Crown Ether Complexation of Scandium(III), Yttrium(III) and Lanthanum(III) Halides. Synthesis and Spectroscopic Characterisation of Anhydrous Cationic Metal–Oxacrown Species and Crystal Structure of a Scandium Benzocrown†

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Halide abstraction reactions of MCl_3 (M = Sc, Y or La) with $SbCl_5$ in the presence of a crown ether provided a series of anhydrous cationic M^{III}-crown compounds of the types [MCl_2(crown)][$SbCl_6$] [M = Sc, crown = 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (benzo-15-crown-5), or 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5)], [$ScCl_2$(12-crown-4)(MeCN)][$SbCl_6$] (12-crown-4 = 1,4,7,10-tetraoxacyclododecane), [M(18-crown-6)$(MeCN)_3$][$SbCl_6$]$_3$ (M = Y or La) and [M(12-crown-4)$(MeCN)_5$][$SbCl_6$]$_3$ (M = Y or La). Analytical and spectroscopic (^1H and ^{13}C NMR) characterisation of these compounds supports their formulation as hexachloroantimonate(V) salts. The structure of [$ScCl_2$(benzo-15-crown-5)][$SbCl_6$] has been determined by X-ray diffraction. Crystals are orthorhombic, space group *Pbca* with *a* = 17.015(10), *b* = 13.296(8), *c* = 22.236(12) Å and *Z* = 8. The cation has a threaded structure with an essentially linear $ScCl_2^+$ unit [Sc–Cl (mean) 2.395 Å, Cl–Sc–Cl 175.5°]. All the oxygen atoms of the oxacrown ligand are coplanar and are bonded to the central scandium atom, Sc–O 2.166(4)–2.223(4) Å, (mean) 2.188 Å with the benzene ring tilted out of this plane at an angle of 24.9°. The resulting geometry of the seven-co-ordinate scandium atom is pentagonal bipyramidal.

It has been established that halide abstraction from covalent metal halides using $SbCl_5$ (or sometimes $SbCl_3$) in the presence of acetonitrile as a suitable donor solvent is a convenient synthetic route to solvated cationic metal species[1,2] [equation (1)].

$$MCl_n + ySbCl_5/SbCl_3 \xrightarrow{MeCN} [MCl_{n-y}(MeCN)_x][SbCl_6]_y/[SbCl_4]_y \quad (1)$$

In turn these cationic species are attractive precursors to anhydrous macrocyclic complexes following direct ligand exchange of the loosely bound acetonitrile molecules.[3] In a recent communication[4] we have described the structure of [$ScCl_2$(18-crown-6)][$SbCl_6$] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) featuring crown ether encapsulation of a chloroscandium(III) monocation. At that time only two scandium(III)–crown ether compounds were known and in both cases the oxacrown is located in the second co-ordination sphere of the metal. Two further examples have appeared in the very recent literature *viz*. [$ScCl_2$(15-crown-5)]Y (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane) where Y = Cl or $CuCl_4$;[5] the X-ray crystal structure of the latter salt confirms insertion of a linear $ScCl_2^+$ unit directly into the cavity of the pentaoxamacrocycle.

In this report we present a fuller account of the patterns of complexation of scandium(III) and the related yttrium(III) and lanthanum(III) chlorides with the macrocyclic polyether ligands 12-crown-4 (1,4,7,10-tetraoxacyclododecane), 15-crown-5 and 18-crown-6.

Experimental

All manipulations involved in the synthesis and characterisation of starting materials and products were carried out using standard Schlenk techniques in conjunction with a conventional dinitrogen atmosphere glove-box. Solvents were stored over CaH_2 and distilled over sodium–benzophenone under a dinitrogen atmosphere prior to use. Acetonitrile was purified following the recommended procedure.[6] The compound [$ScCl_3(thf)_3$] (thf = tetrahydrofuran) was prepared by the method reported by Manzer.[7] Anhydrous $SbCl_5$, YCl_3, $LaCl_3$ and the oxamacrocycles 12-crown-4, 15-crown-5 and 18-crown-6 were used directly as supplied commercially (Aldrich). Infrared spectra were recorded on a Perkin Elmer 580B instrument with samples as Nujol mulls placed between CsI plates. The ^1H (220 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded on a Perkin Elmer R34 spectrometer. Elemental analyses were carried out by Medac Ltd., Brunel University, Uxbridge, Middlesex.

Preparation of the Complexes.—[$ScCl_2$(18-crown-6)][$SbCl_6$]. Addition with stirring of an acetonitrile solution (10 cm^3) of $SbCl_5$ (0.122 g, 0.408 mmol) to an acetonitrile solution (5 cm^3) of [$ScCl_3(thf)_3$] (0.150 g, 0.408 mmol) provided a clear solution. The macrocycle 18-crown-6 (0.108 g, 0.409 mmol) was then added directly to the reaction mixture. After standing overnight, controlled reduction of the solvent volume over 3 h produced a large crop of colourless block crystals (yield 0.25 g, 86%), m.p. 163–164 °C (Found: C, 20.20; H, 3.45; Cl, 39.60. $C_{12}H_{24}Cl_8O_6SbSc$ requires C, 20.15; H, 3.40; Cl, 39.70%). δ_H 4.25 (24 H, s, CH_2); δ_C 73.49 (CH_2). IR: ν(SbCl) 347; ν(ScCl) 399, 291; ν(ligand) 1086, 961, 832 cm^{-1}. UV/VIS: λ_{max}(MeCN) 36 980 cm^{-1}.

[$ScCl_2$(15-crown-5)][$SbCl_6$]. A methodology directly analogous to that used for the 18-crown-6 complex provided diffraction quality crystals directly from the reaction mixture

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(yield 0.17 g, 62%). Reagents used: $SbCl_5$ (0.122 g, 0.408 mmol), $[ScCl_3(thf)_3]$ (0.150 g, 0.408 mmol) and 15-crown-5 (0.090 g, 0.409 mmol) (Found: C, 18.05; H, 3.10. $C_{10}H_{20}Cl_8O_5SbSc$ requires C, 17.90; H, 3.00%). δ_H 4.33 (20 H, s, CH_2); δ_C 73.49 (CH_2). IR: ν(SbCl) 346, ν(ScCl) 427, 291; ν(ligand) 1062, 964, 827 cm^{-1}. UV/VIS: λ_{max}(MeCN) 36 900 cm^{-1}.

$[ScCl_2$(benzo-15-crown-5)]$[SbCl_6]$ (*benzo*-15-*crown*-5 = 2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecine*). A similar method to that used for the 18-crown-6 complex was used. Diffraction quality crystals were obtained directly from the reaction mixture by concentrating the solution over the course of several h (yield 0.25 g, 85%). Reagents used: $SbCl_5$ (0.122 g, 0.408 mmol), $[ScCl_3(thf)_3]$ (0.150 g, 0.408 mmol) and benzo-15-crown-5 (0.109 g, 0.408 mmol) (Found: C, 23.30; H, 2.75. $C_{14}H_{20}Cl_8O_5SbSc$ requires C, 23.40; H, 2.80%). δ_H 7.317 (4 H, s, aromatic), 4.900, 4.593, 4.444, 4.440 (16 H, two AA'BB' m, CH_2); δ_C 144.89, 126.16, 113.78 (aromatic); 73.74, 73.15, 72.08, 71.67 (CH_2). IR: ν(SbCl) 359, 331; ν(ScCl) 418, 406, 287; ν(ligand) 1238, 1058, 755 cm^{-1}. UV/VIS: λ_{max}(MeCN) 33 470, 29 400 (sh) cm^{-1}.

$[ScCl_2$(12-crown-4)(MeCN)]$[SbCl_6]$. Antimony pentachloride (0.220 g, 0.736 mmol) in acetonitrile (10 cm^3) was added to an acetonitrile solution (5 cm^3) of $[ScCl_3(thf)_3]$ (0.27 g, 0.735 mmol), followed by 12-crown-4 (0.129 g, 0.733 mmol). The clear solution was allowed to stand overnight. Controlled reduction of solvent volume over several h failed to produce crystalline material. After removal of all solvent *in vacuo*, the resultant white powder was washed with toluene (3 × 10 cm^3), hexane (2 × 5 cm^3), and dried under vacuum (yield 0.35 g, 71%) (Found: C, 15.85; H, 2.70; N, 2.05. $C_{10}H_{19}Cl_8NO_6SbSc$ requires C, 18.00; H, 2.85; N, 2.10%). δ_H 4.430, 4.499 (16 H, midpoints of AA'BB' m, CH_2); δ_C 73.49 (CH_2). IR: ν(SbCl) 342; ν(ScCl) 424, 322; ν(CN) 2300, 2283 cm^{-1}. UV/VIS: λ_{max}(MeCN) 37 010 cm^{-1}.

[Y(18-crown-6)$(MeCN)_3][SbCl_6]_3$. An acetonitrile solution (35 cm^3) of $SbCl_5$ (1.53 g, 5.12 mmol) was added to an acetonitrile solution (40 cm^3) of YCl_3 (0.25 g, 1.28 mmol). This was stirred and warmed to 50 °C for 2 h prior to the addition of 18-crown-6 (0.338 g, 1.28 mmol) in acetonitrile (25 cm^3). After further stirring overnight all volatiles were removed *in vacuo*. The product was washed with toluene (5 × 20 cm^3) and hexane (2 × 10 cm^3) to produce a fine white powder (yield 1.4 g, 74%) (Found: C, 14.35; H, 2.30; N, 2.70. $C_{18}H_{33}Cl_{18}N_3O_6Sb_3Y$ requires C, 14.60; H, 2.25; N, 2.85%). δ_H 4.178 (24 H, s, CH_2); δ_C 72.695 (CH_2). IR: ν(SbCl) 342; ν(CN) 2302, 2275 cm^{-1}. UV/VIS: λ_{max}(MeCN) 36 930 cm^{-1}.

[Y(12-crown-4)$(MeCN)_5][SbCl_6]_3$. A methodology similar to that for the 18-crown-6 complexes was used. Reagent quantities were $SbCl_5$ (1.60 g, 5.35 mmol), YCl_3 (0.25 g, 1.28 mmol), and 12-crown-4 (0.225 g, 1.28 mmol). A fine white powder was obtained after washing thoroughly with toluene (yield 1.0 g, 66%) (Found: C, 14.15; H, 2.00; N, 5.90. $C_{18}H_{31}Cl_{18}N_5O_4Sb_3Y$ requires C, 14.65; H, 2.10; N, 4.75%). δ_H 4.295, 4.061 (16 H, midpoints of AA'BB' multiplets, CH_2); δ_C 70.480 (CH_2). IR: ν(SbCl) 342; ν(CN) 2311, 2284 cm^{-1}. UV/VIS: λ_{max}(MeCN) 37 010 cm^{-1}.

[La(18-crown-6)$(MeCN)_3][SbCl_6]_3$. An acetonitrile solution (35 cm^3) of $SbCl_5$ (1.25 g, 4.18 mmol) was added to a suspension of $LaCl_3$ (0.250 g, 1.02 mmol) in acetonitrile (40 cm^3). Heating to 70 °C for 20 min provided a clear solution to which 18-crown-6 (0.270 g, 1.03 mmol) was added directly. After stirring overnight, slow reduction of the solvent volume over several hours failed to produce crystalline material. After all volatiles were removed *in vacuo*, the product was washed with toluene (5 × 10 cm^3) and hexane (2 × 10 cm^3) to produce a fine white powder (yield 1.1 g, 70%) (Found: C, 14.15; H, 2.25; N, 2.65. $C_{18}H_{33}Cl_{18}LaN_3O_6Sb_3$ requires C, 14.15; H, 2.25; N, 2.75%). δ_H 4.063 (24 H, s, CH_2); δ_C 72.579 (CH_2). IR: ν(SbCl) 342; ν(CN) 2298, 2268 cm^{-1}. UV/VIS: λ_{max}(MeCN) 36 980 cm^{-1}.

[La(12-crown-4)$(MeCN)_5][SbCl_6]_3$. A similar methodology to that for the 18-crown-6 complexes was used. Reagent quantities were $SbCl_5$ (1.20 g, 4.01 mmol), $LaCl_3$ (0.250 g, 1.02 mmol) and 12-crown-4 (0.180 g, 1.03 mmol). A fine white powder was obtained after washing thoroughly with toluene (yield 1.1 g, 71%) (Found: C, 14.25; H, 2.10; N, 4.95. $C_{18}H_{31}Cl_{18}LaN_5O_4Sb_3$ requires C, 14.20; H, 2.05; N, 4.60%). δ_H 4.146, 3.978 (16 H, midpoints of AA'BB' m, CH_2); δ_C 69.163 (CH_2). IR: ν(SbCl) 342; ν(CN) 2303, 2275 cm^{-1}. UV/VIS: λ_{max}(MeCN) 36 890 cm^{-1}.

X-Ray Crystallography.—Structure of $[ScCl_2$(benzo-15-crown-5)]$[SbCl_6]$. *Crystal data.* $C_{14}H_{20}Cl_8O_5SbSc$, M = 718.64, orthorhombic, space group *Pbca*, a = 17.015(10), b = 13.296(8), c = 22.236(12) Å, U = 5030.5 Å^3, Z = 8, D_c = 2.118 g cm^{-3}, Mo-Kα radiation, λ = 0.710 69 Å, μ(Mo-Kα) = 2.33 mm^{-1}, T = 290 K, R = 0.0388 for 3282 unique observed $[I/\sigma(I) \geqslant 2.0]$ reflections.

A yellow block crystal was obtained from acetonitrile and mounted, under argon, in a Lindemann capillary. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode. Maximum 2θ was 50° with scan range ±0.7° (ω) around the $K\alpha_1$–$K\alpha_2$ angles, scan speed 1.5–15° (ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. The *hkl* ranges were 0–15, 0–20, 0–26. Three standard reflections were monitored every 200 reflections, and showed up to 10% decrease. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 14 reflections (15 < 2θ < 30°). The 5302 reflections collected were processed using profile analysis to give 4452 unique reflections (R_{int} = 0.074), of which 3282 were considered observed $[I/\sigma(I) \geqslant 2.0]$. These were corrected for Lorentz, polarization and absorption effects (by the Gaussian method); minimum and maximum transmission factors were 0.385 and 0.629. Systematic reflection conditions $hk0$, $k = 2n$; $0kl$, $l = 2n$; $h0l$, $h = 2n$, indicate space group *Pbca*. The antimony atom was located by the Patterson interpretation section of SHELXTL PLUS[8] and the light atoms then found by E-map expansion and successive Fourier syntheses. The asymmetric unit contains one ion pair. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.08 Å^2; they were inserted at calculated positions. Final refinement was on F by least-squares methods refining 262 parameters. Largest positive and negative peaks on a final Fourier difference synthesis were of height ±0.6 e Å^{-3}. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0.002$ was used and shown to be satisfactory by a weight analysis. Final R = 0.0388, R' = 0.0443, S = 0.97; $R_{(all\ reflections)}$ = 0.059. Maximum shift/error in final cycle was 0.001. Computing was conducted on a DEC Microvax-II with SHELXTL PLUS. Scattering factors in the analytical form and anomalous dispersion factors are taken from ref. 9. The fractional atomic coordinates are given in Table 1. Selected bond lengths and angles are listed in Table 2.

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

X-Ray analysis of $[ScCl_2$(15-crown-5)]$[SbCl_6]$. The crystals were found to be tetragonal with a = 11.365(4), c = 18.311(7) Å. Diffraction data were taken as above and the apparent space group was found to be $P\bar{4}2c$. The antimony and scandium atoms were located by Patterson methods on sites of symmetry 222 and $\bar{4}$ respectively but it has not been possible to refine the structure below R = 0.22. Clearly, either the oxa ligand is highly disordered, or there is unresolved twinning in the structure (possibly in a lower symmetry space group).

Results and Discussion

In this study of Group 3-crown ether complexation the anhydrous chlorides of M^{III}, M = Y or La have been used directly in the reaction system MCl_3–$SbCl_5$–crown ether–

Table 1 Atomic coordinates (× 10^4) for $[ScCl_2(benzo\text{-}15\text{-}crown\text{-}5)][SbCl_6]$

Atom	*x*	*y*	*z*
Sb	1 260.4(2)	1 709.3(3)	2 311.1(2)
Sc	8 883.0(6)	2 695.3(8)	−70.3(4)
Cl(1)	2 417.7(11)	2 695.2(14)	2 308.6(8)
Cl(2)	117.0(11)	705.2(15)	2 330.0(9)
Cl(3)	486.2(12)	3 171.6(13)	2 424.1(9)
Cl(4)	2 020.5(11)	224.1(13)	2 218.0(8)
Cl(5)	1 173.4(15)	1 865.5(15)	1 274.6(8)
Cl(6)	1 358.9(10)	1 591.1(13)	3 367.1(7)
Cl(7)	7 524.3(8)	2 231.6(12)	−117.1(7)
Cl(8)	10 264.8(8)	3 023.3(12)	06.1(7)
O(1)	8 914(2)	2 022(3)	836(2)
O(4)	8 600(2)	3 867(3)	575(2)
O(7)	8 748(2)	4 083(3)	−570(2)
O(10)	8 977(2)	2 332(3)	−1 020(2)
O(13)	9 160(2)	1 065(3)	−138(2)
C(2)	8 656(4)	2 649(5)	1 337(3)
C(3)	8 889(4)	3 699(5)	1 167(3)
C(5)	8 636(4)	4 892(4)	359(3)
C(6)	8 334(4)	4 882(5)	−269(3)
C(8)	8 595(4)	3 996(6)	−1 201(3)
C(9)	9 119(4)	3 178(5)	−1 418(3)
C(11)	9 405(4)	1 433(5)	−1 163(3)
C(12)	9 117(4)	639(5)	−741(3)
C(14)	8 889(3)	475(4)	340(3)
C(15)	8 756(3)	−543(4)	304(3)
C(16)	8 493(4)	−1 030(5)	806(3)
C(17)	8 342(4)	−522(5)	1 336(3)
C(18)	8 474(4)	510(5)	1 372(3)
C(19)	8 758(3)	998(4)	863(3)

Table 2 Selected bond lengths (Å) and bond angles (°) for $[SbCl_2(benzo\text{-}15\text{-}crown\text{-}5)][SbCl_6]$

Sc–Cl(7)	2.394(2)	Sc–Cl(8)	2.396(2)
Sc–O(1)	2.205(4)	Sc–O(4)	2.171(4)
Sc–O(7)	2.166(4)	Sc–O(10)	2.173(4)
Sc–O(13)	2.223(4)	O(1)–C(2)	1.465(8)
O(1)–C(19)	1.388(7)	O(4)–C(3)	1.424(8)
O(4)–C(5)	1.447(8)	O(7)–C(6)	1.446(8)
O(7)–C(8)	1.428(8)	O(10)–C(9)	1.451(8)
O(10)–C(11)	1.432(8)	O(13)–C(12)	1.456(7)
O(13)–C(14)	1.399(7)	C(2)–C(3)	1.495(10)
C(5)–C(6)	1.483(10)	C(8)–C(9)	1.493(10)
C(11)–C(12)	1.491(9)	C(14)–C(19)	1.374(8)
Cl(7)–Sc–O(1)	87.7(1)	Cl(8)–Sc–O(1)	89.7(1)
Cl(7)–Sc–O(4)	90.0(1)	Cl(8)–Sc–O(4)	92.7(1)
O(1)–Sc–O(4)	72.2(2)	Cl(7)–Sc–O(7)	95.4(1)
Cl(8)–Sc–O(7)	88.8(1)	O(4)–Sc–O(7)	72.9(2)
Cl(7)–Sc–O(10)	88.4(1)	Cl(8)–Sc–O(10)	91.5(1)
O(7)–Sc–O(10)	72.4(2)	Cl(7)–Sc–O(13)	87.2(1)
Cl(8)–Sc–O(13)	88.5(1)	O(1)–Sc–O(13)	70.1(1)
O(10)–Sc–O(13)	72.6(2)		

MeCN. With M = Sc the tris-adduct $[ScCl_3(thf)_3]$ is the most convenient starting material following dehydration of the hexahydrate $ScCl_3{\cdot}6H_2O$ using thionyl chloride and recrystallisation from thf.

During the preliminary stages of the work the objective was the isolation and structural characterisation of the solvated cationic species [equation (1)]. Although the generation of hexachloroantimonate(V) salts was confirmed by electronic and IR spectroscopy, the acute sensitivity of the $[MCl_2(MeCN)_4][SbCl_6]$ salts to traces of air/moisture precluded the isolation of analytically pure materials or of crystals suitable for X-ray diffraction studies. For the reaction of $[ScCl_3(thf)_3]$ with 1 equivalent of antimony pentachloride, colourless needle crystals of $[ScCl_2(MeCN)_4][SbCl_6]$ were isolable reproducibly but it has proved impossible to prevent crystal degradation following removal of solvent.

Reactions with 18-*Crown*-6.—Despite the apparent panacea of direct co-ordination of six available *O*-donor sites to the cationic metal species generated *in situ*, the initial work was plagued by the incursion of an unexpected side-product. Recrystallisation of the products obtained from the reaction systems MCl_3–$SbCl_5$–18-crown-6 (1 : 1 : 1) provided the salt $[(H_3O)(18\text{-}crown\text{-}6)][SbCl_6]$ as beautiful pale yellow crystals in all three cases. The latter was characterised by ^1H NMR spectroscopy and elemental analyses. Clearly the affinity of 18-crown-6 for the H_3O^+ ion [10] surpasses that for the cationic metallo species under investigation and stringent precautions needed to be taken, particularly with solvent purity, to avoid the ingress of water. Formation of the desired crown ether complexes in good yield with zero contamination by hydronium species was eventually realised using a minimalist approach, *viz.* as little solvent as possible (*ca.* 10 cm^3), all reagents added directly to a single reaction vessel within the dinitrogen glovebox and recrystallisation directly from the reaction solvent.

The reaction of $[ScCl_3(thf)_3]$ using 1 equivalent of $SbCl_5$ provided colourless block crystals of $[ScCl_2(18\text{-}crown\text{-}6)][SbCl_6]$ as reported in the preliminary communication.[4] The cation has a threaded structure in which the scandium is seven-co-ordinate (approximately pentagonal bipyramidal) and the crown adopts an unsymmetrical conformation leaving one oxygen site unco-ordinated to the central metal. For yttrium and lanthanium trichlorides, reactions with 1 and 2 equivalents of $SbCl_5$ failed to produce full dissolution of the anhydrous halide (as judged by the unsatisfactory microanalytical data of the products obtained) and were not pursued further. With an excess of $SbCl_5$ (4 equivalents), the salts $[M(18\text{-}crown\text{-}6)(MeCN)_3][SbCl_6]_3$ were isolated as white semi-crystalline solids. By analogy with the reported structures of $[La(18\text{-}crown\text{-}6)(NO_3)_3]$ [11] and $[Y(dibenzo\text{-}18\text{-}crown\text{-}6)(NCS)_3]$ [12] (dibenzo-18-crown-6 = 6,7,9,10,17,18,20,21-octahydrodibenzo-[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine) a nine-co-ordinate metal geometry is postulated with equatorial six-co-ordination by the oxacrown and with the acetonitrile ligands located on opposite sides, two above and one below, of the mean equatorial plane. The room-temperature ^1H and ^{13}C NMR spectra (CD_3CN) show simple singlets, shifted downfield from those of the free ligand. The moderate shift of the lanthanum complex (δ 4.06) compared to that reported for $[La(18\text{-}crown\text{-}6)(NO_3)_3]$ δ 3.80 is in accordance with anionic nitrate co-ordination in the latter compound.

The reaction of $[ScCl_3(thf)_3]$ with 2 equivalents of antimony pentachloride in the presence of the oxacrown was followed by NMR spectroscopy and produced a ^1H spectrum showing a singlet δ 4.25 at the same resonance as that observed for the 1 : 1 product, an AA'BB' multiplet centred on δ 4.26, 4.36 and another singlet further downfield at δ 4.39 with relative intensities 1 : 2 : 1 respectively. For the reaction using 3 equivalents of $SbCl_5$, the ^1H NMR spectrum shows the return of a single resonance at δ 4.41. The sequential downfield shifts are seen to mirror the increasing formal charge on the scandium ions produced in solution following sequential halide abstraction $ScCl_2^+ \longrightarrow ScCl^{2+} \longrightarrow Sc^{3+}$; the presence of three signals is attributed to an equilibrium between species [equation (2)].

$$2[ScCl(18\text{-}crown\text{-}6)(MeCN)]^{2+} \rightleftharpoons [ScCl_2(18\text{-}crown\text{-}6)]^+ + [Sc(18\text{-}crown\text{-}6)(MeCN)_2]^{3+} \quad (2)$$

N.B. a seven-co-ordinate metal geometry and five-co-ordinate crown attachment is assumed throughout (see later NMR discussion). The appearance of three signals in the ^{13}C NMR spectrum of this 1 : 2 reaction mixture is consistent with three separate scandium species being present in solution.

The structure of $[ScCl_2(18\text{-}crown\text{-}6)][SbCl_6]$ shows one of the ring oxygen atoms displaced 4.137 Å from the metal centre and demonstrably not involved in the bonding. A low-temperature ^1H NMR probe indicates that this situation persists in solution. Initial measurements at 240 K (CD_3CN) showed a noticeable broadening but no separation of the singlet at δ 4.25 observed at room temperature. However at 213 K ([$^2H_6$]acetone) the signal splits into two sharp singlets at δ 4.48 and 3.56 with relative intensities 5 : 1. Five-co-ordination would result in non-equivalence between the four α-CH_2 protons of the excluded oxygen atom and the remainder *i.e.* a 1 : 5 ratio. As expected the α-CH_2 resonance shifts upfield towards that of uncomplexed ligand. At 183 K ([$^2H_6$]acetone) the spectrum shows a poorly resolved five-band multiplet (δ 3.4–5.0) which could indicate the presence of more than one independent scandium species in solution, interconverting above 200 K.

Reactions with 15-*Crown*-5 *and Benzo*-15-*crown*-5.—The establishment of $ScCl_2^+$ insertion into the cavity of 18-crown-6 leaving one ring oxygen atom excluded from the co-ordination sphere of the metal suggested that pentaoxamacrocyclic ligands would produce symmetrical $ScCl_2^+$ cavity insertion with a regular pentagonal girdle of oxygen atoms co-ordinated to the metal. Direct treatment of [$ScCl_3(thf)_3$] with 1 equivalent of $SbCl_5$ and the appropriate oxamacrocycle provided the compounds [$ScCl_2$(15-crown-5)][$SbCl_6$] and [$ScCl_2$(benzo-15-crown-5)][$SbCl_6$]. The analytical and spectroscopic data of these complexes establish their ionic identity. The room-temperature ^1H and ^{13}C NMR spectra (CD_3CN) of [$ScCl_2$(15-crown-5)][$SbCl_6$] show singlets shifted downfield from those of free ligand. A variable-temperature scan of the ^1H NMR spectrum shows retention of the sharp singlet (δ 4.33) even down to 177 K ([$^2H_6$]acetone) commensurate with all oxygen atoms involved in metal co-ordination and hence minimal energy barriers between the ligand conformers. In the case of [$ScCl_2$(benzo-15-crown-5)][$SbCl_6$] the room-temperature ^1H NMR spectrum comprises a singlet for the aromatic protons (δ 7.32) and two AA′BB′ multiplets centred on δ 4.90/4.59 and δ 4.45/4.44 for the skeletal ring (CH_2) protons with relative intensities 1 : 2 : 2; the latter corresponds with the expected ratio for a symmetrical cation with a mirror plane running through the aromatic ring centroid, the central metal atom and the oxygen atom furthest from the aromatic ring. Interestingly the independent AA′BB′ system for those carbon atoms nearest the aromatic ring has an AB separation of approximately δ 0.3 whereas the other has a separation of just δ 0.04. This profile is maintained over a temperature scan down to 190 K ([$^2H_6$]acetone). The room-temperature ^{13}C NMR spectrum is consistent with this interpretation *viz.* four signals around δ 70.0 (CH_2) and three signals δ 144.89, 126.16, 113.78 in the aromatic region of the spectrum.

Crystal Structure of [$ScCl_2$(benzo-15-crown-5)][$SbCl_6$].—Crown complexation of the $ScCl_2^+$ cation formed *via* transfer of a chloride ion from scandium trichloride to antimony pentachloride has produced the compound [$ScCl_2$(benzo-15-crown-5)][$SbCl_6$], comprising discrete, mono-charged ions. Two views of the cation structure are shown in Fig. 1 and selected bond lengths and angles are given in Table 2. The torsion angles around the oxacrown ring are listed in Table 3. The hexachloroantimonate anion is close to ideal octahedral with Sb–Cl (mean) 2.363(3) Å, for all except Cl(5); the rather short Sb–Cl distance for Cl(5) [2.319(2) Å] can be attributed to its high thermal motion in the x direction (U_{11} = 0.15 compared to 0.03–0.06 Å^2 in y and z). The most notable feature of the cation is the threading through the crown cavity of an almost linear $ScCl_2^+$ unit [Sc–Cl(mean) 2.395(2) Å, Cl–Sc–Cl 175.5°] exactly as seen in the analogous complexes *viz.* [$ScCl_2$(15-crown-5)]$_2$[$CuCl_4$][Sc–Cl (mean) 2.426 Å, Cl–Sc–Cl 178.1°][5] and [$ScCl_2$(18-crown-6)][$SbCl_6$][Sc–Cl (mean) 2.413 Å, Cl–Sc–Cl 177.2°].[4] All the polyether oxygen atoms are co-ordinated to the scandium ion in a regular fashion with Sc–O 2.166(5)–2.221(5) Å (mean) 2.188 Å close to the distances observed in the corresponding compounds [$ScCl_2$(15-crown-5)]$_2$[$CuCl_4$], Sc–O (mean) 2.125 Å and [$ScCl_2$(18-crown-6)][$SbCl_6$], Sc–O (mean) 2.210 Å. The scandium atom adopts a

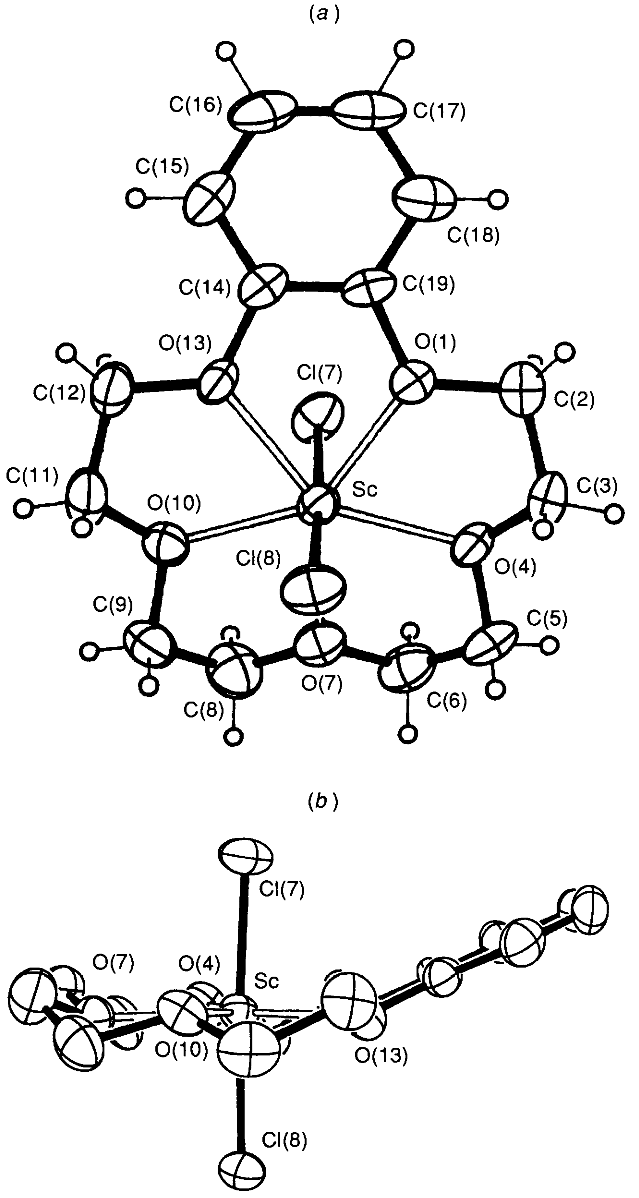

Fig. 1 Views of the [$ScCl_2$(benzo-15-crown-5)]$^+$ cation (*a*) perpendicular and (*b*) parallel to the ligand plane

Table 3 Torsion angles (°) for [$SbCl_2$(benzo-15-crown-5)][$SbCl_6$] *

C(19)–O(1)–C(2)–C(3)	−178.5
O(1)–C(2)–C(3)–O(4)	50.8
C(2)–C(3)–O(4)–C(5)	169.2
C(3)–O(4)–C(5)–C(6)	178.6
O(4)–C(5)–C(6)–O(7)	−49.9
C(5)–C(6)–O(7)–C(8)	−174.4
C(6)–O(7)–C(8)–C(9)	176.7
O(7)–C(8)–C(9)–O(10)	51.1
C(8)–C(9)–O(10)–C(11)	178.0
C(9)–O(10)–C(11)–C(12)	−174.7
O(10)–C(11)–C(12)–O(13)	−50.2
C(11)–C(12)–O(13)–C(14)	177.1
C(12)–O(13)–C(14)–C(19)	−164.7
O(13)–C(14)–C(19)–O(1)	0.1
C(14)–C(19)–O(1)–C(2)	168.7

* Estimated standard deviations are 0.2°.

regular pentagonal-bipyramidal geometry with chlorine atoms directly above and below the equatorial plane of oxygen atoms. The cation exhibits pseudo-mirror symmetry about the plane running through O(7), Sc, Cl(7) and the aromatic ring centroid. Viewing the cation parallel to the O_5-mean plane [Fig. 1(*b*)] it is apparent that the benzene ring is markedly tilted out of this plane with an interplanar angle of 24.9°. Similar tilting has been observed in other benzo-15-crown-5 complexes, *e.g.* $[Ca(NCS)_2(benzo\text{-}15\text{-}crown\text{-}5)(MeOH)]$, 6°; $[Ca(NCS)_2(benzo\text{-}15\text{-}crown\text{-}5)(H_2O)]$, 7° and $[Mg(NCS)_2(benzo\text{-}15\text{-}crown\text{-}5)]$, 22°.[13]

Within the macrocycle, bond lengths and angles are similar to those observed in other such complexes. The usual shortening of the aliphatic C–C bond lengths, compared to the standard value of 1.524 Å is apparent.[14,15] The macrocycle in the present complex has a regular conformation with aliphatic O–C–C–O torsion angles in the range 49.9–51.2°. These are somewhat reduced from an 'ideal' *gauche* angle of 60° but may permit improved binding to the metal ion. The C–O–C–C torsion angles, mean 174.1° show the *anti* preference often manifest by oxacrowns. The five ether oxygen atoms closely define a plane (maximum deviation 0.078 Å) with a slight ripple effect upon passing from O(7) back to the aromatic ring. The scandium ion lies very close to the mean plane (0.008 Å deviation) but is very slightly displaced from the O_5 centroid (0.033 Å) away from the two oxygen atoms nearest to the aromatic ring. This irregularity is also seen[13] in the compound $[Mg(NCS)_2(benzo\text{-}15\text{-}crown\text{-}5]$ where, again, the metal ion is slightly displaced away from the aromatic end of the equatorially oriented macrocycle. The two carbon atoms, C(14) and C(19), forming the bridgehead between the aromatic and aliphatic rings of the macrocycle show somewhat irregular bond angles with mean values for their exocyclic angles of 124.1°.

Reactions with 12-*Crown*-4.—The size of the cavity in 12-crown-4 has been estimated to be less than 1.8 Å in diameter.[16] This suggests that M^{III} cations are more likely to yield compounds with a 'half-sandwich' topology rather than showing direct cavity insertion, *i.e.* the metal atom resides between a macrocyclic ring of oxygen atoms on the one side and a composite of bound single ligands on the other. Certainly 12-crown-4 in its complexes predominantly has C_4 symmetry with all four oxygen atoms conveniently directed to the same side of the crown molecule for maximum bonding interactions with the central metal ion.[17]

The reaction of $[ScCl_3(thf)_3]$ with 1 equivalent of $SbCl_5$ and the oxacrown gives the compound $[ScCl_2(12\text{-}crown\text{-}4)(MeCN)][SbCl_6]$. The analytical and spectroscopic data are consistent with this ionic formulation. A half-sandwich structure is proposed for the cation with a seven-co-ordinate metal geometry (a monocapped trigonal prism comprising the MeCN, the four oxygen atoms of the oxacrown and the two chlorine atoms is one possibility) as found in the other $ScCl_2{}^+$–crown ether complexes described above *but* with the subtle difference that the two chlorine atoms are forced into *cis* positions. Such an arrangement has been noted in the eight-co-ordinate structure of $[YCl_2(12\text{-}crown\text{-}4)(H_2O)(MeOH)]Cl$[17] where the four crown oxygen atoms, the two covalently bound chlorine atoms and the two single ligand molecules form a square-antiprismatic environment to the central metal with the *cis*-chlorine atoms at opposite corners of one square face. In the corresponding reactions with lanthanum and yttrium, 4 equivalents of $SbCl_5$ were necessary to produce complete dissolution of the anhydrous metal chlorides leading to the formation of ionic compounds of the type $[M(12\text{-}crown\text{-}4)(MeCN)_5][SbCl_6]_3$ (M = Y or La). The room-temperature ^1H NMR spectrum of $[ScCl_2(12\text{-}crown\text{-}4)(MeCN)][SbCl_6]$ reveals an AA'BB' multiplet centred on δ 4.43, 4.499 moved downfield by approximately δ 0.9 from the singlet signal of the uncomplexed ligand. Similarly the other two compounds show an AA'BB' multiplet centred, δ 4.15, 3.98 (M = La) and δ 4.29, 4.06 (M = Y). In all three cases the ^{13}C NMR spectrum consists of a singlet. A search of the Cambridge Data Base files reveals four M^{III}–12-crown-4 (M = Y or La) structures *viz.*, $[Y(12\text{-}crown\text{-}4)(NO_3)_3]$,[18] $[YCl_2(12\text{-}crown\text{-}4)(H_2O)(MeOH)]Cl$,[17] $[La(benzo\text{-}12\text{-}crown\text{-}4)(NO_3)_3(H_2O)]\cdot MeCN$[19] (benzo-12-crown-4 = 2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecane) and $[Y(12\text{-}crown\text{-}4)(H_2O)_5]Cl_3\cdot 2H_2O$[17] in which the oxacrown adopts a C_4 conformation with varying degrees of coplanarity for the donor oxygen atoms. In particular the structure of $[Y(12\text{-}crown\text{-}4)(H_2O)_5]Cl_3\cdot 2H_2O$[17] shows the metal surrounded by nine oxygen atoms in a distorted monocapped square antisprismatic arrangement; a similar nine-co-ordinate geometry is proposed for $[M(12\text{-}crown\text{-}4)(MeCN)_5][SbCl_6]_3$ (M = Y or La).

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