Metal-ion Selectivity by Macrocyclic Ligands. Part 3.[1] The Interaction of Mn^{II} and Co^{II} with Pyridinyl-derived N_3O_2 Macrocycles; X-Ray Structures of Endomacrocyclic Complexes of Mn^{II} and Co^{II}†

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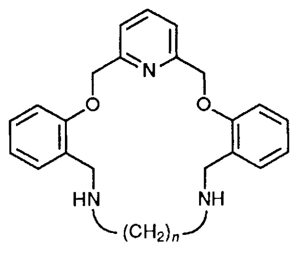
The interaction of Mn^{II} and Co^{II} with the macrocycles L^1 and L^2, each containing an N_3O_2-donor set, has been investigated. Conductometric titration of the 1:1 Mn^{II} complexes with chloride indicated the formation of a 2:1 complex presumably through bridging of a chloride ion. The stability constants of the complexes have been determined in 95% methanol. The X-ray crystal structures of the 1:1 complexes $[MnL^1Br(EtOH)]ClO_4$ and $[CoL^1(NO_3)]NO_3$, have been determined. The metal in $[MnL^1Br(EtOH)]ClO_4$ is seven-co-ordinate and lies within the macrocyclic cavity. The donor set comprises the five macrocyclic donor atoms, a bromide anion and an ethanol molecule. Overall, the co-ordination sphere corresponds to a distorted pentagonal-bipyramidal arrangement. The complex $[CoL^1(NO_3)]NO_3$ also has all donors of the macrocycle co-ordinated together with a nitrate anion. The cobalt is seven-co-ordinated and the co-ordination polyhedron is intermediate between a capped trigonal prism and a pentagonal bipyramid.

In the first two parts of this series the interactions of the oxaazamacrocycles L^1 and L^2 with Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Hg^{II} have been discussed.[1,2] These have shown endo- (Cu^{II}, Ni^{II}, Zn^{II} and Cd^{II}) or exo-macrocyclic (Zn^{II} and Hg^{II}) complexation and the establishment of discrete 2:1 (ligand:metal) complexes for Cu^{II} and Ni^{II}. For the Zn^{II} complexes the nature of the metal incorporation is governed by the nature of the accompanying anion with iodide leading to exo- and nitrate giving endo-macrocyclic complexation. In the endomacrocyclic complexes the aliphatic nitrogen-atom configurations are *S,S* (or *R,R*) whereas in the exomacrocyclic complexes the aliphatic nitrogen-atom configurations are *R,S* (or *S,R*). This paper extends the study to interactions of the oxaazamacrocycles with Co^{II} and Mn^{II} and reports the X-ray crystal structures of the 1:1 endomacrocyclic complexes $[MnL^1Br(EtOH)]ClO_4$ and $[CoL^1(NO_3)]NO_3$.



L^1 $n = 2$
L^2 $n = 3$

Experimental

The details of the physical measurements have been given previously, as have been the syntheses of the macrocyclic ligands and general procedure for the preparation of the metal complexes.[1,2]

Crystal Structure Data and Determination.—Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 four-circle diffractometer by the omega scan method. The data for the manganese complex were collected rapidly since the crystals were prone to sudden decay; no intensity loss was detected during the data collection. Complex scattering factors were taken from ref. 3 and from the program package SHELXTL[4] as implemented on the Data General Nova 3 computer. Unit weights were used throughout the refinements and showed satisfactory convergence. Tables 1 and 2 list atomic positional parameters with estimated standard deviations.

Crystal data for $[CoL^1(NO_3)]NO_3$. $C_{23}H_{25}CoN_5O_8$, $M = 558.41$, crystallises from methanol as dark red prisms, crystal dimensions $0.80 \times 0.30 \times 0.30$ mm. Orthorhombic, space group $Pna2_1$ (C^9_{2v}, no, 33), $a = 16.838(18)$, $b = 12.295(24)$, $c = 11.459(30)$ Å, $U = 2372(8)$ Å^3, $Z = 4$, $D_c = 1.564$ g cm^{-3}, Mo-Kα X-radiation ($\lambda = 0.710\,69$ Å) with graphite monochromator, μ(Mo-Kα) = 7.77 cm^{-1}, $F(000) = 1155.75$.

The 1553 independent reflections (of 2400 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.695 and 0.792). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii xxii.

Table 1 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for [MnL^{1}Br(EtOH)]ClO$_4$*

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn	−481(4)	1562(2)	2240(3)	C(6)	−2707(31)	473(13)	1825(26)
Br	457(4)	1778(2)	4394(3)	C(7)	−3413(30)	1263(13)	2791(26)
Cl(1)	−4381(11)	932(4)	−2132(10)	C(8)	−3690(30)	899(14)	3602(25)
Cl(2)	−4603(43)	985(17)	−2402(36)	C(9)	−4307(33)	1137(15)	4323(30)
O(1)	−2813(22)	1100(8)	2011(17)	C(10)	−4709(34)	1702(14)	4289(28)
O(2)	1839(19)	1209(9)	2533(18)	C(11)	−4434(27)	2081(12)	3526(22)
O(3)	−1311(21)	1339(10)	384(16)	C(12)	−3810(25)	1859(11)	2746(21)
O(4)	−3611(11)	698(4)	−2782(10)	C(13)	−3387(30)	2262(14)	1962(26)
O(5)	−3704(11)	1412(4)	−1503(10)	C(14)	−1526(27)	2835(12)	1693(23)
O(6)	−5642(11)	1118(4)	−2839(10)	C(15)	−45(25)	2875(11)	2013(21)
O(7)	−4585(11)	501(4)	−1392(10)	C(16)	2050(24)	2357(11)	1956(21)
O(8)	−5267(43)	501(17)	−2919(36)	C(17)	2553(27)	1862(12)	1387(22)
O(9)	−5490(43)	1435(17)	−2508(36)	C(18)	3097(25)	1990(11)	494(20)
O(10)	−4002(43)	870(17)	−1284(36)	C(19)	3560(32)	1529(14)	1(27)
O(11)	−3641(43)	1139(17)	−2885(36)	C(20)	3525(35)	957(16)	375(30)
N(1)	−250(20)	545(9)	2669(16)	C(21)	3030(27)	794(12)	1277(22)
N(2)	−1924(20)	2329(9)	2245(19)	C(22)	2564(30)	1274(13)	1705(25)
N(3)	569(22)	2336(8)	1665(16)	C(23)	2215(30)	730(13)	3352(26)
C(1)	970(22)	352(10)	3258(18)	C(24)	−656(58)	1279(20)	−484(40)
C(2)	1175(30)	−179(12)	3839(24)	C(25)	−378(83)	622(24)	−631(64)
C(3)	−17(30)	−478(13)	3783(25)	C(26)	−801(79)	818(15)	−13(51)
C(4)	−1265(25)	−308(11)	3152(20)	C(27)	−337(68)	954(28)	−1056(46)
C(5)	−1426(25)	249(11)	2573(20)				

* Atoms Cl(1), O(4)–O(7) comprise the component of the disordered perchlorate with occupancy 0.76; atoms Cl(2), O(8)–O(11) comprise the component with occupancy 0.24. Atom O(3) with, in turn, the pairs C(24), C(25) and C(26), C(27) comprise the two half-occupancy components of ethanol.

Table 2 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for [CoL^1(NO$_3$)]NO$_3$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	−2086(1)	−686(1)	−2500	C(5)	−2219(5)	−1056(7)	−5105(7)
O(1)	−3227(3)	−662(5)	−3696(5)	C(6)	−3087(5)	−1095(9)	−4849(7)
O(2)	−859(3)	−1556(5)	−2526(7)	C(7)	−4021(5)	−532(7)	−3390(8)
O(3)	−1279(4)	450(7)	−1643(9)	C(8)	−4614(5)	−1097(8)	−3984(8)
O(4)	−1187(5)	2181(6)	−1912(8)	C(9)	−5388(5)	−895(8)	−3662(8)
O(5)	−1904(5)	1169(7)	−3027(7)	C(10)	−5564(5)	−155(8)	−2787(10)
O(6)	−3399(4)	−3325(8)	−3086(8)	C(11)	−4966(5)	356(7)	−2201(8)
O(7)	−2445(5)	−3564(8)	−4291(10)	C(12)	−4173(4)	174(6)	−2482(10)
O(8)	−3198(11)	−4776(10)	−3801(12)	C(13)	−3545(5)	762(7)	−1823(8)
N(1)	−1718(4)	−1001(6)	−4222(6)	C(14)	−3297(5)	−881(7)	−608(7)
N(2)	−2947(4)	−12(6)	−1324(6)	C(15)	−2663(6)	−1714(8)	−349(7)
N(3)	−2352(4)	−2095(5)	−1492(6)	C(16)	−1743(6)	−2957(7)	−1331(10)
N(4)	−1451(5)	1310(8)	−2174(8)	C(17)	−990(5)	−2536(7)	−804(8)
N(5)	−2999(6)	−3876(7)	−3720(8)	C(18)	−707(7)	−2823(8)	275(9)
C(1)	−931(5)	−1085(7)	−4436(8)	C(19)	1(7)	−2430(9)	666(11)
C(2)	−661(6)	−1211(8)	−5583(9)	C(20)	455(7)	−1787(9)	3(10)
C(3)	−1178(7)	−1219(8)	−6469(9)	C(21)	207(6)	−1461(8)	−1102(10)
C(4)	−1973(6)	−1157(8)	−6245(8)	C(22)	−524(5)	−1843(7)	−1477(8)
				C(23)	−401(5)	−1070(8)	−3435(8)

* Atoms N(5), O(6), O(7), O(8) comprise the unco-ordinated nitrate anion.

related to those of the supporting atom, and refined in riding mode. Refinement converged at a final *R* 0.0508 (333 parameters, final mean and maximum Δ/σ 0.010 and 0.062), with allowance for the thermal anisotropy of all non-hydrogen atoms. The correct polarity of the chosen crystal was confirmed by the lower value of *R* (by 0.0018) at convergence. A final difference electron-density synthesis showed minimum and maximum values of −0.30 and +0.37e Å^{-3}.

Crystal data for [MnL^{1}Br(EtOH)]ClO$_4$. $C_{25}H_{31}BrClMnN_3O_7$, $M = 655.83$; crystallises from ethanol–acetonitrile as colourless rectangular prisms, crystal dimensions 0.50 × 0.30 × 0.20 mm. Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 10.308(18)$, $b = 22.576(56)$, $c = 12.263(36)$ Å, $\beta = 107.69(19)°$, $U = 2719(12)$ Å^3, $Z = 4$, $D_c = 1.602$ g cm^{-3}, Mo-Kα X-radiation ($\lambda = 0.710\,69$ Å) with graphite monochromator, μ(Mo-Kα) = 20.68 cm^{-1}, $F(000) = 1339.78$.

The 2035 independent reflections (of 5208 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption by the analysis of eight azimuthal scans (minimum and maximum transmission coefficients 0.439 and 0.661). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The perchlorate anion was found to be rotationally disordered (refined occupancies 0.76:0.24) with approximately coincident chlorines, and each component was refined as a rigid group with T_d symmetry. The co-ordinated ethanol was disordered apparently equally in two orientations with a common oxygen site, and was refined with geometric constraints. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final *R* 0.149 (219 parameters, final

Table 3 Elemental microanalytical,[a] infrared[b] and FAB mass spectral data[c] for the complexes

	Analysis (%)				*m/z*		IR (cm^{-1})		
Complex	C	H	N	Other	[ML–H]$^+$	[ML(X)]$^+$	ν(OH)	ν(NH)	Anion
$MnL^1(NO_3)_2 \cdot 0.5H_2O$	48.6	4.4	12.8		429	492	3425	3255, 3240	1450, 1415, 1385, 1310
	(49.0)	(4.6)	(12.4)						
$MnL^1(ClO_4)_2 \cdot 2H_2O$	41.6	4.4	6.2	10.6 Cl	429	529	3425	3280	1100, 625
	(41.5)	(4.4)	(6.3)	(10.7)					
$MnL^1(ClO_4)Br \cdot 2MeOH$	44.4	5.0	6.2	11.9 Cl, 5.3 Br	429	529, 509, 511	3420	3245	1120, 1110, 1095, 635, 625
	(44.6)	(4.8)	(6.2)	(11.9), (5.3)					
$CoL^1(NO_3)_2 \cdot 0.5H_2O$	48.2	4.6	12.4		433	496	3425	3180	1455, 1385, 1325
	(48.7)	(4.6)	(12.4)						
$CoL^1(ClO_4)_2$	43.8	3.9	6.9	11.5 Cl	433	533		3255, 3225	1100, 625
	(43.6)	(4.0)	(6.6)	(11.2)					

[a] Required values are given in parentheses. [b] As KBr discs. [c] 3-Nitrobenzyl alcohol matrix.

Table 4 Thermodynamic stability constants (log *K*)*

	Mn	Co	Ni	Cu	Zn	Cd
L^1	<4.0	4.51	6.66	13.92	5.91	8.73
L^2	<4.0	4.36	5.15	8.72	5.75	4.19

* In 95% MeOH, 0.1 mol dm^{-3} NEt_4ClO_4 at 25 °C.

mean and maximum Δ/σ 0.015 and 0.074), with allowance for the thermal anisotropy of all non-hydrogen and non-carbon atoms, with the exception of those of the lower occupancy perchlorate component, and of the pyridyl nitrogen. A final difference electron-density synthesis showed minimum and maximum values of -1.21 and $+1.55$ e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

The formation of 1:1 metal-ligand complexes of L^1 with Mn^{II} and Co^{II} was confirmed by elemental microanalysis and fast atom bombardment (FAB) mass spectrometry (Table 3). Solvent molecules were included in the microanalyses when suggested by the IR spectra. Parent peaks in the mass spectra were as expected. Similar reactions with L^2 did not lead to isolable products.

Infrared data (Table 3) showed split and/or shifted amine stretches relative to the free ligand. Anion stretches were often obscured by ligand stretches and were broadened or split due to complexation or hydrogen bonding,[5] therefore the modes of co-ordination, mono- or bi-dentate, were not assigned. Visible spectra of the Co^{II} complexes showed a series of broad overlapping bands at 500–600 nm indicative of a distorted octahedral geometry;[6] $CoL^1(NO_3)_2 \cdot 0.5H_2O$ (in MeOH) λ = 500, 525, 572 and $CoL^1(ClO_4)_2$ (in MeCN) λ = 478, 500, 550 and 585 nm.

Conductometric titrations of $ML^1(ClO_4)_2$; M = Co^{II} or Mn^{II} with NH_4Cl were performed in dimethyl sulphoxide (dmso). For Mn^{II} an inflection at 0.5 mole ratio [NH_4Cl]/[complex] indicted that dimerisation had occurred presumably *via* bridging chloride ions; this type of structure[7–10] has been observed previously for Mn^{II}. For Co^{II} only slight inflections at 0.5 and 1.0 mole ratios were observed but were within experimental error and therefore no definite conclusions were drawn.

Thermodynamic stability constants were determined for Co^{II} and Mn^{II} with L^1 and L^2 in 95% MeOH (25 °C, I = 0.1 mol dm^{-3} NEt_4ClO_4) using the potentiometric (pH) titration method.[1,2] For Co^{II} the stability constants were found to be low (log K = 4.51 for L^1 and 4.36 for L^2) and similar in value to those found for related N_2O_2 macrocycles (log K all <4.5),[11] this raised the possibility that only the aliphatic nitrogen atoms were co-ordinating to the metal. A small drop in stability occurred on moving from L^1 to L^2 and this may be related to the increased chelate ring size between the co-ordinated aliphatic nitrogens.[12] For Mn^{II} stability constants of less than 4 were found for both ligands. Flow-microcalorimetry studies of the Mn–L^1 system enabled the determination of the enthalpy (ΔH°) and entropy (ΔS°) of complexation. (ΔH° = 10.75 kJ mol^{-1}, ΔS° = 73.6 J K^{-1} mol^{-1}). The enthalpy was endothermic and calculations of the entropy indicated that this was the driving force for complexation. In contrast to the complexes obtained for Ni^{II} and Cu^{II}[2] no 1:2 metal:ligand species were observed in this study. A comparison of stability constants for the transition-metal elements used in this study is shown in Table 4. The sequences follow the natural or Irving–Williams stability order[13] with the exception of the pronounced stability of Cd^{II} for L^1 relative to Zn^{II}; the stability of the Cu^{II} complex of L^1 is much enhanced over that of the corresponding Ni^{II} complex.[2]

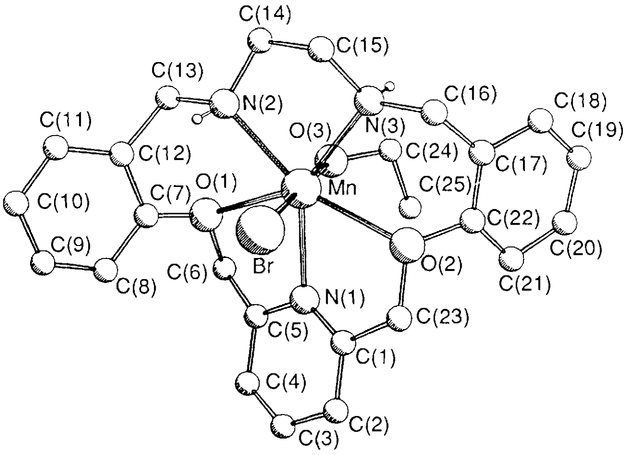


Fig. 1 The molecular structure, with atom labelling, of the cation $[MnL^1Br(EtOH)]^+$

Description of Structures.—$[MnL^1Br(EtOH)]ClO_4$. The structure of the molecule, with atom labelling, is illustrated in Fig. 1: bond lengths and angles with estimated standard deviations are listed in Table 5. The crystal structure is approximately isomorphous to that of $[CdL^1(NO_3)(MeOH)]NO_3$.[1]

The manganese is in a seven-co-ordinate, distorted pentagonal-bipyramidal environment with the macrocyclic donor atoms occupying the equatorial plane (root-mean-square deviation 0.29 Å). The axial sites are filled by the bromide anion, and by an ethanol of solvation. The distorted pentagonal-bipyramidal

Table 5 Bond lengths (Å) and angles (°) for $[MnL^1Br(EtOH)]ClO_4$*

Mn–Br	2.569(8)	Mn–O(1)	2.556(23)	C(5)–C(6)	1.451(35)	C(7)–C(8)	1.385(47)
Mn–O(2)	2.441(21)	Mn–O(3)	2.232(19)	C(7)–C(12)	1.402(39)	C(8)–C(9)	1.348(52)
Mn–N(1)	2.351(21)	Mn–N(2)	2.283(22)	C(9)–C(10)	1.340(46)	C(10)–C(11)	1.360(46)
Mn–N(3)	2.278(22)	Cl(1)–O	1.39	C(11)–C(12)	1.398(42)	C(12)–C(13)	1.482(43)
Cl(2)–O	1.35	O(1)–C(6)	1.444(35)	C(14)–C(15)	1.459(36)	C(16)–C(17)	1.491(40)
O(1)–C(7)	1.337(43)	O(2)–C(22)	1.440(43)	C(17)–C(18)	1.403(42)	C(17)–C(22)	1.383(40)
O(2)–C(23)	1.446(36)	O(3)–C(24)	1.429(64)	C(18)–C(19)	1.361(43)	C(19)–C(20)	1.373(48)
O(3)–C(26)	1.432(59)	N(1)–C(1)	1.319(27)	C(20)–C(21)	1.401(51)	C(21)–C(22)	1.354(43)
N(1)–C(5)	1.357(33)	N(2)–C(13)	1.448(36)	C(24)–C(25)	1.53(7)	C(26)–C(27)	1.53(10)
N(2)–C(14)	1.451(37)	N(3)–C(15)	1.492(33)	N(3) ··· Br^{I}	3.402	H(N3) ··· Br^{I}	2.77
N(3)–C(16)	1.459(33)	C(1)–C(2)	1.378(35)	O(3) ··· O(5)	2.829	H(O3a) ··· O(5)	2.27
C(1)–C(23)	1.517(38)	C(2)–C(3)	1.385(44)	H(O3b) ··· O(5)	2.18	O(3) ··· O(10)	3.090
C(3)–C(4)	1.340(35)	C(4)–C(5)	1.430(34)	H(O3a) ··· O(10)	2.86	H(O3b) ··· O(10)	2.33
Br–Mn–O(1)	103.8(5)	Br–Mn–O(2)	82.2(5)	N(1)–C(1)–C(2)	122.8(23)	N(1)–C(1)–C(23)	120.0(21)
O(1)–Mn–O(2)	136.9(7)	Br–Mn–O(3)	177.8(6)	C(2)–C(1)–C(23)	117.2(21)	C(1)–C(2)–C(3)	113.8(24)
O(1)–Mn–O(3)	74.9(8)	O(2)–Mn–O(3)	97.5(8)	C(2)–C(3)–C(4)	124.8(27)	C(3)–C(4)–C(5)	119.0(25)
Br–Mn–N(1)	88.5(5)	O(1)–Mn–N(1)	69.8(7)	N(1)–C(5)–C(4)	115.1(20)	N(1)–C(5)–C(6)	120.1(23)
O(2)–Mn–N(1)	67.7(7)	O(3)–Mn–N(1)	89.4(7)	C(4)–C(5)–C(6)	124.5(24)	O(1)–C(6)–C(5)	109.8(22)
Br–Mn–N(2)	84.0(6)	O(1)–Mn–N(2)	73.6(7)	O(1)–C(7)–C(8)	126.2(27)	O(1)–C(7)–C(12)	115.4(27)
O(2)–Mn–N(2)	148.9(7)	O(3)–Mn–N(2)	97.2(8)	C(8)–C(7)–C(12)	118.5(30)	C(7)–C(8)–C(9)	118.4(30)
N(1)–Mn–N(2)	139.6(8)	Br–Mn–N(3)	96.1(5)	C(8)–C(9)–C(10)	124.2(35)	C(9)–C(10)–C(11)	119.6(35)
O(1)–Mn–N(3)	143.0(7)	O(2)–Mn–N(3)	76.1(8)	C(10)–C(11)–C(12)	118.7(27)	C(7)–C(12)–C(11)	120.5(26)
O(3)–Mn–N(3)	85.9(8)	N(1)–Mn–N(3)	142.5(8)	C(7)–C(12)–C(13)	118.3(28)	C(11)–C(12)–C(13)	120.7(24)
N(2)–Mn–N(3)	77.9(8)	O–Cl(1)–O	109.5	N(2)–C(13)–C(12)	113.5(22)	N(2)–C(14)–C(15)	110.2(20)
O–Cl(2)–O	109.5	Mn–O(1)–C(6)	107.6(18)	N(3)–C(15)–C(14)	111.8(20)	N(3)–C(16)–C(17)	110.4(19)
Mn–O(1)–C(7)	115.7(16)	C(6)–O(1)–C(7)	117.1(25)	C(16)–C(17)–C(18)	119.3(24)	C(16)–C(17)–C(22)	124.1(28)
Mn–O(2)–C(22)	123.9(15)	Mn–O(2)–C(23)	113.0(18)	C(18)–C(17)–C(22)	116.5(27)	C(17)–C(18)–C(19)	117.8(26)
C(22)–O(2)–C(23)	118.6(23)	Mn–O(3)–C(24)	131.3(23)	C(18)–C(19)–C(20)	121.5(34)	C(19)–C(20)–C(21)	124.3(34)
Mn–O(3)–C(26)	117.8(25)	Mn–N(1)–C(1)	117.4(15)	C(20)–C(21)–C(22)	110.7(28)	O(2)–C(22)–C(17)	109.6(26)
Mn–N(1)–C(5)	115.7(15)	C(1)–N(1)–C(5)	124.3(20)	O(2)–C(22)–C(21)	120.8(26)	C(17)–C(22)–C(21)	129.2(32)
Mn–N(2)–C(13)	123.5(17)	Mn–N(2)–C(14)	108.6(17)	O(2)–C(23)–C(1)	109.0(20)	O(3)–C(24)–C(25)	109.0(47)
C(13)–N(2)–C(14)	113.0(20)	Mn–N(3)–C(15)	104.7(17)	O(3)–C(26)–C(27)	111.1(37)		
Mn–N(3)–C(16)	120.6(14)	C(15)–N(3)–C(16)	114.0(18)				

* Symmetry operation: I $x, 0.5 - y, -0.5 + z$.

geometry has been commonly found for Mn^{II} in the presence of both acyclic[14–17] and cyclic[18–21] imine ligands. The bond lengths between the macrocyclic oxygen donors and the Mn^{II} (2.44, 2.56 Å; Table 5) were found to exceed the sum of the ionic radius for seven-co-ordinate Mn^{II} and the van der Waals radius of oxygen (2.30 Å)[22] and their orientation would suggest an electrostatic interaction. The other metal ion-donor bond lengths were found to lie in the anticipated ranges, Mn–N, 2.28–2.35 and Mn–O, 2.23 Å.[14–21]

The conformation of the macrocycle is roughly that of a chair with the two planar phenyl fragments tilted in opposite directions by approximately 50° to the mean equatorial plane. The nitrogen-atom configurations are *R,R* (or *S,S*), the protons being mutually *trans* to each other. This configuration is emerging as a common feature of endomacrocyclic co-ordination by N_3O_2 macrocycles, and is perhaps related to the minimisation of steric strain in the macrocycle;[1,2] this observation is supported by molecular models.

The co-ordinated ethanol is disordered over two orientations with a common donor oxygen site. The perchlorate anion (which is disordered 0.76:0.24 with approximately coincident chlorines) is not co-ordinated to the metal, but is hydrogen-bonded to the co-ordinated ethanol. It is interesting to note that both ethanol orientations form good hydrogen bonds to the perchlorate of the higher occupancy, whereas only one ethanol orientation forms a well aligned hydrogen bond (at a greater O ··· O separation) with the lower-occupancy disorder component of the perchlorate. This explains the different occupancies of the two disorder components, and the observed splittings of the perchlorate bands in the IR spectrum. Also noteworthy is that there are rather short interactions across the crystallographic inversion centre at (0,0,0) between the symmetry-related terminal methyl carbons C(25) of one of the ethanol orientations (C ··· C 3.18 Å), and by some of its associated hydrogens (H ··· H 2.04 and 2.19 Å). This suggests that such inversion related pairs of complexes have different ethanol orientations, thus justifying the equal occupancies, but giving rise to overall bulk disorder. A further weak hydrogen bond is formed between one of the amine nitrogens and the bromine of a *c*-glide related molecule (N ··· Br 3.401, H ··· Br 2.77 Å).

$[CoL^1(NO_3)]NO_3$. The structure of the molecule, with atom labelling, is illustrated in Fig. 2: bond lengths and angles with estimated standard deviations are listed in Table 6. The crystal structure is isomorphous to that of $[ZnL^1(NO_3)]NO_3$.[1]

The cobalt is in a seven-co-ordinate environment in which all five donor atoms of the macrocycle and two oxygen atoms of an asymmetrically bidentate nitrate ligand form the co-ordination sphere: the second nitrate is a free anion. Seven-co-ordinate complexes of Co^{II} are relatively rare,[23–28] and generally have pentagonal-bipyramidal geometries: here, the co-ordination polyhedron is intermediate between a capped trigonal prism [with N(3) capping the approximately rectangular face defined by O(1), O(2), N(1) and N(2)] and a pentagonal bipyramid [with N(3) and O(5) occupying axial sites].

The Co^{II}-donor bond lengths (Table 6) were found to be in the anticipated range[23–28] for seven-co-ordinate Co^{II} [Co–O(NO_2) 2.18, 2.38, Co–N 2.10–2.15 and Co–O(macrocycle) 2.33, 2.36 Å]. The conformation of the macrocycle is buckled, most noticeably in the region of the diamine fragment. The configurations of the aliphatic nitrogen atoms are again *R,R* (or *S,S*), with the hydrogens being mutually *trans*. The phenyl rings are similarly inclined to the pyridyl ring (43 and 37°) in opposite directions: all three rings are essentially planar.

Both amine nitrogen atoms form hydrogen-bonded interactions to different (symmetry related) free nitrate anions (N ··· O 2.96, 3.01; H ··· O 2.00, 2.13 Å). Thus, the nitrate

Table 6 Bond lengths (Å) and angles (°) for $[CoL^1(NO_3)]NO_3$

Co–O(1)	2.360(7)	Co–O(2)	2.327(7)	C(1)–C(23)	1.453(13)	C(2)–C(3)	1.337(15)
Co–O(3)	2.182(9)	Co–O(5)	2.379(10)	C(3)–C(4)	1.366(15)	C(4)–C(5)	1.376(12)
Co–N(1)	2.104(8)	Co–N(2)	2.145(8)	C(5)–C(6)	1.491(13)	C(7)–C(8)	1.394(13)
Co–N(3)	2.130(8)	O(1)–C(7)	1.392(10)	C(7)–C(12)	1.379(13)	C(8)–C(9)	1.377(13)
O(1)–C(6)	1.443(10)	O(2)–C(22)	1.374(12)	C(9)–C(10)	1.386(15)	C(10)–C(11)	1.364(14)
O(2)–C(23)	1.426(12)	O(3)–N(4)	1.254(13)	C(11)–C(12)	1.391(12)	C(12)–C(13)	1.487(13)
O(4)–N(4)	1.198(12)	O(5)–N(4)	1.252(12)	C(14)–C(15)	1.508(14)	C(16)–C(17)	1.497(14)
O(6)–N(5)	1.199(13)	O(7)–N(5)	1.203(14)	C(17)–C(18)	1.370(14)	C(17)–C(22)	1.392(13)
O(8)–N(5)	1.159(16)	N(1)–C(1)	1.352(11)	C(18)–C(19)	1.363(17)	C(19)–C(20)	1.336(16)
N(1)–C(5)	1.320(11)	N(2)–C(13)	1.498(12)	C(20)–C(21)	1.393(16)	C(21)–C(22)	1.385(13)
N(2)–C(14)	1.471(12)	N(3)–C(15)	1.487(12)	N(3) ··· O(6)	2.956	H(N3) ··· O(6)	2.00
N(3)–C(16)	1.485(12)	C(1)–C(2)	1.399(14)	N(2) ··· O(7^I)	3.005	H(N2) ··· O(7^I)	2.13
O(1)–Co–O(2)	136.1(3)	O(1)–Co–O(3)	139.5(3)	O(4)–N(4)–O(5)	123.1(10)	O(6)–N(5)–O(7)	125.8(10)
O(2)–Co–O(3)	75.4(3)	O(1)–Co–O(5)	86.9(3)	O(6)–N(5)–O(8)	115.2(12)	O(7)–N(5)–O(8)	119.0(12)
O(2)–Co–O(5)	108.9(3)	O(3)–Co–O(5)	54.6(3)	N(1)–C(1)–C(2)	119.8(8)	N(1)–C(1)–C(23)	117.2(8)
O(1)–Co–N(1)	72.4(2)	O(2)–Co–N(1)	69.0(3)	C(2)–C(1)–C(23)	123.0(8)	C(1)–C(2)–C(3)	120.2(10)
O(3)–Co–N(1)	110.9(3)	O(5)–Co–N(1)	84.3(3)	C(2)–C(3)–C(4)	119.7(10)	C(3)–C(4)–C(5)	118.6(9)
O(1)–Co–N(2)	79.1(3)	O(2)–Co–N(2)	141.8(3)	N(1)–C(5)–C(4)	122.7(8)	N(1)–C(5)–C(6)	118.5(7)
O(3)–Co–N(2)	83.7(3)	O(5)–Co–N(2)	82.9(3)	C(4)–C(5)–C(6)	118.6(8)	O(1)–C(6)–C(5)	109.2(7)
N(1)–Co–N(2)	149.2(3)	O(1)–Co–N(3)	98.9(3)	O(1)–C(7)–C(8)	120.5(8)	O(1)–C(7)–C(12)	116.1(7)
O(2)–Co–N(3)	79.6(3)	O(3)–Co–N(3)	114.0(3)	C(8)–C(7)–C(12)	123.3(8)	C(7)–C(8)–C(9)	117.2(9)
O(5)–Co–N(3)	160.8(3)	N(1)–Co–N(3)	114.9(3)	C(8)–C(9)–C(10)	121.0(9)	C(9)–C(10)–C(11)	120.1(8)
N(2)–Co–N(3)	80.3(3)	Co–O(1)–C(6)	113.2(5)	C(10)–C(11)–C(12)	121.4(9)	C(7)–C(12)–C(11)	117.0(8)
Co–O(1)–C(7)	129.6(5)	C(6)–O(1)–C(7)	115.5(6)	C(7)–C(12)–C(13)	123.8(7)	C(11)–C(12)–C(13)	119.2(8)
Co–O(2)–C(22)	118.2(5)	Co–O(2)–C(23)	107.2(5)	N(2)–C(13)–C(12)	111.3(7)	N(2)–C(14)–C(15)	108.6(7)
C(22)–O(2)–C(23)	121.6(6)	Co–O(3)–N(4)	100.2(7)	N(3)–C(15)–C(14)	106.9(7)	N(3)–C(16)–C(17)	112.8(7)
Co–O(5)–N(4)	90.8(6)	Co–N(1)–C(1)	118.2(6)	C(16)–C(17)–C(18)	124.7(9)	C(16)–C(17)–C(22)	117.8(8)
Co–N(1)–C(5)	122.7(6)	C(1)–N(1)–C(5)	119.0(7)	C(18)–C(17)–C(22)	117.5(9)	C(17)–C(18)–C(19)	120.6(10)
Co–N(2)–C(13)	117.4(5)	Co–N(2)–C(14)	109.9(5)	C(18)–C(19)–C(20)	121.6(11)	C(19)–C(20)–C(21)	121.0(11)
C(13)–N(2)–C(14)	113.9(7)	Co–N(3)–C(15)	107.2(5)	C(20)–C(21)–C(22)	116.8(9)	O(2)–C(22)–C(17)	114.2(8)
Co–N(3)–C(16)	120.2(6)	C(15)–N(3)–C(16)	111.0(7)	O(2)–C(22)–C(21)	123.3(8)	C(17)–C(22)–C(21)	122.5(9)
O(3)–N(4)–O(4)	123.1(9)	O(3)–N(4)–O(5)	113.7(9)	O(2)–C(23)–C(1)	103.9(7)		

* Symmetry operation: I $-0.5 - x, 0.5 + y, 0.5 + z$.

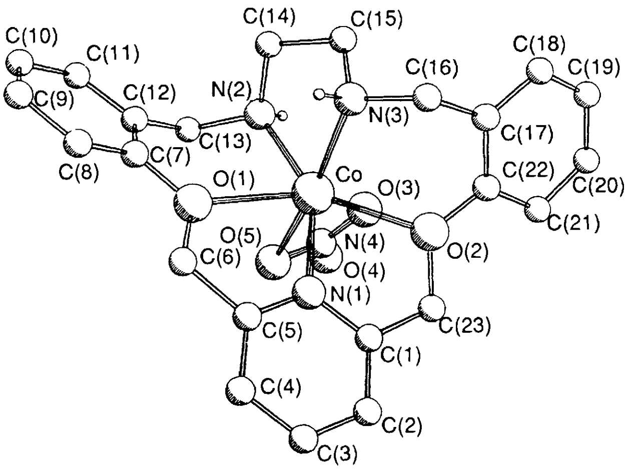
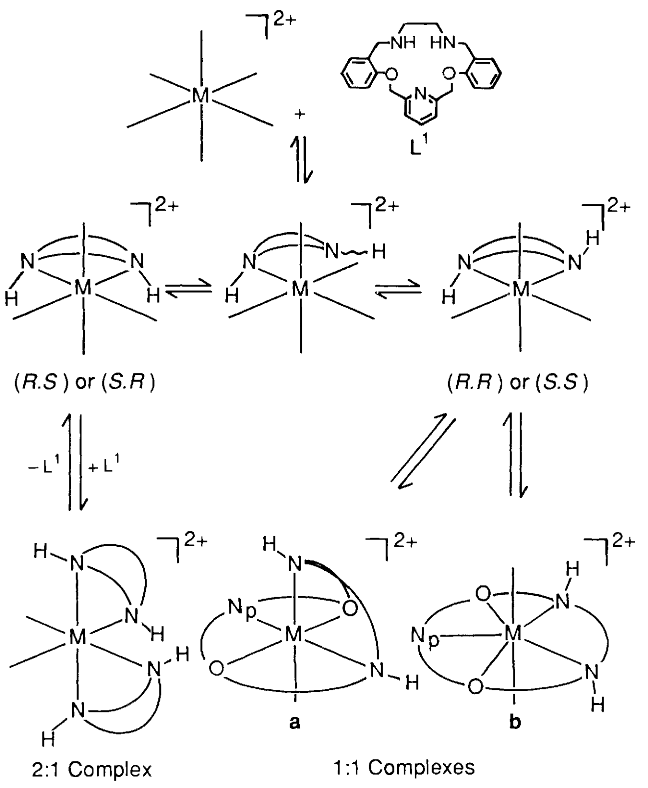


Fig. 2 The molecular structure, with atom labelling, of the cation $[CoL^1(NO_3)]^+$

bridges adjacent cationic complexes by the formation of hydrogen bonds.

Conclusion

On surveying the structural and solution data available for complexes of L^1 a general solution reaction scheme can be advanced (Scheme 1). Initial chelation of L^1 *via* the aliphatic nitrogen atoms leads to exomacrocyclic complexation involving either (*SR*; *RS*) or (*RR*; *SS*) configurations at the nitrogen atoms. These forms can interconvert *via* a monodentate intermediate, and in the exomacrocyclic complexes isolated and characterised by X-ray crystallography $\{[ZnL^1I_2]\cdot H_2O$ and $[HgL^1I_2]\}$ only the (*SR*; *RS*) configurations have been found.[1]



Scheme 1 Proposed solution equilibria available to the metal complexes

Addition of a second molecule of L^2—in this bidentate mode—leads to 2:1 (ligand:metal) complexes of which $[Ni(L^1)_2(NO_3)]NO_3\cdot MeOH$ has been characterised.[2]

The 1 : 1 complexes of types **a** and **b**, in which all of the ligand donor atoms are attached to the metal, are formed from the (*RR*; *SS*) isomer. The conformational differences between type **a** and type **b** are evidenced by analysis of the torsion angles in the complexes.[29] Type **a** has been crystallographically identified for $[CuL^1(H_2O)][ClO_4]_2$,[2] $[NiL^1(I)]I\cdot MeOH$,[2] $[CoL^1(NO_3)]NO_3$ and $[ZnL^1(NO_3)]NO_3$[1] and type **b** has been identified for $[MnL^1Br(EtOH)]ClO_4$ and $[CdL^1(NO_3)(MeOH)]NO_3$.[1]

The equilibria involved will tend to be dynamic with the prospect that various proportions of a number of forms of a given species will be present in solution simultaneously. For example, contributions from both endo- and exo-macrocyclic co-ordination may be simultaneously present under a given set of conditions although only one form may predominate. The nature of the predominant complex species will depend on a number of factors such as: the hole and chelate-ring sizes presented by the ligands; the donor atom type and location within the ligands; the ionic radius, donor-atom and geometric preferences of the cation; the donor-type and denticity of the accompanying anion and solvent molecules; and the conditions under which the reaction is run.

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References

1 Part 2, H. Adams, N. A. Bailey, D. E. Fenton, I. G. Ford, S. J. Kitchen, M. G. Williams, P. A. Tasker, A. J. Leong and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, 1991, 1665.
2 N. A. Bailey, D. E. Fenton, S. J. Kitchen, T. H. Lilley, M. G. Williams, P. A. Tasker, A. J. Leong and L. F. Lindoy, *J. Chem. Soc., Dalton Trans.*, 1991, 627.
3 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
4 G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data (Revision 4), University of Göttingen, 1983.
5 K. Nakamoto, *Infra-red and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1978.
6 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988.
7 E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1976, 162.
8 E. M. Meyer and C. Floriani, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 356.
9 F. H. Kohler, N. Hebendanz, U. Thewalt, B. Kanellakopulos and R. Klenze, *Organometallics*, 1987, **6**, 115.
10 H. Diril, H.-R. Chang, X-Zhang, S. K. Larsen, J. A. Potenza, C. G. Pierpoint, H. J. Schugar, S. S. Isied and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 6207.
11 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.
12 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.
13 H. M. N. H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 1953, 3192.
14 C. Pelizzi, G. Pelizzi, G. Predieri and F. Vitali, *J. Chem. Soc., Dalton Trans.*, 1985, 2387.
15 C. Pelizzi, G. Pelizzi and P. Tarasconi, *J. Chem. Soc., Dalton Trans.*, 1985, 215.
16 C. Pelizzi, G. Pelizzi, G. Predieri and S. Resola, *J. Chem. Soc., Dalton Trans.*, 1982, 1349 and refs. therein.
17 G. J. Palenik and D. W. Wester, *Inorg. Chem.*, 1978, **17**, 864 and refs. therein.
18 M. G. B. Drew, A. H. bin Othman, S. G. McFall and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1977, 558.
19 M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 438.
20 M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 1173.
21 N. W. Alcock, D. C. Liles, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1974, 727.
22 R. D. Shannon, *Acta Crystallogr., Sect. C*, 1976, **32**, 751; L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell Univ. Press, Ithaca, NY, 1960, p. 260, 1984.
23 S. M. Nelson, F. S. Esho, M. G. B. Drew and P. Bird, *J. Chem. Soc., Chem. Commun.*, 1979, 1035.
24 A. H. White and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1977, 1377.
25 A. F. Cameron, D. W. Taylor and R. H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 1972, 1603.
26 G. R. Newkome, V. K. Gupta, F. P. Fronzcek and S. Pappalardo, *Inorg. Chem.*, 1984, **23**, 2400.
27 C. G. W. Ansell, J. Lewis, M. C. Liptrot, P. R. Raithby and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1982, 2557 and refs. therein.
28 E. M. Holt, N. W. Alcock, R. R. Hendrison, G. D. Malpass, R. G. Ghirardelli and R. A. Palmer, *Acta Crystallogr., Sect. B*, 1981, **37**, 1080.
29 M. G. Williams, Ph.D. Thesis, University of Sheffield, 1989.

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