Crown Ether Complexation of Scandium(III). Formation and Spectroscopic Characterisation of $ScCl_2^+$–Oxacrown Species and Crystal Structures of Two Scandium Dibenzocrowns†

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 systems $ScCl_3$–$SbCl_5$–MeCN–crown ether(L), where L = 6,7,9,10,17,18,20,21-octahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclooctadecine (dibenzo-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), have been investigated. Halide abstraction generates the $ScCl_2^+$ cation *in situ* which can be stabilised by macrocyclic complexation with the appropriate cyclic ether. The compound $[ScCl_2(\text{dibenzo-18-crown-6})][SbCl_6]$ was isolated as a white solid and characterised as the hexachloroantimonate(V) salt from microanalytical and spectroscopic (IR, ^1H and ^{13}C NMR) data. Entrapment of a *trans*-$ScCl_2$ unit within the ring cavity involving five-co-ordination of the ring oxygen atoms is seen as the most likely arrangement. Removal of a further chloride ion from this compound, effected by the addition of $SbCl_5$ (three equivalents), provides $[ScCl(\text{dibenzo-18-crown-6})(MeCN)][SbCl_6]_2$ as established by microanalytical and spectroscopic data, and similar cavity entrapment of a *trans*-ScCl(MeCN) unit has been discussed. Solution studies, as monitored by ^1H NMR spectroscopy, indicate that complete removal of chloride ion from $[ScCl(\text{dibenzo-18-crown-6})(MeCN)][SbCl_6]_2$ can be effected but only with a heavy excess (10 equivalents) of $SbCl_5$. The compound $[ScCl_2(\text{dibenzo-24-crown-8})(H_2O)][SbCl_6]\cdot 2MeCN$ **1** was isolated as red crystals and structurally characterised by X-ray diffraction studies. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$ and R 0.0638. The structure consists of $[ScCl_2(\text{dibenzo-24-crown-8})(H_2O)]^+$ cations and $[SbCl_6]^-$ anions with two solvent (MeCN) molecules trapped in the lattice. For the cation the Sc^{III} co-ordination geometry is essentially pentagonal bipyramidal involving two axial chlorine atoms [Sc–Cl 2.387(4) and 2.397(4) Å, Cl–Sc–Cl 173.8(2)°] and five equatorial oxygen atoms comprising four from the crown ether with Sc–O distances in the range 2.184(7)–2.297(7) (mean 2.25 Å) and one from a co-ordinated water molecule [$Sc–O_{water}$ 2.130(8) Å]. The threaded $ScCl_2^+$ unit is located within the ring cavity but in an 'off-centre' position. Intracavity hydrogen bonding of the type $Sc–OH_2\cdots O_{ring}$ is present with $O_{water}\cdots O_{ring}$ 2.65 and 2.75 Å. The compound $[ScCl_2(\text{dibenzo-30-crown-10})(H_2O)_2][SbCl_6]\cdot MeCN\cdot H_2O$ **2** was isolated as yellow needle crystals and characterised crystallographically as the hexachloroantimonate(V) salt. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$ and $R = 0.0639$. There are two solvent molecules (MeCN and H_2O) trapped in the lattice. In the $[ScCl_2(\text{dibenzo-30-crown-10})(H_2O)_2]^+$ cations the Sc^{III} ion is seven-co-ordinate, involving bonds to three oxygens from the crown ether, two chlorine atoms and two water molecules, and shows distorted pentagonal-bipyramidal geometry. The *trans*-$ScCl_2$ unit [Sc–Cl 2.411(3) and 2.419(3) Å, Cl–Sc–Cl 169.3(2)°] is located in an annexe section of the ring with $Sc–O_{ring}$ bond distances ranging between 2.208(8) and 2.280(8) (mean 2.25 Å), $Sc–O_{water}$ 2.148(9) and 2.160(8) Å. Both of the co-ordinated water molecules are involved in a complex pattern of intracavity hydrogen bonding of the type $Sc–OH_2\cdots O_{ring}$ with one molecule forming three $O_{water}\cdots O_{ring}$ close contacts in the range 2.83–2.98 Å and the other forming four such contacts in the range 2.75–3.00 Å.

In previous studies we have shown that crown ether complexation of the $ScCl_2^+$ cation, as generated by halide abstraction from the parent trihalide using antimony(V) chloride in acetonitrile solution, is extremely effective for 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5),[1] 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (benzo-15-crown-5)[1] and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6)[2] [equation (1)]. Independently Strel'tsova *et al.*[3] have described two similar examples, *viz.* $[ScCl_2(\text{15-crown-5})]Cl$ and $[ScCl_2(\text{15-crown-5})]_2[CuCl_4]$. In all these structures the metal sits directly in the ring cavity and exhibits a seven-co-ordinate pentagonal-bipyramidal geometry involving a *trans*-$ScCl_2$ and an equatorial array of five oxygen atoms from the ring. This arrangement is achieved in the case of 18-crown-6 by severe distortion of a $CH_2CH_2OCH_2CH_2$ segment of the ring leaving the oxygen atom in question in an excluded (non-bonding) location, $Sc\cdots O$ 4.137 Å. The only other crown ether–scandium(III) complexes noted in the literature are

$$ScCl_3 + SbCl_5 + MeCN + [\text{crown}] \longrightarrow [ScCl_2(\text{crown})][SbCl_6] \quad (1)$$

---

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

$[Sc(NO_3)_3\cdot$(18-crown-6)$\cdot 3H_2O]$[4] and $[Sc(NO_3)_3\cdot$(benzo-15-crown-5)$\cdot 2H_2O]$[5] but here the metal is attached only indirectly to the crown, *i.e.* with 'second-sphere' complexation *via* hydrogen bonding of the type $O_{crown} \cdots H_2O \cdots Sc$.

The emergence of a favoured seven-co-ordinate role in these crown ether–scandium(III) complexes is striking. Bearing in mind the fact that scandium can and does enjoy higher co-ordination status we have extended our complexation studies of the $ScCl_2^+$ unit to include the more voluminous oxacrown ligands 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]deca-oxacyclotriacontine (dibenzo-30-crown-10). For both these ligands the combination of increased flexibility allied with large cavity size, *i.e.* dibenzo-30-crown-10 has a diameter of *ca.* 4 Å, lends intriguing possibilities in terms of high co-ordination metal geometries. Some measure of the incipient flexibility in the case of dibenzo-30-crown-10 is provided by the complexation profile with the s-block cations M^+ (M = K[6] or Rb[7]) and M^{2+} (M = Ba[8]) whereby the ring completely envelops the central metal with all ten oxygen atoms involved in bonding interactions; for the smaller M = Na, two cations are symmetrically entrapped within the cavity.[9]

Experimental

Manipulations were performed using standard Schlenk techniques together with a conventional dinitrogen atmosphere glove box. Acetonitrile was stored over CaH_2 and distilled under a dinitrogen atmosphere prior to use. The compound $[ScCl_3(thf)_3]$ (thf = tetrahydrofuran) was prepared as described in the literature.[10] Anhydrous $SbCl_5$ and the oxacrown ligands 6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*]-[1,4,7,10,13,16]hexaoxacyclooctadecine (dibenzo-18-crown-6), dibenzo-24-crown-8 and dibenzo-30-crown-10 were used directly as supplied (Aldrich). The IR spectra were recorded as Nujol mulls placed between CsI plates using a Perkin-Elmer 580B instrument, and the ^1H (220 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded using a Bruker AC250 spectrometer. Elemental analyses were carried out by Medac Ltd., Brunel University, Uxbridge, Middlesex.

Preparation of the Complexes.—(*a*) $[ScCl_2$(dibenzo-18-crown-6)$][SbCl_6]$. A solution of $[ScCl_3(thf)_3]$ (0.12 g, 0.326 mmol) dissolved in MeCN (30 cm^3) was added dropwise to a chilled (0 °C) solution of $SbCl_5$ (0.10 g, 0.334 mmol) in MeCN (30 cm^3) to give a clear solution. Following stirring of this solution for 4 h at room temperature, a solution of dibenzo-18-crown-6 (0.12 g, 0.333 mmol) in MeCN (10 cm^3) was added slowly to yield a clear light yellow solution which was stirred at room temperature for 24 h. Slow removal of solvent *in vacuo* provided a very light yellow microcrystalline solid which was washed with toluene (2 × 10 cm^3) and hexane (2 × 10 cm^3) and pumped dry *in vacuo* for several hours (yield 0.21 g, 79%), m.p. 170–172 °C (Found: C, 29.70; H, 2.95; Cl, 34.80. $C_{20}H_{24}Cl_8O_6SbSc$ requires C, 29.65; H, 3.00; Cl, 35.00%). $\delta_H[(CD_3)_2CO]$ 6.92–6.88 (8 H, m, aromatic), 4.16, 3.97 (16 H, midpoints of AA'BB' multiplets, CH_2); $\delta_C[(CD_3)_2CO]$ 147.9, 121.9, 114.0 (aromatic), 70.4, 69.2 (CH_2). IR $\tilde{\nu}/cm^{-1}$(Nujol) 1333, 1259, 1134, 1081, 1047, 1024, 935, 851, 821 (ligand), 345 ν(SbCl), 315 ν(ScCl).

(*b*) $[ScCl$(dibenzo-18-crown-6)$(MeCN)][SbCl_6]_2$. Following the procedures in (*a*) above, the reaction of $[ScCl_3(thf)_3]$ (0.12 g, 0.326 mmol), $SbCl_5$ (0.30 g, 1.002 mmol) and dibenzo-18-crown-6 (0.12 g, 0.333 mmol) provided $[ScCl$(dibenzo-18-crown-6)$(MeCN)][SbCl_6]_2$ as a light tan semicrystalline solid (yield 0.27 g, 72%), m.p. 90–92 °C (Found: C, 22.95; H, 2.80; Cl, 39.90; N, 1.10. $C_{22}H_{27}Cl_{13}NO_6Sb_2Sc$ requires C, 22.95; H, 2.35; Cl, 40.05; N, 1.20%); $\delta_H[(CD_3)_2CO]$ 6.99–6.93 (8 H, m, aromatic), 4.23, 4.04 (16 H, AA'BB' multiplets, CH_2), 2.30 (3 H, s, co-ordinated MeCN); $\delta_C[(CD_3)_2CO]$ 148.9, 129.7, 113.7 (aromatic), 70.4, 68.8 (CH_2). IR $\tilde{\nu}/cm^{-1}$(Nujol) 2363, 2314, 2288 ν(MeCN), 1326, 1281, 1207, 1127, 1098, 1052, 954, 843, 828 (ligand), 340 ν(SbCl), 310 ν(ScCl).

As a separate experiment carried out in an NMR tube a solution of $[ScCl$(dibenzo-18-crown-6)$(MeCN)][SbCl_6]_2$ dissolved in CD_3CN was treated with an excess of $SbCl_5$ (10 drops ≈0.1 g) and the ^1H NMR spectrum re-recorded; δ_H 7.06–6.97 (8 H, m, aromatic), 4.33, 4.19 (16 H, AA'BB' multiplets, CH_2), 2.44 (6 H, s, co-ordinated MeCN).

(*c*) $[ScCl_2$(dibenzo-24-crown-8)$(H_2O)][SbCl_6]\cdot 2MeCN$ **1**. Dropwise addition of an acetonitrile solution (10 cm^3) of $SbCl_5$ (0.10 g, 0.334 mmol) to a chilled (0 °C) solution of $[ScCl_3(thf)_3]$ (0.12 g, 0.326 mmol) in MeCN (30 cm^3) provided a clear solution. After a period of 2 h stirring this solution at room temperature, the oxacrown dibenzo-24-crown-8 (0.15 g, 0.334 mmol) was added directly to give a clear yellowish orange solution, which was stirred at room temperature for 24 h. Removal of solvent gave a red fibrous solid which was washed with toluene (2 × 20 cm^3) and hexane (2 × 20 cm^3) and pumped dry *in vacuo* for several hours. Recrystallisation from acetonitrile–activated charcoal provided the product as ruby-red chunky crystals of X-ray diffraction quality (yield 0.20 g, 67%), m.p. 180–182 °C (Found: C, 33.30; H, 3.90; Cl, 28.20. $C_{28}H_{40}Cl_8N_2O_9SbSc$ requires C, 33.65; H, 4.05; Cl, 28.40%). NMR (CD_3CN): spectra recorded at 61 °C, δ_H 7.08 (8 H, s, aromatic), 4.42 (8 H, s, CH_2), 4.28 (8 H, s, CH_2), 4.15 (8 H, s, CH_2); δ_C 146.0, 124.0, 114.5 (aromatic), 72.6, 71.4, 69.3 (CH_2); at −41.5 °C, δ_H 7.24 [6.94]* (8 H, s, aromatic), 4.65 (16 H, s, CH_2), 4.45 [4.18] (8 H, s, CH_2), 3.98 [3.88] (8 H, s, CH_2); δ_C 148.5 [145.0], 125.3 [122.1], 113.4 [113.0], (aromatic), 76.6 [71.6], 70.3 [69.6], 68.4 [66.6] (CH_2). IR $\tilde{\nu}/cm^{-1}$(Nujol) 1255, 1215, 1124, 1047, 938, 839 (ligand), 3380, 1664 (H_2O), 345 ν(SbCl), 309 ν(ScCl).

(*d*) $[ScCl_2$(dibenzo-30-crown-10)$(H_2O)_2][SbCl_6]\cdot MeCN\cdot H_2O$ **2**. An acetonitrile solution (20 cm^3) of $SbCl_5$ (0.10 g, 0.334 mmol) was added dropwise to a solution of $[ScCl_3(thf)_3]$ (0.123 g, 0.332 mmol) in acetonitrile (30 cm^3) to give a light yellow solution. This solution was stirred at room temperature for 5 h prior to the direct addition of dibenzo-30-crown-10 (0.180 g, 0.335 mmol). The resulting yellow solution was stirred at 30 °C for 48 h. Removal of solvent gave a light yellow solid which was washed with toluene (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3) and pumped dry *in vacuo* for several hours. Recrystallisation from acetonitrile–CH_2Cl_2 (1:1) in the presence of activated charcoal yielded a crop of light yellow needle crystals of X-ray diffraction quality (yield 0.27 g, 82%), m.p. 153–156 °C (Found: C, 33.15; H, 4.40; Cl, 26.05. $C_{30}H_{49}Cl_8NO_{13}SbSc$ requires C, 33.30; H, 4.55; Cl, 26.20%). NMR (CD_3CN): spectra recorded at 61 °C, δ_H 7.04 (8 H, m, aromatic), 4.28 (8 H, s, CH_2), 4.24 (8 H, s, CH_2), 4.03 (16 H, br s, CH_2); δ_C 147.5, 123.5, 115.0 (aromatic), 71.9, 71.7, 71.3, 68.7 (CH_2); at −41.5 °C, δ_H 6.96 (8 H, m, aromatic), 4.24 (8 H, s, CH_2), 4.16 (8 H, s, CH_2), 4.07 (8 H, s, CH_2), 4.02 (8 H, s, CH_2); δ_C 147.3 [146.6], 122.2 [121.4], 112.1 [111.6] (aromatic), 73.7 [71.4], 70.9 [70.8], 69.1 [68.0], 66.7 [64.1] (CH_2). IR $\tilde{\nu}/cm^{-1}$(Nujol) 3502, 3302, 1647 (H_2O), 1325, 1310, 1285, 1252, 1214, 1127, 1097, 1084, 1073, 1056, 1041, 1024, 943, 927 (ligand), 345 ν(SbCl), 320 ν(ScCl).

X-Ray Crystallography.—Crystal data are given in Table 1, together with refinement details. Data for both crystals were collected with Mo-Kα radiation using the MARresearch image plate system. The crystals were positioned at 75 mm from the image plate system, and 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program,[11] and both structures were solved using direct methods with the SHELXS 86 program.[12] Both structures consist of independent cations containing the $ScCl_2^+$ moiety encapsulated within a crown ether with either one or two

---

* Values in square brackets may be due to other isomers.

Table 1 Crystal data and structure refinement for **1** and **2***

Compound	$[ScCl_2(dibenzo\text{-}24\text{-}crown\text{-}8)(H_2O)][SbCl_6]\cdot 2MeCN$ **1**	$[ScCl_2(dibenzo\text{-}30\text{-}crown\text{-}10)(H_2O)_2][SbCl_6]\cdot MeCN\cdot H_2O$ **2**
Empirical formula	$C_{28}H_{40}Cl_8N_2O_9SbSc$	$C_{30}H_{49}Cl_{18}NO_{13}SbSc$
M	998.93	1082.05
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	13.381(8)	11.505(9)
b/Å	9.651(8)	14.410(9)
c/Å	31.685(12)	16.021(9)
α/°	90	73.0(1)
β/°	93.5(1)	77.5(1)
γ/°	90	65.9(1)
Z	4	2
U/Å^3	4084.2	2304.7
D_c/Mg m^{-3}	1.625	1.556
Absorption coefficient/mm^{-1}	1.399	1.251
F(000)	2008	1092
Crystal size/mm	0.3 × 0.25 × 0.25	0.25 × 0.25 × 0.25
θ Range/°	2.21–25.10	1.83–25.04
Index ranges	$-15 \leqslant h \leqslant 15, 0 \leqslant k \leqslant 10, -37 \leqslant l \leqslant 37$	$0 \leqslant h \leqslant 13, -14 \leqslant k \leqslant 16, -18 \leqslant l \leqslant 18$
No. of reflections collected	10 674	6746
No. of independent reflections	6203 (R_{int} = 0.0290)	6746
No. of data, parameters	6203, 426	6746, 480
Parameters a, b in weighting scheme	0.0875, 77.57	0.1933, 18.41
Goodness of fit on F^2	0.988	1.036
R ($wR2$) [$I > 2\sigma(I)$]	0.0638 (0.1454)	0.0639 (0.2024)
R ($wR2$) (all data)	0.1305 (0.2515)	0.1367 (0.3407)
Largest difference peak, hole/e Å^{-3}	0.905, −1.036	1.688, −1.775

* Details in common: $T = 293(2)$ K; $\lambda = 0.710\,71$ Å; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$; refinement by full-matrix least squares on F^2.

additional co-ordinated water molecules, $[SbCl_6]^-$ anions, and lattice solvent molecules. In **1**, the cation and anion were ordered, and all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms on carbon were included in geometric positions while those of the co-ordinated water molecule were located in a Fourier-difference map and refined with constraints on the O–H distance. There were two solvent molecules of MeCN and contributing atoms were refined isotropically. In **2**, there was some disorder in the crown ether and two positions were included for atoms C(17), C(18) and O(19). These two sets of positions were given refineable population parameters that summed to 1.0. All atoms in the cation and anion except for these were given anisotropic thermal parameters. It was also apparent, from a study of their thermal parameters, that C(20) and C(21) also showed signs of disorder but for these atoms we decided that the introduction of two different positions was unnecessary. One MeCN and two water molecules with 50% occupancy were located and these also were refined with isotropic thermal parameters. Both structures were then refined using SHELXL.[13] All calculations were carried out on a Silicon Graphics R4000 workstation at the University of Reading. Positional parameters for **1** and **2** are given in Tables 2 and 3. Dimensions in the cations are compared in Table 4, and torsion angles around the oxacrown rings are given in Table 5.

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

Results and Discussion

A search of the Cambridge Database files (July 1994) reveals 48 structures containing Sc^{III} with a co-ordination number range from 3, *e.g.* $[Sc\{N(SiMe_3)_2\}_3]$,[14] $[Sc\{OC_6H_2Bu^t{}_2Me\}_3]$[15] and $[Li(thf)_3][Li\{Sc(C_2B_9H_{11})(\eta^5\text{-}C_5Me_5)CH(SiMe_3)_2\}_2]$[16] through to 9 as in $[Sc(H_2O)_3(NO_3)_3]\cdot$(18-crown-6)[4] and $[Sc(terpy)(NO_3)_3]$[17] (terpy = 2,2′:6′,2″-terpyridine). Specifically for seven-co-ordination there are two examples in addition to the pentagonal-bipyramidal Sc^{III}–oxacrown species mentioned above, *viz.* $[Sc(L)(H_2O)_2][NO_3]_2[OH]$[18] (L = 2,6-diacetylpyridine bis-semicarbazone) and $[\{(H_2O)_5\text{-}Sc\}(OH)_2\{Sc(H_2O)_5\}][PhSO_3]_4\cdot 4H_2O$.[19] In both cases the metal co-ordination geometry is also pentagonal bipyramidal.

Reactions with Dibenzo-18-*crown*-6.—As previously noted above the resulting complex between 18-crown-6 and $ScCl_2^+$ is unsymmetrical in the sense that one of the ring oxygen atoms is excluded from co-ordination to the metal. From the standpoint of ion–cavity-size compatibility a central location for the metal resulting in six equivalent $Sc\cdots O_{ring}$ bonding interactions—albeit of slightly elongated length with respect to those observed in the seven-co-ordinate structure—and with a resulting six-fold symmetry for the ligand, *i.e.* all of the OCH_2CH_2O units would be in the energetically favourable *gauche* conformation, would seem a more attractive alternative arrangement. In an attempt to enforce this 'idealised' eight-co-ordination dibenzo-18-crown-6 was chosen as ligand in anticipation that the presence of the aromatic rings would sufficiently restrict the flexibility to induce full O-donor involvement. Examples of threaded $[MX_2$(dibenzo-18-crown-6)] structures include M = Hg, X = Cl;[20] M = Tl, X = Me;[21] M = Na, X = H_2O;[22] M = K, X = thf or $O{\equiv}C\text{-}Cr(CO)(CPh{\equiv}CPh)(\eta^4\text{-}C_4Ph_4)$;[23] M = K, X = H_2O or NCS;[24] and M = Na, X = thf.[25] On the other hand it could well be the case that such a symmetrical fit is implausible for the scandium atom; ionic radii Sc^{3+} (six-co-ordinate) 0.885 and Sc^{3+}(eight-co-ordinate) *ca.* 0.78 Å have been estimated.[26]

The reaction with dibenzo-18-crown-6 [equation (1)] provided $[ScCl_2$(dibenzo-18-crown-6)]$[SbCl_6]$ as an off-white semicrystalline solid. Satisfactory microanalytical and spectroscopic data for this product confirm the ionic formulation. The ^1H NMR spectrum ($[^2H_6]$acetone) shows a broad multiplet δ 6.92–6.88 for the aromatic protons and two AA′BB′ multiplets centred on δ 4.16 and 3.97 for the backbone (CH_2) ring protons with relative intensities 1:1:1 and with downfield shifts *ca.* 0.1–0.5 ppm from uncomplexed ligand signals. The ^{13}C NMR spectrum ($[^2H_6]$acetone) shows three distinct signals for the

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

Atom	*x*	*y*	*z*
Sb	3 420(1)	863(1)	1 335(1)
Cl(1)	2 560(3)	−890(4)	950(1)
Cl(2)	4 727(3)	−702(5)	1 508(1)
Cl(3)	2 107(3)	2 405(5)	1 142(1)
Cl(4)	2 609(3)	215(5)	1 937(1)
Cl(5)	4 199(3)	1 550(6)	728(2)
Cl(6)	4 292(4)	2 568(5)	1 728(2)
Sc	−1 019(2)	−3 379(2)	1 024(1)
Cl(11)	498(2)	−4 327(3)	781(1)
Cl(12)	−2 506(2)	−2 233(3)	1 215(1)
O(W1)	−1 289(6)	−5 241(9)	1 360(2)
O(1)	−342(6)	−2 882(8)	1 651(2)
C(2)	490(7)	−1 924(12)	1 665(3)
C(3)	151(9)	−700(11)	1 418(3)
O(4)	−283(5)	−1 235(7)	1 025(2)
C(5)	−578(7)	−280(11)	724(3)
C(6)	−1 080(8)	−820(11)	365(3)
O(7)	−1 211(6)	−2 246(7)	387(2)
C(8)	−1 775(9)	−2 910(12)	41(3)
C(9)	−1 698(10)	−4 419(12)	139(3)
O(10)	−1 966(5)	−4 636(8)	567(2)
C(11)	−2 999(8)	−4 986(13)	609(4)
C(12)	−3 159(10)	−6 496(13)	627(4)
O(13)	−2 783(6)	−6 969(8)	1 040(2)
C(14)	−2 949(8)	−8 417(13)	1 073(4)
C(15)	−2 983(8)	−8 865(13)	1 518(4)
O(16)	−1 995(5)	−8 739(8)	1 718(2)
C(17)	−1 865(9)	−9 310(12)	2 112(4)
C(18)	−990(9)	−8 973(14)	2 334(4)
O(19)	−359(6)	−8 138(10)	2 125(3)
C(20)	438(11)	−7 496(16)	2 369(5)
C(21)	797(10)	−6 426(19)	2 106(5)
O(22)	57(7)	−5 402(10)	2 006(3)
C(23)	20(10)	−4 224(14)	2 271(3)
C(24)	−686(9)	−3 217(14)	2 060(4)
C(25)	−1 397(9)	−13(13)	28(4)
C(26)	−1 172(9)	1 421(14)	66(4)
C(27)	−681(9)	1 966(13)	408(4)
C(28)	−372(8)	1 128(11)	750(4)
C(29)	−2 514(10)	−10 160(14)	2 296(4)
C(30)	−2 317(13)	−10 705(16)	2 691(5)
C(31)	−1 434(14)	−10 344(17)	2 916(5)
C(32)	−797(13)	−9 497(15)	2 744(4)
N(71)	2 684(24)	5 997(35)	1 978(11)
C(72)	2 960(24)	5 897(35)	1 614(11)
C(73)	3 453(23)	5 737(33)	1 219(10)
N(74)	5 915(29)	4 425(46)	−403(12)
C(75)	5 492(23)	3 265(39)	−338(9)
C(76)	4 863(25)	1 897(40)	−386(10)

Table 3 Atomic coordinates (× 10^4) for **2**

Atom	*x*	*y*	*z*
Sb	2247(1)	1674(1)	4213(1)
Cl(1)	2024(4)	1680(3)	2781(2)
Cl(2)	2517(4)	1618(3)	5644(2)
Cl(3)	3605(5)	2600(4)	3648(3)
Cl(4)	4022(4)	109(3)	4227(3)
Cl(5)	900(4)	734(3)	4756(2)
Cl(6)	478(5)	3219(4)	4197(4)
Sc	2418(2)	−2004(2)	1607(1)
Cl(11)	1978(3)	−3549(2)	2398(2)
Cl(12)	2450(3)	−281(2)	911(2)
O(1)	807(8)	−1694(6)	826(5)
C(2)	−417(13)	−911(12)	1071(9)
C(3)	−575(13)	−1145(10)	2040(9)
O(4)	554(8)	−1170(6)	2285(5)
C(5)	543(14)	−1300(13)	3205(8)
C(6)	1615(17)	−1057(12)	3308(9)
O(7)	2699(8)	−1650(6)	2824(5)
C(8)	3838(14)	−1437(9)	2868(9)
C(9)	4544(15)	−2156(9)	3623(9)
O(10)	4982(10)	−3159(6)	3457(5)
C(11)	5745(11)	−3982(8)	4045(7)
C(12)	6099(13)	−4952(10)	3873(8)
O(13)	5613(9)	−4935(6)	3141(6)
C(14)	5844(15)	−5913(10)	2964(10)
C(15)	5168(20)	−5703(12)	2226(11)
O(16)	5415(16)	−5006(12)	1472(10)
C(17A)	6529(50)	−5400(37)	1249(34)
C(18A)	7162(46)	−4656(35)	919(29)
O(19A)	6348(42)	−3620(29)	273(23)
C(17B)	6189(49)	−5198(29)	766(30)
C(18B)	6485(44)	−4372(28)	102(26)
O(19B)	6356(37)	−3622(25)	565(20)
C(20)	6998(22)	−2962(21)	143(21)
C(21)	6281(28)	−1973(19)	−327(26)
O(22)	5256(16)	−1651(12)	−479(11)
C(23)	4780(18)	−714(14)	−1073(12)
C(24)	4348(17)	−849(13)	−1818(10)
O(25)	3379(10)	−1268(8)	−1500(5)
C(26)	2798(13)	−1400(10)	−2080(7)
C(27)	1781(13)	−1740(10)	−1733(8)
O(28)	1619(9)	−1980(7)	−830(5)
C(29)	524(14)	−2192(10)	−423(8)
C(30)	653(13)	−2482(10)	547(8)
C(31)	6164(14)	−3891(11)	4736(8)
C(32)	6882(14)	−4776(15)	5287(10)
C(33)	7241(14)	−5732(13)	5097(10)
C(34)	6868(15)	−5815(11)	4407(10)
C(41)	1084(16)	−1852(12)	−2241(8)
C(42)	1402(20)	−1612(13)	−3163(11)
C(43)	2374(19)	−1323(13)	−3485(10)
C(44)	3099(16)	−1199(11)	−2979(9)
O(W1)	3349(8)	−2421(7)	374(5)
O(W2)	4371(9)	−2969(7)	1829(6)
N(60)	7503(24)	−2510(19)	2268(16)
C(61)	8166(24)	−3228(19)	2713(15)
C(62)	8940(32)	−3946(25)	3346(21)
O(W3)	9946(67)	−4604(49)	−1361(41)
O(W4)	1884(57)	−5707(43)	1712(36)

aromatic carbon atoms at δ 147.9 (for those adjacent to the electronegative oxygen atoms), 121.9 and 114.0 and two signals for the skeletal CH_2 carbon atoms at δ 70.4 and 69.2. Again the downfield shifts of *ca.* 0.05–0.15 ppm reflect encapsulation of the metal within the crown cavity. Characteristic broad and intense bands are observed in the low energy region of the IR spectrum at 345 cm^{-1} ν(Sb–Cl) and 315 cm^{-1} ν(Sb–Cl) respectively. Unfortunately we were unable to grow crystals of suitable quality for X-ray diffraction studies and the question of either total or partial O-donor involvement remains unanswered.

Further halide abstraction leading to $ScCl^{2+}$ and Sc^{3+} solvated species that could be stabilised *in situ via* complexation with dibenzo-18-crown-6 was investigated by using varying amounts of $SbCl_5$ [equation (1)]. Removal of a second chloride ion was only brought about in the presence of three equivalents of antimony(v) chloride to give the tan semicrystalline product [ScCl(dibenzo-18-crown-6)(MeCN)][$SbCl_6$]$_2$. The IR spectrum confirms the presence of co-ordinated acetonitrile with sharp bands at 2363, 2314 and 2288 cm^{-1} ν(C≡N) and strong broad bands in the low energy region are assigned as ν(Sb–Cl) (340) and ν(Sc–Cl) (310 cm^{-1}). The ^1H NMR spectrum shows much the same profile as that observed for the $ScCl_2^+$ product, *i.e.* a broad multiplet δ 6.99–6.93 (relative intensity 8) for the aromatic protons and two AA′BB′ multiplets centred on δ 4.23, 4.04 (relative intensity 16) for the CH$_2$ protons but with an additional sharp singlet δ 2.30 (relative intensity 3) indicative of the co-ordinated solvent (acetonitrile) molecule. The larger downfield shifts of *ca.* 0.1–0.3 ppm compared with those observed for the ScCl$_2$$^+$ complex are seen to reflect the increased formal charge associated with the [ScCl(MeCN)]$^{2+}$ cations. The ^{13}C NMR spectrum is also consistent with this structural analysis with three singlets at δ 148.9, 129.7 and 113.7 associated with the benzene ring and two signals for the framework CH$_2$ linkages at δ 70.4 and 68.8.

Table 4 Selected bond lengths (Å) and angles (°) in compounds **1** and **2**

Compound **1**		Compound **2**	
Sc–O(W2)	2.130(8)	Sc–O(W1)	2.148(9)
Sc–O(1)	2.184(7)	Sc–O(W1)	2.160(8)
Sc–O(10)	2.226(7)	Sc–O(4)	2.208(8)
Sc–O(4)	2.291(7)	Sc–O(7)	2.270(8)
Sc–O(7)	2.297(7)	Sc–O(1)	2.280(8)
Sc–Cl(12)	2.387(4)	Sc–Cl(11)	2.411(3)
Sc–Cl(11)	2.397(4)	Sc–Cl(12)	2.419(3)
O(W1)–Sc–O(1)	78.8(3)	O(W2)–Sc–O(W1)	74.4(3)
O(W1)–Sc–O(10)	76.0(3)	O(W2)–Sc–O(4)	142.0(3)
O(1)–Sc–O(10)	154.1(3)	O(W1)–Sc–O(4)	143.5(3)
O(W1)–Sc–O(4)	148.0(3)	O(W2)–Sc–O(7)	75.4(3)
O(1)–Sc–O(4)	69.3(3)	O(W1)–Sc–O(7)	144.5(3)
O(10)–Sc–O(4)	136.1(3)	O(4)–Sc–O(7)	69.3(3)
O(W1)–Sc–O(7)	145.8(3)	O(W2)–Sc–O(1)	144.0(3)
O(1)–Sc–O(7)	135.4(3)	O(W1)–Sc–O(1)	74.3(3)
O(10)–Sc–O(7)	70.0(3)	O(4)–Sc–O(1)	70.3(3)
O(4)–Sc–O(7)	66.2(2)	O(7)–Sc–O(1)	139.5(3)
O(W1)–Sc–Cl(12)	95.4(3)	O(W2)–Sc–Cl(11)	84.6(3)
O(1)–Sc–Cl(12)	88.5(2)	O(W1)–Sc–Cl(11)	100.9(3)
O(10)–Sc–Cl(12)	88.1(2)	O(4)–Sc–Cl(11)	84.4(2)
O(4)–Sc–Cl(12)	86.9(2)	O(7)–Sc–Cl(11)	94.5(2)
O(7)–Sc–Cl(12)	87.2(2)	O(1)–Sc–Cl(11)	84.1(2)
O(W1)–Sc–Cl(11)	90.7(3)	O(W2)–Sc–Cl(12)	104.9(3)
O(1)–Sc–Cl(11)	93.7(2)	O(W1)–Sc–Cl(12)	86.5(3)
O(10)–Sc–Cl(11)	92.4(2)	O(4)–Sc–Cl(12)	85.1(2)
O(4)–Sc–Cl(11)	88.4(2)	O(7)–Sc–Cl(12)	83.5(2)
O(7)–Sc–Cl(11)	87.2(2)	O(1)–Sc–Cl(12)	90.5(2)
Cl(12)–Sc–Cl(11)	173.8(2)	Cl(11)–Sc–Cl(12)	169.3(2)

In an attempt to effect complete halide abstraction the reaction of [ScCl(dibenzo-18-crown-6)(MeCN)][SbCl$_6$]$_2$ with a large excess of SbCl$_5$ (≈20 equivalents) in acetonitrile and contained in an NMR tube was monitored by ^{1}H NMR spectroscopy. Interestingly the same pattern as noted previously is retained, *i.e.* the aromatic protons appear as a broad multiplet at δ 7.06–6.97, the ring CH$_2$ protons give rise to two AA′BB′ multiplets centred at δ 4.33 and 4.19 and there is a sharp singlet for co-ordinated acetonitrile at δ 2.44; however, there are two significant changes: all these signals have experienced a further pronounced downfield shift and the relative intensity pattern is now 8 : 16 : 6. Clearly the final chloride has been abstracted and the vacant co-ordination site on the scandium has been filled by a second solvent molecule. A *trans*-axial orientation of the [Sc(MeCN)$_2$]$^{3+}$ unit with preservation of the oxacrown ring symmetry seems the most likely outcome.

Reactions with Dibenzo-24-*crown*-8.—Previous metal complexes of this particular oxacrown ligand that have been structurally characterised have featured the s-block metals where, in addition to single entrapment, *e.g.*, for Ba^{2+}[27] and K$^+$[28] there are examples in which two metal ions have been incorporated into the cavity, *i.e.*, Na$^+$[29] and K$^+$.[30] Only two other examples have been listed, *viz.*, [Gd(NO$_3$)$_3$(H$_2$O)$_3$]·(dibenzo-24-crown-8)[31] and [Y(NO$_3$)$_3$(H$_2$O)$_3$]·(dibenzo-24-crown-8).[32] In each case the nine-co-ordinate lanthanide M^{III} ion is bonded to six oxygen atoms from the nitrate anions (bidentate) and three oxygen atoms from the solvate (H$_2$O) molecules in a distorted tricapped trigonal-prismatic metal

Table 5 Bond torsional angles (°) with estimated standard deviations in parentheses for **1** and **2**

Compound **1**			
C(24)–O(1)–C(2)–C(3)	−120(1)	C(12)–O(13)–C(14)–C(15)	−156(1)
O(1)–C(2)–C(3)–O(4)	−49(1)	O(13)–C(14)–C(15)–O(16)	−69(1)
C(2)–C(3)–O(4)–C(5)	−175(1)	C(14)–C(15)–O(16)–C(17)	−170(1)
C(3)–O(4)–C(5)–C(6)	−174(1)	C(15)–O(16)–C(17)–C(18)	−168(1)
O(4)–C(5)–C(6)–O(7)	2(1)	O(16)–C(17)–C(18)–O(19)	−2(2)
C(5)–C(6)–O(7)–C(8)	177(1)	C(17)–C(18)–O(19)–C(20)	166(1)
C(6)–O(7)–C(8)–C(9)	175(1)	C(18)–O(19)–C(20)–C(21)	−165(2)
O(7)–C(8)–C(9)–O(10)	51(1)	O(19)–C(20)–C(21)–O(22)	63(1)
C(8)–C(9)–O(10)–C(11)	94(1)	C(20)–C(21)–O(22)–C(23)	92(2)
C(9)–O(10)–C(11)–C(12)	95(1)	C(21)–O(22)–C(23)–C(24)	170(1)
O(10)–C(11)–C(12)–O(13)	74(1)	O(22)–C(23)–C(24)–O(1)	−58(1)
C(11)–C(12)–O(13)–C(14)	178(1)	C(23)–C(24)–O(1)–C(2)	−77(1)
Compound **2**			
C(30)–O(1)–C(2)–C(3)	105(1)	C(17A)–C(18A)–O(19A)–C(20)	171(4)
O(1)–C(2)–C(3)–O(4)	54(1)	C(15)–O(16)–C(17B)–C(18B)	−169(3)
C(2)–C(3)–O(4)–C(5)	−175(1)	O(16)–C(17B)–C(18B)–O(19B)	28(6)
C(3)–O(4)–C(5)–C(6)	−167(1)	C(17B)–C(18B)–O(19B)–C(20)	158(4)
O(4)–C(5)–C(6)–O(7)	−51(1)	C(18B)–O(19B)–C(20)–C(21)	98(4)
C(5)–C(6)–O(7)–C(8)	178(1)	O(19A)–C(20)–C(21)–O(22)	12(6)
C(6)–O(7)–C(8)–C(9)	90(2)	O(19B)–C(20)–C(21)–O(22)	−7(6)
O(7)–C(8)–C(9)–O(10)	63(1)	C(20)–C(21)–O(22)–C(23)	−169(3)
C(8)–C(9)–O(10)–C(11)	176(1)	C(21)–O(22)–C(23)–C(24)	119(3)
C(9)–O(10)–C(11)–C(12)	177(1)	O(22)–C(23)–C(24)–O(25)	59(2)
O(10)–C(11)–C(12)–O(13)	−1(2)	C(23)–C(24)–O(25)–C(26)	176(1)
C(11)–C(12)–O(13)–C(14)	−175(1)	C(24)–O(25)–C(26)–C(27)	−175(1)
C(12)–O(13)–C(14)–C(15)	175(1)	O(25)–C(26)–C(27)–O(28)	−6(2)
O(13)–C(14)–C(15)–O(16)	54(1)	C(26)–C(27)–O(28)–C(29)	172(1)
C(14)–C(15)–O(16)–C(17A)	61(3)	C(27)–O(28)–C(29)–C(30)	177(1)
C(14)–C(15)–O(16)–C(17B)	98(3)	C(2)–O(1)–C(30)–C(29)	87(1)
C(15)–O(16)–C(17A)–C(18A)	−141(4)	O(28)–C(29)–C(30)–O(1)	56(1)
O(16)–C(17A)–C(18A)–O(19A)	−44(6)		

geometry. Critically the crown ether ligand is associated with the rare earth metal *only via* hydrogen bonding of the type $O_{crown} \cdots H_2O \cdots M^{III}$. Five of the hydrogen atoms associated with the three co-ordinated water molecules are bonded to five of the oxygen atoms of the macrocyclic ring.

The reaction of $[ScCl_3(thf)_3]$ with one equivalent of dibenzo-24-crown-8 and one equivalent of $SbCl_5$ [equation (1)] provided chunky red crystals of $[ScCl_2$(dibenzo-24-crown-8)$(H_2O)][SbCl_6]\cdot 2MeCN$ **1** following recrystallisation of the original product from acetonitrile in the presence of activated charcoal.

Spectroscopic and microanalytical data are in accord with an ionic formulation and an X-ray crystallographic study revealed the structure of **1** as discrete $[ScCl_2$(dibenzo-24-crown-8)-$(H_2O)]^+$ cations and $[SbCl_6]^-$ anions with two solvent (MeCN) molecules in the lattice. The anions are unexceptional with *cis*-Cl–Sb–Cl angles in the range 88.3(2)–91.9(2)° within 2° of the ideal octahedral geometry and Sb–Cl bond distances lying between 2.324(4) and 2.354(4) Å. The cation structure is shown in Fig. 1 together with the atom labelling used. The *trans*-$ScCl_2{}^+$ unit of the threaded cation structure is essentially linear, with Sc–Cl 2.387(4) and 2.397(4) Å, Cl–Sc–Cl 173.8(2)°, with the metal anchored 'off-centre' towards one end of the ring cavity. Along with the two axial chlorine atoms, an equatorial array of five oxygen atoms four of which originate from the crown ether and the other from a 'stray' water molecule complete the seven-co-ordinate, pentagonal-bipyramidal metal environment. These five oxygen atoms lie in a plane around the metal with deviations (oxygen) O(1) 0.07, O(4) −0.02, O(7) −0.35, O(10) 0.08 O(W1), −0.08 and (metal) −0.02 Å. The $Sc-O_{water}$ distance is the shortest bond at 2.130(8) Å. The $Sc-O_{crown}$ bond distances are found in the range 2.184(7)–2.297(7) (mean 2.25 Å) similar to those observed in $[ScCl_2$(18-crown-6)$][SbCl_6]$ (mean 2.210), $[ScCl_2$(benzo-15-crown-5)$][SbCl_6]$ (mean 2.188) and $[ScCl_2$(15-crown-5)$]_2[CuCl_4]$ (mean 2.125 Å). Compound **1** is the first example of direct encapsulation of a lanthanide metal ion by this large-cavity crown ether. With the exception of the synclinal O(4)–C(5)–C(6)–O(7) 2(1)°, the torsion angles (O–C–C–O) of the O(1)–O(10) segment of the ring involved in metal chelation fall within 10° of the all-*gauche* sequence (±60°). Equally, apart from C(24)–O(1)–C(2)–C(3) −120(1), C(8)–C(9)–O(10)–C(11) 94(1) and C(9)–O(10)–C(11)–C(12) 95(1)° all the C–O–C–C torsion angles within this segment lie within 6° of the favoured *trans* conformation (180°) (see Table 5).

Clearly the water molecule completes the five-atom equatorial girdle for a regular pentagonal-bipyramidal geometry in preference to any of the remaining ring oxygen atoms. Of the latter two are ideally positioned, however, for involvement in a simple pattern of intramolecular hydrogen bonding with the included water molecule as shown in Fig. 1 with O(W1) $\cdots$ O(22) 2.65, O(W1) $\cdots$ O(13) 2.75 Å. In a sense the adventitious presence of water molecules (introduced most likely during the recrystallisation process *via* impurities in solvent and/or charcoal) is vital since it is debatable whether the oxacrown alone would be able fully to stabilise the $ScCl_2{}^+$ cation; significant distortion of the ligand would be essential for collective binding of five ring oxygen atoms to the metal. This constraint is removed by the presence of the water molecule in a co-ordination site of the central scandium atom thereby facilitating a favourable conformation complete with intramolecular H-bonding. It was a great pity that we were unable structurally to characterise the $[ScCl_2$(dibenzo-18-crown-6)$]^+$ cation (see above). Since four of the six available oxygen atoms of the ligand are locked in vicinal positions, the adoption of a suitable conformation involving only five of these in a regular pentagonal pattern seems most unlikely. Moreover, even if a water molecule were present it cannot be accommodated in any stabilising intramolecular H-bonding role as observed with the appreciably larger dibenzo-24-crown-8 ligand.

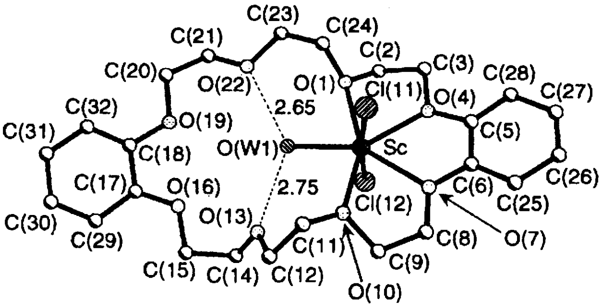

Fig. 1 A view of the $[ScCl_2$(dibenzo-24-crown-8)$(H_2O)]^+$ cation of **1** (with atomic labelling) showing the intracavity hydrogen bonding. Hydrogen-bond distances in Å

*Reactions with Dibenzo-*30-*crown-*10.—The one common factor that has emerged for all the previous $ScCl_2{}^+$–oxacrown compounds is the seeming insistence of the metal for a seven-co-ordinate pentagonal-bipyramidal geometry. What is of interest here is whether a *trans*-$ScCl_2{}^+$ cation can reside within the cavity of this particularly egregious crown ether and still remain within the confines of seven-co-ordination. A further possibility is 'double insertion'; with this extremely large crown macrocycle the cavity is theoretically of sufficient magnitude to house two scandium dichloride units. An example where two cations reside symmetrically within the ring cavity is provided by $[Na_2$-(dibenzo-30-crown-10)$][NCS]_2\cdot H_2O$.[8]

The reaction of $[ScCl_3(thf)_3]$ (1 mol) with dibenzo-30-crown-10 (1 mol) and antimony(V) chloride (1 mol) [equation (1)] gives the compound $[ScCl_2$(dibenzo-30-crown-10)$(H_2O)_2]$-$[SbCl_6]\cdot MeCN\cdot H_2O$ **2**. This product was obtained as light yellow needle crystals following recrystallisation of the original yellow solid from an acetonitrile–dichloromethane (1:1) mixture in the presence of activated charcoal. Microanalytical and spectroscopic data support the ionic formulation. The structure of **2** has been determined by X-ray crystallography and reveals discrete $[ScCl_2$(dibenzo-30-crown-10)$(H_2O)_2]^+$ cations and octahedral $[SbCl_6]^-$ anions together with trapped solvent (H_2O and MeCN) molecules in the lattice. A perspective view of the cation is shown in Fig. 2 together with the atom labelling used. The *trans*-$ScCl_2{}^+$ unit lies in the cavity but is located in an 'annexe' position created by co-ordination to only *three* of the ring oxygen atoms and, unexpectedly, two molecules of water. Unlike the structure of **1** the scandium atom is conspicuously not bonded to any of the vicinal oxygen atoms. The metal co-ordination geometry approximates to a distorted pentagonal bipyramid in which the five oxygens occupy equatorial positions and are essentially coplanar [O(1) 0.15, O(4) 0.05, O(7) −0.22, O(W1) −0.30, O(W2) 0.33 and Sc 0.00 Å]. The $Sc-O_{water}$ bond lengths are 2.160(8) and 2.148(9) Å while $Sc-O_{crown}$ bond lengths are 2.280(8), 2.208(8) and 2.270(8) Å, comparable to those in $[ScCl_2$(dibenzo-24-crown-8)-$(H_2O)]^+$. Interestingly a precedent for this restricted co-ordination to a lanthanide M^{III} ion has been established, *viz.* $[M(NCS)_3$(dibenzo-30-crown-10)$(H_2O)_2]$ where M = Gd[33] or Dy.[34] In both instances yet again only *three* of the ten available ring oxygen atoms are directly linked to the metal which enjoys a co-ordination number of eight with dodecahedral (M = Gd) and square-antiprism (M = Dy) geometries respectively. The co-ordinated water molecules are further implicated in a network of intramolecular hydrogen bonds involving several of the remaining oxygen atoms of the ring.

The presence of the two uninvited water molecules in **2**, introduced almost certainly during the recrystallisation stages, is again seen to be crucial. Intracavity hydrogen bonding of the type $Sc-OH_2 \cdots O_{crown}$ occurs between these two co-ordinated water molecules and the remaining oxygen atoms of the oxacrown ring, *e.g.* O(W1) is involved in three interactions, O(W1)–O(22) 2.78, –O(25) 2.98, –O(28) 2.83 Å, and O(W2) in

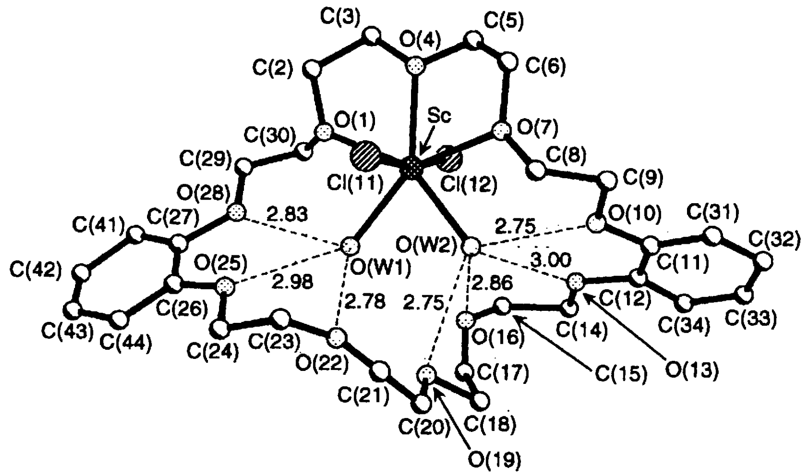

Fig. 2 A view of the $[\mathrm{ScCl_2(dibenzo\text{-}30\text{-}crown\text{-}10)(H_2O)_2}]^+$ cation of **2** (with atomic labelling) showing the intracavity hydrogen bonding. Hydrogen-bond distances in Å

four such stabilising interactions O(W2)–O(10) 2.75, –O(13) 3.00, –O(16) 2.86, –O(19) 2.75 Å. Within the ring segment O(1)–O(7) involved in metal chelation, the O–C–C–O torsion angles (*i.e.*, 54, −51°) approach the favoured *gauche* (60°) conformation and the C–C–O–C torsion angles are extremely close to 180° with the exception of C(6)–O(7)–C(8)–C(9) 90(2), C(30)–O(1)–C(2)–C(3) 105(1) and C(29)–C(30)–O(1)–C(2) 87(1)°. Apart from the latter, which represents a *trans* (177°) to *gauche* (87°) reversal, there are no dramatic changes in torsion angles between complexed and uncomplexed oxacrown ligand which suggests that no significant ring strain has been introduced following insertion of the $\mathrm{ScCl_2}^+$ cation and the attendant intracavity hydrogen-bonding interactions.

Acknowledgements

We thank the SERC for a studentship (to M. D. R.) and the University of Warwick for a postgraduate scholarship (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 to Mrs. Merlin Callaway for typing the manuscript.

References

1 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 1993, 3407.
2 G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1992, 1619.
3 N. R. Strel'tsova, V. K. Bel'skii, B. M. Bulychev and O. K. Kireeva, *Russ. J. Inorg. Chem.*, 1992, **37**, 934 (transl. from *Zh. Neorg. Khim.*, 1992, **37**, 1822).
4 Z. S. Jin, Y. S. Liu, S. G. Zhang, F. L. Yu and J. Z. Ni, *Acta Chim. Sin. Engl. Ed.*, 1987, **45**, 1048.
5 M. Tan, X. M. Gan, N. Tang and J. P. Zou, *Gaodeng Xuexiao Xuebao*, 1988, **9**, 1217.
6 M. A. Bush and M. R. Truter, *J. Chem. Soc., Perkin Trans. 2*, 1972, 345; J. Hasek, D. Hlavata and K. Huml, *Acta Crystallogr., Sect. B*, 1980, **36**, 1782; J. D. Owen, M. R. Truter and J. N. Wingfield, *Acta Crystallogr., Sect. C*, 1984, **40**, 1515.
7 J. Hasek, K. Huml and D. Hlavata, *Acta Crystallogr., Sect. B*, 1979, **35**, 330.
8 Z. Q. Li, H. W. Xu, X. W. Wang and Y. P. Fan, *Jiegou Huaxue*, 1989, **8**, 273; Y. P. Fan, H. W. Xu, Y. H. Wei and Q. P. Hu, *Shandong Daxue. Xuebao, Ziran. Kexueban*, 1991, **26**, 129.
9 J. D. Owen and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1979, 1831.
10 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135.
11 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
12 G. M. Sheldrick, SHELXS 86, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
13 G. M. Sheldrick, SHELXL, Program for crystal structure refinement, University of Göttingen, 1993.
14 J. S. Ghotra, M. B. Hursthouse and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669.
15 P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499.
16 R. E. Marsh, W. P. Schaefer, G. C. Bazan and J. E. Bercaw, *Acta Crystallography., Sect. C*, 1992, **48**, 1416.
17 A. M. Arif, F. A. Hart, M. B. Hursthouse, M. Thornton-Pett and W. Zhu, *J. Chem. Soc., Dalton Trans.*, 1984, 2449.
18 D. D. McRitchie, R. C. Palenik and G. J. Palenik, *Inorg. Chim. Acta*, 1976, **20**, L27.
19 F. Matsumoto, Y. Ohki, Y. Suzuki and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2081.
20 Y. Kawasaki and Y. Matsuura, *Chem. Lett.*, 1984, 155.
21 J. Crowder, K. Hendrick, R. W. Matthews and B. L. Podejma, *J. Chem. Res.*, 1983, (*S*)82, (*M*) 901.
22 M. A. Bush and M. R. Truter, *J. Chem. Soc. B*, 1971, 1440.
23 D. J. Wink, J. R. Fox and N. J. Cooper, *J. Am. Chem. Soc.*, 1985, **107**, 5012.
24 H. Zhang, Y. X. Sun, G. D. Yang, C. Shen and C. C. Jin, *Gaodeng Xuexiao Huaxue Xuebao*, 1986, **7**, 721.
25 T. Mashiko, C. A. Reed, K. J. Haller and W. R. Scheidt, *Inorg. Chem.*, 1984, **23**, 3192.
26 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751; T. J. Anderson, M. A. Neuman and G. A. Melson, *Inorg. Chem.*, 1974, **13**, 1884.
27 D. L. Hughes and J. N. Wingfield, *J. Chem. Soc., Chem. Commun.*, 1977, 804; D. L. Hughes, C. L. Mortimer and M. R. Truter, *Acta Crystallogr., Sect. B*, 1978, **34**, 800.
28 N. P. Rath and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, 1985, 665; T. Gallagher, M. J. Taylor, S. R. Ernst and M. L. Hackert, *Acta Crystallogr., Sect. B*, 1991, **47**, 362.
29 D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1975, 2374; C. Momany, M. L. Hackert, J. Sharma and N. S. Poonia, *J. Incl. Phenom.*, 1987, **5**, 343.
30 M. Mercer and M. R. Truter, *J. Chem. Soc., Dalton Trans.*, 1973, 2469.
31 T. B. Lu, X. M. Gan, M. Y. Tan, C. Z. Li and K. B. Yu, *Polyhedron*, 1993, **12**, 1641.
32 T. B. Lu, X. K. Gan, M. Y. Tan and K. Yu, *Polyhedron*, 1993, **12**, 621.
33 S. Yan, G. Wang, H. G. Wang and X. K. Yao, *Polyhedron*, 1991, **10**, 1889.
34 S. Yang, Z. H. Jiang, D. Liao, G. Wang, R. Wang, H.-G. Wang and X.-K. Yao, *J. Incl. Phenom.*, 1993, **15**, 159.

Received 12*th September* 1994; *Paper* 4/05508J