, $\gamma = 77.31(2)°$, $U = 2664.88$ Å^3, $Z = 2$, $D_c = 1.866$ g cm^{-3}, $F(000) = 1448$, μ(Mo-Kα) = 55.34 cm^{-1}.

[CdL^{4}Br$_2$]·MeCN, $C_{22}H_{33}Br_2CdN_5$, $M = 651.7$, monoclinic, space group $P2_1/n$, $a = 16.035(4)$, $b = 14.537(3)$, $c = 11.532(3)$ Å, $\beta = 107.48(2)°$, $U = 2564.04$ Å^3, $Z = 4$, $D_c = 1.688$ g cm^{-3}, $F(000) = 1296$, μ(Mo-Kα) = 38.47 cm^{-1}.

Data were collected in the range θ = 3–23° for the free macrocycles and 3–25° for the cadmium(II) complexes, using a Philips PW1100 four-circle diffractometer as described previously.[8] Crystal dimensions: L^3, 0.38 × 0.26 × 0.20; L^4, 0.48 × 0.24 × 0.16; [CdL^{3}Br]$_2$[CdBr$_4$]·MeOH, 0.25 × 0.27 × 0.19; [CdL^{4}Br$_2$]·MeCN, 0.27 × 0.35 × 0.41. Absorption corrections were applied to the metal complexes.[9] Equivalent reflections were averaged to give the following unique data with $I > 3\sigma(I)$; L^3, 1160; L^4, 1506; [CdL^{3}Br]$_2$[CdBr$_4$]·MeOH, 3865; [CdL^{4}Br$_2$]·MeCN, 2387.

Structure solution and refinement. The structures of the free macrocycles L^3 and L^4 were solved by direct methods.[10] All the non-hydrogen atoms were located from subsequent Fourier-difference maps. The amine hydrogen atoms were included at observed positions revealed by a Fourier-difference map calculated using data with $(\sin\theta)/\lambda < 0.35$. In the final cycles of full-matrix least-squares refinement, anisotropic thermal parameters were assigned to the nitrogen atoms and the unsubstituted carbon atoms of the phenylene rings in L^3 and to the nitrogen atoms and the carbon atoms of the five-carbon bridge in L^4. Refinement in these and the following structures was based on F values using a weighting scheme of $w = 1/[\sigma^2(F_o)]$ and converged at R and R' values of 0.0657 and 0.0663 for L^3 and 0.0797 and 0.0761 for L^4.

For the complex [CdL^{4}Br$_2$]·MeCN the cadmium and bromine atoms were located from a Patterson synthesis.[10] The remaining non-hydrogen atoms and the amine hydrogen atoms were found from subsequent Fourier-difference syntheses. Two carbon atoms, C(10a) and C(10b), were each disordered over two sites in the ratio 0.8:0.2 and during refinement the associated carbon–carbon bond lengths were constrained to 1.54(2) Å. All the non-hydrogen atoms, except the minor components of C(10a) and C(10b), were assigned anisotropic thermal parameters and refinement converged to $R = 0.0416$, $R' = 0.0393$.

The structure of [CdL^{3}Br]$_2$[CdBr$_4$]·MeOH was solved by direct methods. The methanol solvent was disordered over two sites in the occupancy ratio 0.7:0.3. Anisotropic thermal parameters were assigned to the cadmium and bromine atoms, all the nitrogen atoms and the methylene carbon atoms of the macrocycles and to the oxygen and carbon atoms of the major component of the methanol molecule. Refinement converged to $R = 0.0600$ and $R' = 0.0593$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/96.

Results and Discussion

Preparation and characterisation of the macrocycles and complexes

The macrocycles L^1–L^4 were synthesised using a similar procedure to that reported previously.[2,7] Satisfactory microanalyses were obtained in each case and the compounds were characterised by infrared and multinuclear NMR spectroscopy.

The ^1H, ^{13}C and ^{15}N NMR spectra were assigned using ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY) plots; potentially ambiguous assignments were resolved by a combination of ^1H–^{15}N COSY and ^{13}C INADEQUATE (incredible natural abundance double quantum transfer experiment) in the case of the most soluble compounds L^2 and L^4. The number and multiplicity of the observed signals in the respective spectra indicate that corresponding nuclei in the a and b halves of the macrocycles exhibit chemical shift equivalence.

The ^1H NMR spectrum of each compound shows broadened signals for the anilino N(2)H and the benzylamino N(1)H protons. They are quite distinct and range from δ 1.1 to 1.2 for N(1)H and δ 6.0 to 6.8 for N(2)H with the latter being obscured by the phenyl-H signals in cases except for L^2. A further difference in the ^1H spectrum of L^2 is observed in the complex signal from the four H(1) protons on the C_2 bridge between the anilino N atoms. This signal collapses to a singlet on deuteriation, indicating spin–spin coupling between these protons and the anilino protons. The latter was confirmed by the ^1H–^1H COSY contour plot for L^2. Similar coupling is not noticeable in the spectra of the other macrocycles; this may reflect a restriction on the δ–λ conformation exchange rate for the C_2 bridge.

The ^{15}N-{^1H} NMR spectrum of compound L^2 shows two sharp signals at δ 38.0 and 60.4, assigned to the benzylamino N(1) and anilino N(2) nitrogen atoms, respectively. For L^4 the corresponding signals occur at δ 35.8 and 63.7. In the proton-undecoupled spectra of L^2 and L^4 one-bond spin–spin coupling is evident only for the anilino N atoms (with $^1J_{NH}$ = 84 and 85 Hz, respectively), consistent with sp^2 hybridisation of the anilino atoms.[11] No such coupling is observed for the benzylamino N atoms, presumably reflecting a faster rate of exchange of the NH protons with those of the environment.

Zinc(II) and cadmium(II) bromide and iodide complexes of L^3 and L^4 were prepared by mixing solutions of the macrocycle in acetonitrile or dichloromethane with solutions of the metal halide in acetonitrile, dichloromethane or methanol, either at room temperature or at reflux. With the exception of the cadmium(II) bromide complex of L^3, microanalyses are compatible with formulation as $[ML]X_2$, $[MLX]X$ or $[MLX_2]$ (M = Zn or Cd, X = Br or I). The latter was confirmed for $[CdL^4Br_2]$ by subsequent X-ray structural study. A parallel investigation of the cadmium(II) bromide complex of L^3 shows it is of type $[CdL^3Br]_2[CdBr_4]$.

X-Ray diffraction studies

The structures of compounds L^3 and L^4 are shown in Fig. 1. The bond lengths and interbond angles (supplementary data) throughout each macrocycle are comparable with those reported for L^1, L^5 and L^6 previously.[2,12] In each of these three compounds, the two intramolecular hydrogen bonds involve interaction of the anilino hydrogen atoms with the lone pairs on the adjacent benzylamino nitrogen atoms (Table 3) and the geometry of these bonds is constrained by the cyclic nature of the compounds. This situation is manifested again in L^4, but in L^3 the relevant distances and angle in the a half of the macrocycle are strikingly dissimilar to those in the other compounds and in the b half of L^3, indicating a difference in the hydrogen-bonding pattern for L^3. Here, one of the intramolecular hydrogen bonds is replaced by a very weak intermolecular hydrogen bond across a crystallographic centre of symmetry (Fig. 2), between the lone pair of the benzylamino atom, N(1a), and the anilino hydrogen atom of a neighbouring molecule (at $1 - x$, $-y$, $-z$) [N(1a)···N(2a′) 3.51, N(1a)···H′ 2.50 Å, N(2a′)···H–N(1a) 155°]. The formation of this bond is associated with a conformation of the *o*-aminobenzyl group (Fig. 2) which places the anilino hydrogen atom, HN(2a), in an unfavourable position to interact with the lone pair on the adjacent benzylamino nitrogen atom, N(1a).

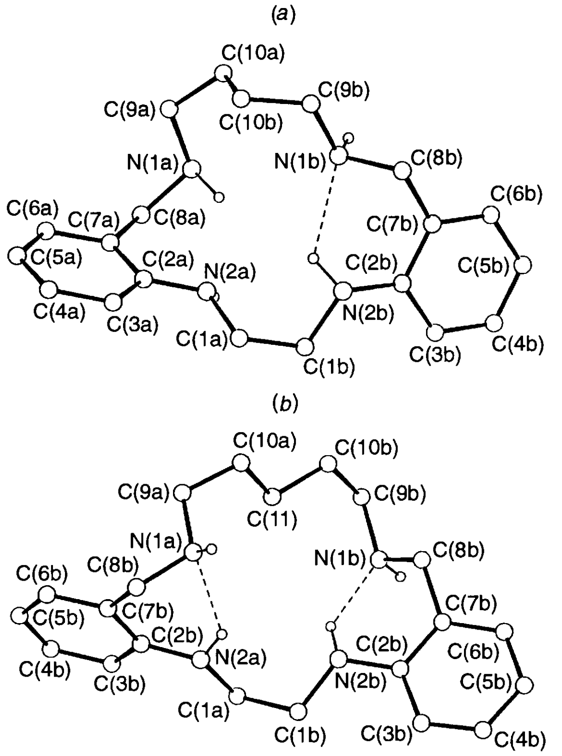

Fig. 1 The structures of (*a*) the 16-membered macrocycle L^3 and (*b*) the 17-membered macrocycle L^4. Intramolecular hydrogen bonds are indicated by dashed lines

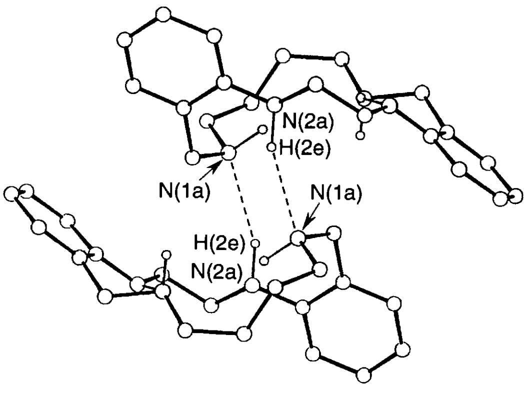

Fig. 2 The intermolecular hydrogen bonding in the solid-state structure of compound L^3

As might be expected, increasing the lop-sidedness of the compounds in the series L^1–L^6 leads to a significant increase in the 'bite' distance between the benzylamino nitrogen atoms; the N(1a)···N(1b) distances in the 14-membered (L^1),[12] the two 15-membered (L^5 and L^6)[2] and the 16- and 17-membered rings (L^3 and L^4) are 2.90, 3.27, 3.79, 3.76 and 5.38 Å, respectively. The much less symmetrical structure of the 16-membered L^3, concomitant with the intermolecular hydrogen-bonded structure in the solid state, would account for this distance being shorter than expected. Hole sizes, defined by the mean distance of the four nitrogen atoms from their centroid, vary more

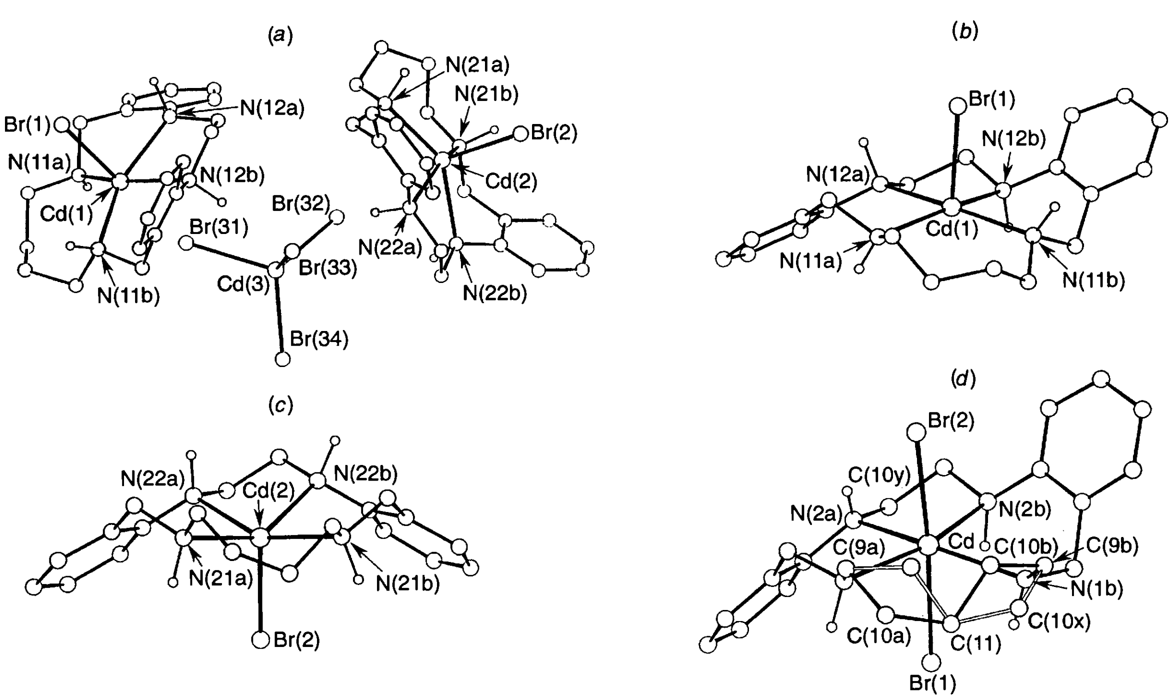

Fig. 3 The structures of (*a*) $[CdL^3Br]_2[CdBr_4]$, (*b*) *rac*-$[CdL^3Br]^+$, (*c*) *meso*-$[CdL^3Br]^+$ in the complex $[CdL^3Br]_2[CdBr_4]$ and (*d*) $[CdL^4Br_2]$. The open bonds connect the minor components of the disordered carbon atoms to those of full site occupancy. Atom labels in the macrocyclic ligands correspond to those used in Fig. 1

Table 1 Selected bond lengths (Å) in the cadmium(II) complexes of L^3 and L^4

	rac-$[CdL^3Br]^+$		*meso*-$[CdL^3Br]^+$		$[CdL^4Br_2]$·MeCN	
	Part a	Part b	Part a	Part b	Part a	Part b
Cd–N(1)	2.276(15)	2.257(14)	2.332(13)	2.247(15)	2.370(7)	2.370(6)
Cd–N(2)	2.427(13)	2.390(14)	2.339(13)	2.431(17)	2.450(6)	2.440(7)
Cd–Br	2.660(3)		2.574(3)		2.793(1)	2.695(1)

$[CdBr_4]^{2-}$

Cd(3)–Br(31)	2.613(2)	Cd(3)–Br(32)	2.596(2)	Cd(3)–Br(33)	2.597(3)	Cd(3)–Br(34)	2.561(3)

Table 2 Interbond angles (°) in the co-ordination spheres

	rac-$[CdL^3Br]^+$	*meso*-$[CdL^3Br]^+$	$[CdL^4Br_2]$
N(1a)–Cd–N(1b)	110.1(6)	106.0(5)	115.5(2)
N(1a)–Cd–N(2a)	85.0(5)	86.2(5)	86.3(2)
N(1a)–Cd–N(2b)	156.7(5)	145.9(5)	161.1(2)
N(1b)–Cd–N(2a)	160.9(5)	151.9(6)	152.6(3)
N(1b)–Cd–N(2b)	86.5(5)	83.5(5)	82.6(2)
N(2a)–Cd–N(2b)	75.9(5)	73.2(5)	74.8(2)
N(1a)–Cd–Br(1)	96.5(4)	—	74.8(2)
N(1b)–Cd–Br(1)	95.0(4)	—	78.3(2)
N(2a)–Cd–Br(1)	94.6(4)	—	88.0(2)
N(2b)–Cd–Br(1)	98.2(4)	—	93.9(2)
N(1a)–Cd–Br(2)	—	105.1(4)	91.8(2)
N(1b)–Cd–Br(2)	—	102.5(4)	105.6(2)
N(2a)–Cd–Br(2)	—	98.3(4)	89.0(2)
N(2b)–Cd–Br(2)	—	104.5(4)	88.1(2)
Br(1)–Cd–Br(2)	—	—	175.8(1)

systematically in the same series of compounds: 2.02, 2.10, 2.14, 2.22 and 2.41 Å. While this increase in cavity size might suggest that the larger rings will better accommodate larger metal ions, it should be noted that there are much larger deviations from planarity of the N_4-donor set in the more lop-sided compounds (see below), and thus the 'goodness of fit' will also depend on the requirement of the metal ion to approach a regular co-ordination geometry.

The structure of $[CdL^3Br]_2[CdBr_4]$ [Fig. 3(*a*)] consists of two cationic complexes of cadmium(II) each co-ordinated to all four nitrogen donors of the macrocycle and to an axial bromide ligand. These two complexes sandwich a tetrabromocadmate(II) anion in such a way that two of its bromine atoms are directed towards the cadmium atoms of each cation [Cd(1) ··· Br(31) 3.09, Cd(2) ··· Br(32) 3.53 Å]. The Cd–Br bond lengths in $[CdBr_4]^{2-}$ are well within the range (2.529–2.685 Å) reported for this anion in six other reported structure determinations.[13,14]

The conformations of the macrocyclic ligand in each complex are markedly different; in that containing Cd(1) the benzo rings are inclined to opposite sides of the N_4-donor plane with the amine hydrogen atoms alternately above and below the plane giving the *R*,*R*,*R*,*R* (or *S*,*S*,*S*,*S*) sequence of absolute configurations of the nitrogen atoms [Fig. 3(*b*)]. In contrast, the complex containing Cd(2) [Fig. 3(*c*)] has the benzo rings inclined to the same side of the N_4-donor plane as the co-ordinated bromine atom with the two anilino hydrogen atoms on the same side and the two benzylamino hydrogen atoms on the opposite side giving absolute configurations of *R*,*S*,*R*,*S* (or *S*,*R*,*S*,*R*). These configurations of the ligand are conveniently referred to as *rac* and *meso*, respectively. The *rac* configuration has been previously observed[12,15] in the nickel(II) complexes of L^1 and L^2 and the *meso* in $[ZnL^2I]I$,[16] $[ZnL^2(NO_3)(H_2O)]NO_3$, $[CdL^2(NO_3)]NO_3$ and $[CdL^6(NO_3)]NO_3$.[2]

The seven-membered chelate rings in *rac*- and *meso*-$[CdL^3Br]^+$ adopt distorted skew and chair conformations, respectively. The results from preliminary molecular mechanics

Table 3 Hydrogen bonding in the free macrocycles: interatomic distances (Å) and angles (°) at the amine hydrogen atoms[a]

Compound	N(1)···N(2)	N(1)···H	N(1)···H–N(2)
L^1	2.83	2.01	137
	2.78	1.99	134
L^3	(3.09	2.83	93)[b]
	2.87	2.24	125
L^4	2.89	2.27	135
	2.87	2.04	137
L^5	2.82	1.99	140
	2.82	2.00	135
L^6	2.82	2.20	120
	2.87	2.05	130

[a] For each compound the first and second rows refer to the a and b halves, respectively. [b] The H atom here is not aligned for intramolecular hydrogen bonding (see text and Fig. 2).

calculations on the individual *rac* and *meso* complexes using established procedures,[2] although only semiquantitative, suggest that both structures have quite similar strain energies, in accordance with their coexistence in the unit cell.

The complex $[CdL^4Br_2]$ [Fig. 3(*d*)] consists of a pseudo-octahedral geometry in which the cadmium atom is co-ordinated to all four nitrogen donors of the macrocycle and to two *trans*-axial bromide ligands. The macrocycle conformation differs from that in *rac*-$[CdL^3Br]^+$ in the configurations of the amine hydrogen atoms. Here one of the hydrogen atoms, HN(1b), is on the opposite side of the N_4 plane to the others, giving a *R*,*S*,*R*,*R* (or *S*,*R*,*S*,*S*) sequence.

The Cd–Br distances in these complexes compare well with those found[14,17] in related complexes of macrocycles, *e.g.* L^7 and L^8. Bonds are longer in complexes which have two axial bromide ligands {2.775(3) and 3.037(3) Å in the bromide-bridged polymeric cationic complex[14] $[\{CdL^7Br\}_n]^+$} and shorter in discrete cationic complexes with only one axial bromide {2.582(1) Å in $[CdL^8Br]^+$}.

The eight-membered chelate ring in $[CdL^4Br_2]$ contains two disordered carbon atoms giving two alternative twist-boat conformations [Fig. 3(*d*)].

There is no significant increase in Cd–N bond lengths on increasing the ligand ring size from 15- to 16-membered. However, these bonds are longer in the 17-membered complex, $[CdL^4Br_2]$. For complexes of the N_4 macrocycles with two anilino and two benzylamino donors (L^2–L^6), many of the Cd–N bond lengths fall below the range [2.325(6)–2.47(3) Å] found with aliphatic tetraaza ligands 1,5,9,13-tetraazacyclohexadecane,[18] 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane[19] and the dicadmium(II) complex of 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane.[20]

In general terms, increasing ring size in the series L^2–L^6 has the effect of allowing a cadmium atom to approach closer to the centre of the N_4 cavity and to form a six-co-ordinate *trans*-dibromo complex of the largest ring, L^4. Thus, with the exception of the *rac* form of the complex $[CdL^3Br]$, the displacement of the cadmium atom from the mean plane of the N_4-donor set decreases as the ring size increases: $[CdL^2(NO_3)]^+$, 0.61; $[CdL^6(NO_3)]^+$, 0.49; *rac*-$[CdL^3Br]^+$, 0.53; *meso*-$[CdL^3Br]^+$, 0.25; $[CdL^4Br_2]$, 0.19 Å.

Five-co-ordinate complexes are formed by the 15-membered L^2 and its C-butylated homologue L^6; transoid co-ordination of a second nitrate or aqua ligand is apparently sterically hindered by the macrocyclic ligand in these compounds. In the complexes of the 16-membered ring L^3 a relatively weak interaction between the cadmium atom and a second (*trans*-axial) bromine atom gives the complex a structure intermediate between five- and six-co-ordinate, in accordance with the trends just discussed.

Conclusion

Despite the 'lop-sidedness' of the larger rings in this series of macrocycles, they successfully accommodate cadmium(II) ions in their donor-set cavities. Their ability to do this appears to depend on a combination of flexibility coupled with the lack of strong directional requirements for bond formation by the cadmium ion with its d^{10} electronic configuration.

In the following paper a related study is presented outlining the complexation of L^3 and L^4 with high-spin nickel(II), a metal ion characterised by much stronger directional requirements in its bonding behaviour.

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