Unusual Crown Ether Encapsulation of a Chloroscandium(III) Cation. Structure of Threaded [ScCl$_2$(18-crown-6)][SbCl$_6$]

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Halide abstraction from ScCl$_3$ using SbCl$_5$ provides the ScCl$_2^+$ cation, which is stabilised by crown ether complexation to give the ionic complex [ScCl$_2$(18-crown-6)][SbCl$_6$]; the cation has a threaded structure in which the scandium is seven-coordinate (approximately pentagonal bipyramidal) and the crown adopts an unsymmetrical conformation leaving one oxygen site uncoordinated to the central metal.

The burgeoning interest in the structural–coordination chemistry of scandium, despite the high material cost, embraces neutral molecular species, as typified by ScCl$_3$·3thf[1] and ionic Sc^{3+} complexes such as Sc(acac)$_3$[2] and [Sc(H$_2$O)$_4$(C$_7$H$_7$SO$_3$)$_2$][C$_7$H$_7$SO$_3$]·2H$_2$O (thf = tetrahydrofuran, Hacac = pentane-2,4-dione, C$_7$H$_7$SO$_3$ = toluene-*p*-sulfonate anion).[3] Bearing in mind the relatively small size of scandium [Sc^{3+} (six-coordinate) 0.885 Å][4] in relation to the other lanthanides the variety of coordination geometries observed is quite remarkable. A search of the Cambridge Data Base files reveals 40 scandium-containing structures encompassing the coordination number range from 3, as in [Sc{N(SiMe$_3$)$_2$}$_3$][5] right through to 9, as in [Sc(NO$_3$)$_3$(terpy)] (terpy = 2,2′:6′,2″-terpyridine);[6] coordination numbers 4 (12 examples), 6 (11 examples) and 8 (8 examples) predominate. In this report we describe the synthesis and structure of [ScCl$_2$(18-crown-6)][SbCl$_6$], which represents the first example of (*i*) a discrete ScCl$_2^+$ complexed cation and (*ii*) direct encapsulation of scandium by a crown ether in this case the archetypal 18-crown-6.

Direct addition of an acetonitrile solution of SbCl$_5$ (0.22 g, 0.736 mmol) to a chilled and stirred solution of ScCl$_3$ (0.12 g, 0.785 mmol) in acetonitrile (25 cm^3) provided a clear solution. Subsequent addition of 18-crown-6 (0.20 g, 0.758 mmol) in acetonitrile (25 cm^3) to this solution was followed by heating (50 °C) and stirring for 6 h. Removal of solvent under vacuum gave a white microcrystalline solid, which was washed with toluene and dried *in vacuo*. Recrystallisation from acetonitrile–dichloromethane provided the product as colourless block crystals (yield 0.46 g, 87%). Microanalysis data were satisfactory: ν_{max}/cm^{-1} (mull) 291, 399, (Sc–Cl), 347 (Sb–Cl); λ_{max}/cm^{-1} (MeCN) 36, 900 (SbCl$_6^-$); δ, ^{1}H[4.25, CH$_2$(singlet)], ^{13}C[73.49, CH$_2$(singlet)].†

The structure of the title compound consists of discrete scandium cations [ScCl$_2$(18-crown-6)]$^+$ and octahedral SbCl$_6^-$ counteranions. Two crystallographically independent molecules (**1** and **2**) are observed but variations in the separate Sc–O and Sc–Cl bond distances (and angles) are without chemical significance. The cation structure is shown in Fig. 1; the SbCl$_6^-$ anions are unexceptional with regular octahedral coordination about Sb atoms, Sb-Cl (mean) 2.339 Å, ClSbCl (mean) 90.0 and 178.8°.

The most remarkable feature of the cation is that the ScCl$_2^+$ unit is threaded through the centre of the oxacrown *cf.* rotoxane-like structure, but with only five of the crown oxygens coordinated to the central metal Sc–O 2.190(5)–2.229(5) Å (molecule **1**). These five oxygen atoms lie on a quasi-equatorial plane around the central metal; deviations from this mean plane are (oxygen) + 0.0512, −0.1450, +0.0696, −0.1496, +0.1738 and (metal) +0.0053 Å. Taken in conjunction with the two (axial) chlorine atoms, Cl–Sc–Cl 176.5(1)°, this gives the metal a seven-coordinate, approximately pentagonal-bipyramidal, geometry. The remaining oxygen atom lies well outside this plane (+1.3015 Å) and is clearly not involved in coordination to the metal Sc···O 4.137 Å. The present structure provides only the third example of a seven-coordinate Sc^{III} species: previous examples are [Sc(dapsc)(H$_2$O)$_2$][NO$_3$]$_2$[OH], mean Sc–O 2.110 Å [dapsc = 2,6-diacetylpyridine bis(semicarbazone)][7] and [(H$_2$O)$_5$Sc(μ-

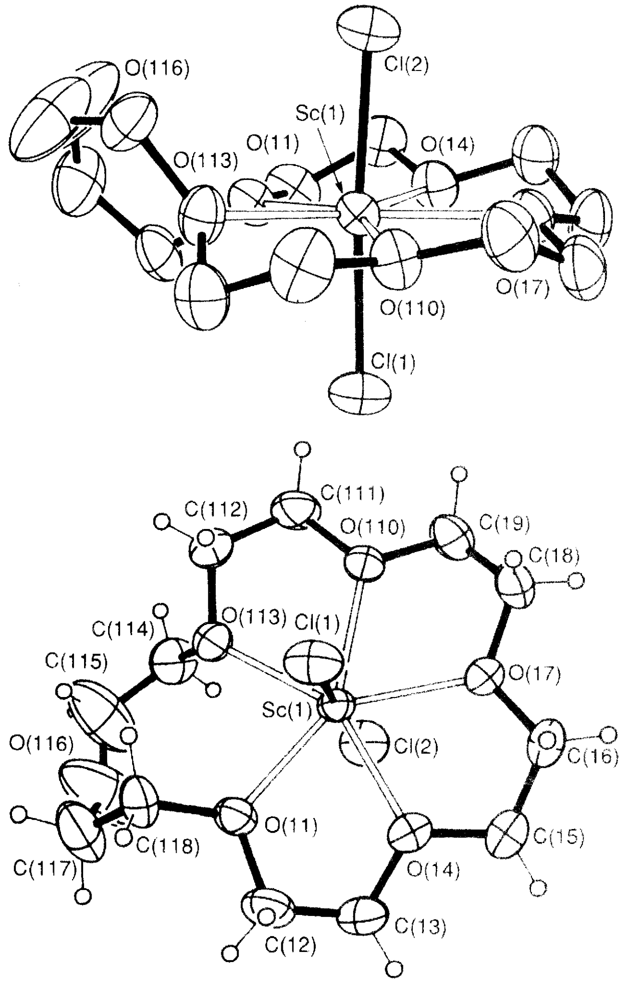

Fig. 1 Views of the [ScCl$_2$(18-crown-6)]$^+$ cation, parallel and perpendicular to the mean ring plane

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† *Crystal data*: [C$_{12}$H$_{24}$O$_6$ScCl$_2$]$^+$[SbCl$_6$]$^-$ M = 714.62, triclinic, space group $P\bar{1}$, a = 7.363(2), b = 18.822(6), c = 19.164(6) Å, α = 105.38(3), β = 100.18(3), γ = 90.90(3)°, V = 2514.80 Å^3, Z = 4, D_c = 1.89 g cm^{-3}, Mo-Kα radiation, λ = 0.71069 Å, μ(Mo-Kα) = 2.22 mm^{-1}, T = 290 K, R = 0.056, R_W = 0.063, for 6663 unique observed [$I/\sigma(I) \geqslant 2.0$] reflections.

The colourless block crystal was mounted under argon in a Lindemann tube. Data were collected with a Siemens R3m four-circle diffractometer in the w-2θ mode to maximum 2θ of 50°. The structure was solved by direct methods. No absorption correction was made. Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.08 Å^2, inserted at calculated positions and not refined. Final refinement was on F by least-squares method refining 509 parameters including an isotropic extinction parameter. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ with g = 0.003625 was used and shown to be satisfactory by a weight analysis. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$OH)_2Sc(H_2O)_5]$ $[C_6H_5SO_3]_4 \cdot 4H_2O$ ($C_6H_5SO_3$ = benzenesulfonate anion),[8] mean Sc–O(H_2O) axial 2.146, equatorial 2.227 and Sc–O (OH, bridge) 2.072 Å. The Sc–Cl bond distances 2.402(3), 2.418 Å are similar to those in $ScCl_3 \cdot 3thf$ (mean 2.41 Å);[1] this is a little surprising since some shortening might be anticipated as a reflection of the cationic nature of the $ScCl_2$ unit.

Another point of interest is that the metal resides directly within the ring cavity. Only two examples of a crown ether–scandium(III) complex have been reported in the literature *viz.*, $Sc(NO_3)_3 \cdot (18\text{-crown-}6) \cdot 3H_2O$[9] and $Sc(NO_3)_3 \cdot$benzo15-crown-5$\cdot 2H_2O$[10] but both of these are 'second sphere' complexes *i.e.* the scandium is merely held in proximity to the crown by hydrogen bonding of the type $O_{crown} \cdots H_2O \cdots Sc$. In our approach we have used anhydrous scandium(III) chloride in the reaction system $ScCl_3/SbCl_5$/18-crown-6/MeCN. Halide abstraction by $SbCl_5$ provides the $ScCl_2^+$ unit, presumably initially as the solvated species $[ScCl_2(MeCN)_n]^+$ where $n \geqslant 4$, which is then readily stabilised by crown complexation with the ubiquitous 18-crown-6.

A third significant feature relates to the unsymmetrical conformation adopted by the crown. From the viewpoint of size compatibility the 18-crown-6 has in effect constricted its cavity by exclusion of one of the oxygen atoms in order to better accommodate the $ScCl_2^+$ unit. The resulting distorted-crown conformation allows effective penta-atom 'shrink wrapping'[11] of the metal but, surprisingly, without any discernible shortening of the Sc–O bond distances. The values observed here lie well within the general range for Sc^{3+} *e.g.* four-coordinate $(\eta^5\text{-}C_5Me_5)_2Sc(p\text{-}MeC_6H_5CO_2)$, Sc–O (mean) 2.172 Å,[12] six-coordinate $ScCl_3 \cdot 3thf$,[1] Sc–O 2.147(7)–2.236(8) Å and eight-coordinate $[HSc(C_7H_5O_2)_4]_2$[13] ($C_7H_5O_2$ = tropolonate anion), Sc–O 2.161(3)–2.310 Å. The ring segment embracing the five bonding oxygen atoms approximates to the symmetrical 'crown' conformation (D_{3d}) and shows O–C–C–O torsion angles close to the 'all *gauche*' sequence (± 60°) with values in the range 49.7–55.1°. For the irregular section of the ring torsion angles around the 'excluded' oxygen atom O(116) give some indication of the extent of distortion *e.g.* in cation (**1**) O(113)–C(114)–C(115)–O(116) 76.9° and, in particular C(112)–O(113)–C(114)–C(115) 113.4° and C(117)–O(116)–C(115)–C(114) 108.1° For a direct comparison 18-crown-6 exhibits a similarly unsymmetrical conformation in $MgCl_2$(18-crown-6) in which a five atom girdle of oxygen atoms surrounds the metal in an approximate coplanar array Mg–O 2.15–2.33 Å leaving the sixth oxygen in a non-bonding peripheral location Mg···O 4.378 Å.[14] Interestingly, in the hydrated sodium thiocyanate complex of 18-crown-6[15] five oxygen atoms again form a more or less pentagonal girdle arrangement around the central metal. Here, however, the remaining oxygen atom is coordinated to the metal and (along with a coordinated H_2O molecule) occupies an axial position of the resulting distorted pentagonal bipyramid structure.

Involvement of all six available oxygens of 18-crown-6 in coordination to $ScCl_2^+$ can be envisaged *e.g.* trigonal prismatic distortion of the crown as witnessed in $[BiCl_2(18\text{-crown-}6)]^+$,[16] but this would necessitate a *cis*-chloro arrangement with each halogen capping a (rectangular) face. Further investigations of the coordination chemistry of $ScCl_2^+$ with macrocyclic ligands are now in progress.

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