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FULL PAPER

Zinc and cadmium complexes of an 18-membered N_4O_2 oxaaza-Schiff base macrocycle and the corresponding reduced form†

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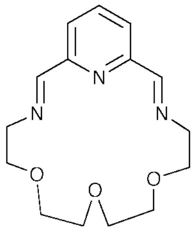
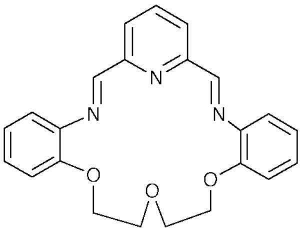
The metal templated (Cd and Zn) cyclocondensation of 2,6-pyridinedicarbaldehyde and 1,5-bis(2-aminophenoxy)-3-azapentane is reported together with the crystal structures of two mononuclear cadmium macrocyclic Schiff base complexes, [CdL^1(NO$_3$)$_2$] **1** and [CdL^1(H$_2$O)$_2$][ClO$_4$]$_2$ **2** and a dinuclear, μ-hydroxy-bridged zinc macrocyclic Schiff base complex [Zn$_2$L$^1{}_2$(OH)][ClO$_4$]$_3$·CH$_3$CN **3·**CH$_3$CN. The corresponding reduced macrocycle, L^2, has been synthesised by using the Mn^{II}-templated cyclocondensation of 2,6-pyridinedicarbaldehyde and 1,5-bis(2-aminophenoxy)-3-azapentane in methanol followed by an *in situ* reductive demetallation of the Schiff base macrocyclic manganese(II) complex using excess sodium borohydride. The crystal structures of the free macrocycle L^2, [CdL^2(NO$_3$)$_2$] **4** and [CdL^2(CH$_3$CN)$_2$][ClO$_4$]$_2$ **5** are reported.

Introduction

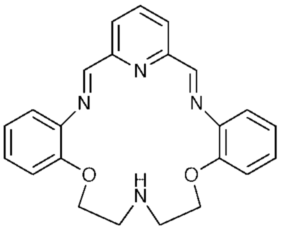
The synthesis of oxaaza Schiff base macrocyclic ligands by the metal templated cyclocondensation of 2,6-dicarbonylpyridines and α,ω-diaminoethers is well documented.[1,2] Metal complexes of both '1 + 1' diimine and '2 + 2' tetraimine macrocycles were reported and it was first suggested that for 18-membered ring macrocycles (L^a, generated from 1,5-diamino-3-oxapentane, and L^b, generated from 1,5-bis(2-aminophenoxy)-3-oxapentane) the ionic size of the templating cation exercised a major influence on macrocycle formation.[3] Alkaline earth cations such as Ca^{2+}, Sr^{2+} and Ba^{2+}, the trivalent lanthanide cations and Pb^{2+} were all shown to be effective at producing complexes of L^a and L^b by this route whereas the transition metals did not do so.

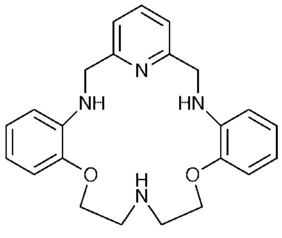

L^a


L^b

Recently it has been shown that if 1,13-diamino-4,7,10-trioxatridecane is reacted with 2,6-pyridinedicarbaldehyde in the presence of copper(II) and nickel(II) templates then copper can serve to produce a 20-membered '1 + 1' macrocycle and nickel(II) will generate a 40-membered '2 + 2' macrocycle.[4] The reaction paths are dominated by the binding of the metal to the pyridinyl head units. It is therefore necessary to think beyond a simple size control parameter. In this case the additional methylene groups give the macrocycle an extra mobility which allows the metal to attain a preferential site geometry. A balance between cationic size, the bonding preference of the cation, the nature of the donor atoms present and their disposition within the macrocyclic framework is therefore required to effect cyclocondensation.

In the present study we have modified the donor atom sequence of the precursor diamine for macrocycle L^B by replacing the oxygen atom present at the 3-position of the ether linker with a secondary amino-group. This change was made to enhance the opportunity to use templates other than 'hard' metals and introduces into the macrocycle a functional group to which pendant arms can be attached. In the present work we report the application of zinc(II), cadmium(II) and manganese(II) as templating devices together with the X-ray crystal structures of the Schiff base macrocyclic complexes [CdL^1(NO$_3$)$_2$] **1**, [CdL^1(H$_2$O)$_2$][ClO$_4$]$_2$ **2**, and [Zn$_2$L$^1{}_2$(OH)][ClO$_4$]$_3$·CH$_3$CN **3·**CH$_3$CN. The structure of the reduced macrocycle L^2 and its cadmium complexes, [CdL^2(NO$_3$)$_2$] **4** and [CdL^2(CH$_3$CN)$_2$][ClO$_4$]$_2$ **5** are also reported.‡


L^1


L^2

Experimental

Elemental analyses were carried out on a Carlo Erba Ea 1108. IR Spectra were recorded as KBr discs using a Bruker IFS-66V spectrophotometer. ^{1}H NMR spectra were recorded using

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† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4131/

‡ L^1 = 10,16-dioxa-3,13,23,29-tetraazatetracyclo[23.3.1.0^{4,9}.0^{17,22}]nonacosa-1(29),2,4(9),5,7,17,19,21,23,25,27-undecaene. L^2 = 10,16-dioxa-3,13,23,29-tetraazatetracyclo[23.3.1.0^{4,9}.0^{17,22}]nonacosa-1(29),4(9),5,7,17,19,21,25,27-nonaene.

Bruker DPX250 and Bruker AMX300 spectrometers. Mass spectra were recorded using a Kratos-MS-50 spectrometer with 3-nitrobenzyl alcohol used as the matrix for FAB spectra. Conductivity measurements were recorded on a WTW LF-3 spectrometer using 10^{-3} M acetonitrile solutions of the complexes.

Synthetic procedures

2,6-Pyridinedicarbaldehyde was prepared by the literature method[5] as was *N*,*N*-bis-[2-(2-aminophenoxy)ethyl]formamide.[6]

1,5-Bis(2-aminophenoxy)-3-azapentane. This triamine precursor was prepared by deformylation of *N*,*N*-bis-[2-(2-aminophenoxy)ethyl]formamide. 4 mmol of *N*,*N*-bis-[2-(2-aminophenoxy)ethyl]formamide were dissolved in ethanol (30 ml), NaOH (0.6 g) was added and the solution was refluxed for 12 hours. When cold the solution was evaporated to dryness under reduced pressure and the residue dissolved in water (50 ml) prior to extraction with $CHCl_3$ (3 × 50 ml). The combined extracts were dried over magnesium sulfate, filtered and evaporated, under reduced pressure, to leave a cream powder. Yield: 95% (Found: C, 66.7; H, 7.3; N, 14.7. Calc. for $C_{16}H_{21}N_3O_2$: C, 66.9; H, 7.3; N, 14.6%). Mass spectral parent ion: *m*/*z* 288. IR (KBr disc): $\nu(NH_2)$ 3360, 3450 cm^{-1}. ^{1}H NMR ($CDCl_3$), δ 6.91–6.70 (m, 8H, C_6H_4), 4.26 (t, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.09 (t, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$), 3.71 (br, 4H, NH_2).

Metal complexes of the diimine macrocycle. 2,6-Pyridinedicarbaldehyde (0.5 mmol) and the requisite metal nitrate or perchlorate (0.5 mmol) were dissolved in refluxing acetonitrile (30 ml). To this a solution of 1,5-bis(2-aminophenoxy)-3-azapentane (0.5 mmol) in acetonitrile (20 ml) was added dropwise. The resultant solution was refluxed for 2 hours, cooled, and filtered. The volume of the filtrate was reduced to 20 ml and the solution was left standing for crystallisation.

$[Zn_2L^1_2(OH)][ClO_4]_3$ **3**. Yield: 61% (Found: C, 44.1; H, 3.6; N, 9.3. Calc. for $C_{46}H_{45}N_8O_{17}Cl_3Zn_2$: C, 45.3; H, 3.7; N, 9.2%). Mass spectral parent ion: *m*/*z* 549, 449. IR (KBr disc): ν(C=N) 1621 cm^{-1}, $\nu(ClO_4^-)$ 1103, 624 cm^{-1}. ^{1}H NMR (CD_3CN), δ 8.44 (t, 1H, py), 8.07 (d, 2H, py), 7.55–7.13 (m, 8H, C_6H_4), 8.84 (s, 2H, HC=N), 4.10, 3.75 (m, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$) 2.76, 2.54 (m, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 407 Ω^{-1} cm^2 mol^{-1} (3 : 1 electrolyte).

$[ZnL^1(NO_3)_2]$. Yield: 43% (Found: C, 46.2; H, 4.0; N, 13.3. Calc. for $C_{23}H_{22}N_6O_8Zn\cdot H_2O$: C, 46.5; H, 4.0; N, 14.2%). Mass spectral parent ion: *m*/*z* 512, 450. IR (KBr disc): ν(C=N) 1620 cm^{-1}, (NO_3^-) 1384, 1449 cm^{-1}. ^{1}H NMR (CD_3OD), δ 8.57 (t, 1H, py), 8.29 (d, 2H, py), 7.77–7.30 (m, 8H, C_6H_4), 9.16 (s, 2H, HC=N), 4.44 (br, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.03 (br, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 139 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte).

$[CdL^1(H_2O)_2][ClO_4]_2$ **2**. Yield: 78% (Found: C, 37.9; H, 3.5; N, 7.9. Calc. for $C_{23}H_{26}N_4O_{12}Cl_2Cd$: C, 37.6; H, 3.5; N, 7.6%). Mass spectral parent ion: *m*/*z* 599, 498. IR (KBr disc): ν(C=N) 1625 cm^{-1}, $\nu(ClO_4^-)$ 1093, 623 cm^{-1}. ^{1}H NMR (CD_3CN), δ 8.53 (t, 1H, py), 8.27 (d, 2H, py), 7.70–7.19 (m, 8H, C_6H_4), 9.13 (s, 2H, HC=N), 4.58, 4.45 (br, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.30, 3.17 (br, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 298 Ω^{-1} cm^2 mol^{-1} (2 : 1 electrolyte).

$[CdL^1(NO_3)_2]$ **1**. Yield: 76% (Found: C, 44.2; H, 4.0; N, 13.4. Calc. for $C_{23}H_{22}N_6O_8Cd$: C, 44.3; H, 3.5; N, 13.5%). Mass spectral parent ion: *m*/*z* 562, 499. IR (KBr disc): ν(C=N) 1628 cm^{-1}, (NO_3^-) 1309, 1384, 1419 cm^{-1}. ^{1}H NMR (CD_3OD), δ 8.46 (t, 1H, py), 8.22 (d, 2H, py), 7.63–7.13 (m, 8H, C_6H_4), 9.15 (s, 2H, HC=N), 4.47 (br, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.30 (br, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 117 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte).

The metal-free reduced macrocycle L^2. 2,6-Pyridinedicarbaldehyde (1 mmol) and $Mn(NO_3)_2\cdot 4H_2O$ (1 mmol) were dissolved in methanol (50 ml). The solution was stirred vigorously and heated while a solution of 1,5-bis(2-aminophenoxy)-3-azapentane (1 mmol) in methanol (50 ml) was added. The resultant solution was refluxed for 2 hours and cooled. Sodium borohydride (4 mmol) was then added slowly and carefully. The resulting precipitate was filtered off and recrystallised from hot acetonitrile. Yield: 65% (Found: C, 70.3; H, 6.3; N, 14.1. Calc. for $C_{23}H_{26}N_4O_2$: C, 70.8; H, 6.7; N, 14.4%). Mass spectral parent ion: *m*/*z* 391. IR (KBr disc): ν(NH) 3354, 3282 cm^{-1}. ^{1}H NMR (CD_3CN), δ 7.75 (t, 1H, py), 7.35 (d, 2H, py), 6.93–6.59 (m, 8H, C_6H_4), 5.42 (t, 4H, NH), 4.42 (d, 4H, $NHCH_2$), 4.12 (t, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.07 (t, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$); ^{13}C NMR, δ 156.4 (py), 137.6 (py), 120.5 (py), 47.5 ($NHCH_2$), 109.8, 110.0, 116.1, 120.7, 146.2 (C_6H_4), 67.0 (OCH_2), 26.3 ($NHCH_2$).

Metal complexes of the reduced macrocycle. The following procedure was used in all cases. The ligand (0.05 mmol) and appropriate hydrated metal salt (nitrate or perchlorate) (0.05 mmol) were mixed in warm acetonitrile (50 ml). The solution was refluxed for 2 hours and filtered while hot. The volume of the filtrate was reduced to 20 ml and the solution was left standing for crystallisation.

$[ZnL^2][NO_3]_2$. Yield: 43% (Found: C, 46.6; H, 4.1; N, 14.1. Calc. for $C_{23}H_{26}N_6O_8Zn$: C, 47.6; H, 4.5; N, 14.5%). Mass spectral parent ion: *m*/*z* 391. IR (KBr disc): ν(NH) 3360, 3390 cm^{-1}, $\nu(NO_3^-)$ 1318, 1384, 1400 cm^{-1}. ^{1}H NMR (CD_3CN), δ 8.12 (t, 1H, py), 7.55 (d, 2H, py), 7.26–6.88 (m, 8H, C_6H_4), 6.14 (t, 2H, NH), 4.63 (d, 4H, $NHCH_2$), 4.33 (t, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.64 (t, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 114 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte).

$[ZnL^2(H_2O)_2][ClO_4]_2$. Yield: 40% (Found: C, 40.2; H, 4.0; N, 8.3. Calc. for $C_{23}H_{30}N_4O_{12}Cl_2Zn$: C, 40.0; H, 4.3; N, 8.1%). Mass spectral parent ion: *m*/*z* 553, 453. IR (KBr disc): ν(NH) 3264 cm^{-1}, $\nu(ClO_4^-)$ 1121, 1089, 624 cm^{-1}. ^{1}H NMR (CD_3CN), δ 8.08 (t, 1H, py), 7.54 (d, 2H, py), 7.31–7.09 (m, 8H, C_6H_4), 5.66 (t, 2H, NH), 4.61 (d, 4H, $NHCH_2$), 4.44 (t, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.13 (t, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 294 Ω^{-1} cm^2 mol^{-1} (2 : 1 electrolyte).

$[CdL^2(NO_3)_2]$ **4**. Yield: 76% (Found: C, 41.4; H, 4.0; N, 12.6. Calc. for $C_{23}H_{26}N_6O_8Cd\cdot 2H_2O$: C, 41.6; H, 4.7; N, 12.7%). Mass spectral parent ion: *m*/*z* 566, 501. IR (KBr disc): ν(NH) 3226, 3267, 3321 cm^{-1}, $\nu(NO_3^-)$ 1036, 1302, 1384, 1410 cm^{-1}. ^{1}H NMR (CD_3CN), δ 8.08 (t, 1H, py), 7.58 (d, 2H, py), 7.11–6.87 (m, 8H, C_6H_4), 5.54 (t, 2H, NH), 4.52 (d, 4H, $NHCH_2$), 4.30 (t, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.23 (t, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 146 Ω^{-1} cm^2 mol^{-1} (1 : 1 electrolyte).

$[CdL^2(CH_3CN)_2][ClO_4]_2$ **5**. Yield: 78% (Found: C, 41.0; H, 4.6; N, 10.6. Calc. for $C_{27}H_{32}N_6O_{10}Cl_2Cd$: C, 41.3; H, 4.1; N, 10.7%). Mass spectral parent ion: *m*/*z* 603, 501. IR (KBr disc): ν(NH) 3239, 3281 cm^{-1}, $\nu(ClO_4^-)$ 1121, 623 cm^{-1}. ^{1}H NMR (CD_3CN), δ 8.18 (t, 1H, py), 7.67 (d, 2H, py), 7.18–6.84 (m, 8H, C_6H_4), 5.31 (t, 2H, NH), 4.43 (d, 4H, $NHCH_2$), 4.76, 3.78 (m, 4H, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2NH}$), 3.21 (t, 4H, $\mathrm{OCH_2C}\mathit{H}_2\mathrm{NH}$). Λ_M (acetonitrile): 284 Ω^{-1} cm^2 mol^{-1} (2 : 1 electrolyte).

X-Ray crystallography

All crystals were obtained by slow recrystallisation of the compound from acetonitrile. The details of the X-ray crystal data, and of the structure solution and refinement, are given in Table 1. Measurements were made on a Siemens SMART CCD area diffractometer for the free macrocycle L^2, a Siemens P4 four-circle diffractometer for complex **4**, and a Bruker SMART CCD area diffractometer for complexes **1**, **2**, **3**$\cdot CH_3CN$ and **5**.

The programs used were Siemens SMART and SAINT for control and integration software and SHELXTL as imple-

Table 1 Crystal data, structure solution and refinement

	$[CdL^1(NO_3)_2]$ **1**	$[CdL^1(H_2O)_2]$-$[ClO_4]_2$ **2**	$[Zn_2L^1_2(OH)][ClO_4]_3\cdot CH_3CN$ **3**$\cdot CH_3CN$	Free macrocycle L^2	$[CdL^2(NO_3)_2]$ **4**	$[CdL^2(CH_3CN)_2]$-$[ClO_4]_2$ **5**
Chemical formula	$C_{23}H_{22}CdN_6O_8$	$C_{23}H_{26}CdCl_2N_4O_{12}$	$C_{48}H_{48}Cl_3N_9O_{17}Zn_2$	$C_{23}H_{28}N_4O_3$	$C_{23}H_{26}CdN_6O_8$	$C_{27}H_{32}CdCl_2N_6O_{10}$
Formula weight	622.87	733.78	1260.04	408.49	626.90	783.89
T/K	150(2)	150(2)	293(2)	293(2)	293(2)	293(2)
Crystal system, space group	Monoclinic, $P2(1)/n$	Monoclinic, $C2/c$	Monoclinic, $P2_1/c$	Orthorhombic, $Cmc21$	Monoclinic, $P2(1)/n$	Orthorhombic, $P2(1)2(1)2(1)$
a/Å	7.9479(13)	31.382(7)	19.5154(10)	21.7074(3)	11.891(5)	8.72260(5)
b/Å	12.605(2)	10.683(2)	12.2075(6)	12.1388(2)	12.824(6)	10.5384(6)
c/Å	23.682(4)	18.127(4)	22.3744(12)	7.9913(2)	16.724(7)	34.657(2)
β/°	95.467(18)	116.983(6)	96.8220(10)		105.48(3)	
V/Å^3	2361.7(7)	5415.2(19)	5292.6(5)	2105.72(7)	2457.7(19)	3187.0(3)
Z	4	8	4	4	4	4
μ/mm^{-1}	0.988	1.076	1.139	0.087	0.950	0.917
Reflections collected	15442	17448	34249	7640	5413	21043
Independent reflections	5685 ($R_{int} = 0.0587$)	6471 ($R_{int} = 0.0735$)	12571 ($R_{int} = 0.0698$)	2338 ($R_{int} = 0.0217$)	4296 ($R_{int} = 0.0957$)	2338 ($R_{int} = 0.0217$)
Final $R1$, $WR2$ indices [$I > 2\sigma(I)$]	0.0370, 0.0897	0.0453, 0.1053	0.0534, 0.1337	0.0365, 0.0856	0.0657, 0.1715	0.0349, 0.0731
(all data)	0.0478, 0.0952	0.0623, 0.1134	0.0903, 0.1539	0.0471, 0.0947	0.1153, 0.2119	0.0430, 0.0826

mented on the Viglen Pentium computer; XSCANS was used for the P4.[7]

CCDC reference number 186/1686.

See http://www.rsc.org/suppdata/dt/1999/4131/ for crystallographic files in .cif format.

Results and discussion

Macrocyclic Schiff base complexes

The diimine macrocyclic complexes were synthesised by the metal templated cyclocondensation of 2,6-pyridinedicarbaldehyde and 1,5-bis(2-aminophenoxy)-3-azapentane in refluxing acetonitrile in the presence of the appropriate zinc(II) or cadmium(II) salt demonstrating that it is indeed possible to use metals other than the alkaline earth metals as templates when the donor set in the 18-membered ring macrocycle is changed from N_3O_3 to N_4O_2. The complexes were characterised by elemental analysis, IR, NMR (^1H and ^{13}C) and FAB MS. The IR of the complexes showed no bands corresponding to NH_2 and C=O groups and were consistent with the formation of imine linkages. For the perchlorate complexes absorptions attributable to ionic perchlorate were found,[8] and for the nitrate complexes it was possible to distinguish the vibrations associated with coordinated nitrate as well as a band at 1384 cm^{-1} arising from ionic nitrate;[9] the ν_1–ν_4 separation suggested that at least one nitrate would be bidentate. The FAB MS of the complexes gave highest peaks corresponding to $[MLX]^+$; in the case of $[Zn_2L^1_2(OH)][ClO_4]_3$ **3** the hydroxide bridge is cleaved and no higher peaks were detected. The molar conductivity of complex **1** in acetonitrile indicated that this nitrate complex is a 1:1 electrolyte; in the crystalline state, as discussed below, the nitrate anions in **1** are coordinated to the metal but one is more distant than the other and so might be more readily displaced in solution. The cadmium perchlorate complex **2** is a 2:1 electrolyte and the zinc perchlorate complex **3** is a 3:1 electrolyte.[10] This reflects the weaker coordinating ability of perchlorate relative to nitrate and this is further shown in the crystalline state where the perchlorate anions are non-coordinated. The NMR spectra of the complexes are unremarkable and are reported in the Experimental section.

The X-ray structure analyses of three of the complexes confirm that the metal cation has been incorporated on complexation to generate endomacrocyclic complexes; both cadmium complexes **1** and **2** are mononuclear whereas the zinc perchlorate complex is an uncommon μ-hydroxo-bridged dinuclear species **3**.

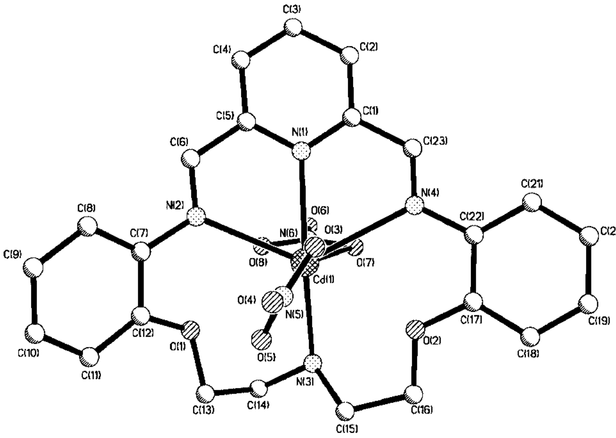


Fig. 1 The molecular structure of complex **1**, $[CdL^1(NO_3)_2]$. Selected bonds and angles: Cd(1)–O(3), 2.376(2); Cd(1)–N(2), 2.556(2); Cd(1)–N(1), 2.389(2); Cd(1)–O(7), 2.595(2); Cd(1)–N(3), 2.397(2); Cd(1)–N(4), 2.658(2); Cd(1)–O(8), 2.544(2) Å. O(3)–Cd(1)–N(1), 83.90(8); O(3)–Cd(1)–O(7), 145.17(7); O(3)–Cd(1)–N(3), 119.60(8); N(1)–Cd(1)–O(7), 81.91(7); N(1)–Cd(1)–N(3), 155.98(7); N(3)–Cd(1)–O(7), 75.61(7); O(3)–Cd(1)–O(8), 155.82(7); O(8)–Cd(1)–O(7), 49.23(6); N(1)–Cd(1)–O(8), 79.82(7); N(2)–Cd(1)–O(7), 121.73(6); N(3)–Cd(1)–O(8), 79.14(7); O(3)–Cd(1)–N(4), 75.64(7); O(3)–Cd(1)–N(2), 80.18(7); N(1)–Cd(1)–N(4), 64.83(7); N(1)–Cd(1)–N(2), 66.30(7); N(3)–Cd(1)–N(4), 113.58(7); N(3)–Cd(1)–N(1), 119.37(7); O(8)–Cd(1)–N(4), 112.55(7); O(8)–Cd(1)–N(2), 79.95(6); N(2)–Cd(1)–N(4), 127.02(7)°.

The structures of the cadmium complexes of L^1

The molecular structures of the cationic unit present in the cadmium complexes, **1** and **2**, are given in Figs. 1 and 2 respectively, together with selected bond lengths and angles relating to the coordination environment of the metal. In **1** the metal is seven-coordinate with a distorted capped trigonal prismatic (1:4:2) geometry arising from coordination by the four N atoms of the macrocycle, and three O atoms from a monodentate nitrate [Cd(1)–O(3), 2.38 Å] and an asymmetric, bidentate nitrate [Cd(1)–O(8), 2.54 Å; Cd(1)–O(7), 2.60 Å] sited *trans* to the macrocyclic plane and in **2** the metal is six-coordinate with a distorted octahedral geometry arising from coordination by the four N atoms of the macrocycle, and two O atoms from water molecules sited *trans* to the macrocyclic plane. These O atoms are asymmetrically bound, Cd(1)–O(11), 2.26 Å and Cd(1)–O(12), 2.36 Å. The perchlorate anions are non-coordinating and so the cadmium structures reflect the relative coordinating abilities of the nitrate and perchlorate anions.

Table 2 Structures of zinc complexes with single hydroxide bridges

Compound	Zn···Zn/Å	Zn–O–Zn/°	Coordination numbers (and geometries)	Ref.
$[(L^A)Zn_2(\mu\text{-}OH)(2\text{-hydroxypyridinate})][ClO_4]_3$ [b]	3.46	n/r [a]	6 (distorted O_h) and 5 (intermediate between square bipyramid and trigonal bipyramid)	22
$[(L^B)Zn_2(\mu\text{-}OH)][ClO_4]_3$ [b]	3.54	137.1	6 and 6 (both distorted trigonal prisms)	23
$[(L^C)Zn_2(\mu\text{-}OH)][ClO_4]_3$ [b]	3.63	140.2	4 and 4 (both distorted tetrahedra)	15
$[(L^DH)_2Zn_2(\mu\text{-}OH)][PF_6]$ [b]	3.08	131	6 and 6 (both distorted octahedra)	24
$[(L^E)_3Zn\text{-}(\mu\text{-}OH)\text{-}Zn(L^E)_3][ClO_4]_3$ [b]	3.54	137	4 and 4 (both distorted tetrahedra)	14
$[(L^F)Zn_4(\mu\text{-}OH)_2(\mu\text{-}O_2CMe)_2][ClO_4]_2\cdot 2H_2O$ [b]	3.40 3.41	n/r [a]	5 and 5 (both trigonal bipyramid)	25
$[(L^1)_2Zn\text{-}(\mu\text{-}OH)\text{-}Zn][ClO_4]_3$ [b]	3.60	141	5 and 5 (both distorted square coplanar)	This work

[a] n/r = not reported. [b] Abbreviations of ligands: L^A = 4,7,10,23-tetramethyl-17-oxa-1,4,7,10,13,23-hexaazabicyclo[11.7.5]pentacosane, L^B = 1,4,7,16,19,22-hexaaza-10,13,25,28-tetraoxacyclotriacontane, L^C = α,α′-bis(bis(2-pyridylethyl)amino)-*m*-xylene, L^D = 4,7-di(2-hydroxybenzyl)-1-oxa-4,7-dioxacyclononane, L^E = 5-*tert*-butylpyrazole, L^1 = 10,16-dioxa-3,13,23,29-tetraazatetracyclo[23.3.1.0^{4,9}.0^{17,22}]nonacosa-1(29),2,4(9),5,7,17,19,21,23,25,27-undecaene, L^F = [2 + 2] macrocycle derived from 2,6-diformyl-4-methylphenol and 1,11-diamino-3,6,9-trioxaundecane.

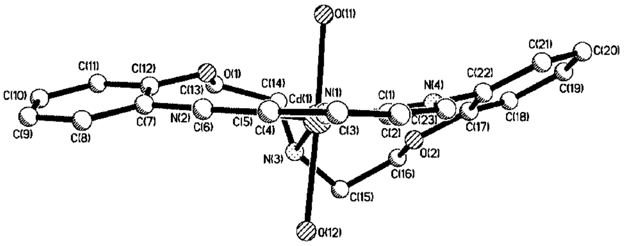


Fig. 2 The molecular structure of the cation from complex **2**, $[CdL^1(H_2O)_2][ClO_4]_2$, viewed in the plane of the pyridinyl head group. Selected bonds and angles: Cd(1)–O(11), 2.256(2); Cd(1)–N(3), 2.371(3); Cd(1)–O(12), 2.359(2); Cd(1)–N(4), 2.540(3); Cd(1)–N(1), 2.363(3); Cd(1)–N(2), 2.585(3) Å. O(11)–Cd(1)–N(1), 177.71(9); N(1)–Cd(1)–N(4), 66.80(9); O(11)–Cd(1)–N(3), 99.17(9); N(3)–Cd(1)–N(4), 122.75(9); O(12)–Cd(1)–N(3), 80.46(9); O(11)–Cd(1)–N(2), 93.97(8); O(11)–Cd(1)–O(8), 96.56(9); O(12)–Cd(1)–N(2), 83.80(8); O(12)–Cd(1)–O(8), 83.52(8); N(1)–Cd(1)–N(2), 67.45(6); N(1)–Cd(1)–O(8), 162.56(9); N(3)–Cd(1)–N(2), 104.08(8); O(11)–Cd(1)–N(2), 83.64(9); N(4)–Cd(1)–N(2), 133.12(8); O(12)–Cd(1)–N(2), 98.25(9)°.

The geometric distortion in the complexes arises in part from the distortion of the rectangular arrangement of the ligand N atoms. This is imposed by rigidity of the pyridinyldiimino-fragment within the ligand framework. In **1** the plane containing N(1)N(2)N(3)N(4) has an r.m.s. deviation from planarity of 0.308 Å and the Cd(1) is displaced from this towards the monodentate nitrate by 0.1826 (0.0012) Å. In **2** the corresponding plane containing N(1)N(2)N(3)N(4) has a smaller r.m.s. deviation from planarity of 0.179 Å and the Cd(1) is now displaced from this towards the water molecule containing O(12) by 0.1276 (0.0013) Å [N(2)Cd(1)N(4)]. In both complexes the Cd–N_{imine} distances (2.5–2.6 Å) are longer than the Cd–N_{py} (*ca.* 2.37 Å) and Cd–N_{amine} (*ca.* 2.38 Å) and the O_{ether} atoms at the distances of Cd–O(1), 2.90 Å and Cd–O(2), 2.77 Å in **1** and Cd–O(1), 2.97 Å and Cd–O(2), 2.72 Å in **2** from the metal leading to weak, long range interactions.

The pyridine and benzenes are all coplanar and the bonds and angles within the macrocyclic framework are as expected. The macrocycle is somewhat buckled in each case. For **1** the plane derived from N(2)C(6)C(5)N(1)C(1)C(23)N(4) and the phenyl rings C(7)–C(12) and C(17)–C(22) are inclined at 43.7 and 23.7° respectively to this plane and the dihedral angle between the two aromatic rings is 53.1°. In **2** the plane derived from N(2)C(6)C(5)N(1)C(1)C(23)N(4) and the phenyl rings C(7)–C(12) and C(17)–C(22) are more shallowly inclined at 13.7 and 28.8°; the dihedral angle between the two aromatic rings is now 33.5°.

One of the noncoordinated perchlorate anions in **2** is weakly involved in hydrogen bonding with a coordinated water molecule, O(7)···O(11), 2.76 Å and there are further weak hydrogen bonds from the water molecules to perchlorate anions in the symmetry related positions shown—O(11)···O(9) (−*x* + 1, *y*, −*z* + 3/2), 2.84 Å, O(12)–H(3W)···O(5) (*x* − 1/2, *y* − 1/2, −*z*), 2.81 Å and O(12)–H(4W)···O(4) (−*x* + 1, *y*, −*z* + 3/2), 2.97 Å.

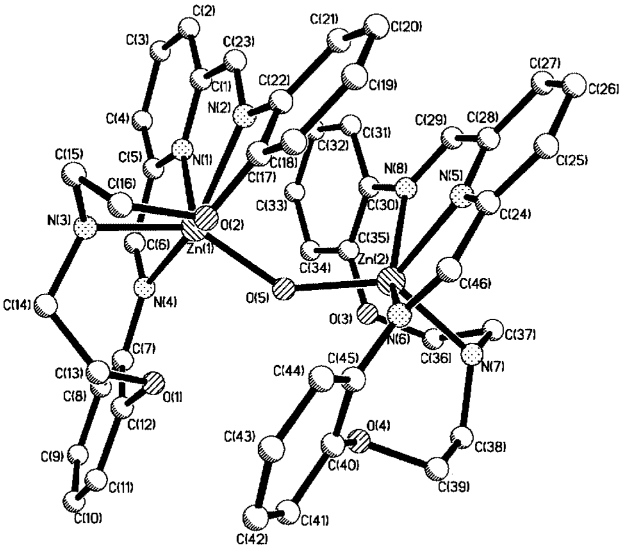
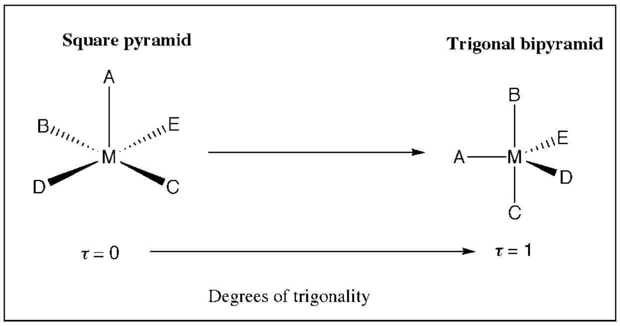


Fig. 3 The molecular structure of the cation from complex $\mathbf{3}\cdot CH_3CN$, $[Zn_2L^1_2(OH)][ClO_4]_3\cdot CH_3CN$. Selected bonds and angles: Zn(1)–O(5), 1.904(2); Zn(2)–O(5), 1.910(2); Zn(1)–N(3), 2.066(3); Zn(2)–N(5), 2.107(3); Zn(1)–N(1), 2.094(3); Zn(2)–N(7), 2.108(3); Zn(1)–N(2), 2.249(3); Zn(2)–N(8), 2.279(3); Zn(1)–N(4), 2.426(3); Zn(2)–N(6), 2.323(3) Å. O(5)–Zn(1)–N(3), 136.14(11); O(5)–Zn(2)–N(5), 129.92(10); O(5)–Zn(1)–N(1), 121.73(10); O(5)–Zn(2)–N(7), 128.95(10); N(3)–Zn(1)–N(1), 101.24(11); N(5)–Zn(2)–N(7), 101.12(11); O(5)–Zn(1)–N(2), 97.98(10); O(5)–Zn(2)–N(8), 97.81(10); N(3)–Zn(1)–N(2), 101.65(11); N(5)–Zn(2)–N(8), 73.50(11); N(1)–Zn(1)–N(2), 74.77(10); N(7)–Zn(2)–N(8), 97.60(10); O(5)–Zn(1)–N(4), 96.82(9); O(5)–Zn(2)–N(6), 95.19(10); N(3)–Zn(1)–N(4), 87.73(10); N(5)–Zn(2)–N(6), 72.37(11); N(1)–Zn(1)–N(4), 72.06(10); N(7)–Zn(2)–N(6), 99.99(10); N(2)–Zn(1)–N(4), 146.69(10); N(8)–Zn(2)–N(6), 143.95(10); Zn(1)–O(5)–Zn(2), 141.50 (12)°.

The structure of the dinuclear zinc complex of L^1

The molecular structure of the cationic unit present in the dinuclear zinc complex, $\mathbf{3}\cdot CH_3CN$, is given in Fig. 3, together with selected bond lengths and angles relating to the coordination environment of the metal. The zinc atoms are 3.60 Å apart and the Zn–O–Zn angle is 141.5°. Although there are numerous examples of zinc complexes with multiple hydroxo bridges instances of unsupported, or single, μ-hydroxo bridged complexes are less evident.[12,13] Details of the structures of such complexes are given in Table 2. It is noted that for the first four complexes the dinuclear moiety is held within a single ligand framework and so a direct structural comparison can only be made with $[(L^E)_3Zn\text{–}OH\text{–}(L^E)_3][ClO_4]_3$ in which the two zinc atoms are four coordinate, there is a Zn···Zn separation of 3.54 Å and the Zn–O–Zn angle is 137°.[14] In the complex

$[(L^C)Zn_2OH][ClO_4]_3$ the two zinc atoms are both in distorted tetrahedral environments but slight differences in the bonds and angles lead to inequivalent zinc-containing sites.[15] A similar situation exists in **3**·CH_3CN where although the Zn–OH distances are similar [Zn(1)–O(5), 1.904(2) Å and Zn(2)–O(5), 1.910(2) Å] the molecule is not symmetric as there are differences in the metal coordination geometries and the macrocyclic configurations as discussed below.



Addison *et al.* have formulated an algebraic expression which has proven to be extremely useful for assessing the degree of trigonality (τ) in a given five-coordinate transition metal complex. τ is considered as the index of trigonality within the structural continuum between ideal square pyramidal and perfectly trigonal bipyramidal geometry and is defined by the expression $\tau = (\beta - \alpha)/60$.[16] In a typical square pyramidal molecule there is an apex A and an equatorial plane defined by BCDE. The apical donor atom A should not be designated as any of the atoms which are associated with the two largest angles (α,β) at the metal centre. Consequently the limiting cases are $\tau = 0$ for the square pyramid and $\tau = 1$ for the trigonal bipyramid. In the present case, where the zinc atoms are both five coordinated by four macrocycle N atoms and the bridging O atom of the coordinated hydroxide, it is possible to use this formula to show that the geometry at Zn(2) is distorted square pyramidal with $\tau = 0.23$. The geometry is such that the amino nitrogen atom N(7) is at the apex and the base is provided by the plane O(5)N(5)N(8)N(6) which has an r.m.s. deviation from planarity of 0.178 Å. Applying the same criteria to Zn(1) gives a less clear result. The differences of largest angles gives a τ value of 0.18 with the pyridine nitrogen atom N(1) at the apex and O(5)N(2)N(3)N(4) as the basal plane. This plane however is considerably distorted with a r.m.s. deviation from planarity of 0.699 Å. If the second largest angular difference is used then the amino nitrogen N(3) becomes the apex and so the ligand configuration is similar to that found at Zn(2). The τ factor is now 0.41 indicating a significant distortion towards trigonal bipyramidal and the basal plane, formed by O(5)N(2)N(1)N(4), has a much reduced mean displacement of 0.293 Å. For completeness it is noted that the second largest angular differences found at Zn(2) give rise to a τ value of 0.25 with pyridine nitrogen atom N(5) at the apex and O(5)N(6)N(7)N(8) as the basal plane, the deviation from planarity of which is 0.781 Å. The ambiguity in using the τ formula in this case is ascribed to the distortions caused by geometric constraints imposed by the semi-flexible macrocyclic ligand.

In both macrocyclic units the $Zn–N_{imine}$ distances (2.25–2.42 Å) are longer than the $Cd–N_{py}$ (*ca.* 2.1 Å) and $Cd–N_{amine}$ (*ca.* 2.1 Å) with the O_{ether} atoms at distances of Zn(1)–O(1) 2.81 Å, Zn(1)–O(2) 2.84 Å, Zn(2)–O(3) 2.86 Å, and Zn(2)–O(4), 2.90 Å suggesting weaker interactions. The pyridine and benzenes are all coplanar and the bonds and angles within the macrocyclic framework are as expected. Each of the macrocycles are buckled; in the macrocycle ligating Zn(1) the plane derived from N(2)C(23)C(1)N(1)C(5)C(6)N(4) has the phenyl rings C(7)–C(12) and C(17)–C(22) inclined at 12.1 and 28.3° respectively to this plane with a dihedral angle between the two aromatic rings of 20.6°. In the macrocycle ligating Zn(2) the plane derived from N(8)C(29)C(28)N(5)C(24)C(46)N(6) has the phenyl rings C(30)–C(35) and C(40)–C(45) inclined at 36.6 and 38.6° respectively to this plane; the dihedral angle between the two aromatic rings is now 57.5°.

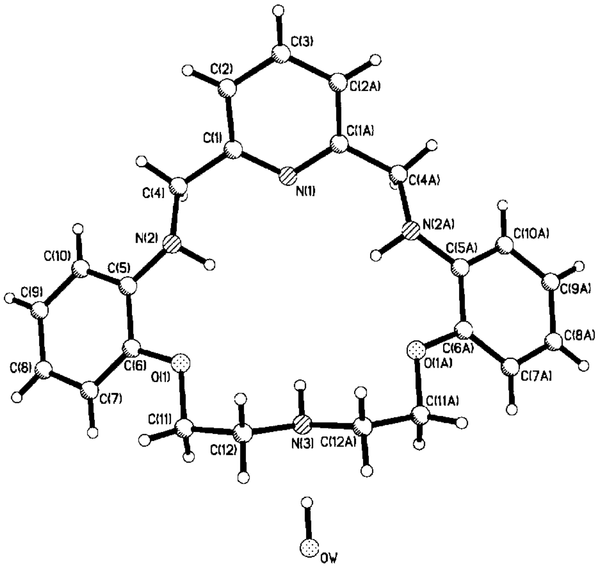


Fig. 4 The molecular structure of the free macrocycle L^2.

The three non-coordinated perchlorate anions are disordered with occupancies of 53 and 47% for the two components of $Cl(1)O_4$, 71 and 29%, for the two components of $Cl(2)O_4$ and 54 and 46%, for the two components of $Cl(3)O_4$.

The free reduced macrocycle L^2

Tetrahydroborate reduction of a range of Schiff base diimine macrocyclic complexes, prepared by template synthesis on manganese(II) or lead(II) has afforded a useful route to the corresponding metal-free macrocycles.[11] In the present study the manganese(II) templated cyclocondensation of 2,6-pyridinedicarbaldehyde and 1,5-bis(2-aminophenoxy)-3-azapentane in methanol followed by an *in situ* reductive demetallation of the Schiff base macrocyclic manganese(II) complex using excess sodium borohydride readily gave the metal-free macrocyclic ligand L^2—it is possible to isolate the Schiff base complex but crystals suitable for X-ray analysis have so far proved elusive. The reduced form of macrocycle L^B was only obtained when lead(II) was used as the template and so the change in donor set is important in modifying the conditions required to produce L^2. Macrocycle L^2 was characterised by elemental analysis, IR, NMR (^1H and ^{13}C) and FAB MS. The IR showed no bands corresponding to NH_2, C=O or C=N groups and bands were observed ascribable to the secondary amines present in L^2. The FAB MS gave a parent peak at *m*/*z* 391 $[L^2 + 1]^+$ confirming that a macrocycle derived from a 1 + 1 condensation had been formed. The NMR data are summarised in the Experimental section.

The X-ray crystal structure of the ligand L^2, recrystallised from acetonitrile, confirmed the macrocyclic nature of the product (Fig. 4). The bond lengths and angles do not show any significant deviations from the expected values. The macrocyclic ring is somewhat bent, having a butterfly shape, with the benzene rings forming a dihedral angle of 57.3° and the pyridine ring lying at an angle of 48.4° to them. There is a water of crystallisation a hydrogen atom of which undergoes a weak hydrogen bonded interaction with N(3), [N(3)···O(2), 2.86 Å].

The metal complexes of L^2

The zinc(II) and cadmium(II) complexes of L^2 were synthesised by reaction of the ligand and the appropriate metal salt in refluxing acetonitrile. The complexes were characterised by elemental analysis, IR, NMR (^{1}H and ^{13}C) and FAB MS. The IR of the complexes showed no bands corresponding to NH_2, C=O or C=N groups but gave bands *ca.* 3250 cm^{-1} corresponding to the secondary amine present. For the perchlorate complexes a splitting of the band at 1100 cm^{-1} suggests that there could be a possible coordination of the perchlorate group but such a splitting can also arise from hydrogen bonding to anion-coordinated perchlorate, loss of symmetry occurring in both cases. As found for the Schiff base complexes the vibrations associated with a coordinated nitrate were noted together with a band arising from ionic nitrate. The FAB MS of the complexes gave highest peaks corresponding to $[MLX]^+$ and the molar conductivities of the complexes in acetonitrile indicated that the nitrate complexes were 1 : 1 electrolytes and that the perchlorate complexes were 2 : 1 electrolytes suggesting a similar solution behaviour as found for the complexes of L^1. The NMR spectra of the complexes showed, in general, downfield shifts of signals on coordination suggesting an interaction of the metal with all available donor atoms. No clear pattern of shift emerged to support the metal–donor interactions noted in the crystal structures. The 1 : 1 stoichiometry of the complexes in solution was established by NMR titrimetry in CD_3CN. For the cadmium complexes **5** and **6** the metal ion must be strongly complexed because there is an immediate ingrowth of the signals due to the metal complex when the metal salt solution is added to the ligand solution. In contrast only broad signals occur as the formation of $[ZnL^2(NO_3)_2]$ procedes; this may be due to an exchange process indicating a weaker coordination of the zinc although the presence of different conformers in solution cannot be discounted. Certain oxaazamacrocycles have been shown to exhibit a marked preference for cadmium over zinc and it has been suggested that this arises from 'structural dislocations', abrupt changes in coordination geometry, between the respective complexes.[17–21] It is possible to speculate that this is the case here but in the absence of crystals of the zinc complex it has not been possible to determine the precise nature of the bonding to the macrocycle.

The structures of the cadmium complexes of L^2

X-Ray structure analysis confirmed that both **4** and **5**, were mononuclear endomacrocyclic complexes. The molecular structures of the cationic unit present in the cadmium complexes, **4** and **5**, are given in Figs. 5 and 6 respectively, together with selected bond lengths and angles relating to the coordination environment of the metal. In **4** the metal is again seven-coordinate with a distorted capped trigonal prismatic (1 : 4 : 2) geometry arising from coordination by the four N atoms of the macrocycle, and three O atoms from a monodentate nitrate [Cd(2)–O(6), 2.38 Å] and an asymmetric, bidentate nitrate [Cd(2)–O(3), 2.53 Å; Cd(2)–O(4), 2.61 Å] sited *trans* to the macrocyclic plane and in **5** the metal is also seven-coordinate but with a pentagonal bipyramidal geometry arising from coordination by the four N atoms and one ether oxygen atom, O(2), of the macrocycle, and two N atoms from acetonitrile molecules sited *trans* to the macrocyclic plane. These N atoms are symmetrically bound, Cd(1)–N(5), 2.44 Å and Cd(1)–N(6), 2.41 Å. The perchlorate anions are non-coordinating and so the structures again reflect the relative coordinating abilities of the nitrate and perchlorate anions. One of the perchlorate cations is disordered with occupancies of 60 and 40%, for the two components present. The Flack parameter for **5** is −0.040(19).

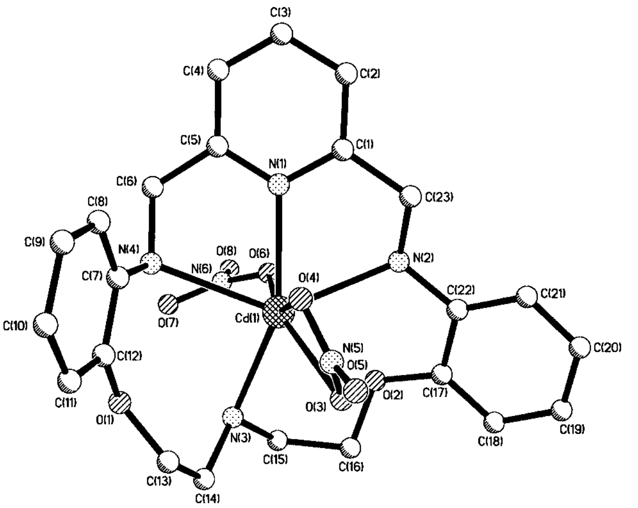


Fig. 5 The molecular structure of complex **4**, $[CdL^2(NO_3)_2]$. Selected bonds and angles: Cd(1)–N(3), 2.370(7); Cd(1)–O(3), 2.530(11); Cd(1)–N(1), 2.378(6); Cd(1)–N(4), 2.558(7); Cd(1)–O(6), 2.385(8); Cd(1)–O(4), 2.610(11); Cd(1)–N(2), 2.466(7) Å. N(3)–Cd(1)–N(1), 154.4(3); N(3)–Cd(1)–O(3), 83.1(3); N(3)–Cd(1)–O(6), 83.2(3); N(1)–Cd(1)–N(4), 90.9(3); N(1)–Cd(1)–O(6), 81.4(3); N(3)–Cd(1)–N(4), 68.3(2); N(3)–Cd(1)–N(2), 129.4(2); O(8)–Cd(1)–N(4), 87.8(3); N(1)–Cd(1)–N(2), 68.6(2); N(2)–Cd(1)–N(4), 136.8(2); O(6)–Cd(1)–N(2), 83.1(2); O(3)–Cd(1)–N(4), 120.6(3); O(3)–Cd(1)–O(3), 84.4(2); N(1)–Cd(1)–O(4), 120.2(3); N(3)–Cd(1)–O(3), 118.5(3); N(3)–Cd(1)–O(4), 74.9(3); N(1)–Cd(1)–O(3), 149.1(3)°.

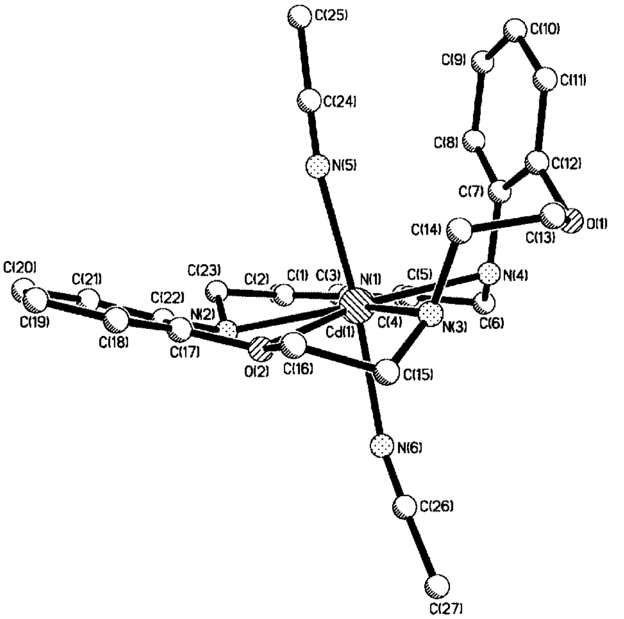
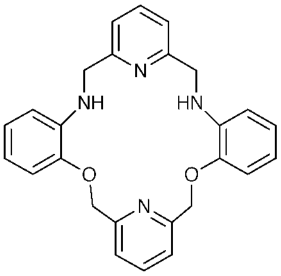


Fig. 6 The molecular structure of the cation from complex **5**, $[CdL^2(CH_3CN)_2][ClO_4]_2$, viewed along the plane of the pyridinyl head group. Selected bonds and angles: Cd(1)–N(1), 2.330(3); Cd(1)–N(5), 2.438(3); Cd(1)–N(3), 2.368(3); Cd(1)–O(2), 2.486(2); Cd(1)–N(6), 2.413(3); Cd(1)–N(4), 2.583(3); Cd(1)–N(2), 2.423(3) Å. N(11)–Cd(1)–N(1), 153.55(10); N(1)–Cd(1)–O(2), 135.63(9); N(11)–Cd(1)–N(3), 91.35(10); N(3)–Cd(1)–O(2), 69.95(9); N(12)–Cd(1)–N(3), 84.82(11); N(6)–Cd(1)–O(2), 83.05(10); N(11)–Cd(1)–N(8), 70.67(9); N(2)–Cd(1)–O(2), 65.20(9); N(12)–Cd(1)–N(8), 135.11(10); N(5)–Cd(1)–O(2), 89.92(10); N(1)–Cd(1)–N(8), 88.20(11); N(1)–Cd(1)–N(4), 68.69(9); N(11)–Cd(1)–N(2), 92.89(10); N(3)–Cd(1)–N(4), 85.25(9); N(11)–Cd(1)–N(2), 93.87(10); N(6)–Cd(1)–N(4), 91.77(11); N(11)–Cd(1)–N(2), 172.88(12); N(2)–Cd(1)–N(4), 139.34(9); N(11)–Cd(1)–N(2), 87.81(10); N(5)–Cd(1)–N(4), 95.09(10)°.

The geometric distortion in **4** again arises in part from the distortion of the rectangular arrangement of the ligand N atoms. In **4** the plane containing N(1)N(2)N(3)N(4) has an r.m.s. deviation from planarity of 0.067 Å and the Cd is displaced from this by 0.2665 (0.0045) Å towards the bidentate nitrate anion, in contrast to the pattern observed for **1**. In **4** the corresponding plane containing N(1)N(2)N(3)N(4) has an r.m.s. deviation from planarity of 0.021 Å and the Cd is now displaced from this by 0.0819 (0.0015) Å towards the N(5) atom of a coordinated acetonitrile molecule. In both complexes the Cd–N$_{amine}$ distances, relating to the amines derived from the reduced imines, (2.4–2.6 Å) are longer than the Cd–N$_{py}$ (*ca.* 2.36 Å) and remaining Cd–N$_{amine}$ (*ca.* 2.37 Å). The Cd–O$_{ether}$

distance in **5** is 2.49 Å and the remaining O_{ether} atoms lie at distances from the metal of 3.93 Å [Cd–O(1)] in **5** and 3.44 Å [Cd–O(1)] and 2.68 Å [Cd–O(2)] in **4**; the latter may be viewed as a weak long range interaction.

The pyridine and benzenes are each coplanar and the bonds and angles within the macrocyclic framework are as expected. The macrocycle L^2 is significantly buckled in each complex relative to the buckling of L^1 in its complexes, thus reflecting the greater flexibility inherent in the reduced ligand. For **4** the plane derived from N(4)C(6)C(5)N(1)C(1)C(23)N(2) and the phenyl rings C(7)–C(12) and C(17)–C(22) are inclined at 72.0 and 20.4 Å respectively; the dihedral angle between the phenyl rings is much increased from that in the complexes of L^1 at 88.2 Å. In **5** the plane derived from N(2)C(23)C(1)N(1)C(5)C(6)N(4) and the phenyl rings C(7)–C(12) and C(17)–C(22) are inclined at 94.7 and 163.0 Å respectively; the dihedral angle between the phenyl rings is again much increased from that in the complexes of L^1 at 101.4 Å.



L^G

The structures of the cadmium complexes may be compared with that of $[CdL^G(MeOH)_{0.5}(H_2O)_{0.5}(NO_3)][ClO_4]$ derived from the related macrocycle L^G.[20] In this complex a more symmetric coordination environment is found even though the ligand adopts a very twisted conformation. The cadmium is eight coordinated by all six donor atoms of the ligand together with a monodentate nitrate anion in one 'axial' site with the remaining axial site occupied by a water molecule in one half of the molecules and a methanol in the remaining half. The Cd–N distances in this molecule range from 2.43 to 2.58 Å and the Cd–O distances from 2.35–2.42 Å. It is possible that the presence of the two pyridine groups in L^G allow a more cadmium compatible macrocyclic cavity to be formed than can occur with the more flexible macrocycle L^2.

Conclusions

Mononuclear cadmium(II) macrocyclic Schiff base complexes and a dinuclear, μ-hydroxy-bridged zinc(II) macrocyclic Schiff base complex have been prepared by the metal templated cyclocondensation of 2,6-pyridinedicarbaldehyde and 1,5-(2-aminophenoxy)-3-azapentane. This has provided a new oxaaza macrocyclic ligand and the opportunity to utilise the amino-group in the linker unit to introduce a range of pendant arms. Mononuclear cadmium(II) and zinc(II) complexes of the corresponding reduced macrocycle, L^2, have also been synthesised. Comparison of the crystal structures of the cadmium(II) complexes $[CdL^1(NO_3)_2]$ **1**, $[CdL^1(H_2O)_2][ClO_4]_2$ **2**, $[CdL^2(NO_3)_2]$ **4** and $[CdL^2(CH_3CN)_2][ClO_4]_2$ **5** show that there is an enhancement of ligand flexibility on reduction which is manifest by the more 'cleft'-like conformation found in the complexes of L^2. The nitrate anions are metal coordinated whereas the perchlorate anions are not, clearly indicating their relative coordinating strengths. The complex $[Zn_2L^1_2(OH)][ClO_4]_3\cdot CH_3CN$ provides a rare example of an unsupported dinuclear μ-hydroxy-bridged complex.

Acknowledgements

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