Studies of the Reaction System $[ScCl_3(thf)_3]$–$SbCl_5$–L (thf = tetrahydrofuran, L = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane): Unexpected Formation and Crystal Structure of $[H_2L]Cl_2{\cdot}ScCl_3(H_2O)_3{\cdot}3H_2O$†

Gerald R. Willey,*[a] **Paul R. Meehan,**[a] **Martin D. Rudd**[a] **and Michael G. B. Drew**[b]
[a] *Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*
[b] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD, UK*

The reaction system $[ScCl_3(thf)_3]$–$SbCl_5$–cryptand 222 (L) (thf = tetrahydrofuran, cryptand 222 = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) has been studied as a possible route to scandium(III)–cryptate complexation. The compound $[H_2L]Cl_2{\cdot}ScCl_3(H_2O)_3{\cdot}3H_2O$ **1** was isolated as yellow crystals. Microanalytical and spectroscopic (IR, ^1H) data and a crystal-structure determination provided complete identification of **1**. Crystals are monoclinic, space group *C*2/*c* with a = 29.008(14), b = 8.369(7), c = 26.356(14) Å, β = 94.6(1)° and Z = 8. The molecular structure consists of discrete $[H_2L]^{2+}$ cations, two accompanying chloride anions, a molecule of $[ScCl_3(H_2O)_3]$ and three water molecules trapped in the lattice. The diprotonated di-*endo* cryptand cation binds two protons within the intramolecular cavity with an N···N separation of 6.34(4) Å. The encapsulated protons are covalently bound to the nitrogen atoms and each NH centre is involved in weak intracavity hydrogen-bonding interactions with the three adjacent oxygen atoms [N···O 2.84(2) (two), 2.83(2) Å and 2.74(2), 2.71(2), 2.72(2) Å]. The structure of the molecular adduct $[ScCl_3(H_2O)_3]$ shows a central six-co-ordinate scandium atom with a near-idealised *mer*-octahedral geometry [mean Sc–Cl 2.417(7), mean Sc–O 2.122(14) Å].

The large macrobicycle $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ or cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane, L) forms a series of inclusion complexes (cryptates) with a variety of metal ions.[1,2] Encapsulation of the metal cation in the intramolecular cavity involving all eight heteroatoms (two N plus six O) is typical for s-block elements M^+ (M = Na,[3] K,[4] Li,[5] Rb or Cs[6]) and M^{2+} (M = Ca[7] or Ba[8]), f-block elements M^{3+} (M = Eu,[9] La,[10] Sm[11] or Nd[12]), p-block elements (*e.g.* Pb^{2+} [13] or Tl^+ [14]) and, quite recently, the first examples from the transition-metal (d block) elements *viz.* $[MnL][CF_3SO_3]_2$,[15] $[CdL][CdCl_4]$ and $[HgL][Hg_2Cl_6]$.[16]

Recent studies in these laboratories have demonstrated that the *trans*-$ScCl_2^+$ cation, as generated by *in situ* halide abstraction of $ScCl_3$ using $SbCl_5$ (1 mol) in acetonitrile solution, can be stabilised by macrocyclic complexation using crown ethers, *e.g.*, 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (benzo-15-crown-5), 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), 6,7,9,10,12,13,20,21,23,24,-26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (dibenzo-24-crown-8) and 6,7,9,10,12,13,15,-16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b*,*q*][1,4,7,-10,13,16,19,22,25,28]decaoxacyclotriacontine (dibenzo-30-crown-10); all the resulting structures show cavity entrapment with a common seven-co-ordinate pentagonal-bipyramidal metal geometry.[17] Recognition of the great flexibility of L, with a diagonal N···N separation distance 6.87 Å, coupled with the successful isolation of $[MnL][CF_3SO_3]_2$ [diagonal N···N separation distance 4.46 Å and effective ionic radius Mn^{2+} (eight-co-ordinate) estimated at 1.10 Å[18]] encouraged us to attempt the encapsulation of Sc^{3+} [effective ionic radius Sc^{3+} (eight-co-ordinate) estimated at 1.01 Å[18]], to be introduced by *in situ* halide abstraction of the parent halide using a healthy excess (6–8 mol) of $SbCl_5$.

Although this objective proved to be elusive the interesting compound $[H_2L]Cl_2{\cdot}ScCl_3(H_2O)_3{\cdot}3H_2O$ **1** was isolated and has been structurally characterised by X-ray diffraction studies.

Experimental

All reactions and manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. Solvents were dried over CaH_2–P_4O_{10} and distilled under dinitrogen prior to use. The compound $[ScCl_3(thf)_3]$ (thf = tetrahydrofuran) was prepared as described in the literature.[19] The cryptand (L) was obtained from Aldrich and purified by recrystallisation from benzene. The IR spectra were recorded as Nujol mulls (CsI plates) on a Perkin-Elmer 580B spectrophotometer, ^1H (220 MHz) NMR spectra using a Bruker AC250 spectrometer. Microanalytical data were obtained using a Leeman Labs Inc., PS 1000 sequential inductively coupled plasma (ICP) spectrometer and a Leeman Labs Inc., CE440 elemental (C,H,N) analyser.

Preparation of $[H_2L]Cl_2{\cdot}ScCl_3(H_2O)_3{\cdot}3H_2O$ **1**.—A solution of $SbCl_5$ (0.40 g, 1.34 mmol) in acetonitrile (20 cm^3) was added dropwise to a stirred, chilled (0 °C) solution of $[ScCl_3(thf)_3]$ (0.12 g, 0.334 mmol) in acetonitrile (25 cm^3). The resulting solution was stirred at room temperature for 6 h and then transferred very slowly, *via* a stainless-steel transfer needle fitted with a glass frit attachment, directly into a solution of L (0.12 g, 0.330 mmol) in benzene (20 cm^3). Further stirring (24 h) at 50 °C produced a light yellow solution which was concentrated *in vacuo* to a volume of approximately 15 cm^3. Controlled cooling in a refrigerator at −30 °C resulted in the deposition of a crop of pale yellow needles which were collected, washed with diethyl ether (3 × 20 cm^3) and pumped dry *in vacuo* for several

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: cal = 4.184 J.

Table 1 Crystal data and structure refinement for compound **1**

Empirical formula	$C_{18}H_{50}Cl_5N_2O_{12}Sc$
M	708.81
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	29.008(14)
b/Å	8.369(7)
c/Å	26.356(14)
β/°	94.6(1)
U/Å^3	6378.2
Z	8
D_c/Mg m^{-3}	1.476
T/K	293(2)
λ/Å	0.710 70
Absorption coefficient/mm^{-1}	0.70
F(000)	2992
Crystal size/mm	0.3 × 0.15 × 0.2
θ Range/°	2.01–25.03
Index ranges	$0 \leqslant h \leqslant 34$, $-9 \leqslant k \leqslant 9$, $-30 \leqslant l \leqslant 30$
No. of reflections collected	8316
No. of independent reflections	5093 (R_{int} = 0.0497)
Refinement method	Full-matrix least squares on F^2
Data, parameters	5093, 374
Goodness of fit on F^2	1.090
$R1$, $wR2$ [$I > 4\sigma(I)$, 2134 data]	0.0666, 0.1918
$R1$, $wR2$ (all data)	0.1199, 0.2833
Largest difference peak, hole/e Å^{-3}	0.610, −0.780

Weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.17P)^2 + 69.07P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2 Atomic coordinates (× 10^4) for compound **1**

Atom	x	y	z
Sc	1 245(1)	9 620(3)	819(1)
Cl(1)	1 858(1)	9 744(4)	249(1)
Cl(2)	543(2)	9 563(5)	1 253(2)
Cl(3)	1 756(2)	9 605(5)	1 590(2)
O(1)	795(4)	9 552(13)	129(4)
O(2)	1 227(4)	12 103(11)	813(4)
O(3)	1 227(4)	7 076(10)	781(4)
N(100)	1 666(4)	4 604(12)	−594(4)
N(200)	1 006(5)	5 408(14)	−2 753(4)
C(11)	2 014(5)	3 297(14)	−563(5)
C(12)	1 870(5)	1 973(15)	−939(5)
O(13)	1 822(4)	2 647(11)	−1 459(4)
C(14)	2 222(7)	3 006(20)	−1 668(6)
C(15)	2 149(7)	3 135(20)	−2 234(6)
O(16)	1 858(4)	4 388(13)	−2 367(4)
C(17)	1 775(9)	4 539(24)	−2 897(7)
C(18)	1 413(7)	5 623(34)	−3 030(7)
C(31)	1 866(6)	6 154(16)	−392(5)
C(32)	2 110(5)	6 986(13)	−795(4)
O(33)	1 765(4)	7 531(10)	−1 167(3)
C(34)	1 956(6)	8 081(18)	−1 617(5)
C(35)	1 584(7)	8 765(18)	−1 951(6)
O(36)	1 245(4)	7 681(11)	−2 096(4)
C(37)	921(7)	8 215(21)	−2 489(6)
C(38)	728(9)	6 907(26)	−2 734(9)
C(21)	1 259(6)	4 155(17)	−345(5)
C(22)	827(5)	4 994(16)	−576(5)
O(23)	769(4)	4 551(11)	−1 096(3)
C(24)	513(5)	3 110(17)	−1 204(5)
C(25)	619(6)	2 402(18)	−1 663(5)
O(26)	551(4)	3 443(10)	−2 081(4)
C(27)	678(8)	2 826(20)	−2 537(6)
C(28)	689(8)	4 102(22)	−2 900(6)
Cl(4)	464(2)	4 560(4)	785(2)
Cl(5)	1 976(1)	4 595(4)	845(1)
O(50)	983(4)	9 201(12)	−868(4)
O(60)	−284(6)	2 286(19)	1 421(6)
O(70)	−18(7)	7 904(22)	40(7)

Table 3 Selected torsion angles (°) for the $[H_2L]^{2+}$ cation in compound **1**

C(21)–N(100)–C(11)–C(12)	76(1)
C(31)–N(100)–C(11)–C(12)	−158(1)
N(100)–C(11)–C(12)–O(13)	59(2)
C(11)–C(12)–O(13)–C(14)	74(2)
C(12)–O(13)–C(14)–C(15)	161(1)
O(13)–C(14)–C(15)–O(16)	64(2)
C(14)–C(15)–O(16)–C(17)	−179(2)
C(15)–O(16)–C(17)–C(18)	169(2)
O(16)–C(17)–C(18)–N(200)	−46(3)
C(28)–N(200)–C(18)–C(17)	−78(2)
C(38)–N(200)–C(18)–C(17)	156(2)
C(21)–N(100)–C(31)–C(32)	−152(1)
C(11)–N(100)–C(31)–C(32)	83(1)
N(100)–C(31)–C(32)–O(33)	70(1)
C(31)–C(32)–O(33)–C(34)	−169(1)
C(32)–O(33)–C(34)–C(35)	−174(1)
O(33)–C(34)–C(35)–O(36)	−61(2)
C(34)–C(35)–O(36)–C(37)	−169(1)
C(35)–O(36)–C(37)–C(38)	156(2)
O(36)–C(37)–C(38)–N(200)	−29(3)
C(18)–N(200)–C(38)–C(37)	−63(3)
C(28)–N(200)–C(38)–C(37)	164(2)
C(11)–N(100)–C(21)–C(22)	−152(1)
C(31)–N(100)–C(21)–C(22)	82(1)
N(100)–C(21)–C(22)–O(23)	60(1)
C(21)–C(22)–O(23)–C(24)	87(2)
C(22)–O(23)–C(24)–C(25)	−156(1)
O(23)–C(24)–C(25)–O(26)	−56(2)
C(24)–C(25)–O(26)–C(27)	176(2)
C(25)–O(26)–C(27)–C(28)	−167(2)
O(26)–C(27)–C(28)–N(200)	59(3)
C(18)–N(200)–C(28)–C(27)	111(2)
C(38)–N(200)–C(28)–C(27)	−120(2)

hours at room temperature (yield 0.07 g, 34%), m.p. 176–178 °C (Found: C, 29.95; H, 7.00; Cl, 24.90; N, 3.65. Calc. for $C_{18}H_{50}Cl_5N_2O_{12}Sc$: C, 30.50; H, 7.10; Cl, 25.00; N, 3.95%). IR $\tilde{\nu}$/cm^{-1} (Nujol) 3354s (br) (H_2O), 3160s [ν(NH)], 1746m, 1620s (br) (H_2O), 1302m, 1261w, 1230m, 1117vs, 1067s, 1022s, 961s, 931s, 908s, 834m, 818m, 808m, 722m, 669m, 570m, 532m, 496m, 466w, 393w and 340s [ν(ScCl)].

X-Ray Crystallography.—Crystal data are given in Table 1, together with refinement details. Data were collected with Mo-Kα radiation using the MARresearch image plate system. The crystal was positioned 75 mm from the image plate and 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[20] The structure was solved using direct methods with the SHELXLS 86 program.[21] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on carbon were included in geometric positions. The two protons on the bridgehead nitrogen atoms were clearly discernible in a Fourier-difference map and were included in the refinement. Default C–H and N–H distances of 0.97 and 0.91 Å respectively were used. Four of the six hydrogen atoms on the water molecules bonded to the metal atom were located but the other two together with those of the solvent water molecules could not be located. The structure was then refined using SHELXL 93.[22] All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. The fractional atomic coordinates for compound **1** are listed in Table 2, selected torsion angles for $[H_2L]^{2+}$ in Table 3, selected intermolecular hydrogen-bonding contacts in Table 4 and selected bond parameters for the *mer*-$[ScCl_3(H_2O)_3]$ moiety in Table 5.

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

Table 4 Intermolecular hydrogen bonds (Å) for compound **1**

O(1) ··· O(70)	2.726	O(3) ··· Cl(4)	3.057
O(1) ··· O(50)	2.742	O(50) ··· O(33)	2.830
O(2) ··· Cl(5$^{\text{III}}$)	3.007	O(60) ··· O(23$^{\text{I}}$)	3.087
O(2) ··· Cl(4$^{\text{III}}$)	3.019	O(60) ··· O(50$^{\text{II}}$)	2.705
O(3) ··· Cl(5)	3.001		

Symmetry elements: I $0.5 - x, 1.5 - y, -z$; II $0.5 - x, 0.5 + y, 0.5 - z$; III $0.5 - x, y - 0.5, 0.5 - z$.

Table 5 Bond lengths (Å) and angles (°) for the metal in compound **1**

Sc–O(2)	2.078(10)	Sc–Cl(2)	2.413(6)
Sc–O(3)	2.132(9)	Sc–Cl(3)	2.419(4)
Sc–O(1)	2.155(9)	Sc–Cl(1)	2.419(5)
O(2)–Sc–O(3)	175.9(4)	O(1)–Sc–Cl(3)	178.1(3)
O(2)–Sc–O(1)	90.4(4)	Cl(2)–Sc–Cl(3)	94.9(2)
O(3)–Sc–O(1)	85.5(4)	O(2)–Sc–Cl(1)	88.4(4)
O(2)–Sc–Cl(2)	90.1(4)	O(3)–Sc–Cl(1)	91.7(4)
O(3)–Sc–Cl(2)	89.1(4)	O(1)–Sc–Cl(1)	84.4(3)
O(1)–Sc–Cl(2)	85.5(3)	Cl(2)–Sc–Cl(1)	169.8(2)
O(2)–Sc–Cl(3)	91.5(3)	Cl(3)–Sc–Cl(1)	95.2(2)
O(3)–Sc–Cl(3)	92.6(3)		

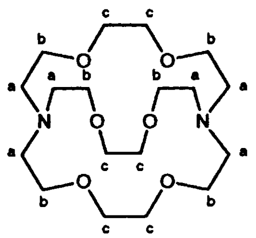
Results and Discussion

Compound **1** was isolated from the $ScCl_3(thf)_3$–$SbCl_5$–L system as yellow needles. Consideration of the microanalytical and spectroscopic data gave a clear pointer that it was not the desired product but rather a protonated cryptand species. The ^1H NMR spectrum revealed conspicuous downfield chemical shifts for the H^a, H^b and H^c protons (Table 6) and the appearance of a signal at δ 6.59 typical for NH^+. The greatest change occurs for the H^a protons ($\Delta = 0.89$ ppm) as might be expected since these are adjacent to the bridgehead nitrogen atoms and are clearly the most sensitive to NH^+ formation. This trend has been noted for cryptand 222–metal complexation where these N–CH_2 protons show shifts which vary according to both cation size and charge (*e.g.* K^+, $\Delta = 0.15$; Ca^{2+}, $\Delta = 0.35$ ppm).[23] The H^b protons experience a shift of 0.24 ppm and now appear further downfield than either H^a or H^c in line with previous observations for metal–cryptate 222 formation.[24] The IR spectrum contains broad asymmetric bands at 3354 and 1620 cm^{-1} confirming the presence of water molecules, an intense band at 3160 cm^{-1} [ν(NH)] and a strong fairly broad band in the low-energy region at 340 cm^{-1} [ν(ScCl)] together with a characteristic range of ligand bands.

The formation of compound **1** is most likely the result of hydrolysis reactions resulting from adventitious water intrusion. Despite rigorous drying procedures, contamination of the solvents and a drop in quality of the in-house dinitrogen supply are considered to be the most likely sources. Subsequent limited hydrolysis of $SbCl_5$ releases hydrogen chloride which provides a ready source of H^+, for cryptand protonation, and chloride counter anions. The molecular structure of **1** is of considerable interest and novelty: it consists of discrete $[H_2L]^{2+}$ cations, two accompanying chloride counter anions, an included molecular adduct $[ScCl_3(H_2O)_3]$ together with three solvent (H_2O) molecules trapped in the lattice. Previous cryptand and protonated cryptand structures include: cryptand 111 (4,10,15-trioxa-1,7-diazabicyclo[5.5.5]heptadecane) and its mono- and di-protonated forms,[25] the diprotonated form of cryptand 211 (4,7,13,18-tetraoxa-1,10-diazabicyclo[8.5.5]icosane),[26] cryptand 221 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane) (as a co-crystallised species with an iron porphyrin complex)[27] and its diprotonated form.[28] The structure of uncomplexed cryptand 222 is published[29] but this is, surprisingly, the first identification of a protonated species. This is particularly astonishing given that there are 147 crystal structures involving this cryptand or its substituted analogues listed in the Cambridge Crystallographic Database. Most of the metal–cryptand 222 complexes that have been reported feature eight-co-ordinate cations with the metal encapsulated within the cavity and bonded to all six oxygen atoms and the two nitrogen atoms. For the smaller cations such as Na^+, however, the co-ordination sphere can be somewhat irregular in that whereas all six oxygen atoms are invariably bonded to the metal the two nitrogens are often located much further away and may or may not be considered within bonding distance(s). For the transition-metal complexes typical bond dimensions include: Mn^{II}, Mn–O 2.393(2) Å identical by symmetry and, within experimental error, the same as Mn–N [2.406(4) Å];[15] Cd^{II}, Cd–O 2.426(7)–2.492(7), Cd–N 2.431(8) Å; Hg^{II}, Hg–O 2.68(1)–2.72(1), Hg–N 2.17(2) Å;[16] in comparison the corresponding dimensions in the complex $[NaL]_3[Sb_7Mo(CO)_3]$[30] are Na–O 2.44(2)–2.66(2), Na–N 2.67(2), 2.75(2) Å.

As an evaluation of bond length–metal geometry variations for metal–cryptate 222 systems we have carried out molecular mechanics calculations using the CERIUS 2 software[31] and the Universal force field. We calculated the hole size for the macrocycle using our established method,[32] where we fix the bond length between the metal and donor atom at specific values in turn by incorporating a large force constant for the harmonic bond-stretch term. For each particular M–L distance the energy is minimised. The resulting value is a measure of how well the macrocycle can adapt to fit in with specific M–L distances. A plot of *E vs.* M–L distance can then provide the ideal distances for encapsulation of the macrocycle. Rather than incorporate two ideal distances (for M–N and M–O), M–O was set at a specific value and then M–N set at a distance 0.15 Å greater. This was in accord with the experimental data from crystal structures. We did not include angles around the metal in the molecular mechanics summation so that there would be no restriction on co-ordination geometry, but van der Waals interactions between donor atoms were included. The plot of *E vs.* M–O distance for complexes of cryptand 222 (Fig. 1) shows that the most favoured M–O distance is *ca.* 2.85 Å; interestingly the K–O bond dimensions for $[KL]^+$ compounds[4] are found in the range 2.774(6)–2.853(6) Å reflecting the excellent fit for this particular cation. The curve is quite steep for smaller M–O distances and indicates that the cryptand cannot easily adapt for the smaller metal ions. A search of the Cambridge Crystallographic Database for comparable structures with incipient Sc–O bond distances in the range 2.8–2.9 Å provided scant encouragement. The most relevant examples to emerge derive from Sc^{III}–oxacrown cations of the type $[ScCl_2(crown)]^+$ which feature a seven-co-ordinate pentagonal-bipyramidal metal environment comprising an equatorial plane of five oxygen and two axial chlorine atoms. Typical examples include: $[ScCl_2(benzo\text{-}15\text{-}crown\text{-}5)]^+$, Sc–$O_{crown}$ 2.166(4)–2.223(4); $[ScCl_2(15\text{-}crown\text{-}5)]^+$, Sc–$O_{crown}$ 2.09(2)–2.12(2); $[ScCl_2(18\text{-}crown\text{-}6)]^+$, Sc–$O_{crown}$ (only five of the six oxygens bonded to the metal) 2.190(5)–2.229(5); $[ScCl_2(dibenzo\text{-}24\text{-}crown\text{-}8)(H_2O)]^+$, Sc–$O_{crown}$ (only four of the eight oxygens bonded to the metal) 2.184(7)–2.297(7); $[ScCl_2(dibenzo\text{-}30\text{-}crown\text{-}10)(H_2O)_2]^+$, Sc–$O_{crown}$ (only three of the ten oxygens bonded to the metal) 2.208(8)–2.280(8) Å.[17] These bond dimensions, and taking into account Fig. 1, would indicate that scandium(III) is rather on the small side to fit snugly, *i.e.* eight-co-ordinate, into the cavity of L. An alternative consideration is whether the cryptand could form a six-co-ordinate metal complex with the available oxygen atoms to the exclusion of the two nitrogens. There are no clear examples of this particular binding mode in the Database; all structures (even those with Na^+) have both nitrogen atoms directed towards the metal (*endo*) even if they are much further away than the oxygen set. We note also that the arrangement of the six oxygen atoms around the metal can be considered to be closer to an octahedral rather than a trigonal-prismatic

Table 6 Proton NMR data for compound **1** and L



Compound	δ N-CH$_2$ (a)	O-CH$_2$CH$_2$-NH$_2$ (b)	O-CH$_2$CH$_2$-O (c)	[NH]$^+$
1	3.47 (br m, 12 H)	3.78 (br t, 12 H)	3.68 (s, 12 H)	6.59 (br, 2 H)
L	2.58 (t, 12 H)	3.54 (t, 12 H)	3.61 (s, 12 H)	

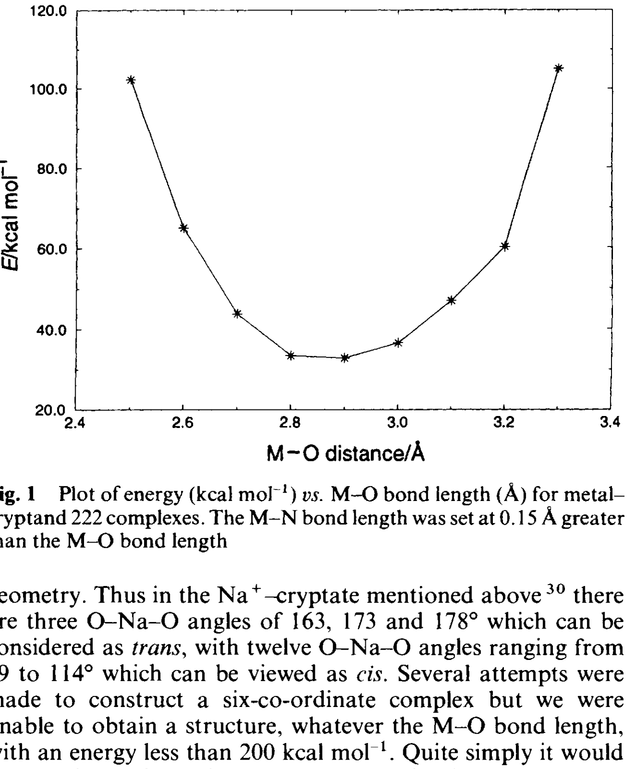


Fig. 1 Plot of energy (kcal mol^{-1}) *vs.* M–O bond length (Å) for metal–cryptand 222 complexes. The M–N bond length was set at 0.15 Å greater than the M–O bond length

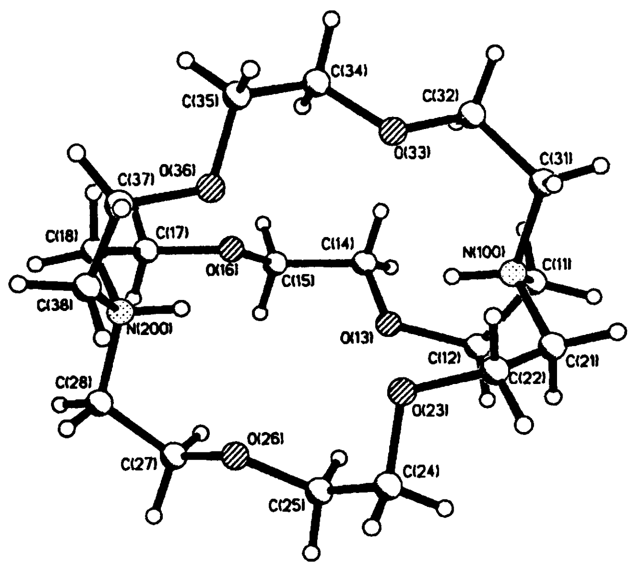


Fig. 2 A view of the [H$_2$L]$^{2+}$ cation of compound **1** with the atomic numbering scheme used

geometry. Thus in the Na$^+$-cryptate mentioned above[30] there are three O–Na–O angles of 163, 173 and 178° which can be considered as *trans*, with twelve O–Na–O angles ranging from 69 to 114° which can be viewed as *cis*. Several attempts were made to construct a six-co-ordinate complex but we were unable to obtain a structure, whatever the M–O bond length, with an energy less than 200 kcal mol^{-1}. Quite simply it would appear that L is unable to provide a suitable/acceptable co-ordination sphere for the relatively small scandium(III) ion.

The structure of the [H$_2$L]$^{2+}$ cation is shown in Fig. 2 together with the atom notation used. The framework dimensions are as expected. With both protons lying within the molecular cavity the molecule is clearly in an *endo–endo* conformation thereby encouraging all the oxygen atoms to assume their closest approach positions and orientate their lone pairs towards the centre of the cavity for maximum N–H ··· O interactions. This point is reinforced by a comparison of O–C–C–O torsion angles, *viz.* whereas uncomplexed L shows values of −175, −178, 179 (mean 177°)[29] the corresponding values for compound **1** are 64(2), −61(2), −56(2)° (*cf.* [KL]$^+$, mean O–C–C–O 51°).[4] Both nitrogen atoms enjoy an essentially tetrahedral environment: N(100), mean C–N–C 112°; N(200), mean C–N–C 113°. Evidently the size of the cavity of L is extremely variable *e.g.* inclusion of Cs$^+$ results in N ··· N 6.1 Å[6] whereas inclusion of Mn^{2+} results in N ··· N 4.46 Å.[15] Here, and as if to emphasise the great flexibility of this cryptand, the N ··· N separation has decreased to 6.34(4) Å compared to 6.87 Å in the uncomplexed cryptand, a reduction of some 8% in the accommodation of the two protons. Each NH centre is involved in weak hydrogen-bonding interactions with its three nearest-neighbour oxygen atoms and allowing for the general floppiness of the CH$_2$–CH$_2$ linkages there is an approximate C_3 axis along the N ··· N direction coincident with the N–H bonds. The N ··· O separations [*i.e.* around N(100), 2.84(2) (two), 2.83(2) Å; around N(200), 2.74(2), 2.71(2), 2.72(2) Å] are perceptibly shortened with respect to the free cryptand [*e.g.* 2.942(3), 3.094(3), 3.041(3) and 3.045(3), 2.940(3), 2.959(3) Å][29] as a direct reflection of this intracavity hydrogen bonding. A similar pattern is noted in the O ··· O separations: for the diprotonated form presented here the range is 3.59(3)–3.89(3) Å whereas the uncomplexed macrocycle shows a range between 3.744(4) and 4.697(4) Å with the majority in excess of 4.0 Å.

The structure of the included [ScCl$_3$(H$_2$O)$_3$] molecule is shown in Fig. 3 complete with the atom labelling used. Individual six-co-ordinate scandium atoms adopt a *mer*-octahedral geometry with Sc–Cl bond distances 2.413(6), 2.419(4), 2.419(5), and Sc–O bond distances 2.078(10), 2.132(9), 2.155(9). These bond dimensions compare favourably with those observed in the analogous *mer*-[ScCl$_3$(thf)$_3$][33] Sc–Cl 2.406(4), 2.420(4), 2.415(4) Å, Sc–O 2.236(8), 2.147(7), 2.164(7) Å which, up until now, has been the sole representative of six-co-ordinate (O_h) [ScCl$_3$L'$_3$] species for monodentate (L') ligands.

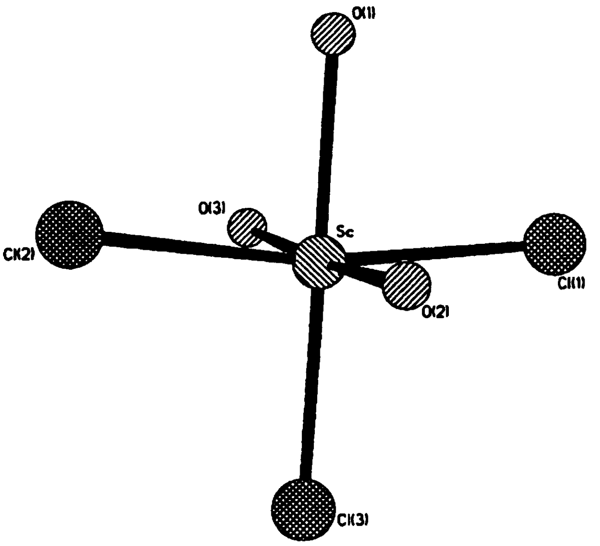


Fig. 3 Structure of the $[ScCl_3(H_2O)_3]$ moiety of compound **1**

In contrast the Sc–O bond length (mean 2.07 Å) noted for $[Sc(acac)_3]$[34] (acac = acetylacetonate) reflects an inherent ionic character. As indicated in Table 5, whereas the *cis* interbond angles O–Sc–O [mean 88(2)°], O–Sc–Cl [mean 89(3)°] for compound **1** do not differ in a significant sense from the ideal (90°), the *cis* angles Cl–Sc–Cl [mean 95.1(2)°] do show a slight abnormality.

There is an extensive intermolecular hydrogen-bonding pattern in the structure as shown in Table 4. Thus for the cation, each of the three water molecules that are co-ordinated to the Sc atom is involved in two hydrogen bonds; one water molecule, O(1), is linked to two of the lattice water molecules whilst the other two, O(2), O(3), are in contact distance with each of the two chloride ions. In addition there are two hydrogen bonds from lattice water molecules to the oxygen atoms in the cryptate.

Acknowledgements

We thank the SERC for a studentship (to M. D. R.) and the University of Warwick for a postgraduate studentship (to P. R. M.). Financial support by the SERC and the University of Reading for the image plate system is gratefully acknowledged. We are indebted to Mr. A. W. Johans for technical assistance with the X-ray crystallographic studies and acknowledge the use of the SERC funded Chemical Databank Service at Daresbury.

References

1 J.-M. Lehn, *Science*, 1985, **227**, 849.
2 R. Hilgenfield and W. Saenger, in *Host Guest Complex Chemistry/Macrocycles*, eds. F. Vögtle and E. Weber, Springer, Berlin, 1985, pp. 43–124.
3 D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 396; K. Plossl, G. Huttner and L. Zsolnai, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 446; F. Ettel, G. Huttner, L. Zsolnai and C. Emmerich *J. Organomet. Chem.*, 1991, **414**, 71.
4 D. Moras, B. Metz and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 383; R. C. Burns and J. D. Corbett, *Inorg. Chem.*, 1981, **20**, 4433; M. Bjorgvinsson, J. F. Sawyer and G. J. Schrobilgen, *Inorg. Chem.*, 1991, **30**, 2231.
5 D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 400; C. Cambillau, G. Bram, J. Corset and C. Riche, *Nouv. J. Chim.*, 1979, **3**, 9.
6 D. Moras, B. Metz and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 388; R. H. Huang, D. L. Ward, M. E. Kuchenmeister and J. L. Dye, *J. Am. Chem. Soc.*, 1987, **109**, 5561.
7 B. Metz, D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1377.
8 B. Metz, D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1382; R. Zagler and B. Eisenmann, *Z. Naturforsch., Teil B*, 1991, **46**, 593.
9 M. Giampolini, P. Dapporto and N. Nardi, *J. Chem. Soc., Dalton Trans.*, 1979, 974; G. Yang, S. Liu and Z. Jin, *Inorg. Chim. Acta*, 1987, **131**, 125.
10 F. A. Hart, M. B. Hursthouse, K. M. A. Malik and S. Moorhouse, *J. Chem. Soc., Chem. Commun.*, 1978, 550; J. Mao and Z. Jin, *Polyhedron*, 1994, **13**, 319.
11 J. H. Burns, *Inorg. Chem.*, 1979, **18**, 3044.
12 F. Benetollo, G. Bombieri, A. Cassol, G. de Paoli and J. Legendziewicz, *Inorg. Chim. Acta*, 1985, **110**, 7.
13 B. Metz and R. Weiss, *Inorg. Chem.*, 1974, **13**, 2094.
14 D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, 1973, **29**, 1059.
15 K. S. Hagen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 764.
16 J. Pickardt and B. Kühn, *Z. Naturforsch., Teil B*, 1994, **49**, 1031.
17 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1992, 1619; *J. Chem. Soc., Dalton Trans.*, 1993, 3407; G. R. Willey, P. R. Meehan, M. D. Rudd and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1995, 811.
18 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
19 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135.
20 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
21 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
22 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinement, University of Göttingen, 1993.
23 D. Parker, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 1.
24 B. Dietrich, J.-M. Lehn and J.-P. Sauvage, *Tetrahedron*, 1973, **29**, 1647.
25 H.-J. Brügge, D. Carboo, K. von Deuten, A. Knöchel, J. Kopf and W. Dreissig, *J. Am. Chem. Soc.*, 1986, **108**, 107.
26 B. G. Cox, J. Murray-Rust, P. Murray-Rust, N. van Truong and H. Schneider, *J. Chem. Soc., Chem. Commun.*, 1982, 377; P. Luger, J. Buschmann, A. Knöchel, D. Tiemann and M. Patz, *Acta Crystallogr., Sect. C*, 1991, **47**, 1860.
27 R. Weiss, M. Schappacher, L. Ricard, G. Riviere, A. Mitschler and C. Caron, *J. Am. Chem. Soc.*, 1979, **101**, 7401.
28 J. G. Mao, Z. S. Jin and J. Z. Ni, *Jiegou Huaxue*, 1992, **11**, 302.
29 B. Metz, D. Moras and R. Weiss, *J. Chem. Soc., Perkin Trans. 2*, 1976, 423.
30 U. Bolle and W. Tremel, *J. Chem. Soc., Chem. Commun.*, 1994, 217.
31 CERIUS 2 version 1.5, Molecular Simulations Inc., Cambridge and Waltham, MA, 1994.
32 M. G. B. Drew, S. Hollis and P. C. Yates, *J. Chem. Soc., Dalton Trans.*, 1985, 1820.
33 J. L. Atwood and K. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 921.
34 T. J. Anderson, M. A. Neuman and G. A. Melson, *Inorg. Chem.*, 1973, **12**, 927.

Received 23*rd March* 1995; *Paper* 5/01878A