Interaction of Related Open-chain and Macrocyclic Ligands incorporating Oxygen- and Nitrogen-donor Atoms with Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II}. *X*-Ray Structures of a Seven-co-ordinate Zinc(II) Complex as well as Seven- and Eight-co-ordinate Cadmium(II) Derivatives†

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The interaction of Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Cd^{II} with an O_2N_3-donor open-chain ligand has been investigated and the properties of the resulting 1 : 1 complexes compared with those of two related macrocyclic derivatives. The log *K* values have been determined in 95% methanol (I = 0.1 mol dm^{-3}, NEt_4ClO_4). *X*-Ray structures of the cadmium complexes of the open-chain ligand (L^1) and the cyclic derivative (L^3) are presented. The open-chain ligand complex is seven-co-ordinate with an approximate pentagonal-bipyramidal co-ordination geometry: nitrate ions occupy axial sites with the O_2N_3-donor set of the organic ligand co-ordinating equatorially. The complex of the macrocycle (L^3) (O_2N_4-donor set) is eight-co-ordinate with the six macrocyclic donor atoms showing only a small deviation from planar co-ordination while the backbone of the macrocycle is not flat but adopts a puckered arrangement. A nitrate ion occupies one 'axial' co-ordination site while the second site is occupied by a water in half of the molecules and a methanol in the remaining half. Solution studies indicate that this latter cadmium complex is substantially more stable than its zinc analogue, an observation which may reflect the better accommodation of the larger cadmium ion by this (18-membered ring) macrocycle relative to Zn^{II}. Molecular-mechanics calculations provide no evidence of any mismatch between the macrocyclic cavity and the cadmium ion. The *X*-ray structure of the zinc complex of the related O_2N_3-donor macrocycle (L^2) has also been determined; Zn^{II} is seven-co-ordinate with the macrocycle binding to this ion *via* its five donor groups in an approximately pentagonal-planar fashion. The axial sites are occupied by a nitrate ion and a water molecule, respectively.

There are many chemical and biochemical processes where the ability of an organic substrate to behave in a selective manner towards particular metal ions is central to their function. Nevertheless, in general, the factors underlying the metal-ion selective behaviour of many multi-donor systems (especially when they incorporate mixed donor atoms) remain poorly understood.

Recent studies have involved an investigation of the co-ordination behaviour of series of mixed-donor macrocycles (mainly oxygen–nitrogen donor systems) with selected transition- and post-transition-metal ions in order to elucidate the factors governing metal-ion recognition by such systems.[1,2] The study now reported is an extension of these investigations involving the ligands L^1—L^3 and has afforded an opportinity to compare the properties of related (mixed-donor) open-chain and macrocyclic ligand complexes. In particular, it was of interest to study the effects of the additional constraints present in the macrocyclic systems and also to investigate whether a 'macrocyclic effect'[3,4] operates in the case of the cyclic systems.

Experimental

The solution equilibrium and other physical measurements were performed as described previously.[2,5] The syntheses of L^1, L^2, and L^3 have been reported previously.[2]

Preparation of the Complexes.—All metal complexes were dried over P_2O_5 in a vacuum before analysis. Yields were in the range 20—60%.

Complexes of type $ML^1(NO_3)_2{\cdot}nH_2O$ (M = Cu^{II}, Co^{II}, Ni^{II}, or Zn^{II}; n = 0, 0.5, or 2) were synthesized by the following general procedure. A warm ethanol solution (30 cm^3) of L^1 (3 mmol) was added slowly to a warm stirred ethanol solution (10 cm^3) of the metal nitrate (3 mmol). Butanol (10—20 cm^3) was added, and the solution was then concentrated on a steam-bath. The *product* which precipitated was filtered off then washed with acetone.

The complex $[CdL^1(NO_3)_2]$ was obtained by mixing L^1 (3 mmol) in warm ethanol (20 cm^3) with a warm aqueous solution (10 cm^3) of cadmium nitrate (3 mmol). Slow cooling of the solution resulted in the formation of small crystals of *product*. A portion of the solution containing this product was refrigerated for 2 months after which crystals suitable for the *X*-ray diffraction study had formed.

The complex $ZnL^2(NO_3)_2{\cdot}H_2O$ was prepared by the slow addition of a methanol solution (10 cm^3) of zinc nitrate (3 mmol) to a hot stirred solution of L^2 (3 mmol) in ethanol (20

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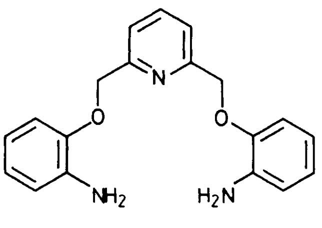
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



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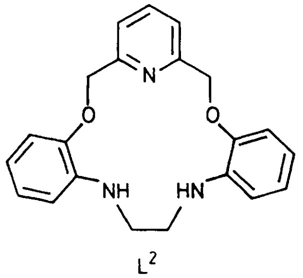

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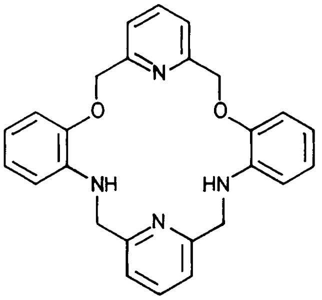

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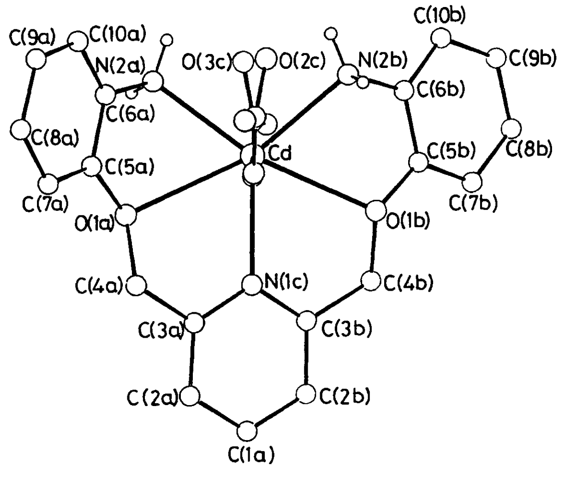


Figure 1. The *X*-ray structure of [CdL^1(NO$_3$)$_2$]

cm^3). The solution was allowed to stand overnight in a stoppered flask during which time colourless crystals of the *product* formed. This was removed by filtration and washed with ethanol then acetone.

The complex [ZnL^3(NO$_3$)$_2$] was obtained by a similar procedure to the above except that the reaction solution was evaporated to one third of its original volume and excess of diethyl ether was then added (with scratching) to induce crystallization. A fine cream *product* formed which was filtered off and washed with ethanol then acetone.

Complexes [CdL^2(ClO$_4$)$_2$] and [CdL^3(MeOH)$_{0.5}$(H$_2$O)$_{0.5}$(NO$_3$)]ClO$_4$ were obtained by mixing warm methanol solutions of cadmium nitrate and L^2 or L^3 as described above followed by the addition of excess of lithium perchlorate in methanol (10 cm^3). The compound [CdL^2(ClO$_4$)$_2$] precipitated almost immediately; the solution containing the complex of L^3 was evaporated to approximately one third of its original volume and then cooled to induce crystallization. Both *products* were obtained as crystalline solids. Larger crystals of the latter complex formed in the filtrate and one of these was used for the *X*-ray crystallographic characterization.

X-Ray Structural Analyses.—Single-crystal *X*-ray analyses were carried out for each of the complexes [CdL^1(NO$_3$)$_2$] (**1**), [ZnL^2(H$_2$O)(NO$_3$)]NO$_3$ (**2**), and [CdL^3(MeOH)$_{0.5}$(H$_2$O)$_{0.5}$(NO$_3$)]ClO$_4$ (**3**). Data were collected using crystals of dimensions 0.47 × 0.16 × 0.10 mm for (**1**), 0.32 × 0.26 × 0.13 mm for (**2**), and 0.28 × 0.16 × 0.15 mm for (**3**) on a Philips PW1100 diffractometer with a constant scan width of 0.90° for (**1**) and (**2**) and 1.10° for (**3**) and a scan speed of 0.05° s^{-1} in the θ range 3—25° (using graphite crystal-monochromated Mo-K_α radiation with a θ—2θ scan mode); no significant change occurred in three reference reflections which were checked every 5 h. Lorenz polarization corrections were applied to all sets of data and equivalent reflections were merged to give a total of 3 090 unique reflections for (**1**), 3 331 for (**2**), and 1 195 for (**3**) with $I/\sigma(I) > 3.0$. Individual weights of $1/\sigma^2(I)$ were assigned to each reflection and refinement converged at R 0.0247 and R' 0.0258 for the complex (**1**), R 0.0848 and R' 0.0835 for (**2**), and R 0.0771 and R' 0.0759 for (**3**), where $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$.

The metal atoms were located from Patterson syntheses. The remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. In the case of compound (**3**), a peak of *ca.* 3 e Å^{-3} within bonding distance of O(2) was observed. This peak was included in the model as a carbon atom C(2) with a population parameter of 0.5 corresponding to a random 50:50 distribution of the complexes [CdL^3(MeOH)(NO$_3$)]$^+$ and [CdL^3(H$_2$O)(NO$_3$)]$^+$ in the crystal. This disorder accounts for the poor diffraction of the crystals at high angle. Due to the resultant shortage of data for complex (**3**) the atoms of the two phenylene rings were constrained to idealised geometry (C–C 1.395 Å). In the final stages of full-matrix refinement anisotropic thermal parameters were assigned to all non-hydrogen atoms for complex (**1**) and the cadmium and zinc for (**2**) and (**3**), respectively. For complex (**1**), all the hydrogen atoms were located in a final Fourier-difference synthesis and were assigned a fixed thermal parameter of 0.08 Å^2. For complex (**3**) all the hydrogen atoms were included at idealized positions with fixed thermal parameters of 0.10 Å^2. For complex (**2**), the thermal parameters for the aromatic and aliphatic hydrogens were separately tied to free variables and refined to values of 0.087 and 0.077 Å^2, respectively.

Major computations were performed using the SHELX program.[6] Neutral scattering factors,[7] corrected for the real and imaginary parts of the anomalous scattering,[8] were used for all atoms.

The final atomic co-ordinates for complexes (**1**)—(**3**) are listed in Table 1, selected bond lengths in Table 2, and selected angles in Table 3. The structures are shown in Figures 1, 2, and 3, respectively.

Crystal data. Complex (**1**). C$_{19}$H$_{19}$CdN$_5$O$_8$, $M = 557.8$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.502(2)$, $b = 7.294(2)$, $c = 12.038(2)$ Å, $\alpha = 91.20(2)$, $\beta = 107.37(2)$, and $\gamma = 90.22(2)$°, $U = 1\,047.4$ Å^3, $Z = 2$, $D_c = 1.77$ g cm^{-3}, $F(000) = 560$, μ(Mo-K_α) = 9.91 cm^{-1}.

Table 1. Fractional atomic co-ordinates for complexes (**1**)—(**3**)

Atom	*x*	*y*	*z*
(*a*) $[\mathrm{CdL^1(NO_3)_2}]$ (**1**)			
Cd	−0.163 42(2)	0.243 76(3)	0.148 50(2)
N(1c)	−0.286 6(2)	0.229 5(3)	0.267 4(2)
C(1c)	−0.422 7(3)	0.171 4(6)	0.408 4(3)
C(2a)	−0.467 3(3)	0.170 0(5)	0.289 9(3)
C(3a)	−0.397 7(2)	0.203 4(4)	0.221 5(3)
C(4a)	−0.448 8(2)	0.222 9(4)	0.093 5(3)
O(1a)	−0.374 1(2)	0.150 2(3)	0.034 2(2)
C(5a)	−0.391 1(3)	0.208 5(4)	−0.078 1(3)
C(7a)	−0.490 4(3)	0.279 7(4)	−0.147 1(3)
C(8a)	−0.494 6(3)	0.346 2(5)	−0.256 0(3)
C(9a)	−0.400 6(3)	0.339 0(5)	−0.294 2(3)
C(10a)	−0.302 1(3)	0.262 6(5)	−0.225 6(3)
C(6a)	−0.297 0(3)	0.194 5(4)	−0.117 4(3)
N(2a)	−0.197 0(2)	0.124 5(3)	−0.038 7(2)
N(2b)	0.014 7(2)	0.371 2(4)	0.186 0(2)
C(6b)	0.089 8(3)	0.328 1(4)	0.297 3(3)
C(10b)	0.203 2(3)	0.300 2(6)	0.315 0(4)
C(9b)	0.271 3(3)	0.261 5(8)	0.426 2(5)
C(8b)	0.227 6(3)	0.244 8(6)	0.517 0(4)
C(7b)	0.113 5(3)	0.269.0(5)	0.500 3(3)
C(5b)	0.046 4(3)	0.307 9(4)	0.389 9(3)
O(1b)	−0.068 0(2)	0.331 8(3)	0.363 0(2)
C(4b)	−0.119 9(3)	0.248 0(5)	0.439 9(3)
C(3b)	−0.243 8(3)	0.228 3(4)	0.384 1(3)
C(2b)	−0.309 8(3)	0.202 1(6)	0.456 8(3)
O(2a)	−0.257 8(2)	0.521 4(3)	0.091 6(2)
O(2b)	−0.283 0(2)	0.743 5(4)	−0.029 0(3)
O(2c)	−0.141 3(2)	0.568 7(4)	−0.005 1(3)
O(3a)	−0.103 0(2)	−0.035 7(3)	0.241 9(2)
O(3b)	0.026 3(3)	−0.240 1(4)	0.271 7(2)
O(3c)	0.001 2(2)	−0.054 7(4)	0.129 4(3)
N(2)	−0.227 1(2)	0.613 8(4)	0.018 5(3)
N(3)	−0.024 8(2)	−0.111 4(4)	0.214 1(2)
H(na1)	−0.142 20	0.144 30	−0.059 90
H(na2)	−0.205 00	0.006 70	−0.029 20
H(nb1)	0.039 90	0.340 30	0.132 00
H(nb2)	−0.003 30	0.480 70	0.186 90
(*b*) $[\mathrm{ZnL^2(H_2O)(NO_3)]NO_3}$ (**2**) (molecule 1)			
Zn(1)	0.235 16(18)	0.100 43(12)	0.178 40(4)
N(2a)	0.020 7(11)	0.060 9(7)	0.152 3(2)
N(2b)	0.182 9(12)	−0.053 9(8)	0.202 0(3)
N(1c)	0.406 4(12)	0.222 0(8)	0.185 2(3)
O(1a)	0.136 0(11)	0.250 5(8)	0.158 5(2)
O(1b)	0.445 8(10)	0.038 7(7)	0.217 2(2)
O(2a)	0.114 4(12)	0.169 3(8)	0.220 9(2)
O(3a)	0.369 9(11)	0.015 5(8)	0.147 1(2)
O(3b)	0.299 1(13)	0.125 2(9)	0.110 2(3)
O(3c)	0.464 6(14)	0.006 1(9)	0.099 7(3)
N(3a)	0.377 8(15)	0.048 4(11)	0.119 0(3)
C(1c)	0.615 2(19)	0.379 2(13)	0.197 4(4)
C(2a)	0.477 4(18)	0.402 4(13)	0.179 9(4)
C(3a)	0.375 9(17)	0.317 1(12)	0.174 9(3)
C(4a)	0.228 7(17)	0.339 0(12)	0.156 1(4)
C(5a)	−0.013 0(15)	0.249 9(11)	0.146 1(3)
C(8a)	−0.090 2(16)	0.338 8(11)	0.136 3(3)
C(9a)	−0.244 3(17)	0.327 2(12)	0.124 0(3)
C(10a)	−0.310 6(16)	0.230 6(10)	0.120 9(3)
C(11a)	−0.226 0(15)	0.140 6(11)	0.130 6(3)
C(6a)	−0.075 3(15)	0.151 1(10)	0.142 3(3)
C(7a)	−0.059 7(15)	−0.016 3(10)	0.172 2(3)
C(2b)	0.650 5(18)	0.282 2(11)	0.208 1(4)
C(3b)	0.540 8(16)	0.203 4(11)	0.201 7(3)
C(4b)	0.584 9(16)	0.094 0(11)	0.211 2(4)
C(5b)	0.454 3(16)	−0.068 0(11)	0.215 7(3)
C(8b)	0.584 0(19)	−0.126 1(13)	0.222 1(4)
C(9b)	0.581 9(19)	−0.236 3(13)	0.219 5(4)
C(10b)	0.448 6(20)	−0.284 7(14)	0.210 6(4)
C(11b)	0.308 3(18)	−0.230 1(12)	0.204 4(4)
C(6b)	0.319 2(16)	−0.118 0(11)	0.207 0(3)
C(7b)	0.056 6(16)	−0.099 7(11)	0.182 3(3)
H(n2a)	0.047 10	0.027 30	0.129 10
H(n2b)	0.146 70	−0.045 90	0.226 60
N(1)	−0.048 4(21)	−0.027 4(14)	0.269 0(4)
O(11)	−0.027 0(27)	−0.125 0(17)	0.265 2(5)
O(12)	0.077 4(20)	0.022 7(14)	0.265 9(4)
O(13)	−0.161 1(25)	0.014 2(18)	0.277 8(5)
O(14)	−0.086 7(43)	0.059 6(29)	0.257 7(9)
O(15)	−0.158 4(61)	−0.080 6(45)	0.283 0(12)
O(16)	0.061 4(84)	−0.074 1(59)	0.266 4(16)
(molecule 2)			
Zn(2)	0.263 61(19)	0.241 08(12)	0.458 08(4)
N(2x)	0.318 7(13)	0.167 9(8)	0.410 7(3)
N(2y)	0.467 3(12)	0.330 4(8)	0.446 4(3)
N(1z)	0.104 2(13)	0.211 0(8)	0.496 1(3)
O(1x)	0.071 4(10)	0.110 1(7)	0.439 0(2)
O(1y)	0.342 7(10)	0.335 0(7)	0.503 2(2)
O(2x)	0.405 8(11)	0.120 2(8)	0.481 3(2)
O(3x)	0.080 8(11)	0.339 0(7)	0.443 5(2)
O(3y)	0.188 9(13)	0.404 4(9)	0.401 2(3)
O(3z)	−0.051 1(16)	0.429 4(11)	0.408 1(3)
N(3x)	0.074 2(17)	0.392 4(11)	0.417 5(3)
C(1z)	−0.091 3(21)	0.170 5(14)	0.544 4(5)
C(2x)	−0.124 5(20)	0.126 4(14)	0.513 9(4)
C(3x)	−0.019 5(18)	0.152 4(12)	0.490 0(4)
C(4x)	−0.063 5(17)	0.118 9(12)	0.456 0(4)
C(5x)	0.056 8(16)	0.118 9(11)	0.406 4(3)
C(8x)	−0.084 1(19)	0.098 8(12)	0.388 4(4)
C(9x)	−0.088 2(19)	0.107 1(12)	0.354 9(4)
C(10x)	0.041 5(19)	0.133 6(13)	0.339 1(4)
C(11x)	0.179 0(18)	0.152 4(11)	0.357 2(4)
C(6x)	0.183 4(16)	0.145 4(10)	0.390 2(3)
C(7x)	0.439 8(16)	0.230 1(11)	0.396 0(3)
C(2y)	0.032 8(19)	0.230 6(13)	0.551 6(4)
C(3y)	0.130 0(16)	0.249 0(12)	0.525 1(3)
C(4y)	0.267 0(17)	0.314 9(12)	0.532 8(4)
C(5y)	0.492 2(16)	0.361 7(11)	0.504 4(3)
C(8y)	0.579 2(19)	0.389 3(12)	0.533 2(4)
C(9y)	0.730 6(18)	0.414 1(12)	0.530 2(4)
C(10y)	0.802 1(19)	0.410 8(12)	0.502 3(4)
C(11y)	0.716 9(17)	0.383 9(11)	0.473 1(4)
C(6y)	0.562 0(15)	0.359 7(10)	0.474 6(3)
C(7y)	0.550 6(16)	0.266 1(12)	0.421 8(3)
H(n2x)	0.367 00	0.090 60	0.414 50
H(n2y)	0.433 90	0.405 30	0.436 00
N(2)	0.427 9(19)	0.449 1(13)	0.067 6(5)
O(21)	0.413 5(50)	0.461 8(37)	0.095 7(11)
O(22)	0.582 5(29)	0.455 1(19)	0.060 6(6)
O(23)	0.335 9(28)	0.440 3(18)	0.043 7(6)
O(24)	0.334 9(43)	0.373 5(31)	0.078 2(9)
O(25)	0.494 5(46)	0.429 5(28)	0.045 5(9)
O(26)	0.457 3(36)	−0.496 1(25)	0.091 3(8)

Table 1 (*continued*)

Atom	x	y	z	Atom	x	y	z
(*c*) $[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]ClO_4$ (**3**)							
Cd	0.099 0(2)	0.197 5(1)	0.161 7(2)	C(4b)	0.042 2(24)	0.314 0(12)	0.359 7(22)
N(1c)	0.098 7(19)	0.318 8(9)	0.166 8(21)	C(11b)	−0.014 6(15)	0.209 7(10)	0.523 1(19)
N(2a)	0.273 5(18)	0.147 6(12)	0.094 6(18)	C(12b)	−0.036 8(15)	0.154 6(10)	0.590 7(19)
N(2b)	−0.076 6(18)	0.147 7(12)	0.225 3(19)	C(13b)	−0.075 1(15)	0.095 8(10)	0.538 6(19)
N(3c)	0.096 9(21)	0.076 5(9)	0.152 3(19)	C(14b)	−0.091 2(15)	0.092 2(10)	0.418 8(19)
O(1a)	0.204 2(16)	0.256 5(10)	0.007 3(16)	C(6b)	−0.069 0(15)	0.147 2(10)	0.351 2(19)
O(1b)	−0.007 0(16)	0.256 7(11)	0.325 5(16)	C(5b)	−0.030 7(15)	0.206 0(10)	0.403 3(19)
C(1c)	0.071 0(23)	0.455 2(15)	0.154 5(25)	C(7b)	−0.099 4(23)	0.085 3(16)	0.163 7(28)
C(2a)	0.110 2(24)	0.420 9(14)	0.062 3(26)	C(8b)	0.001 1(20)	0.047 8(14)	0.158 2(21)
C(3a)	0.122 4(25)	0.352 0(14)	0.072 7(21)	C(9b)	0.000 3(26)	−0.022 0(14)	0.156 7(25)
C(4a)	0.158 7(16)	0.314 4(10)	−0.025 9(16)	O(2)	0.210 6(16)	0.184 9(12)	0.338 4(18)
C(11a)	0.215 4(13)	0.219 5(8)	−0.194 5(16)	C(2)	0.211 8(87)	0.118 9(55)	0.405 3(76)
C(12a)	0.238 0(13)	0.167 8(8)	−0.269 1(16)	O(31)	−0.002 6(18)	0.190 3(12)	−0.015 6(17)
C(13a)	0.271 8(13)	0.106 1(8)	−0.224 8(16)	O(32)	−0.141 4(22)	0.229 8(13)	−0.139 1(26)
C(14a)	0.283 1(13)	0.096 1(8)	−0.105 8(16)	O(33)	−0.120 8(25)	0.259 6(15)	0.038 0(27)
C(6a)	0.260 5(13)	0.147 9(8)	−0.031 1(16)	N(3)	−0.088 4(27)	0.225 7(15)	−0.040 1(29)
C(5a)	0.226 6(13)	0.209 6(8)	−0.075 5(16)	Cl	0.102 4(7)	0.401 2(3)	0.662 0(7)
C(7a)	0.284 1(23)	0.081 8(16)	0.142 3(29)	O(1c1)	0.151 2(7)	0.440 5(3)	0.754 9(7)
C(8a)	0.185 6(22)	0.041 4(14)	0.140 5(25)	O(2c1)	0.061 1(7)	0.444 8(3)	0.575 4(7)
C(9a)	0.188 0(25)	−0.028 1(14)	0.139 9(24)	O(3c1)	0.176 0(7)	0.353 7(3)	0.625 6(7)
C(10c)	0.090 4(25)	−0.060 4(15)	0.141 9(26)	O(4c1)	0.015 8(7)	0.367 0(3)	0.711 2(7)
C(2b)	0.049 3(24)	0.421 2(13)	0.254 8(26)	H(n2a)	0.344 20	0.176 30	0.120 60
C(3b)	0.066 2(23)	0.352 6(13)	0.256 9(21)	H(n2b)	−0.139 10	0.182 40	0.198 10

Table 2. Selected bond lengths (Å) for complexes (**1**)—(**3**)

(*a*) $[CdL^1(NO_3)_2]$ (**1**)							
Cd–N(1c)	2.398(3)	Cd–O(1a)	2.660(2)	C(5a)–C(6a)	1.396(5)	C(6a)–N(2a)	1.428(4)
Cd–N(2a)	2.315(3)	Cd–N(2b)	2.322(3)	N(2a)–H(na1)	0.813(3)	N(2a)–H(na2)	0.879(3)
Cd–O(1b)	2.566(2)	Cd–O(2a)	2.357(2)	N(2b)–C(6b)	1.430(4)	N(2b)–H(nb1)	0.830(3)
Cd–O(3a)	2.364(2)	N(1c)–C(3a)	1.345(4)	N(2b)–H(nb2)	0.831(3)	C(6b)–C(5b)	1.388(6)
N(1c)–C(3b)	1.346(4)	C(3a)–C(4a)	1.492(4)	C(5b)–O(1b)	1.382(4)	O(1b)–C(4b)	1.425(5)
C(4a)–O(1a)	1.431(4)	O(1a)–C(5a)	1.381(4)	C(4b)–C(3b)	1.498(5)		
(*b*) $[ZnL^2(H_2O)(NO_3)]NO_3$ (**2**)							
Zn(1)–N(2a)	2.172(10)	Zn(2)–N(2x)	2.235(11)	N(2b)–H(n2b)	1.079(11)	N(2y)–H(n2y)	1.082(11)
Zn(1)–N(2b)	2.253(11)	Zn(2)–N(2y)	2.186(11)	N(1c)–C(3a)	1.308(18)	N(1z)–C(3x)	1.327(19)
Zn(1)–N(1c)	2.163(11)	Zn(2)–N(1z)	2.177(11)	N(1c)–C(3b)	1.349(17)	N(1z)–C(3y)	1.300(18)
Zn(1)–O(1a)	2.241(10)	Zn(2)–O(1x)	2.471(9)	O(1a)–C(4a)	1.396(18)	O(1x)–C(4x)	1.405(18)
Zn(1)–O(1b)	2.502(9)	Zn(2)–O(1y)	2.286(9)	O(1a)–C(5a)	1.373(16)	O(1x)–C(5x)	1.344(17)
Zn(1)–O(2a)	2.264(10)	Zn(2)–O(2x)	2.172(10)	O(1b)–C(4b)	1.436(17)	O(1y)–C(4y)	1.439(18)
Zn(1)–O(3a)	2.090(10)	Zn(2)–O(3x)	2.092(10)	O(1b)–C(5b)	1.365(17)	O(1y)–C(5y)	1.348(17)
N(2a)–C(6a)	1.470(16)	N(2x)–C(6x)	1.445(17)	C(3a)–C(4a)	1.493(20)	C(3x)–C(4x)	1.493(21)
N(2a)–C(7a)	1.480(16)	N(2x)–C(7x)	1.474(18)	C(5a)–C(6a)	1.379(19)	C(5x)–C(6x)	1.360(20)
N(2a)–H(n2a)	1.081(10)	N(2x)–H(n2x)	1.082(11)	C(7a)–C(7b)	1.515(19)	C(7x)–C(7y)	1.475(20)
N(2b)–C(6b)	1.451(17)	N(2y)–C(6y)	1.438(17)	C(3b)–C(4b)	1.496(20)	C(3y)–C(4y)	1.484(21)
N(2b)–C(7b)	1.459(17)	N(2y)–C(7y)	1.516(18)	C(5b)–C(6b)	1.373(19)	C(5y)–C(6y)	1.396(20)
(*c*) $[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]ClO_4$ (**3**)							
Cd–N(1c)	2.433(19)	Cd–N(2a)	2.575(23)	N(2b)–H(n2b)	1.078(23)	N(3c)–C(8a)	1.33(4)
Cd–N(2b)	2.572(23)	Cd–N(3c)	2.428(18)	N(3c)–C(8b)	1.34(3)	O(1a)–C(4a)	1.34(3)
Cd–O(1a)	2.586(20)	Cd–O(2)	2.416(20)	O(1a)–C(5a)	1.39(3)	O(1b)–C(4b)	1.35(3)
Cd–O(31)	2.350(20)	N(1c)–C(3a)	1.33(3)	O(1b)–C(5b)	1.40(3)	C(3a)–C(4a)	1.47(3)
N(1c)–C(3b)	1.34(3)	N(2a)–C(6a)	1.46(3)	C(6a)–C(5a)	1.395	C(7a)–C(8a)	1.48(4)
N(2a)–C(7a)	1.43(4)	N(2a)–H(n2a)	1.082(22)	C(3b)–C(4b)	1.47(4)	C(6b)–C(5b)	1.395
N(2b)–C(6b)	1.46(3)	N(2b)–C(7b)	1.46(4)	C(7b)–C(8b)	1.47(4)	C(8b)–C(9b)	1.40(4)

Complex (**2**). $C_{21}H_{21}N_5O_9Zn$, $M = 552.81$, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$), $a = 8.733(2)$, $b = 12.762(3)$, $c = 41.131(3)$ Å, $\beta = 92.80(2)°$, $U = 4\,578.61$ Å^3, $Z = 8$, $D_c = 1.649$ g cm^{-3}, $F(000) = 2\,272$, $\mu(\text{Mo-}K_\alpha) = 10.71$ cm^{-1}.

Complex (**3**). $C_{26.5}H_{27}CdClN_5O_{10}$, $M = 723.4$, monoclinic, space group $P2_1/n$ (non-standard $P2_1/c$), $a = 12.530(3)$, $b = 20.051(4)$, $c = 11.625(3)$ Å, $\beta = 94.02(2)°$, $U = 2\,913.47$ Å^3, $Z = 4$, $D_c = 1.649$ g cm^{-3}, $F(000) = 1\,464$, $\mu(\text{Mo-}K_\alpha) = 8.12$ cm^{-1}.

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

Table 3. Selected interbond angles (°) for complexes (**1**)—(**3**)

(*a*) $[CdL^1(NO_3)_2]$ (**1**)

O(1a)–Cd–N(1c)	65.3(1)	N(2a)–Cd–N(1c)	126.8(1)	C(4a)–O(1a)–Cd	110.3(1)	C(5a)–O(1a)–Cd	105.4(2)
N(2a)–Cd–O(1a)	63.1(1)	N(2b)–Cd–N(1c)	130.9(1)	C(5a)–O(1a)–C(4a)	115.9(2)	C(6a)–C(5a)–O(1a)	114.2(2)
N(2b)–Cd–O(1a)	159.9(1)	N(2b)–Cd–N(2a)	102.3(1)	N(2a)–C(6a)–C(5a)	117.4(3)	C(6a)–N(2a)–Cd	112.4(2)
O(1b)–Cd–N(1c)	66.4(1)	O(1b)–Cd–O(1a)	131.7(1)	H(na1)–N(2a)–Cd	108.5(2)	H(na1)–N(2a)–C(6a)	112.1(3)
O(1b)–Cd–N(2a)	162.6(1)	O(1b)–Cd–N(2b)	65.5(1)	H(na2)–N(2a)–Cd	102.5(2)	H(na2)–N(2a)–C(6a)	110.0(2)
O(2a)–Cd–N(1c)	82.2(1)	O(2a)–Cd–O(1a)	74.2(1)	H(na2)–N(2a)–H(na1)	110.9(3)	C(6b)–N(2b)–Cd	114.2(2)
O(2a)–Cd–N(2a)	95.5(1)	O(2a)–Cd–N(2b)	94.8(1)	H(nb1)–N(2b)–Cd	108.3(2)	H(nb1)–N(2b)–C(6b)	112.0(3)
O(2a)–Cd–O(1b)	97.9(1)	O(3a)–Cd–N(1c)	80.8(1)	H(nb2)–N(2b)–Cd	97.6(2)	H(nb2)–N(2b)–C(6b)	109.0(3)
O(3a)–Cd–O(1a)	99.3(1)	O(3a)–Cd–N(2a)	95.3(1)	H(nb2)–N(2b)–H(nb1)	115.1(3)	C(5b)–C(6b)–N(2b)	118.5(3)
O(3a)–Cd–N(2b)	95.7(1)	O(3a)–Cd–O(1b)	74.6(1)	C(7b)–C(5b)–C(6b)	122.0(3)	O(1b)–C(5b)–C(6b)	114.9(3)
O(3a)–Cd–O(2a)	163.0(1)	C(3a)–N(1c)–Cd	122.1(2)	C(5b)–O(1b)–Cd	110.1(2)	C(4b)–O(1b)–Cd	112.8(2)
C(3b)–N(1c)–Cd	119.9(2)	C(3b)–N(1c)–C(3a)	117.7(3)	C(4b)–O(1b)–C(5b)	115.4(2)	C(3b)–C(4b)–O(1b)	110.9(3)
C(4a)–C(3a)–N(1c)	118.7(3)	O(1a)–C(4a)–C(3a)	109.3(2)	C(4b)–C(3b)–N(1c)	120.0(3)	C(2b)–C(3b)–N(1c)	122.5(3)

(*b*) $[ZnL^2(H_2O)(NO_3)]NO_3$ (**2**)

N(2b)–Zn(1)–N(2a)	79.8(4)	N(2y)–Zn(2)–N(2x)	79.3(4)	C(6b)–N(2b)–Zn(1)	111.8(8)	C(6y)–N(2y)–Zn(2)	113.7(8)
N(1c)–Zn(1)–N(2a)	143.5(4)	N(1z)–Zn(2)–N(2x)	136.4(4)	C(7b)–N(2b)–Zn(1)	105.9(8)	C(7y)–N(2y)–Zn(2)	106.6(8)
N(1c)–Zn(1)–N(2b)	136.4(4)	N(1z)–Zn(2)–N(2y)	143.6(4)	C(7b)–N(2b)–C(6b)	116(1)	C(7y)–N(2y)–C(6y)	114(1)
O(1a)–Zn(1)–N(2a)	73.1(3)	O(1x)–Zn(2)–N(2x)	67.1(4)	H(n2b)–N(2b)–Zn(1)	113.3(7)	H(n2y)–N(2y)–Zn(2)	109.9(7)
O(1a)–Zn(1)–N(2b)	145.3(4)	O(1x)–Zn(2)–N(2y)	146.2(4)	H(n2b)–N(2b)–C(6b)	101.3(9)	H(n2y)–N(2y)–C(6y)	102.9(9)
O(1a)–Zn(1)–N(1c)	71.7(4)	O(1x)–Zn(2)–N(1z)	70.2(4)	H(n2b)–N(2b)–C(7b)	108(1)	H(n2y)–N(2y)–C(7y)	110(1)
O(1b)–Zn(1)–N(2a)	146.2(3)	O(1y)–Zn(2)–N(2x)	149.0(4)	C(3a)–N(1c)–Zn(1)	119.7(9)	C(3x)–N(1z)–Zn(2)	120.5(9)
O(1b)–Zn(1)–N(2b)	66.9(3)	O(1y)–Zn(2)–N(2y)	71.8(4)	C(3b)–N(1c)–Zn(1)	121.2(9)	C(3y)–N(1z)–Zn(2)	120.4(9)
O(1b)–Zn(1)–N(1c)	70.2(4)	O(1y)–Zn(2)–N(1z)	71.9(4)	C(3b)–N(1c)–C(3a)	119(1)	C(3y)–N(1z)–C(3x)	119(1)
O(1b)–Zn(1)–O(1a)	139.6(3)	O(1y)–Zn(2)–O(1x)	141.9(3)	C(4a)–O(1a)–Zn(1)	120.1(8)	C(4x)–O(1x)–Zn(2)	111.1(8)
O(2a)–Zn(1)–N(2a)	92.8(4)	O(2x)–Zn(2)–N(2x)	86.8(4)	C(5a)–O(1a)–Zn(1)	118.2(8)	C(5x)–O(1x)–Zn(2)	106.9(8)
O(2a)–Zn(1)–N(2b)	83.9(4)	O(2x)–Zn(2)–N(2y)	90.7(4)	C(5a)–O(1a)–C(4a)	121(1)	C(5x)–O(1x)–C(4x)	117(1)
O(2a)–Zn(1)–N(1c)	88.1(4)	O(2x)–Zn(2)–N(1z)	86.1(4)	C(4b)–O(1b)–Zn(1)	109.8(7)	C(4y)–O(1y)–Zn(2)	117.5(8)
O(2a)–Zn(1)–O(1a)	76.4(4)	O(2x)–Zn(2)–O(1x)	91.4(3)	C(5b)–O(1b)–Zn(1)	109.0(7)	C(5y)–O(1y)–Zn(2)	114.6(8)
O(2a)–Zn(1)–O(1b)	89.2(3)	O(2x)–Zn(2)–O(1y)	82.6(3)	C(5b)–O(1b)–C(4b)	116(1)	C(5y)–O(1y)–C(4y)	120(1)
O(3a)–Zn(1)–N(2a)	94.2(4)	O(3x)–Zn(2)–N(2x)	101.1(4)	C(4a)–C(3a)–N(1c)	120(1)	C(4x)–C(3x)–N(1z)	120(1)
O(3a)–Zn(1)–N(2b)	86.8(4)	O(3x)–Zn(2)–N(2y)	104.1(4)	C(3a)–C(4a)–O(1a)	107(1)	C(3x)–C(4x)–O(1x)	108(1)
O(3a)–Zn(1)–N(1c)	92.6(4)	O(3x)–Zn(2)–N(1z)	78.8(4)	C(6a)–C(5a)–O(1a)	114(1)	C(6x)–C(5x)–O(1x)	118(1)
O(3a)–Zn(1)–O(1a)	115.9(4)	O(3x)–Zn(2)–O(1x)	79.4(3)	C(5a)–C(6a)–N(2a)	118(1)	C(5x)–C(6x)–N(2x)	115(1)
O(3a)–Zn(1)–O(1b)	79.1(3)	O(3x)–Zn(2)–O(1y)	96.6(4)	C(7b)–C(7a)–N(2a)	107(1)	C(7y)–C(7x)–N(2x)	109(1)
O(3a)–Zn(1)–O(2a)	167.2(4)	O(3x)–Zn(2)–O(2x)	164.2(4)	C(4b)–C(3b)–N(1c)	120(1)	C(4y)–C(3y)–N(1z)	121(1)
C(6a)–N(2a)–Zn(1)	115.0(7)	C(6x)–N(2x)–Zn(2)	112.7(8)	C(3b)–C(4b)–O(1b)	107(1)	C(3y)–C(4y)–O(1y)	108(1)
C(7a)–N(2a)–Zn(1)	107.6(7)	C(7x)–N(2x)–Zn(2)	108.7(8)	C(8b)–C(5b)–O(1b)	125(1)	C(8y)–C(5y)–O(1y)	125(1)
C(7a)–N(2a)–C(6a)	113(1)	C(7x)–N(2x)–C(6x)	117(1)	C(6b)–C(5b)–O(1b)	115(1)	C(6y)–C(5y)–O(1y)	115(1)
H(n2a)–N(2a)–Zn(1)	108.2(6)	H(n2x)–N(2x)–Zn(2)	110.7(7)	C(5b)–C(6b)–N(2b)	118(1)	C(5y)–C(6y)–N(2y)	117(1)
H(n2a)–N(2a)–C(6a)	102.0(8)	H(n2x)–N(2x)–C(6x)	101.8(9)	C(7a)–C(7b)–N(2b)	110(1)	C(7x)–C(7y)–N(2y)	109(1)
H(n2a)–N(2a)–C(7a)	110.5(9)	H(n2x)–N(2x)–C(7x)	106(1)				

(*c*) $[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]ClO_4$ (**3**)

N(2a)–Cd–N(1c)	113.5(8)	N(2b)–Cd–N(1c)	112.2(8)	H(n2a)–N(2a)–C(6a)	108(2)	H(n2a)–N(2a)–C(7a)	109(2)
N(2b)–Cd–N(2a)	134.3(7)	N(3c)–Cd–N(1c)	178.7(8)	C(6b)–N(2b)–Cd	107(1)	C(7b)–N(2b)–Cd	109(2)
N(3c)–Cd–N(2a)	66.7(8)	N(3c)–Cd–N(2b)	67.6(8)	C(7b)–N(2b)–C(6b)	119(2)	H(n2b)–N(2b)–Cd	106(1)
O(1a)–Cd–N(1c)	64.0(7)	O(1a)–Cd–N(2a)	58.9(7)	H(n2b)–N(2b)–C(6b)	107(2)	H(n2b)–N(2b)–C(7b)	107(2)
O(1a)–Cd–N(2b)	149.9(6)	O(1a)–Cd–N(3c)	115.5(7)	C(8a)–N(3c)–Cd	122(2)	C(8b)–N(3c)–Cd	116(2)
O(2)–Cd–N(1c)	94.9(8)	O(2)–Cd–N(2a)	76.3(7)	C(8b)–N(3c)–C(8a)	122(2)	C(4a)–O(1a)–Cd	112(1)
O(2)–Cd–N(2b)	99.8(7)	O(2)–Cd–N(3c)	86.4(8)	C(5a)–O(1a)–Cd	108(1)	C(5a)–O(1a)–C(4a)	119(2)
O(2)–Cd–O(1a)	110.2(7)	O(31)–Cd–N(1c)	94.6(8)	C(5b)–O(1b)–C(4b)	123(2)	C(4a)–C(3a)–N(1c)	119(2)
O(31)–Cd–N(2a)	97.5(7)	O(31)–Cd–N(2b)	78.8(7)	C(3a)–C(4a)–O(1a)	112(2)	C(5a)–C(6a)–N(2a)	113(2)
O(31)–Cd–N(3c)	84.0(8)	O(31)–Cd–O(1a)	72.0(7)	C(6a)–C(5a)–O(1a)	115(2)	C(8a)–C(7a)–N(2a)	116(2)
O(31)–Cd–O(2)	170.1(8)	C(3a)–N(1c)–Cd	119(2)	C(7a)–C(8a)–N(3c)	114(2)	C(9a)–C(8a)–N(3c)	123(3)
C(3b)–N(1c)–Cd	122(2)	C(3b)–N(1c)–C(3a)	119(2)	C(4b)–C(3b)–N(1c)	117(2)	C(3b)–C(4b)–O(1b)	109(2)
C(6a)–N(2a)–Cd	105(1)	C(7a)–N(2a)–Cd	107(2)	C(5b)–C(6b)–N(2b)	115(2)	C(6b)–C(5b)–O(1b)	114(2)
C(7a)–N(2a)–C(6a)	113(2)	H(n2a)–N(2a)–Cd	114(1)	C(8b)–C(7b)–N(2b)	109(2)	C(7b)–C(8b)–N(3c)	124(2)

Results and Discussion

Characterization of the Solid Complexes.— Cobalt-, nickel-, copper-, zinc-, and cadmium(II) complexes of the open-chain ligand L^1 have been prepared together with zinc and cadmium complexes of the related macrocyclic systems L^2 and L^3. Cobalt-, nickel-, and copper(II) complexes of L^2 and nickel and copper complexes of L^3 were reported in an earlier paper.[2] Each of the solid products has a 1:1 (ligand:metal) stoicheiometry; physical properties and microanalytical data for the new complexes are listed in Tables 4 and 5.

The i.r. spectrum of each complex confirmed the presence of water (or methanol) that was suggested to be present from the microanalytical data. In all cases the expected lowering of the NH stretching frequencies of the unco-ordinated amine groups on complex formation was observed. Because of the complexity of the spectra in the region of the nitrate absorptions, it was

Table 4. Physical data for the complexes of L^1—L^3

Complex	Colour	$\mu_{eff.}$ [a]	I.r.[b]/cm^{-1} H_2O	I.r.[b]/cm^{-1} NH_2	Visible spectra[c]
$[CoL^1(NO_3)_2]$	Pink	4.99		3 320, 3 300	560(sh)
$[NiL^1(NO_3)_2]\cdot 2H_2O$	Green	3.15	3 400	3 320, 3 250	625, 1 100
$[CuL^1(NO_3)_2]\cdot 0.5H_2O$	Green	1.99	3 400(br)	3 200	375(sh), 770(br)
$[ZnL^1(NO_3)_2]\cdot 0.5H_2O$	Off white		3 450	3 290, 3 230, 3 200	
$[CdL^1(NO_3)_2]$	White			3 215, 3 140	
$[ZnL^2(H_2O)(NO_3)]NO_3$	White		3 400(br)	3 245, 3 180	
$[CdL^2(ClO_4)_2]$	White			3 230	
$[ZnL^3(NO_3)_2]$	Cream			3 230	
$[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]ClO_4$	Off white		3 450	3 295, 3 200(br)	

[a] At 298 K. [b] Nujol mull. [c] Solid as Nujol mull. Wavelength in nm. All spectra also contained a strong charge-transfer band which extended from the u.v. region into the visible region.

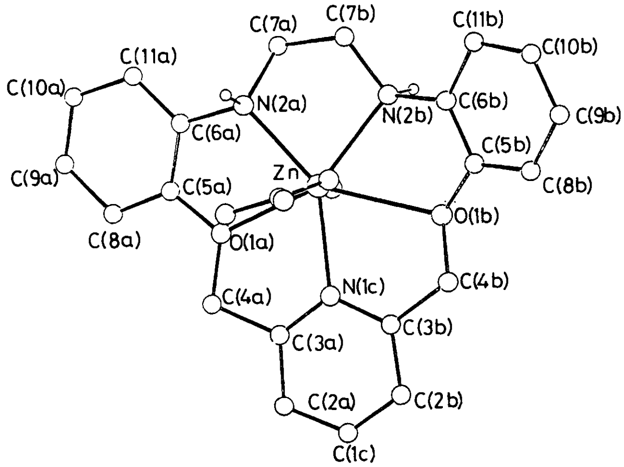


Figure 2. One of the two crystallographically independent seven-co-ordinate cations $[ZnL^2(H_2O)(NO_3)]^+$. Suffixes x, y, and z replace a, b, and c in labels for equivalent atoms in the other $[ZnL^2(H_2O)(NO_3)]^+$ unit

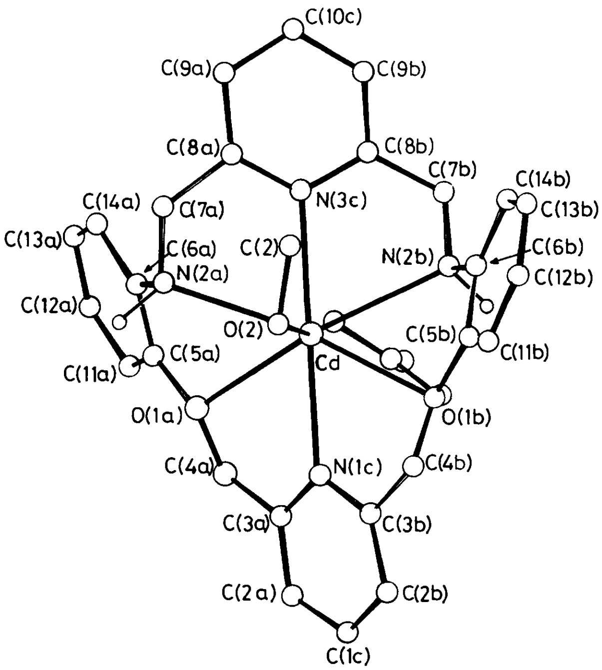


Figure 3. The *X*-ray structure of $[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]^+$

inappropriate to attempt an analysis of the latter for the present complexes.

The magnetic moments for the paramagnetic complexes are unremarkable and fall in the ranges expected for (high-spin) species of Co^{II}, Ni^{II}, and Cu^{II}. The visible spectra are consistent with the complexes of Co^{II} and Ni^{II} having pseudo-octahedral geometries while the (characteristic) broad spectral pattern observed for the copper complex is not, by itself, sufficient to enable a reliable structural assignment.

Stability Constant Measurements.—The protonation constants for L^1 in 95% MeOH (I = 0.1 mol dm^{-3}, NEt_4ClO_4) were determined potentiometrically by pH titration and processed using the programs MINIQUAD[9] and/or SUPERQUAD.[10] The following values were obtained; log K_1 = 4.80, log K_2 = 3.94, and log K_3 = *ca.* 2.08. The corresponding values for L^2 and L^3 have been published previously.[2] The log K values for the respective 1:1 complexes were obtained under similar conditions to those mentioned above. A summary of the stability constant data is given in Table 6.

The log K value for the copper complex of the open-chain ligand L^1 is lower than those for the two related complexes of the cyclic species L^2 and L^3. In particular, comparison with the value for the copper complex of L^2 (which contains the same number and sequence of donor groups as L^1) indicates that a quite significant macrocyclic effect[3,11] occurs for the cyclic species. Incorporation of an additional donor group in the ring, as occurs in L^3, results in the expected further increase in stability for the corresponding copper complex.

For the other metal systems, the respective log K values tend to be quite small and because of the considerable uncertainties associated with such values it is not possible to comment on their relative magnitudes. However, it is clear that L^3 shows a very marked preference for Cd^{II} over Zn^{II}. In recent work, a similar tendency has been documented for a number of macrocyclic ligand systems and, at least in some cases, the observed difference in affinity for Cd^{II} over Zn^{II} has been postulated to reflect the presence of a structural 'dislocation' between the respective complexes.[12] Such dislocations arise when the balance between the metal co-ordination requirements and ligand flexibility culminate in an abrupt change in co-ordination geometry between the complexes of interest.[1,5,12,13] Because of constraints inherent in their cyclic nature, it is expected that macrocyclic ligand complexes will be especially prone to displaying dislocation behaviour. It should be noted that L^3 incorporates two additional features which may help promote dislocation discrimination. First, it contains a mixed donor set and secondly it incorporates significant unsaturation in the carbon backbone. Thus, the presence of ether donors may serve

Table 5. Analytical data for the complexes

Complex	Analysis* (%)		
	C	H	N
$[CoL^1(NO_3)_2]$	45.1 (45.2)	3.8 (3.8)	13.6 (13.9)
$[NiL^1(NO_3)_2]\cdot 2H_2O$	42.4 (42.3)	3.9 (4.3)	12.8 (13.0)
$[CuL^1(NO_3)_2]\cdot 0.5H_2O$	44.2 (44.1)	3.8 (3.9)	13.5 (13.5)
$[ZnL^1(NO_3)_2]\cdot 0.5H_2O$	43.9 (43.9)	3.8 (3.9)	13.4 (13.5)
$[CdL^1(NO_3)_2]$	41.0 (40.9)	3.4 (3.4)	12.4 (12.6)
$[ZnL^2(NO_3)_2]\cdot H_2O$	45.7 (45.6)	4.2 (4.0)	12.6 (12.6)
$[CdL^2(ClO_4)_2]$	38.7 (38.3)	3.3 (3.2)	6.5 (6.4)
$[ZnL^3(NO_3)_2]$	50.9 (50.9)	3.7 (3.9)	13.8 (13.7)
$[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]ClO_4$	43.7 (44.0)	3.8 (3.8)	9.2 (9.7)

* Calculated values are given in parentheses.

Table 6. The log *K* values for L^1—L^3 with divalent metal ions[a]

Metal ion	L^1	L^2	L^3
Co^{II}	<3	<4[b]	<4[b]
Ni^{II}	<3	<4[b]	4.6[b]
Cu^{II}	3.6	6.8[b]	11.1[b]
Zn^{II}	<3	3.9	<3
Cd^{II}	<3	[c]	6.0

[a] In 95% MeOH; $I = 0.1$ mol dm^{-3}, NEt_4ClO_4. [b] Data taken from ref. 2. [c] Insoluble.

to provide labile sites where the dislocation may initiate while the degree of unsaturation present reduces the number of sterically favourable conformations possible and tends to increase the prospect that dislocation behaviour will be observed.

The origins of the considerable difference in stability between the zinc and cadmium complexes of L^3 cannot be rationalized with certainty from the data available. However, from macrocyclic hole-size considerations,[1,14] it seemed likely that the cadmium ion is large enough to occupy the cavity of this 18-membered ring and interact with all six donors without inducing major strain in the ring system. In contrast, from space-filling molecular models it appears that substantial ring-size contraction (with a corresponding increase in ring strain) will occur if the zinc complex was to adopt a similar geometry to that postulated for the cadmium species. Alternatively, ligand folding or non-co-ordination of particular donor atoms of the macrocycle may be induced in the case of the zinc complex; such non-co-ordination of ether oxygen groups in mixed-donor macrocycles has been documented by *X*-ray studies for related zinc complexes.[12,15]

It is pertinent to the above discussion that the 18-membered O_4N_2-donor macrocycle, diaza-18-crown-6, also exhibits a strong preference for cadmium over zinc;[16] once again, this presumably reflects a significant structural difference between the corresponding complexes. For this system the respective stabilities (log *K* values, determined under identical conditions to those employed in the present study) are < 2.5 (zinc complex) and 7.2 (cadmium complex). In view of the above, it is of interest that an *X*-ray diffraction study of $[CdCl_2(18\text{-crown-}6)]$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane) shows that it contains the metal in a hexagonal-bipyramidal (O_6Cl_2-donor) environment.[17]

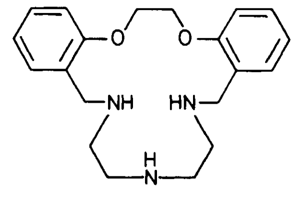
X-Ray Structural Studies.—The *X*-ray structure of $[CdL^1(NO_3)_2]$ confirms that all five donor atoms of L^1 co-ordinate to Cd^{II} in an approximately planar array while two monodentate nitrate ions occupy axial sties such that the overall co-ordination geometry is distorted pentagonal bipyramidal (Figure 1). Lists of bond distances and angles for the complex are given in Tables 2 and 3. The cadmium to ether bond lengths, Cd–O(1a) 2.660(2) and Cd–O(1b) 2.566(2) Å, are somewhat elongated reflecting, in part, the inherently weak affinity[18] of this donor type for ions such as Cd^{II} while all the remaining metal–donor distances appear unremarkable. The co-ordination of the organic ligand is far from a regular pentagonal arrangement; the (donor–Cd–donor) bond angles associated with chelate ring formation range from 63.1(1)° for O(1a)–Cd–N(2a) to 66.4(1)° for O(1b)–Cd–N(1c) while the N(2a)–Cd–N(2b) angle, involving the terminal amine donors, is 102.3°. It is of relevance to the present discussion that the *X*-ray structures of related six- and seven-co-ordinate cadmium complexes involving co-ordination of an equatorial quinquedentate ligand and monodentate axial ligand(s) have been reported previously.[12,19] For example, the complex $[CdL^4(NO_3)_2]$, which also has the five donors of the macrocycle co-ordinated in a distorted pentagonal-planar manner, has similarly elongated cadmium–ether bonds (2.614 and 2.732 Å, respectively.)[12]

An *X*-ray structure determination of $[ZnL^2(H_2O)(NO_3)]NO_3$ (Figure 2) reveals two crystallographically independent seven-co-ordinate complexes which have very similar geometries. A distorted pentagonal-bipyramidal co-ordination sphere is observed in each case with significant puckering of the O_2N_3-donor sets (maximum deviations of macrocycle donors from the mean ZnO_2N_3 planes are 0.29 and 0.15 Å in molecules 1 and 2, respectively). The hole sizes[14] in the two molecules are very similar at 2.26 and 2.27 Å, respectively. As might be expected, the pyridine nitrogen atom provides the strongest bond to zinc in both.

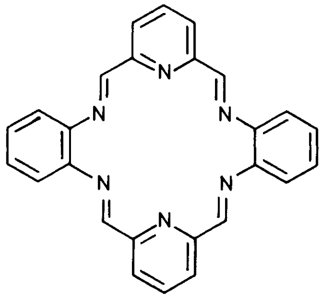
Interestingly in both complex cations, the zinc atom is significantly displaced to one side of the macrocycle cavity, bonding more strongly to one of the *o*-phenoxyaniline groups [the O(1a)/N(2a) unit in molecule 1 and the O(1y)/N(2y) unit in molecule 2] than the other. This displacement of the zinc from the centroid of the donor set (0.36 and 0.14 Å in molecules 1 and 2, respectively) is accompanied by a slight displacement of the nitrato and water donors from axial sites towards the more weakly bonded side of the molecule. This suggests that the O_2N_3-donor cavity in L^2, formed largely by relatively weak ether and anilino donors, does not provide a particularly good fit for divalent zinc in a pentagonal-bipyramidal geometry.

The structure of the macrocyclic ligand derivative $[CdL^3(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)]ClO_4$ confirms that all six donor atoms of the macrocycle co-ordinate to the central cadmium ion (in accordance with inference from the stability constant data) (Figure 3). One 'axial' site in the complex is occupied by a monodentate nitrate while the remaining axial position is occupied by a water in half of the molecules and a methanol in the remaining half (see Experimental section). The microanalytical data for this compound support the crystallographic evidence that the solid complex contains approximately equal proportions of the monohydrate and monomethanol species. The overall co-ordination geometry is distorted hexagonal bipyramidal with the macrocycle co-ordinating approximately equatorially. Although rare, eight-co-ordination for Cd^{II} in macrocyclic complexes is not unknown;[17,20] for example, the compound $[CdL^5(H_2O)(ClO_4)]ClO_4\cdot MeOH$ also has the ligand co-ordinated in an equatorial fashion with a water and a perchlorate ion in axial positions.[20]

Even though the co-ordinated macrocycle adopts a very twisted conformation in the above complex of L^3 (the dihedral angle between the pyridine ring planes is 63.6°), the donor atoms still show only a minor distortion from planarity [the deviations from the best plane through the O_2N_4-donor set are respectively N(2a) + 0.69, N(2b) − 0.65, O(1a) − 0.67, O(1b) + 0.68, N(1c) − 0.03, and N(2c) − 0.02 Å]. Nevertheless, the deviations still tend to be significantly greater than



L^4



L^5

Table 7. Force-field parameters involving Cd^{II} used in the MM2 program

	r_0/Å	$k_r{}^a$/mdyn $Å^{-1}$
Bond stretching		
Cd-N(pyridyl)	2.42	2.0
Cd-N(anilino)	2.55	1.5
Cd-O(aromatic ether)	2.65	0.4
	θ/°	k_θ/°
Angle bending^b		
RC-N(pyridyl)-Cd	120.0	0.45
RC-N(anilino)-Cd	109.5	0.50
RC-O-Cd	109.5	0.50
RC-O-C	120.0	0.60
R-C-N-C	117.0	0.50

[a] dyn = 10^{-5}N. [b] R = Aryl.

those that occur in the related open-chain cadmium complex discussed earlier [deviations of the donor atoms of L^1 from the best plane through the O_2N_3-donor set are O(1a) + 0.23, O(1b) − 0.18, N(2a) − 0.29, N(2b) + 0.26, and N(1c) − 0.03 Å].

In the complex of L^3 the macrocycle adopts a quite twisted configuration (Figure 3). The overall structure apparently represents a lower-energy arrangement than one containing the macrocycle co-ordinated in a more symmetrical configuration. In order to probe the relative merits of these different possibilities, a molecular-mechanics investigation of this system was initiated.

Molecular-mechanics Studies.—The molecular-mechanics calculations were based on Allinger's MM2 force field.[21] Initially a set of force-field parameters for those parts of the molecule involving the Cd^{II} were derived by a trial-and-error procedure in which the calculated structure was matched to that found by *X*-ray diffraction. An excellent match of the *X*-ray structure was achieved using the parameters listed in Table 7.

In an extension of this study, a new set of atom co-ordinates was generated by removing the co-ordinates for the cadmium ion from the *X*-ray atom co-ordinate set. The resultant 'free ligand' was then minimized (using the 'organic' MM2 force field). The ligand structure [Figure 4(*a*)] calculated in this manner was considerably different from its structure in the starting complex. The cadmium ion was then re-inserted in the macrocyclic cavity and the new complex geometry thus generated was again minimized. The resultant structure was found to contain the macrocycle in a conformation which was virtually identical to that in the *X*-ray structure (small variations in the torsional angles involving the cadmium and expected minor differences involving the axial ligands were the main deviations in the structure). Excluding distances and angles associated with the axial groups, all (corresponding) calculated and found bond distances and angles in the structure agreed within 0.05 Å (and usually less than 0.02 Å) and 6° (and usually less than 3°), respectively. The overall steric energy for this structure was also near identical (within 1 kJ mol^{-1}) to that for the structure generated by direct minimization of the *X*-ray co-ordinates.

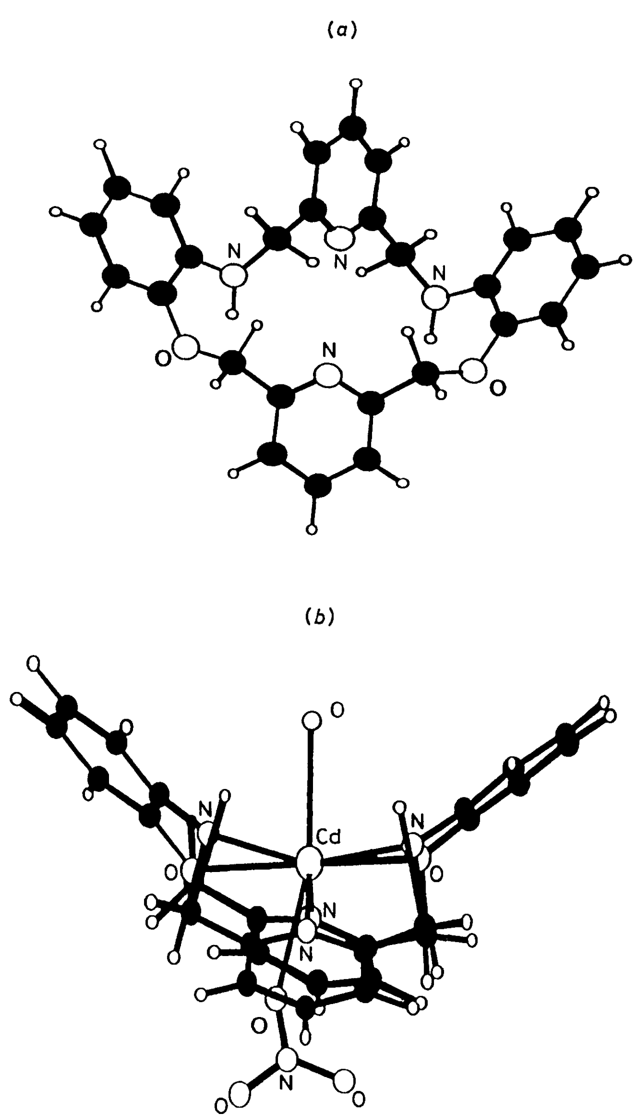


Figure 4. Calculated structures using molecular mechanics: (*a*) the minimized structure of free L^3 (see text) and (*b*) an alternative 'more symmetrical' structure for the cadmium complex of L^3

Inspection of molecular models indicated the possibility of an alternative configurational isomer containing a more symmetrical arrangement of the co-ordinated ligand. This latter isomer has the pyridyl rings tilted to one side of the donor atom plane while each *o*-phenylene ring is tilted to the opposite side of this plane. The molecular-mechanics parameters listed in Table 7 were used to model this latter isomer. A new set of 'flatter' starting co-ordinates was first obtained by 'manual' manipulation of the *X*-ray co-ordinates such that all carbon atoms in the structure were approximately planar. Minimization of this structure resulted in generation of the required second isomer; details of the structure are given in Figure 4(*b*). The calculated hole size in this arrangement, at 2.55 Å, remained identical to that found in the initial (*X*-ray) isomer. In accordance with the latter being the experimentally observed geometry, its calculated steric energy was found to be 5.0 kJ mol^{-1} lower than that for the alternative arrangement shown in Figure 4(*b*) (the magnitude of this difference is only approximate since the force-field elements given in Table 7 were not calibrated with respect to energy, only in terms of geometry).

Finally, in view of the earlier discussion, it is worth noting that both the *X*-ray data and the molecular-mechanics calculations for complex (**3**) provide little evidence of any mismatch between the size of the cadmium ion and the macrocyclic cavity adopted by L^3 in this complex.

Acknowledgements

We thank the S.E.R.C. and ICI Organics Division for a co-operative award and the Australian Research Council and the Australian Institute for Nuclear Science and Engineering for support.

References

1 L. F. Lindoy, *Prog. Macrocyclic Chem.*, 1987, **3**, 53.

2 D. E. Fenton, B. P. Murphy, A. J. Leong, L. F. Lindoy, A. Bashall, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1987, 2543.

3 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1969, **91**, 6540; D. K. Cabbiness and D. W. Margerum, *ibid.*, 1970, **92**, 2151; F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, 1974, **13**, 2941.

4 L. F. Lindoy, 'The Chemistry of Macrocyclic Ligand Complexes,' Cambridge University Press, Cambridge, 1989.

5 K. R. Adam, A. J. Leong, L. F. Lindoy, H. C. Lip, B. W. Skelton, and A. H. White, *J. Am. Chem. Soc.*, 1983, **105**, 4645.

6 G. M. Sheldrick, SHELX 76 program system, University of Cambridge, 1976.

7 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

8 D. T. Cromer and D. Libermann, *J. Chem. Phys.*, 1970, **53**, 1891.

9 P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

10 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.

11 R. D. Hancock and V. J. Thom, *J. Am. Chem. Soc.*, 1982, **104**, 291.

12 K. R. Adam, K. P. Dancey, A. J. Leong, L. F. Lindoy, B. J. McCool, M. McPartlin, and P. A. Tasker, *J. Am. Chem. Soc.*, 1988, **110**, 8471.

13 K. R. Adam, C. W. G. Ansell, K. P. Dancey, L. A. Drummond, A. J. Leong, L. F. Lindoy, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1986, 1011.

14 K. Henrick, P. A. Tasker, and L. F. Lindoy, *Prog. Inorg. Chem.*, 1985, **33**, 1.

15 L. F. Lindoy, H. C. Lip, J. H. Rea, R. J. Smith, K. Henrick, M. McPartlin, and P. A. Tasker, *Inorg. Chem.*, 1980, **19**, 3360.

16 G. Anderegg, *Helv. Chim. Acta*, 1981, **64**, 1790.

17 C. R. Paige and M. F. Richardson, *Can. J. Chem.*, 1984, **62**, 332.

18 R. M. Izatt, D. J. Eatough, and J. J. Christensen, *Struct. Bonding (Berlin)*, 1973, **16**, 166; R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Am. Chem. Soc.*, 1976, **98**, 7620; R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshaw, L. D. Hansen, and J. J. Christensen, *ibid.*, p. 7626.

19 S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. B. Othman, and N. B. Mason, *J. Chem. Soc., Chem. Commun.*, 1977, 167; M. G. B. Drew, S. Hollis, S. G. McFall, and S. M. Nelson, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1595; M. G. B. Drew, S. G. McFall, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1979, 575.

20 M. G. B. Drew, J. de O. Cabral, M. F. Cabral, F. S. Esho, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1979, 1033.

21 N. L. Allinger, *J. Am. Chem. Soc.*, 1977, **99**, 8127.

Received 15*th August* 1989; *Paper* 9/03487K