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Structure–Function Relationships in the Interaction of Zinc(II) and Cadmium(II) with an Extended Range of 16- to 19-Membered Macrocycles Incorporating Oxygen, Nitrogen, and Sulfur Donor Atoms

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The interaction of zinc(II) and cadmium(II) with a series of potentially quinquedentate macrocycles incorporating nitrogen, oxygen, and/or sulfur donor atoms is reported. These ligands form part of an extended array in which a systematic variation in donor atom pattern and ring size is present (and against which structure–function relationships are more clearly seen). Stability constants for the 1:1 (metal:ligand) complexes have been determined in 95% methanol (I = 0.1 M, NEt_4ClO_4) at 25 °C. The factors influencing the stabilities of individual zinc(II) and cadmium(II) complexes are discussed in the light of a range of crystallographic and other data. The X-ray structures of five complexes, isolated during the study, are reported. $[Zn(\mathbf{L1})](ClO_4)_2$ crystallized in the monoclinic space group $P2_1/c$, with a = 12.766(2) Å, b = 9.127(2) Å, c = 20.975(4) Å, β = 97.90(2)°, and Z = 4. All five donor atoms of the macrocycle are coordinated to the zinc cation, which exhibits a distorted trigonal bipyramidal geometry. $[Zn(CH_3C_6H_4SO_3)(\mathbf{L1})]CH_3C_6H_4SO_3$ crystallized in the monoclinic space group $P2_1/c$ with a = 9.655(2) Å, b = 13.605(3) Å, c = 26.721(5) Å, β = 97.94(2)°, and Z = 4. The zinc atom is six coordinate with a distorted octahedral geometry made up of all five donor atoms of the N_4O macrocyclic ligand and an oxygen atom, O(11), of a coordinated 4-toluenesulfonate anion, *trans* to N(2b). $[Cd(ClO_4)(\mathbf{L3})(CH_3OH)]ClO_4$ crystallized in the triclinic space group $P\bar{1}$, a = 14.204(2) Å, b = 10.892(2) Å, c = 9.268(2) Å, α = 109.85(2)°, β = 108.19(2)°, γ = 97.12(2)°, and Z = 2. The coordination sphere approximates a pentagonal bipyramid with the donor atoms of the macrocycle in the equatorial positions while the axial sites are occupied by O(1) of a perchlorate anion and O(11) of a coordinated methanol molecule. $[Zn(NO_3)(\mathbf{L15})(H_2O)]ClO_4{\cdot}C_2H_5OH$ crystallized in the monoclinic space group $P2_1/c$ (nonstandard setting $P2_1/n$) with a = 26.654(5) Å, b = 10.819(2) Å, c = 10.691(2) Å, β = 95.12(2)°, and Z = 4. The zinc atom is six coordinate with the complex cation exhibiting a distorted-octahedral geometry comprising the three nitrogen donor atoms of the O_2N_3 macrocyclic ligand [namely, N(1a), N(1b) and N(1c)] in a facial arrangement, a water molecule *trans* to N(1c), and O(1) and O(2) of a chelating bidentate nitrate anion. $[Cd(NO_3)_2(\mathbf{L15})]_2{\cdot}2C_2H_5OH$, crystallized in the monoclinic space group $P2_1/c$ with a = 9.228(4) Å, b = 14.008(3) Å, c = 22.235(3) Å, β = 97.21(2)°, and Z = 2. In contrast to the above zinc complex, this species is binuclear with the two cadmium ions separated by 4.17 Å and linked by two single oxygen (from nitrate) bridges across a centre of inversion; each Cd–O(bridging) distance is 2.474(5) Å. The cadmium atoms are seven coordinate with coordination of each being completed by the three nitrogens of the macrocyclic ligand and a bidentate nitrate ion.

Introduction

The metal ion chemistry of polydentate ligands has now been investigated for more than a century. Nevertheless, it is still often difficult to predict the binding preferences of such ligands—especially when mixed donor atom species are involved. In previous studies we have investigated structure–function relationships in the (transition and post transition) metal ion chemistry of closely related macrocyclic ligands chosen from the series **L1–L24**.[1–4] For example, a number of O_2N_3-donor systems of the above type, incorporating 17–19-membered rings, have been demonstrated to exhibit metal ion recognition behavior.[1,2] In these studies, ring-size variation was found to induce "structural dislocations" and thereby alter the relative thermodynamic stabilities of particular cobalt(II), nickel(II), zinc(II), and cadmium(II) complexes. That is, when metal complexation occurs along a series of closely related ligands showing a gradation in properties, the buildup of strain from one complex to the next may cause a major change in the structure of adjacent complexes in the series. The dislocation behavior may occur at different points along the series for different metal ions. As a consequence, enhanced discrimination may result. Such discrimination differs from the usual type observed for many macrocyclic systems[5] since it does not necessarily depend on the match of the radius of the metal ion to the available macrocyclic cavity.

Our previous studies in this area[1,2] have aided the understanding of particular observed metal ion recognition behavior; they also serve as a background upon which the design of new discrimination reagents may be based. Apart from the implications for metal ion discrimination, it has been our experience that the investigation of systems showing a stepwise variation in structure (such as occurs along the series **L1–L24**) tends to lead to a more complete

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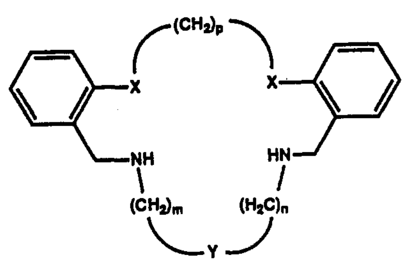

	X	Y	m	n	p
L1	NH	NH	2	2	2
L2	NH	S	2	2	2
L3	NH	O	2	2	2
L4	NH	NH	3	3	3
L5	O	NH	2	2	1
L6	O	S	2	2	1
L7	O	O	2	2	1
L8	O	NH	2	2	2
L9	O	S	2	2	2
L10	O	O	2	2	2
L11	O	NH	3	2	2
L12	O	NH	3	3	2
L13	O	NH	4	2	2
L14	O	S	3	3	2
L15	O	NH	2	2	4
L16	O	S	2	2	4
L17	O	O	2	2	4
L18	S	NH	2	2	1
L19	S	S	2	2	1
L20	S	NH	2	2	2
L21	S	S	2	2	2
L22	S	O	2	2	2
L23	S	NH	3	3	2
L24	S	S	2	2	3

understanding of the complexation behavior of individual members of the series.

As an extension of our previous study,[2] we now present the results of a comparative investigation of the interaction of zinc(II) and cadmium(II) with the above ligand series.

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 197 spectrophotometer. Positive-ion fast atom bombardment (FAB) mass spectra were determined using a JEOL-DX300 spectrometer (samples in 3-nitrobenzyl alcohol). Conductance measurements were obtained using a Philips conductivity bridge type PR 9501; all measurements were performed in methanol at *ca.* 10^{-3} M (and 23 °C). The procedures employed, the apparatus used, and the method of processing the data for the potentiometric determination of the protonation constants and the corresponding metal complex stability constants (in 95% methanol, $I = 0.1$ M, NEt_4ClO_4; 25 °C) were identical to those described previously.[3] The protonation constants for **L1**–**L24** have been reported previously;[3,4] errors represent the average deviation from the mean obtained for separate experimental determinations (rounded to one significant figure).

Macrocycle and Selected Complex Synthesis. The synthesis and characterization of the macrocyclic ligands **L1**–**L24** are described elsewhere.[6,7]

Safety Note. Perchlorate salts of metal complexes of organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with extreme caution. So far, we have not observed any difficulties with the perchlorate-containing complexes described in this report.

[Zn(NO$_3$)(L5)]ClO$_4$·0.5C$_2$H$_5$OH. Zinc nitrate hexahydrate (0.09 g) in boiling ethanol (10 mL) and lithium perchlorate (0.09 g) were added sequentially to a stirred boiling solution of **L5** (0.10 g). The solution was filtered and cooled. After 24 h, an off-white crystalline product had separated; yield 0.05 g. Anal. Calcd for $C_{20}H_{28}ClN_4O_{9.5}Zn$: C, 41.8; H, 4.9; N, 9.7. Found: C, 41.8; H, 4.8; N, 9.9. FAB mass spectrum: *m/z* 454, [Zn(NO$_3$)(**L5**)]$^+$.

[Zn(NO$_3$)(L15)(H$_2$O)]ClO$_4$·C$_2$H$_5$OH. In a similar manner, zinc nitrate hexahydrate (0.08 g), lithium perchlorate (0.09 g), and **L15** (0.10 g) gave the product as a white powder which was recrystallized from methanol; yield 0.05 g. Anal. Calcd for $C_{24}H_{39}ClN_4O_{11}Zn$: C, 43.6; H, 6.0; N, 8.5. Found C, 43.6; H, 6.0; N, 8.5. FAB mass spectrum: *m/z* 495, [Zn(NO$_3$)(**L15**)]$^+$.

[Zn(NO$_3$)(L18)]ClO$_4$·0.25H$_2$O. In a similar manner, zinc nitrate hexahydrate (0.083 g), lithium perchlorate (0.09 g), and **L18** (0.10 g) gave the product as a pale yellow crystalline solid; yield 0.08 g. Anal. Calcd for $C_{19}H_{25.5}ClN_4O_{7.25}S_2Zn$: C, 38.6; H, 4.4; N, 9.5. Found: C, 38.6; H, 4.4; N, 9.8. FAB mass spectrum: *m/z* 485, [Zn(NO$_3$)(**L18**)]$^+$.

[Cd(NO$_3$(L5)]ClO$_4$·0.5C$_2$H$_5$OH. Cadmium nitrate tetrahydrate (0.09 g) in boiling ethanol (10 mL) was added to a stirred boiling solution of **L5** (0.10 g) in ethanol (10 mL). The volume of the solution was reduced to 10 mL. Following the subsequent addition to lithium perchlorate (0.1 g), a white powder separated. The powder was isolated and recrystallized from ethanol; yield 0.05 g. Anal. Calcd for $C_{20}H_{28}CdClN_4O_{9.5}$: C, 38.5; H, 4.5; N, 9.0. Found: C, 38.7; H, 4.3; N, 8.8. FAB mass spectrum: *m/z* 503, [Cd(NO$_3$)(**L5**)]$^+$.

[Cd(NO$_3$)(L9)]NO$_3$. Cadmium nitrate tetrahydrate (0.34 g) in boiling ethanol (15 mL) was added to a stirred boiling solution of **L9** (0.33 g) in ethanol (15 mL). The solution was filtered and cooled. After 24 h a pale yellow crystalline product had separated; yield 0.32 g. Anal. Calcd for $C_{20}H_{26}CdN_4O_8S$: C, 40.4; H, 4.4; N, 9.4. Found: C, 40.2; H, 4.5; N, 9.3. FAB mass spectrum: *m/z* 534, [Cd(NO$_3$)(**L9**)]$^+$.

[Cd(NO$_3$)(L10)]NO$_3$. In a similar manner, cadmium nitrate tetrahydrate (0.09 g) and **L10** gave the product as a white crystalline solid; yield 0.10 g. Anal. Calcd for $C_{20}H_{26}CdN_4O_9$: C, 41.5; H, 4.5; N, 9.7. Found: C, 41.4; H, 4.7; N, 9.5. FAB mass spectrum: *m/z* 518, [Cd(NO$_3$)(**L10**)]$^+$.

[Cd(NO$_3$)$_2$(L15)]$_2$·2C$_2$H$_5$OH. In a similar manner, cadmium nitrate tetrahydrate (0.083 g) and **L15** (0.10 g) gave the product as an off white crystalline solid; yield 0.07 g. Anal. Calcd for $C_{48}H_{74}Cd_2N_{10}O_{18}$ C, 44.2; H, 5.7; N, 10.8. Found: C, 44.2; H, 5.5; N, 11.1. FAB mass spectrum: *m/z* 545, [Cd(NO$_3$)(**L15**)]$^+$.

[Cd(NO$_3$)(L18)]ClO$_4$. In a similar manner to that used for the synthesis of the cadmium(II) complex of **L5**, cadmium nitrate tetrahydrate (0.09 g) and **L18** (0.10 g) gave the product as a white crystalline solid; yield 0.03 g. Anal. Calcd for $C_{19}H_{25}CdClN_4O_7S_2$: C, 36.0; H, 4.0; N, 8.8. Found: C, 36.1; H, 4.0; N, 8.9. FAB mass spectrum: *m/z* 535, [Cd(NO$_3$)(**L18**)]$^+$.

X-ray Structure Determinations. Crystal data are listed in Table 1. A suitable crystal of [Zn(**L1**)](ClO$_4$)$_2$ was obtained from a methanol solution containing a 1:1 mixture of zinc perchlorate and **L1**. A similar procedure was used to obtain crystalline [Zn(CH$_3$C$_6$H$_4$SO$_3$)(**L3**)]CH$_3$C$_6$H$_4$SO$_3$, starting from zinc tosylate and **L3**. Data were collected on a Philips PW1100 diffractometer in the θ range 3–25° (in octants $\pm h,k,l$ for the monoclinic and $\pm h,\pm k,l$ for the triclinic crystals, respectively), with a scan width of 0.80°, using the technique previously described.[8] No absorption corrections were applied. Equivalent reflections were averaged to give the following unique data with $I > 3\sigma(I)$: [Zn(**L1**)](ClO$_4$)$_2$, 1566; [Zn(CH$_3$C$_6$H$_4$SO$_3$)(**L3**)]CH$_3$C$_6$H$_4$SO$_3$, 2558; [Cd(ClO$_4$)(**L3**)(CH$_3$OH)]ClO$_4$, 2454; [Zn(NO$_3$)(**L15**)(H$_2$O)]ClO$_4$·C$_2$H$_5$OH, 3599; [Cd(NO$_3$)$_2$(**L15**)]$_2$·2C$_2$H$_5$OH, 3546. The metal atom was located from a Patterson synthesis.[9] The positions of the remaining non-hydrogen atoms were found from subsequent Fourier and difference-Fourier syntheses. The C-bonded H atoms were placed in geometrically idealized positions (C–H 1.08 Å), and constrained to ride on the relevant C atom. For [Zn(**L1**)](ClO$_4$)$_2$ the positions of the N-bonded H atoms

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Table 1. Brief X-ray Details for $[Zn(\mathbf{L1})](ClO_4)_2$ (**I**), $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$ (**II**), $[Cd(ClO_4)(\mathbf{L3})(CH_3OH)]ClO_4$ (**III**), $[Zn(NO_3)(\mathbf{L15})(H_2O)]ClO_4{\cdot}C_2H_5OH$ (**IV**), and $[Cd(NO_3)_2(\mathbf{L15})]_2{\cdot}2C_2H_5OH$ (**V**)

	I	II	III	IV	V
formula	$ZnC_{20}H_{29}Cl_2N_5O_8$	$ZnC_{34}H_{42}N_4O_7S_2$	$CdC_1H_{32}Cl_2N_4O_{10}$	$ZnC_4H_{39}ClN_4O_{11}$	$Cd_2C_{48}H_{74}N_{10}O_8$
fw	603.8	748.2	683.8	660.4	1304.0
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	12.766(2)	9.655(2)	14.204(2)	26.654(5)	9.228(4)
b, Å	9.127(2)	13.605(3)	10.892(2)	10.819(2)	14.008(3)
c, Å	20.975(4)	26.721(5)	9.268(2)	10.691(2)	22.235(3)
α, deg			109.85(2)		
β, deg	97.90(2)	97.94(2)	108.19(2)	95.12(2)	97.21(2)
γ, deg			97.12(2)		
V, Å^3	2420.7	3476.3	1337.8	3070.7	2851.5
Z	4	4	2	4	2
D(calc),g/cm^3	1.66	1.43	1.70	1.43	0.915
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69	0.710 69
Mo Kα, cm^{-1}	12.19	8.21	9.73	8.89	9.66
R; R' [a]	0.080; 0.082	0.064; 0.064	0.052; 0.055	0.045; 0.047	0.049; 0.049
T, K	290	290	290	290	290

[a] Where $R' = \sum\|F_o| - |F_c\|w^{1/2}/\sum|F_o|w^{1/2}$, using a weighting scheme of $w = 1/[\sigma^2(F_o)]$.

were found from a difference-Fourier synthesis. The located N-bonded H atoms were given fixed isotropic thermal parameters of 0.08 Å^2, and their positions were not refined. In the final cycles of full-matrix refinement the metal and chlorine atoms were assigned anisotropic thermal parameters. For $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$, the positions of H(N2a) and H(N2b) were found from the Fourier and difference-Fourier syntheses while H(N1a) and H(N1b) were placed in geometrically idealized positions and constrained to ride on the N atom. The methyl and N-bonded H atoms were given fixed isotropic thermal parameters of 0.08 Å^2. The remaining H atoms were divided into aliphatic, macrocyclic aromatic, and 4-toluenesulfonate aromatic groups, and each group was assigned a separate isotropic thermal parameter, which was refined. In the final cycles of full-matrix refinement the zinc, nitrogen, oxygen, and sulfur atoms were assigned anisotropic thermal parameters. For $[Cd(\mathbf{L3})(CH_3OH)(ClO_4)]ClO_4$, the positions of the N-bonded H atoms were found from the difference-Fourier synthesis. The located N-bonded H atoms were given fixed isotropic thermal parameters of 0.08 Å^2, and their positions were not refined. The O-bonded H-atom of the methanol molecule was not found. In the final cycles of full-matrix refinement all of the atoms except those of carbon and hydrogen were assigned anisotropic thermal parameters. For $[Zn(NO_3)(\mathbf{L15})(H_2O)]ClO_4{\cdot}C_2H_5OH$, the positions of the N-bonded and water H atoms were found from the difference-Fourier synthesis. The C-bonded H atoms had thermal parameters tied to free variables for each of the aromatic, macrocyclic aliphatic, and ethanolic methylene hydrogen atoms, which were refined. The methyl and O-bonded H atoms in the ethanol molecule could not be found and were not included in the structure for refinement. The located N- and O-bonded H atoms were given fixed isotropic thermal parameters of 0.08 Å^2, and their positions were not refined. In the final cycles of blocked full-matrix refinement the non-hydrogen atoms were assigned anisotropic thermal parameters. For $[Cd(NO_3)_2(\mathbf{L15})]_2{\cdot}2C_2H_5OH$, the positions of the N- and O-bonded H atoms were again found from a difference-Fourier synthesis. Thermal parameters for the aromatic and aliphatic C-bonded H atoms were tied to single free variables, which were refined. The located N- and O-bonded H atoms were given fixed isotropic thermal parameters of 0.08 Å^2, and their positions were not refined. In the final cycles of full-matrix refinement, all atoms except hydrogens were assigned anisotropic thermal parameters.

In all cases, a final difference-Fourier map showed no significant regions of electron density. Selected atom coordinates and bond lengths and angles are given in Tables 2 and 3, while details of the structures are given in Figure 1 and Table 4. Additional data for all structures has been deposited as supplementary material.

Table 2. Atomic Coordinates for the Coordination Sphere in Complexes (a) $[Zn(\mathbf{L1}](ClO_4)_2$, (b) $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$, (c) $[Cd(ClO_4(\mathbf{L3})(CH_3OH)]ClO_4$, (d) $[Zn(NO_3)(\mathbf{L15})$ $(H_2O)]ClO_4{\cdot}C_2H_5OH$, and (e) $[Cd(NO_3)(\mathbf{L15})]_2{\cdot}2C_2H_5OH$

atom	x	y	z	U_{iso},[a] Å^2
		(a) $[Zn(\mathbf{L1})](ClO_4)_2$		
Zn	0.2666(1)	0.1639(2)	0.1216(1)	0.032(1)
N(1a)	0.3482(9)	0.0992(13)	0.0492(5)	0.032(3)
N(1b)	0.2621(9)	0.0856(13)	0.2138(5)	0.032(3)
N(1c)	0.1720(10)	−0.0308(15)	0.0936(6)	0.047(4)
N(2a)	0.3709(9)	0.3548(14)	0.1398(5)	0.032(3)
N(2b)	0.1501(9)	0.3179(13)	0.1244(5)	0.030(3)
		(b) $[N(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$		
Zn	0.23518(13)	0.22297(8)	0.23016(4)	0.0357(7)
N(1a)	0.1719(8)	0.0755(5)	0.2287(3)	0.035(5)
N(1b)	0.1851(8)	0.3712(5)	0.2169(3)	0.038(5)
O(1c)	0.0748(7)	0.2133(5)	0.1611(3)	0.059(5)
N(2a)	0.4085(8)	0.1992(5)	0.2869(3)	0.034(5)
N(2b)	0.4011(8)	0.2290(5)	0.1820(3)	0.033(5)
O(11)	0.0979(7)	0.2442(4)	0.2957(2)	0.043(4)
		(c) $[Cd(ClO_4)(\mathbf{L3})(CH_3OH)]ClO_4$		
Cd	0.23325(5)	0.17737(7)	0.18798(8)	0.0329(4)
N(1a)	0.2595(5)	−0.0289(7)	−0.0003(8)	0.037(4)
N(1b)	0.2621(5)	0.3814(7)	0.1583(9)	0.043(5)
O(1c)	0.3852(6)	0.1944(6)	0.0305(7)	0.050(4)
N(2a)	0.1693(5)	0.0309(7)	0.3246(8)	0.034(4)
N(2b)	0.1169(5)	0.2937(7)	0.3844(8)	0.035(4)
O(1)	0.0889(4)	0.1330(6)	0.0375(7)	0.075(5)
O(11)	0.3490(4)	0.2340(6)	0.3744(7)	0.049(4)
		(d) $[Zn(NO_3)(\mathbf{L15})(H_2O)]ClO_4{\cdot}C_2H_5OH$		
Zn	0.06276(2)	0.12988(4)	0.19087(5)	
N(1a)	0.0943(1)	0.1216(3)	0.0189(3)	
N(1c)	0.0914(1)	0.2742(3)	0.3123(3)	
O(1)	0.0181(1)	0.2763(3)	0.1046(3)	
O(2)	0.0001(1)	−0.0021(3)	0.1603(3)	
O(4)	0.0042(1)	0.0871(3)	0.3395(3)	
		(e) $[Cd(NO_3)(\mathbf{L15}){\cdot}2C_2H_5OH$		
Cd	0.17180(5)	0.09752(3)	0.00753(2)	
N(1a)	0.2587(5)	0.2390(3)	−0.0328(3)	
N(1b)	0.0974(7)	0.1300(4)	0.1032(3)	
N(1c)	0.3900(6)	0.1264(3)	0.0695(2)	
O(1)	0.1440(5)	0.0409(3)	−0.0973(2)	
O(2)	0.3586(6)	0.0172(3)	−0.0520(2)	
O(4)	−0.0923(5)	0.0657(3)	−0.0189(2)	

[a] $U_{iso} = (U_{11} + U_{22} + U_{33})/3$.

Results and Discussion

Isolation and Characterization of Selected Metal Complexes. Zinc(II) and cadmium(II) complexes of a selection of the present macrocycles have been isolated from the reaction of the metal nitrate in boiling ethanol with the appropriate macrocycle. In the majority of instances lithium perchlorate was added to the reaction solution to induce precipitation of individual complexes as their perchlorate salts. Microanalysis of the solid products indicated that all have 1:1 (metal:ligand) stoichiometries; the zinc complexes of **L5**, **L15**, and **L18** as well as the cadmium complexes of **L5** and **L18** contain one nitrate and one perchlorate per metal ion, whereas the remaining complexes contain two nitrate anions per complex. Physical data for each of these species are presented in Table 5.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Complexes with Standard Deviations in Parentheses

(a) $[Zn(\mathbf{L1})](ClO_4)_2$			
Zn–N(1a)	2.042(12)	Zn–N(1b)	2.070(12)
Zn–N(2a)	2.194(12)	Zn–N(2b)	2.054(12)
Zn–N(1c)	2.183(13)		
N(1b)–Zn–N(1a)	132.1(5)	N(2a)–Zn–N(1a)	90.0(5)
N(2a)–Zn–N(1b)	101.9(4)	N(2b)–Zn–N(1a)	131.6(5)
N(2b)–Zn–N(1b)	95.5(5)	N(2b)–Zn–N(2a)	82.9(5)
N(1c)–Zn–N(1a)	83.4(5)	N(1c)–Zn–N(1b)	83.4(5)
N(1c)–Zn–N(2a)	173.3(5)	N(1c)–Zn–N(2b)	100.9(5)
(b) $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$			
Zn–O(1c)	2.242(7)	Zn–N(1a)	2.096(7)
Zn–N(1b)	2.092(8)	Zn–N(2a)	2.123(7)
Zn–N(2b)	2.190(8)	Zn–O(11)	2.355(7)
N(1a)–Zn–O(1c)	76.2(3)	N(1b)–Zn–O(1c)	78.5(3)
N(1b)–Zn–N(1a)	149.3(3)	N(2a)–Zn–O(1c)	164.9(3)
N(2a)–Zn–N(1a)	93.8(3)	N(2a)–Zn–N(1b)	114.1(3)
N(2b)–Zn–O(1c)	89.8(3)	N(2b)–Zn–N(1a)	105.1(3)
N(2b)–Zn–N(1b)	92.0(3)	N(2b)–Zn–N(2a)	81.8(3)
O(11)–Zn–O(1c)	102.9(2)	O(11)–Zn–N(1a)	86.5(3)
O(11)–Zn–N(1b)	82.3(3)	O(11)–Zn–N(2a)	87.5(3)
O(11)–Zn–N(2b)	164.7(2)		
(c) $[Cd(ClO_4)(\mathbf{L3})(CH_3OH)]ClO_4$			
Cd–O(1c)	2.546(7)	Cd–N(1a)	2.386(6)
Cd–N(1b)	2.314(8)	Cd–N(2a)	2.415(8)
Cd–N(2b)	2.489(6)	Cd–O(1)	2.463(6)
Cd–O(11)	2.340(6)		
N(1a)–Cd–O(1c)	68.4(2)	N(1b)–Cd–O(1c)	68.8(2)
N(1b)–Cd–N(1a)	126.7(3)	N(2a)–Cd–O(1c)	133.7(2)
N(2a)–Cd–N(1a)	79.8(2)	N(2a)–Cd–N(1b)	153.2(2)
N(2b)–Cd–O(1c)	147.6(2)	N(2b)–Cd–N(1a)	143.6(2)
N(2b)–Cd–N(1b)	81.5(3)	N(2b)–Cd–N(2a)	72.7(2)
O(1)–Cd–O(1c)	113.1(2)	O(1)–Cd–N(1a)	79.6(2)
O(1)–Cd–N(1b)	89.3(3)	O(1)–Cd–N(2a)	92.2(2)
O(1)–Cd–N(2b)	78.1(2)	O(11)–Cd–O(1c)	78.1(2)
O(11)–Cd–N(1a)	109.1(2)	O(11)–Cd–N(1b)	91.5(3)
O(11)–Cd–N(2a)	81.7(2)	O(11)–Cd–N(2b)	90.4(2)
O(11)–Cd–O(1)	168.2(2)		
(d) $[Zn(NO_3)(\mathbf{L15})(H_2O)]ClO_4{\cdot}C_2H_5OH$			
Zn–N(1a)	2.091(4)	Zn–N(1b)	2.127(3)
Zn–N(1c)	2.141(4)	Zn–O(1)	2.199(3)
Zn–O(2)	2.370(4)	Zn–O(4)	2.085(3)
N(1b)–Zn–N(1a)	114.7(1)	N(1c)–Zn–N(1a)	84.5(1)
N(1c)–Zn–N(1b)	82.8(1)	O(1)–Zn–N(1a)	101.6(1)
O(1)–Zn–N(1b)	142.5(1)	O(1)–Zn–N(1c)	91.8(1)
O(2)–Zn–N(1a)	157.2(1)	O(2)–Zn–N(1b)	87.5(1)
O(2)–Zn–N(1c)	93.4(1)	O(2)–Zn–O(1)	55.7(1)
O(4)–Zn–N(1a)	93.9(1)	O(4)–Zn–N(1b)	96.9(1)
O(4)–Zn–N(1c)	178.1(1)	O(4)–Zn–O(1)	89.6(1)
O(4)–Zn–O(2)	88.5(1)		
(e) $[Cd(NO_3)_2(\mathbf{L15})]_2{\cdot}2C_2H_5OH$			
Cd–N(1a)	2.356(5)	Cd–N(1b)	2.360(6)
Cd–N(1c)	2.328(5)	Cd–O(1)	2.445(5)
Cd–O(2)	2.561(5)	Cd–O(4)	2.474(5)
N(1b)–Cd–N(1a)	109.4(2)	N(1c)–Cd–N(1a)	76.6(2)
N(1c)–Cd–N(1b)	76.2(2)	O(1)–Cd–N(1a)	84.8(2)
O(1)–Cd–N(1b)	156.1(2)	O(1)–Cd–N(1c)	126.9(2)
O(2)–Cd–N(1a)	83.7(2)	O(2)–Cd–N(1b)	147.3(2)
O(2)–Cd–N(1c)	78.1(2)	O(2)–Cd–O(1)	50.3(1)
O(4)–Cd–N(1a)	115.7(2)	O(4)–Cd–N(1b)	81.9(2)
O(4)–Cd–N(1c)	157.6(2)	O(4)–Cd–O(1)	74.5(2)
O(4)–Cd–O(2)	120.3(2)		

The attempted isolation of the zinc(II) and cadmium(II) complexes of most of the macrocycles incorporating less than three nitrogen donors resulted in the separation of crystalline products whose microanalytical and other data indicated that they were monoprotonated ligand salts.

The infrared spectra of the solid complexes were consistent with the presence of solvent molecules and perchlorate ions where they were suggested to be present from the microanalytical data. Thus, when the complexes were formulated as containing water and/or alcohol, absorptions in the 3400–3600-cm^{-1} region were observed. The perchlorate-containing complexes each yielded a spectrum which contained the expected strong absorption near 1080 cm^{-1}. No clear splitting of this band was evident although it is quite asymmetric in most cases; from the infrared data it is difficult to decide whether or not the perchlorate ion is coordinated to the metal in individual complexes. The presence of macrocyclic ligand bands partially obscured the nitrate absorptions and no assignment was attempted. The infrared spectra of all complexes contain bands in the region 3200–3300 cm^{-1} which are assigned to the (coordinated) secondary amines. Conductance values for the cadmium(II) complexes in methanol fall in the expected range (80–115 S cm^{-2} mol^{-1})[10] for 1:1 electrolytes in this solvent (see Table 5) while the zinc(II) complexes yielded values which were higher than this. Thus, under the conditions of measurement, there is a greater tendency towards ionization of both anions in these latter species.

The fast atom bombardment (FAB) mass spectra of the respective solid complexes are consistent with the presence of 1:1 (metal to macrocycle) stoichiometries in which one nitrate ion is associated with the complex cation: in each case, a peak corresponding to $[M(NO_3)(\text{macrocycle})]^+$ was observed. Taken together with the conductance data these results suggest that each of the complexes incorporates at least one nitrate in its co-ordination shell.

Discussion of the X-ray Structures. X-ray structures were obtained for the complexes listed in Table 4; the approximate coordination geometries of the complexes are also summarized in the table.

In $[Zn(\mathbf{L1})](ClO_4)_2$, the Zn–N bond lengths involving the three equatorial donor atoms, N(1a), N(1b), and N(2b), are not significantly different from each other, [mean Zn–N 2.056(7) Å], and are slightly shorter than the distances to the axial nitrogen atoms, N(1c) and N(2a), [mean Zn–N 2.189(9) Å]. The metal ion is slightly displaced (0.04 Å) from the plane of best fit made by it and the equatorial N atoms [N(1a), –0.02 Å; N(1b), –0.01 Å; and N(2b), –0.01 Å] toward N(2a). The three five-membered chelate rings subtend an average angle of 83.2(3)° at the zinc atom while the six-membered chelate rings make larger angles of 90.0(5) [N(2a)–Zn–N(1a)] and 95.5(5)° [N(2b)–Zn–N(1b)]. The largest angle is made by the six-membered chelate ring whose two N-donor atoms, N(2b) and N(1b), both occupy equatorial positions (where the optimum angle would be 120°) whereas the other rings link axial–equatorial sites (where a smaller angle would suffice). The configuration of the asymmetric nitrogen atoms N(1a), N(1b), N(2a), and N(2b) is *SRRR* (or *RSSS*). This arrangement is also found in the zinc and cadmium complexes of the related ON$_4$ donor macrocycle, namely $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$ and $[Cd(ClO_4)(\mathbf{L3})(CH_3OH)]ClO_4$. The complex cation is strongly hydrogen bonded to the perchlorate anions with H(N2a)···O(1) = 2.19 Å, H(N1a)···O(3)′ = 1.93 Å and H(N2b)···O(6)″ 2.24 Å; where O(3)′ and O(6)″ are related to O(3) and O(6) by the screw axis and glide plane, respectively.

In $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$, the two longest bonds to the metal involve the oxygen donors: Zn–O(11) is 2.355(7) Å, and Zn–O(1c) is 2.242(7) Å. The zinc–nitrogen bond lengths lie in the range 2.092(7)–2.190(8) Å. The chiral centers at the nitrogen atoms have a *RSSS* (or *SRRR*) configuration for N(1a), N(2a), N(2b), and N(1b), respectively. Such an overall arrangement has been found in the cadmium complex of the related 17-membered, ON$_4$ macrocycle **L3** (see below) and the zinc complex of the 17-membered, N$_5$ macrocycle **L1** (discussed above). In the latter complex the zinc atom is five-coordinate

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[10] Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

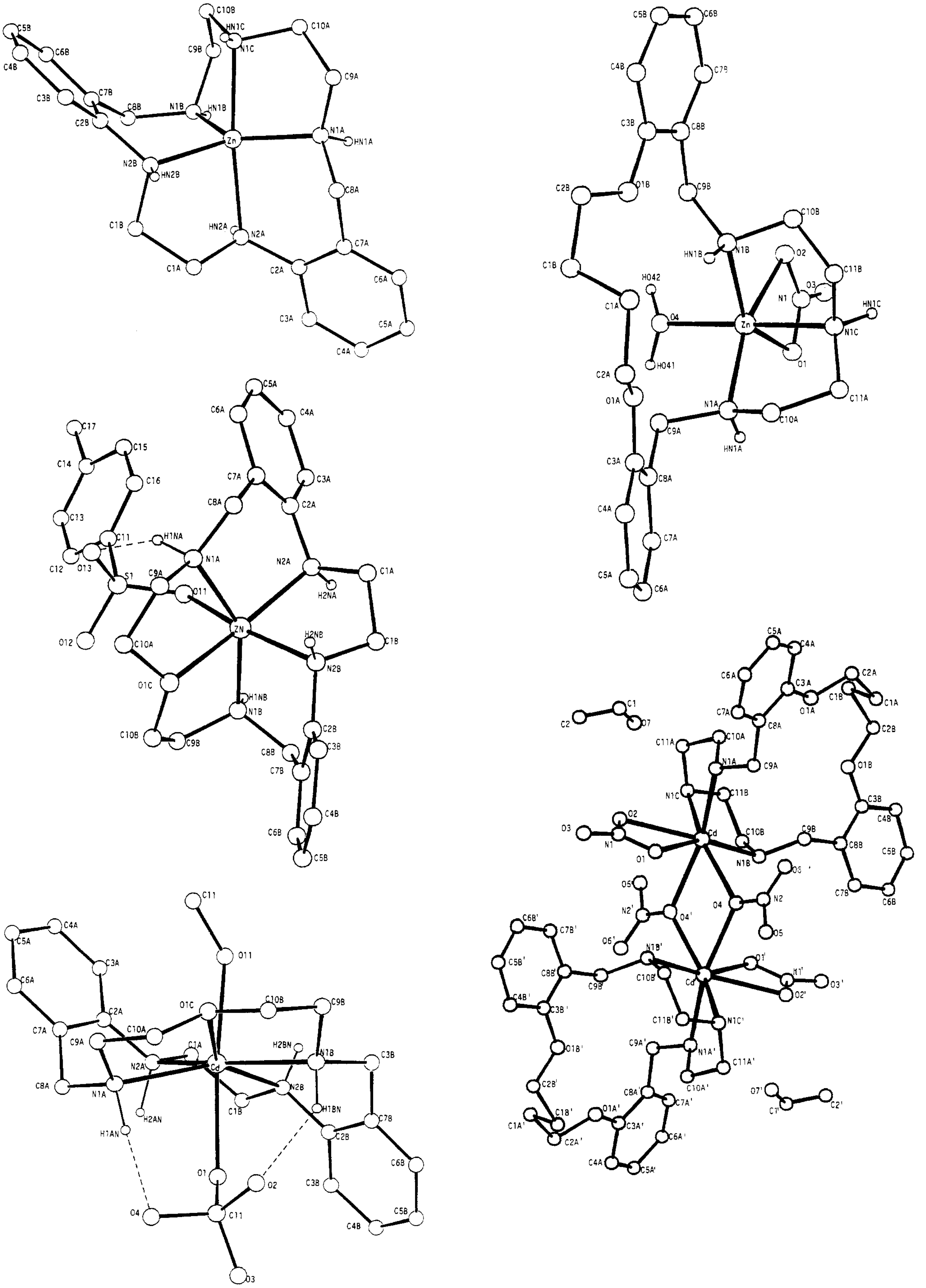

Figure 1. X-ray diffraction structures of the cations in (a, top left) [ZnL1])ClO$_4$)$_2$, (b, middle left) [Zn(CH$_3$C$_6$H$_4$SO$_3$)(**L3**)]CH$_3$C$_6$H$_4$SO$_3$, (c, bottom left) [Cd(ClO$_4$)(**L3**)(CH$_3$OH)]ClO$_4$, (d, top right) [Zn(NO$_3$)(**L15**)(H$_2$O)]ClO$_4$·C$_2$H$_5$OH, (e, bottom right) [Cd(NO$_3$)$_2$(**L15**)]$_2$·2C$_2$H$_5$OH

Table 4. Summary of Metal Coordination Spheres from X-ray Data

complex	coordination no.	coordination geometry[a]	macrocycle donor set coordinated
$[Zn\mathbf{L1}]^{2+}$	5	distort tbp	N_5
$[Zn(CH_3C_6H_4SO_3)\mathbf{L3}]^+$	6	distort oc	N_4O
$[Cd(ClO_4)\mathbf{L3}(CH_3OH)]^+$	6	distort oct	N_4O
$[Zn(NO_3)\mathbf{L15}(H_2O)]^+$	6	distort oct	N_3
$[Cd(NO_3)_2\mathbf{L15}]_2$	7	distort capped oct	N_3

[a] Distort tbp: distorted trigonal bipyramidal. Distort oct: distorted octahedral.

Table 5. Physical Data for the Zinc(II) and Cadmium(II) Complexes of Selected Macrocyclic Ligands

complex	Λ,[a] S cm^{-2} mol^{-1}	IR,[b] cm^{-1} ν(OH)	ν(NH)	anion
$[Zn(NO_3)(\mathbf{L5})]ClO_4\cdot 0.5C_2H_5OH$	148	3500 (br)	3205	1070
$[Zn(NO_3)(\mathbf{L15})(H_2O]\cdot ClO_4\cdot C_2H_5OH$	131	3420	3300, 3260	1060
$[Zn(NO_3)(\mathbf{L18})]ClO_4\cdot 0.25H_2O$	125	3500 (br)	3280, 3290	1060
$[Cd(NO_3)(\mathbf{L5})]ClO_4\cdot 0.5C_2H_5OH$	112	ca. 3500 (br)	3260	1065
$[Cd(NO_3)(\mathbf{L9})]NO_3$	109		3275	
$[Cd(NO_3)(\mathbf{L10})]NO_3$	95		3260	
$[Cd(NO_3)_2(\mathbf{L15})]_2\cdot 2C_2H_5OH$	104	3450	3280	
$[Cd(NO_3)(\mathbf{L18})]ClO_4$	126		3310, 3250	1060 (br)

[a] In methanol (23 °C). [b] Nujol mull.

Table 6. Stability Constants[a] for the Zinc(II) and Cadmium(II) Complexes of **L1–L24** [95% methanol; I = 0.1 M (NEt_4ClO_4) at 25 °C]

ligand	ring size	donor set	log *K* ZnL	CdL
L1	17	N_5	11.9	12.1
L2	17	N_4S	8.9	9.2
L3	17	N_4O	7.8	10.0
L4	20	N_5	5.6	5.8
L5	16	N_3O_2	6.5	7.3
L6	16	N_2O_2S	*b*	*b*
L7	16	N_2O_3	*b*	3.5
L8	17	N_3O_2	7.5[c]	8.7[c]
L9	17	N_2O_2S	<3.5	4.4(2)
L10	17	N_2O_3	<3.5	5.3
L11	18	N_3O_2	7.1[c]	7.9[c]
L12	19	N_3O_2	6.6[c]	5.3[c]
L13	19	N_3O_2	6.0[c]	5.0[c]
L14	19	N_2O_2S	<3.5	<3.5
L15	19	N_3O_2	7.3(2)	7.2
L16	19	N_2O_2S	3.6(3)	3.8
L17	19	N_2O_3	3.8	<3.5
L18	16	N_3S_2	5.6	6.6(2)
L19	16	N_2S_3	*b*	~3.3
L20	17	N_3S_2	6.3	7.8
L21	17	N_2S_3	*b*	~3.3
L22	17	N_2S_2O	*b*	4.4
L23	19	N_3S_2	5.4	4.6
L24	18	N_2S_3	*b*	<3.5

[a] All values ± 0.1 unless otherwise indicated. [b] Precipitation. [c] From ref 3.

with an approximately trigonal bipyramidal coordination geometry. The nickel(II) complex of the 17-membered ON_2S_2 macrocycle has a related distorted octahedral geometry with a water molecule occupying the sixth coordination site.[3] In the present complex there is evidence of an intramolecular hydrogen bond between the coordinated amino and 4-toluenesulfonate groups, H(N1a)···O(13) (1.94 Å). The complex is also strongly hydrogen-bonded to neighboring 4-toluenesulfonate anions with H(N2b)···O(21) (1.85 Å), and H(N1b)···O(23)′ (2.13 Å) and H(N2a)···O(22)′ (1.72 Å).

In the complex cation, $[Cd(ClO_4)(\mathbf{L3})(CH_3OH)]^+$, the cadmium to donor-atom bond lengths range from 2.314(8) Å [Cd–N(1b)] to 2.546(7) Å [Cd–O(1c)]. The macrocyclic donor atoms show significant deviations [O(1c), 0.54; N(1a), –0.63; N(2a), 0.43; N(1b), –0.21; and N(2b), –0.13 Å] from the plane of best fit that they and the metal cation (–0.01 Å) define. The five- and six-membered chelate rings subtend average angles of 70.0(1) and 80.7(2)° at the metal atom, respectively. The overall arrangement gives rise to *SRRR* (or *RSSS*) configurations for N(1a), N(1b), N(2a), and N(2b), respectively—with three [H(N1a), H(N1b) and H(N2b)] of the four N-bonded H atoms lying on the same side of the coordination plane while the phenylene rings lie on opposite sides of the plane to each other. As mentioned previously, this is similar to the arrangements found in $[Zn(\mathbf{L1})](ClO_4)_2$ and $[Zn(CH_3C_6H_4SO_3)(\mathbf{L3})]CH_3C_6H_4SO_3$. Both perchlorate anions in the present complex are strongly hydrogen bonded to the macrocycle, with H(N1a)···O(4) being 1.96 Å, H(N1b)···O(2) being 2.12 Å, and H(N2b)···O(5) being 2.23 Å. In addition, O(3) of the coordinated perchlorate is hydrogen bonded to H(N2a)′ of the complex cation, related by the center of inversion [H(N2a)′···O(3) 1.88 Å]. Thus the overall structure may be thought of as consisting of dimers whose halves are linked by two hydrogen bonds across the inversion center.

$[Zn(NO_3)(\mathbf{L15})(H_2O)]ClO_4\cdot C_2H_5OH$ has a coordination geometry related to that of the zinc complex of the 17-membered, O_2N_3 donor macrocycle **L8**, determined previously.[2] For the complex cation, the two longest bonds to the metal atom are made by the chelating nitrate with Zn–O(1) [2.199(3) Å] being somewhat shorter than Zn–O(2) [2.370(4) Å], giving an unsymmetric bidentate mode of coordination. The remaining zinc–donor atom bond lengths lie in the range 2.085(3)–2.141(4) Å. The asymmetric nitrogen atoms, N(1a) and N(1b), have *RR* (or *SS*) configurations, respectively. There are strong hydrogen-bonding interactions in the structure, with H(N1c)···O(6)′ = 2.13 Å (0.5 + *x*, 0.5 – *y*, 0.5 + *z*), H(O41)···O(8)″ = 1.69 Å (0.5 – *x*, 0.5 + *y*, 0.5 – *z*), and H(O42)···O(9)‴ = 1.69 Å (0.5 – *z*, 0.5 + *y*, 0.5 + *z*) linking the complex to neighboring perchlorate anions and to the ethanol of solvation. There is also a longer intramolecular contact, H(N1b)···O(1b), of 2.31 Å.

In contrast to the above zinc complex, $[Cd(NO_3)_2(\mathbf{L15})]_2\cdot 2C_2H_5OH$ is binuclear with the two cadmium ions separated by 4.17 Å and linked by two single oxygen (from nitrate) bridges across a center of inversion (Figure 1); each Cd–O(bridging) distance is 2.474(5) Å. This mode of nitrate bridging is unusual (although not unique).[11] It is noted that other dimeric cadmium complexes of macrocyclic ligands have been reported.[12,13] An ethanol of solvation per cadmium is also present. These ethanol molecules are disordered (as is shown by the large thermal parameters); efforts to determine the nature of the disorder were unsuccessful.

As mentioned previously, this cadmium complex was found to be a 1:1 electrolyte in methanol (Table 5), and thus the complex does not maintain its dimeric structure in this ionizing solvent.

Stability Constants. Stability constants for the 1:1 (L:M) zinc(II) and cadmium(II) complexes were determined potentiometrically in 95% methanol (Table 6), using conditions identical to those employed in our earlier studies.[2-4] As expected, there is a strong dependence of the respective stabilities on the donor atom set present—with the constants varying by more than 8 orders of magnitude along the series. In particular, the magnitude of a particular log *K* value is strongly influenced by the number of nitrogen donors present, with the contribution to overall stability

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(11) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev.* **1971**, *17*, 3536 and references therein.

(12) Drew, M. G. B.; Hollis, S.; McFall, S. G.; Nelson, S. M. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1595.

(13) Nelson, S. M.; McFall, S. G.; Drew, M. G. B.; Othman, A. H. B.; Mason, N. B. *J. Chem. Soc., Chem. Commun.* **1977**, 167.

falling in the order: NH(aliphatic) > NH(anilino). Thus, the 17-membered ring **L1**, with its N_5 donor set, yields complexes which are significantly more stable than those of any of the other ligands in the series. Indeed, for all three 17-membered systems where X = NH, the stabilities of the corresponding complexes are (as expected[14]) consistently higher than their analogues for which X = O or S. The stabilities of the complexes of both metals also show the expected dependence on the nature of the Y donor.

The effect of macrocyclic ring size (and concomitant chelate ring sizes) on complex stability are evident from the data presented in Table 6. The stabilities of the 16-membered ring complexes tend to be lower than the corresponding 17-membered ring systems—undoubtedly reflecting, at least in part, the potential to form "less stable" 4-membered chelate rings in the former. Complexes of the larger rings also tend to be of lower stability than their 17-membered ring analogues. For example, comparison of the results for the 20-membered ring (N_5 donor) macrocycle (**L4**) with those for the 17-membered analogue (**L1**), shows that **L4** yields zinc(II) and cadmium(II) complexes which are more than 6 orders of magnitude less stable than the corresponding complexes of **L1**. Provided all donor atoms coordinate, the chelate rings in the former complexes will be all six membered whereas **L1** will yield complexes incorporating two six-membered and three (more favored) five-membered chelate rings. In this context, the X-ray structures of the zinc complexes of **L1** and **L3** and the cadmium complex of **L3** confirm coordination of the five macrocyclic donors in each case in the solid state (see earlier discussion). Although caution needs to be exercised when discussing solution behavior with respect to solid-state geometries, it appears likely that coordination of all donors will be maintained in solution for these systems with X = NH.

The complexes of the macrocycles incorporating O_3N_2 and O_2N_2S donor sets mostly gave log *K* values which are less than 4, and such values are not of high accuracy. Because of this no detailed comparison of these systems is attempted here.

The previously reported X-ray structure of the zinc nitrate complex of **L8** (17-membered ring, O_2N_3 donor set) indicates that coordination of the ether donors does not occur in the solid; however, the corresponding cadmium nitrate complex of this ligand does have these donors coordinated.[2] This system thus appears to be poised between coordination and non coordination of the ether donors—a situation conducive to structural dislocation behavior of the type mentioned previously. Indeed, our earlier study of the stabilities of the zinc and cadmium complexes of the 17–19-membered pentadentate macrocycles incorporating O_2N_3 donor sets (namely, **L8**, **L11**–**L13**) strongly suggested that a structural dislocation occurs in solution on passing from the cadmium(II) complex of the 18-membered ring to that of a 19-membered ring.[2] Thus, when zinc(II) and cadmium(II) react with the above 17–19-membered rings the stability trends for each ion parallel each other for the first two ligands [with the stability constants falling in the order cadmium(II) > zinc(II)]. However, on passing to the 19-membered ligand complexes, a dislocation of the overall log *K* trend is evident for cadmium(II) but not for zinc (II). Thus, for cadmium(II) there is a larger than expected decrease in stability: the 19-membered ring complexes of this ion are 10^2–10^3 less stable than the corresponding 18-membered ring complex. The 19-membered ring cadmium(II) species are now of lower stability than their zinc(II) analogues.

The observed dislocation along the cadmium(II) series thus appears to reflect a cross over from coordination of the ether groups in the 17- and 18-membered ring complexes to their noncoordination in the 19-membered ring complexes. The crystal structure of the cadmium(II) complex of **L12** (19-membered) confirms that the ether oxygens are not coordinated in the solid state.[2] The present results extend this study. The behavior of the related O_2N_3-donor 19-membered ring (**L15**)—containing four methylene groups linking the oxygen donors—is of interest in this respect.

Not surprisingly, the stabilities of the complexes of the 19-membered ring macrocycles **L12** and **L15** show a significant dependence on the respective (alternate) chelate ring patterns that are possible. For example, the cadmium(II) complex of **L15** is about 100 times more stable than the corresponding complex of **L12**. In the latter species, as mentioned above, noncoordination of the ether donors has been postulated to occur in solution (and was confirmed in the solid state);[2] the ligand forms two 6-membered chelate rings involving the N_3 donor string. In contrast, even though the overall macrocyclic ring size of **L15** equals that of **L12**, the chelate rings formed by the N_3 donor string of **L15** are five membered and this is undoubtedly a major contribution to the enhanced stability of both complexes of this latter ligand (relative to those of **L12**). Further, by analogy with the complexes of **L12**, it appears unlikely that the ether donors of **L15** (which would yield a seven-membered chelate ring on coordination) coordinate in either the zinc(II) or cadmium(II) complexes. In accordance with this, the X-ray crystal structures of both complexes show noncoordination of these groups in the solid. As expected from the points just discussed, the observed stability difference between the zinc(II) complexes of the 17-membered macrocycle **L8** and the 19-membered species **L15** is only about 0.2 log units—in accordance with both macrocycles being bound to zinc solely via their (identical) $-NHCH_2CH_2NHCH_2CH_2NH-$ fragments.

Generally, similar trends in the stability patterns to those discussed above for the O_2N_3 donor systems are observed for the complexes of the 16- to 19-membered ligands **L18**, **L20**, and **L23**, incorporating thioether donors at the X positions. However, in all cases the log *K* values obtained for each of the latter complexes are somewhat lower than those obtained for the corresponding O_2N_3 donor systems (compare the values obtained for **L5**, **L8**, and **L12**)—presumably reflecting different electronic and/or steric influences (perhaps involving different solvation patterns) in the two sets of complexes. Thus, in parallel to the proposed noncoordination of the ether groups in the zinc complexes of the O_2N_3 systems,[2] similar noncoordination of the thioether donors in each of the present zinc(II) complexes appears likely; the low affinity of zinc(II) for thioether donors is well documented.[15] Once again, the data are in accordance with a structural dislocation occurring between the cadmium complexes of **L20** (17-membered ring) and **L23** (19-membered ring).[16]

Clearly the results discussed above provide additional evidence for the existence of a discrimination mechanism that while receiving little attention in the past, appears to have important implications for understanding metal ion discrimination behavior across a range of other chemical and biochemical systems.

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Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, and full bond lengths and angles for all structures (55 pages). Ordering information is given on any current masthead page.

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