Group 12 Complexes of *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (L). Crystal Structures of $[Zn_2(OH)L][ClO_4]_3$ and $[Cd_2Cl(L)][CF_3SO_3]_3$ together with Formation Constant Determinations and pK_a Measurements for the Aquated Bimetallic Species†

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The complex-forming properties of the ligand *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (L) with zinc(II), cadmium(II) and mercury(II) have been investigated by synthesis, X-ray crystallography and potentiometric titration. With zinc(II) in aqueous or aqueous methanol solution the only complexes which could be isolated were salts of the μ-hydroxo-bridged bimetallic cation $[Zn_2(OH)(L)]^{3+}$, although potentiometric titration data suggest the presence of small amounts of $[Zn(H_3L)]^{5+}$ at low pH. Crystallographic data for $[Zn_2(OH)(L)]^{3+}$ indicate that each zinc(II) ion is five-co-ordinate, being bound by a pair of tertiary amines, a pair of primary amines and the bridging hydroxide. The μ-hydroxo group could not be replaced, in attempted substitution reactions, by other potentially bridging anions. The pK_a for the aqua species which leads to the μ-hydroxo species is < 5.3. Complexation with cadmium(II) and mercury(II) leads to both mono- and bi-metallic species. The monometallic species are the first isolated and can be recognised spectroscopically by the relatively high-field ^{13}C NMR chemical shift for the carbon atoms β to nitrogen. In the bimetallic complexes the tendency for μ-hydroxo formation is lower than for zinc(II) and it is possible to isolate $[Cd_2L]^{4+}$ to which Cl^- can be added forming $[Cd_2Cl(L)]^{3+}$. X-Ray crystallography indicates a structure for $[Cd_2Cl(L)]^{3+}$ which is qualitatively similar to that of $[Zn_2(OH)(L)]^{3+}$. In aqueous solution the species $[Cd_2(OH)(L)]^{3+}$ can be detected from potentiometric titration data and forms in response to a pK_a value of < 6.6 for the aquated precursor. The pK_a values for the corresponding cobalt(II), nickel(II) and copper(II) aquated species were measured, for comparison, and found to be 7.3, 9.0 and 7.7, respectively.

Murase and co-workers[1-4] have reported the synthesis of a variety of tetraaza macrocycles which have 2-aminoethyl groups appended to the four nitrogen atoms, and their transition-metal complexes. Considerable information has been gathered on the solid-state structures of these complexes, from which it is clear that the ligand has a tendency to bind two transition-metal ions, in exocyclic positions, and that the two metal ions, once bound, are able to trap, usually as bridging entities, co-ordinating anions of suitable dimensions.[5-8] Solution studies have shown that the binding constants for these bridging anions are several orders of magnitude higher than those for the same anion when bound in a monodentate fashion to the same transition-metal ion,[9-11] suggesting that these systems may have an application as anion-sequestering reagents. Incorporation of an anion with a strong bridging tendency into a complex free of strongly bridging anions is believed to involve a pre-equilibrium between the type 1 configuration, shown for *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (L) in Fig. 1, and the type 2 configuration in which the ligand is in the *trans* I configuration and the two metal ions are on the same side of the macrocyclic ring.[11] This was suggested on the basis of structural studies of both $[Ni_2L][ClO_4]_4$ and $[Cu_2(L)(ClO_4)_2][ClO_4]_2$ which revealed type 1 structures whereas the bridged structures are, of necessity, type 2.[1-8] Electronic spectral changes that occur when $[Cu_2(L)(ClO_4)_2][ClO_4]_2$ is dissolved in water suggest that the energy barrier for interconversion between types 1 and 2 may be quite small.[11]

To shed further light on this we set out to examine the binding properties of L with the diamagnetic Group 12 ions, zinc(II), cadmium(II), and mercury(II), with the intention of looking for effects in the ^{13}C NMR spectra of the complexes, when recorded over a wide temperature range, which might clarify the situation in the same way that it has for some of the hydroxyethyl analogues of these ligands.[12-14] Unfortunately, the low solubility, or inaccessibility, in the case of zinc(II), of non-bridged bimetallic Group 12 complexes prevented us from doing this, however other interesting features concerning the chemistry of the L complexes of this triad emerged. In particular, the aquated dizinc(II) complex shows a very low pK_a such that formation of a μ-hydroxo complex, the structure of which we have verified by X-ray crystallography, dominates the chemistry of this system under aqueous conditions. A related observation was made recently by Bencini *et al.*,[15] where the smallest member of a set of polyazamacrocycles, each capable of binding two zinc(II) ions, appeared, from potentiometric titration work, to form $[Zn_2(OH)([24]aneN_8)]^{3+}$, but not $[Zn_2([24]aneN_8)]^{4+}$ ($[24]aneN_8$ = 1,4,7,10,13,16,19,22-octaazacyclotetracosane), whereas with the larger ligands in the series only analogues of the latter species were observed. In

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

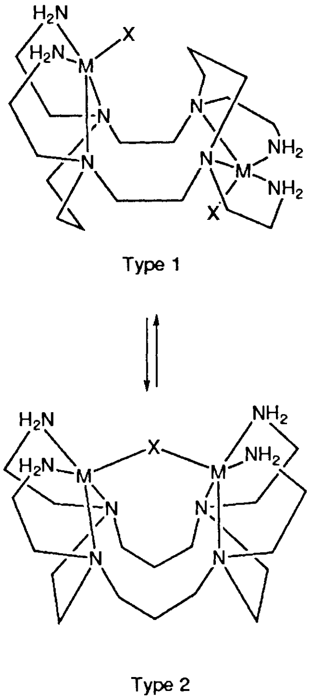

Fig. 1 Co-ordination modes thought accessible to L complexes when X is an anion, such as ClO_4^-, with only a weak tendency to bridge the metal ions (ref. 11)

contrast to zinc(II) and the transition-metal ions studied to date, cadmium(II) and mercury(II) both form isolable monometallic complexes of L, on which we also report.

Results and Discussion

Co-ordination with Zinc(II).—Combination of $Zn(ClO_4)_2 \cdot 6H_2O$ with L in either 1:1 or 2:1 molar ratio, in methanol, results in a precipitate which analyses as $[Zn_2(OH)L][ClO_4]_3$ and which displays a conductivity, in dimethylformamide (dmf), typical of a 3:1 electrolyte. Suspecting that this might be a μ-hydroxo species, similar to that observed by Murase and co-workers[2,8] on combining cobalt(II) with L in aqueous solution, but cognisant of the fact that monohydroxo-bridged dizinc(II) complexes are rare, and that only a single example has been structurally characterised previously,[16] we determined the structure of this complex by X-ray diffraction and verified this. Suitable crystals were obtained by diffusion of methanol vapour into a dilute aqueous solution of the complex. The structure (Fig. 2) is remarkably similar to that of the cobalt(II) analogue,[8] both qualitatively and quantitatively, supporting various other observations which, either directly or indirectly, have suggested that the interchange of cobalt(II) and zinc(II) can occur with negligible perturbation of a metal-ion binding cavity.[18]

Crystallographic data, atomic coordinates, and selected interatomic distances and angles are given in Tables 1, 2 and 3, respectively. Each zinc ion has approximately square-pyramidal co-ordination geometry and is displaced [0.671(4) and 0.710(4) Å for Zn(1) and Zn(2) respectively] from the mean basal plane formed by two nitrogen atoms from the macrocyclic ring and two pendant amino groups, in the direction of the bridging hydroxo group. The two zinc ions are separated by 3.737(1) Å and the two Zn–O bond lengths are similar [1.944(5) and 1.930(5) Å for Zn(1)–O and Zn(2)–O, respectively]. The Zn(1)–O–Zn(2) angle is 149.5(3)°. The hydrogen atom of the bridging hydroxide group could not be located in Fourier difference maps. The possibility of it being involved in intramolecular hydrogen bonding in the cation is stereochemically excluded (Fig. 2), but there is the possibility of weak hydrogen-bonded interactions with a neighbouring perchlorate anion [O ··· O(3) 3.09(1) and O ··· O(4) 3.13(1) Å].

Table 1 Crystallographic data[a]

	$[Zn_2(OH)L][ClO_4]_3$	$[Cd_2Cl(L)][CF_3SO_3]_3$
Empirical formula	$C_{18}H_{45}Cl_3N_8O_{13}Zn_2$	$C_{21}H_{44}Cd_2ClF_9N_8O_9S_3$
M	818.8	1080.2
Space group	$P2_1/c$	$P2_1/n$
a/Å	9.272(1)	14.099(1)
b/Å	16.423(1)	14.889(1)
c/Å	20.529(1)	18.853(1)
β/°	91.04(1)	99.95(2)
U/Å^3	3125.5(4)	3898.1(8)
F(000)	1696	2160
D_c/g cm^{-3}	1.740	1.840
D_m[b]/g cm^{-3}	1.74(1)	1.83(2)
Crystal dimensions/mm	0.085 × 0.20 × 0.33	0.033 × 0.19 × 0.25
μ/cm^{-1}	19.11	14.10
Transmission coefficient	0.52–0.60	0.75–0.89
θ_{max}/°	22	20
hkl	−9 to 9, 0–17, 0–21	−13 to 13, 0–14, −18 to 18
Scan width/°	1.0 + 0.35tanθ	0.9 + 0.35tanθ
No. of reflections measured	4043	7285
No. used in refinement	2853	3049
R_{int}	—	0.046
No. of parameters refined	398	477
Extinction factor, g	23(3) × 10^2	—
R[c]	0.067	0.065
R'	0.093	0.085
Goodness of fit	2.68	1.62
Final shift/error	0.01	0.38

[a] Details in common: $Z = 4$; $T = 293(2)$ K; scan mode ω–θ. [b] By flotation in a dibromomethane–isopropyl alcohol mixture. [c] $R = \Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma|F_o|^2$.

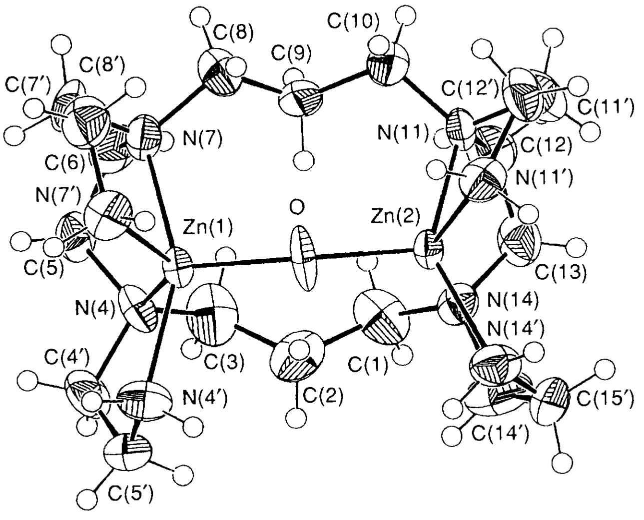

Fig. 2 An ORTEP[17] drawing of $[Zn_2(OH)L]^{3+}$ showing thermal ellipsoids of the non-hydrogen atoms at the 50% probability level

The stability of the hydroxo bridge is such that it predominates in the presence of chloride or bromide even though the former of these two ions has been shown to act as an alternative to hydroxide as the bridging species in the dicobalt(II) analogue.[2] Thus, using the methods detailed in the Experimental section, attempted bridge-substitution reactions led to $[Zn_2(OH)(L)][ClO_4]_2Cl$ and $[Zn_2(OH)L]Br_3$, which

Table 2 Atomic positional parameters with estimated standard deviations in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(*a*) $[Zn_2(OH)L]^{3+}$				(*b*) $[Cd_2Cl(L)]^{3+}$			
Zn(1)	0.240 9(1)	0.085 62(5)	0.223 80(4)	Cd(1)	0.348 46(5)	0.248 46(6)	0.596 54(4)
Zn(2)	0.251 4(1)	0.145 37(5)	0.399 49(4)	Cd(2)	0.394 15(6)	0.099 04(6)	0.403 39(4)
C(1)	0.454(1)	0.282 3(6)	0.330 4(5)	C(1)	0.154 4(8)	0.159 4(9)	0.375 8(7)
C(2)	0.481(1)	0.220 7(6)	0.278 6(5)	C(2)	0.164 2(8)	0.154 1(8)	0.458 0(7)
C(3)	0.422(1)	0.242 9(6)	0.212 3(5)	C(3)	0.127 9(8)	0.239 4(9)	0.486 4(7)
N(4)	0.367 5(8)	0.174 9(4)	0.172 0(3)	N(4)	0.177 7(7)	0.265 8(8)	0.559 9(6)
C(4′)	0.484(1)	0.126 4(6)	0.139 8(4)	C(4′)	0.133 0(8)	0.214 9(9)	0.614 7(8)
C(5′)	0.543(1)	0.060 4(6)	0.180 8(5)	C(5′)	0.191(1)	0.218(1)	0.689 3(7)
N(4′)	0.424 7(8)	0.011 4(4)	0.206 9(4)	N(4′)	0.289 9(6)	0.185 8(6)	0.689 4(5)
C(5)	0.262(1)	0.208 9(5)	0.122 5(4)	C(5)	0.168 8(8)	0.363 7(9)	0.570 3(7)
C(6)	0.123(1)	0.233 7(6)	0.151 0(4)	C(6)	0.228 5(9)	0.419 2(8)	0.528 7(7)
N(7)	0.062 3(7)	0.167 2(4)	0.188 5(3)	N(7)	0.332 2(6)	0.395 3(6)	0.541 0(4)
C(7′)	−0.027(1)	0.113 4(6)	0.146 1(4)	C(7′)	0.383 4(9)	0.453 8(8)	0.599 1(6)
C(8′)	−0.049(1)	0.031 9(6)	0.176 1(5)	C(8′)	0.481 0(9)	0.415 2(9)	0.633 5(6)
N(7′)	0.092 8(8)	−0.003 6(4)	0.194 5(3)	N(7′)	0.474 2(6)	0.325 2(6)	0.661 2(5)
C(8)	−0.032(1)	0.197 4(6)	0.243 4(4)	C(8)	0.374 6(8)	0.403 3(8)	0.476 3(6)
C(9)	0.049 0(9)	0.249 7(5)	0.290 5(4)	C(9)	0.348 6(9)	0.324 9(8)	0.425 7(6)
C(10)	−0.010(1)	0.249 8(6)	0.357 7(5)	C(10)	0.403 0(9)	0.314 9(8)	0.364 0(7)
N(11)	0.103 2(7)	0.246 4(4)	0.409 5(3)	N(11)	0.385 4(6)	0.229 3(6)	0.325 8(5)
C(11′)	0.036(1)	0.230 5(7)	0.473 8(5)	C(11′)	0.462 6(9)	0.210 3(9)	0.282 5(6)
C(12′)	−0.019(1)	0.145 0(6)	0.479 9(4)	C(12′)	0.555 1(9)	0.182 1(8)	0.327 7(7)
N(11′)	0.093 0(7)	0.086 5(4)	0.457 5(3)	N(11′)	0.543 6(6)	0.105 8(7)	0.373 2(5)
C(12)	0.188(1)	0.322 9(5)	0.414 4(5)	C(12)	0.291 6(8)	0.228 5(8)	0.277 8(5)
C(13)	0.341(1)	0.311 6(5)	0.431 9(4)	C(13)	0.237 5(8)	0.138 1(9)	0.275 2(7)
N(14)	0.412 2(7)	0.248 6(4)	0.395 8(3)	N(14)	0.227 4(6)	0.104 6(7)	0.346 8(5)
C(14′)	0.546(1)	0.217 6(6)	0.427 5(6)	C(14′)	0.193 0(9)	0.009 5(9)	0.344 6(8)
C(15′)	0.522(1)	0.154 5(6)	0.479 1(4)	C(15′)	0.261(1)	−0.056(1)	0.339(1)
N(14′)	0.420 4(8)	0.092 5(4)	0.454 4(4)	N(14′)	0.354 5(7)	−0.045 8(7)	0.385 1(5)
O	0.228 5(7)	0.087 3(3)	0.318 2(2)	Cl	0.422 1(2)	0.118 0(2)	0.538 2(1)

Table 3 Selected bond lengths (Å) and angles (°)

$[Zn_2(OH)L][ClO_4]_3$		$[Cd_2Cl(L)][CF_3SO_3]_3$	
Zn(1)–O	1.944(5)	Cd(1)–Cl	2.540(3)
Zn(1)–N(7′)	2.089(7)	Cd(1)–N(7′)	2.277(9)
Zn(1)–N(4′)	2.129(7)	Cd(1)–N(4′)	2.26(1)
Zn(1)–N(4)	2.169(7)	Cd(1)–N(4)	2.401(9)
Zn(1)–N(7)	2.241(7)	Cd(1)–N(7)	2.418(9)
Zn(2)–O	1.930(5)	Cd(2)–Cl	2.520(3)
Zn(2)–N(14′)	2.101(7)	Cd(2)–N(14′)	2.24(1)
Zn(2)–N(11′)	2.137(7)	Cd(2)–N(11′)	2.278(9)
Zn(2)–N(11)	2.167(6)	Cd(2)–N(11)	2.419(9)
Zn(2)–N(14)	2.260(6)	Cd(2)–N(14)	2.409(8)
O–Zn(1)–N(7′)	104.3(3)	Cl–Cd(1)–N(7′)	106.1(3)
O–Zn(1)–N(4′)	103.5(3)	Cl–Cd(1)–N(4′)	104.5(3)
O–Zn(1)–N(4)	121.5(2)	Cl–Cd(1)–N(4)	115.0(3)
O–Zn(1)–N(7)	104.9(2)	Cl–Cd(1)–N(7)	121.3(2)
N(7′)–Zn(1)–N(4′)	94.3(3)	N(7′)–Cd(1)–N(4′)	98.5(3)
N(7′)–Zn(1)–N(4)	133.8(3)	N(7′)–Cd(1)–N(4)	138.5(4)
N(7′)–Zn(1)–N(7)	81.3(3)	N(7′)–Cd(1)–N(7)	77.6(3)
N(4′)–Zn(1)–N(4)	82.3(3)	N(4′)–Cd(1)–N(4)	77.6(3)
N(4′)–Zn(1)–N(7)	151.5(3)	N(4′)–Cd(1)–N(7)	133.5(3)
N(4)–Zn(1)–N(7)	80.8(3)	N(4)–Cd(1)–N(7)	76.3(3)
O–Zn(2)–N(14′)	109.2(3)	Cl–Cd(2)–N(14′)	104.8(3)
O–Zn(2)–N(11′)	101.1(3)	Cl–Cd(2)–N(11′)	104.9(2)
O–Zn(2)–N(11)	113.6(2)	Cl–Cd(2)–N(11)	120.2(2)
O–Zn(2)–N(14)	113.8(2)	Cl–Cd(2)–N(14)	114.4(2)
N(14′)–Zn(2)–N(11′)	91.6(3)	N(14′)–Cd(2)–N(11′)	102.8(4)
N(14′)–Zn(2)–N(11)	137.2(3)	N(14′)–Cd(2)–N(11)	133.9(3)
N(14′)–Zn(2)–N(14)	80.9(3)	N(14′)–Cd(2)–N(14)	76.5(3)
N(11′)–Zn(2)–N(11)	81.4(3)	N(11′)–Cd(2)–N(11)	76.5(3)
N(11′)–Zn(2)–N(14)	144.9(3)	N(11′)–Cd(2)–N(14)	139.6(3)
N(11)–Zn(2)–N(14)	81.3(2)	N(11)–Cd(2)–N(14)	76.2(3)
Zn(1)–O–Zn(2)	149.5(3)	Cd(1)–Cl–Cd(2)	121.2(1)

both display a ^{13}C NMR spectrum identical to that shown by $[Zn_2(OH)L][ClO_4]_3$ strongly suggesting that the cation is the same in each case.

Owing to the current interest in the acidic properties of zinc(II)-bound water and its relevance to hydrolytic enzymes such as carbonic anhydrase and carboxypeptidase,[19–21] we were interested in measuring the pK_a of the bound water molecule, which, presumably, acts as a precursor to the hydroxo bridge. This pK_a value relates to a water molecule polarised by two metal ions and is of particular relevance to an understanding of the mechanism of recently reported enzymes which contain two zinc(II) ions, in close proximity, at the active site.[20] Speciation diagrams for the zinc(II)–L system at 1 : 1 and 2 : 1 metal : ligand ratios, derived from potentiometric titration data, are shown in Fig. 3. It may be seen that the monometallic species $[Zn(H_3L)]^{5+}$, present in low concentration at low pH and presumably five-co-ordinate with a single pendant arm bound, is replaced by the bimetallic hydroxo-bridged species at higher pH without detectable intervention of an aqua species. Since the intermediate aqua species is not observed it is only possible to calculate that its pK_a value (25 °C) is < 5.3, and not the actual value. However, it is clear from this datum that the effect of the Lewis acidity of two zinc(II) ions on the bound water molecule, compared to one, is manifested through a lowering of the acidity constant by two orders of magnitude: pK_a values for aquated monozinc(II) polyamines are typically in the range 7.0–8.5 (refs. 19 and 21). Formation constants and pK_a values for the aquated bimetallic complexes of L with a range of different metal ions were measured in this work and are given in Table 4 for comparison. It is particularly interesting that although $[Zn_2(OH)L][ClO_4]_3$ and $[Co_2(OH)L][ClO_4]_3$ are structurally very similar the pK_a values for their aquated precursors differ quite significantly, with the cobalt(II) complex having a pK_a of 7.3 and thus being considerably less acidic. Speciation diagrams for the cobalt(II) system are shown in Fig. 4.

Co-ordination with Cadmium(II).—In contrast to the behaviour of L with all other metal ions studied to date, cadmium(II) [and also mercury(II), see below] forms a monometallic complex. Thus, combination of equimolar

Table 4 Formation constants of metal complexes of L and pK_a values for the aquated dimetallic species[a]

	$\log_{10} \beta$				
	Co^{2+}	Ni^{2+}	Cu^{2+}[b]	Zn^{2+}	Cd^{2+}
Overall reaction					
$M + L + 4H^+ \rightleftharpoons MLH_4$	—	—	44.2(1)	—	—
$M + L + 3H^+ \rightleftharpoons MLH_3$	—	33.7(1)	41.4(1)	34.47(5)	< 34.5[c]
$M + L + 2H^+ \rightleftharpoons MLH_2$	—	28.00(5)	36.7(3)	—	29.9(1)
$M + L + H^+ \rightleftharpoons MLH$	—	19.7(1)	28.1(5)	—	22.2(1)
$M + L \rightleftharpoons ML$	—	10.8(1)	19.9(2)	—	13.4(1)
$2M + L \rightleftharpoons M_2L$	13.9(1)	15.5(1)	31.7(2)	< 19.6[c]	< 17.5[c]
$2M + L \rightleftharpoons M_2L(OH) + H^+$	6.6(1)	6.4(1)	24.1(3)	14.33(8)	10.9(1)
Derived reaction					
$M + ML \rightleftharpoons M_2L$	—	4.7(2)	11.8(4)	—	< 4.1
$M_2L + OH^- \rightleftharpoons M_2L(OH)$	6.4(2)	4.6(2)	6.1(5)	> 8.4	> 7.1

	p$K_a(M_2L)$				
Reaction	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$M_2L \rightleftharpoons M_2L(OH) + H^+$	7.3(1)	9.0(1)	7.65(5)	< 5.3	< 6.6

[a] Determined by glass-electrode potentiometry at 25 °C in water at constant ionic strength ($I = 0.1$ mol dm^{-3}, NEt_4ClO_4). A value of 13.7(1) was obtained for the apparent pK_w under these conditions. [b] The copper–L system has also been studied at higher ionic strength ($I = 0.5$ mol dm^{-3}, $NaNO_3$) by Evers *et al.*[9] [c] These upper bounds were determined on the basis that if the stability constant was greater than, or equal to, this value then, under the conditions of our titrations (*ca.* 10^{-3} mol dm^{-3} concentrations of reactants), the corresponding metal complex would become 5% or more of the total metal concentration at some stage during the titration. At these concentrations it would have been necessary to include the constant in our model to achieve a satisfactory correlation between the experimental and theoretical titration curves.

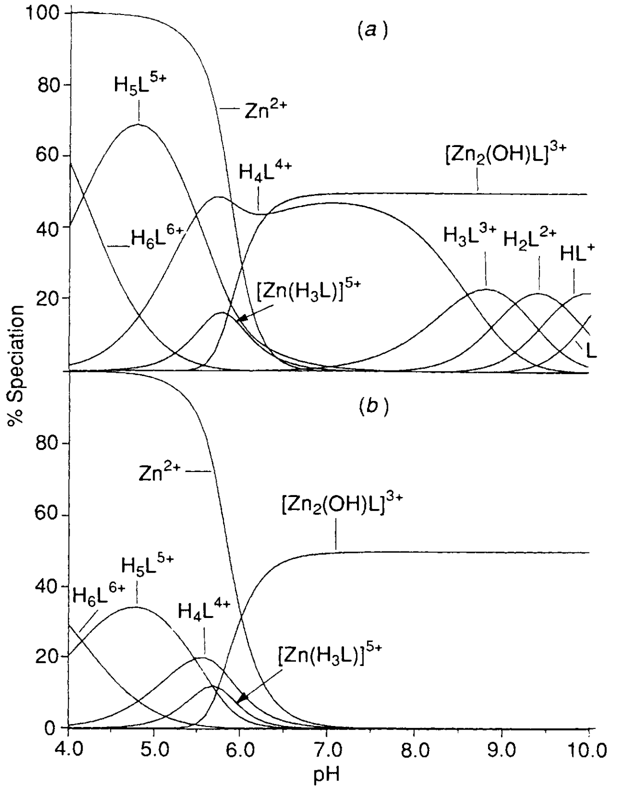

Fig. 3 Speciation diagrams for the zinc(II)–L system (10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} aqueous NEt_4ClO_4: (*a*) 1 : 1, (*b*) 2 : 1 Zn^{2+} : L. Percentage abundances are relative to the number of moles of zinc(II) present

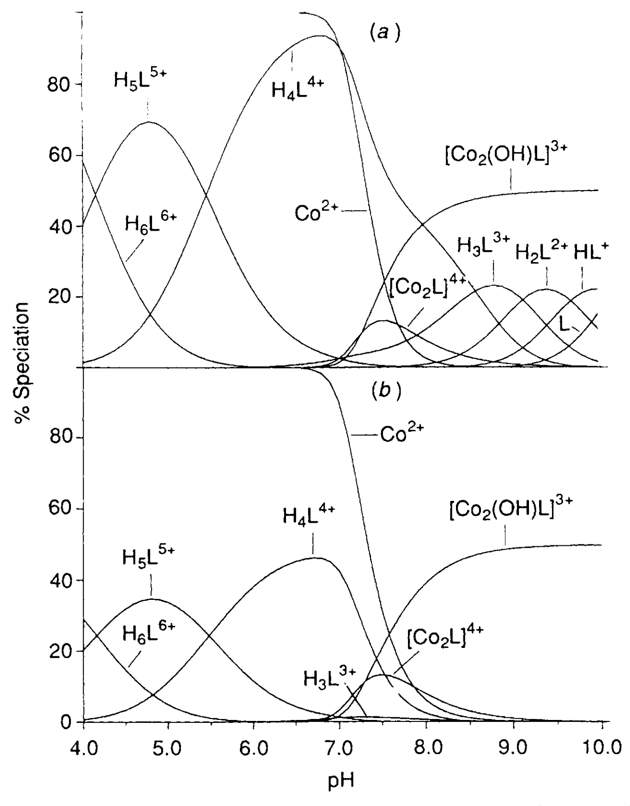

Fig. 4 Speciation diagrams for the cobalt(II)–L system (10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} aqueous NEt_4ClO_4: (*a*) 1 : 1, (*b*) 2 : 1 Co^{2+} : L. Percentage abundances are relative to the number of moles of cobalt(II) present

amounts of cadmium perchlorate hexahydrate and L in methanol yields a white powder which analyses as $[CdL][ClO_4]_2$ and behaves as a 2 : 1 electrolyte in dmf. Under the same conditions the same reagents in a 2 : 1 ratio give a much less soluble precipitate which analyses as $[Cd_2L][ClO_4]_4$ and behaves as a 4 : 1 electrolyte in dmf. The ^{13}C NMR spectra, recorded in D_2O at 365 K, of the two adducts are markedly different, particularly in terms of the resonance position for the ring carbon atoms which are β to the ring nitrogen atoms (the medial carbons). In $[CdL][ClO_4]_2$ these atoms resonate at δ 23.7 which is within the normal region for this resonance in monometallic cyclam (1,4,8,11-tetraazacyclotetradecane) type complexes;[12,13] with $[Cd_2L][ClO_4]_4$, however, this resonance occurs well downfield, at δ 33.0, even though the resonance positions for the other carbon atoms differ to a much smaller extent. The large downfield shift experienced only by the medial carbon atom appears to be a characteristic of type 2 bimetallic species, whether or not a bridging group is present, as both the bimetallics characterised by X-ray diffraction in this work, $[Zn_2(OH)L][ClO_4]_3$ and $[Cd_2Cl(L)][CF_3SO_3]_3$, which are type 2 structures, show the same effect, having chemical shift values for their medial carbon atoms of δ 30.0 and 32.8 respectively. In $[Hg_2L][ClO_4]_4$ (to be discussed below), however, the effect is less marked with the medial carbons resonating at δ 25.3, which probably indicates that in this complex the linking groups are dimethylene and that the medial carbon atoms form a part of the quadridentate assembly bound to each metal ion (type 1 structure). Although the formation of monometallic complexes has no precedent in L chemistry it does appear to be the common binding mode for the closely related 3-aminopropyl analogue.[22,23]

Speciation diagrams for the cadmium(II)–L system in water are shown in Fig. 5 and provide additional information concerning the complexation. It is clear that whereas the zinc(II) system showed evidence for a five-co-ordinate complex as the only monometallic species, the cadmium(II) system shows, instead, a strong tendency for potentially six- $\{[Cd(H_2L)]^{4+}\}$, seven- $\{[Cd(HL)]^{3+}\}$ and eight-co-ordinate $([CdL]^{2+})$ monometallics to form. Although the actual co-ordination number in each case is not known it is likely that it is the stabilisation achieved by cadmium(II) in adopting a co-ordination number greater than five, the maximum achievable in the bimetallic complexes, that militates against the pre-eminence of bimetallic species in the cadmium(II) system.

The formation of the bimetallic $[Cd_2L][ClO_4]_4$ in aqueous methanol without the imposition of a hydroxo bridge is indicative of the lower acidity of the larger cadmium(II) ion compared to zinc(II).[19] Our potentiometric data give a value of 6.6 as the upper limit for the pK_a (25 °C) of the bound water molecule necessary for the formation of the hydroxo-bridged species observed in aqueous solution (Fig. 5). The non-bridged species is able to capture monovalent anions other than hydroxide, a fact which became apparent when we carried out the synthesis in the presence of 1 mol equivalent of chloride. From this reaction a precipitate analysing as $[Cd_2Cl(L)][ClO_4]_3$ was isolated, which gave a conductivity characteristic of a 3:1 electrolyte, in dmf solution, and displayed a resonance attributable to the medial carbon atoms at δ 32.7 in the ^{13}C NMR spectrum, all suggesting that chloride had been incorporated into a bridging position. To verify this we carried out an X-ray diffraction analysis of the corresponding triflate salt, which occurs as crystals better suited for the purpose.

Single crystals of $[Cd_2Cl(L)][CF_3SO_3]_3$ were formed during the slow evaporation of a methanol solution of the compound. The structure of the cation, shown in Fig. 6, confirms the presence of the bridging chloride. Both cadmium atoms exhibit distorted square-pyramidal sterochemistry with the bridging halide ion at the apical site and a basal plane consisting of a pair of 1,4-related ring nitrogen atoms and two pendant amino groups. The Cd(1)–Cl and Cd(2)–Cl distances are similar being 2.540(3) and 2.520(3) Å respectively. The intercadmium separation is 4.409(1) Å and the two ions are both displaced from their basal plane towards the bridging halide by 0.803(6) and 0.834(6) Å respectively. The Cd(1)–Cl–Cd(2) angle is 121.2(1)°.

Co-ordination with Mercury(II).—The behaviour of L with mercury(II) is similar to that with cadmium(II) in that both mono- and bi-metallic complexes could be produced. The bimetallic tetraperchlorate salt (4:1 electrolyte) was isolated from methanol, and as noted above appears from the ^{13}C NMR spectrum to have a type 1 structure. This is supported by the fact that when a single equivalent of Cl^- is added to it, producing $[Hg_2Cl(L)][ClO_4]_3$, a 3:1 electrolyte, the ^{13}C NMR spectrum of this compound indicates that the two halves of the bimetallic species are non-equivalent, showing that the chloride is terminal, on one of the two mercury(II) ions, and not bridging. Potentiometric titration of protonated L–mercury(II) mixtures indicated that strong complexation takes place at very low pH (pH < 3), preventing the formation of HgO unless the number of equivalents of mercury(II) exceeded 2.

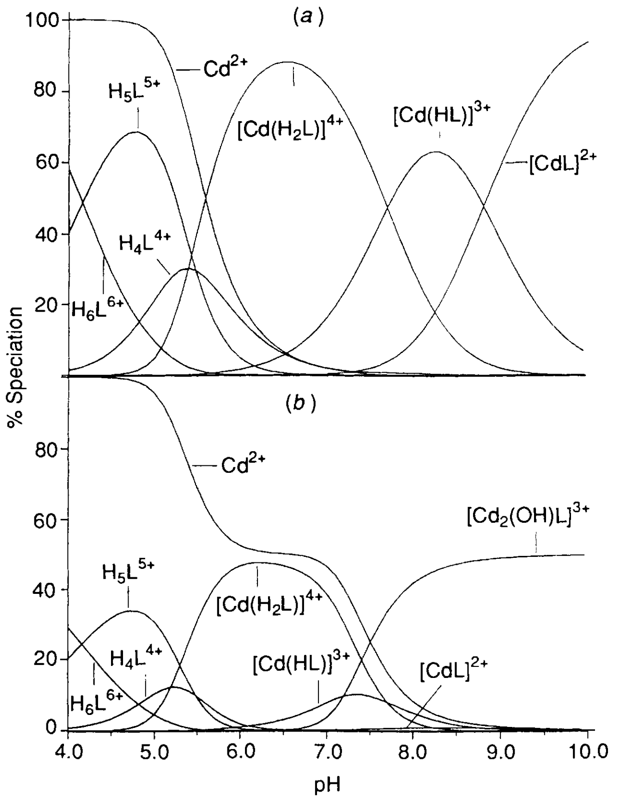

Fig. 5 Speciation diagrams for the cadmium(II)–L system (10^{-3} mol dm^{-3}) in 0.1 mol dm^{-3} aqueous NEt_4ClO_4: (*a*) 1:1, (*b*) 2:1 Cd^{2+}:L. Percentage abundances are relative to the number of moles of cadmium(II) present

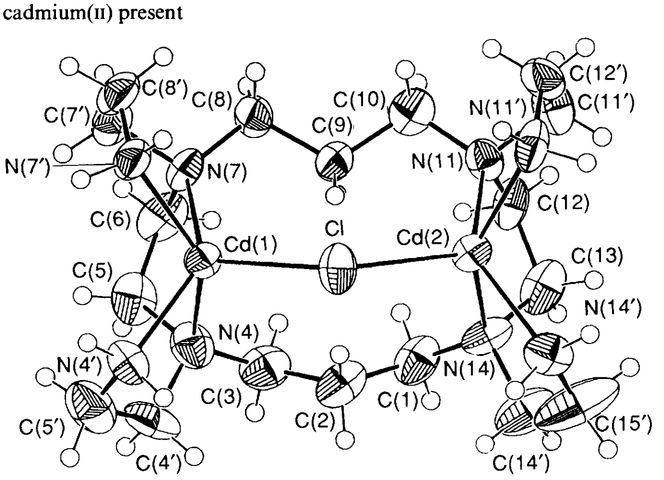

Fig. 6 An ORTEP drawing of $[Cd_2Cl(L)]^{3+}$ showing thermal ellipsoids of the non-hydrogen atoms at the 50% probability level

pK_a *Values for* L.—The pK_a values measured at an ionic strength (*I*) of 0.1 mol dm^{-3} (NEt_4ClO_4), and used in this work, are reported in Table 5. They are qualitatively similar to those previously determined at higher ionic strength (I = 0.5 mol dm^{-3}, $NaNO_3$),[9] but slight differences emerged. Thus, the first four constants lie bunched at between pH 8.6 and 10.2, while the

Table 5 Stepwise acid dissociation constants[a] of the protonated octaamine ligand L

	pK_a[b]		
Step	0.1 mol dm^{-3} NEt_4ClO_4[c]	0.5 mol dm^{-3} $NaNO_3$[d]	ΔpK_a[e]
1	10.14(2)	10.10(3)	−0.04(5)
2	9.67(2)	10.05(2)	0.38(4)
3	9.12(3)	9.41(4)	0.29(7)
4	8.59(3)	9.00(3)	0.41(6)
5	5.48(1)	6.08(7)	0.60(8)
6	4.16(4)	4.84(7)	0.68(11)
7	—	1.8(1)	—
7 + 8[f]	4.15(15)	—	—

[a] Determined by glass-electrode potentiometry at 25 °C in water at constant ionic strength as indicated. [b] The stepwise equilibrium constants K_{a1}, K_{a2}, *etc.* refer to the equations $HL^+ \rightleftharpoons L + H^+$, $H_2L^{2+} \rightleftharpoons HL^+ + H^+$, *etc.*, where p$K_a = -\log_{10}K_a$. [c] This work. These constants are averaged from four separate titrations, the numbers in parentheses referring to the maximum variation found in the least significant figure exhibited by different titrations. [d] From ref. 9. [e] The difference in pK_a between values determined at I = 0.1 and 0.5 mol dm^{-3}. [f] This constant refers to the reaction $H_8L^{8+} \rightleftharpoons H_6L^{6+} + 2H^+$.

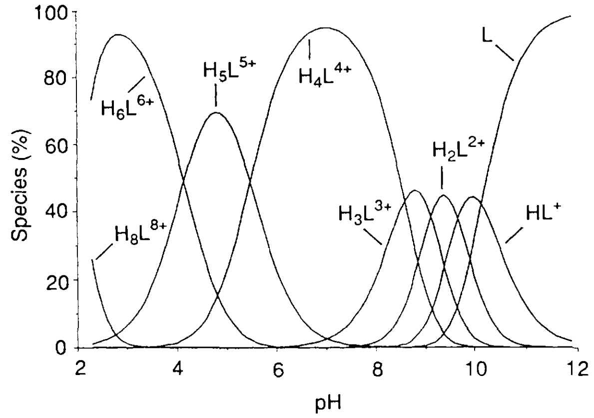

Fig. 7 Relative percentages of different species in a 1.00 × 10^{-3} mol dm^{-3} solution of L in water at an ionic strength of 0.1 mol dm^{-3} (NEt_4ClO_4) as determined using the data in Table 5. The pH range shown is typical of one of the titrations used to determine the pK_a values

other constants lie below pH 6.1 leading to a well defined end-point in the titration curve at about pH 7. The four pK_a values above pH 7.0 presumably represent the protonation of the primary amino pendant arms which can best adopt conformations to minimise electrostatic repulsions. In general the pK_a values are slightly smaller when determined at lower ionic strength, with more noticeable deviations for the smaller pK_a values (up to a 0.68 pH unit difference for pK_{a6}). This is consistent with the larger degree of stabilisation expected for a highly charged (protonated) species in a solution of higher ionic strength. Whereas Evers *et al.*[9] found pK_{a1} and pK_{a2} to be abnormally close when I = 0.5 mol dm^{-3} (Table 5) no such effect was apparent at lower ionic strength. We found that a model that assumed pK_{a8} > pK_{a7} (*i.e.* where the last two protonation steps occur together) better fitted the data at very low pH, rather than a single value for pK_{a7}. A similar result was determined for cyclam itself where pK_{a4} > pK_{a3} for the last two steps.[24,25] The relative concentration of each species as a function of pH is shown in Fig. 7.

Experimental

The ^{13}C NMR spectra were recorded using a JEOL FX90Q spectrometer at 365 K in D_2O or in [$^2H_7$]dmf at ambient temperature. Chemical shifts in D_2O are quoted with respect to internal 1,4-dioxane, for which the resonance position was taken as δ 67.00, and in [$^2H_7$]dmf with respect to the central peak of the upfield solvent multiplet, taken as δ 29.00. Conductivity measurements were made on 10^{-3} mol dm^{-3} solutions in dmf at 293 K using a Phillips PW9504 conductivity bridge. Elemental analyses were performed by the Australian Microanalytical Service. The ligand L and its octahydrobromide were prepared according to the method of Murase *et al.*[2] Cadmium triflate sesquihydrate was prepared from cadmium chloride and silver triflate (Aldrich) by the literature method.[26]

Syntheses.—[$Zn_2(OH)L$][ClO_4]$_3$. A solution of zinc perchlorate hexahydrate (0.30 g, 0.80 mmol) dissolved in methanol (10 cm^3) was added dropwise, over a period of 10 min, to a refluxing solution of L (0.15 g, 0.4 mmol) in methanol (10 cm^3). The resulting slurry was refluxed for 1 h, cooled to room temperature and then filtered. The white powder was washed with methanol (2 × 5 cm^3) and dried under vacuum giving the pure product (0.31 g, 95%) (Found: C, 26.6; H, 5.4; N, 13.8. $C_{18}H_{45}Cl_3N_8O_{13}Zn_2$ requires C, 26.4; H, 5.5; N, 13.7%); ^{13}C NMR (D_2O): δ 57.0 (4C), 53.5 (4C), 51.1 (4C), 36.4 (4C, CH_2NH_2) and 30.0 (2C, $CH_2CH_2CH_2$); Λ_M = 227 Ω^{-1} cm^2 mol^{-1} (dmf) (3:1).[27]

[$Zn_2(OH)L$][ClO_4]$_2$Cl. A solution of L (0.15 g, 0.4 mmol) in methanol (10 cm^3) was added dropwise over a period of 10 min to a stirred refluxing solution containing zinc perchlorate hexahydrate (0.23 g, 0.6 mmol) and zinc chloride (0.03 g, 0.2 mmol) in methanol (10 cm^3). After stirring and refluxing the reaction mixture for 30 min it was cooled to room temperature and filtered. The coarse white precipitate was washed with methanol (2 × 5 cm^3) and dried under vacuum giving the pure product (0.21 g, 70%) (Found: C, 28.6; H, 5.9; Cl, 14.1; N, 14.8. $C_{18}H_{45}Cl_3N_8O_9Zn_2$ requires C, 28.6; H, 6.0; Cl, 14.1; N, 14.9%); Λ_M = 210 Ω^{-1} cm^2 mol^{-1} (dmf) (3:1).[27]

[$Zn_2(OH)L$]Br_3. The compound L·8HBr (1 g, 0.98 mmol) was dissolved in water (50 cm^3). Basic zinc carbonate ($ZnCO_3$·2ZnO·3H_2O, 0.49 g, 1.4 mmol) was added to the solution and the mixture was heated at 80 °C for 1 h. The solution was then filtered and the filtrate concentrated to 10 cm^3 before slowly adding ethanol (40 cm^3). The product, which precipitated as a fine white powder, was filtered off and dried under vacuum (0.72 g, 96%) (Found: C, 28.3; H, 5.8; N, 14.4. $C_{18}H_{45}Br_3N_8OZn_2$ requires C, 28.4; H, 6.0; N, 14.7%); Λ_M = 72 Ω^{-1} cm^2 mol^{-1} (dmf) (1:1), 436 Ω^{-1} cm^2 mol^{-1} (water) (3:1).[27]

[CdL][ClO_4]$_2$. A solution of cadmium perchlorate hexahydrate (0.17 g, 0.4 mmol) in methanol (10 cm^3) was added dropwise to a stirred refluxing solution of L (0.15 g, 0.4 mmol) in methanol (10 cm^3). A white powder precipitated towards the end of the addition. The slurry was refluxed for 30 min before allowing it to cool to room temperature and filtering off the precipitated solid. The solid was washed with methanol (2 × 5 cm^3) and dried under vacuum giving the pure product (0.17 g, 62%) (Found: C, 31.7; H, 6.3; N, 16.2. $C_{18}H_{44}CdCl_2N_8O_8$ requires C, 31.6; H, 6.5; N, 16.4%); ^{13}C NMR (D_2O): δ 58.8 (4C), 55.9 (4C), 52.2 (4C), 35.3 (4C, CH_2NH_2) and 23.7 (2C, $CH_2CH_2CH_2$); Λ_M = 163 Ω^{-1} cm^2 mol^{-1} (dmf) (2:1).[27]

[Cd_2L][ClO_4]$_4$. A solution of cadmium perchlorate hexahydrate (0.34 g, 0.8 mmol) in methanol (10 cm^3) was added dropwise over 10 min to a stirred refluxing solution of L (0.15 g, 0.4 mmol) in methanol (10 cm^3). Immediate precipitation of a white solid occurred. The slurry was stirred for 1 h whilst allowing it to cool to room temperature. The product was filtered off, washed with methanol (2 × 5 cm^3) and dried under vacuum (0.24 g, 60%) (Found: C, 21.9; H, 4.2; Cd, 22.6; Cl, 14.3; N, 11.5. $C_{18}H_{44}Cd_2Cl_4N_8O_{16}$ requires C, 21.7; H, 4.5; Cd, 22.6; Cl, 14.3; N, 11.3%); ^{13}C NMR (D_2O): δ 57.5 (4C), 52.3 (4C), 51.5 (4C), 36.9 (4C, CH_2NH_2) and 33.0 (2C, $CH_2CH_2CH_2$); Λ_M = 285 Ω^{-1} cm^2 mol^{-1} (dmf) (4:1).[27]

$[Cd_2Cl(L)][ClO_4]_3$. The ligand L (0.15 g, 0.4 mmol) dissolved in methanol (10 cm^3) was added dropwise over a period of 10 min to a stirred refluxing solution of cadmium perchlorate hexahydrate (0.25 g, 0.6 mmol) and cadmium chloride hemipentahydrate (0.05 g, 0.2 mmol) in methanol (10 cm^3). After stirring the resulting suspension for 30 min and cooling it to room temperature the precipitated product was filtered off, washed with methanol (2 × 5 cm^3) and dried under vacuum (0.31 g, 83%) (Found: C, 23.3; H, 4.6; N, 11.8. $C_{18}H_{44}Cd_2Cl_4N_8O_{12}$ requires C, 23.2; H, 4.8; N, 12.0%); ^{13}C NMR (D_2O): δ 57.5 (4C), 52.2 (4C), 51.5 (4C), 36.8 (4C, CH_2NH_2) and 32.7 (2C, $CH_2CH_2CH_2$); $\Lambda_M = 216\ \Omega^{-1}\ cm^2\ mol^{-1}$ (dmf) (3:1).[27]

$[Cd_2Cl(L)][CF_3SO_3]_3$. This compound was prepared in the same way as the perchlorate salt by substituting cadmium triflate sesquihydrate for cadmium perchlorate hexahydrate. Yield: 95% (Found: C, 23.6; H, 4.0; Cl, 3.5; N, 10.2. $C_{21}H_{44}Cd_2ClF_9N_8O_9S_3$ requires C, 23.4; H, 4.1; Cl, 3.3; N, 10.4%); ^{13}C NMR (D_2O): δ 120.1 (3C, q, J = 316 Hz, CF_3), 57.5 (4C), 52.2 (4C), 51.5 (4C), 36.8 (4C, CH_2NH_2) and 32.8 (2C, $CH_2CH_2CH_2$); $\Lambda_M = 227\ \Omega^{-1}\ cm^2\ mol^{-1}$ (dmf) (3:1).[27]

$[HgL][ClO_4]_2$. This compound was prepared in the same way as for the cadmium(II) analogue except that the reaction was conducted at 0 °C and with mercury(II) perchlorate trihydrate replacing the cadmium(II) salt. Yield: 56% (Found: C, 28.2; H, 5.5; N, 14.3. $C_{18}H_{44}Cl_2HgN_8O_8$ requires C, 28.0; H, 5.7; N, 14.5%); ^{13}C NMR ([$^2H_7$]dmf): δ 55.7 (4C), 54.8 (4C), 51.9 (4C), 36.8 (4C, CH_2NH_2) and 25.0 (2C, $CH_2CH_2CH_2$); $\Lambda_M = 144\ \Omega^{-1}\ cm^2\ mol^{-1}$ (dmf) (2:1).[27]

$[Hg_2L][ClO_4]_4$. This compound was synthesised in the same way as $[HgL][ClO_4]_2$ except that 2 mol equivalents of $Hg(ClO_4)_2 \cdot 3H_2O$ were used instead of 1. Yield: 88% (Found: C, 18.2; H, 4.0; N, 9.3. $C_{18}H_{44}Cl_4Hg_2N_8O_{16}$ requires C, 18.5; H, 3.8; N, 9.6%); ^{13}C NMR ([$^2H_7$]dmf): δ 54.4 (4C), 51.0 (4C), 50.5 (4C), 38.1 (4C, CH_2NH_2), and 25.3 (2C, $CH_2CH_2CH_2$); $\Lambda_M = 278\ \Omega^{-1}\ cm^2\ mol^{-1}$ (dmf) (4:1).[27]

$[Hg_2Cl(L)][ClO_4]_3$. This complex was produced at 0 °C using the same method as employed for $[Cd_2Cl(L)][ClO_4]_3$, but with substitution of the appropriate mercury(II) salts. Yield: 87% (Found: C, 19.7; H, 4.1; N, 10.1. $C_{18}H_{44}Cl_4Hg_2N_8O_{12}$ requires C, 19.5; H, 4.0; N, 10.1%); ^{13}C NMR ([$^2H_7$]dmf): δ 57.0 (2C), 55.0 (2C), 51.5 (4C), 51.3 (2C), 50.9 (2C), 37.9 (2C), 36.4 (2C), 32.2 (1C) and 26.1 (1C); $\Lambda_M = 217\ \Omega^{-1}\ cm^2\ mol^{-1}$ (dmf) (3:1).[27]

Potentiometric Titrations.—The potentiometric titrations were carried out under an inert atmosphere of water-saturated nitrogen in a water-jacketed vessel maintained at 25 °C. Data were obtained from 10 cm^3 aliquots of solution containing 0.010 mol dm^{-3} $HClO_4$, 0.100 mol dm^{-3} NEt_4ClO_4, and approximately 1.0×10^{-3} mol dm^{-3} of L titrated with 0.10 mol dm^{-3} NEt_4OH. A Metrohm E665 Dosimat autoburette equipped with a burette (5 cm^3) was used to deliver the titrant and the potential was measured by an Orion Ross Sure Flow 81-72BN combination electrode connected to an Orion SA 720 pH meter. The autoburette and pH meter were interfaced to an IBM compatible personal computer which controlled the addition of titrant using a locally written program so that successive additions of titrant resulted in a decrease of 4 mV in the potential reading. The electrode was calibrated by a titration in the absence of ligand and fitting the resulting data from this strong acid–strong base titration by the Nernst equation. The pK_a and stability constants were determined using the program SUPERQUAD.[28] Stability constant data were gathered from solutions to which 0.1 mol dm^{-3} metal perchlorate solution was added so as to give a metal-to-ligand ratio in the range 0.5:1 to 2:1. At least three titrations, with different ratios, were performed for each metal ion.

Structural Analyses.—Suitable single crystals of $[Zn_2(OH)L][ClO_4]_3$ were obtained by diffusion of methanol vapour into an aqueous solution of the complex, whilst those of $[Cd_2Cl(L)][CF_3SO_3]_3$ were obtained by the slow evaporation of a methanolic solution of the complex. Space groups were determined from precession photographs. Unit-cell and intensity data were measured with a CAD-4 diffractometer using graphite-monochromated Mo-Kα X-radiation. Unit-cell data (Table 1) were determined from a least-squares fit to a setting angle of 25 reflections chosen widely in reciprocal space each at four different values of ψ in the ranges 2θ 15–21 (Zn) and 14–20° (Cd). Three reflections monitored every 120 min of exposure time showed no significant variation in intensity. Absorption corrections were applied (Gaussian quadrature, 8 × 8 × 8 grid).

Crystal structures were solved by Patterson and Fourier methods. Hydrogen atoms were placed in calculated positions with arbitrarily assigned isotropic thermal parameters. The hydrogen atom of the hydroxide group of the zinc complex was not included. Non-hydrogen atomic coordinates and, with the exception of those of the carbon atom of the third triflate anion, anisotropic thermal parameters were refined by full-matrix least squares minimising $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Values of $\sigma^2(F_o^2)$ were obtained from a combination of counting statistics and mean deviations where available. A Zachariasen extinction correction was refined in both cases but it was only significant in the case of Zn and was not included in the final cycles of the cadmium refinement. Hydrogen-atom coordinates and thermal parameters were not refined.

Computer programs of the XTAL system[29] were used in the structure solution and refinement. The program CRYLSQ[30] was used in least-squares refinement with neutral atom scattering factors for all atoms. A refinement summary is given in Table 1. The final positional coordinates for the complex cations are given in Table 2 and atom labelling is shown in Figs. 2 and 6. The possibility that the thermal ellipsoid of the hydroxide oxygen atom, in the zinc complex, which is elongated normal to the plane of the bonds to Zn, represents an approximation to a positional disorder in the oxygen atom cannot be discounted, but there is no discernible reason why it should be disordered. The atomic positions in the third triflate anion were not well defined and, in particular, the anisotropic thermal parameters of the carbon atom were physically impossible. A model with two half-occupancy carbon atoms about 0.5 Å apart [C(3′) and C(3″)] with isotropic thermal parameters gave a smoother difference map and resulted in a significantly lower value of R after refinement. This disordered model is reported herein. The perchlorate and triflate anions are all subject to large 'thermal' motion bordering on disorder and there are many peaks in the final difference maps in the region of these ions in the range −0.7 to +1.0 e $Å^{-3}$ for the zinc complex and −0.8 to +0.8 e $Å^{-3}$ for the cadmium complex.

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

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