Hydrothermal synthesis of Group 13 metal trifluoride complexes with neutral N-donor ligands†‡

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The reactions of the hydrated Group 13 fluorides, MF$_3$·3H$_2$O (M = Al, Ga or In) with 2,2′:6′:2″-terpyridyl, 2,2′-bipyridyl or 1,10-phenanthroline under hydrothermal conditions (180 °C/15 h) produced high yields of the complexes [MF$_3$(terpy)·3H$_2$O], [MF$_3$(bipy)(OH$_2$)·2H$_2$O] and [MF$_3$(phen)(OH$_2$)]. X-Ray crystal structures of [MF$_3$(terpy)·3H$_2$O (M = Al or Ga), [MF$_3$(bipy)(OH$_2$)]·2H$_2$O and [GaF$_3$(phen)(OH$_2$)] show that all of them contain distorted octahedral geometries at the metal with mer-trifluoride coordination. Extensive H-bonding (F⋯H–OH) links the molecules. The complexes have been further characterised by microanalysis, IR, $^1$H, $^{19}$F($^1$H) and $^{27}$Al NMR spectroscopy. In contrast, reactions of the trifluorides with the acyclic triamine, $N,N,N',N''$-pentamethyldiethylenetriamine, under similar hydrothermal conditions results in cleavage of the triamine and ring-closure to form the 1,1,4-trimethylpiperazinium cation, [Me$_2$N-(CH$_2$)$_2$NMe(CH$_2$)$_2$]$^+$, with fluorometallate anions, and confirmed by X-ray analysis of [Me$_2$NICH$_2$]NMe-(CH$_2$)$_2$Al$_2$F$_8$(OH$_2$)$_2$·2H$_2$O. The strongly H-bonded [GaF$_3$(terpy)]·3H$_2$O was also obtained by Cl/F exchange from [GaCl$_3$(terpy)] and [NBu$_4$]F or [K(2,2,2-crypt)]F. Crystalisation of a mixture of [NH$_4$]$_3$[PF$_6$] and [GaF$_3$(terpy)]·3H$_2$O from aqueous solution produced the edge-bridged cationic complex, ([GaF$_3$(terpy)F]$_2$–(μ-F))$_2$[PF$_6$]$_2$. The synthesis of the more sterically bulky [GaCl$_3$(Bu$_3$-terpy)] (Bu$_3$-terpy = 4,4′-tris-2,2′-6′:2″-terpyridyl) and the crystal structure of [GaCl$_3$(Bu$_3$-terpy)][GaCl$_4$], which contains a trigonal bipyramidal cation, are also reported.

Introduction

The anhydrous Group 13 metal fluorides MF$_3$ (M = Al, Ga or In) are inert polymeric solids and generally unreactive towards neutral ligands. This has hindered attempts to explore their coordination chemistry, hence very few adducts have been described.1 The hydrates, MF$_3$·3H$_2$O, are more reactive, but have very poor solubility in organic solvents or water.1 Two structural forms of AlF$_3$·3H$_2$O are known, the α-form with discrete [AlF$_3$(OH)$_2$]$_3$ molecules, and the β-form which is a polymer, ([AlF$_3$(OH)$_2$]$_n$(μ-F)$_m$)$_n$H$_2$O.2 The structure of GaF$_3$·3H$_2$O is unclear, but InF$_3$·3H$_2$O is also a fluoride bridged polymer.2 Prolonged reflux of GaF$_3$·3H$_2$O with pyridine in thf afforded the mer octahedral complex [GaF$_3$(py)$_3$],3 whilst the reaction of GaF$_3$·3H$_2$O with 1,4,7-tris(2-amino-3,5-di-tert-butylbenzyl)-1,4,7-triazacyclononane (L) under reflux conditions in ethanol, followed by crystallisation from MeOH, afforded [GaF$_3$(L)]·6MeOH, as an $N_6$-symmetric MeOH hexamer.4 Complexes of aluminium, gallium and indium fluorides with neutral NH$_3$ ligands have been formed from the reaction of AlN or InN with NH$_4$F in supercritical ammonia at 400 °C, from NH$_4$F or NH$_4$HF$_2$ and elemental Ga, and from [NH$_4$(MF)$_6$] and gaseous NH$_3$ or MF$_3$·3H$_2$O and liquid NH$_3$.5–9 The structures are usually polymeric with F-bridges. Studies in aqueous solution of various ethylenediamine derivatives of Al and Ga contain the mer-diamine:AlF$_3$ system12 have also been reported. The X-ray crystal structures of [InF$_3$(2,2′-bipy)(OH$_2$)]·2H$_2$O and [InF$_3$(phen)(OH$_2$)] obtained during the latter study have been described.12,13 The complexes [MF$_3$(4,4′-bipy)] (M = Ga and In) were formed hydrothermally from the respective MF$_3$·3H$_2$O and 4,4′-bipyridyl in aqueous HF at 180 °C.14 Hydrothermal synthesis has also been used with other N-donor ligands such as the macrocyclic Me$_3$-tacn and BzMe$_2$-tacn (Me$_3$-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, BzMe$_2$-tacn = 1,4,4-dimethyl-7-benzyl-1,4,7-triaza-
cyclohexanone, L’) to form $\text{fac-}[\text{MF}_3(L')]\cdot x\text{H}_2\text{O}$ for each of aluminium, gallium and indium. The compounds formed with Me$_2$-tacn were found to crystallise as tetrahydrates, and excessive hydrogen bonding interactions between the water molecules of crystallisation and the coordinated fluorides were observed.

An alternative method for the production of the metal-fluoro complexes is to first synthesise the metal chloride analogue and then perform a halide exchange reaction using reagents such as Me$_2$SiF or Me$_2$SnF. For example, $[\text{AlF}_2(py)_4]\text{Cl}$ was successfully formed from the reaction of $[\text{AlCl}_3(py)_6] (n = 1$ to 3) with Me$_2$SiF in pyridine.

The use of aluminium$^{15}$ and gallium$^{17}$ fluoride complexes incorporating $^{19}$F as a radioisotope, has attracted much recent interest as diagnostic imaging agents for PET (positron emission tomography). Key to their potential clinical suitability is the ability to incorporate the short-lived $^{19}$F isotope (t$_{1/2}$ = 110 min.) rapidly and cleanly in water; the resulting aluminium fluoride complexes are stable under physiological conditions,$^{15}$ while the gallium fluoride radio-product is stable in phosphate buffered saline (PBS) solution.$^{17}$ A fuller understanding of the coordination chemistry of these Group 13 fluorides is expected to contribute to advancing the design of the next generation of $^{19}$F imaging agents.

Here we report on the systematic study of the preparation, spectroscopic and structural features of several series of complexes of the three Group 13 trifluorides with bi- and polydentate N-donor ligands, to explore the suitability of hydrothermal synthesis for other neutral ligands. The work also investigates the effect of replacing amine with neutral N-heterocyclic ligands, and introducing the mer-trifluoride geometry, rather than the fac geometry present in the $[\text{MF}_3(R_3\text{tacn})]$ systems.

**Experimental**

The $\text{AlF}_3\cdot 3\text{H}_2\text{O}$ (M = Al, Ga or In), $\text{GaCl}_3$, $2,2'$-bipyridyl, 1,10-phenanthroline, $2,2':6',2''$-terpyridyl, 4,4',4''-tris-$t$-butyl-$2,2':6',2''$-terpyridyl ($\text{Bu}_3$-terpy), and $N,N',N'',N'''$-pentamethyldiethylenetriamine (PMDTA), were obtained from Sigma-Aldrich or Alfa-Aesar and used as supplied. Solvents were dried diethylenetriamine (PMDTA), were obtained from Sigma-Aldrich or Alfa-Aesar and used as supplied. Solvents were dried and layered with hexane. A pale yellow precipitate formed over-night. Yield 0.042 g, 67%. Spectroscopic data matched that via Method 1.

**Method 1**

$\text{AlF}_3\cdot 3\text{H}_2\text{O}$ (0.010 g, 0.72 mmol) was suspended in freshly distilled water (7 mL) and terpy (0.169 g, 0.72 mmol) was then added. The suspension was transferred into a Teflon container and loaded into a stainless steel high pressure vessel (Parr) and heated to 180 °C for 15 h. The vessel was then allowed to cool. A pale yellow solution had formed, a small aliquot of which was retained to grow crystals. For the remaining reaction mixture the solvent was removed in vacuo, yielding a pale orange solid. Yield: 0.18 g, 70%. IR (Nujol, $\nu$/cm$^{-1}$): 3370 ($\nu$ O-H), 1640 ($\delta$ H-O-H) 656, 631, 620 (Al-F). $^1$H NMR (298 K): $\delta$ = 8.90 (d, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.76 (d, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.54 (d, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.39 (t, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.28 (t, $J_{HH}$ 8.0 Hz, [H], ArH), 7.83 (t, $J_{HH}$ 6.0 Hz, [2H], ArH), 4.87 (s, H$_2$O). $^{19}$F$^1$H NMR (298 K): $\delta$ = –162.0 (d, $J_{FF}$ 2.3 Hz, [2F]), –177.3 (t, $J_{FF}$ 2.3 Hz, [F]). $^{27}$Al NMR (298 K): $\delta$ = 167.6 (br). Microanalyses on several batches, which were pure by spectroscopic analysis (including the single crystals), consistently gave H and N content as expected, but very variable (low) C content for this complex. Slow evaporation of the reaction solvent gave crystals suitable for X-ray diffraction.

$\text{GaF}_3\cdot \text{terpy}\cdot \text{H}_2\text{O}$

**Method 1**: Method as for $[\text{AlF}_3\cdot \text{terpy}]\cdot \text{H}_2\text{O}$ using $\text{GaF}_3\cdot \text{H}_2\text{O}$ (0.200 g, 1.11 mmol) and terpy (0.259 g, 1.11 mmol). Orange solid. Yield 0.366 g, 80%. Required for $C_{15}H_{17}F_3GaN_3O_3$: C, 43.3; H, 4.1; N, 10.6. Found: C, 43.3; H, 4.0; N, 10.3%. IR (Nujol, $\nu$/cm$^{-1}$): 3407 ($\nu$ O-H), 1644 ($\delta$ H-O-H) 548, 504, 490(sh) (Ga-F). $^1$H NMR (298 K): $\delta$ = 9.04 (d, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.80 (d, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.78 (d, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.64 (t, $J_{HH}$ 8.0 Hz, [H], ArH), 8.49 (t, $J_{HH}$ 8.0 Hz, [2H], ArH), 8.03 (t, $J_{HH}$ 6.0 Hz, [2H], ArH), 4.87 (s, H$_2$O). $^{19}$F$^1$H NMR (298 K): $\delta$ = –156.3 (s, [2F]), –189.7 (s, [F]); (183 K $\delta$ = –154.5 (s, [2F]), –188.9 (s, [F]). Slow evaporation of the reaction solvent gave crystals suitable for X-ray diffraction.

**Method 2**: A suspension of $[\text{GaCl}_3\cdot \text{terpy}]$ (0.06 g, 0.15 mmol) in anhydrous MeCN (5 mL) was treated with 0.45 mL (0.45 mmol) of a 1.0 M solution of $[\text{NBu}_3]$F in thf. Addition of the fluoride source resulted in the dissolution of the chloride precursor and the formation of a pale yellow solution. The mixture was stirred at room temperature for 1 h and then the volatiles were removed in vacuo to yield a yellow gum. This was dissolved in anhydrous MeCN (ca. 2 mL) and layered with hexane. A pale yellow precipitate formed over-night. Yield 0.042 g, 67%. Spectroscopic data matched those obtained via Method 1.

**Method 3**: $[\text{GaCl}_3\cdot \text{terpy}]$ (0.020 g, 0.050 mmol) was suspended in anhydrous MeCN (5 mL). A solution of $[\text{K}(2.2.2$-
F). 1H NMR (298 K): 1.11 mmol) and bipy (0.158 g, 1.11 mmol). Pale pink solid. X-ray di in the formation of orange crystals suitable for single crystal tion was left to evaporate slowly at room temperature, resulting in vacuo daltontrans. This journal is © The Royal Society of Chemistry 2015

[AlF3(bipy)(OH2)]·2H2O

Method as for [AlF3(terpy)]·3H2O using InF3·3H2O (0.100 g, 0.44 mmol). Pale orange solid. Yield: 0.20 g, 47%.

[AlF3(phen)(OH2)]·2H2O

Method as for [AlF3(terpy)]·3H2O, but using InF3·3H2O (0.200 g, 0.44 mmol) and phen (0.226 g, 1.45 mmol). White solid. Yield: 0.254 g, 62%. Required for C12H10F3GaN2O (324.9): C, 31.4; H, 3.6; N, 10.0%. IR (Nujol, υ/cm−1): 1360, 1291 (Ga, F), 1670 (δ H–O–H), 637, 608 (Al–F).

[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using InF3·3H2O (0.200 g, 0.45 mmol) and phen (0.261 g, 1.45 mmol). White solid. Yield: 0.254 g, 62%. Required for C12H10AlF5N2O2 (282.2): C, 51.1; H, 3.6; N, 9.9. Found: C, 50.9; H, 3.4; N, 10.0%. IR (Nujol, υ/cm−1): 3200br (υ O–H), 1670 (δ H–O–H), 637, 608 (Al–F).

[AlF3(phen)(OH2)]·2H2O

Method as for [AlF3(terpy)]·3H2O using InF3·3H2O (0.200 g, 0.45 mmol) and phen (0.261 g, 1.45 mmol). White solid. Yield: 0.254 g, 62%. Required for C12H10AlF5N2O2 (282.2): C, 51.1; H, 3.6; N, 9.9. Found: C, 50.9; H, 3.4; N, 10.0%. IR (Nujol, υ/cm−1): 3200br (υ O–H), 1670 (δ H–O–H), 637, 608 (Al–F).

[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using InF3·3H2O (0.200 g, 0.45 mmol) and phen (0.261 g, 1.45 mmol). White solid. Yield: 0.254 g, 62%. Required for C12H10AlF5N2O2 (282.2): C, 51.1; H, 3.6; N, 9.9. Found: C, 50.9; H, 3.4; N, 10.0%. IR (Nujol, υ/cm−1): 3200br (υ O–H), 1670 (δ H–O–H), 637, 608 (Al–F).

[AlF3(phen)(OH2)]·2H2O

Method as for [AlF3(terpy)]·3H2O using InF3·3H2O (0.200 g, 0.45 mmol) and phen (0.261 g, 1.45 mmol). White solid. Yield: 0.254 g, 62%. Required for C12H10AlF5N2O2 (282.2): C, 51.1; H, 3.6; N, 9.9. Found: C, 50.9; H, 3.4; N, 10.0%. IR (Nujol, υ/cm−1): 3200br (υ O–H), 1670 (δ H–O–H), 637, 608 (Al–F).

[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using InF3·3H2O (0.200 g, 0.45 mmol) and phen (0.261 g, 1.45 mmol). White solid. Yield: 0.254 g, 62%. Required for C12H10AlF5N2O2 (282.2): C, 51.1; H, 3.6; N, 9.9. Found: C, 50.9; H, 3.4; N, 10.0%. IR (Nujol, υ/cm−1): 3200br (υ O–H), 1670 (δ H–O–H), 637, 608 (Al–F).
A solution of terpy (0.258 g, 1.11 mmol) in anhydrous CH2Cl2 (5 mL) was added dropwise to a solution of GaCl3 (0.195 g, 1.11 mmol) in 5 mL anhydrous CH2Cl2. A white precipitate formed upon addition of the ligand. The mixture was stirred at room temperature for 1 h. The precipitate was isolated by filtration, washed with hexane and dried in vacuo. White solid. Yield: 0.062 g, 77%. Required for C14H42Al2F8N4O4 (536.4): C, 31.4; H, 7.8; N, 9.0.

[GalCl(terpy)]·3H2O

A solution of Bu4-terpy (0.111 g, 0.278 mmol) in anhydrous CH2Cl2 (5 mL) was added dropwise to a solution of GaCl3 (0.025 g, 0.139 mmol) in anhydrous CH2Cl2 (5 mL). A white precipitate formed upon addition of the ligand. The mixture was stirred at room temperature for 1 h. The solid of the ligand resulted in the formation of a white precipitate. The mixture was stirred at room temperature for 1 h. The product was isolated by filtration, washed with MeCN, producing a white powder. Yield: 0.44 g, 58%. Required for C27H35Cl3GaN3·CH2Cl2 (662.60): C, 50.7; H, 5.6; N, 6.3.

[cMe2N(CH2)2NMe(CH2)2]Cl

Method as for [AlF3(bipy)(OH2)]·2H2O, but using AlF3·3H2O (0.200 g, 1.45 mmol) and PMDTA (0.3 mL, 1.45 mmol). A brown gum was obtained after removing the solvent. This was washed with MeCN, producing a white powder. Yield: 0.44 g, 58%. Required for C10H25Al2F10N4O4 (536.4): C, 31.4; H, 7.8; N, 10.4. Found: C, 31.3; H, 7.8; N, 10.4%. IR (Nujol, v/cm⁻¹): 3370 br (ν O–H), 1673 (ν C=O), 1216 s (ν C–N), 1172 s (ν C–F), 1140 s (ν C–F), 1013 s (ν C–F), 999 s (ν C–F), 906 s (ν C–F). 1H NMR (CD3CN, 298 K): δ = 4.87 (s, H2O), 3.35 (t, JHH 6.0 Hz, [4H], CH3), 3.07 (s, [6H], Me), 2.67 (br s, [4H], CH2CH2), 2.32 (s, [3H], Me). 13C{1H} NMR (CD3CN, 298 K): δ = 48.7 (s, H2O), 3.35 (t, JHH 6.0 Hz, [4H], CH3), 3.07 (s, [6H], Me), 2.67 (br s, [4H], CH2CH2), 2.32 (s, [3H], Me). 19F{1H} NMR (CD3CN, 298 K): δ = 44.18 (s), 48.84 (s), 61.59 (s). IR (Nujol, v/cm⁻¹): 3420 br (ν O–H), 1673 (δ H–O–H), 518 br, 477 br (Ga–F).

A small number of crystals obtained from the Ga and In reaction mixtures were found to be [cMe2N(CH2)2NMe(CH2)2]Cl (see text and ESI‡).

X-Ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 μm focus) with the crystal held at 100 K (N2 cryostream). Structure solution and refinements were performed with either SHELX (S/L)97 or SHELX(L/S)2013‡ and were straightforward, except where detailed below. H atoms bonded to C were placed in calculated positions using the default C–H distance and refined using a riding model. In the case of the [AlF3(bipy)(OH2)]·2H2O structure, the H-atoms on the co-crystallised water molecules were not located in the difference map. While not included in the refinement, the H-atoms are inferred from the H-bonding distances of F⋯O and O⋯O and are thus included in the formulae. The H-atoms on both the coordinated and co-crystallised water molecules could not be located in the structure of [cMe2N(CH2)2NMe(CH2)2]AlF3(OH2)3·2H2O. While not included in the refinement, the H-atoms are similarly inferred and included in the formulae. CCDC numbers 1053047–1053048 and 1053152–1053158.

Results and discussion

The unreactive and poorly soluble nature of the MF3·3H2O makes reaction with neutral ligands in organic solvents difficult or impossible. We therefore used the hydrothermal approach (180 °C/15 h) and found this gave high yields of [MF3(terpy)]·3H2O (below). The same approach was then extended to reactions with N,N,N′,N″-pentamethyldiethyl- 

[cMe2N(CH2)2NMe(CH2)2]AlF3(OH2)3·2H2O

Required for C10H25Al2F10N4O4 (536.4): C, 31.4; H, 7.8; N, 10.4%. Found: C, 26.7; H, 6.4; N, 9.8%. 1H NMR (CD3CN, 298 K): δ = 4.87 (s, H2O), 3.35 (t, JHH 6.0 Hz, [4H], CH3), 3.07 (s, [6H], Me), 2.67 (br s, [4H], CH2CH2), 2.32 (s, [3H], Me). 13C{1H} NMR (CD3CN, 298 K): δ = 48.7 (s, H2O), 3.35 (t, JHH 6.0 Hz, [4H], CH3), 3.07 (s, [6H], Me), 2.67 (br s, [4H], CH2CH2), 2.32 (s, [3H], Me). 19F{1H} NMR (CD3CN, 298 K): δ = 44.18 (s), 48.84 (s), 61.59 (s). IR (Nujol, v/cm⁻¹): 3420 br (ν O–H), 1673 (δ H–O–H), 518 br, 477 br, (Ga–F).
Table 1  Crystallographic parameters

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* Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. b R₁ = Σ||Fᵢ|| - |Fᵢ||/Σ|Fᵢ||; wR₂ = [Σw(Fᵢ² - Fᵢ)²/ΣwFᵢ²]¹/².

than 90°/180°, whereas the F–Al–F and (cis) F–Al–N angles are close to those expected for an octahedron.

There is extensive H-bonding between the fluoride ligands and the lattice water molecules (Fig. 2), as well as π-stacking of the aromatic rings (Fig. 3).

The Al–F bond lengths are very similar to those observed in fac-[AlF₆(Me₃-tacn)]·4H₂O, but the Al–N bonds are shorter by ∼0.05 Å, suggesting the macrocyclic ring may limit the close approach of the N atoms to the metal centre. The molecular structure of [GaF₆(terpy)]·3H₂O is very similar to that of the Al(n) complex (Fig. 4) with the Ga–F bonds ca. 0.1 Å longer than the corresponding Al–F, whilst the Ga–N and Al–N are little different.

As found in the aluminium complex, the structure of [GaF₆(terpy)]·3H₂O shows extensive H-bonding as shown in Fig. 5 as well as π-stacking interactions of 3.57 and 3.62 Å (see ESI Fig. S1†), although the arrangements differ in detail. The Ga–F distances are very similar to those found in fac-[GaF₆(Me₃-tacn)]·4H₂O. The Ga–N distances are also not significantly different to those found in the [GaX₃(terpy)] (X = Cl or Br), although the extensive H-bonding in the fluoride complex is absent in the structures of the heavier halides. The single bond covalent radii of Al(n) and Ga(m) are quoted in standard texts as nearly identical (∼1.25 Å), although the ionic radius of Ga³⁺ is ∼0.07 Å larger than that of Al³⁺. The limited number of structurally characterised complexes of the trifluorides limits detailed comparisons, but it seems that the metal-donor bond length may be very sensitive to the electronegativity of the donor atom, with little difference between Al–L.
and Ga–L with heavier donor ligands and halides, but significant differences in the M–F bond lengths. The effects of solvent molecules and hydrogen bonding also complicates the interpretation of small differences in metal-donor bond lengths, and these may be a significant factor in the extensively hydrogen bonded metal fluoride complexes.

Interpretation of the spectroscopic properties (Experimental section) of the three terpy complexes is straightforward. The IR spectra show strong, very broad features due to the $\nu$(OH) and $\delta$(HOH) modes of the water and three $\nu$(MF) stretches, as expected for a mer-trifluoride (theory $2A_1 + B_1$). The $^1$H NMR spectra in CD$_3$OD exhibit sharp multiplet resonances for the terpy protons and a broad signal for the water, whilst the $^{19}$F($^1$H) NMR spectra show two resonances in a 2 : 1 ratio due to $F_{\text{trans}}$ and $F_{\text{trans}}$, respectively. The $^{19}$F($^1$H) resonances for the [AlF$_3$(terpy)] show doublet and triplet $^J_{FF}$ couplings of 23 Hz, but for the gallium and indium complexes only broad singlets are observed over the temperature range 298–183 K. The aluminium complex also exhibited a $^{27}$Al NMR resonance at $\delta = 16.7$ as a broad singlet with no resolved $^J_{AA}$ coupling, which is in the range expected for six-coordinate aluminium.

Neither the gallium nor indium complex exhibited a metal nucleus resonance, probably due to fast quadrupolar relaxation. The multinuclear NMR data show that the molecular structures of these complexes are maintained in MeOH solution.
The synthesis of the [GaF₆(terpy)] by halide exchange was also explored. The [GaCl₃(terpy)] precursor was made in high yield by reaction of GaCl₃ with terpy in anhydrous CH₂Cl₂ solution, and its composition confirmed by microanalysis and spectroscopically. Complete fluorination of [GaCl₃(terpy)] in MeCN solution was achieved at room temperature with [Bu₄NF] in the or [K(2.2.2-crypt)][F] in MeCN; the [GaF₆(terpy)] produced was spectroscopically identical to samples produced by the hydrothermal route, and crystals obtained using the [Bu₄NF] route had the same unit cell. Fluorination with [K(2.2.2-crypt)][F] was also successful at 80 °C in MeCN, confirming the gallium species is thermally stable under these conditions. The [GaCl₃(terpy)] was relatively poorly soluble in organic solvents and in an attempt to increase the solubility, the corresponding complex of 4,4′-tris-terpyridyl, [GaCl₃(terpy)], was prepared. Its properties were very similar to the terpy complex (Experimental section), but it was in fact rather less soluble in common organic solvents. However, crystals grown from the filtrate from one synthesis were found to be [GaCl₃(Bu₃-terpy)][GaCl₄]·CH₂Cl₂, containing a five-coordinate cation. This minor by-product probably results from the presence of a small excess of GaCl₃ in the synthesis, which extracts a chloride from the neutral species to form the stable [GaCl₄]⁻ anion. The structure of the cation is shown in Fig. 6. The geometry is a distorted trigonal bipyramid with apical N, distorted by the steric constraints of the Bu₃-terpy (N₃-Ga₁-N₁ = 155.1(2)°), as also found in the neutral [GaCl₃(terpy)] complex above. Comparisons of the bond lengths between [GaCl₃(Bu₃-terpy)]⁺ and [GaCl₃(terpy)],¹³ as expected, show shorter bonds in the five-coordinate cation (Ga–Cl = 2.169(2), 2.195(2), Ga–N = 1.995(5)–2.092(5) Å) compared to the six-coordinate neutral complex (Ga–Cl = 2.251(5)–2.4118(6), Ga–N = 2.0412(5)–2.1024(15) Å).

\[
[\text{Ga(terpy)F}_2(\mu-F)_2][\text{PF}_6]_2·4\text{H}_2\text{O}
\]

The fac-[GaF₆(BzMe₂-tacn)] has been shown to function as a neutral ‘metalloligand’ through the coordinated fluorides towards alkali metal and ammonium cations in aqueous solution, leading to supramolecular arrays with Ga–F–M linkages,²⁵ whilst combination of Ga₃⁺ and fac-[GaF₆(Me₂-tacn)] leads to [Gd₂Ga₄]⁻ cores that are of interest as molecular magnets.²⁶ A key feature of these systems is that the three facial Ga–F bonds remain intact throughout. To explore if the meridional trifluoride arrangement present in [GaF₆(terpy)] could function in a similar manner, a H₂O-MeCN solution containing [GaF₃(Me₃-tacn)] was allowed to evaporate slowly. Orange crystals formed and an X-ray structure analysis on these showed that rather than forming an ammonium-metalloligand complex, the dimer, ([Ga(terpy)F]₂(μ-F)₂)[PF₆]₂·4H₂O had formed.

The centrosymmetric cation (Fig. 7) contains six-coordinate gallium, severely distorted from regular octahedral by the steric constraints of the terpy ligand (N₁–Ga₁–N₃ = 153.85(10)°), and the fluoride bridges are asymmetric (Ga₁–F₁ = 1.889(2), Ga₁–F₁a = 2.003(2) Å). There is extensive hydrogen bonding linking the lattice water molecules, the cations and the [PF₆]⁻ anions (Fig. 8). The complex, formed by dissociation of one fluoride from each gallium centre, followed by dimerisation, dissolves in CD₃OD with decomposition and formation of a white precipitate. The ¹³⁵F{¹H} NMR spectrum of the supernatant shows only [GaF₆(terpy)] and [PF₆]⁻ as significant species.

\[
[\text{MF}_₃(\text{diimine})(\text{OH}_2)]·\text{nH}_2\text{O}
\]

The hydrothermal method also proved a suitable route to obtain [MF₃(bipy)(OH₂)]·2H₂O and [MF₃(phen)(OH₂)] in good yields. The structures of [InF₃(phen)(OH₂)] and [InF₃(bipy)-(OH₂)]·2H₂O obtained from samples made from aqueous HF solution have been reported previously.¹⁵ The [MF₃(bipy)-(OH₂)]·2H₂O (M = Al or Ga) are monoclinic, P2₁/n, with six-coordinate metal centres and a mer-fluoride arrangement,
More electronegative donors have the greatest di-
complex as expected, but here the di-
corresponding bond lengths all increase in the indium
lattice water and
are less clear, with all showing an increase of
∼0.15–0.2 Å over
the gallium analogue. In all of the complexes H-bonding to
the lattice water and π-stacking of the aromatic rings is also
evident (Fig. 11–13 and S21).
Overall, the structural data reinforce earlier conclusions that trends in the bond lengths in comparable Al and Ga complexes often differ from those predicted on the basis of simple Lewis acidity in the gas phase;22,27–29 other factors, including the presence or absence of lattice solvent and hydrogen bonding also need to be considered.13,19,21,22 The effects are less noticeable at indium, where corresponding bonds are typically ∼0.2 Å longer than for Ga, reflecting the increased radius of the metal centre.

Using the same hydrothermal route with 1,10-phenanthroline in place of 2,2′-bipyridyl, gave [MF₃(phen)(OH₂)], notably without lattice water (in contrast to the terpy and bipy complexes above). The structure of crystals of [GaF₃(phen)(OH₂)] is shown in Fig. 14, and the [InF₃(phen)(OH₂)] is isomorphous.13 Corresponding bond lengths are again ∼0.15–0.20 Å longer for the indium complex. The [GaF₃(phen)(OH₂)] also shows π-stacking of the aromatic rings (Fig. S3†) and intermolecular F⋯H hydrogen bonding, in this case involving the coordinated water molecules (Fig. 15).

The IR spectra of the [MF₃(phen)(OH₂)] complexes show quite weak features due to ν(OH) and δ(HOH), whereas in the hydrated [MF₃(bipy)(OH₂)]·2H₂O the corresponding features
are much stronger and show several overlapping bands. The $\nu$(MF) fall in energy as expected Al > Ga > In, but for the corresponding Al and Ga complexes (less clearly in the In complexes), those in [MF$_3$(bipy)(OH$_2$)]·2H$_2$O occur at lower frequency than in [MF$_3$(phen)(OH$_2$)], which is probably due to the extensive hydrogen bonding in the former.

The multinuclear NMR data show interesting trends as the metal is changed. The complexes were insoluble or very poorly soluble in chlorocarbons and CD$_3$CN, and therefore spectra were obtained from freshly prepared solutions in CD$_3$OD. The solutions decompose slowly forming F$^-$ or HF$_2$-, qualitatively the indium complexes seem less stable in solution than those of the lighter metals. At 183 K, all six complexes show two resonances with relative intensities 1:2 in the $^{19}$F{1H} NMR spectra, consistent with the solid state structures. On warming, the fluorine resonances of the indium complexes are lost, and those of the gallium complexes and of [AlF$_3$(bipy)-(OH$_2$)] broaden and then coalesce; only the $^{19}$F{1H} NMR spectrum of [AlF$_3$(phen)(OH$_2$)] shows two fluorine resonances at room temperature. The $^1$H NMR spectra of the aluminium complexes show inequivalent pyridyl rings, as expected from the static structures, but those of the gallium and indium show broad resonances even at low temperatures. The temperature dependence of the spectra is consistent with reversible ligand dissociation, possibly of the water, to give a fluxional five-coordinate intermediate, the dissociation increasing with decreased Lewis acid strength Al > Ga > In.

Reactions of MF$_3$·3H$_2$O with PMDTA

PMDTA, Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$NMe$_2$, is a flexible, aliphatic acyclic triamine analogue of Me$_3$-tacn and terpy, and its reactions with the hydrated Group 13 fluorides were explored to provide a third series of complexes for comparison. In contrast to the reactions with the other two N$_3$-donor ligands, the hydrothermal route using PMDTA resulted in cleavage of the triamine and the formation of the 1,1,4-trimethylpiperazinium cation, [Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]$^+$. After removing all volatiles from the reaction mixtures and washing the residue with MeCN, the $^1$H and $^{13}$C{1H} NMR spectra show the cyclic cation to be the only organic species in the bulk products. For the aluminium reaction, crystals were obtained, showing the solid contained [cMe$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$][AlF$_3$(OH$_2$)$_2$]·2H$_2$O. The anion (Fig. 16) has been obtained previously as the [NMe$_4$]$^+$ salt, and breaks up in solution to form [AlF$_4$]$^-$, which was identified by a combination of $^{27}$Al ($\delta$ = 48.7 (s)) and $^{19}$F{1H} NMR data ($\delta$ = −194.6, 6 lines, $J_{AF}$ = 38 Hz). In the cases of the gallium and indium reactions, a few crystals of the same cation were obtained as the chloride salt, from traces of chloride in the reaction. The structure of [cMe$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]Cl has been reported previously and the crystals obtained in this study were identical, and hence are not discussed further (see ESI†). The data on the bulk product from the gallium reaction fitted the constitution [cMe$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$][GaF$_6$(OH$_2$)$_2$]·2H$_2$O, analogous to the aluminium complex, although in the absence of X-ray structural data, the anion present cannot be confirmed. The relative instability of the fluoro-metallate anions in solution and the sensitivity of the $^{19}$F chemical shifts to solvent, make identification of the anions uncertain without structural data. The reactions of the MF$_3$·3H$_2$O with PMDTA were also attempted in refluxing methanol solution, since it was reasoned that the milder conditions (compared to the hydrothermal preparations) might have prevented cleavage of the PMDTA. No reaction occurred in the case of indium fluoride, whilst with AlF$_3$·3H$_2$O, $^1$H and $^{19}$F{1H} NMR spectra of the crude product showed protonated PMDTA and [AlF$_4$]$^-$ as the only significant species. The contrast between the instability of PMDTA and the robust Me$_3$-tacn which has similar groups in these Group 13 fluoride reactions may be due to the ring structure of the latter preventing close approach of an amine.
function polarised by coordination to the metal, to the next CH2NMe unit, which is presumably the first stage in C-N bond fission and formation of the small ring.

Conclusions

Hydrothermal synthesis using MF3·3H2O as the metal source has been shown to be a convenient method to form a range of complexes of the otherwise rather intractable Group 13 trifluorides with nitrogen heterocycles in high yield. X-ray crystallographic studies show all of the new complexes contain a mer arrangement of fluorides, contrasting with the fac geometry present in the triaza-macroyclic complexes reported previously. Extensive H-bonding and π-stacking networks are present in the complexes of all three imines with the three metal ions, although the details differ. These studies significantly extend the known coordination chemistry of the Group 13 trifluorides. The relatively high stability of the trifluorides with nitrogen heterocycles in high yield. X-Ray crystallographic studies show all of the new complexes contain a mer arrangement of fluorides, contrasting with the fac geometry present in the triaza-macroyclic complexes reported previously.

Future work will aim to establish whether the hydrothermal approach is also suitable for oxygen donor ligands and whether soft donor ligands such as thioethers or phosphines can form complexes with the Group 13 trifluorides.

Acknowledgements

We thank EPSRC and GE Healthcare for support (EP/I501673/1, EP/L505651/1 and EP/103394/1).

References


23 $^{27}$Al [I = 5/2, 100% abundance, $\gamma = 26.08$ MHz, $Q = 0.149 \times 10^{-28}$ m$^3$, $R_C = 1170$, $^{69}$Ga [I = 3/2, 60.4% abundance, $\gamma = 26.08$ MHz, $Q = 0.149 \times 10^{-28}$ m$^3$, $R_C = 1170$].
24.07 MHz, $Q = 0.178 \times 10^{-28} \text{ m}^2$, $R_C = 237$ $^{71}\text{Ga}$ [$I = 3/2$, 39.6% abundance, $\Xi = 30.58$ MHz, $Q = 0.112 \times 10^{-28} \text{ m}^2$, $R_C = 322$] $^{115}\text{In}$ [$I = 9/2$, 95.7% abundance, $\Xi = 22.04$ MHz, $Q = 1.16 \times 10^{-28} \text{ m}^2$, $R_C = 1920$].


