Group 3 metal trihalide complexes with neutral N-donor ligands – exploring their affinity towards fluoride†

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Fluorination of [ScCl3(Me3-tacn)] (Me3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) and [ScCl3(BnMe2-tacn)] (BnMe2-tacn = 1,4-dimethyl-7-benzyl-1,4,7-triazacyclononane) by Cl/F exchange with 3 mol. equiv. of anhydrous [NMe4]F in CH3CN solution yields the corresponding [ScF2(R3-tacn)] (R3 = Me3 or BnMe2). These are the first examples of scandium fluoride complexes containing neutral co-ligands. The fluorination occurs stepwise, and using a deficit of [NMe4]F produced [ScF2Cl(Me3-tacn)]. Attempts to fluorinate [YCl3(Me3-tacn)], [YI3(Me3-tacn)], [LaCl3(Me3-tacn)(OH2)] or [MCl3(terpy)] (M = Sc, Y or La; terpy = 2,2′:6′:2′-terpyridyl) using a similar method were unsuccessful, due to the Cl/F exchange being accompanied by loss of the neutral ligand from the metal centre. Fluorination of [ScCl3(Me3-tacn)] or [ScCl3(terpy)] with Me3SnF was also successful. The products were identified as the very unusual heterobi-metallic [Sc(Me3-tacn)F2(µ-F)SnMe3Cl] and [Sc(terpy)F(µ-F)2(SnMe3Cl)2], in which the Me3SnCl formed in the reaction behaves as a weak Lewis acid towards the scandium fluoride complex, linked by Sc–F–Sn bridges. [Sc(terpy)F(µ-F)2(SnMe3Cl)2] decomposes irresolvably in solution but, whilst multinuclear NMR data show that [Sc(Me3-tacn)F2(µ-F)SnMe3Cl] is dissociated into the [ScF3(Me3-tacn)] and Me3SnCl in CH3CN solution, the bimetallic complex reforms upon evaporation of the solvent. The new scandium fluoride complexes and the chloride precursors have been characterised by microanalysis, IR and multinuclear NMR (1H, 19F, 45Sc) spectroscopy as appropriate. X-ray crystal structures provide unambiguous evidence for the identities of [Sc(Me3-tacn)F2(µ-F)SnMe3Cl], [ScF2Cl(Me3-tacn)], [YCl3(Me3-tacn)], [YCl3(terpy)] and [[Y(Me3-tacn)]2(µ-O)], [ScCl3(terpy)], [YCl3(terpy)(OH2)], and [[La(terpy)(OH2)Cl2]2(µ-C12)]. Once formed, the [ScF2(R3-tacn)] complexes are stable in water and unaffected by a ten-fold excess of Cl– or MeCO2–, although they are immediately decomposed by excess F–. The potential use of [ScF3(R3-tacn)] type complexes as platforms for 18F PET (positron emission tomography) radiopharmaceuticals is briefly discussed. Attempts to use the Group 3 fluoride "hydrates", MF3·xH2O, as precursors were unsuccessful; no reaction with R3-tacn or terpy occurred either on reflux in CH3CN or under hydrothermal conditions (H2O, 180° C, 15 h). PXRD data showed that these "hydrates" actually contain the anhydrous metal trifluorides with small amounts of surface or interstitial water.

Introduction

The coordination chemistries of scandium and yttrium have been explored much less than those of the other 3d and 4d metals. The presence of colourless metal ions, in a single (3+) oxidation state and with closed shell configurations (hence no magnetic or d–d spectroscopic fingerprints), coupled with their limited availability, low purity and high cost, restricted early work.1,2 Often their chemistry was included in studies of the lanthanide elements, which tended to see similarities rather than explore differences.2 More recent work3 has shown that there are significant differences, especially for scandium, and the structural chemistry of scandium is surprisingly diverse.4 A rich, but synthetically challenging, organometallic chemistry of both metals has been explored in recent years,2 and C–H bond activation, ethene, styrene and α-olefin polymerisation, and aromatic C–F bond activation have all been...
observed in appropriate systems. Scandium fluoride has attracted considerable interest due to its negative thermal expansion, and nanocrystals of ScF₃ doped with lanthanide ions exhibit tuneable luminescent properties. As expected for oxophilic metal ions, the coordination chemistry with neutral ligands has been dominated by oxoanions – nitrate, triflate, carboxylates, etc., with much less work on the metal halides. Apart from a range of fluoro-aniions mostly made by solid state syntheses, complexes containing ScF or Y-F bonds are very rare and contain charged N- or C-donor co-ligands, e.g. [ScL₂-F₂(SnMe₃Br₂)]⁻ [L = N,N'-1,3-dimethyl-1,3-propanediylidene]bis[N,N'-diethyl-1,2-ethanediaminato] made from [ScLBr₃] and Me₃SnF, [Sc(MeC(N(2,6-iPrC₆H₃))₂-C₅H₄NSi(NEt₂)₂)], [Sc₂(μ-F)₂{Fe(C₅H₄NSiBuMe₂)₂}]₂ and [Sc₂(μ-F)₃]. Attempts to prepare complexes of ScF₃ or YF₃ with neutral donor ligands, such as R₃P, have failed, whilst treatment of [ScCl(μ-C₆H₄H(2,6-Me₂))]₂ with [Me₃NF] in CH₂Cl₂ resulted in liberation of the diphosphine and precipitation of ScF₃.

In an effort to develop new PET (positron emission tomography) imaging agents, the ability of Group 13 metal (Al, Ga or In) aza-macrocycle complexes to undergo Cl/F exchange, including in some cases with radiofluorido, under mild conditions and in aqueous solution has been demonstrated. These include both the neutral trifluoride complexes, [MF₂(R₁-tacn)] [M = Al, Ga; R₁-tacn = 1,4,7-trimethyl-1,4,7-triazaacyclononane, 1,4-dimethyl-7-benzyl-1,4,7-triazaacyclononane] and anionic complexes, [M(ν₂F)₂R₂-tacn] (H₂R₂-taca = 1-R,1,4,7-triazaacyclononane-4,7-dicarboxylic acid; R = benzyl or a peptide conjugate). The ideal requirements for PET imaging agents are that the metal complex precursor can be rapidly radiofluorinated in a single step, with minimal subsequent purification needed, and that the resulting complex is stable in water, to reaction with other competitive anions and at near neutral pH. The present work sought to establish whether Group 3 metal centres (Sc, Y or La) could offer prospects as alternative reagents for radiofluorination as potential future PET platforms and therefore explores the synthesis, properties and stability of the metal trifluoride complexes with tridentate neutral N₃-donor ligands, R₁-tacn and 2,2'-6'2'-terpyridyl.

**Experimental**

All complex syntheses were carried out using standard Schlenk and vacuum line techniques. Samples were handled and stored in a glove box under a dry dinitrogen atmosphere to exclude moisture, which decomposes many of the samples. [ScCl₃(thf)]₃ and [YCl₃(thf)]₃[YCl₃(thf)]₃ were prepared by the literature methods. 2,2'-6'2'-terpyridyl was obtained from Sigma-Aldrich and dried in vacuo prior to use. 1,4,7-Trimethyl-1,4,7-triazaacyclononane and 1,4-dimethyl-7-benzyl-1,4,7-triazaacyclononane were prepared as described previously. Anhydrous [NMe₄]F was obtained by recrystallising the commercial sample (Aldrich) from PrOH as described. Infrared spectra were recorded as Nujol mulls between CsI plates using a PerkinElmer Spectrum 100 spectrometer over the range 4000–200 cm⁻¹.¹⁹H,¹⁹F,⁴⁵Sc NMR spectra were recorded from CH₂Cl₂/CD₂Cl₂ or CH₃CN/CD₃CN solutions using a Bruker AV400 spectrometer and referenced to TMS via the residual solvent resonance, CFCl₃ and [Sc(H₂O)₆]³⁺ in water at pH = 1. Microanalyses were undertaken by London Metropolitan University. n-Hexane was dried by distillation from sodium and CH₂Cl₂ and CH₃CN from CaH₂.

**Metal trifluoride “hydrates”**

ScF₃·xH₂O. Sc₂O₃ (2.9 g, 0.021 mol), and a 6 M solution of HCl (43 mL) were heated to reflux for 3 h, during which period the mixture changed from a cloudy white suspension to a clear yellow solution. The solvent was removed in vacuo whilst heating at 65 °C. ScCl₃·6H₂O was obtained as a white solid. This was dissolved in water in a plastic beaker and 6 mL of 40% HFₐq (CARE) were added causing the precipitation of a white solid. The mixture was heated to boiling and the solvent evaporated, giving a white gel-like solid. A portion of the gel was suspended in water, causing the formation of the solid, which was isolated by evaporation of the solvent. The same procedure was repeated portion by portion and the solid combined (3.94 g, 93%).

YF₃·xH₂O. Method 1: Y₂(SO₄)₃·8H₂O (3.0 g, 4.92 mmol) was dissolved in water. 5 mL of a solution of 40% HFₐq was added and a white precipitate formed. The precipitate was left to settle overnight. The solution was filtered and the solid washed with water and dried in vacuo (1.07 g, 75%).

Method 2: Y₂(SO₄)₃·8H₂O (3.0 g, 4.92 mmol) was suspended in hot water (80 °C) until most of the solid dissolved. The liquid was decanted off from any residue and a solution of 40% HFₐq (3 mL) was added to the solution. A white solid precipitated immediately. The reaction was left stirring for 1.5 h and then the solid was left to settle overnight. The solution was decanted off and the solid dried overnight in a desiccator (1.24 g, 86%).

LaF₃·xH₂O. LaCl₃·7H₂O (5.0 g, 13.5 mmol) was dissolved in water (30 mL). 40% HFₐq (1.5 mL) was diluted in water (10 mL) and added dropwise to the solution, giving a white gelatinous material which was stirred for 1 h. This solid was collected by evaporating the solvent off at 110 °C, leaving a fine white solid. Yield: 2.50 g, 95%.

**Metal complexes**

[ScCl₃(terpy)]. A solution of terpy (0.055 g, 0.24 mmol) in 3 mL of CH₃CN was added to a solution of [ScCl₃(thf)] (0.076 g, 0.24 mmol) in 5 mL of CH₃CN, causing the immediate precipitation of a white solid. After a few minutes, the solid was filtered off, washed with n-hexane and dried in vacuo. Yield: 0.054 g, 60%. Required for C₅H₄N₅Cl₃Sc: C, 46.8; H, 2.9; N, 10.9. Found: C, 46.7; H, 3.1; N, 11.1%.¹⁹H NMR (CD₃CN, 298 K): δ = 9.25 (s, [2H], Ar); 8.30 (m, [7H], Ar). ⁴⁵Sc NMR (CD₂Cl₂, 298 K): δ = 254 (s, br). IR (Nujol, cm⁻¹): 292, 339, 337 (Sc–Cl). Colourless crystals were obtained from slow diffusion of Et₂O into a concentrated solution of the complex in CH₃CN.
A solution of terpy (0.046 g, 0.20 mmol) was added to a solution of [YCl3(thf)3][YCl3(thf)2] (0.08 g, 0.09 mmol) in anhydrous CH2CN, causing the immediate precipitation of a white solid. After 30 minutes, the white solid was filtered, washed with n-hexane and dried in vacuo. Yield: 0.051 g, 61%. Required for C10H14Cl2LaO2: C, 34.0; H, 4.2; N, 7.2%. 1H NMR (CD3CN, 298 K): δ = 9.84 (m, [2H], Ar), 8.48 (m, [2H], Ar), 8.39 (m, [3H], Ar), 8.17 (t, [2H], Ar), 7.69 (t, [2H], Ar), 2.15 (s, H2O). IR (Nujol, ν/cm-1): 3338, 1641 (H2O), 272, 262(sh) (Y-Cl). Colourless crystals were grown by placing the Schlenk tube containing the filtrate in the freezer (-18 °C) for a few days.

LaCl3(terpy)(OH2)-4H2O. LaCl3·7H2O (0.108 g, 0.40 mmol) was dissolved in ethanol (10 mL). Terpy (0.098 g, 0.42 mmol) was suspended in ethanol (10 mL) and the reagents combined. A white precipitate formed, which was stirred for 45 min. The solvent was then removed by filtration and the solid washed with ethanol, then diethyl ether and dried in vacuo. Yield: 0.09 g, 40%. Required for C10H8Cl2LaO2: C, 29.3; H, 3.9; N, 7.5%. 1H NMR (CD3OD, 298 K): δ = 9.37 (m, br, [2H], Ar), 8.59 (m, br, [3H], Ar), 8.40 (m, br, [2H], Ar), 8.29 (m, br, [2H], Ar), 7.77 (m, br, [2H], Ar), 4.85 (H2O). IR (Nujol, ν/cm-1): 3369, 1633 (H2O), 209, 205 (La-Cl). Colourless crystals of terpy-H2OCl3La were obtained by layering an ethanol solution of LaCl3·7H2O with an equimolar solution of terpy in ethanol, and leaving undisturbed for 48 h.

[AuCl3(terpy)(OH2)]-H2O. AuCl3·7H2O (0.113 g, 0.29 mmol) was dissolved in ethanol (10 mL). Terpy (0.069 g, 0.30 mmol) was dissolved in ethanol (5 mL) and added dropwise. After stirring for 2 h, a white precipitate had formed. The precipitate was collected via filtration, washed with diethyl ether (2 mL) and then dried in a desiccator for one hour, leaving a white powder. Yield: 0.120 g, 77%. Required for C10H8Cl2AuO2: C, 33.8; H, 2.5; N, 7.9. Found: C, 33.7; H, 2.5; N, 7.7%. 1H NMR (CD3OD, 298 K): δ = 9.41 (d, [2H], Ar), 8.72 (d, [2H], Ar), 8.67 (m, [3H], Ar), 8.51 (t, [2H], Ar), 8.35 (t, [2H], Ar). IR (Nujol, ν/cm-1): 3424, 1657 (H2O) 205, 201 (La-Cl). Colourless crystals of [AuCl3(terpy)(OH2)] were grown by layering an ethanol solution of AuCl3·6H2O with an equimolar solution of terpy in ethanol, and leaving undisturbed for 48 h.

[ScCl3(terpy)(OH2)]. ScCl3·6H2O (0.063 g, 0.29 mmol) was dissolved in ethanol (10 mL). Terpy (0.046 g, 0.20 mmol) was dissolved in ethanol (5 mL) and added dropwise. After stirring for 2 h, a white precipitate had formed. The precipitate was collected via filtration, washed with diethyl ether (2 mL) and then dried in a desiccator for one hour, leaving a white powder. Yield: 0.109 g, 54%. Required for C10H8Cl2ScO2: C, 34.4; H, 4.0; N, 5.7%. Found: C, 34.8; H, 3.9; N, 6.9%. 1H NMR (CD3CN, 298 K): δ = 6.88 (br, [2H], Ar-CH2), 8.48 (br, [3H], Ar-CH2), 8.05 (br, [2H], Ar-CH2), 7.95 (br, [2H], Ar-CH2), 7.45 (br, [2H], Ar-CH2), 0.60 (s). 19F NMR (CD3CN, 298 K): δ = -37.7 (br s, [2F]), -53.5 (br s, [F]). 31P NMR (CD3CN, 298 K): δ = 64 (s, br). IR (Nujol, ν/cm-1): 389, 509, 544 (Sc-F), 270 (Sn-Cl).

[ScF3(terpy)]. [ScF3(terpy)] (0.05 g, 0.15 mmol) was dissolved in acetonitrile (10 mL). A solution of Me2-tacn (0.044 g, 0.26 mmol) in acetonitrile (10 mL) was added. The reaction mixture was heated to 40 °C until a clear solution was obtained. After cooling, the volatiles were removed in vacuo to 5 mL causing the precipitation of a white solid, which was filtered and dried in vacuo (0.078 g, 47%). Required for C10H22F3I3N3Sc: C, 20.5; H, 3.7; N, 9.0. Found: C, 21.2; H, 3.9; N, 8.4%. 1H NMR (CD3CN, 298 K): δ = 3.46 (m, [6H], CH3), 3.12 (s, [9H], CH3), 2.92 (m, [6H], CH3), 1.98 (s, CH3CN). IR (Nujol, ν/cm-1): 2253, 2187 (CH3CN). Crystals suitable for single crystal X-ray analysis were obtained from a separate reaction by placing the Schlenk flask in the freezer (-18 °C). After a few days, two different crystal morphologies were found, which were identified by single crystal X-ray diffraction to be [Y1(terpy)-1.5CH3CN] and [Y1(terpy)-1.5CH3CN]2. The latter formed via hydrolysis from trace water ingress into the flask during crystallisation in the freezer.
solution of the complex. The reaction was left stirring for 90 minutes. Some white solid was evident throughout the reaction. The volatiles were removed in vacuo and the resulting white solid was washed with CH₂Cl₂, filtered and dried in vacuo (0.041 g, 97%). Required for C₄H₆F₃Cl₂Sc-Cl: C, 36.4; H, 6.4; N, 5.6. Found: C, 37.0; H, 6.3; N, 5.7.

[Sc₂(Me₃-tacn)F₆] (Me₃-tacn): 1590540, [ScI₂(Me₃-tacn)]: 1590541, [YI₂(Me₃-tacn)]: 1590542, [La(terpy)(OH₂)Cl₂]₂ (Me₃-tacn): 1590543, [ScF₃(Me₃-tacn)]: 1590544, [Sc(Me₃-tacn)F₂(µ-F)SnMe₃Cl]: 1590545, [Sc(Me₃-tacn)F₂(µ-F)SnMe₃Cl]: 1590546, [Mf₃·3H₂O] (M = Sc, Y, La) to form analogous metal trifluoride ligand complexes. Literature data on the hydrates is sparse and the amount of water present apparently variable, although “x” typically appears to be less than one.

The addition of a fluoride source, either KF or aqueous HF, to aqueous solutions of yttrium or lanthanum salts, gave immediate white precipitates, MF₃·H₂O. Using scandium salts and aqueous HF also gave ScF₃·H₂O, but using alkali metal fluorides gave mixtures, and in one case pure KSc₂F₇, which was identified by its PXRD pattern (see ESI†). The PXRD patterns obtained from MF₃·xH₂O sometimes showed rather broad reflections, but corresponded to the patterns reported for anhydrous MF₃ (Fig. 1 and ESI†).

Thus, we conclude that the MF₃·xH₂O actually comprise of the “anhydrous” MF₃ polymer, with water of crystallisation on the surface or occupying voids in the crystal lattice, rather than coordinated to the metal ion. This also explains the range of values of “x” in MF₃·xH₂O reported in the limited literature available.† Attempts to react the MF₃·H₂O with terpy or Me₃-tacn under hydrothermal conditions (180 °C, 15 h) were unsuccessful, with the MF₃·xH₂O being recovered, although with noticeably increased crystallinity (sharper PXRD patterns).

These results explain why ‘hydrated’ Group 3 fluorides are not a viable entry into the coordination chemistry of these fluorides with neutral ligands. This contrasts sharply with the Group 13 fluoride hydrates, and the Group 4 compounds, [M₂F₇(OH₂)] (M = Zr, Hf), whose crystal structures show the water is coordinated to the metal, from which it can be displaced by neutral ligands. These are effective synths for wider coordination chemistry. We reported previously that
Many trichloride complexes of Sc(III), Y(III) and La(III) with chloride/iodide precursor complexes are likely to be viable synthons for neutral ligand complexes. Chloride/iodide precursor complexes

the f-block tetrafluorides, \([\text{MF}_2\cdot\text{H}_2\text{O}]\) \((\text{M} = \text{Ce, Th})\) have very limited coordination chemistry \((\text{CeF}_2\cdot\text{H}_2\text{O} \text{ dissolves only very slowly in refluxing dms})\). They too are likely to contain only lattice/surface water.32 The wider implications of these results in metal fluoride coordination chemistry suggest that for other metals, only those ‘hydrated’ fluorides that contain water within the metal coordination sphere, are likely to be viable synthons for neutral ligand complexes.

**Chloride/iodide precursor complexes**

Many trichloride complexes of Sc(III), Y(III) and La(III) with neutral ligands are highly moisture sensitive and must be synthesised and handled in anhydrous systems. In work with other early d-block systems, we noted that the corresponding metal iodides and iodo-complexes were often more soluble in weakly coordinating solvents, probably due to lower lattice energy, although the gain in solubility comes at the cost of even greater moisture sensitivity.17,33,34 In the present study we synthesised complexes with \(\text{Me}_2\text{tacn}\) and terpy, which give examples of pseudo-octahedral complexes with \(\text{fac}\) and \(\text{mer}\) geometries for scandium, respectively, although for Y and La higher coordination numbers were often produced. The known26 \([\text{MCl}_3\text{(Me}_3\text{tacn)}]\) \((\text{M} = \text{Y, Sc})\) were made from \([\text{ScCl}_3\text{(thf)}]_2\) or \([\text{YCl}_3\text{(thf)}]_2\) and the triaza macrocycle in anhydrous acetonitrile. The corresponding \([\text{ScCl}_3\text{(BnMe}_2\text{tacn)}]\) was prepared similarly, whilst reaction of \([\text{LaF}_3\text{·7H}_2\text{O}]\) in EtOH yielded \([\text{LaCl}_3\text{(Me}_3\text{tacn)}\text{(OH}_2\text{)}]\) as a white powdered solid. All complexes have been characterised spectroscopically \((\text{IR, }1^\text{H}, 45^{\text{Sc}}\text{ NMR, Table 1, as appropriate})\) and by microanalysis.

Treatment of \(\text{YI}_3\) with one molar equivalent of \(\text{Me}_2\text{tacn}\) in anhydrous acetonitrile under a dinitrogen atmosphere formed a light yellow, extremely moisture sensitive solid, identified as \([\text{YI}_3\text{(Me}_3\text{tacn)}]\)·\(\text{CH}_3\text{CN}\) (Fig. 2), with the expected tridentate \(\text{Me}_3\text{tacn}\) and three mutually \(\text{facial}\) iodoses completing the distorted octahedral environment, and the partial hydrolysis product, \([\text{YI}_2\text{(Me}_3\text{tacn)}]_2\text{(\mu-O)}]\) (Fig. 3), formed \textit{via} reaction with trace water. The \(\text{Y}	ext{–N}\) bond distances in \([\text{YI}_3\text{(Me}_3\text{tacn)}]\) are similar to those reported in functionalised tacn complexes, e.g. \([\text{[iPr}_2\text{-tacn(CH}_2\text{SiMe}_3\text{)}]Y(\text{CH}_2\text{SiMe}_3)}_2\text{[Cu} \text{II}\text{]}\).35

Table 1

| Complex | \(\delta^{45}\text{Sc}/\text{ppm}\) | \(\delta^{19}\text{F}/\text{ppm}\) |
|---------|--------------------------|--------------------------|
| \([\text{ScCl}_3\text{(Me}_2\text{tacn)}]\) | +300 | — |
| \([\text{ScCl}_3\text{(BnMe}_2\text{tacn)}]\) | +302 | — |
| \([\text{ScFCl}_3\text{(Me}_2\text{tacn)}]\) | +219 | 77.2 |
| \([\text{ScF}_2\text{Cl(Me}_3\text{tacn)}]\) | +155 | 40.1 |
| \([\text{ScF}_3\text{(Me}_2\text{tacn)}]\) | 104 | 7.7 (q, \(J_{\text{Sc-F}} = 219\) Hz) |
| \([\text{ScF}_3\text{(terpy)}]\) | 104 | 10.1 |
| \([\text{ScCl}_3\text{(terpy)}]\)^b | +64 | — |
| \([\text{ScF}_3\text{(terpy)}]\)^b | +254 | — |

\(\text{CH}_3\text{CN}/\text{CD}_3\text{CN except.}^b \text{CH}_3\text{Cl}_2/\text{CD}_2\text{Cl}_2\).

LaCl\(_3\)·7H\(_2\)O with Me\(_2\)tacn in EtOH yielded \([\text{LaCl}_3\text{(Me}_2\text{tacn)}\text{(OH}_2\text{)}]\) as a white powdered solid. All complexes have been characterised spectroscopically (IR, \(1^\text{H}, 45^{\text{Sc}}\text{ NMR, Table 1, as appropriate}) and by microanalysis.

Fig. 1 PXRD patterns obtained from the attempted synthesis of yttrium fluoride hydrate. (A) PXRD of anhydrous YF\(_3\). A. K. Cheetham and N. Norman, \textit{Acta Chem. Scand.}, Ser. A, 1974, \textbf{28}, 55; (B) YF\(_3\)·H\(_2\)O (this work); (C) YF\(_3\)·H\(_2\)O after heating under hydrothermal conditions.

Fig. 2 Structure of \([\text{YI}_3\text{(Me}_3\text{tacn)}]\)·\(\text{CH}_3\text{CN}\) with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Select bond lengths (Å) and angles (°): Y1–I1 = 2.9671(8), Y2–I2 = 2.9509(9), Y1–I3 = 2.9460(8), Y1–N1 = 2.468(6), Y1–N2 = 2.480(5), Y1–N3 = 2.4767(7), I3–Y1–N1 = 160.9(1), I2–Y1–N3 = 162.3(2), I1–Y1–N2 = 161.6(1), I1–Y1–I2 = 99.59(2), I3–Y1–I2 = 98.87(2), I3–Y1–N2 = 94.5(1), N1–Y1–N2 = 72.0(2).
Fig. 3 The structure of \([\text{YI}_2(\text{Me}_3\text{tacn})_2(\mu-O)]\cdot\text{CH}_3\text{CN}\) with atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–I1 = 3.0213(6), Y1–I2 = 2.9969(7), Y1–O1 = 2.0332(5), Y1–N2 = 2.580(5), Y1–N1 = 2.473(5), Y1–N3 = 2.495(5), Y1–O1–Y1 = 180.00(3), I2–Y1–I1 = 93.991(19), O1–Y1–I2 = 104.69(2), O1–Y1–I2 = 104.12(2), O1–Y1–N2 = 156.16(11), O1–Y1–N1 = 90.72(11), O1–Y1–N3 = 93.79(11).

The reaction of \([\text{ScCl}_3(\text{thf})_3]\) with terpy in anhydrous CH\(_3\)CN gave \([\text{ScCl}_3(\text{terpy})]\) (Fig. 4). The extended crystal structure of \([\text{ScCl}_3(\text{terpy})]\) shows π-stacking interactions (3.82 Å) between the aromatic ring of the terpy ligand of the adjacent molecule, connecting them into 1D zig-zag chains (see ESI Fig. S4†).

Reaction of \([\text{YCl}_3(\text{thf})_3]\) with terpy in CH\(_3\)CN yields the colourless complex \([\text{YCl}_3(\text{terpy})(\text{OH}_2)]\) incorporating adventitious water and characterised spectroscopically and by microanalysis. Confirmation of the seven-coordinate geometry follows from a crystal structure determination (Fig. 5).

The crystal structure (Fig. 5) shows a pentagonal-bipyramidal coordination around the metal centre with the Y–Cl bond lengths in the axial positions shorter than that in the equatorial plane. The angle between the yttrium centre and the nitrogen atoms is less than the 72° value expected for the perfect pentagonal-bipyramidal conformation, due to the rigid terpy ligand and the equatorial plane is puckered. Furthermore, the packing in the crystal structure shows both H-bonding (Cl⋯HOH) between adjacent molecules to form associated dimers, and weak π-stacking (4.04 Å) linking the dimers into zig-zag chains (Fig. S5†). The bond lengths are generally shorter than in the eight-coordinate \([\text{YCl}_3(\text{terpy})\cdot\text{H}_2\text{O}]]\) (see ESI Fig. S4†).

Using the heavier f-block ions, La(m) and Lu(m), \([\text{LaCl}_3(\text{terpy})(\text{OH}_2)]\cdot4\text{H}_2\text{O}\) and \([\text{LuCl}_3(\text{terpy})(\text{OH}_2)]\) were obtained via reaction of LaCl\(_3\)·7H\(_2\)O or LuCl\(_3\)·6H\(_2\)O, respectively, with one mol. equiv. of terpy in ethanol. X-ray crystallographic analyses show that the La(m) complex exists as a chloro-bridged dimer, \([\text{La}(\text{terpy})(\text{OH}_2)\text{Cl}_2]\cdot[\mu-\text{Cl}])_2\) (Fig. 6) involving eight-coordinate La(m) with adjacent molecules linked into chains via H-bonding interactions between the coordinated water molecule on one La(m) centre and the Cl ligands on adjacent molecules (Fig. S6†). On the other hand, [\([\text{LuCl}_3(\text{terpy})(\text{OH}_2)]\)] (Fig. S7†) is a seven-coordinate monomer, isostructural with the Y(m) analogue above (and hence also displaying the same H-bonding and π-stacking interactions in the solid state).

Chloride(iodide)/fluoride exchange reactions using \([\text{NMe}_4]^+\)\text{F}^- Addition of three mol. equiv. of anhydrous \([\text{NMe}_4]^+\text{F}^-\) to a CH\(_3\)CN solution of \([\text{ScCl}_3(\text{Me}_3\text{tacn})]\) gave a colourless solution whose \(^{19}\text{F}(\text{H})\) and \(^{45}\text{Sc} N\text{MR spectra}\) each showed three
broadened resonances at 77.2, 40.1 and 7.7 ppm (19F{1H}) and 219, 155 and 104 ppm (45Sc) (Fig. 7, Table 1), corresponding to [ScFCl2(Me3-tacn)] (very minor), [ScF2Cl(Me3-tacn)] and [ScF3(Me3-tacn)], respectively. The modest quadrupole moment of 45Sc (I = 7/2) means that resonances are observed in many systems, but couplings to other nuclei are often lost in the line broadening, unless the scandium is in a high symmetry environment.17,34,38,39 Since these complexes are the first examples of scandium fluoride species with neutral ligands, there are no comparable literature data, but the chemical shifts of the chloro-species are reasonable compared to data on other ScCl3 adducts.34,38,39

Adding further small aliquots of [NMe4]F in CH3CN initially led to depletion of the resonances assigned to the mixed chloro/fluoro complexes, and enhancement of the broadened quartet at δ = 104 ppm, attributed to [ScF3(Me3-tacn)] (Fig. 7). The broad quartet shows coupling to three equivalent fluorides with 1JScF = 219 Hz (since the efg is small). However, excess fluoride caused complete loss of all the 45Sc and 19F{1H} resonances from the tacn complexes (see below).

The 19F{1H} and 45Sc NMR data for the fluorination reaction are also strongly indicative of the fluorination of [ScCl3(Me3-tacn)] occurring in a stepwise manner. Further confirmation of this follows from a single crystal X-ray structure determination on [ScF2Cl(Me3-tacn)], a few crystals of which were grown by concentrating the NMR solution in acetonitrile (Fig. 8). The complex is six-coordinate with the three nitrogen atoms of the ligand coordinated to the metal in a facial conformation, while the three other positions are occupied by two fluorine atoms and one chlorine, with no evidence for disorder being present. As expected, the Sc–F bonds are significantly shorter than the Sc–Cl bond (1.94 against 2.44 Å). The analogous [ScCl3(BnMe2-tacn)] shows similar behaviour with [NMe4]F, with [ScF3(BnMe2-tacn)] showing a broad 45Sc NMR resonance at 104 ppm, with δ(19F{1H}) = 10.1 ppm.

Fig. 6 Crystal structure of [{La(terpy)(OH2)Cl2(μ-Cl)2} with ellipsoids drawn at 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): La1–Cl1 = 2.8385(9), La1–Cl2 = 2.8014(8), La1–Cl3 = 2.8895(9), La1–N1 = 2.638(3), La1–N2 = 2.678(3), La1–N3 = 2.658(3), La1–O1 = 2.576(3), La1–Cl3 = 2.9209(9), Cl1–La1–Cl2 = 144.65(2), Cl1–La1–Cl2 = 86.82(2), Cl1–La1–O1 = 72.14(7), Cl2–La1–O1 = 78.77(7), Cl3–La1–O1 = 140.69(7), N3–La1–N1 = 123.52(9), N3–La1–O1 = 145.03(9), N5–La1–N2 = 62.21(9).

Fig. 7 Fluorination of [ScCl3(Me3tacn)]: A: 45Sc NMR showing the species [ScFCl2(Me3tacn)] (219 ppm), [ScF2Cl(Me3tacn)] (155 ppm) and [ScF3(Me3tacn)] (104 ppm) when a deficit of [NMe4]F is used; B: 45Sc NMR of [ScF3(Me3tacn)] showing the quartet at 104 ppm (1JScF = 219 Hz).

Fig. 8 Crystal structure of [ScF2Cl(Me3-tacn)] with ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Select bond lengths (Å) and angles (°): Sc1–F1 = 1.947(3), Sc1–F2 = 1.940(3), Sc1–Cl1 = 2.444(2), Sc1–N1 = 2.339(5), Sc1–N2 = 2.364(4), Sc1–N3 = 2.334(4), Cl1–Sc1–F1 = 101.7(1), Cl1–Sc1–N1 = 162.4(1), Cl1–Sc1–N2 = 89.9(1), F1–Sc1–F2 = 103.3(1), N2–Sc1–N3 = 74.6(1), F1–Sc1–N3 = 158.8(1).
Attempts to react [ScCl₃(terpy)] with dry [NMe₄]F in CH₂CN on an NMR scale caused complete loss of the resonances from the trichloro complex, without the appearance of any new resonances in either the ⁴⁵Sc or ¹⁹F spectra.

The reaction of [YCl₃(Me₃-tacn)] with three equivalents of [NMe₄]F in CH₂CN resulted in a white precipitate that was insoluble in CH₂CN or CH₂Cl₂ and the ¹H NMR spectrum of the solution showed liberation of Me₃-tacn, whilst the ¹⁹F NMR spectrum showed only small amounts of free fluoride. Similar results were obtained using [YI₃(Me₃-tacn)], and it was concluded that Cl⁻/F⁻ exchange resulted in decomposition and loss of the Me₃-tacn from the yttrium. Similar decomposition occurred using [La(Cl)(Me₃-tacn)(OH₂)].

Chloride/fluoride exchange reactions using Me₃SnF

Me₃SnF is a useful fluorinating agent, its polymeric structure makes it insoluble in most solvents, but it dissolves as the Cl⁻/F⁻ exchange reaction proceeds, and usually, the Me₃SnCl (which contains tbp tin centres weakly chlorine-bridged into polymeric chains) formed is easily removed from the products by washing with hexane. The reagent does not provide free fluoride ions so an excess can be used without the risk of the decomposition observed using [NMe₄]F. The fac-octahedral trifluoro complexes [ScF₃(R₃-tacn)] were readily obtained by treatment of the trichloro species with three mol. equiv. of Me₃SnF (and adding excess Me₃SnF has no further effect) (Fig. 9). The broad “doublets” observed in the ¹⁹F{¹H} NMR spectra result from partial collapse of the couplings to ⁴⁵Sc (I = 7/2) in the low symmetry environments.

However, the product obtained had a microanalysis corresponding to [Sc(Me₃-tacn)F₂(µ-F)SnMe₃Cl]; note that whilst three equivalents of Me₃SnCl are produced in the reaction, only one is retained in the scandium complex.

Fig. 10 Crystal structure of [Sc(Me₃-tacn)F₂(µ-F)SnMe₃Cl] with atom numbering scheme. Ellipsoids are shown at the 50% probability level. The only similar complex to have been reported is [ScCl₂(µ-F)₂(SnMe₃Br₂)] (ₗ = N₄N⁺(1,3-dimethyl-1,3-propanediylidiline)bis[N4, N₂-diethyl-1,2-ethanediamine]), made from [ScLBr₃] and Me₃SnF.

The ⁴⁵Sc and ¹⁹F{¹H} NMR spectra of [Sc(Me₃-tacn)F₂(µ-F)SnMe₃Cl] in CH₂CN are identical, as are the ¹H resonances of the Me₃-tacn moieties, whilst the ¹H resonances of the Me₃-tacn moieties, whilst the ¹H
NMR resonance of the Me3SnCl in the former complex is consistent with the free organotin, indicating the adduct is dissociated in solution. Me3SnF is a weak Lewis acid and complexes such as [Me3SnCl(Ph3PO)] also appear largely dissociated in solution.45 However, attempts to crystallise [ScF3(Me3-tacn)] from solutions of [Sc(Me3-tacn)F2(µ-F)SnMe3Cl] failed with the bimetallic species reformed in the isolated solid. This contrasts with [Sc(µ-F)2(Me3SnBr)2] which decomposes when the mother liquor is removed.13 Gently heating a finely ground sample of [Sc(Me3-tacn)F2(µ-F)SnMe3Cl] (40 °C) under vacuum leads to partial removal of the Me3SnCl, but complete removal of the tin species could not be achieved without decomposition of the scandium moiety.

The reaction of [ScCl3(terpy)] with three equivalents of Me3SnF gave a white solid identified by microanalysis and multinuclear NMR as [Sc(terpy)F(µ-F)2(SnMe3Cl)2]. The 19F{1H} NMR (CD3CN) δ = −37.7 (br s, [2F]), −53.3 (br s, [F]) and 45Sc NMR δ = 64 (s, br) are consistent with the formulation. However, in contrast to [Sc(Me3-tacn)F2(µ-F)SnMe3Cl], [Sc(terpy)F(µ-F)2(SnMe3Cl)2] is unstable in solution and slowly deposits a white insoluble solid.

The reaction of [YCl3(Me3-tacn)] with Me3SnF in CH3CN resulted in decomposition, and no YF3 complex was identified.

Unlike the trichloro analogues, which are very hydrolytically sensitive, solutions of [ScF3(Me3-tacn)] and [ScF3(BnMe2-tacn)] in water at neutral pH are stable for many weeks, monitored by 19F and 45Sc NMR spectroscopy, and to heating aqueous solutions at 80 °C for several hours. The complexes are decomposed by excess F− and by Na2PO3 and Na2CO3 (which have a pH ~ 9), but are stable to a 10-fold excess of Cl− or MeCO2−.

Conclusions
The [ScF3(Me3-tacn)] and [ScF3(BnMe2-tacn)], which represent the first reported examples of scandium fluoride complexes with neutral co-ligands, have been prepared by Cl/F exchange reactions from the corresponding chlorides, using [NMMe3]F. Attempts to isolate similar complexes of Y or La, or [ScF3(terpy)] have been unsuccessful. In these cases fluorination is accompanied by dissociation of the neutral ligands and formation of insoluble MF3. Highly unusual [Sc(terpy)F(µ-F)2(SnMe3Cl)2] and [Sc(Me3-tacn)F2(µ-F)SnMe3Cl] have been isolated using Me3SnF as the fluoride source. The high stability of [ScF3(R3-tacn)] in water over a range of temperatures and pHs, as well as towards common ions such as Cl− or MeCO2−, indicates that they are worthy further examination to determine their potential as possible carriers for 19F in PET imaging radio-tracers.

The decomposition of analogous Y and La trichloride complexes upon attempted fluorination, indicates that the R3-tacn or terpy ligands are insufficiently strongly bound to these metal ions to prevent their dissociation and formation of MF3 polymer. Since Y and La are larger than Sc, tetra-azamacrocycles (cyclen or cyclam) may be better suited. Alternatively, anionic pendant arm ligands such as the H2-R-NOTA type, which will bind more strongly, may be better for these oxophilic metal centres. These possibilities will be investigated in future work.

Conflicts of interest
There are no conflicts to declare.

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