

Primary and secondary coordination of crown ethers to scandium(III). Synthesis, properties and structures of the reaction products of $\text{ScCl}_3(\text{thf})_3$, $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with crown ethers

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The synthesis and spectroscopic characterisation of $[\text{ScCl}(\text{15-crown-5})(\text{MeCN})][\text{SbCl}_6]_2$, $[\text{ScCl}_2(\text{18-crown-6})][\text{FeCl}_4]$ and $[\text{ScCl}_2(\text{15-crown-5})][\text{FeCl}_4]$ ($[\text{15-crown-5}] = 1,4\text{-dithia-7,10,13-trioxacyclopentadecane}$) are reported, the last containing the first example of thioether-scandium(III) coordination. The structure of $[\text{ScCl}(\text{15-crown-5})(\text{MeCN})][\text{SbCl}_6]_2$ reveals a pentagonal bipyramidal cation with axial Cl and MeCN, whilst $[\text{ScCl}_2(\text{18-crown-6})][\text{FeCl}_4]$ is also pentagonal bipyramidal with axial Cl ligands. ^1H and ^{45}Sc NMR spectroscopies have been used to study the speciation in the $\text{ScCl}_3/\text{18-crown-6}$ system in the presence of the Lewis acids SbCl_5 and FeCl_3 in anhydrous MeCN. Hydrolysis of any of the above complexes and of $[\text{Sc}(\text{12-crown-4})_2]^{3+}$ (formed from $\text{ScCl}_3(\text{thf})_3$, crown and SbCl_5), results in the formation of $[\text{ScCl}_3(\text{H}_2\text{O})_3]\cdot\text{crown}$, the solution NMR spectra of which show a common scandium species and uncomplexed crown ether. The structure of $[\text{ScCl}_3(\text{H}_2\text{O})_3]\cdot\text{18-crown-6}$ reveals a *mer* octahedral scandium species which is hydrogen bonded *via* the scandium-coordinated water to the 18-crown-6 (secondary coordination) leading to infinite chains. Similar complexes have been isolated directly from reaction of $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ and the crown ethers in absolute ethanol, including $[\text{ScCl}_3(\text{H}_2\text{O})_3]_n \cdot (\text{crown})$ ($n = 1$ or 2 , crown = 18-crown-6; $n = 2$, crown = 15-crown-5 or 12-crown-4). Hydrated scandium nitrate and the crown ethers react in ethanol solution to form a surprisingly diverse range of structural types containing the crown ethers hydrogen bonded to the scandium-aquo-nitrato or scandium-aquo-hydroxo-nitrato complexes. X-Ray crystal structures are reported for $[\text{Sc}(\text{H}_2\text{O})_2(\text{NO}_3)_3] \cdot (\text{12-crown-4})_2$, $[\text{Sc}(\text{H}_2\text{O})_4(\text{NO}_3)_2][\text{NO}_3] \cdot \text{15-crown-5}$ and $[\text{Sc}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6(\text{OH})_2](\text{NO}_3)_2 \cdot \text{12-crown-4}$. However, in the related $[\text{Sc}_2(\text{NO}_3)_4(\text{H}_2\text{O})_4(\text{OH})_2][\text{Na}(\text{12-crown-4})_2](\text{NO}_3) \cdot (\text{H}_2\text{O})_3$, the hydrogen bonding occurs between the lattice water and the scandium dimer unit.

Introduction

Crown ethers are probably best known as effective ligands for hard metal ions, especially those of groups 1 and 2, although they also coordinate to the metals and metalloids of the p-block and to many transition metals.¹ Scandium(III) is the largest and hardest of the 3d M(III) ions and is highly oxophilic. Anhydrous scandium salts are known to react with crown ethers to form complexes where the scandium is directly coordinated (primary coordination) to the ether oxygens.^{2–5} There is also a small number of crystal structure reports of hydrated scandium nitrate species hydrogen bonded to crown ethers (secondary coordination).² In view of the expected affinity of crown ethers for the hard Sc(III) ion, we have investigated the factors influencing primary *versus* secondary coordination in these systems. Surprisingly, as we describe below, we found that even traces of water result in displacement of the crown ether from the scandium, and solids isolated from these systems show the crown H-bonded to scandium-coordinated water. This behaviour contrasts with that in many other systems where trace hydrolysis causes loss of co-ligands, but retention of the crown coordination. For example, initial hydrolysis of $[\text{TiCl}_4(\text{18-crown-6})]$ results in formation of complexes such as $[(\text{18-crown-6})\text{Cl}_3\text{Ti}-\text{O}-\text{TiCl}_3(\text{18-crown-6})]$.⁶ Complexes of crown ethers with lanthanide metals, where the crown is coordinated to 8- or 9-coordinate lanthanide or hydrogen bonded to lanthanide coordinated water ligands have been studied in detail by Rogers and co-workers.⁷ Here we describe detailed studies of the reactions of anhydrous and hydrated scandium chloride and hydrated scandium nitrate with three crown ethers (12-crown-4, 15-crown-5, and 18-crown-6) and explore their structural features.

Experimental

^1H NMR spectra were obtained on Bruker AC300 or DPX400 spectrometers, and ^{45}Sc NMR on the latter at 97.16 MHz and referenced to 1 mol dm⁻³ aqueous scandium nitrate at pH 1. Other physical measurements were made as described previously.⁸ $\text{Sc}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Strem), 12-crown-4, 15-crown-5 and 18-crown-6 (Aldrich) were used as received and $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$,⁹ and $[\text{ScCl}_3(\text{thf})_3]$ ¹⁰ and the thia-oxa-crown 1,4-dithia-7,10,13-trioxacyclopentadecane, $[\text{15-crown-5}]$ ¹¹ were made by literature methods. Anhydrous MeCN and thf were freshly distilled under nitrogen from P_4O_{10} and Na/benzophenone respectively and handled in a dry box. All samples of the anhydrous complexes were made using Schlenk techniques and handled in a dry box ($\text{H}_2\text{O} < 5\text{ppm}$).

$[\text{ScCl}(\text{MeCN})(\text{15-crown-5})][\text{SbCl}_6]_2 \cdot \text{MeCN}$

A solution of SbCl_5 (0.24 g, 0.84 mmol) in anhydrous MeCN (5 ml) was added to a solution of $[\text{ScCl}_3(\text{thf})_3]$ (0.15 g, 0.42 mmol) in MeCN (10 ml) and the solution was stirred under nitrogen for 15 min. The 15-crown-5 (0.09 g, 0.42 mmol) was added and the reaction mixture allowed to stand for several days under a nitrogen atmosphere. Colourless crystals formed slowly which were filtered off and dried *in vacuo*. Yield 0.23 g, 84%. (Found: C, 15.9; H, 2.4; N, 1.8. Calc. for $\text{C}_{14}\text{H}_{26}\text{Cl}_3\text{N}_2\text{O}_5\text{Sb}_2\text{Sc}$: C, 16.0; H, 2.5; N, 2.7%). IR (Nujol mull)/cm⁻¹: 2332w, 2303w, 1349m, 1267m, 1246m, 1128w, 1058s, 965s, 939m, 821m, 449s, 441s, 344vs. ^1H NMR ($d^3\text{-MeCN}$): 4.3 (m). ^{45}Sc NMR (MeCN): 99.5.

$[\text{ScCl}_2(\text{18-crown-6})][\text{FeCl}_4]$

A solution of FeCl_3 (0.08 g, 0.42 mmol) in MeCN (5 ml) was added to a solution of $[\text{ScCl}_3(\text{thf})_3]$ (0.15 g, 0.42 mmol) in

MeCN (10 ml) and the mixture stirred for 30 min under nitrogen. A solution of 18-crown-6 (0.11 g, 0.42 mmol) in MeCN (5 ml) was added and the reaction mixture was left to stand in a refrigerator for 24 h. Yellow crystals formed which were filtered off and dried *in vacuo*. Yield 0.09 g, 37%. (Found: C, 24.7; H, 4.1. Calc. for $C_{12}H_{24}Cl_6FeO_6Sc$: C, 24.9; H, 4.1%). IR (Nujol mull)/ cm^{-1} : 1261m, 1152w, 1089s, 1020m, 960m, 797m, 449m, 389s. 1H NMR (d^3 -MeCN): 4.3 (m). ^{45}Sc NMR (MeCN): 132.

[$ScCl_2([15]aneS_2O_3)[FeCl_4]$]

A solution of [$ScCl_3(thf)_3$] (0.15 g, 0.42 mmol) in MeCN (5 ml) was added to a solution of $FeCl_3$ (0.08 g, 0.42 mmol) in MeCN (5 ml) and the mixture stirred for 1 h. A solution of $[15]aneS_2O_3$ (0.11 g, 0.42 mmol) in MeCN (5 ml) was added, the solution concentrated to ca. 5 ml and refrigerated for 3 d producing a yellow solid. This was filtered off and dried *in vacuo*. Yield 0.12 g, 49%. (Found: C, 21.7; H, 3.5. Calc. for $C_{10}H_{20}Cl_6FeO_3S_2Sc$: C, 21.2; H, 3.5%). IR (Nujol mull)/ cm^{-1} : 1302w, 1260m, 1246m, 1169sh, 1111s, 1021sh, 968m, 933m, 839m, 798m, 594m, 466s, 382vs. 1H NMR (CD_2Cl_2): 3.70–3.35 (m). ^{45}Sc NMR (MeCN): 200.

[$Sc(H_2O)_2(NO_3)_3 \cdot (12-crown-4)$]

A solution of 12-crown-4 (0.176 g, 1.0 mmol) in boiling ethanol (5 ml) was added to a hot solution of $Sc(NO_3)_3 \cdot 5H_2O$ (0.32 g, 1.0 mmol) in ethanol (15 ml) and the mixture refluxed for 1 h. Evaporation to dryness produced a gum, which was redissolved in a small amount of ethanol and slowly evaporated under reduced pressure. On standing at room temperature a few crystals separated along with an oil. The crystals were identified by a crystal structure (below). IR (Nujol mull)/ cm^{-1} : 3580br, 2665m, 1650m, 1587m, 1305w, 1168w, 1157w, 1088w, 1024w, 972m, 931m, 897m, 852m, 813w, 770m, 637w, 560w, 519w. 1H NMR (d^6 -acetone): 3.6 (s), 4.5 (br,s). ^{45}Sc NMR (Me_2CO): –1.0 (br).

[$Sc_2(NO_3)_2(H_2O)_6(OH)_2(NO_3)_2 \cdot 12-crown-4$]

On one occasion, the reaction mixture above was left to stand after concentration to small volume and deposited a few crystals identified by X-ray crystallography as the complex above. Insufficient material was obtained for spectroscopic study.

[$Sc_2(NO_3)_4(H_2O)_4(OH)_2[Na(12-crown-4)_2](NO_3) \cdot (H_2O)_3$]

In an attempt to improve the yield of the complex described above, the gum produced was redissolved in ethanol (2 ml) and 1 mol dm^{-3} aqueous NaOH (5 drops) added. A few crystals separated which were identified by an X-ray study (below).

[$Sc(H_2O)_4(NO_3)_2NO_3 \cdot 15-crown-5$]

A solution of 15-crown-5 (0.04 g, 0.2 mmol) in ethanol (5 ml) was added dropwise to a hot solution of $Sc(NO_3)_3 \cdot 5H_2O$ (0.12 g, 0.4 mmol) in ethanol (5 ml) and the mixture refluxed for 1 h. Concentration to small volume and refrigeration produced a white powder which was filtered off and dried *in vacuo*. Yield 0.05 g, 50%. (Found: C, 23.0; H, 5.4; N, 8.1. Calc. for $C_{10}H_{28}N_3O_{18}Sc$: C, 22.9; H, 5.3; N, 8.0%). IR (Nujol mull)/ cm^{-1} : 3400br, 3200br, 1645m, 1537m, 1279m, 1121w, 1098m, 1056w, 1023m, 964w, 944m, 833m, 808m, 757m. 1H NMR (d^6 -acetone): 3.6 (s), 4.4 (br,s). ^{45}Sc NMR (Me_2CO): +2.0.

[$Sc(H_2O)_3(NO_3)_3 \cdot 18-crown-6$]

A solution of 18-crown-6 (0.058 g, 0.22 mmol) in ethanol (5 ml) was added dropwise to a hot solution of $Sc(NO_3)_3 \cdot 5H_2O$ (0.15 g, 0.45 mmol) in ethanol (15 ml) and the mixture refluxed for 1 h. Concentration to small volume and refrigeration produced a white powder which was filtered off and dried *in vacuo*. Yield 0.05 g, 40%. (Found: C, 25.8; H, 5.2; N, 7.2. Calc. for

$C_{12}H_{30}N_3O_{18}Sc$: C, 26.2; H, 5.5; N, 7.7%). IR (Nujol mull)/ cm^{-1} : 3400br, 3200br, 1645m, 1304w, 1170w, 1153w, 1077w, 1020w, 965m, 936m, 919w, 892m, 844m, 810w, 769m, 562w, 450w. 1H NMR (d^6 -acetone): 3.6 (s), 4.0 (br,s). ^{45}Sc NMR (Me_2CO): +5.0.

[$ScCl_3(H_2O)_3 \cdot 12-crown-4$]

To a boiling ethanol (15 ml) solution of $ScCl_3 \cdot 6H_2O$ (0.22 g, 0.85 mmol), a solution of 12-crown-4 (0.07 g, 0.42 mmol) in ethanol (5 ml) was added dropwise and the solution refluxed for 1 h. All the solvent was removed and the residue washed with ice-cold ethanol (1 ml), filtered off and dried *in vacuo*. Yield 0.08 g, 35%. (Found: C, 16.2; H, 4.6. Calc. for $C_8H_{28}Cl_6O_{10}Sc_2$: C, 16.4; H, 4.8%). IR (Nujol mull)/ cm^{-1} : 3300br, 1620m, 1304w, 1166w, 1155w, 1047s, 1021w, 966m, 938m, 908w, 891m, 855m, 810w, 765m. 1H NMR (d^6 -acetone): 3.6 (s), 4.0 (br,s). ^{45}Sc NMR (EtOH): 153.

[$ScCl_3(H_2O)_3 \cdot 15-crown-5$]

Was made similarly to the above from $ScCl_3 \cdot 6H_2O$ (0.14 g, 0.55 mmol) and 15-crown-5 (0.06 g, 0.27 mmol) in ethanol. Concentration of the solution to a small volume yielded a white solid which was filtered off and dried *in vacuo*. Yield, 0.085 g, 50%. (Found: C, 19.0; H, 4.9. Calc. for $C_{10}H_{32}Cl_6O_{11}Sc_2$: C, 19.0; H, 5.0%). IR (Nujol mull)/ cm^{-1} : 3400br, 1636m, 1304w, 1263w, 1125w, 1060m, 965m, 936m, 919w, 889w, 825m, 771w. 1H NMR (d^6 -acetone): 3.6 (s), 4.7 (br,s). ^{45}Sc NMR (EtOH): 152.

[$ScCl_3(H_2O)_3 \cdot 18-crown-6$]

Was made similarly to the above from $ScCl_3 \cdot 6H_2O$ (0.16 g, 0.60 mmol) and 18-crown-6 (0.08 g, 0.30 mmol) in ethanol. Concentration of the solution to a small volume yielded a white solid which was filtered off and dried *in vacuo*. Yield 0.06 g, 30%. (Found: C, 21.7; H, 5.9. Calc. for $C_{12}H_{36}Cl_6O_{12}Sc_2$: C, 21.4; H, 5.4%). IR (Nujol mull)/ cm^{-1} : 3400br, 3190br, 1635m, 1569w, 1303w, 1259w, 1169m, 1140m, 1093s, 956s, 837m, 768m. 1H NMR (d^6 -acetone): 3.6 (s), 4.6 (br,s). ^{45}Sc NMR (EtOH): 153.

[$ScCl_3(H_2O)_3 \cdot 18-crown-6$]

To a solution of [$ScCl_3(thf)_3$] (0.15 g, 0.42 mmol) in MeCN (10 ml) was added a solution of 18-crown-6 (0.11 g, 0.42 mmol) in MeCN (10 ml). The solution was allowed to evaporate in air over about 1 week when colourless crystals formed, which were filtered off and dried *in vacuo*. Yield 0.09 g, 46%. (Found: C, 30.8; H, 5.5. Calc. for $C_{12}H_{30}Cl_3O_9Sc$: C, 30.7; H, 6.4%). IR (Nujol mull)/ cm^{-1} : 3410br, 3222br, 1631m, 1300m, 1262w, 1140m, 1101m, 958s, 817m, 439m, 334m. 1H NMR (d^6 -acetone): 3.6 (s), 4.2 (s). ^{45}Sc NMR (EtOH): 152.

X-Ray crystallographic studies

Crystals of [$ScCl(MeCN)(15-crown-5)[SbCl_6]_2 \cdot MeCN$], [$ScCl_2(18-crown-6)[FeCl_4]$], [$Sc(H_2O)_2(NO_3)_3 \cdot (12-crown-4)_2$], [$Sc_2(OH)_2(H_2O)_6(NO_3)_2(NO_3)_2 \cdot 12-crown-4$ and [$Sc_2(NO_3)_4(H_2O)_4(OH)_2[Na(12-crown-4)_2](NO_3) \cdot (H_2O)_3$ were obtained from the reaction mixtures as described above. The crystals of [$Sc(H_2O)_4(NO_3)_2NO_3 \cdot 15-crown-5$ and [$ScCl_3(H_2O)_3 \cdot 18-crown-6$ were obtained by slow evaporation of ethanol solutions. Crystallographic data were obtained using a Nonius Kappa CCD diffractometer fitted with Mo radiation and graphite monochromator (Table 1). The data were corrected for absorption using SORTAV,¹² and structure solution and refinement were generally routine.^{13–15} Methylene hydrogen atoms on the crown residue were placed in calculated positions, whereas H atoms bonded to O atoms (OH and H_2O) were convincingly located in later electron-density maps in all but a few cases and introduced

Table 1 Crystallographic data for Sc complexes^a

Compound	[ScCl(MeCN)- (15-crown-5)]SbCl ₆ z· MeCN	[ScCl ₂ (18-crown-6)]FeCl ₄	[ScCl ₃ (H ₂ O) ₃]·18-crown-6	[Sc ₂ (NO ₃) ₄ (H ₂ O) ₄ (OH) ₂]- [Na(12-crown-4)] ₂ (NO ₃) ₃ · (H ₂ O) ₃	[Sc ₂ (NO ₃) ₂ (H ₂ O) ₆ (OH) ₂]- (NO ₃) ₂ ·12-crown-4	[Sc(NO ₃) ₃ (H ₂ O) ₂] (12-crown-4) ₂
Formula	C ₁₄ H ₂₆ Cl ₁₃ N ₂ O ₅ Sb ₂ Sc	C ₁₂ H ₂₄ Cl ₆ FeO ₆ Sc	C ₁₂ H ₃₀ Cl ₃ O ₉ Sc	C ₁₆ H ₄₈ N ₁₅ NaO ₃₂ Sc ₂	C ₈ H ₃₀ N ₄ O ₂₄ Sc ₂	C ₁₆ H ₃₆ N ₃ O ₁₉ Sc
<i>M</i>	1051.68	577.82	469.67	935.50	656.28	619.44
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Triclinic	Orthorhombic
Space group	<i>Pbca</i> (no. 61)	<i>Pna2</i> ₁ (no. 33)	<i>Pbcn</i> (no. 60)	<i>P1</i> (no. 2)	<i>P1</i> (no. 2)	<i>P2</i> ₁ <i>2</i> ₁ <i>2</i> ₁ (no. 18)
<i>a</i> /Å	21.209(2)	19.2026(15)	10.7210(10)	8.7342(10)	7.5712(15)	11.6362(15)
<i>b</i> /Å	13.4224(10)	11.2156(10)	14.8569(15)	13.4735(15)	9.2350(15)	13.432(3)
<i>c</i> /Å	24.800(2)	21.0990(15)	13.2776(15)	16.842(3)	9.862(3)	8.7311(10)
<i>a</i> /°	90.0	90.0	90.0	100.341(4)	85.497(7)	90.0
<i>β</i> /°	90.0	90.0	90.0	98.989(4)	84.869(8)	90.0
<i>γ</i> /°	90.0	90.0	90.0	93.665(7)	69.545(15)	90.0
<i>U</i> /Å ³	7060.0(10)	4544.1(6)	2114.9(4)	1917.2(4)	642.7(2)	1364.7(3)
<i>D</i> _{calc} /g cm ⁻³	1.979	1.689	1.475	1.621	1.696	1.507
<i>Z</i>	8	8	4	2	1	2
<i>F</i> (000)	4064	2344	984	976	340	652
Crystal size/mm	0.36 × 0.24 × 0.16	0.26 × 0.26 × 0.20	0.30 × 0.26 × 0.20	0.32 × 0.30 × 0.26	0.26 × 0.20 × 0.10	0.28 × 0.20 × 0.18
No. reflections measured	38521	33479	17374	26054	8198	9719
No. unique reffns (<i>R</i> _{int})	8017 (0.107)	10116 (0.060)	2415(0.073)	6636 (0.058)	2801 (0.085)	3109 (0.050)
2 θ (max)/°	55.0	55.0	54.9	50.0	54.9	54.9
Max., min. transmission	0.8822, 0.7992	0.8875, 0.8157	0.9492, 0.7854	0.8954, 0.8798	0.9230, 0.8746	0.8857, 0.8521
No. of data in refinement	8017	10116	2415	6636	2801	3109
No. params/restraints	335/0	470/1	125/3	493/3	191/6	185/2
Flack parameter	n.a.	0.09(1)	n.a.	n.a.	n.a.	0.00(3)
μ /cm ⁻¹	27.19	16.67	7.65	4.79	6.36	3.58
<i>S</i>	0.952	0.992	1.036	1.019	1.027	1.015
Max. shift/e.s.d.	0.003	0.001	0.001	0.001	0.000	0.000
Residual e-density/e Å ⁻³	-0.97 to +0.94	-0.56 to +0.44	-0.39 to +0.37	-0.56 to +1.01	-0.47 to +0.34	-0.37 to +0.22
<i>R</i> ^b (<i>I</i> > 2 σ (<i>I</i>))	0.042 (4920 refs)	0.039 (7859 refs)	0.038 (1767 refs)	0.050 (4294 refs)	0.041 (2053 refs)	0.041 (2506 refs)
<i>R</i> (all data)	0.098	0.065	0.062	0.090	0.069	0.060
<i>wR2</i> ^c (all data)	0.086	0.080	0.092	0.145	0.098	0.088

^aIn common: λ (Mo-K α) = 0.71073 Å; *T* = 120 K. ^b*R* = $\Sigma||F_o| - \Sigma||F_c| - |F_c|/\Sigma|F_o|$. ^c*wR2* = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for [ScCl(MeCN)(15-crown-5)][SbCl₆]₂·MeCN

Sc(1)–Cl(1)	2.361(2)	Sc(1)–N(1)	2.272(4)
Sc(1)–O(1)	2.135(3)	Sc(1)–O(4)	2.154(3)
Sc(1)–O(2)	2.155(3)	Sc(1)–O(5)	2.176(3)
Sc(1)–O(3)	2.164(3)		
C–O	1.444(6)–1.469(6)	C–C (ring)	1.477(7)–1.501(7)
Sb(1)–Cl	2.356(1)–2.382(1)		
Sb(2)–Cl	2.356(1)–2.372(1)		
O(1)–Sc(1)–O(2)	71.2(1)	O(5)–Sc(1)–O(1)	71.7(1)
O(2)–Sc(1)–O(3)	72.1(1)	N(1)–Sc(1)–Cl(1)	178.2(1)
O(3)–Sc(1)–O(4)	71.5(1)	O(5)–Sc(1)–Cl(1)	92.14(9)
O(4)–Sc(1)–O(5)	72.5(1)	O(4)–Sc(1)–Cl(1)	95.7(1)

Table 3 Selected bond lengths (Å) and angles (°) for [ScCl₂(18-crown-6)][FeCl₄]

Sc(1)–Cl(1)	2.435(1)	Sc(1)–Cl(2)	2.413(1)
Sc(1)–O(1)	2.195(2)	Sc(1)–O(5)	2.243(2)
Sc(1)–O(2)	2.192(2)	Sc(1)–O(6)	2.210(2)
Sc(1)–O(3)	2.230(2)		
Sc(2)–Cl(3)	2.425(1)	Sc(2)–Cl(4)	2.402(1)
Sc(2)–O(7)	2.264(2)	Sc(2)–O(11)	2.213(2)
Sc(2)–O(9)	2.216(2)	Sc(2)–O(12)	2.202(2)
Sc(2)–O(10)	2.200(2)		
C–O	1.417(4)–1.473(4)	C–C	1.483(5)–1.503(5)
Fe(1)–Cl	2.179(1)–2.202(1)		
Fe(2)–Cl	2.184(1)–2.202(1)		
O(1)–Sc(1)–O(2)	70.76(9)	O(6)–Sc(1)–O(1)	69.60(9)
O(2)–Sc(1)–O(3)	71.68(8)	Cl(1)–Sc(1)–Cl(2)	177.96(5)
O(3)–Sc(1)–O(5)	77.50(9)	O(1)–Sc(1)–Cl(1)	85.58(7)
O(5)–Sc(1)–O(6)	71.72(8)	O(3)–Sc(1)–Cl(1)	95.50(7)
O(7)–Sc(2)–O(9)	77.85(9)	O(12)–Sc(2)–O(7)	72.28(9)
O(9)–Sc(2)–O(10)	70.66(8)	Cl(3)–Sc(2)–Cl(4)	176.35(4)
O(10)–Sc(2)–O(11)	71.11(9)	O(11)–Sc(2)–Cl(3)	86.47(7)
O(11)–Sc(2)–O(12)	68.96(9)	O(9)–Sc(2)–Cl(3)	95.12(7)

Table 4 Selected bond lengths (Å) and angles (°) for [ScCl₃(H₂O)₃]₂·18-crown-6

Sc(1)–O(4)	2.177(2)	Sc(1)–Cl(1)	2.4403(6)
Sc(1)–O(5)	2.142(1)	Sc(1)–Cl(2)	2.4267(8)
C–O	1.419(3)–1.446(3)	C–C	1.441(3)–1.484(4)
O(4)–Sc(1)–O(5)	81.89(4)	O(4)–Sc(1)–Cl(1)	88.14(2)
O(5)–Sc(1)–O(5i)	163.78(8)	O(4)–Sc(1)–Cl(2)	180.00
Cl(1)–Sc(1)–Cl(2)	91.86(2)	O(5)–Sc(1)–Cl(1)	89.79(5)
Cl(1)–Sc(1)–Cl(1i)	176.27(3)	O(5)–Sc(1)–Cl(2)	98.11(4)

Symmetry operation: $i = -x, y, -z + 3/2$.**Table 5** Selected bond lengths (Å) and angles (°) for [Sc(NO₃)₃(H₂O)₂]₂·(12-crown-4)₂

Sc(1)–O(1)	2.252(2)	Sc(1)–O(4)	2.201(2)
Sc(1)–O(3)	2.268(1)	Sc(1)–O(6)	2.105(2)
C–O	1.417(3)–1.444(3)	C–C	1.492(3)– 1.505(4)
O(1)–Sc(1)–O(1i)	56.98(7)	O(3)–Sc(1)–O(4)	57.58(5)
O(6)–Sc(1)–O(6i)	153.64(9)		

Symmetry operation: $i = -x, -y, z$.

into the model with either fixed or restrained positions (using DFIX command; target 0.84(2) Å). Selected bond lengths and angles are presented in Tables 2–7.

CCDC reference numbers 196080–196085 (for the compounds in Tables 4, 3, 5, 6, 2 and 7 respectively).

See <http://www.rsc.org/suppdata/dt/b2/b210458j/> for crystallographic data in CIF or other electronic format.

Results and discussion

Anhydrous ScCl₃ systems

The reaction of [ScCl₃(thf)₃], SbCl₅ and 15-crown-5 in a 1 : 1 : 1 mol ratio in anhydrous MeCN produces white [ScCl₂(15-crown-5)][SbCl₆]₂,³ which has been shown (as the [CuCl₄]²⁻ salt⁵) to contain a 7-coordinate *trans* pentagonal bipyramidal

Table 6 Selected bond lengths (Å) and angles (°) for [Sc₂(NO₃)₂(H₂O)₆(OH)₂](NO₃)₂·12-crown-4

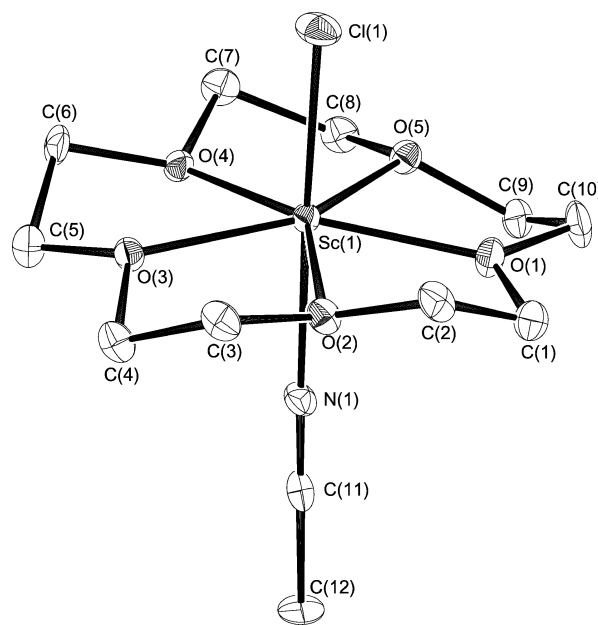
Sc(1)–O(1)	2.261(2)	Sc(1)–O(6)	2.101(2)
Sc(1)–O(2)	2.366(2)	Sc(1)–O(7)	2.050(2)
Sc(1)–O(4)	2.128(2)	Sc(1)–O(7i)	2.064(2)
Sc(1)–O(5)	2.186(2)	Sc(1) ⋯ Sc(1i)	3.296(1)
C(1)–C(2)	1.511(4)	C(3)–C(4)	1.488(4)
C–O	1.431(3)–1.435(3)		
O(1)–Sc(1)–O(2)	55.23(6)	O(7)–Sc(1)–O(7i)	73.54(7)
Sc(1)–O(7)–Sc(1i)	106.46(7)		

Symmetry operation: $i = 1 - x, -y, 1 - z$.**Table 7** Selected bond lengths (Å) and angles (°) for [Sc₂(NO₃)₄(H₂O)₄(OH)₂][Na(12-crown-4)₂](NO₃)·(H₂O)₃

Sc(1)–O(1)	2.346(2)	Sc(2)–O(9)	2.089(2)
Sc(1)–O(2)	2.345(2)	Sc(2)–O(10)	2.033(2)
Sc(1)–O(4)	2.298(3)	Sc(2)–O(11)	2.155(3)
Sc(1)–O(5)	2.337(2)	Sc(2)–O(12)	2.174(2)
Sc(1)–O(7)	2.170(2)	Sc(2)–O(13)	2.352(2)
Sc(1)–O(8)	2.153(3)	Sc(2)–O(14)	2.291(2)
Sc(1)–O(9)	2.039(2)	Sc(2)–O(16)	2.341(2)
Sc(1)–O(10)	2.087(2)	Sc(2)–O(17)	2.355(2)
Sc(1) ⋯ Sc(2)	3.324(1)		
Na(1)–O(19)	2.465(3)	Na(1)–O(23)	2.499(3)
Na(1)–O(20)	2.490(3)	Na(1)–O(24)	2.449(3)
Na(1)–O(21)	2.503(3)	Na(1)–O(25)	2.449(3)
Na(1)–O(22)	2.431(3)	Na(1)–O(26)	2.475(3)
C–O	1.416(4)–1.436(4)	C–C	1.502(5)–1.518(5)
O(1)–Sc(1)–O(2)	54.38(9)	O(13)–Sc(2)–O(14)	54.89(9)
O(4)–Sc(1)–O(5)	55.02(9)	O(16)–Sc(2)–O(17)	54.28(9)
O(9)–Sc(1)–O(10)	72.52(9)	O(9)–Sc(2)–O(10)	72.61(9)
Sc(1)–O(9)–Sc(2)	107.3(1)	Sc(1)–O(10)–Sc(2)	107.6(1)

scandium cation; we have observed the same monocation. However, when we conducted the reaction with a 1 : 2 [ScCl₃(thf)₃] : SbCl₅ ratio, the MeCN solution deposited white crystals identified as [ScCl(15-crown-5)(MeCN)][SbCl₆]₂·MeCN by analysis and spectroscopy and confirmed by an X-ray crystallographic study. The IR spectrum shows both coordinated and lattice MeCN (2332, 2303 cm⁻¹), [SbCl₆]⁻ ($\nu_3 = 344$ cm⁻¹) and $\nu_{\text{Sc-Cl}} = 441$ cm⁻¹. The ⁴⁵Sc NMR resonance of this cation in rigorously anhydrous MeCN solution is δ 99.5, (which compares with $\delta = 130$ in [ScCl₂(15-crown-5)]⁺). The structure of the cation in [ScCl(15-crown-5)(MeCN)][SbCl₆]₂·MeCN is the expected *trans* pentagonal bipyramid and is shown in Fig. 1, and selected bond lengths and angles are given in Table 2. Comparison of the dimensions with those of [ScCl₂(15-crown-5)]⁺,⁵ show very similar Sc–O distances, whilst the Sc–Cl bond is slightly shorter in the dication (2.361(2) Å) than in the monocation (2.426(8) Å). Several attempts using excess SbCl₅ in these reactions failed to remove the last chloride ligand from the scandium, monitoring the reaction by ⁴⁵Sc NMR showed only [ScCl(15-crown-5)(MeCN)]²⁺ was present.

The reaction of [ScCl₃(thf)₃], SbCl₅ and 18-crown-6 in anhydrous MeCN in a 1 : 1 : 1 mol ratio affords [ScCl₂(18-crown-6)]SbCl₆ which also contains a pentagonal bipyramidal cation, in this case one crown ether oxygen is uncoordinated.³ Attempts to remove further chlorines by reaction with stoichiometric amounts of SbCl₅ gave complex mixtures,³ and an *in situ* study using ⁴⁵Sc NMR spectroscopy as the solution probe gave confusing results.¹⁶ We suspected that the problem might be that SbCl₅ is such a powerful Lewis acid that it also reacts with other bases in the system as well as abstracting chloride and this prevents control of the Sc : SbCl₅ stoichiometry. Use of FeCl₃, a weaker Lewis acid, avoids this problem and the reaction of [ScCl₃(thf)₃], FeCl₃ and 18-crown-6 in a 1 : 1 : 1 ratio cleanly produces [ScCl₂(18-crown-6)]FeCl₄ as

**Fig. 1** The structure of the cation in [ScCl(MeCN)(15-crown-5)][SbCl₆]₂·MeCN showing the atom labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and the H atoms are omitted for clarity.

yellow–green crystals. The crystal structure of this material (Fig. 2, Table 3) shows two similar independent cations differing only in the conformation of the ring at the uncoordinated oxygen (O(4)). Comparison of these and the [ScCl₂(18-crown-6)]SbCl₆,³ shows only small differences in bond lengths and angles at the scandium centre which are not chemically significant. However, the structure provides a clear starting point for

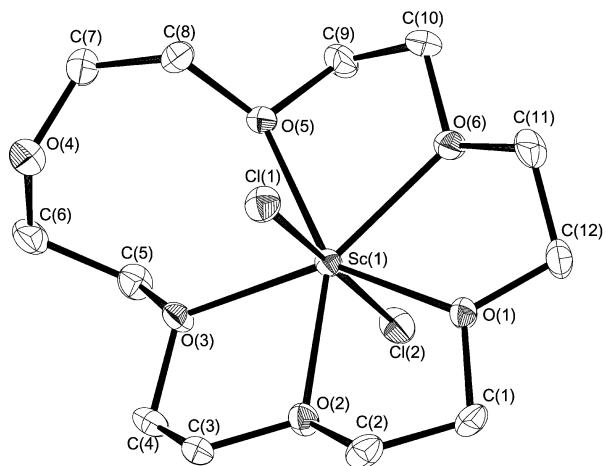


Fig. 2 The structure of the cation involving Sc(1) in $[\text{ScCl}_2(18\text{-crown-6})]\text{FeCl}_4$ showing the atom labelling scheme. The Sc(2) species is similar, differing in the conformation at C(7) and O(4). Displacement ellipsoids are drawn at the 50% probability level and the H atoms are omitted for clarity.

attempting to identify other solution species. In solution in anhydrous MeCN, $[\text{ScCl}_2(18\text{-crown-6})]\text{FeCl}_4$ exhibits a single ^{45}Sc NMR resonance at δ 132 ($W_{1/2} = 600$ Hz), attributable to the ‘ ScCl_2O_5 ’ cation and notably no other scandium-containing species was evident. This contrasts with the reports^{3,16} of several species in solutions of the $[\text{SbCl}_6]^-$ salt. The resonance broadens and shifts slightly on cooling but no other species are seen. Addition of aliquots of FeCl_3 results in diminution and then loss of the resonance due to the dichloroacation and the stepwise appearance of new features at δ 101 and -2 which can be attributed respectively to $[\text{ScCl}(18\text{-crown-6})]^{2+}$ and $[\text{Sc}(18\text{-crown-6})]^{3+}$ species, presumably with MeCN completing the coordination spheres. When the ratio Sc : FeCl_3 is $1 : \geq 4$ only the $\delta -2$ resonance is present. The progressive low frequency shift in the ^{45}Sc resonance as chloride is replaced by oxygen or nitrogen is consistent with the results in the 15-crown-5 system described above, and also with $\text{ScCl}_3\text{-R}_3\text{PO}$ systems.⁹ Re-examination of the $[\text{ScCl}_3(\text{thf})_3]/18\text{-crown-6}/\text{SbCl}_5/\text{MeCN}$ system varying the Sc : SbCl_5 ratio shows species with $\delta(^{45}\text{Sc}) = 130, 95,$ and -19 , although their relative abundances are not readily related to the Sc : SbCl_5 ratio. The first two are assigned to the dichloro- and monochloro-cations respectively, the last is unassigned (and notably absent in the FeCl_3 reactions), but a possibility is that it corresponds to $[\text{Sb}(18\text{-crown-6}\cdot\text{SbCl}_5)(\text{MeCN})_3]^{3+}$ where the SbCl_5 has coordinated to the one remaining ‘free’ oxygen in the crown ether.

The reaction of $[\text{ScCl}_3(\text{thf})_3]$, SbCl_5 , SbCl_3 and 12-crown-4 in a 1 : 1 : 2 : 2 mol ratio in MeCN forms $[\text{Sc}(12\text{-crown-4})_2][\text{SbCl}_6][\text{Sb}_2\text{Cl}_8(\text{MeCN})_2]\cdot 2\text{MeCN}$. An X-ray crystallographic study¹⁷ showed the presence of a square antiprismatic $[\text{Sc}(12\text{-crown-4})_2]^{3+}$ cation, readily identified in solution by a ^{45}Sc NMR resonance at δ 25. The reaction of $[\text{ScCl}_3(\text{thf})_3]$, SbCl_5 , and 12-crown-4 in a 1 : 1 : 1 mol ratio in MeCN gives a poorly soluble white powder which was formulated³ as $[\text{ScCl}_2(12\text{-crown-4})(\text{MeCN})]\text{SbCl}_6$. We too have isolated a compound with very similar spectroscopic data, but have been unable to obtain crystals to unequivocally establish the cation present. An *in situ* NMR study of this system reported¹⁶ two ^{45}Sc NMR resonances at δ 25 and 153 attributed to $[\text{Sc}(12\text{-crown-4})_2]^{3+}$ and $[\text{ScCl}_2(12\text{-crown-4})]^+$, but from our work we believe that the latter is due to the ubiquitous hydrolysis product $[\text{ScCl}_3(\text{H}_2\text{O})_3]$ (see below). In our hands, a solution of pre-isolated ‘ $[\text{ScCl}_2(12\text{-crown-4})(\text{MeCN})]\text{SbCl}_6$ ’ in rigorously anhydrous MeCN shows resonances at δ 25 and 205 in *ca.* 1 : 1 ratio, the latter very similar to that observed when $[\text{ScCl}_3(\text{thf})_3]$ is dissolved in

MeCN. Since 12-crown-4 is too small to encapsulate Sc^{3+} , it behaves differently to the larger crowns. Without an X-ray crystal structure the nature of this species remains unclear, but the data would fit a formulation $[\text{Sc}(12\text{-crown-4})_2][\text{SbCl}_6]_2[\text{ScCl}_4(\text{MeCN})_2]^{\dagger}$.

The thia-oxa-crown $[\text{15}]_{\text{ane}}\text{S}_2\text{O}_3$ reacted with $[\text{ScCl}_3(\text{thf})_3]$ and FeCl_3 in anhydrous MeCN to form yellow $[\text{ScCl}_2([\text{15}]_{\text{ane}}\text{S}_2\text{O}_3)]\text{FeCl}_4$. The complex is poorly soluble in MeCN and very readily hydrolysed, but in anhydrous CD_2Cl_2 the ^1H NMR spectrum contains overlapping multiplets at δ 3.35–3.70 which compares with 2.72(t), 2.87(s) CH_2S , 3.64(s), 3.75(t) CH_2O in the ‘free’ ligand.¹¹ The high frequency shift of the CH_2S resonances indicates coordination of the thioether functions to the scandium, and this is supported by the ^{45}Sc NMR data ($\delta = 200$), (compare $\delta = 130$ in $[\text{ScCl}_2(15\text{-crown-5})]^+$). Unfortunately we have been unable to obtain a crystal for an X-ray study, but this complex appears to be the first example of coordination of thioether donors to scandium(III).

Hydrated scandium chloride systems

The anhydrous scandium chloride/crown ether systems are very moisture sensitive, even traces of water from laboratory solvents are sufficient to generate a new species which is common to all of the systems, with a ^{45}Sc NMR resonance at *ca.* 153 (± 3), $W_{1/2}$ 500–1100 Hz (the resonances are concentration and solvent dependent). The corresponding ^1H NMR spectra showed the presence of uncoordinated crown ether. The same species is the only scandium-containing product formed when any of the anhydrous scandium chloride-crown complexes are dissolved in absolute ethanol, and a solution of $\text{ScCl}_3\cdot 6\text{H}_2\text{O}$ in absolute ethanol has δ 150, suggesting the common species responsible for this resonance is $[\text{ScCl}_3(\text{H}_2\text{O})_3]$. Crystals were obtained by allowing a solution of $[\text{ScCl}_2(18\text{-crown-6})]\text{SbCl}_6$ in MeCN to evaporate exposed to air, and the structure solution revealed a *mer*- $[\text{ScCl}_3(\text{H}_2\text{O})_3]\cdot 18\text{-crown-6}$ network (Fig. 3(a) and (b), Table 4) where the crown is hydrogen bonded to the scandium-coordinated water ligands (secondary coordination). The structure consists of a neutral $[\text{ScCl}_3(\text{H}_2\text{O})_3]$ residue with an approximately octahedral scandium atom. The 18-crown-6 has a crystallographic centre of symmetry and is H-bonded to the scandium residue through three $\text{O}-\text{H}\cdots\text{O}$ H-bonds (*ca.* 2.8 Å). All the H atoms bonded to the water molecules were clearly identified in later electron-density maps. Every water H atom is involved in H-bonding to the crown (all crown O atoms are used) the result being the formation of chains of alternating scandium groups and crowns in the *c* direction.

The ready displacement of the crown ether by even traces of water with retention of the chloride ligands was unexpected, and contrasts with other systems. For example trace hydrolysis of $[\text{TiCl}_4(18\text{-crown-6})]$ results in one or more of the chloride ligands being replaced by $\mu\text{-O}$ linkages, but the direct crown ether–Ti coordination remains.⁶ This led us to investigate the products formed by reaction of $\text{ScCl}_3\cdot 6\text{H}_2\text{O}$ and the three crown ethers in absolute ethanol. The reaction of $\text{ScCl}_3\cdot 6\text{H}_2\text{O}$ with the crowns in absolute ethanol was carried out in 2 : 1 ratios. The products are highly soluble, evaporation tends to produce viscous oils and it is difficult to isolate crystals or even powders. However, we have isolated solids with stoichiometries $[\text{ScCl}_3(\text{H}_2\text{O})_3]_2\cdot 18\text{-crown-6}$, $[\text{ScCl}_3(\text{H}_2\text{O})_3]_2\cdot 15\text{-crown-5}$ and $[\text{ScCl}_3(\text{H}_2\text{O})_3]_2\cdot 12\text{-crown-4}$ (Experimental). As expected, the spectroscopic properties of these complexes are very similar and all show ^1H NMR spectra consistent with ‘free’ crowns, and the ^{45}Sc NMR (ethanol solution) show only the δ 153

[†] A solution of $[\text{ScCl}_3(\text{thf})_3]$ in MeCN shows $\delta(^{45}\text{Sc}) = 205$ which on treatment with a large excess of LiCl is converted to a sharper resonance at δ 217 possibly due to $[\text{ScCl}_4(\text{MeCN})_2]^-$. However in the absence of excess Cl^- , $[\text{ScCl}_4(\text{MeCN})_2]^-$ probably decomposes to $[\text{ScCl}_3(\text{MeCN})_3]$ so the result is inconclusive. The literature ^{45}Sc chemical shift of $[\text{ScCl}_3(\text{MeCN})_3]$ in MeCN is 201.¹⁸

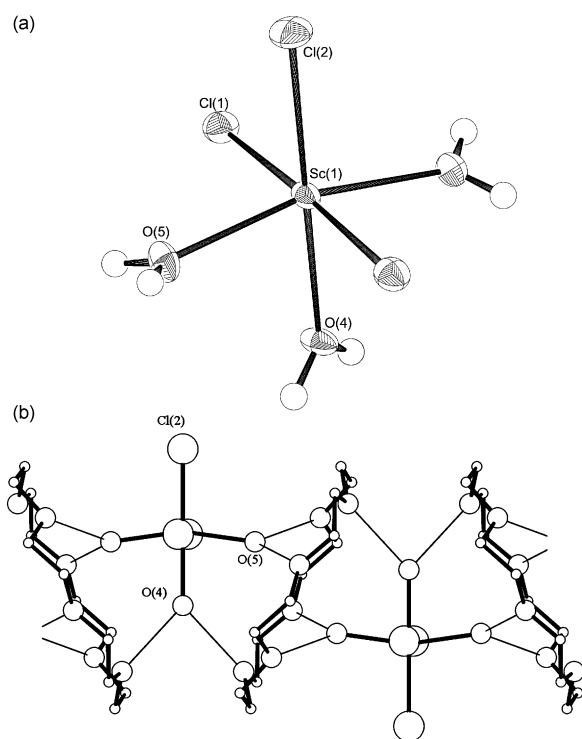


Fig. 3 The structure of $[\text{ScCl}_3(\text{H}_2\text{O})_3]\cdot 18\text{-crown-6}$ (a) shows the Sc(1) group with the atom labelling scheme and the 2-fold symmetry lying along O(4), Sc(1) and Cl(2). Displacement ellipsoids are drawn at the 50% probability level; (b) view down the a direction showing the chain of O–H \cdots O bonds between the Sc groups and the crown parallel to the c direction. The H-bonding is indicated by single lines and the H atoms are omitted for clarity.

resonance of $[\text{ScCl}_3(\text{H}_2\text{O})_3]$. We have also obtained the 1 : 1 species $[\text{ScCl}_3(\text{H}_2\text{O})_3]\cdot 18\text{-crown-6}$ directly from $\text{ScCl}_3\cdot 6\text{H}_2\text{O}$ and 18-crown-6.

Hydrated scandium nitrate systems

The products of the reactions of $\text{Sc}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ with the three crowns in absolute ethanol are very soluble and correspondingly difficult to isolate as solids. From $\text{Sc}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ and 18-crown-6, the product was $[\text{Sc}(\text{H}_2\text{O})_3(\text{NO}_3)_3]\cdot 18\text{-crown-6}$. The structure of this compound has been described previously,¹⁹ and our crystals had the same unit cell. The IR spectrum shows the characteristic features of H_2O , 18-crown-6 and a weak band at 810 cm^{-1} assigned as ν_2 of a coordinated nitrate group,^{8,20} (the other nitrate modes are obscured by absorptions of the crown ether). The ^1H NMR spectrum in d^6 -acetone shows “free” crown ether and water, whilst the ^{45}Sc NMR resonance ($\delta = +5$) is reasonable for scandium in an O-donor environment (compare $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ ($\delta = 0$) or $[\text{Sc}(\text{NO}_3)_3(\text{OPPh}_3)_2]$ ($\delta = -7.5$)⁸). The $[\text{Sc}(\text{H}_2\text{O})_4(\text{NO}_3)_2]\text{NO}_3\cdot 15\text{-crown-5}$ has similar ^1H and ^{45}Sc NMR spectra, including $\delta(^{45}\text{Sc}) \delta = +2$, but the IR spectrum shows two weak $\nu_2(\text{NO}_3)$ modes at 833 and 808 cm^{-1} consistent with the presence of both ionic and coordinated nitrate groups.^{8,20} The structure (below) shows eight-coordinate scandium and differs from the complex reported by Gan *et al.*,²¹ $[\text{Sc}(\text{H}_2\text{O})_2(\text{NO}_3)_3]\cdot 15\text{-crown-5}$, which contains only two water and three bidentate nitrate ligands.

The 12-crown-4 complexes proved particularly difficult to isolate in useful quantities. The $[\text{Sc}(\text{H}_2\text{O})_2(\text{NO}_3)_3]\cdot (12\text{-crown-4})_2$, which separated in very poor yield as crystals from $\text{Sc}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ and 12-crown-4 in ethanol, also contains eight-coordinate scandium, the IR spectrum confirming the absence of ionic nitrate groups, whilst the ^{45}Sc NMR resonance is at $\delta = -1$. Crystallisation over a longer period of time yielded a few crystals of a second species identified by X-ray crystallography

as $[\text{Sc}_2(\text{H}_2\text{O})_6(\text{OH})_2(\text{NO}_3)_2](\text{NO}_3)_2\cdot 12\text{-crown-4}$, a dihydroxy-bridged Sc dimer cation. Insufficient material was obtained to permit spectroscopic or analytical characterisation, and in attempt to improve the yield, the reaction was repeated in the presence of base (aqueous NaOH). Only a few crystals were obtained from this reaction also, but these proved to be $[\text{Sc}_2(\text{NO}_3)_4(\text{H}_2\text{O})_4(\text{OH})_2]\cdot [\text{Na}(12\text{-crown-4})_2]\text{NO}_3\cdot (\text{H}_2\text{O})_3$. Most interestingly, the scandium is present as another hydroxy-bridged dimer whilst the two 12-crown-4 ligands sandwich a Na^+ , further evidence of the weak affinity of Sc^{3+} for the crown which coordinates preferentially to the larger and singly charged sodium.

The crystal structures of the four new scandium nitrate complexes are described below, three of these contain the crown ether hydrogen bonded to the water ligands of the scandium residues (secondary coordination), but provide a range of different supramolecular arrays. The structure of $[\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_3]\cdot 18\text{-crown-6}$ has been described three times (initially in space group $Pna2_1$ and later in the centrosymmetric $Pnma$).¹⁹ The latter space group shows a scandium residue with mirror symmetry; the nine-coordinate Sc atom is coordinated by three bidentate nitrate groups and three essentially *mer* water molecules (Sc–O(H) 2.205, 2.228; Sc–O(N) 2.249–2.363 Å). Hydrogen atomic coordinates were not available, but calculation of O \cdots O distances between the crown and the Sc residue showed four distances < 3.0 Å (shortest 2.79 Å) involving both crystallographically distinct O(H₂) and all O atoms of the crown. These distances are typical of H-bonded interactions and result in chains of alternating Sc residues and crowns, giving an infinite 1-dimensional network. The H-bonding pattern in this compound is similar to that described above for $[\text{ScCl}_3(\text{H}_2\text{O})_3]\cdot 18\text{-crown-6}$. We have also isolated this compound as shown by the measured cell dimensions (see Experimental).

The crystals obtained from the $\text{Sc}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ and 15-crown-5 are of stoichiometry $[\text{Sc}(\text{NO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)\cdot 15\text{-crown-5}$.[‡] Unfortunately, we were only able to obtain rather poor quality crystals of this material and although the structure did not refine well it did establish the gross crystal structure. The structure clearly shows some important differences from the 18-crown-6 system above. The cation contains eight-coordinate Sc from two bidentate NO_3 ligands and four water ligands (Sc–O(H) 2.134(8)–2.232(7), Sc–O(N) 2.184(8)–2.249(7) Å) (see Fig. 4). The 15-crown-5 ring is disordered (mainly in the region of the ring which is not involved in H-bonding), this was partially modelled for two fractionally occupied atoms where individual atom sites were recognised but clearly, from the adp values, the disorder is more extensive. No attempt was made to introduce H atoms on the O atoms and evidence for H-bonding between two of the H_2O ligands and four of the five O atoms of the crown comes from O \cdots O distances (*ca.* 2.8 Å). The H-bonding involves the two mutually *trans* coordinated H_2O ligands, each of which forms two H-bonds to two of the crown O-atoms. The result is infinite chains of alternating Sc cations and 15-crown-5 molecules. In addition there is H-bonding between the water (O(10), O(11)) and the ionic nitrate anion.

With 12-crown-4 we obtained crystals of stoichiometry $[\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_2]\cdot (12\text{-crown-4})_2$. The structure consists of neutral $[\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_2]$ groups with an eight-coordinate Sc atom with three symmetrically bidentate NO_3 groups. The group has crystallographic 2-fold symmetry and the H_2O ligands make

[‡] Crystal data for $[\text{Sc}(\text{NO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)\cdot (\text{C}_{10}\text{H}_{20}\text{O}_5)$: $\text{C}_{10}\text{H}_{20}\text{N}_3\text{O}_{18}\text{Sc}$, $M_r = 523.31$, orthorhombic, space group $Pbca$ (no. 61), $a = 8.666(2)$, $b = 15.767(6)$, $c = 31.740(9)$ Å, $U = 4337.1(2.5)$ Å³, $Z = 8$, $T = 120$ K, $F(000) = 2192$. 8116 Reflections measured ($R_{\text{int}} = 0.11$) 2868 unique reflections (1726 with $I > 2\sigma(I)$) (288 parameters, 18 restraints). $R1$ ($I > 2\sigma(I)$) = 0.12 with disorder in the crown ring.

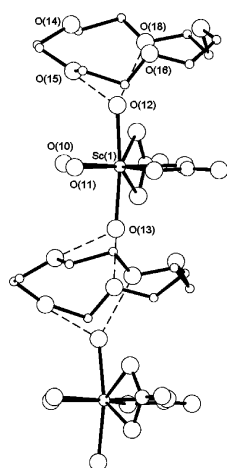


Fig. 4 The structure of $[\text{Sc}(\text{NO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)\cdot 15\text{-crown-5}$ showing the $\text{O}-\text{H}\cdots\text{O}$ H-bonded chain between the Sc cation and the crown (H-bonds as dotted lines) lying parallel to the b direction. A partial atom labelling scheme is shown with O(10)–O(13) being coordinated water molecules. O(17A) (not labelled) is in a disordered part of the crown and is not involved in H-bonding. H atoms are omitted for clarity.

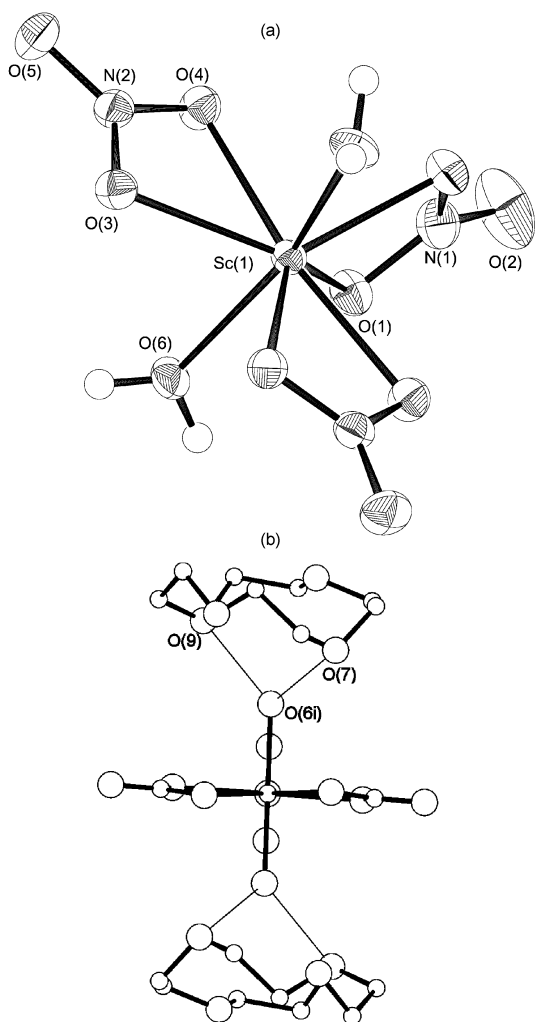


Fig. 5 The structure of $[\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_2]\cdot (12\text{-crown-4})_2$ (a) shows the Sc(1) group with the atom labelling scheme and the 2-fold symmetry in the c direction passing through Sc(1), N(1) and O(2). Displacement ellipsoids are drawn at the 50% probability level; (b) view down the c direction showing the $\text{O}-\text{H}\cdots\text{O}$ bonds (thin lines) between O(6i) of the Sc group and the crown. (Symmetry operation: $i = 1/2+x, 1/2-y, -z$).

an $\text{O}-\text{Sc}-\text{O}$ angle of $153.64(9)^\circ$ (Table 5 and Fig. 5(a)). Each H_2O ligand forms two H-bonds with the 12-crown-4 with $\text{O}-\text{H}\cdots\text{O}$ bonds (*ca.* 2.7 Å). Only two of the four crown O atoms are involved in H-bonding and the H-bonding pattern results in a discrete species $(12\text{-crown-4})\cdot[\text{Sc}(\text{NO}_3)_3(\text{H}_2\text{O})_2]\cdot(12\text{-crown-4})$ (Fig. 5(b)).

A few crystals of a second species, $[\text{Sc}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6(\text{OH})_2](\text{NO}_3)_2\cdot 12\text{-crown-4}$, were obtained when crystallisation occurred over a prolonged period of time. The structure of this consists of a centrosymmetric cation with the Sc atoms linked *via* bridging OH groups. Each Sc is coordinated by a symmetrically bonded NO_3 ligand, three water ligands and the two OH groups and is thus seven-coordinate (Table 6 and Fig. 6(a)). The shortest $d(\text{Sc}-\text{O})$ is provided by the $\text{Sc}-\text{O}(\text{H})$ bond and the longest by the $\text{Sc}-\text{O}(\text{N})$ of the coordinated nitrate. The 12-crown-4 is also centrosymmetric with all the O atoms involved in H-bonding to H_2O ligands on the cation. Every H(O) atom is involved in H-bonding either to the crown or the O of a nitrate (either ionic or coordinated) with $d(\text{O}\cdots\text{O}) < 3.0$ Å. The H-bonding between the crown and the dimeric cation creates chains of these alternating groups aligned in the c direction. H-bonding to the ionic nitrate cross-links the parallel chains to give a 2-dimensional network (Fig. 6(b)).

The structure of the related $[\text{Sc}_2(\text{NO}_3)_4(\text{H}_2\text{O})_4(\text{OH})_2][\text{Na}(12\text{-crown-4})_2](\text{NO}_3)\cdot(\text{H}_2\text{O})_3$ also consists of neutral dinuclear $[\text{Sc}_2(\text{NO}_3)_4(\text{H}_2\text{O})_4(\text{OH})_2]$ units with eight-fold coordination to

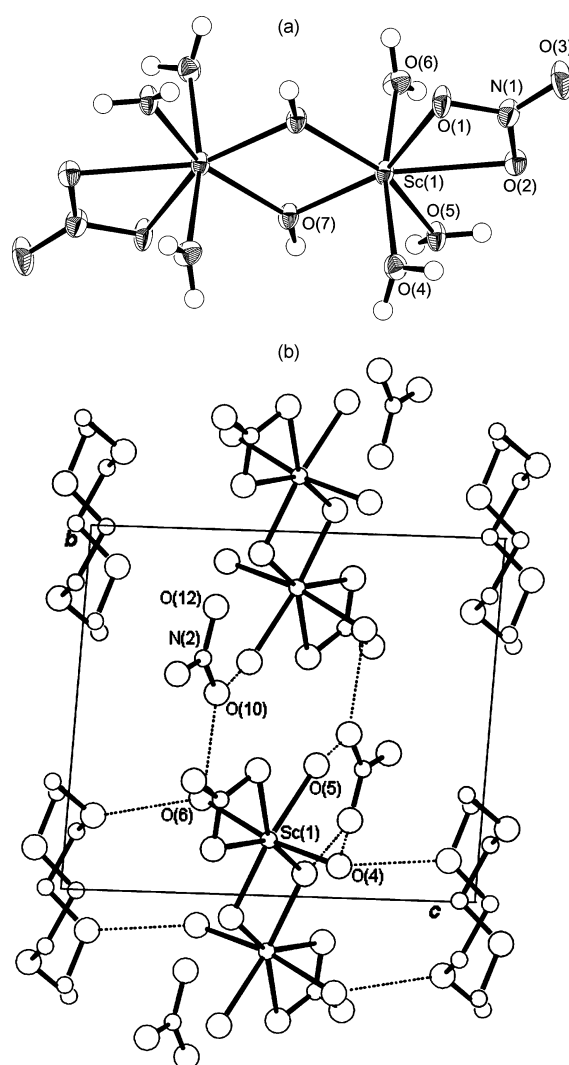


Fig. 6 The structure of $[\text{Sc}_2(\text{NO}_3)_2(\text{H}_2\text{O})_6(\text{OH})_2](\text{NO}_3)_2\cdot 12\text{-crown-4}$ (a) shows the centrosymmetric cation with the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level; (b) shows part of the 2-dimensional sheet formed by the $\text{O}-\text{H}\cdots\text{O}$ H-bonding (indicated by dotted lines).

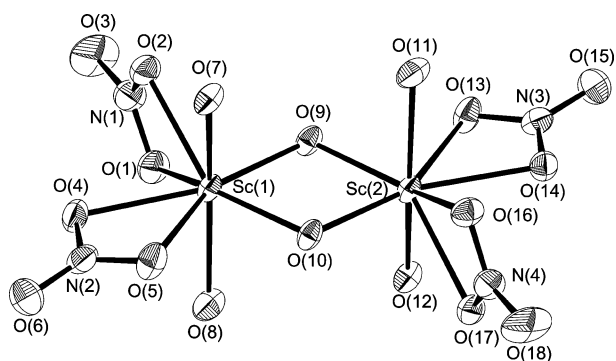


Fig. 7 The structure of $[\text{Sc}_2(\text{NO}_3)_4(\text{H}_2\text{O})_4(\text{OH})_2][\text{Na}(12\text{-crown-4})_2](\text{NO}_3)\cdot(\text{H}_2\text{O})_3$, showing the scandium dimer with the atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and the H atoms are omitted for clarity.

each Sc by two symmetrical NO_3 ligands, two water molecules and two bridging OH groups (Table 7 and Fig. 7). In this species the 12-crown-4 molecules are involved in primary coordination to an eight-coordinate Na ion. The ionic nitrate group is disordered over two sites (N(5A)/(5B)) with the added complication of an overlapping (disordered) water molecule (O(32A)/(32B)). Two other hydrate water molecules were located, and all of the H atoms bonded to O, except for the disordered O(32A)/(32B), were located from the difference maps. In this species the H-bonding occurs between coordinated and solvate water and bridging OH groups, with the shortest $\text{O} \cdots \text{O}$ distances *ca.* 2.7–2.8 Å. The crown is not involved in secondary coordination, presumably since the O atoms are directly coordinated to the Na^+ .

These results show a surprising dependence of the supramolecular structure with the particular crown ether, and the reaction conditions. However, there are some recurring motifs observed in the present work. When the scandium residue (monomer or dimer) : crown ratio is 1 : 1, chains of alternating groups (scandium residue \cdots crown \cdots scandium residue \cdots) are found. With a scandium residue : crown ratio of 1 : 2, a discrete species was observed (crown \cdots scandium residue \cdots crown). We also note that not all the crown ether oxygens are involved in H-bonding in some cases.

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