Synthesis and Co-ordination Chemistry of the Sterically Demanding Pendant-arm Macrocycle *N,N′,N″*-Tris[(2*R*)-2-hydroxy-3-methylbutyl]-1,4,7-triazacyclononane†

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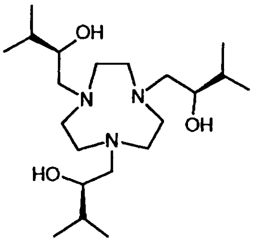
The sterically demanding pendant-arm macrocycle *N,N′,N″*-tris[(2*R*)-2-hydroxy-3-methylbutyl]-1,4,7-triazacyclononane H_3L has been synthesised. Owing to its bulky isopropyl arms the formation of dimeric species is prevented which is in contrast to the behaviour of the analogous ligand with methyl substituted arms, *N,N′,N″*-tris[(2*S*)-2-hydroxypropyl]-1,4,7-triazacyclononane (H_3L'). The preparation of complexes of V^{IV}, Cr^{III}, Mn^{IV} Ni^{II}, Cu^{II} and Zn^{II} with H_3L is described and the crystal structures and some spectroscopic properties of $[Mn^{IV}L][PF_6]\cdot H_2O$ and $[Ni^{II}(H_3L)][NO_3][PF_6]$ determined.

The small triaza macrocycle 1,4,7-triazacyclononane ([9]ane-N_3) has been N-substituted with a variety of pendant arms.[1] We have extensively investigated the chemistry of the ligand with hydroxypropyl arms, *N,N′,N″*-tris[(2*S*)-2-hydroxypropyl]-1,4,7-triazacyclononane (H_3L') and can briefly summarise its co-ordination chemistry as follows. With divalent metal ions, such as Mn^{II}[2] or Ni^{II},[3] H_3L' remains protonated and forms monomeric complexes {$[Mn(H_3L')]^{2+}$, $[Ni(H_3L')]^{2+}$}. With ions in higher oxidation states dimeric species are formed in which one half of the dimer contains deprotonated L′ acting as an alkoxide ligand and the other half contains H_3L', the halves being joined by three hydrogen bridges. Examples of homonuclear dimers are $[Co^{III}(L'\cdot H_3L')Co^{III}]^{3+}$[4] and $[Cr^{III}(L'\cdot H_3L')Cr^{III}]^{3+}$.[5] Manganese forms a mixed-valent dimer $[Mn^{IV}(L'\cdot H_3L')Mn^{II}]^{3+}$[2] and vanadium, in the presence of zinc, forms a mixed-metal dimer $[V^{IV}(L'\cdot H_3L')Zn^{II}]^{3+}$.[6]

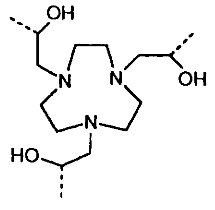
We wished to synthesise mononuclear complexes of the higher valent ions, particularly of Mn^{IV} and V^{IV}. Molecular models suggested that dimerisation would be prevented if the substituent on the arm was more bulky than a methyl group. We have therefore prepared *N,N′,N″*-tris[(2*R*)-2-hydroxy-3-methylbutyl]-1,4,7-triazacyclononane (H_3L) a bulky arm macrocyclic ligand with an isopropyl group on the pendant arm. We report in this work the synthesis of the ligand and its complexes with V^{IV}, Cr^{III}, Mn^{IV}, Ni^{II}, Cu^{II} and Zn^{II} and the crystal structures of $[Mn^{IV}L][PF_6]\cdot H_2O$ and $[Ni^{II}(H_3L)][NO_3][PF_6]$.

Experimental

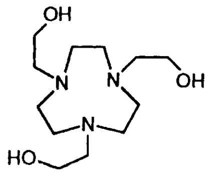
Synthesis of (2R)-2-*Isopropyloxirane*.—This was based upon the method of Koppenhoefer and Schurig.[7] The initial step was the preparation of (2*S*)-2-chloro-3-methylbutanoic acid by the diazotisation of valine in aqueous hydrochloric acid. Subsequent reduction with lithium aluminium hydride in diethyl ether afforded (2*S*)-2-chloro-3-methylbutan-1-ol which was cyclised to (2*R*)-2-isopropyloxirane using aqueous potassium hydroxide. The oxirane was distilled as it was formed to prevent alkaline hydrolysis. (**CAUTION**: A well ventilated fume cupboard should be used. Oxiranes are suspect carcinogens. Exposure to even low concentrations of (2*R*)-2-isopropyloxirane may cause drowsiness and severe headaches.)



H_3L



H_3L'



H_3L''

Synthesis of N,N′,N″-*Tris*[(2R)-2-*hydroxy*-3-*methylbutyl*]-1,4,7-*triazacyclononane* H_3L.—In a 25 cm^3 round bottomed flask, 1,4,7-triazacyclononane (1.05 g, 8.13 mmol) was dissolved in dry absolute ethanol (10 cm^3). The solution was cooled and (2*R*)-2-isopropyloxirane (2.45 g, 28 mmol) was added in one portion and the flask securely stoppered and allowed to stand at room temperature for 10 d. Solvents were removed to afford the required product as a viscous yellow oil, which upon refrigeration crystallised as fine needles with a sharp melting point. The material was sufficiently pure to be used without further purification. Yield 3.15 g (quantitative). ^1H NMR ($CDCl_3$): δ 0.83 [m, 18 H, $CH(CH_3)_2$], 1.53 [m, 3 H, $CH(CH_3)_2$], 2.33–2.82 (m, 18 H, NCH_2), 3.33 (m, 3 H, *CH*OH) and 5.47 (br s, 3 H, OH).

The macrocycle H_3L was taken up in absolute ethanol (50 cm^3) in a volumetric flask to give a 0.162 mol dm^{-3} (63 mg cm^{-3}) solution which was used in the preparations below. It is of note that the ligand is rather insoluble in water.

Synthesis of Complexes of H_3L.—$[V^{IV}L][PF_6]$. A portion (4 cm^3, 252 mg, 0.651 mmol) of the ligand solution was placed in a dry Schlenk tube and the solvent removed *in vacuo*. The ligand was then dissolved in tetrahydrofuran (thf) (20 cm^3). In a second Schlenk tube, sodium hydride (60% suspension in oil, 233 mg, 5.83 mmol) was washed with 3 × 20 cm^3 portions of light petroleum (b.p. 40–60 °C) and pumped dry. The ligand solution was added to the sodium hydride under nitrogen. After

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

Table 1 Experimental data for the crystallographic studies[a]

Molecular formula	$C_{21}H_{42}F_6MnN_3O_3P\cdot H_2O$	$C_{21}H_{45}F_6N_4NiO_6P$
M	602.5	653.28
Crystal system	Monoclinic	Cubic
Space group	$P2_1$ (no. 4, $C^2{}_2$)	$P2_13$ (no. 198, T^4)
a/Å	8.4160(7)	14.106(2)
b/Å	11.992(1)	
c/Å	14.222(1)	
β/°	103.934(7)	
U/Å^3	1392.1(2)	2806.6(5)
Z	2	4
D_c/g cm^{-3}	1.44	1.546
F(000)	634	1376
μ(Mo-Kα)/cm^{-1}	5.8	8.29
T/K	298	298
Crystal size/mm	0.65 × 0.5 × 0.25	0.5 × 0.5 × 0.5
2θ range/°	$2 < \theta < 26$	$2 < \theta < 25$
Standards	1 3 7, 4 4 2, 2 6 3	8 0 2, 6 5 1, 3 4 1
Total no. of reflections	6137	1031
No. independent	5456	927
No. used in refinement	4588	820
Observability criterion, n in $I > n\sigma(I)$	3.0	2.0
No. of refined parameters	270	122
R[b]	0.040	0.025
R'[c]	0.049	0.031
Largest remaining feature in electron density map/e Å^{-3}	+0.33 (max.), −0.51 (min.)	+0.37 (max.), −0.36 (min.)

[a] Details in common: θ–2θ scan mode; standards measured every 2 h; no decay observed. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|/\Sigma wF_o{}^2]^{\frac{1}{2}}$.

effervescence had subsided (approximately 1 h) the solution was filtered under nitrogen through a small pad of Celite. In a separate Schlenk tube, VCl_3 (102 mg, 0.654 mmol) was dissolved in dry tetrahydrofuran–acetonitrile (15 cm^3, 5:1) under nitrogen. The ligand solution was then added and a grey-green colour was produced. The solution was refluxed under nitrogen for 6 h. The Schlenk tube was then opened to the air and left to stand overnight. The solvent was pumped off and water cautiously added followed by an aqueous solution of $[NH_4][PF_6]$. The purple solid which precipitated was washed with water, dried and recrystallised from acetonitrile. Yield 610 mg (80%) (Found: C, 43.20; H, 7.35; N, 7.15. $C_{21}H_{42}F_6N_3O_3PV$ requires C, 43.5; H, 7.3; N, 7.3%).

$[Cr^{III}(H_3L)][PF_6]_3$. A portion (3 cm^3, 189 mg, 0.488 mmol) of the ligand solution was placed in a dry Schlenk tube and the solvent was removed *in vacuo*. The ligand was then dissolved in dry tetrahydrofuran (15 cm^3). In a second Schlenk tube sodium hydride (60% suspension in oil, 75 mg, 4.37 mmol) was washed with 3 × 20 cm^3 portions of dry light petroleum (b.p. 40–60 °C) and then dried *in vacuo*. The ligand solution was then added to the sodium hydride (with caution) under nitrogen. After effervescence had subsided (approximately 1 h) the solution was filtered under nitrogen through a small pad of Celite. In a separate Schlenk tube $[Cr^{III}Cl_3(thf)_3]$ was dissolved in dry tetrahydrofuran (15 cm^3) under nitrogen. The ligand solution was then added and an intense green colour was produced. The solution was refrigerated for 24 h and solvents were then removed *in vacuo*. Water (10 cm^3) was then added and a pale purple solution was produced, and on addition of concentrated hydrochloric acid an intense pink solution was obtained. An excess of $[NH_4][PF_6]$ was then added and the solution was allowed to stand overnight in a 50 cm^3 beaker at room temperature. The required product was formed as intense pink needles which were filtered off on a glass sinter and washed with small portions of cold 12.5 mol dm^{-3} hydrochloric acid. Yield 121 mg (28%) (Found: C, 30.00; H, 6.40; N, 4.70. $C_{21}H_{45}CrF_{18}N_3O_3P_3$ requires C, 28.85; H, 5.20; N, 4.80%).

$[Mn^{IV}L][PF_6]\cdot H_2O$. In a 25 cm^3 beaker $MnCl_2\cdot 4H_2O$ (61.4 mg, 0.324 mmol) was dissolved in water (2 cm^3). A portion of the ligand solution (2 cm^3, 126 mg, 0.325 mmol) was then added and immediately a dark brown colour was produced. The mixture was allowed to evaporate to dryness and was redissolved in water (5 cm^3). An excess of $[NH_4][PF_6]$ dissolved in water (1 cm^3) was added. A brown precipitate formed and the solution was refrigerated overnight. The solid was filtered off, washed with water and air-dried. The material was recrystallised by the slow evaporation of a covered acetone solution to give the required product as massive black crystals. Yield 101 mg (51%) (Found: C, 42.30; H, 7.45; F, 18.75; N, 7.00. $C_{21}H_{42}F_6MnN_3O_3P\cdot H_2O$ requires C, 41.85; H, 7.35; F, 18.90; N, 6.95%).

$[Ni(H_3L)][NO_3][PF_6]$. In a 5 cm^3 beaker $Ni(NO_3)_2\cdot 6H_2O$ (94.0 mg, 0.323 mmol) was dissolved in absolute ethanol (2 cm^3). A portion of the ligand solution (2 cm^3, 126 mg, 0.325 mmol) was added and there was a colour change from intense green to blue (a small amount of nickel hydroxide was produced but this redissolved as the reaction proceeded). The solution was allowed to evaporate to dryness, producing a lilac coloured glass. This was redissolved in water (2 cm^3) and an excess of $[NH_4][PF_6]$ dissolved in water (1 cm^3) was added. Immediately a purple precipitate was formed. The solution was refrigerated overnight, and the product filtered off, washed with water and recrystallised by slow evaporation of an acetonitrile solution. It was collected by filtration and washed with acetone to give purple triangular pyramidal crystals. Yield 212 mg (89%) (Found: C, 38.05; H, 6.85; N, 8.35. $C_{21}H_{45}F_6N_4NiO_6P$ requires C, 38.60; H, 6.95; N, 8.60%).

$[Cu(H_3L)][PF_6]_2$. The method was analogous to that used for $[Ni(H_3L)][NO_3][PF_6]$. Copper(II) nitrate trihydrate (78 mg, 0.323 mmol) was treated with 2 cm^3 of the ligand solution. The hexafluorophosphate salt was recrystallised by the slow evaporation of a water–acetonitrile (1:1) solution to give the product as lustrous plates. Attempts to grow crystallographic quality crystals failed. Yield 91 mg (38%) (Found: C, 33.75; H, 5.85; N, 5.50. $C_{21}H_{45}CuF_{12}N_3O_3P_2$ requires C, 34.05; H, 6.10; N, 5.65%).

$[Zn(H_3L)][PF_6]_2\cdot 3H_2O$. The method was analogous to that for $[Ni(H_3L)][NO_3][PF_6]\cdot H_2O$. Zinc nitrate hexahydrate (95 mg, 0.319 mmol) was treated with 2 cm^3 of the ligand solution. The product was recrystallised by the slow evaporation of a methanol solution to yield the product as white needles. Yield 112 mg (43%) (Found: C, 31.75; H, 6.40; N, 5.20. $C_{21}H_{51}F_{12}N_3O_6P_2Zn$ requires C, 31.65; H, 6.45; N, 5.25%).

Crystal Structure Determination of $[Mn^{IV}L][PF_6]\cdot H_2O$ **1** *and* $[Ni(H_3L)][NO_3][PF_6]$ **2**.—Details of the data collection procedures and structural refinements are given in Table 1. Data were collected on an Enraf–Nonius CAD4 automated diffractometer with graphite-monochromated X-radiation (λ = 0.710 69 Å). Unit-cell parameters were determined by refinement of the setting angles of 25 reflections using the SET4 routine. Absorption (DIFABS[8]) (max., min. corrections 1.08 and 0.86) (**1**) and Lorentz-polarisation corrections were also applied.

The statistics of the normalised structure factors and systematic absences uniquely indicated the non-centrosymmetric space groups $P2_1$ (**1**) or $P2_13$ (**2**). The structures were solved by heavy-atom methods for the Mn atom and subsequent electron density difference syntheses (**1**) or by direct methods (SHELXS 86[9]) (**2**). Refinement was by full-matrix least squares minimising the function $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory; $\sigma(F_o)$ was estimated from counting statistics. All non-hydrogen atoms were allowed anisotropic thermal motion. The aliphatic C–H hydrogen atoms were included at calculated positions (C–H 1.0 Å) (the positions of the O–H hydrogens of **2** were determined from a Fourier difference map), and were allowed to

Table 2 Final positional parameters (fractional coordinates) with estimated standard deviations (e.s.d.s) in parentheses for the complex $[MnL][PF_6]\cdot H_2O$ **1**

Atom	*X/a*	*Y/b*	*Z/c*
Mn	0.235 86(5)	0.000 00	0.226 93(3)
P	0.848 28(12)	−0.001 12(14)	0.570 74(6)
F(1)	0.685 4(15)	0.073 7(10)	0.561 9(8)
F(1A)	0.710 7(16)	−0.099 2(8)	0.561 1(14)
F(2)	0.882(2)	0.024(2)	0.677(1)
F(2A)	0.690 9(15)	0.030 1(16)	0.585 8(12)
F(3)	0.878 1(16)	−0.093 7(8)	0.645 7(6)
F(3A)	0.970 6(14)	−0.096 2(12)	0.580 9(18)
F(4)	0.769 2(15)	−0.081 3(10)	0.489 3(8)
F(4A)	0.940 1(10)	0.084 7(8)	0.647 5(11)
F(5)	0.935(3)	0.098(2)	0.560(2)
F(5A)	0.807 3(15)	−0.004 3(24)	0.459 4(6)
F(6)	1.028 2(9)	−0.026 5(9)	0.556 1(5)
F(6A)	0.836(2)	0.089(2)	0.488(1)
N(1)	0.002 8(3)	0.053 7(3)	0.222 9(2)
N(4)	0.290 3(4)	0.069 8(3)	0.362 4(2)
N(7)	0.173 7(3)	−0.136 0(2)	0.297 0(2)
O(1)	0.143 7(3)	−0.054 5(2)	0.106 8(1)
O(100)	0.540 5(5)	0.012 4(6)	0.074 8(3)
O(4)	0.301 1(3)	0.134 6(2)	0.189 5(1)
O(7)	0.432 6(3)	−0.071 5(2)	0.242 0(2)
C(2)	0.021 5(6)	0.154 1(3)	0.284 4(3)
C(3)	0.143 6(6)	0.131 4(4)	0.378 9(3)
C(5)	0.338 9(5)	−0.022 5(3)	0.432 8(2)
C(6)	0.217 9(6)	−0.118 4(4)	0.403 2(3)
C(8)	−0.008 3(5)	−0.151 0(4)	0.259 1(3)
C(9)	−0.090 1(5)	−0.038 8(3)	0.259 1(3)
C(111)	−0.062 9(5)	0.077 1(3)	0.118 0(3)
C(112)	−0.017 2(4)	−0.017 8(3)	0.060 4(2)
C(113)	−0.027 2(5)	0.010 0(4)	−0.046 3(2)
C(114)	0.082 1(8)	0.101 6(4)	−0.059 8(3)
C(115)	0.002 9(8)	−0.095 8(4)	−0.099 2(3)
C(411)	0.430 6(5)	0.145 0(3)	0.359 4(2)
C(412)	0.387 2(5)	0.208 2(3)	0.264 1(3)
C(413)	0.535 5(6)	0.255 1(4)	0.234 7(3)
C(414)	0.637 5(6)	0.328 4(4)	0.317 3(4)
C(415)	0.489 5(7)	0.319 2(5)	0.143 5(4)
C(711)	0.270 2(5)	−0.227 7(3)	0.265 9(3)
C(712)	0.443 5(5)	−0.184 7(3)	0.274 9(3)
C(713)	0.545 5(6)	−0.252 5(4)	0.222 2(5)
C(714)	0.593 5(10)	−0.364 9(6)	0.269 0(6)
C(715)	0.461 8(9)	−0.270 7(6)	0.115 1(5)

Table 3 Final positional parameters (fractional coordinates) with e.s.d.s in parentheses for the complex $[Ni(H_3L)][PF_6][NO_3]$ **2**

Atom	*X/a*	*Y/b*	*Z/c*
Ni	0.692 18(3)	0.692 18	0.692 18
P	0.475 62(10)	0.475 62	0.475 62
F(1)	0.455 7(2)	0.583 4(2)	0.500 3(2)
F(2)	0.450 8(3)	0.495 8(3)	0.367 5(2)
N(1)	0.652 47(19)	0.774 98(17)	0.805 26(21)
N(100)	0.110 7(2)	0.110 7	0.110 7
O(1)	0.584 43(18)	0.606 28(17)	0.747 53(18)
O(100)	0.182 7(2)	0.067 2(2)	0.084 2(2)
C(1)	0.716 9(3)	0.755 3(2)	0.886 2(2)
C(2)	0.552 3(2)	0.751 1(2)	0.826 6(2)
C(3)	0.538 9(3)	0.644 6(2)	0.831 8(2)
C(4)	0.661 7(2)	0.874 4(2)	0.770 5(3)
C(5)	0.434 7(3)	0.614 0(3)	0.836 1(3)
C(6)	0.375 9(3)	0.645 3(3)	0.751 2(3)
C(7)	0.390 1(3)	0.648 3(4)	0.928 8(3)
H(01)	0.585(3)	0.546(3)	0.755(3)

ride on their attached C atom with one common unrefined isotropic thermal parameter (0.08 Å) used. The $[PF_6]^-$ unit in **1** was disordered, and this was modelled by two orientations with site occupancies of 0.58 and 0.42. A water molecule was also found in **1** but the H atoms could not be detected. Refinement of **1** using a total of 270 parameters converged at $R(R') = 0.040$ (0.049), with mean and maximum Δ/σ values of 0.001 and 0.005 respectively. The final electron density difference map showed no peaks of chemical significance (max. $\Delta\rho = +0.33$, min. $\Delta\rho = -0.51$ e $Å^{-3}$ in the vicinity of the Mn atom). The estimated standard deviation (e.s.d.) of an observation of unit weight (S) was 1.33. The correctness of the enantiomer was confirmed by refinement of the η parameter[10] which converged to a value of 1.03(4), with $(1 + |\eta|)/\sigma(\eta) = 47.2$. Refinement using the inverted configuration converged with significantly higher residuals $R(R') = 0.048$ (0.061). Refinement of **2** using a total of 122 parameters converged at $R(R') = 0.025$ (0.031), with mean and maximum Δ/σ values of 0.002 and 0.014 respectively. The final electron density map showed no peaks of chemical significance (max. $\Delta\rho = +0.37$, min. $\Delta\rho = -0.36$ e $Å^{-3}$). The e.s.d. of an observation of unit weight (S) was 1.77. The correctness of the enantiomer was confirmed by refinement of the η parameter which converged to a value of 1.02(5), with $(1 + |\eta|)/\sigma(\eta) = 37.3$. Refinement using the inverted configuration converged with significantly higher residuals $R(R') =$ 0.042 (0.054). Neutral-atom scattering factors were taken from ref. 11 with corrections applied for anomalous scattering. All calculations were carried out on a microVAX 3600 computer using the Glasgow GX suite of programs.[12] Final positional parameters for the two complexes are given in Tables 2 and 3 (**1** and **2** respectively).

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

Results and Discussion

The macrocycle H_3L is prepared in quantitative yield by reaction of [9]aneN_3 with (2*R*)-2-isopropyloxirane. As was the case for H_3L' attack is at the less hindered carbon atom of the epoxide, with retention of configuration at the substituted carbon, resulting in a 100% regio- and stereo-specific reaction.

Synthesis of Metal Complexes of H_3L.—Metal complexes were synthesised by two different methods. The divalent ion complexes $\{[Ni(H_3L)][NO_3][PF_6]$, $[Cu(H_3L)][PF_6]_2$ and $[Zn(H_3L)][PF_6]_2\cdot 3H_2O\}$ were prepared by mixing equimolar quantities of H_3L and the appropriate metal nitrate salt followed by addition of $[NH_4][PF_6]$. The complex $[Mn^{IV}L][PF_6]\cdot H_2O$ was prepared in an analogous manner but the complex was allowed to oxidise in air to the tetravalent state before addition of $[NH_4][PF_6]$. The complexes of Cr^{III} and V^{IV}, $[Cr(H_3L)][PF_6]_3$ and $[VL][PF_6]$ were prepared by first deprotonating H_3L using sodium hydride in thf, followed by addition of the appropriate anhydrous metal salt $\{[CrCl_3(thf)_3]$ or $VCl_3\}$.

As expected all the complexes of H_3L are monomers indicating that the bulk of the isopropyl arms has prevented dimerisation. As was found for H_3L' the air-stable oxidation states formed by H_3L are V^{IV}, Cr^{III}, Mn^{IV} and Ni^{II}. No attempt was made to prepare the cobalt or iron complexes.

Structure and Spectroscopy of $[MnL][PF_6]\cdot H_2O$.—The structure of the $[MnL]^+$ cation is shown in Fig. 1; selected bond lengths and angles are collected in Table 4. As anticipated the structure is monomeric, the isopropyl arms on the ligand effectively preventing dimerisation. This is shown clearly in the stereoview of **1** (Fig. 2) where the isopropyl groups can be seen to project out in front of the *O,O′,O″* face of the molecule. The structure of $[MnL]^+$ is very similar to those of $[MnL']^+$ and

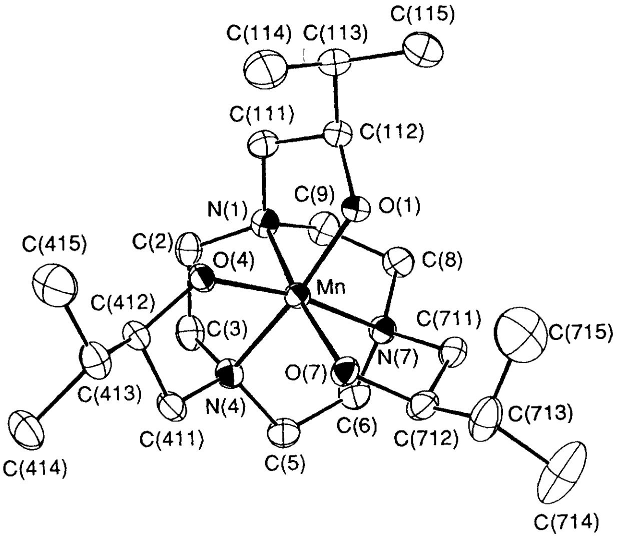

Fig. 1 View of the cation of complex **1** looking down the C_3 axis

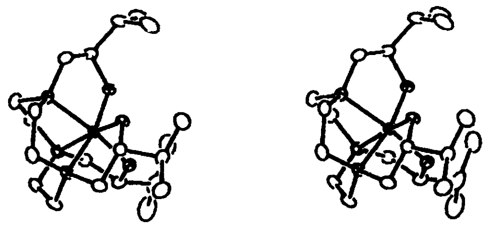

Fig. 2 Stereoview of the cation of complex **1**

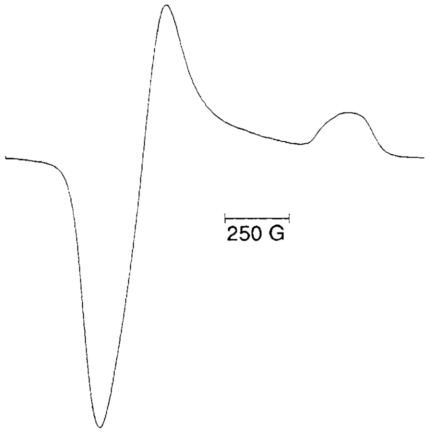

Fig. 3 The X-band (ν = 9.34 GHz) EPR spectrum of a frozen (77 K) solution of complex **1** in MeCN (G = 10^{-4} T)

Table 4 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

$[MnL][PF_6]\cdot H_2O$ **1**			
Mn–N(1)	2.052(3)	Mn–N(4)	2.049(3)
Mn–N(7)	2.044(3)	Mn–O(1)	1.819(3)
Mn–O(4)	1.825(3)	Mn–O(7)	1.831(3)
N(1)–Mn–N(4)	83.9(2)	N(1)–Mn–N(7)	84.8(2)
N(4)–Mn–N(7)	83.9(2)	O(1)–Mn–O(4)	97.7(1)
O(1)–Mn–O(7)	96.3(1)	O(4)–Mn–O(7)	97.0(1)
N(1)–Mn–O(1)	84.2(2)	N(1)–Mn–O(4)	93.8(2)
N(4)–Mn–O(4)	84.1(2)	N(7)–Mn–O(7)	84.2(2)
$[Ni(H_3L)][PF_6][NO_3]$ **2**			
Ni–N(1)	2.055(3)	Ni–O(1)	2.095(3)
O(1)–H(01)	0.86(5)		
N(1)–Ni–N(1)	85.7(2)	O(1)–Ni–O(1)	93.8(1)
N(1)–Ni–O(1)	80.9(1)		

Table 5 A comparison of selected geometric parameters of complexes **1** and **2** with those of related compounds. The twist angle φ is defined in ref. 2

Complex	M–N/Å	M–O/Å	φ/°	Ref.
1	2.048*	1.825*	10.8*	This work
$[Mn(L'\cdot H_3L')Mn]^{3+}$†	2.051	1.857	10.9	2
$[MnL'']^+$	2.044*	1.836*	9.4*	2
$[Co(L'\cdot H_3L')Co]^{3+}$	1.944	1.939	10.2	4
2	2.055	2.095	18.0	This work
$[Ni(H_3L')]^{2+}$	2.064*	2.083*	17.5*	3

* Average values. † For Mn^{IV} part.

$[MnL'']^+$ [L'' = *N*,*N'*,*N''*-tris(2-hydroxyethyl)-1,4,7-triazacyclononane];[2] in all three complexes the ligand is deprotonated, the bond lengths and angles are similar and the twist away from octahedral geometry is almost identical. The geometries of the three complexes are compared in Table 5. The average Mn–O bond length in **1** is slightly shorter than in the other two complexes. This is presumably because the oxygen atoms make no hydrogen-bonded contacts in **1** thus increasing the p_π–d_π overlap. The absolute configuration of **1** is Λ(δλ) consistent with the *R* configuration of the isopropyl groups on the exocyclic rings.

The intramolecular properties of the two monomeric manganese(IV) complexes are, however, different. In $[MnL'']^+$ the *O*,*O'*,*O''* face makes weak hydrogen-bonded contacts with the methylene residues of a second molecule in the unit cell giving a pseudo dimeric structure. In $[MnL]^+$ the *O*,*O'*,*O''* face is too congested for this to occur and the molecular structure consists of independent molecules. Even the water molecule in the lattice is not within hydrogen bonding distance of the cation.

The electronic and circular dichroism (CD) spectra of $[MnL]^+$ are quite similar to those of $[MnL']^+$. There are four prominent electronic transitions at λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 585 (1200), 400 (3000), 300 (8000) and 250 (2900) and a shoulder at 440. The intensities of the electronic transitions (and the values of the dissymmetry ratios, Δε/ε) indicate that they are charge-transfer transitions—presumably alkoxide $\longrightarrow$ Mn^{IV}. The CD spectra are more complicated indicating underlying (possibly d–d) transitions.

The ESR spectrum of $[MnL]^+$ in frozen (77 K) MeCN solution (kindly obtained by Dr. L. J. Yellowlees, University of Edinburgh) is shown in Fig. 3. There are two components with *g* values of 3.674 and 1.922. The spectrum is typical for a d^3 ion with axial symmetry in a strong ligand field and confirms the Mn^{IV} oxidation state. A number of tetragonally and trigonally distorted manganese(IV) complexes have been reported with similar ESR spectra.[13] The zero-field splitting is estimated to be approximately 1.54 cm^{-1} which reflects the large trigonal distortion of the complex.

The cyclic voltammogram of **1** in acetonitrile (dried with molecular sieves to remove the lattice water) shows two irreversible reductions at −0.58 and −0.79 V (*vs.* Ag–Ag$^+$). The reduction processes are presumably $Mn^{IV} \longrightarrow Mn^{III}$ (which is Jahn–Teller unstable) and $Mn^{III} \longrightarrow Mn^{II}$ (which is labile).

Structure and Spectroscopy $[Ni(H_3L)][NO_3][PF_6]$.—The structure of the $[Ni(H_3L)]^{2+}$ cation is shown in Fig. 4 and selected bond lengths and angles given in Table 4. The complex has exact C_3 symmetry with a twist away from octahedral geometry of 18°. The O–H groups form a three-dimensional hydrogen bonding network with the nitrate ion.

The absorption and CD spectra of $[Ni(H_3L)]^{2+}$ (as the chloride salt) are shown in Fig. 5. There are two interesting features. The intensity of the absorption spectrum is high for a complex with saturated ligators (ε for all three bands of

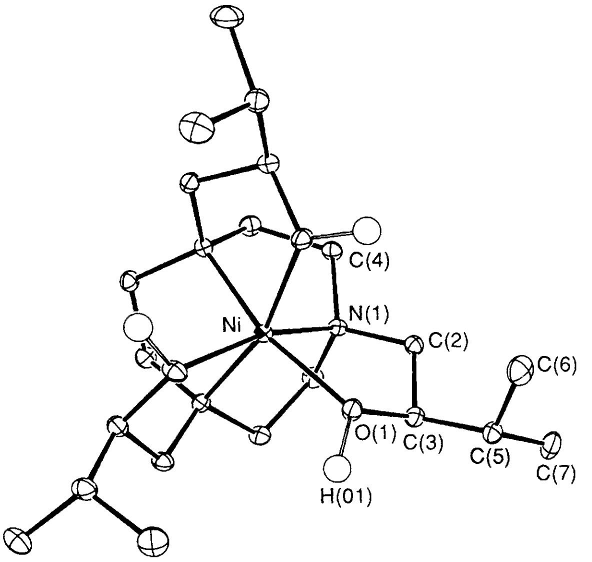

Fig. 4 View of the cation of complex **2** looking down the C_3 axis

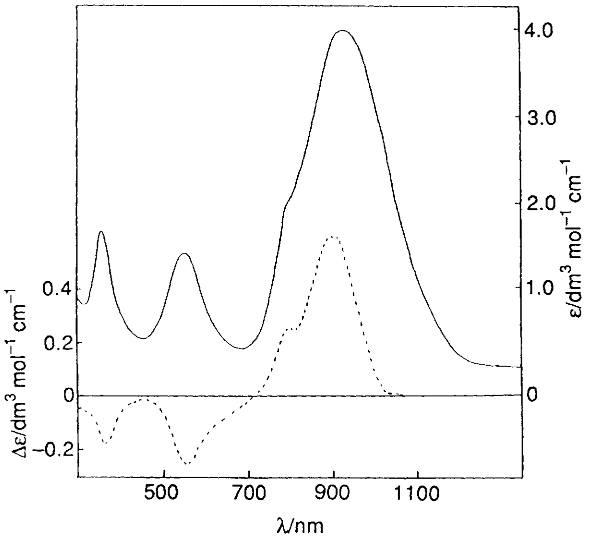

Fig. 5 Absorption and CD spectra of an aqueous solution (4×10^{-2} mol dm^{-3}) of $[Ni(H_3L)]Cl_2$

$[Ni(OH_2)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ (en = ethylenediamine) lie in the range 2–9 dm^3 mol^{-1} cm^{-1} [14]) whereas in **2** the intensities lie in the range 13–40. secondly the intensity of the magnetic dipole allowed $^4A_2 \longrightarrow {}^4T_2$ transition (at 931 nm) is more than twice that of the other two bands [$^4A_2 \longrightarrow {}^4T_1$ and $^4T_1(P)$]. Again this is quite different from typical O_h or D_3 complexes of Ni^{II} where the magnetic dipole transition invariably has the lowest intensity.

The CD spectra are typical for tris-chelates of Ni^{II} in that both higher energy bands have a single signed CD (T_1 splits into $A_2 + E$ in D_3 symmetry and the $A_2 \longrightarrow A_2$ component of the transition is symmetry forbidden). The lowest energy (magnetic dipole allowed) band is of one sign down to the photomultiplier cut-off of 1000 nm. The dissymmetry factors for the three transitions are of comparable magnitude and in the range expected for magnetic dipole allowed transitions ($\Delta\varepsilon/\varepsilon$ = 1.65, 2.15 and 1.25×10^{-2} for the $^4A_2 \longrightarrow {}^4T_2$, $^4T_1$ and $^4T_1(P)$ transitions respectively). This is in marked contrast to typical D_3 tris-chelates where the dissymmetry factors of the magnetic dipole forbidden $^4A_2 \longrightarrow {}^4T_1$ and $^4T_1(P)$ transitions are almost an order of magnitude smaller than that of the magnetic dipole allowed transition.[15] This must reflect the fact that the three transitions are extensively mixed in the strongly trigonally distorted complex $[Ni(H_3L)]^{2+}$.

$[VL]^+$, $[Cr(H_3L)]^{3+}$, $[Cu(H_3L)]^{2+}$ *and* $[Zn(H_3L)]^{2+}$.—The vanadium(IV) complex $[VL]^+$, as expected, contains a deprotonated L ligand. It has similar spectroscopic properties, and is slightly more air stable than the mixed-metal analogue $[V^{IV}(L'\cdot H_3L')Zn^{II}]^{3+}$.[6] The two vanadium species will be fully discussed in a subsequent paper.

The chromium complex, $[Cr(H_3L)]^{3+}$, isolated from acid solution, contains protonated H_3L. The complex is acidic and slowly deprotonates in acetonitrile or diethyl ether to give a mixture of $[Cr(H_3L)]^{3+}$ and [CrL] (and probably the various intermediate complexes). In acetonitrile with a drop of triethylamine the complex fully deprotonates to give [CrL]. The Δ and B values of the protonated and deprotonated complexes are consistent with alcohol and alkoxide ligators respectively $\{[Cr(H_3L)]^{3+}$, Δ = 19 150 cm^{-1}, B = 740 cm^{-1}; [CrL], Δ = 17 000 cm^{-1}, B = 600 cm$^{-1}\}$. The protonation behaviour of $[Cr(H_3L)]^{3+}$ is consistent with that of the dimers $[M(L'\cdot H_3L')M]^{3+}$, M = Cr^{III} and Co^{III}, except that in the latter case the hydrogen bridged dimeric structure is formed in the neutral pH region (*i.e.* water at pH 7 or acetonitrile) while with the bulky H_3L a mixture containing both protonated and deprotonated monomeric species is formed.

The copper and zinc complexes have not been structurally characterised; $[Cu(H_3L)]^{2+}$ has a single absorption and CD band (at 720 nm) suggesting a geometry close to octahedral. The complex $[Zn(H_3L)]^{2+}$ shows seven sharp resonances in the ^{13}C NMR spectrum indicating that the complex has exact C_3 symmetry and suggesting octahedral co-ordination.

Conclusion

We have synthesised the sterically demanding pendant arm macrocycle H_3L and prepared and characterised its complexes with V^{IV}, Cr^{III}, Mn^{IV}, Ni^{II}, Cu^{II} and Zn^{II}. The ligand, which has bulky isopropyl arms, prevents the formation of dimeric species which is a feature of the chemistry of the analogous ligand with methyl substituted arms (H_3L'). The crystal structures of $[Mn^{IV}L][PF_6]\cdot H_2O$ and $[Ni^{II}(H_3L)][NO_3][PF_6]$ have been determined.

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