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, MF3·3H2O (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 [MF3(terpy)·3H2O], [MF3(bipy)(OH2)·2H2O] and [MF3(phen)(OH2)]. X-ray crystal structures of [MF3(terpy)·3H2O (M′ = Al or Ga), [MF3(bipy)(OH2)]·2H2O and [GaF3(phen)(OH2)] 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, 1H, 19F{1H} and 27Al 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, [Me2N(CH2)2NMe(CH2)2]+, with fluorometallate anions, and confirmed by X-ray analysis of [cMe2N-(CH2)3]NMe(CH2)3]+, with fluorometallate anions, and confirmed by X-ray analysis of [cMe2NICH2](NMe4)(CH2)3] with [AlF3(L)·2H2O]. The strongly H-bonded [GaF3(terpy)]·3H2O was also obtained by Cl/F exchange from [GaCl3(terpy)] and [NBu4]F or [K(2,2,2-crypt)]F. Crystallisation of a mixture of [NH4]3[MF6] and [GaF3(terpy)]·3H2O from aqueous solution produced the edge-bridged cationic complex, [(GaF3(terpy)F2)- (µ-F)]2[PF6]3. The synthesis of the more sterically bulky [GaCl3(terpy)] (Bu3-terpy = 4,4′-tris-2,2′-6,2″-terpyridyl) and the crystal structure of [GaCl3(terpy)]·2H2O, which contains a trigonal bipyramidal cation, are also reported.

Introduction

The anhydrous Group 13 metal fluorides MF3 (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, MF3·3H2O, are more reactive, but have very poor solubility in organic solvents or water.1 Two structural forms of AlF3·3H2O are known, the a-form with discrete [AlF2(OH)3] molecules, and the β-form which is a polymer, [AlF3(OH2)2(µ-F)]nH2O.2 The structure of GaF3·3H2O is unclear, but InF3·3H2O is also a fluoride bridged polymer.2 Prolonged reflux of GaF3·3H2O with pyridine in thf afforded the mer octahedral complex [GaF3(py)3]3 whilst the reaction of GaF3·3H2O 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 [GaF3(L)·6MeOH, as an S6-symmetric MeOH hexamer.4 Complexes of aluminium, gallium and indium fluorides with (neutral) NH3 ligands have been formed from the reaction of AlN or InN with NH4F in supercritical ammonia at 400 °C, from NH4F or NH4HF2 and elemental Ga, and from [NH4][MF6] and gaseous NH3, or MF3·3H2O and liquid NH3.5-9 The structures are usually polymeric with F-bridges. Studies in aqueous solution of various ethylenediamine derivatives of Al and Ga10,11 and of the indium fluoride-2,2′-bipyridyl-H2O-HF system12 have also been reported. The X-ray crystal structures of [InF3(2,2′-bipy)(OH2)]·2H2O and [InF3(phen)(OH2)] obtained during the latter study have been described.12,13 The complexes [MF3(4,4′-bipy)][M = Ga and In] were formed hydrothermally from the respective MF3·3H2O 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 Me3-tacn and BzMe2-tacn (Me3-tacn = 1,4,7-triazacyclononane, BzMe2-tacn = 1,4,4-methyl-7-benzyl-1,4,7-triaza-
cyclononane, L’) to form fac-[MF₃(L’)]·xH₂O for each of aluminium, gallium and indium. The compounds formed with Me₂-tacn were found to crystallise as tetrahydrates, and extensive 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 Me₃SiF or Me₃SnF. For example, [AlF₃(py)]Cl was successfully formed from the reaction of [AlCl₃(py)]ₙ (n = 1 to 3) with Me₃SiF in pyridine.

The use of aluminium¹⁵ and gallium¹⁷ fluoride complexes incorporating ¹⁸F 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 ¹⁸F isotope (t₁/₂ = 110 min.) rapidly and cleanly in water; the resulting aluminium fluoride complexes are stable under physiological conditions, while the gallium fluoride radio-product is stable in phosphate buffered saline (PBS) solution. 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 ¹⁸F 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 [MF₃(R₃-tacn)] systems.

**Experimental**

The MF₃·H₂O (M = Al, Ga or In), GaCl₃, 2,2’-bipyridyl, 1,10-phenanthroline, 2,2’:6’,2’-terpyridyl, 4,4’,4”-tris-2-buty1,2,2’:6’,2’-terpyridyl (Bu₃-terpy), and N,N,N’,N”,N”-pentamethyl-dienylentriamine (PMDTA), were obtained from Sigma-Aldrich or Alfa-Aesar and used as supplied. Solvents were dried by distillation prior to use, CH₂Cl₂ and CH₃CN from CaH₂, diethylenetriamine (PMDTA), were obtained from Sigma-Aldrich. All preparations of chloro-complexes were performed under an atmosphere of dry N₂ using Schlenk techniques and spectroscopic samples were prepared in a dry, N₂-purged glove box. Hydrothermal preparations were conducted in a 23 mL Teflon reactor vessel placed in a Parr stainless steel bomb. H NMR spectra were recorded in CD₂OD on a Bruker AVII 400 spectrometer and referenced to the residual proton resonance. ¹⁹F H NMR spectra were recorded in CD₂OD on Bruker AVII 400 and DPPX400 spectrometers, with CFCl₃ as external reference. ²⁷Al, ⁷¹Ga and ¹¹⁵In NMR spectra were recorded in CH₃OH/CD₂OD on a Bruker AVII 400 NMR spectrometer and were referenced to [Al(OH₂)₆]³⁺, [Ga(OH₂)₆]³⁺ and [In(OH₂)₆]³⁺, respectively, in H₂O/D₂O at pH = 1. Infra-red spectra were recorded as Nujol mulls between CsI plates on a Perkin Elmer Spectrum100 spectrometer over the range 4000–2000 cm⁻¹. Microanalyses were undertaken by London Metropolitan University.

**[AlF₃(terpy)]·3H₂O**

AlF₃·H₂O (0.100 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, ν/cm⁻¹): 3370 (ν O–H), 1640 (δ H–O–H) 656, 631, 620 (Al–F). H NMR (298 K): δ = 8.90 (d, JHH 8.0 Hz, [2H], ArH), 8.76 (d, JHH 8.0 Hz, [2H], ArH), 8.54 (d, JHH 8.0 Hz, [2H], ArH), 8.39 (t, JHH 8.0 Hz, [2H], ArH), 8.28 (t, JHH 8.0 Hz, [H], ArH), 7.83 (t, JHH 6.0 Hz, [2H], ArH), 4.87 (s, H₂O). ¹⁹F(¹H) NMR (298 K): δ = −162.0 (d, ¹²FF 23 Hz, [2F]), −177.3 (t, ¹²FF 23 Hz, [F]). ²⁷Al NMR (298 K): δ = 16.7 (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.

**[GaF₃(terpy)]·3H₂O**

**Method 1:** Method as for [AlF₃(terpy)]·3H₂O using GaF₃·H₂O (0.200 g, 1.11 mmol) and terpy (0.259 g, 1.11 mmol). Orange solid. Yield 0.366 g, 80%. Required for C₁₃H₁₂F₃GaN₂O₄ (414.0): C, 43.5; H, 4.1; N, 10.2. Found: C, 43.3; H, 4.0; N, 10.3%. IR (Nujol, ν/cm⁻¹): 3407 (ν O–H), 548, 504, 490(sh) (Ga–F). H NMR (298 K): δ = 9.04 (d, JHH 8.0 Hz, [2H], ArH), 8.80 (d, JHH 8.0 Hz, [2H], ArH), 8.78 (d, JHH 8.0 Hz, [2H], ArH), 8.64 (t, JHH 8.0 Hz, [H], ArH), 8.49 (t, JHH 8.0 Hz, [2H], ArH), 8.03 (t, JHH 6.0 Hz, [2H], ArH), 4.87 (s, H₂O). ¹⁹F(¹H) NMR (298 K): δ = −156.3 (s, [2F]), −189.7 (s, [F]); (183 K) δ = −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 [GaCl₃(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 [NBu₃]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 a minimum volume of CH₂Cl₂ (ca. 2 mL) and layered with hexane. A pale yellow precipitate formed over night. Yield 0.042 g, 67%. Spectroscopic data matched that observed for Method 1 and recrystallisation from CH₂Cl₂/hexane yielded small crystals whose unit cell dimensions matched those of the crystals obtained via Method 1.

**Method 3:** [GaCl₃(terpy)] (0.020 g, 0.050 mmol) was suspended in anhydrous MeCN (5 mL). A solution of [K(2,2,2-
[Ga(terpy)(μ-F3)2][PF6]2·4H2O

\[ \text{[Ga(terpy)(μ-F3)2][PF6]2·4H2O} \]

The reaction was left to evaporate slowly at room temperature, resulting in the formation of orange crystals suitable for single crystal X-ray diffraction. Required for C30H30F16Ga2N6O4P2: C, 34.5; H, 3.1; N, 8.6. Found: C, 35.6; H, 4.1; N, 8.2%. IR (Nujol, ν/cm⁻¹): 3533, 3422 (ν O–H), 1760 w (ν O–F). 19F{1H} NMR (298 K): δ = 157.8 (br s [2F]), 181.6 (br s [2F]). 27Al NMR (298 K): δ = 446, 422 br, 405(sh) (Al F). 

[InF3(bipy)(OH2)]·2H2O

Yield: 0.17 g, 50%. Required for C10H14F3InN2O3 (357.0): C, 39.0; H, 2.7; N, 7.6. Found: C, 39.2; H, 2.8; N, 7.7%. IR (Nujol, ν/cm⁻¹): 3360 br, 3177 (ν O–H), 1660 w (δ O–H–O), 543, 511 (Ga–F).

[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using AlF3·3H2O (0.200 g, 0.11 mmol) and phen (0.200 g, 1.45 mmol). Pale red solid. Yield 0.315 g, 79%. Required for C12H10AlF3N2O (324.9): C, 44.4; H, 3.1; N, 8.5%. IR (Nujol, ν/cm⁻¹): 3200 br (ν O–H), 1680 (δ O–H–O), 560, 543, 511 (Ga–F).

[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using AlF3·3H2O (0.200 g, 0.11 mmol) and phen (0.200 g, 1.45 mmol). Pale red solid. Yield 0.315 g, 79%. Required for C12H10AlF3N2O (324.9): C, 44.4; H, 3.1; N, 8.5%. IR (Nujol, ν/cm⁻¹): 3200 br (ν O–H), 1680 (δ O–H–O), 560, 543, 511 (Ga–F).

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[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using AlF3·3H2O (0.200 g, 0.11 mmol) and phen (0.200 g, 1.45 mmol). Pale red solid. Yield 0.315 g, 79%. Required for C12H10AlF3N2O (324.9): C, 44.4; H, 3.1; N, 8.5%. IR (Nujol, ν/cm⁻¹): 3200 br (ν O–H), 1680 (δ O–H–O), 560, 543, 511 (Ga–F).

[AlF3(phen)(OH2)]

Method as for [AlF3(terpy)]·3H2O using AlF3·3H2O (0.200 g, 0.11 mmol) and phen (0.200 g, 1.45 mmol). Pale red solid. Yield 0.315 g, 79%. Required for C12H10AlF3N2O (324.9): C, 44.4; H, 3.1; N, 8.5%. IR (Nujol, ν/cm⁻¹): 3200 br (ν O–H), 1680 (δ O–H–O), 560, 543, 511 (Ga–F).
[1H, ArH], 9.02–8.96 (br [3H], ArH), 8.29–8.07 (br, m, [4H], ArH), 4.87 (s, H2O); (183 K): 9.28 (s), 8.98 (s), 8.76 (s), 8.33–8.22 (m), 7.95 (m). 13F{1H} NMR (298 K): not observed; (183 K): δ = 157 (br [F]), 199 (br, [2F]).

[GaCl3(terpy)]

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 product was isolated by filtration, washed with hexane and dried in vacuo. White solid. Yield: 0.402 g, 88%. Required for C15H11Cl3GaN3·CH2Cl2 (662.60): C, 50.7; H, 5.6; N, 6.3.

[GaCl3(Bu3-terpy)]

A solution of Bu3-terpy (0.111 g, 0.278 mmol) in anhydrous CH2Cl2 (5 mL) was added dropwise to a solution of GaCl3 (0.195 g, 0.278 mmol) in 5 mL anhydrous CH2Cl2 and dried in vacuo. White solid. Yield: 0.062 g, 77%. Required for C22H21Cl3GaN3·CH2Cl2 (662.60): C, 50.7; H, 5.6; N, 6.3. Found: C, 50.4; H, 5.6; N, 6.5%. 1H NMR (CD3CN, 298 K): δ = 1.42 (s, [18H], Bu), 1.44 (s, [9H], Bu), 7.47–7.46 (br m, [2H], ArH), 8.50 (br s, [2H], ArH), 8.61–8.60 (br m, [2H], ArH), 8.77 (br s, [2H], ArH).

The same reaction performed in a 1:1 stoichiometric ratio gave a spectroscopically identical product. However, crystals formed from the filtrate gave the ionic by-product [GaCl3(Bu3-terpy)][GaCl4(CH2Cl)2].

[cMe2N(CH3)2NMe(CH2)2][AlF3(OH2)]·2H2O

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 C13H23Al3F4O4 (536.4): C, 31.4; H, 7.8; N, 10.4. Found: C, 31.3; H, 7.8; N, 10.4%. IR (Nujol, ν/cm–1): 3370 br (ν O–H), 1673 (δ H–O–H), 616 br, 569 br, (Al–F). 1H NMR (CD3CN, 298 K): δ = 4.87 (s, H2O), 3.35 (t (ν HH 6.0 Hz), [4H], CH2), 3.07 (s, [H8], CH2).

13F{1H} NMR (CD3CN, 298 K): δ = 1.11 mmol) in 5 mL anhydrous CH2Cl2. A white precipitate 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 a further 10 mL CH2Cl2 in vacuo. The reaction solvent gave crystals suitable for X-ray analysis. X-ray diﬀraction. The corresponding gallium and indium fluoride reactions were conducted similarly.

[Me2N(CH2)2NMe(CH2)2][Ga2F8(OH2)2]·2H2O

Required for C31H24F2Ga2N4O4 (619.9): C, 27.0; H, 6.8; N, 9.0. Found: C, 26.7; H, 6.4; N, 9.8%. 1H NMR (CD3CN, 298 K): δ = 4.87 (s, H2O), 3.35 (t (ν HH 6.0 Hz), [4H], CH2), 3.07 (s, [H8], CH2), 2.67 (br s, [4H], CH2), 2.32 (s, [3H], Me). 13F{1H} NMR (CD3CN, 298 K): δ = −194.6 (6 lines 1JMF = 38 Hz).

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'‘-pentamethyldiethylentriamine (PMDTA), and to the diimines, 2,2'-bipyridyl and 1,10-phenanthroline.

[MF₃(terpy)]·3H₂O (M = Al, Ga or In)

The reaction of the MF₃·3H₂O with terpy in a 1:1 molar ratio in water at 180 °C/15 h, followed by removal of the solvent in vacuo at room temperature, gave high yields of the [MF₃(terpy)]·3H₂O as pale orange solids. Slow evaporation of a small portion of the mother liquor at ambient temperatures gave crystals of [MF₃(terpy)]·3H₂O (M = Al or Ga). For M = Al, the structure shows (Fig. 1) a distorted octahedral geometry about the aluminium, the distortions being largely due to the rigid terpy ligand which results in N–Al–N angles significantly less...
Table 1  Crystallographic parameters

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<td>10.460(2)</td>
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<tr>
<td>β/°</td>
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<td>123.374(4)</td>
<td>78.064(12)</td>
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<tr>
<td>U/Å³</td>
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<td>78.682(16)</td>
<td>62.738(8)</td>
<td>85.448(14)</td>
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<td>4</td>
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<td>1</td>
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<tr>
<td>μ(Mo-Kα)/mm⁻¹</td>
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<td>2.111</td>
<td>0.214</td>
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<tr>
<td>F(000)</td>
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<td>848</td>
<td>5785</td>
<td>17 446</td>
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<tr>
<td>Total number reflections</td>
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<td>16 476</td>
<td>23 822</td>
<td>3925</td>
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<tr>
<td>R₁</td>
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<td>0.141</td>
<td>0.035</td>
<td>0.079</td>
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<tr>
<td>Unique reflections</td>
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<td>2870</td>
<td>2822</td>
<td>3925</td>
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<tr>
<td>No. of parameters, restraints</td>
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<td>379, 0</td>
<td>170, 6</td>
<td>271, 0</td>
</tr>
<tr>
<td>R₁, wR₂ [I &gt; 2σ(I)]</td>
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<td>0.086, 0.192</td>
<td>0.078, 0.212</td>
<td>0.043, 0.109</td>
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<tr>
<td>R₁, wR₂ (all data)</td>
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<td>0.125, 0.211</td>
<td>0.098, 0.231</td>
<td>0.049, 0.111</td>
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</table>

Common items: T = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. 

The Al–F bond lengths are very similar to those observed in fac-[GaF₄(terpy)]·4H₂O. The Al–N bonds are shorter by ~0.05 Å, suggesting the macrocyclic ring may be shorter 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).

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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 $F_{trans}$ and $F_{trans}$, 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 $J_{AF}$ 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 [GaF₄(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 thf or [K(2.2.2-crypt)]F in MeCN; the [GaF₄(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',4''-tris-(t-butyl)-2,2',6',2''-terpyridyl, [GaCl₃(Bu₃-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)]·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)], 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 = 2.2511(5)–2.4118(6), Ga–N = 2.0412(5)–2.1024(15) Å).

![Fig. 5 View showing the H-bonding network (red) in [GaF₃(terpy)]·3H₂O.](image)

![Fig. 6 The structure of the cation in [GaCl₃(Bu₃-terpy)][GaCl₄] with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga₁–N₁ = 2.092(5), Ga₁–N₂ = 1.995(5), Ga₁–N₃ = 2.066(5), Ga₁–Cl₁ = 2.195(2), Ga₁–Cl₂ = 2.169(2), N₂–Ga₁–N₃ = 77.9(2), N₁–Ga₁–N₂ = 77.3(2), N₁–Ga₁–N₃ = 155.1(2), N₂–Ga₁–Cl₁ = 125.6(8), N₃–Ga₁–Cl₁ = 97.7(6), N₁–Ga₁–Cl₂ = 95.7(8), N₂–Ga₁–Cl₁ = 120.2(8), N₃–Ga₁–Cl₁ = 96.8(16), N₁–Ga₁–Cl₂ = 114.10(8).](image)
which means the neutral bipy ligand is trans to OH₂/F (Fig. 9 and 10).

For [InF₃(bipy)(OH₂)]·2H₂O,¹³ In−F₁trans = 2.065(2), 2.070(2), In−F₂trans = 2.002(3), In−N₁trans = 2.260(4), In−N₁transo = 2.243(4), In−O = 2.130(4) Å. Comparing the bond lengths in the three compounds reveals some interesting trends. The M−N distances are only slightly different (≤0.02 Å) between Al and Ga, whereas the M−F and M−O distances increase by between 0.06–0.1 Å; as noted with the terpy compounds above, the more electronegative donors have the greatest differences. The corresponding bond lengths all increase in the indium complex as expected, but here the differences with donor type 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).

Fig. 7 The structure of the centrosymmetric cation in [[Ga(terpy)F₂]₂(µ-F)₂]PF₆₂·4H₂O with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1−F₂ = 1.8564(17), Ga1−F₁ = 1.889(2), Ga1−F₁a = 2.003(2), Ga1−N₁ = 2.026(2), Ga1−N₁ = 2.095(3), Ga1−N₁ = 2.110(2), F₂−Ga1−F₁ = 98.39(8), F₂−Ga1−F₁a = 174.58(7), F₁−Ga1−F₁a = 76.19(9), F₂−Ga1−N₁ = 97.02(8), F₂−Ga1−N₁ = 88.40(9), F₁a−Ga1−N₁ = 102.47(9), F₁−Ga1−N₁ = 92.37(9), N₁−Ga1−N₁ = 77.26(10), N₁−Ga1−N₁ = 103.67(9), F₁−Ga1−N₁ = 93.03(9), N₂−Ga1−N₁ = 77.34(9), N₁−Ga1−N₁ = 153.85(10), Ga1−F₁−Ga1a = 103.81(9).

Fig. 8 View showing the H-bonding network (red) in [[Ga(terpy)F₂]₂(µ-F)₂][PF₆]₂·4H₂O.

Fig. 9 The structure of the Al complex in [AlF₃(bipy)(OH₂)]·2H₂O with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except those on the coordinated water) are omitted for clarity. Selected bond lengths (Å) and angles (°): Al1−F₁ = 1.786(2), Al1−F₂ = 1.781(2), Al1−F₃ = 1.743(2), Al1−O₁ = 1.900(2), Al1−N₁ = 2.050(3), Al1−N₂ = 2.072(3), F₂−Al1−F₁ = 93.35(11), F₁−Al1−F₁ = 92.22(11), F₃−Al1−O₁ = 97.24(10), F₂−Al1−O₁ = 88.30(11), F₁−Al1−O₁ = 91.16(11), F₃−Al1−N₁ = 92.19(10), F₂−Al1−N₁ = 90.08(10), F₁−Al1−N₁ = 91.55(10), F₂−Al1−N₂ = 86.50(11), F₁−Al1−N₂ = 88.32(11), O₁−Al1−N₁ = 92.39(11), N₁−Al1−N₂ = 78.18(11).

Fig. 10 The structure of Ga species in [GaF₃(bipy)(OH₂)]·2H₂O with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except those on the coordinated water) are omitted for clarity. Selected bond lengths (Å) and angles (°): Ga1−F₁ = 1.8892(15), Ga1−F₂ = 1.8442(17), Ga1−F₃ = 1.8857(14), Ga1−O₁ = 1.962(2), Ga1−N₁ = 2.093(2), Ga1−N₂ = 2.064(3), F₂−Ga1−F₁ = 92.41(7), F₁−Ga1−F₁ = 90.74(7), F₁−Ga1−F₃ = 175.68(7), F₂−Ga1−O₁ = 96.70(8), F₃−Ga1−O₁ = 87.76(7), F₁−Ga1−O₁ = 88.94(7), F₂−Ga1−N₂ = 92.28(9), F₃−Ga1−N₂ = 90.64(8), F₁−Ga1−N₂ = 92.19(8), F₃−Ga1−N₁ = 87.52(7), F₁−Ga1−N₁ = 89.86(7), O₁−Ga1−N₁ = 92.67(8), N₂−Ga1−N₁ = 78.35(9).
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; other factors, including the presence or absence of lattice solvent and hydrogen bonding also need to be considered. 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. 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 υ(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 [MF₃(bipy)(OH₂)]·2H₂O occur at lower frequency than in [MF₃(phen)(OH₂)] 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 CD₃CN, and therefore spectra were obtained from freshly prepared solutions in CD₃OD. The solutions decompose slowly forming F⁻ or HF₂⁻, 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 ¹⁹F{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 and aluminium complexes show inequivalent pyridyl rings, as expected from the static structures, but those of the gallium and indium complexes show inequivalent pyridyl rings, as expected from the static structures, but those of the gallium and indium complexes 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 MF₃·3H₂O with PMDTA**

PMDTA, Me₂N(CH₂)₂NMe(CH₂)₂NMe₂, is a flexible, aliphatic acyclic triamine analogue of Me₃-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 N₃-donor ligands, the hydrothermal route using PMDTA resulted in cleavage of the triamine and the formation of the 1,1,4-trimethylpiperazinium cation, [cMe₃N(CH₂)₂NMe(CH₂)₂]⁺. After removing all volatiles from the reaction mixtures and washing the residue with MeCN, the ¹H and ¹³C{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 [cMe₃N(CH₂)₂NMe(CH₂)₂][AlF₃(phen)(OH₂)]·2H₂O. The anion (Fig. 16) has been obtained previously as the [NMe₄]⁺ salt,³² and breaks up in solution to form [AlF₄]⁻, which was identified by a combination of ²⁷Al (δ = 48.7 [s]) and ¹⁹F{¹H} NMR data (δ = -194.6, 6 lines, J = 38 Hz).³²

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 [cMe₃N(CH₂)₂NMe(CH₂)₂]Cl has been reported previously³¹ 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 [cMe₃N(CH₂)₂NMe(CH₂)₂][GaF₆(phen)(OH₂)]·2H₂O, 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 ¹⁹F chemical shifts to solvent,³⁰,³² make identification of the anions uncertain without structural data. The reactions of the MF₃·3H₂O 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 AlF₃·3H₂O, ¹H and ¹⁹F{¹H} NMR spectra of the crude product showed protonated PMDTA and [AlF₄]⁻ as the only significant species. The contrast between the instability of PMDTA and the robust Me₃-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-macrocyclic complexes15 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 trifluoride complex contrasts with the moisture sensitivity of complexes containing gallium, indium and thallium trifluorides. However, this work has also shown that unlike [GaF3(BzMe2-tacn)]·4H2O, which is stable towards alkali metal or ammonium salts in aqueous MeCN, forming heterometallic (or mixed gallium-ammonium) complexes, competitive ions such as [NH4]+ and [PF6]−, [GaF3(terpy)]·3H2O reacts, with loss of a fluoride ligand, to form the dinuclear product, [[Ga(terpy)F2](µ-F)2]·[PF6]−·4H2O.

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 fluorides.

Acknowledgements

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References

23 23Al [I = 5/2, 100% abundance, Σ = 26.08 MHz, 0 = 0.149 × 10−28 m², R_C = 1170], 69Ga [I = 3/2, 60.4% abundance, Σ =
24.07 MHz, \( Q = 0.178 \times 10^{-28} \text{ m}^2, R_C = 237 \) \(^{71}\text{Ga} \ [I = 3/2, 39.6\% \text{ abundance}, \Xi = 30.58 \text{ MHz}, Q = 0.112 \times 10^{-28} \text{ m}^2, R_C = 322] \(^{115}\text{In} \ [I = 9/2, 95.7\% \text{ abundance}, \Xi = 22.04 \text{ MHz}, Q = 1.16 \times 10^{-28} \text{ m}^2, R_C = 1920].


