Complexes of aluminium, gallium and indium trifluorides with neutral oxygen donor ligands: Synthesis, properties and reactions

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ABSTRACT

The $MF_3\cdot3H_2O$ (M = Al, Ga or In) dissolve in hot dimethylsulfoxide (dmso) to form $[MF_3(OH_2)_2(dmso)]$; further dmso is not incorporated even after prolonged reflux. The X-ray structure of $[GaF_3(OH_2)_2(dmso)]$ shows *mer* fluorides and *trans* OH_2 ligands. The $[GaF_3(OH_2)_2(dmso)]$ reacts with Me_3tacn (1,4,7-trimethyl-1,4,7-triazacyclononane) or 2,2′-bipyridyl to give good yields of $[GaF_3(Me_3tacn)]\cdot xH_2O$ and $[GaF_3(bipy)(OH_2)]\cdot2H_2O$ at room temperature, previously obtained from $GaF_3\cdot3H_2O$ by a hydrothermal route. $[MF_3(OH_2)_2(dmso)]$ (M = Al or Ga) do not react with R_3PO (R = Me or Ph) in CH_2Cl_2 or MeOH, but with pyNO (pyridine-N-oxide), the products were $[AlF_3(OH_2)_2(pyNO)]$ and $[GaF_3(OH_2)_2(pyNO)]\cdot pyNO\cdot H_2O$. The structure of the latter shows equal numbers of the geometric isomers with *mer–trans* and *mer–cis* geometries, as well as lattice pyNO and H_2O. Pentamethyldiethylenetriamine (PMDTA) and $[GaF_3(OH_2)_2(dmso)]$ react to produce the zwitterion $[GaF_4(PMDTAH)]\cdot2H_2O$, which contains κ^2-PMDTA with the 'free' NMe_2 group protonated to balance the charge of the GaF_4^- unit. Crystals of $[\subset Me_2N(CH_2)_2NMe(CH_2)_2]_2[Ga_2F_8(OH_2)_2]\cdot H_2O$ containing a 1,1,4-trimethylpiperazinium cation, were obtained as a minor by-product. The anion is an edge-shared fluoride-bridged dimer, with the coordinated water ligands arranged *anti*. Attempts to prepare complexes with phosphine or thioether ligands by Cl/F exchange from the corresponding chloro-complexes with $[NMe_4]F$ were unsuccessful, halide exchange being accompanied by liberation of the soft donor ligand. X-ray structures are also reported for $[Me_2NH_2][trans\text{-}GaF_4(OH_2)_2]$ and $[AlCl_3(OAsPh_3)]$.

1. Introduction

The anhydrous trifluorides of aluminium, gallium and indium are inert polymers containing six-coordinate metal centres, and are unreactive towards neutral ligands [1,2]. The hydrates, $MF_3\cdot3H_2O$[1], are also very poorly soluble in water and organic solvents, but somewhat more reactive (although the reactivity varies from batch to batch – see further below) and, as a consequence, the coordination chemistry of these three fluorides was little explored until recently [3].

Aluminium [4–8] and gallium [9,10] fluoride complexes incorporating ^{18}F as a radiolabel, have attracted much interest as diagnostic imaging agents for positron emission tomography [11]. Key to their potential clinical suitability is the ability to incorporate the short-lived ^{18}F isotope ($t_{1/2}$ = 110 min) rapidly, preferably using aqueous conditions and that the resulting complexes are stable under physiological conditions. A fuller understanding of the coordination chemistry of these Group 13 fluorides is key to advancing the design of next generation ^{18}F imaging agents.

In previous studies [9,10,12] we found that using hydrothermal reactions (180 °C/15 h) the $MF_3\cdot3H_2O$ react with bi- or poly-dentate nitrogen donor ligands, including 2,2′,6′2″-terpyridyl (terpy), 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy) or 1,4,7-trimethyl-1,4,7,-triazacyclononane (Me_3tacn) to give good yields of the complexes *mer*-$[MF_3(terpy)]\cdot3H_2O$, *mer*-$[MF_3(bipy)(OH_2)]\cdot2H_2O$, *mer*-$[MF_3(phen)(OH_2)]$ and *fac*-$[MF_3(Me_3tacn)]\cdot4H_2O$, respectively. However, under similar conditions N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDTA) was cleaved to give the cyclic 1,1,4-trimethylpiperazinium cation, $[\subset Me_2N(CH_2)_2NMe(CH_2)_2]^+$ [9,10]. Several of the complexes were also made by Cl/F exchange from the corresponding chloro-complexes and $[Me_4N]F$ in anhydrous MeCN [9,10,12]. Apart from the hydrates,

aquo-fluoro-anions such as $[Al_2F_8(OH_2)_2]^{2-}$ or $[GaF_4(OH_2)_2]^-$ [3,9,10,13,14] and the aquo-imine complexes listed above, complexes of these fluorides with neutral oxygen donor ligands appear to be limited to the cation in $[AlF_2(thf)_4][\{(SiMe_3)_3C\}_2Al_2F_5]$ [15]. In this work we describe attempts to prepare Group 13 fluoride complexes with a range of oxygen donor ligands, as well as (unsuccessful) attempts to incorporate soft donor phosphines and thioethers.

2. Results and discussion

2.1. Metal trifluoride hydrates

During the work on the imine complexes described above, we observed that the reactivity and yields obtained from commercial samples of the $MF_3 \cdot 3H_2O$ varied widely [9,10,12], and since such effects could be crucial with less strongly binding ligands, we first examined the syntheses of $MF_3 \cdot 3H_2O$ and also compared data on various commercial samples. Differing reactivities between samples of some metal fluorides or fluoride hydrates is a common observation in this area [1,2,16–18], and may reflect different structural forms, but can also be due to such factors as particle size and the drying regime used in their synthesis. Two forms of $AlF_3 \cdot 3H_2O$ are known, the α-form has discrete octahedral molecules, $[AlF_3(OH_2)_3]$ (R-3), whilst the more stable β-form is a fluoride bridged polymer, $[\{AlF_2(OH_2)_2(\mu\text{-}F)\}_n] \cdot nH_2O$ (P4/n) [19]. The structure of $GaF_3 \cdot 3H_2O$ is less clear, whilst hydrated indium trifluoride has the same polymeric structure as β-$AlF_3 \cdot 3H_2O$ (P4/n) [20]. We prepared $AlF_3 \cdot 3H_2O$ by precipitation of cold aqueous aluminium sulfate solution with 10% HF, and $MF_3 \cdot 3H_2O$ (M = Ga or In) by dissolving freshly precipitated $M(OH)_3$ in aqueous HF, and drying the white powders *in vacuo* at ambient temperature [21]. PXRD studies showed that the hydrated AlF_3 precipitated from cold aqueous solution was the α-form, $[AlF_3(OH_2)_3]$ (R-3) as reported [19]. The PXRD of the precipitated indium fluoride hydrate confirmed it was the chain polymer $[\{InF_2(OH_2)_2(\mu\text{-}F)\}_n] \cdot nH_2O$ [20]. PXRD data on the freshly prepared sample and on commercial samples of $GaF_3 \cdot 3H_2O$ showed them all to have the rhombohedral structure (R-3) found in α-$[AlF_3(OH_2)_3]$; the PXRD data and the Rietveld fit are shown in Fig. 1.

Commercial samples of $AlF_3 \cdot 3H_2O$ were mostly the β-form $[\{AlF_2(OH_2)_2(\mu\text{-}F)\}_n] \cdot nH_2O$ (P4/n) [19], although one commercial sample of "$AlF_3 \cdot 3H_2O$" had a very complex PXRD pattern and we were unable to identify the species present.

The freshly prepared $MF_3 \cdot 3H_2O$ in general were more reactive than the commercial samples and when attempting the syntheses with weaker donor ligands, their use is preferred. For aluminium, the lower reactivity of the commercial samples may be due to the polymeric β-form, but for the Ga and In compounds, which have the same structures as the freshly made samples, it must reflect particle size or surface properties. Similar behaviour was noted in studies of SnF_2 and CeF_4 complexes [17,18].

2.2. Hydrothermal routes

Initial syntheses used the hydrothermal approach, which successfully produced the imine complexes via reaction of $MF_3 \cdot 3H_2O$ with the ligands in water (180 °C/15 h) [9,10,12]. The ligands used were Ph_3PO, $Ph_2P(O)CH_2P(O)Ph_2$, dmso and 12-crown-4, but in all cases, even with a large excess of ligand, the reactants were recovered unchanged, and we concluded that these ligands cannot compete for the metal centre with the large excess of water present. The hydrothermal reactions of $MF_3 \cdot 3H_2O$ (M = Al or Ga) with Ph_3AsO gave very small amounts of colourless crystals, identified by their ^{19}F NMR resonance at δ = −89 as Ph_3AsF_2 [22]. Since
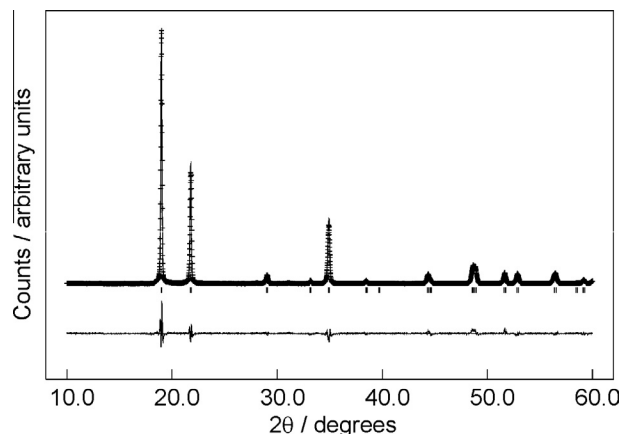

Fig. 1. Fit to the powder XRD pattern of $GaF_3 \cdot 3H_2O$ (Rw_p = 13.4%, R_p = 10.3%). Crosses mark the data points, upper continuous line the fit, and lower continuous line the difference. Tick marks show the positions of allowed reflections in R-3. Cell dimensions: a = 9.3812(3) and c = 4.73971(19) Å, with F and O disordered on a single site; no attempt was made to model H positions. The Ga–F/O distance is 1.845(3) Å.

Ph_3AsO is converted into Ph_3AsF_2 by aqueous HF [23], this is ascribed to a small amount of hydrolysis of the metal trifluoride.

2.3. Solution syntheses

The $MF_3 \cdot 3H_2O$ (M = Al or Ga) did not dissolve or react with MeCN or thf under prolonged reflux. Refluxing $GaF_3 \cdot 3H_2O$ with N, N-dimethylformamide gave some colourless crystals, which were shown by their X-ray crystal structure to be $[Me_2NH_2][trans\text{-}GaF_4(OH_2)_2]$, resulting from cleavage of the solvent, along with a white solid containing a mixture of species, hence this reaction was not pursued further. The structure of the $[Me_2NH_2][trans\text{-}GaF_4(OH_2)_2]$ (Fig. 2) reveals a centrosymmetric anion and with N–H···F hydrogen bonding linking the cations and anions into a 3D network (Fig. S1 in Supporting information). In freshly prepared CD_3OD the anion exhibits a broad singlet at δ = −174.8 in the $^{19}F\{^1H\}$ NMR spectrum, while the $[NMe_2H_2]^+$ cation has δ(^1H) = 2.67 (s, Me). The structure of $[LH_2][cis\text{-}GaF_4(OH_2)_2] \cdot H_2O$ (L = 4,4'-trimethylenedipyridine) has been reported [13], with bond lengths of Ga–F = 1.853(2)–1.882(2) Å and Ga–O = 2.017(2), 2.026(2) Å.

In contrast, the $MF_3 \cdot 3H_2O$ (M = Al or Ga) dissolved quite readily in hot dmso, and following work-up of the colourless solutions, $[MF_3(OH_2)_2(dmso)]$ were obtained in good yields (Scheme 1). A freshly prepared sample of $InF_3 \cdot 3H_2O$ dissolved only very slowly in hot dmso, giving the corresponding $[InF_3(OH_2)_2(dmso)]$ in low yield (12%). Somewhat unexpectedly, refluxing these mono-dmso adducts with further dmso, using longer reaction times, or adding dry molecular sieves, failed to displace the coordinated water from these species.

The structure of $[GaF_3(OH_2)_2(dmso)]$ (Fig. 3a) shows a six-coordinate gallium centre with a *mer*-GaF_3 arrangement and with the O-coordinated dmso *trans* to F. The bond lengths are unexceptional and the d(S–O) is little different to that in 'free' dmso [24]. There is also significant intermolecular F···H–O hydrogen bonding evident in the crystal structure (Fig. 3b), involving the coordinated water molecules in one Ga species with the F^- ligands in adjacent molecules. This gives rise to an extended network in the solid state.

The IR spectra of the three $[MF_3(OH_2)_2(dmso)]$ complexes show bands assigned to water, O-coordinated dmso ($\nu_{SO} \sim 1000$ cm^{-1}) [24], and broad features at lower energy that are attributed to terminal M–F stretching vibrations, strongly suggesting that they all have similar geometries. In CD_3OD solution the $[AlF_3(OH_2)_2(dmso)]$

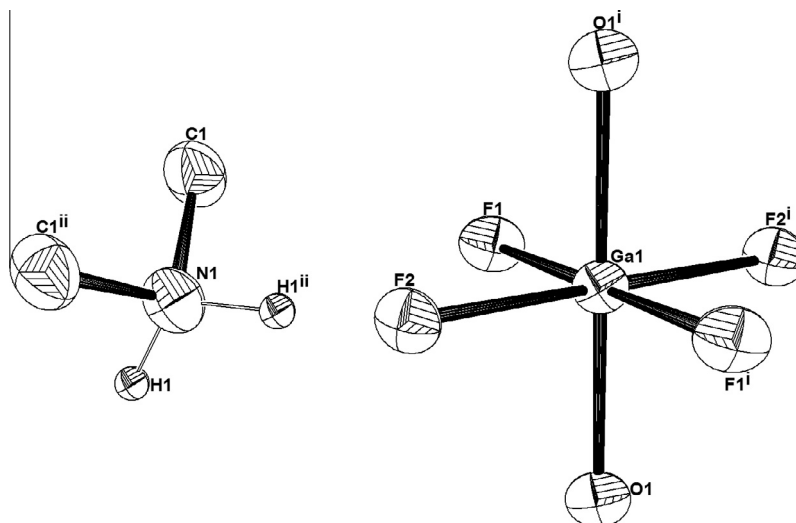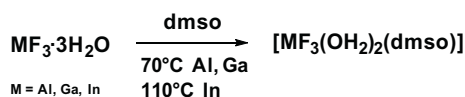**Fig. 2.** The structure of [Me$_2$NH$_2$][*trans*-GaF$_4$(OH$_2$)$_2$] with ellipsoids drawn at the 50% probability level. Hydrogen atoms on the water ligands and methyl carbons are omitted. Selected bond lengths (Å) and angles (°): Ga1–F1 = 1.8595(18), Ga1–F2 = 1.8974(18), Ga1–O1 = 1.987(2), F1–Ga1–F2 = 90.18(8), F1–Ga1–F2^i = 89.82(8), F1–Ga1–O1 = 91.35 (8), F1–Ga1–O1^i = 88.65(8), F2–Ga1–O1 = 89.92(8), F2–Ga1–O1^i = 90.08(8). Symmetry codes: $-x$, $y + 1/2$, $-z + 1/2$.

Scheme 1. Method for the preparation of [MF$_3$(OH$_2$)$_2$(dmso)].

exhibits a singlet at $\delta = -10.1$ in the ^{27}Al NMR spectrum, consistent with six-coordinate Al [9,10], and two ^{19}F{^{1}H} NMR resonances (integrals 2:1), consistent with the solid state structure being retained in solution. However, the ^{19}F{^{1}H} NMR spectrum of [GaF$_3$(OH$_2$)$_2$(dmso)] in CD$_3$OD at ambient temperature shows only a broad singlet, which resolves on cooling the solution into two resonances, suggesting the complex is dynamic at room temperature. The [InF$_3$(OH$_2$)$_2$(dmso)] does not exhibit a ^{19}F{^{1}H} NMR resonance at ambient temperatures, but shows three main resonances at low temperatures, indicative of decomposition in solution.

A number of reactions of the soluble, molecular [MF$_3$(OH$_2$)$_2$-(dmso)] with other neutral ligands were then attempted (Scheme 2). [GaF$_3$(OH$_2$)$_2$(dmso)] reacts readily with Me$_3$tacn in CH$_2$Cl$_2$ or with bipy in MeOH at room temperature to give good yields of [GaF$_3$(Me$_3$tacn)]·xH$_2$O and [GaF$_3$(bipy)(OH$_2$)]·2H$_2$O, providing alternative routes to these species directly from the trifluoride precursor under much milder reaction conditions than the hydrothermal method used previously [10,12].

Phosphine oxides have been shown to form stable complexes with many p-block fluorides [3], including SiF$_4$ [25], GeF$_4$ [26], SnF$_4$ [27], SnF$_2$ [18], TeF$_4$ [28], AsF$_3$ [29] and SbF$_3$ [29]. It was somewhat unexpected, therefore, that all attempts to form phosphine oxide complexes by refluxing [MF$_3$(OH$_2$)$_2$(dmso)] (M = Al or Ga) with Ph$_3$PO, Me$_3$PO or R$_2$P(O)CH$_2$P(O)R$_2$ (R = Me or Ph) in CH$_2$Cl$_2$, MeOH, or EtOH solution were unsuccessful, only the starting materials were recovered. The failure of the hydrothermal route has been noted above; similarly, the MF$_3$·3H$_2$O did not react with R$_3$PO in refluxing MeOH or CH$_2$Cl$_2$.

Use of pyridine N-oxide as a ligand was more successful, and reaction of [AlF$_3$(OH$_2$)$_2$(dmso)] with two mol. equivalents of pyNO in MeOH gave [AlF$_3$(OH$_2$)$_2$(pyNO)] as a white solid. The corresponding reaction of [GaF$_3$(OH$_2$)$_2$(dmso)] with three mol. equivalents of pyNO produced a colourless oil, which, over several days, deposited a quantity of colourless crystals. The latter had the analytical

composition GaF$_3$(OH$_2$)$_3$(pyNO)$_2$. The structure (Fig. 4) shows two geometric isomers of [GaF$_3$(OH$_2$)$_2$(pyNO)] present in equal ratio, both have *mer*-trifluoride coordination, and with lattice pyNO and H$_2$O also present. The Ga1-centred molecule has *trans*–OH$_2$ ligands and with pyNO *trans* to F, whilst Ga2 has *cis*–OH$_2$ ligands, with pyNO *trans* to OH$_2$. The molecules are linked into dimers by F···H–O hydrogen bonding. The lattice pyNO is also involved in H-bonding to the coordinated H$_2$O ligands. The Ga–F, Ga–OH$_2$ and Ga–ONpy bond distances are similar in the two isomers.

In CD$_3$OD solution at 298 K the ^{1}H NMR spectrum of [GaF$_3$-(OH$_2$)$_2$(pyNO)]·pyNO·H$_2$O exhibits only three resonances associated with the pyNO, and the corresponding ^{19}F{^{1}H} NMR spectrum is a broad singlet. This shows that the complex is exchanging or dissociating the neutral ligands in solution. At 183 K the ^{1}H NMR spectrum has six broad C–H resonances and the ^{19}F{^{1}H} NMR spectrum contains three overlapping resonances $\delta = -174.1, -175.0, -176.5$.

The corresponding [AlF$_3$(OH$_2$)$_2$(pyNO)] shows two sharp ^{19}F {^{1}H} NMR resonances (integrals 2:1) in CD$_3$OD solution at 298 K, suggesting the complex is stable in solution, and that only one isomer is present. The increasing lability of neutral ligands in the fluoride complexes as Group 13 is descended is also found in other systems [9,10,12]. The IR spectrum of the Al complex shows v (NO) at 1154 cm^{-1}, significantly lower than the value in pyNO itself (1265 cm^{-1}), and the values in [AlX$_3$(pyNO)] (X = Cl or Br) (both 1204 cm^{-1}) [30]. [GaF$_3$(OH$_2$)$_2$(pyNO)]·pyNO also exhibits v (NO) at 1154 cm^{-1} for the coordinated ligand, and 1265 cm^{-1} for the lattice pyNO, which compare with values of 1198 and 1192 cm^{-1} for the [GaX$_3$(pyNO)] (X = Cl or Br) respectively [31,32].

Since the coordinated water ligands are not displaced completely by other O-donor ligands, whereas Me$_3$-tacn is successful in this respect, and the structure of [GaF$_3$(py)$_3$] has been reported [33], we also reacted [GaF$_3$(OH$_2$)$_2$(dmso)] with pyridine. [GaF$_3$(OH$_2$)$_2$(dmso)] dissolves partially in pyridine, and after filtration to remove the solid (which contains a complex mixture of products by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy), some crystals formed from the mother liquor after a few days. The crystal structure confirmed these to be *mer*–*trans*-[GaF$_3$(OH$_2$)(py)$_2$] (Fig. 5a); the Ga–F and Ga–N bond distances are similar to those in *mer*-[GaF$_3$(py)$_3$] [33].

The structure shows the molecules are associated into a 3D network arising through both hydrogen bonding between the fluoride
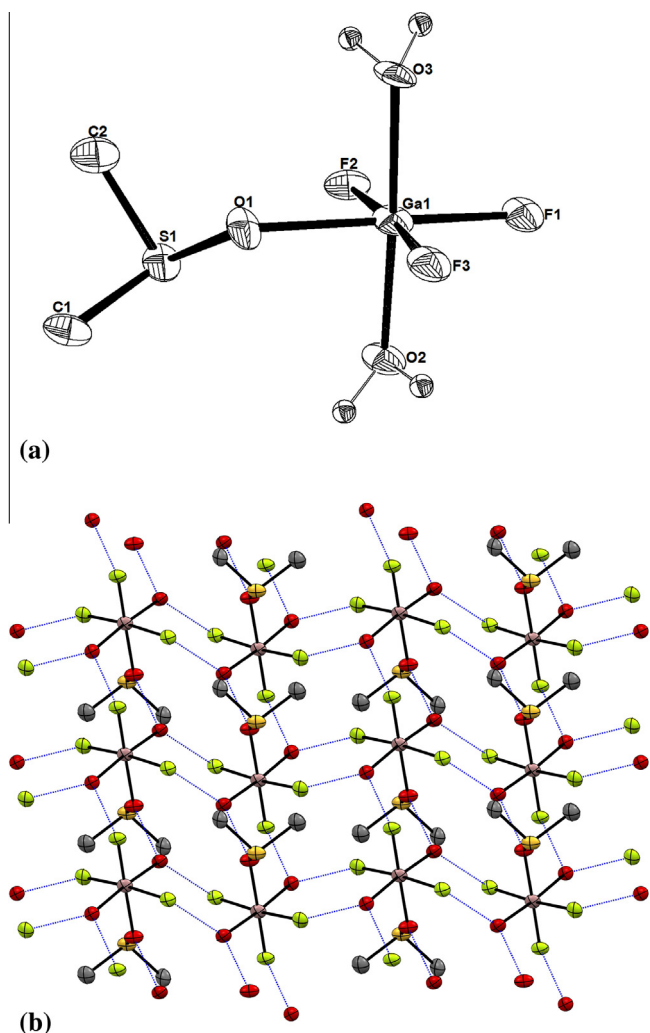
(a)

(b)

Fig. 3. (a) The structure of *mer–trans*-[GaF$_3$(OH$_2$)$_2$(dmso)] with ellipsoids drawn at the 50% probability level. Methyl group hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ga1–F1 = 1.865(7), Ga1–F2 = 1.870(5), Ga1–F3 = 1.876(5), Ga1–O3 = 1.993(6), Ga1–O1 = 2.042(8), Ga1–O2 = 1.972(7), S1–O1 = 1.549(8), F1–Ga1–F2 = 92.0(3), F1–Ga1–O3 = 92.7(3), F1–Ga1–F3 = 94.7(3), F1–Ga1–O2 = 90.9(3), F2–Ga1–O3 = 91.8(3), F2–Ga1–O1 = 88.5(3), F2–Ga1–O2 = 90.2(3), O3–Ga1–O1 = 87.7(3), F3–Ga1–O3 = 88.4(2), F3–Ga1–O1 = 84.8(3), F3–Ga1–O2 = 89.2(3), O2–Ga1–O1 = 88.7(3), S1–O1–Ga1 = 124.4(4); (b) The H-bonding network (blue) in the crystal structure of [GaF$_3$(OH$_2$)$_2$(dmso)] (colour key: pink = Ga, yellow = S, green = F, red = O, grey = C). (Color online.)

Scheme 2. Reactions of [MF$_3$(OH$_2$)$_2$(dmso)].
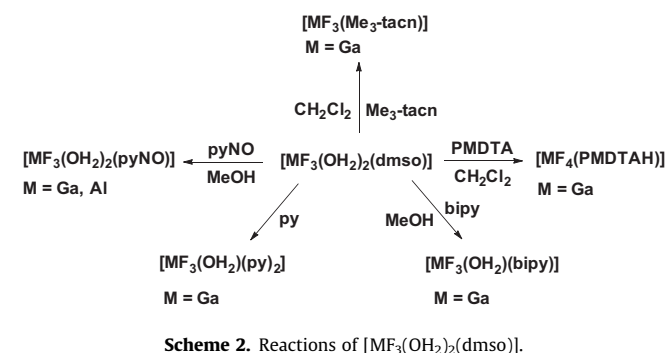
and the retained OH$_2$ ligands, as well as through π-stacking of the pyridine rings in the solid state, as shown in Figs 5b and c.

In an effort to obtain [GaF$_3$(OH$_2$)(py)$_2$] as a single product, the reaction was repeated in MeOH solution with two molar equivalents of py, however, ^{1}H and ^{19}F{^{1}H} NMR spectra of the

product after work-up showed a similar complicated mixture of species present. Hence, this was not pursued further.

We reported previously [12] that the reaction of PMDTA with GaF$_3$·3H$_2$O under hydrothermal conditions resulted in cleavage of the triamine to give a complex formulated as [⊂Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]$_2$[Ga$_2$F$_8$(OH$_2$)$_2$]·2H$_2$O, with a 1,1,4,-trimethylpiperazinium cation, on the basis of analytical and spectroscopic data, and by analogy with the crystallographically characterised, [⊂Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]$_2$[Al$_2$F$_8$(OH$_2$)$_2$]·2H$_2$O [12]. In contrast, reaction of [GaF$_3$(OH$_2$)$_2$(dmso)] with PMDTA in CH$_2$Cl$_2$ solution at room temperature gave the zwitterionic complex [GaF$_4$(PMDTAH)]·2H$_2$O, which contains κ^2 coordinated triamine, with the free NMe$_2$ group protonated to balance the charge of the GaF$_4^-$ unit (Fig. 6).

In solution the complex slowly decomposes, and crystals obtained by diffusion of hexane into a CH$_2$Cl$_2$ solution of [GaF$_4$(PMDTAH)]·2H$_2$O over several weeks, confirmed the formation of the dianion [⊂Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]$_2$[Ga$_2$F$_8$(OH$_2$)$_2$]·2H$_2$O (Fig. 7). The geometry is similar to that of the aluminium analogue [12], although the crystals are not isomorphous. The Ga–O and Ga–F bonds are ~0.07–0.08 Å longer than the corresponding bonds to aluminium. The anion appears to be unstable in solution (as is the aluminium analogue [12]) since in CD$_3$OD solution only a broad singlet ^{19}F{^{1}H} NMR resonance is observed at δ = −162.

2.4. Attempted Cl/F exchange reactions from [MCl$_3$(L)], L = OPR$_3$ or OAsR$_3$

A further possible entry route to fluoro-Group 13 complexes is via Cl$^-$/F$^-$ exchange using a fluoride source, such as [Me$_4$N]F, and the corresponding chloro-complexes [3,9,10,12]. In order to explore this with Group 13 fluoride complexes and phosphine oxide and arsine oxide ligands, the distorted tetrahedral [AlCl$_3$(OPR$_3$)] (R = Me or Ph) and [GaCl$_3$(OPMe$_3$)] complexes were prepared from the appropriate MCl$_3$ and ligand in anhydrous CH$_2$Cl$_2$ solution [34,35]. In a similar reaction, AlCl$_3$ with OAsPh$_3$ in a 1:1 mol. ratio in CH$_2$Cl$_2$ afforded [AlCl$_3$(OAsPh$_3$)], which appears to be the first example of an aluminium(III) halide–arsine oxide complex. The complex is a distorted tetrahedron (Fig. 8) with a bent Al–O–As linkage (146.7(3)°), in contrast to the linear Al–O–P linkage of [AlCl$_3$(OPPh$_3$)] [34]. The d(Al–O) and d(Al–Cl) are similar to those in the Ph$_3$PO complex (1.733(4) and 2.099(2) Å, respectively) [34]. The ^{27}Al NMR spectrum shows a singlet at δ = 93.1, which compares to [AlCl$_3$(OPPh$_3$)] (δ = 90) [34].

A solution of [AlCl$_3$(OAsPh$_3$)] in CH$_2$Cl$_2$ deposited crystals of Ph$_3$AsCl$_2$ (identified by a unit cell comparison with literature data [36]) after a week in a freezer (−18 °C). The conversion of OAsR$_3$ to R$_3$AsCl$_2$ under mild conditions by GeCl$_4$ has been observed previously [26].

Treatment of a solution of either [GaCl$_3$(OPMe$_3$)] or [AlCl$_3$(OPMe$_3$)] with three molar equivalents of [NMe$_4$]F in dry CH$_2$Cl$_2$ instantly produced white precipitates, and the phosphine oxide was liberated from the metal (confirmed by ^{31}P NMR spectroscopy). Thus, halide exchange also fails to generate phosphine oxide complexes of these metal ions.

2.5. Attempts to obtain soft donor ligand complexes

Given the difficulties of displacing water from MF$_3$·3H$_2$O or [MF$_3$(OH$_2$)$_2$(dmso)] by hard oxygen donor ligands, the direct reaction of these reagents with phosphine or thioether donors was considered highly unlikely to be successful, and efforts were therefore centred on Cl/F exchange under anhydrous conditions from corresponding chloro-complexes. Treatment of the diphosphine complexes, *trans*-[AlCl$_2${o-C$_6$H$_4$(PMe$_2$)$_2$}$_2$][AlCl$_4$] [37], *trans*-[GaCl$_2${o-C$_6$H$_4$(PMe$_2$)$_2$}$_2$][GaCl$_4$] [38] or [In$_2$Cl$_6${o-C$_6$H$_4$(PMe$_2$)$_2$}$_2$]
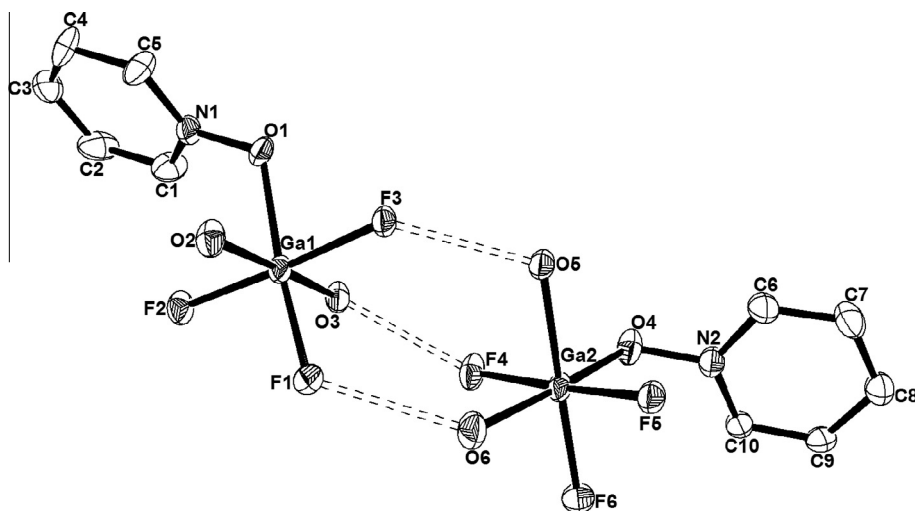
Fig. 4. The structure of the two geometric isomers in [GaF$_3$(OH$_2$)$_2$(pyNO)]·pyNO·H$_2$O showing the hydrogen bonding and with ellipsoids drawn at the 50% probability level. The lattice pyNO and H$_2$O are omitted for clarity. Hydrogen atoms on the coordinated water and pyNO are not shown. Selected bond lengths (Å) and angles (°): Ga1-centred molecule (*mer–trans*) Ga1–F1 = 1.879(4), Ga1–F2 = 1.856(4), Ga1–F3 = 1.858(4), Ga1–O1 = 1.997(5), Ga1–O2 = 1.982(5), Ga1–O3 = 2.003(5), F1–Ga1–O2 = 89.3(2), F1–Ga1–O3 = 91.9(2), F2–Ga1–F1 = 93.86(19), F2–Ga1–O1 = 92.57(19), F2–Ga1–O2 = 88.9(2), F2–Ga1–O3 = 88.22(19), F3–Ga1–F1 = 91.11(19), F3–Ga1–O1 = 82.56(19), F3–Ga1–O2 = 94.1(2), F3–Ga1–O3 = 88.67(19), O1–Ga1–O3 = 90.0(2), O2–Ga1–O1 = 89.1(2); Ga2-centred molecule (*mer–cis*) Ga2–F4 = 1.855(4), Ga2–F5 = 1.863(4), Ga2–F6 = 1.866 (4), Ga2–O4 = 1.985(5), Ga2–O5 = 1.995(5), Ga2–O6 = 2.013(6), F4–Ga2–F6 = 93.41(19), F4–Ga2–O4 = 86.0(2), F4–Ga2–O5 = 87.33(19), F4–Ga2–O6 = 88.0(2), F5–Ga2–F6 = 90.32(19), F5–Ga2–O4 = 95.6(2), F5–Ga2–O5 = 88.96(19), F5–Ga2–O6 = 90.3(2), F6–Ga2–O4 = 90.0(2), F6–Ga2–O6 = 90.1(2), O4–Ga2–O5 = 89.3(2), O5–Ga2–O6 = 90.7(2).

[39] with six molar equivalents of anhydrous [NMe$_4$]F [40,41] in anhydrous CD$_2$Cl$_2$ solution produced immediate white precipitates. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the supernatant liquids showed only o-C$_6$H$_4$(PMe$_2$)$_2$, and the solution did not exhibit any ^{19}F resonances. The white precipitates, after separation and drying showed strong IR features at 960–970 cm^{-1} ([NMe$_4$]$^+$) and ~665 cm^{-1} (M = Al), ~ 560–520 cm^{-1} (M = Ga) and ~ 470 cm^{-1} (M = In) which are assigned as M–F stretches. We conclude therefore that in these compounds fast Cl/F exchange occurs with "naked" fluoride, but this is accompanied by dissociation of the diphosphine from the metal centre, and the "MF$_3$" produced then polymerise and precipitate. Similar results were obtained in studies of Cl/F exchange in some hard d-block systems including zirconium and hafnium diphosphines [16], and it seems that the hard Lewis acidic metal centres often prefer to form M–F–M bridges rather than coordinate to soft phosphines [3]. The reaction of [AlCl$_3$(PMe$_3$)] [37] with [NMe$_4$]F in anhydrous CH$_2$Cl$_2$ similarly liberated PMe$_3$. [AlF$_3$(PMe$_3$)] has been predicted to be a stable complex by DFT calculations (although with AlF$_3$ a weaker Lewis acid than AlCl$_3$ towards PMe$_3$); the calculations refer to the gas phase molecular monomer [42], and naturally did not consider the formation of AlF$_3$ polymer as a decomposition route. [AlCl$_3$(SMe$_2$)] [43] was also decomposed with loss of the dimethylsulfide on treatment with [NMe$_4$]F in CH$_2$Cl$_2$.

3. Experimental

3.1. General information

The MF$_3$·3H$_2$O (M = Al, Ga or In), 2,2′-bipyridyl, 1,4,7-trimethyl-1,4,7-triazacyclononane (Me$_3$-tacn), N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMDTA), Ph$_3$PO, Me$_3$PO, Ph$_3$AsO and pyNO were obtained from Sigma–Aldrich or Alfa-Aesar. Solvents were dried by distillation prior to use, CH$_2$Cl$_2$ and CH$_3$CN from CaH$_2$, methanol from magnesium/diiodine. Hydrothermal preparations were conducted in a 23 mL Teflon reactor vessel placed in a Parr stainless steel autoclave [12]. ^{1}H NMR spectra were recorded in CD$_3$OD on a Bruker AVII 400 spectrometer and referenced to the residual proton resonance. ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded in CD$_3$OD using a Bruker AVII 400 spectrometer, with CFCl$_3$ and H$_3$PO$_4$ respectively as external references. ^{27}Al NMR spectra were recorded with a Bruker DPX400 spectrometer and referenced to external [Al(H$_2$O)$_6$]$^{3+}$ in H$_2$O at pH = 1. Infra-red spectra were recorded as Nujol mulls between CsI plates on a Perkin Elmer Spectrum100 spectrometer over the range 4000–200 cm^{-1}. Microanalyses were undertaken by London Metropolitan University

CARE: concentrated aqueous solutions of HF cause serious burns on skin contact and should be handled with due care, and appropriate personal safety equipment worn.

3.2. AlF$_3$·3H$_2$O

In a Teflon beaker, Al$_2$(SO$_4$)$_3$·16H$_2$O (4.05 g, 6.42 mmol) was dissolved in freshly distilled water (15 mL). After adding HF$_{(aq)}$ 40% (2 mL, 46.0 mmol), a white precipitate formed immediately. The white solid was filtered off, rinsed with water (20 mL) and dried *in vacuo*. Yield: 1.58 g, 89%. IR (Nujol/cm^{-1}): ~3500 (vbr) (O–H, H$_2$O), 1670 (br) (H–O–H), 585 (m), 545 (m) (Al–F).

3.3. GaF$_3$·3H$_2$O

Ga(NO$_3$)$_3$·xH$_2$O (4.08 g, 15.9 mmol) was dissolved in freshly distilled water (15 mL). A solution of KOH (~5 M) in water (10 mL) was added, giving a white precipitate of Ga(OH)$_3$. The precipitate was filtered off, rinsed with water and suspended in HF 40% (10 mL, 230 mmol) in a Teflon beaker. The mixture was heated to 100 °C giving a clear solution, which was cooled to ambient temperature. Ethanol (20 mL) was added to the mixture, causing the precipitation of GaF$_3$·3H$_2$O. The product was filtered off and dried *in vacuo*. Yield: 1.61 g, 56%. IR (Nujol/cm^{-1}) 3500 (br), 3180 (br) (O–H, H$_2$O), 1659 (m) (H–O–H), 450 (vbr) (Ga–F).

3.4. InF$_3$·3H$_2$O

In$_2$(SO$_4$)$_3$·xH$_2$O (3.3 g, ~6.4 mmol) was dissolved in hot freshly distilled water (50 mL). A concentrated solution of NaOH (5 mL of 10 M) was added until a white solid precipitated. The solid was filtered off and washed with water. The solid was then suspended again in water (10 mL) in a Teflon beaker and HF 40% (5 mL, 115 mmol) were added, giving a clear solution. After several
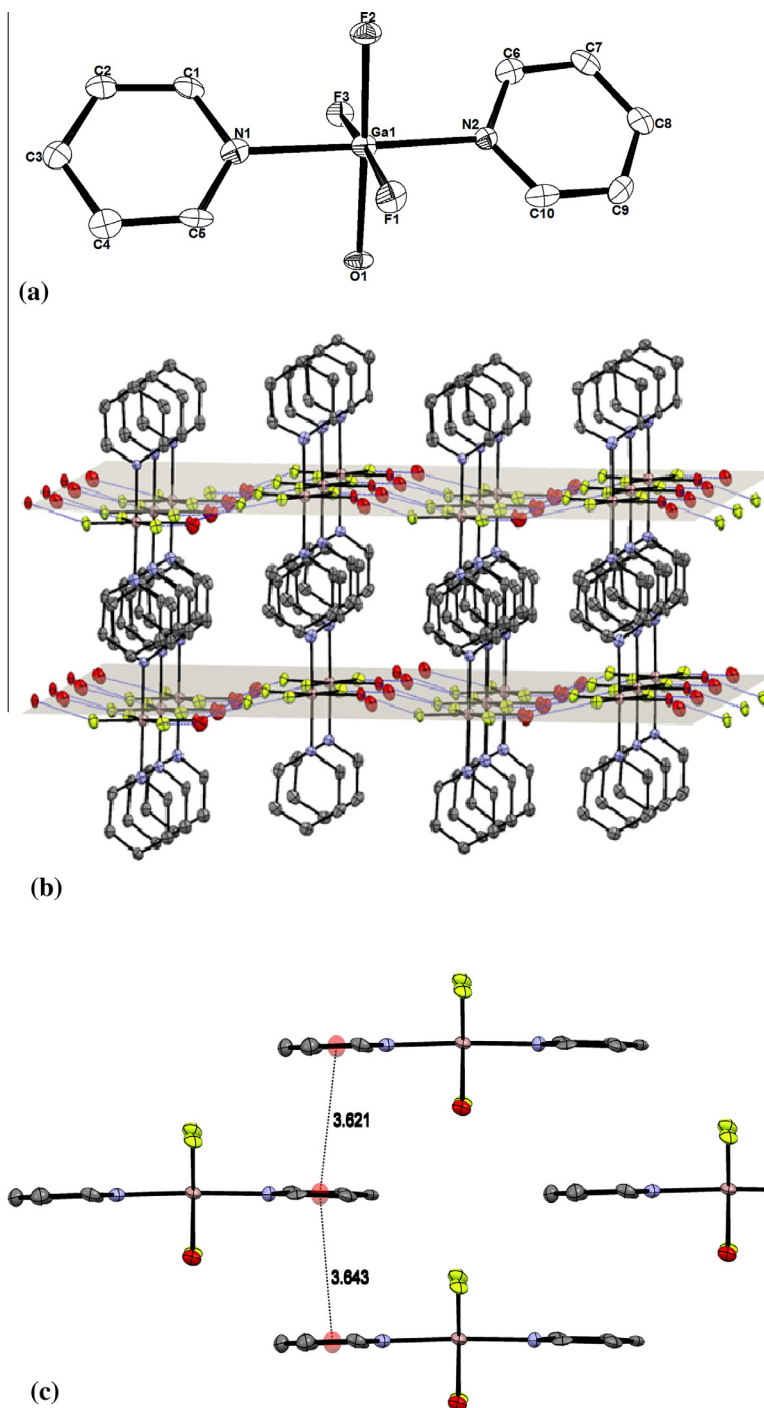
Fig. 5. (a) The structure of *mer–trans*-[GaF$_3$(OH$_2$)(py)$_2$] with ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ga1–N2 = 2.074(7), Ga1–N1 = 2.093 (7), Ga1–F2 = 1.889(6), Ga1–F3 = 1.867(6), Ga1–F1 = 1.854(6), Ga1–O1 = 2.014(7), F2–Ga1–N2 = 90.8(4), F2–Ga1–N1 = 89.2(4), F3–Ga1–N2 = 88.8(3), F3–Ga1–N1 = 88.2(3), F3–Ga1–F2 = 93.0(3), F3–Ga1–O1 = 87.4(3), F1–Ga1–N2 = 91.2(3), F1–Ga1–N1 = 91.8(3), F1–Ga1–F2 = 94.2(3), F1–Ga1–O1 = 85.5(3); (b) View of the hydrogen bonding in [Ga (F$_3$(OH$_2$)(py)$_2$] shown in grey; (c) view of the π-stacking.

minutes a white solid started to precipitate and the mixture was allowed to stand overnight. The solvent was decanted off and the solid dried *in vacuo*. Yield: 0.89 g, 62%. IR (Nujol/cm^{-1}): 3350 (br) (O–H, H$_2$O), 1640 (m) (H–O–H), 452 (vbr) (In–F).

3.5. [AlF$_3$(OH$_2$)$_2$(dmso)]

AlF$_3$·3H$_2$O (0.10 g, 0.72 mmol) was added to dmso (30 mL) and stirred. The mixture was gradually heated to 75 °C and left at this

temperature for 10 min, causing complete dissolution to give a colourless solution. After cooling, the solution was filtered to remove any solid deposited, and the solvent was removed *in vacuo*, giving a white solid. Yield: 0.104 g, 72%. Required for C$_2$H$_{10}$AlF$_3$O$_3$S: C, 12.1; H, 5.1. Found: C, 12.1; H, 4.9%. IR (Nujol/cm^{-1}): 3410 (br) (O– H, H$_2$O), 1660 (m) (H–O–H), 1010 (br) (S=O), 524 (br) (Al–F). ^{1}H NMR (CD$_3$OD, 298 K): δ = 2.66 (s, Me). 4.85 (s, H$_2$O). ^{19}F{^{1}H} NMR (CD$_3$OD, 298 K): δ = −173.6 (s, [2F]), −177.2 (s [F]); (183 K): −171.8 (br s, [2F]), −176.5 (s, [F]). ^{27}Al NMR (CD$_3$OD, 298 K): δ = −10.1 (s).
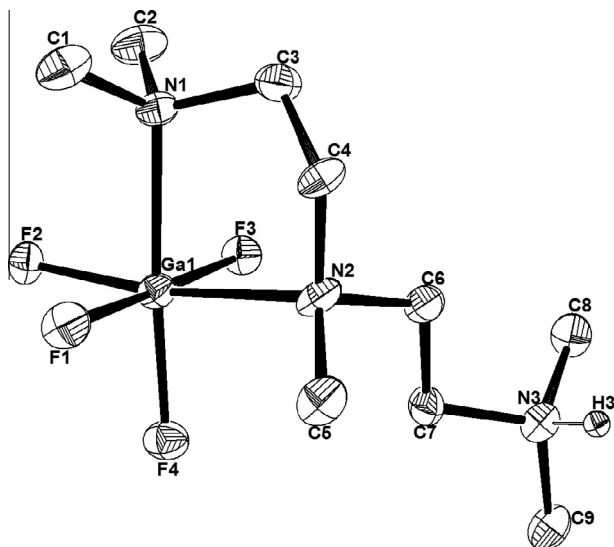
Fig. 6. The structure of [GaF$_4$(PMDTAH)].2H$_2$O with ellipsoids drawn at the 50% level. Selected bond lengths (Å) and angles (°): Ga1–F1 = 1.8641(16), Ga1–F2 = 1.8850(15), Ga1–F3 = 1.8687(15), Ga1–F4 = 1.8417(17), Ga1–N1 = 2.153(2), Ga1–N2 = 2.192(2), F1–Ga1–F2 = 91.14(6), F1–Ga1–N1 = 90.00(7), F1–Ga1–N2 = 88.16(6), F2–Ga1–N1 = 87.11(8), F3–Ga1–F2 = 91.55(6), F3–Ga1–N1 = 87.32(7), F3–Ga1–N2 = 88.73(6), F4–Ga1–F1 = 92.26(6), F4–Ga1–F2 = 95.96(7), F4–Ga1–F3 = 90.27(6), F4–Ga1–N2 = 93.08(8), N1–Ga1–N2 = 83.87(8).

3.6. [GaF$_3$(OH$_2$)$_2$(dmso)]

GaF$_3$·3H$_2$O (0.290 g, 1.6 mmol) was added to dmso (40 mL) and stirred. The mixture was gradually heated to 85 °C and left at this temperature for 10 min, causing almost complete dissolution of the solid. After cooling, the solvent was removed *in vacuo* giving a white solid. The solid was dissolved in methanol (10 mL), the solution was filtered to remove the unreacted GaF$_3$·3H$_2$O and the solvent removed again, giving a white solid. Yield: 0.278 g, 72%. Required for C$_2$H$_{10}$F$_3$GaO$_3$S: C, 10.0; H, 4.2. Found: C, 10.1; H, 4.1%. IR (Nujol/cm^{-1}): ~3400 (vbr) (O–H, H$_2$O), ~3180 (sh) (O–H, H$_2$O), 1605 (br) (H–O–H), 1004 (br) (S=O), 496 (br) (Ga–F). ^{1}H NMR (CD$_3$OD, 298 K): δ = 2.66 (s, Me), 4.92 (s, H$_2$O). ^{19}F{^{1}H} NMR (CD$_3$OD, 298 K): δ = –177.4 (br s); (183 K): –175.0 (br s [2F]), –176.6 (s, [F]).

3.7. [InF$_3$(OH$_2$)$_2$(dmso)]

InF$_3$·3H$_2$O (0.21 g, 0.92 mmol) was added to dmso (40 mL) and stirred. The mixture was gradually heated to 110 °C, leading to partial dissolution. The mother liquor was decanted off and, after cooling, the solvent was removed *in vacuo* giving a white solid. Yield: 0.032 g, 12%. Required for C$_2$H$_{10}$F$_3$InO$_3$S: C, 8.4; H, 3.5. Found: C, 8.5; H, 3.3%. IR (Nujol/cm^{-1}): 3320 (br) (O–H, H$_2$O), 1643 (m, H–O–H), 1001 (br) (S=O), 464 (br) (In–F). ^{1}H NMR (CD$_3$OD, 298 K): δ = 2.66 (s, Me), 4.86 (s, H$_2$O) ^{19}F{^{1}H} NMR (CD$_3$OD, 298 K): not observed; (183 K): δ = –133.5 (s), –136.7 (br), –187.65 (s).

3.8. [AlF$_3$(OH$_2$)$_2$(pyNO)]

[AlF$_3$(OH$_2$)$_2$(dmso)] (0.05 g, 0.25 mmol)) was suspended in MeOH (5 mL). A solution of pyNO (0.05 g, 0.57 mmol) in MeOH (5 mL) was added. After 2 h the solvent was removed under *vacuo* and the resulting white solid was washed with CH$_2$Cl$_2$ (5 mL) and dried *in vacuo*. Yield: 0.049 g, 90%. Required for C$_5$H$_9$AlF$_3$NO$_3$: C, 27.9; H, 4.2; N, 6.6. Found: C, 28.0; H, 4.1; N, 6.6%. IR (Nujol/cm^{-1}): 3606 (vb) (O–H, H$_2$O), 1605 (br) (H–O–H), 1154 (br) (N–O), 565 (br) (Al–F). ^{1}H NMR (CD$_3$OD, 298 K): δ = 4.85 (s, H$_2$O), 7.57 (s, [2H]), 7.65 (s, [H]), 8.36 (s, [2H]). ^{19}F{^{1}H} NMR (CD$_3$OD, 298 K): δ = –173.7 (s, [2F]), –177.3 (s, [F]).

3.9. [GaF$_3$(OH$_2$)$_2$(pyNO)]·pyNO·H$_2$O

[GaF$_3$(OH$_2$)$_2$(dmso)] (0.05 g, 0.21 mmol) was dissolved in MeOH (15 mL). pyNO (0.08 g, 0.62 mmol) was added, giving a colourless solution. After 7 h the solvent was removed *in vacuo* giving a colourless oil. After several days the oil partially solidified into crystals, which were manually separated from the oil and dried *in vacuo*. Yield: 0.043 g, 56%. Required for C$_{10}$H$_{16}$GaF$_3$N$_2$O$_5$: C, 32.4; H, 4.3; N, 7.6. Found: C, 32.3; H, 4.2; N, 7.4%. IR (Nujol/cm^{-1}): 3616 (br) (O–H, H$_2$O), 1605 (br, H–O–H), 1265, 1154, (br) (N–O), 565, 555 (Ga–F). ^{1}H NMR (CD$_3$OD, 298 K): δ = 4.86 (s, H$_2$O), 7.57 (s, [2H]), 7.65 (s, [H]), 8.36 (s, [2H]); (183 K): 7.65 (s), 7.75 (s), 7.77 (br s), 8.06 (br s), 8.46 (s), 8.73 (br s). ^{19}F{^{1}H} NMR (CD$_3$OD, 298 K): δ = –176.9 (s); (183 K): –174.1, –175.0, –176.5.
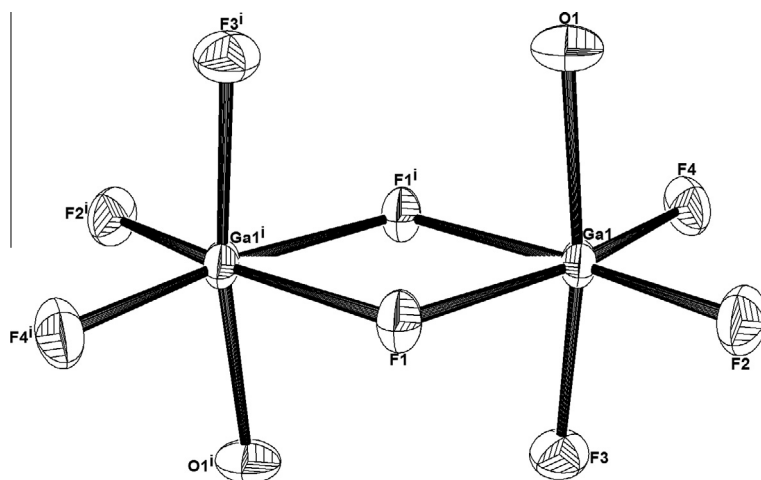
Fig. 7. The anion in [⊂Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]$_2$[Ga$_2$F$_8$(OH$_2$)$_2$]·2H$_2$O with ellipsoids drawn at the 50% probability level. The H-atoms on the water molecules were not located in the difference map. Selected bond lengths (Å) and angles (°): Ga1–F1 = 2.002(2), Ga1–F1 = 1.965(2), Ga1–F2 = 1.832(2), Ga1–F3 = 1.856(3), Ga1–F4 = 1.833(2), Ga1–F1^i = 1.965(2), Ga1–O1 = 1.946(3), F1–Ga1–F1^i = 76.37(12), F2–Ga1–F1 = 91.34(11), F2–Ga1–F3 = 93.37(12), F2–Ga1–F4 = 100.65(12), F2–Ga1–O1 = 90.74(13), F3–Ga1–F1^i = 88.59(11), F3–Ga1–F1 = 86.34(11), F4–Ga1–F1^i = 91.60(11), F4–Ga1–F3 = 94.05(12), F4–Ga1–O1 = 92.47(12), O1–Ga1–F1^i 85.81(12), O1–Ga1–F1 = 86.16(12), Ga1–F1–Ga1^i = 103.63(12). Symmetry codes: –x, y + 1/2, –z + 1/2.

Fig. 8. The structure of the Al1-centred molecule of [AlCl₃(OAsPh₃)]·0.5CH₂Cl₂ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level. H atoms and solvate molecules are omitted for clarity. The other crystallographically independent molecule is similar. Selected bond lengths (Å) and angles (°): Al1–O1 = 1.735(5), Al1–Cl1 = 2.124(3), Al1–Cl2 = 2.118(3), Al1–Cl3 = 2.144(3), As1–O1 = 1.687(5),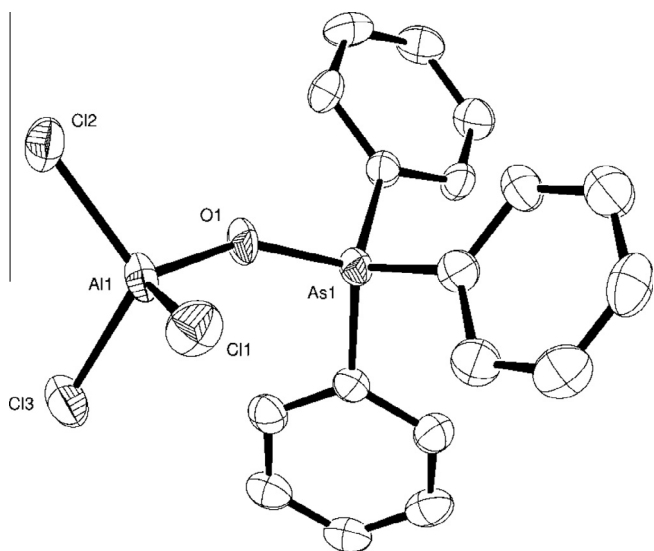 O1–Al1–Cl1 = 110.7(2), O1–Al1–Cl2 = 105.5(2), O1–Al1–Cl3 = 109.5(2), Cl1–Al1–Cl2 = 110.44(13), Cl1–Al1–Cl3 = 108.21(13), Cl2–Al1–Cl3 = 112.47(13), Al1–O1–As1 = 146.7(3).

3.10. [GaF₄(PMDTAH)]

[GaF₃(OH₂)₂(dmso)] (0.06 g, 0.25 mmol) was suspended in CH₂Cl₂ (5 mL). PMDTA (0.06 mL, 0.30 mmol) was added giving a clear solution after few minutes. After 2 h the solvent was removed *in vacuo* and the resulting solid washed with hexane, giving a white solid which was dried *in vacuo*. Yield: 0.04 g, 50%. Required for $C_9H_{24}F_4GaN_3$: C, 33.8; H, 7.6; N, 13.1. Found: C, 33.8; H, 7.7; N, 13.0%. IR (Nujol/cm⁻¹): 536, 524, 504 (Ga–F). ¹H NMR (CD₂Cl₂, 298 K): δ = 2.42 (s, [3H]), 2.57 (s, [6H]), 2.60 (s, [6H]), 2.95 (td, [4H]), 3.44 (td, [4H]), 3.46 (s, H). ¹³C{¹H} NMR (CD₂Cl₂, 298 K): δ = 40.80 ([C]), 44.82 ([C]), 48.57 ([C]), 49.71 ([C]), 54.78 ([2C]), 56.23 ([2C]), 56.74 ([C]). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = −156.1 (br s, [F]), −168.2 (br s, [2F]), −194.6 (br s, [F]). Evaporation of a CD₂Cl₂ solution gave crystals of [GaF₄(PMDTAH)]·2H₂O suitable for X-ray diffraction. Diffusion of hexane into a solution of the product in CH₂Cl₂ gave a few crystals after several weeks, which were shown to be [⊂Me₂N(CH₂)₂NMe(CH₂)₂]₂[Ga₂F₈(OH₂)₂]·2H₂O.

3.11. [GaF₃(Me₃tacn)]·xH₂O

[GaF₃(OH₂)₂(dmso)] (0.07 g, 0.29 mmol) was suspended in CH₂Cl₂ (8 mL). Me₃tacn (0.07 mL, 0.36 mmol) was added, giving a clear solution after ~2 min. After 2 h hexane (10 mL) was added and a white solid precipitated. The solid was filtered, washed with hexane and dried *in vacuo*. Yield: 0.08 g, 81%. Required for $C_9H_{23}F_3GaN_3O$: C, 34.2; H, 7.3; N, 13.3. Found: C, 33.9; H, 8.4; N, 12.7%. IR (Nujol/cm⁻¹): 3425 (br) (O–H), 1666 (br) (H–O–H), 520, 485 (Ga–F). ¹H NMR (CD₃CN, 298 K): δ = 2.63 (s, [9H]), 2.72 (m, [6H],), 2.85 (m, [6H]). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = −181.6 (br q). Colourless crystals were grown by adding hexane into a CH₂Cl₂ solution of the product and cooling in a freezer.

3.12. [GaF₃(OH₂)(bipy)]·2H₂O

[GaF₃(OH₂)₂(dmso)] (0.050 g, 0.21 mmol) was added to MeOH (10 mL) giving a colourless solution. A solution of bipy in MeOH (10 mL) was added. After 4 h the solvent was removed *in vacuo* giving a white solid. The solid was dissolved in the minimum amount of MeOH and left in the fridge overnight, causing the formation of crystals suitable for X-ray diffraction. Yield: 0.042 g, 60%. Required for $C_{10}H_{14}F_3GaN_2O_3$: C, 35.7; H, 4.2; N, 8.3. Found: C, 35.6; H, 4.1; N, 8.2%. IR (Nujol, ν/cm⁻¹): 3500, 3380 (br) (O–H, H₂O), 1660 (br) (O–H), 576, 539 (Ga–F). ¹H NMR (CD₃OD, 298 K): δ = 9.08 (br, [2H], ArH), 8.67 (br d, J_{HH} 8 Hz, [2H], ArH), 8.40 (br t, J_{HH} 7 Hz, [2H], ArH), 7.91 (br t, J_{HH} 6 Hz, [2H], ArH). ¹⁹F{¹H} NMR (CD₂Cl₂, 298 K): δ = −176.5.

3.13. [AlCl₃(OPMe₃)]

Under a dry dinitrogen atmosphere, a solution of OPMe₃ (0.060 g, 0.65 mmol) in CH₂Cl₂ (5 mL) was added to a suspension of AlCl₃ (0.088 g, 0.66 mmol) in CH₂Cl₂ (5 mL). The resulting solution was stirred for 1 h, then concentrated to about 2 mL *in vacuo*. The resulting white precipitate was isolated, washed with hexane (5 mL) and dried *in vacuo* to yield a white powder. Yield: 0.070 g, 48%. Required for $C_3H_9AlCl_3OP$: C, 16.0; H, 4.0. Found: C, 15.2; H, 4.5%. ¹H NMR (CD₂Cl₂, 295 K): δ = 1.92 (d, $^2J_{HP}$ 13.5 Hz). ³¹P{¹H} NMR (CH₂Cl₂, 295 K): δ = 70.0 (s). ²⁷Al NMR (CH₂Cl₂, 295 K): δ = 91.4 (s). IR (Nujol, ν/cm⁻¹): 1149 (s) (P=O), 495 (vs), 392 (br m) (Al–Cl).

3.14. [AlCl₃(OAsPh₃)]

Under a dry dinitrogen atmosphere, a solution of OAsPh₃ (0.301 g, 0.93 mmol) in CH₂Cl₂ (5 mL) was added to a suspension of AlCl₃ (0.128 g, 0.95 mmol) in CH₂Cl₂ (5 mL). The reaction was stirred for 2 h, then the colourless solution was decanted off to leave a white solid. The solid was washed with hexane (5 mL) and dried *in vacuo* to give a white powder. A second crop was obtained by layering the supernatant with hexane (5 mL) and later concentrating it to about 4 mL *in vacuo*, whereupon a white powder precipitated out. This was isolated by filtration and dried *in vacuo*. Block colourless crystals suitable for single crystal X-ray diffraction study were grown from the filtrate upon cooling to –18 °C. Combined yield: 0.135 g, 32%. Required for $C_{18}H_{15}AlAsCl_3O$: C, 47.4; H, 3.3. Found: C, 47.3; H, 3.4%. ¹H NMR (CD₂Cl₂, 295 K): δ = 7.59–8.06 (m, C₆H₅). ²⁷Al NMR (CH₂Cl₂, 295 K): δ = 93.1 (s). IR (Nujol, ν/cm⁻¹): 929 (s) (As = O), 491 (s), 392 (m) (Al–Cl).

4. 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(S/L)2013 [44] 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. The crystal quality for [GaF₄(PMDTAH)]·2H₂O and [GaF₃(OH₂)₂(pyNO)]·pyNO·H₂O was rather poor, leading to higher than normal residuals, hence detailed comparisons of bond lengths and angles require caution. Except for [NMe₂H₂][GaF₄(OH₂)₂] and [GaF₃(OH₂)₂(dmso)], the H atoms on the water molecules were not located in the difference map.

Table 1
Crystal data and structural refinement details.[a]

Compound	[Me$_2$NH$_2$][trans-GaF$_4$(OH$_2$)$_2$]	[GaF$_3$(OH$_2$)$_2$(dmso)]	[GaF$_3$(OH$_2$)$_2$(pyNO)]·pyNO·H$_2$O	[GaF$_3$(OH$_2$)(py)$_2$]·H$_2$O
Formula	C$_2$H$_{12}$F$_4$GaNO$_2$	C$_2$H$_{10}$F$_3$GaO$_3$S	C$_{20}$H$_{32}$F$_6$Ga$_2$N$_4$O$_{10}$	C$_{10}$H$_{14}$F$_3$GaN$_2$O$_2$
M	227.85	240.87	741.94	320.95
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	C2/c (no.15)	P$\bar{1}$ (no. 2)	P$\bar{1}$ (no. 2)	P2$_1$ (no. 4)
a (Å)	6.8849(10)	4.951(3)	9.395(6)	7.220(2)
b (Å)	7.6680(10)	7.808(5)	11.274(8)	11.123(3)
c (Å)	14.5718(10)	9.556(6)	15.285(10)	8.111(2)
α (°)	90	93.469(12)	95.773(18)	90
β (°)	97.153(4)	93.421(15)	107.49(2)	115.353(5)
γ (°)	90	94.188(16)	109.552(15)	90
U (Å^3)	763.31(16)	367.0(4)	1418.1(16)	588.6(3)
Z	4	2	2	2
μ (Mo Kα)/mm^{-1}	3.627	4.040	1.997	2.372
$F(0\,0\,0)$	456	240	752	316
Total no. reflections	2641	4454	24366	4940
R_{int}	0.043	0.128	0.112	0.051
Unique reflections	872	1427	5555	1959
No. of parameters/restraints	50, 0	93, 2	397, 24	163, 15
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.031, 0.073	0.094, 0.240	0.087, 0.245	0.054, 0.140
R_1, wR_2 (all data)	0.044, 0.078	0.120, 0.261	0.101, 0.254	0.062, 0.145

Compound	[GaF$_4$(PMDTAH)]·2H$_2$O	[Me$_2$N(CH$_2$)$_2$NMe(CH$_2$)$_2$]$_2$·[Ga$_2$F$_8$(OH$_2$)$_2$]·2H$_2$O	[AlCl$_3$(OAsPh$_3$)]·0.5CH$_2$Cl$_2$
Formula	C$_9$H$_{24}$F$_4$GaN$_3$O$_2$	C$_{14}$H$_{46}$F$_8$Ga$_2$N$_4$O$_6$	C$_{18.5}$H$_{16}$AlAsCl$_4$O
M	352.06	657.99	498.01
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2$_1$/n (no.14)	P2$_1$/c (no. 14)	P$\bar{1}$ (no. 2)
a (Å)	11.819(7)	10.262(4)	9.3430(18)
b (Å)	9.993(6)	7.592(3)	13.727(3)
c (Å)	12.973(8)	16.436(8)	16.894(3)
α (°)	90	90	99.220(3)
β (°)	97.800(10)	98.398(11)	90.170(4)
γ (°)	90	90	97.248(4)
U (Å^3)	1518.0(16)	1266.7(9)	2121.1(7)
Z	4	2	4
μ (Mo Kα)/mm^{-1}	1.857	2.226	2.153
$F(0\,0\,0)$	728	694	996
Total no. reflections	15289	11243	19433
R_{int}	0.221	0.047	0.050
Unique reflections	3491	2491	9548
No. of parameters/restraints	177, 2	175, 28	469, 0
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.071, 0.137	0.046, 0.122	0.084, 0.217
R_1, wR_2 (all data)	0.154, 0.168	0.062, 0.134	0.112, 0.235

[a] Common items: T = 100 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°.
[b] $R_1 = \Sigma||F\sigma| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma wFo^2]^{1/2}$.

Powder X-ray diffraction data were collected on a Bruker D2 diffractometer using Cu K$_\alpha$ X-rays and refined using the GSAS package [45,46].

5. Conclusions

This work has prepared and characterised several new complexes of the three Group 13 trifluorides with neutral oxygen donor ligands. In general the complexes are significantly less stable than those with N-donor ligands reported previously and in most cases the neutral ligands are partially dissociated in solution, the dissociation increasing Al < Ga < In. The high affinity of the trifluoro-metal centre for coordinated water is also notable; the significant extent of the H-bonding involving the coordinated water may play a role in the preferential isolation of the aquo-complexes from solution. The failure to obtain complexes with soft donor ligands such as phosphines or thioethers either directly or via Cl$^-$/F$^-$ exchange, has parallels in other metal fluoride systems, but the failure to obtain complexes with phosphine oxides (O-donors) was unexpected.

Appendix A. Supplementary data

CCDC 1429857-1429863; contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Other supplementary data: Original NMR and IR data for the complexes and PXRD data for the MF$_3$·3H$_2$O (M = Al or In) is available via http://dx.doi.org/105258/SOTON/385412. A view of the hydrogen bonded network present in the crystal structure of [NMe$_2$H$_2$][GaF$_4$(OH$_2$)$_2$] is available as supplementary data to this manuscript. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.12.032.

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