Introduction

Aluminium chloride is widely used both in the laboratory and industry as a Friedel–Crafts catalyst for alkylation and acylation reactions, and also catalyses condensation, isomerisation and polymerisation reactions.1 The reactions depend upon the strong Lewis acidity which produces incipient carbocations in the single complex of a neutral thioether co-ordinated to AlX3 is the recently reported† [AlCl3(thianthrene)], although there are a few AlMe3 complexes with thiamacrocycles.9 There are no reports of studies with telluroethers, and the single complex of a selenium ligand is [AlCl3(selenoxan)], characterised only by microanalysis.10 Recent studies of gallium(III) halides GaX3 (X = Cl, Br or I) with chalcogenoethers have established that most contain pseudo-tetrahedral gallium centres [GaX3L] (L = Me2S, Me2Se, Me2Te, etc.) or dinoxor-[GaX3] (X = Cl, Br, I) at X=3637

Thio-, seleno- and telluro-ether complexes of aluminium(III) halides: synthesis, structures and properties†

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The reaction of AlCl3 with Me2E (E = S, Se or Te) in CH2Cl2 under rigorously anhydrous conditions gave the pseudo-tetrahedral complexes [AlCl3R2E]. The [AlX3Me2E] (X = Br or I, E = Se; X = Br, E = Te) were made from toluene solution since attempted syntheses in CH2Cl2 resulted in substantial chloride incorporation. The synthesis of [AlCl3]2(o-C6H4H2(CH2SeU))] in which the ligand bridges two tetrahedral aluminium centres, and of the six-coordinate trans-[AlX3(Me(CH2)2EMe2)][AlX4] (X = Cl or Br, E = S, and X = Cl, E = Se) and cis-[AlX3(MeS(CH2)2SMe2)][AlX4] are reported. The tripodal thioether forms [AlCl2(MeC(CH2SMe)3)], which is a chain polymer with κ3-coordinated ligand and a tbp arrangement at Al(III). Chalcenoether macrocycle complexes [AlCl3([9]aneS3)], [AlCl3([14]aneS4)][AlCl4] and [AlCl3([16]aneSe4)][AlCl4] are also described. All complexes were characterised by microanalysis, IR and multinuclear NMR (1H, 27Al, 77Se or 125Te) spectroscopy as appropriate. In CH2Cl2 solution [AlCl3(Me2Si)] with added Me2S forms [AlCl3(Me2Si2)], and the [AlX2(Se(CH2)2EMe2)][AlX4] exist as mixtures of cis and trans isomers which undergo rapid exchange at ambient temperatures. X-Ray crystal structures are reported for [AlCl3(Me2Se), [AlX2(Se(CH2)2EMe2)][AlCl4] (E = S or Se), cis-[AlX3(MeS(CH2)2SMe2)][AlX4], [AlCl2(MeC(CH2SMe)3)] and for the sulfonium salt [Me2SH][AlCl4]. The aluminium halide chalcenoether chemistry is compared with the corresponding gallium and indium systems, and the relative Lewis acidities of the metals discussed. Attempts to use [AlCl3(Bu2E)] (E = Se or Te) as LPCVD reagents to form aluminium chalcogenide films were unsuccessful.

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trans-[GaCl3(macrocycle)][GaCl4]. The larger indium centre forms 4-, 5- or 6-coordinate complexes of types [InX3(R2E)] [E = S, Se or Te], [InX4(RE(CH2)2ER2)] [E = S, Se or Te], [InX5(RE(CH2)2ER2)] [E = S, Se or Te], [InX6(RE(CH2)2ER2)] [E = S, Se or Te]. cis-[InCl3(14aneS4)][InCl4] and trans-[InCl3(16aneSe4)][InCl4].

We have recently reported that [GaCl3(μ-Bu)E] [E = S or Te] or [GaCl3(μ-C6H4(SMe)2)E] [E = S or Te] are effective single source precursors for low pressure chemical vapour deposition (LPCVD) of Ga2E3 thin films, and that preferential deposition occurs onto TiN in photolithographically patterned SiO2/TiN substrates.17 Here we report systematic studies of the reactions of AlCl3 [X = Cl, Br or I] with a range of thio-, seleno- and telluro-ethers, detailed spectroscopic and structural data, and comparisons with their gallium and indium analogues. We also explored whether selected complexes would function as CVD reagents for deposition of aluminium chalcogenide films.

Results and discussion

Aluminium trihalides (AlX3 [X = Cl, Br or I]), are strong hard Lewis acids with a very high affinity for water.2 Successful synthesis of their complexes with soft donor ligands such as thio-, seleno- and telluro-ethers requires anhydrous AlX3 or AlCl3/Me2S, rigorously anhydrous solvents and ligands and exclusion of water at all stages of the manipulations. Trace water displaces the neutral complex is an oil at room temperature, the others crystalline. The moisture sensitivity of the halides and the complexes is much greater than observed in the corresponding gallium(III) systems.12,13 The higher reactivity of the aluminium halides also affects the choice of solvent for the synthesis. Whilst complexes of AlCl3 are readily made in anhydrous CH2Cl2, use of this solvent for the AlBr3 or AlI3 reactions results in incorporation of substantial amounts of chloride into the products, and the heavier halides are best made from anhydrous toluene solution. Similar observations were made by Burford et al.19 in AlX3/R3PO/CH2Cl2 systems. However, the pre-isolated pure [AlX3L] [X = Br or I] react only slowly with CH2Cl2 (or CD2Cl2), which remains the NMR solvent of choice, as non-coordinating and useable down to 180 K. The reactivity of AlCl3 in CH2Cl2 has been ascribed to the formation of the intermediate carbenium ion [CH2Cl][AlCl4],8,20 and in previous studies of GaCl3 complexes of thioethers we observed the formation of [μ-o-C6H4(SMe2CH2Cl)]2[AlCl4] when [GaCl3(μ-o-C6H4(SMe)2)] is allowed to stand in CH2Cl2 solution for several days.13 Cleavage of C–Se or C–Te bonds is also observed, e.g. the formation of the selenium cation in [μ-C6H4(SMe2)SeMe]2[AlCl4] from μ-C6H4(SMe2)SeMe2.12 In the aluminium systems many of the complexes degrade on standing in solution at ambient temperatures (below), hence rapid isolation of the complexes from solution is advisable. Decomposition in solution is much slower at low temperatures, permitting growth of X-ray quality crystals overnight at −18 °C.

Table 1. 27Al NMR data

| Compound | δ (27Al), 298 K | δ (27Al), 190 K | Comments |
|----------|----------------|----------------|----------|
| [AlCl3]− | 103.5          | 103.6          | W1/2 ~ 5 Hz |
| [AlBr3]− | 80.6           | 81.4           | W1/2 ~ 15 Hz |
| [AlI3]−  | −23.0          | −23.0          | W1/2 ~ 25 Hz |
| [AlCl3(Me2S)] | 111.6            | 111.2          | No change with added Me2S |
| [AlBr3(Me2S)] | 111.5            | 111.0          | No change with added Me2S |
| [AlI3(Me2S)] | 38.5            | 38.4           | No change with added Me2S |
| [AlCl3(Se)] | 110.5            | 110.1         | No change with added Me2S |
| [AlBr3(Se)] | 110.0            | 110.0         | No change with added Me2S |
| [AlI3(Se)]  | 109.9            | 109.9          | No change with added Me2S |
| [AlCl3(Se)] | 92.6             | 92.6           | No change with added Me2S |
| [AlBr3(Se)] | 92.6             | 92.6           | No change with added Me2S |
| [AlI3(Se)]  | 92.6             | 92.6           | No change with added Me2S |
| [AlCl3(SiMe3)] | 105.5            | 105.5          | Only anion resonance seen |
| [AlBr3(SiMe3)] | 105.4            | 105.4          | Only anion resonance seen |
| [AlI3(SiMe3)] | 105.4            | 105.4          | Only anion resonance seen |

a Chemical shifts relative to [Al(H2O)4]3+ in H2O at pH = 1. b In CH2Cl2–CD2Cl2 solution at temperature specified.
made in the spectra of many of the aluminium complexes in this work, and are probably due to solid state effects, such as lower site symmetry or cation–anion interactions. The $^1$H NMR spectrum of [AlCl$_3$(Me$_2$S)] in CD$_2$Cl$_2$ (295 K) shows a singlet at $\delta = 2.53$ which does not change significantly on cooling the solution to 190 K. Addition of aliquots of Me$_2$S to the solution produces progressive shifts in the single resonance to low frequency, and on cooling to 185 K, two broad resonances are resolved at $\delta = 2.24$ and 2.20, suggesting ligand exchange is slowing, but that the low temperature limit has not been reached. The latter shift is similar to that of free Me$_2$S ($\delta = 2.15$), whilst the former is assigned to a new aluminium complex. The $^{27}$Al NMR spectra are more informative (Table 1). At ambient temperatures a broad singlet at $\delta = 111.6$ is present in the spectrum of [AlCl$_3$(Me$_2$S)], which is little changed on cooling the solution to 190 K. However, addition of 1 mol. equivalent of Me$_2$S to the solution generates a new resonance at $\delta = 73.5$ ($W_{1/2} = 650$ Hz), and this resonance is unchanged upon addition of more Me$_2$S and shows only a small low frequency drift on cooling the solution to 190 K. The new $^{27}$Al chemical shift is in the range expected for five-coordinate Al species.$^{21}$ The combination of the $^1$H and $^{27}$Al NMR results show that in the presence of excess Me$_2$S in CH$_2$Cl$_2$ solution the 2:1 complex [AlCl$_3$(Me$_2$S)$_2$] forms; further addition of Me$_2$S does not produce any evidence for a 3:1 complex. As noted above, work-up of the solution results in decomposition to reform [AlCl$_3$(Me$_2$S)]. Five-coordination is established in the solid state with aluminium–phosphine complexes, e.g. [Al(PEt$_3$)$_2$], which has a tbp geometry with axial phosphines.$^{22}$

The complexes [AlX$_3$(Me$_2$S)] (X = Br or I) are generally similar to the chloride complex, and exhibit progressively lower frequency shifts in the $^{27}$Al NMR spectra as the halogen becomes heavier (Table 1). However, although the $^1$H NMR spectra show fast exchange with added Me$_2$S in CH$_2$Cl$_2$ solution, no new resonances were evident in the $^{27}$Al NMR spectra in the presence of a large excess of Me$_2$S, indicating that in these cases 2:1 complexes do not form. The [AlX$_3$(Me$_2$E)] (X = Cl, Br, E = Se or Te) were obtained in high yields and their $^1$H NMR and IR spectroscopic properties are similar to those of the thioether analogues. The $^{27}$Al NMR spectra (Table 1) show only small low frequency shifts along the series E = S > Se > Te, and no new complexes are formed by adding excess Me$_2$E to CH$_2$Cl$_2$ solutions of the appropriate [AlX$_3$(Me$_2$E)]. [AlCl$_3$(Me$_2$Se)] shows a $^{77}$Se NMR chemical shift of $\delta = -11.3$, which corresponds to a small low frequency coordination shift ($\Delta = -11.3$); this can be compared with small high frequency coordination shifts observed in [GaX$_3$(Me$_2$Se)].$^{12}$ Although high frequency coordination shifts are seen in most transition metal selenoether (and telluroether) complexes, in p-block complexes both high and low frequency shifts are seen in different systems, and the causes are not understood.$^{23}$ We were unable to observe a $^{77}$Se NMR resonance from [AlBr$_3$(Me$_2$Se)] or $^{125}$Te resonances from [AlX$_3$(Me$_2$Te)] over the temperature range 295–190 K, presumably due to fast exchange. The solutions of the selenoether and telluroether complexes develop new resonances on standing, some of which may be due to Me$_2$E$_2$, Me$_2$E$^+$ or Me$_2$EX$_2$ from their chemical shifts, but given the sensitivity of $^{77}$Se and $^{125}$Te chemical shifts to concentration, solvent etc.$^{21,24}$ their identification was not pursued. They do, however, provide evidence of the fragility in solution of the AlX$_3$ complexes with the heavier chalcogenoethers.

In view of the scarcity of aluminium complexes of the heavier chalcogenoethers, structures of three examples, [AlCl$_3$(Me$_2$Se)], [AlCl$_3$(Me$_2$Te)] and [AlBr$_3$(Me$_2$Te)] were determined. The structures (Fig. 1–3) are isomorphous (orthorhombic, Pbcm) and show the expected pseudo-tetrahedral geometry. The bond lengths are mostly unexceptional, although the Al–Te distances in [AlX$_3$(Me$_2$Te)] (X = Cl or Br) are the same within experimental error.

Storing a solution of [AlCl$_3$(Me$_2$S)] in CH$_2$Cl$_2$ in the refrigerator, produced a few small crystals which were identified as the sulfonium salt [Me$_2$SH][AlCl$_3$] (Fig. 4), by the X-ray structure solution, and probably formed by adventitious hydrolysis. Solid sulfonium salts are rare, but we have previously obtained examples from serendipitous hydrolysis of some niobium(v) fluoride–thioether complexes,$^{25}$ the formation being promoted by “anhydrous” conditions and a large weakly coordinating solvent.
adducts described above, it was expected that flexible dithioethers or diselenoethers (L–L) would produce complexes of the type $[X_3Al(\mu-L)]AlX_3]$. In fact this was only true for the bulky $\alpha$-xyllyl-backboned dithioether, $\alpha$-$\text{C}_6\text{H}_4(\text{CH}_2\text{SeMe})_2$, which gave yellow crystals of $[[\text{AlCl}_2]_2(\mu-\alpha$-$\text{C}_6\text{H}_4(\text{CH}_2\text{Se})_2)]]$. The crystals were of modest quality and had the characteristics of a modulated structure (see Experimental), and thus comparison of the detailed bond lengths and angles is not warranted. However, they are isomorphous with the gallium(III) analogue, and serve as an example of this structure type (Fig. 5).

The spectroscopic data are consistent with four-coordinate aluminium in solution. The corresponding diselenoether $\alpha$-$\text{C}_6\text{H}_4(\text{CH}_2\text{SeEt})_2$ was completely converted to the selenonium cation $[\alpha$-$\text{C}_6\text{H}_4(\text{CH}_2\text{SeEt})_2][\text{AlCl}_4]_2$ upon reaction with $\text{AlCl}_3$ in $\text{CH}_2\text{Cl}_2$ (see ESI†). The same selenonium cation is formed upon reaction of this ligand with $\text{GaCl}_3$ or $\text{InCl}_3$.12,15

Unexpectedly, reaction of $\text{AlX}_3$ with $\text{MeE}(\text{CH}_2)_2\text{EMe}$ ($E = S$ or Se) failed to give $[\text{X}_3\text{Al}(\mu-\text{MeE}(\text{CH}_2)_2\text{EMe})_2][\text{AlX}_4]$ and the products had an $\text{AlX}_3 : \text{MeE}(\text{CH}_2)_2\text{EMe}$ ratio of 1 : 1 irrespective of the ratio of reactants used. Crystals of three examples were grown and showed the presence of pseudo-octahedral cations and tetrahedral anions, $[\text{AlX}_3(\text{MeE}(\text{CH}_2)_2\text{EMe})_2][\text{AlX}_4]$ ($X = \text{Cl}$, $E = S$ or Se; $X = I$, $E = S$). The structures of $[\text{AlCl}_3(\text{MeE}(\text{CH}_2)_2\text{EMe})_2][\text{AlCl}_4]$ (Fig. 6 and 7) reveal centrosymmetric cations (trans isomer) with identical $d(\text{Al}-\text{Cl})$, which are as expected longer than in the four-coordinate complexes. The $d(\text{Al}-\text{S})$ and $d(\text{Al}-\text{Se})$ differ by $\sim0.14$ Å, which approximates to the difference in covalent radii of the chalcogens.26 The bond angles around the aluminium show only small deviations from 90°.

Although both of the structures contain the chalcogeno-ether in the DL conformation, the two crystals are not isomorphous and in the selenoether complex there are short contacts $\text{Se}_2 \cdots \text{Se}^\prime$ (3.436 Å) and $\text{Se}_3 \cdots \text{Se}^\prime$ (3.542 Å). These link $\text{Al}_2$-centred cations into chains through $\text{Se}^\prime$ (along the $a$ direction)

**Complexes with bidentate ligands**

By analogy with the corresponding GaX$_3$ adducts,12 and considering the preference for four-coordination in $[\text{AlX}_3(\text{R}_{2}\text{E})]$

![Fig. 3](image3.png) The structure of $[\text{AlBr}_3(\text{Me}_2\text{Te})]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = x$, $y$, $3/2 - z$. Selected bond lengths (Å) and angles (°): $\text{Al} - \text{Br} = 2.286(3)$, $\text{Al} - \text{Br} = 2.287(2)$, $\text{Al} - \text{Te} = 2.692(4)$, $\text{Br} - \text{Al} - \text{Br} = 111.19(9)$, $\text{Br} - \text{Al} - \text{Br} = 114.01(15)$, $\text{Br} - \text{Al} - \text{Te} = 106.34(12)$, $\text{Br} - \text{Al} - \text{Te} = 106.80(9)$.

![Fig. 4](image4.png) The structure of $[\text{Me}_2\text{SH}][\text{AlCl}_4]$ showing the S$_2$ centred cation and the H-bond (dashed bond) to an adjacent Cl atom. Ellipsoids are drawn at the 50% probability level and H atoms on C are not shown. The difference map gave yellow crystals of $[(\text{AlCl}_3)_2(\mu-\text{MeSE})_2][\text{AlCl}_4]_2$ upon reaction with $\text{AlCl}_3$ in $\text{CH}_2\text{Cl}_2$ (see ESI†). The same selenonium cation is formed upon reaction of this ligand with $\text{GaCl}_3$ or $\text{InCl}_3$.12,15

**Fig. 5** The structure of $[\text{AlCl}_3(\alpha$-$\text{C}_6\text{H}_4(\text{CH}_2\text{Se})_2)_2][\text{AlCl}_4]_2$ showing the atom labelling scheme. The crystals had the properties of a modulated structure and the solution shown was derived from a smaller subcell. For this reason bond lengths and angles are less reliable than usual and not presented here.

![Fig. 6](image6.png) The structure of $[\text{AlBr}_3(\text{Me}_2\text{Te})]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms on C are not shown. The difference map gave yellow crystals of $[(\text{AlCl}_3)_2(\mu-\text{MeSE})_2][\text{AlCl}_4]_2$ upon reaction with $\text{AlCl}_3$ in $\text{CH}_2\text{Cl}_2$ (see ESI†). The same selenonium cation is formed upon reaction of this ligand with $\text{GaCl}_3$ or $\text{InCl}_3$.12,15

![Fig. 7](image7.png) The structure of $[\text{AlCl}_3(\alpha$-$\text{C}_6\text{H}_4(\text{CH}_2\text{Se})_2)_2][\text{AlCl}_4]_2$ showing the atom labelling scheme. The crystals had the properties of a modulated structure and the solution shown was derived from a smaller subcell. For this reason bond lengths and angles are less reliable than usual and not presented here.
and similarly, the Al3-centred cations are linked into chains through Se3 (again along the a direction) (Fig. 8).

The structure of the [AlI2{MeS(CH2)2SMe}2][AlCl4] (Fig. 9) also contains a pseudo-octahedral cation, but this has a cis-geometry and with the dithioethers in the meso form. In cis-[AlI2{MeS(CH2)2SMe}2] the Al–Strans distances are longer by ~0.1 Å than Al–Strans, but the Al–Strans distances are not significantly different to those in trans-[AlCl2{MeS(CH2)2SMe}2][AlCl4].

The Nujol mull IR spectra for these salts all confirm the presence of [AlIxt]+, but the Al–X stretches of the cations could not be identified with certainty. The solution speciation is less clear, and all the complexes are extremely moisture sensitive in solution. All four complexes show 27Al resonances assignable to the [AlIxt]− (Table 1), but only [AlCl2{MeS(CH2)2SMe}2]-[AlCl4] shows a second resonance (δ 27Al = 37.4) which is assigned to the six-coordinate cation. For the other complexes it is likely that the increasing electric field gradients promote fast quadrupolar relaxation, resulting in the loss of the cation resonance.

At room temperature a CD2Cl2 solution of [AlCl3{MeS-(CH2)2SMe}2][AlCl4] shows singlet CH3 (δ = 2.26) and CH2 (δ = 3.08) resonances. On cooling to 223 K the spectrum shows three CH3 resonances (δ = 2.26, 2.50, 2.66) and overlapping CH2 resonances (δ = 3.08–3.31), which we tentatively assign to a mixture of cis and trans isomers of [AlCl2{MeS(CH2)2SMe}2]3+, the changes reversing on warming the solution. The bromo- and iodo-complexes behave similarly. Notably, none of the complexes show resonances due to free dithioether, which would seem to rule out significant amounts of [AlCl2{MeS-(CH2)2SMe}2]3+, being present. At 185 K further splitting of the resonances is evident, which is probably due to slowing of the pyramidal inversion at S, leading to separate resonances for the individual inveritomers. The solutions decompose slowly on standing.

The trans-[AlCl2{MeSe(CH2)2SeMe}2][AlCl4] exhibits a singlet 77Se NMR resonance at room temperature (δ = 95.5) which is a low frequency coordination shift (δ = –25.3) and singlet Cx (δ = 2.36) and CH2 (δ = 3.21) resonances in the 1H NMR spectrum. Cooling the solution to 190 K produces little change in the 1H NMR spectrum, although the 77Se resonance is lost below ~240 K. In the selenoether complex only the trans isomer appears to be present in significant amounts. On standing, new resonances grow in due to decomposition. Attempts to record spectra in CD3CN solution resulted in displacement of the thio- or seleno-ethers by the nitrile.

Reaction of AlCl3 with the ditelluroether BuTe(CH2)3TeBu produced a mixture of species resulting from ligand fragmentation. The 1H NMR spectrum of the product showed multiple resonances for the t-butyI groups and the CH3 units. Multiple signals were also observed in the 125Te NMR spectrum, whilst the 27Al NMR spectrum indicated the presence of [AlCl4]−. Very air sensitive, yellow crystals were isolated of one of the decomposition products, which proved to be BuTe(CH2)3Te-(Bu)Te(CH3)2TeBu][AlCl4], derived from fragmentation of the ditelluroether (see ESI†).

Polydentates and macrocycles

The reaction of the tripodal trithioether MeC(CH2SMe)3 with AlCl3 in a 1 : 1 molar ratio in anhydrous CH2Cl2 gave colourless crystals whose structure (Fig. 10) showed a chain polymer with the ligand binding as a bridging bidentate with one uncoordinated –CH2SMe arm. The structure forms a chain in the a direction. The geometry at aluminium is a distorted trigonal bipyramid with equatorial chlorines and there are two slightly different aluminium environments in the unit cell.

In solution the 1H NMR spectrum shows single, sharp –CH3, –SMe and –CMe resonances consistent with fast exchange. Attempts to isolate complexes with higher AlCl3: triad stoichiometries were unsuccessful. The [AlCl3{MeC-(CH2SMe)3}] stoichiometry contrasts with the gallium complex...
form similarly intractable 1 : 1 complexes with this ligand,
precluding solution measurements. Both gallium and indium
macrocycle is displaced by coordinating solvents like MeCN,
anes4 and [16]aneSe4) and the far IR spectra confirmed the
an equimolar amount of AlCl3 in toluene gave a white powder,
2.533(5), Al1
lengths (Å) and angles (°): Al1
probability level and H atoms are omitted for clarity. Selected bond
showing the atom labelling scheme. Ellipsoids are drawn at the 50%
Lewis acidity falls $\text{AlCl}_3 > \text{AlBr}_3 > \text{AlI}_3$, and $\text{AlCl}_3 > \text{AlBr}_3 > \text{GaCl}_3 > \text{GaBr}_3$ (ref. 27–31 and references therein). One should note in passing that the order with halogen is reversed for boron. The modelling work is based upon gas phase molecules and does not take into account solid state effects (lattice energies, intermolecular interactions and packing effects), or the effects of lattice solvent, which may complicate the interpretation of experimental data, and in some cases lead to apparently anomalous results.\(^{30}\) The various contributions listed above, means that interpreting changes in metal–ligand bond lengths simply in terms of Lewis acidity must be done with care, and one might expect the occasional anomaly, but as a result of recent studies, there are sufficient data available to attempt some comparisons for Al/Ga/In–Group 16 donor complexes. Table 2 shows some illustrative data.

The data show firstly, that if one compares complexes of the same element with the same coordination number, the M–X distances seem unaffected by the specific chalcogen donor type present, which is consistent with the metal–halogen being the dominant interaction. A similar comparison of the M–E bond lengths shows that these increase (sometimes only marginally) with halide, Cl < Br < I, consistent with the trends deduced for lighter donor atoms. The M–X, and M–E bond lengths in comparable complexes of Al and Ga are also nearly identical, consistent with their almost identical covalent radii, resulting from the “3d block contraction”, \(i.e.\) the increased nuclear charge resulting from the 3d metals only partially screened by the d electron shell.\(^{26}\) As expected, In–X and In–E bonds are typically \(~0.2\) Å longer. A very recent dft study\(^{31}\) suggested that whilst Ga and In halide complexes of Me$_2$Se had a high degree of covalency in the M–Se bonds, those of aluminium had a markedly higher electrostatic component to the bonding. Our experimental data reported in the present paper, show no evidence for a significant change in the bonding type present along the series of group 16 donor complexes, the differences noted being due to the higher Lewis acidity of Al(III). We note that the dft calculations predict\(^{31}\) an Al–Se bond length (for the gas phase molecule) of 2.53 Å compared to the X-ray crystallographic result (for the solid) of 2.48(2) Å.

Our data also show the ready formation of six-coordinate cations with aluminium, [AlX$_3$(I–L)$_3$]$^+$, contrasting with the reluctance of gallium to exceed four-coordination, except in macrocyclic compounds, cannot be due to steric effects, but must be a further consequence of the stronger Lewis acidity of aluminium. These differences must originate in the donor/acceptor orbital energy match (or mis-match) rather than in charge/radius effects. The larger indium centre has a less clear preference, easily accommodating four-, five- or six-coordination depending upon the ligand and reaction conditions.

**Conclusions**

Chalcogenoether complexes of aluminium(III) halides with four-, six- and (rarely) five-coordinate metal centres have been prepared, and their structures and properties compared with those of the heavier analogues GaX$_3$ and InX$_3$. The aluminium complexes are extremely moisture sensitive, and complexes with selenium or tellurium ligands are prone to slow E–C bond cleavage in solution. Nonetheless, the formation and structural characterisation of telluroether complexes of the hard AlX$_3$ acceptors is notable. In contrast to the gallium complexes, it does not appear that the aluminium systems are suitable for LPCVD applications. The detailed study of Al(III) complexes with soft, modest donor chalcogenoethers has confirmed the trends in Lewis acidity observed with hard O or N donor ligands and are broadly in line with expectations based upon the dft calculations. The work further demonstrates that a significant range of chalcogenoether complexes with hard p-block Lewis acids are obtainable despite the hard/soft-acceptor/donor mismatch.
Table 2  Structural data on Group 16 ligand adducts of Al, Ga and In halides

| Compound | M−X/Å | M−E/Å | Coordination number of M | Reference |
|----------|-------|-------|--------------------------|-----------|
| [AlCl₃(MeSe)] | 2.121(2), 2.113(1) | 2.486(2) | 4 | This work |
| [AlCl₃(MeTe)] | 2.1207(6), 2.1295(10) | 2.6871(9) | 4 | This work |
| [AlBr₃(MeTe)] | 2.286(3), 2.287(2) | 2.692(4) | 4 | This work |
| trans-[AlCl₃(MeS(CH₂)₂SMe)] | 2.2131(10) | 2.4595(11), 2.4809(10) | 6 | This work |
| cis-[AlCl₃(Me(CH₂)₂SMe)] | 2.612(4), 2.635(4) | 2.431(4)−2.546(5) | 6 | This work |
| trans-[AlCl₃(Me₄Se)] | 2.2112(2) | 2.590(13), 2.6232(13) | 6 | This work |
| [GaCl₃(MeS(CH₃)₂SMe)] | 2.4907(7)−2.5316(7) | 2.4048(12) | 4 | This work |
| [GaCl₃(o-C₆H₄(CH₂)₂SMe)] | 2.1478(14)−2.1650(15) | 2.3573(15) | 4 | This work |
| [GaCl₃(MeSe)] | 2.1606(8), 2.1700(10) | 2.4673(7) | 4 | This work |
| [GaI₃(MeS)] | 2.5209(2)−2.5277(2) | 2.479(2) | 4 | This work |
| [GaCl₃(BuSe(CH₂)₄SeBu)] | 2.149(2)−2.166(2) | 2.468(1) | 4 | This work |
| [GaCl₃(BuTe(CH₂)₄TeBu)] | 2.158(3)−2.181(3) | 2.6378(14), 2.6356(13) | 13 | This work |
| trans-[GaCl₃([16]aneSe₄)] | 2.276(3)−2.296(3) | 2.482(4)−2.518(4) | 6 | This work |
| trans-[GaCl₃([16]aneSe₂Me)] | 2.3038(11), 2.3202(12) | 2.590(6)−2.6106(8) | 6 | This work |
| InBr₃(MeSe)] | 2.4901(12), 2.4981(7) | 2.6455(11) | 15 | This work |
| [(InCl₃)₂{MeS(CH₂)₂SMe}] | 2.4243(1), 2.4457(1) | 2.7722(6), 2.7802(6) | 14 | This work |
| trans-[InCl₃([16]aneSe₄)] | 2.4237(18), 2.393(18) | 2.645(2)−2.696(2) | 6 | This work |
| trans-[InBr₃([16]aneSe₄)] | 2.5775(5), 2.5918(5) | 2.6518(10)−2.690(11) | 15 | This work |
| trans-[InBr₃(MeS(CH₂)₂SMe)] | 2.6076(15), 2.6113(15) | 2.7370(16)−2.7762(15) | 15 | This work |
| trans-[InBr₃([16]aneSe₂Me)] | 2.475(2) | 2.7199(10), 2.7394(11) | 16 | This work |

*a Terminal M−X.

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm⁻¹. ¹H NMR spectra were recorded using a Bruker AV300 spectrometer. ⁷⁷Se{¹H}, ¹²⁵Te{¹H} and ²⁷Al NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external neat SeMe₂, TeMe₂ and aqueous [Al₂H₆O₆]⁺ at pH = 1, respectively. Microanalyses were undertaken by Medac Ltd or London Metropolitan University. Solvents were dried prior to use: toluene by distillation and stored under dinitrogen over molecular sieves. Other thiol- and telluroethers were made by literature methods and stored under dinitrogen over molecular sieves. Other thiol- and telluroethers were made by literature methods and stored under dinitrogen over molecular sieves.

[AlCl₃(MeEST)]: MeEST (0.09 g, 1.5 mmol) was added dropwise to a suspension of AlCl₃ (0.2 g, 1.5 mmol) in anhydrous CH₂Cl₂ (25 mL) with stirring to give a colourless solution. HCl was slowly bubbled through the solution for ~30 seconds. After stirring for 30 minutes, some white precipitate formed. The white solid was collected by filtration and dried in vacuo. The volume of the pale yellow filtrate was reduced to ~10 mL. Colourless crystals suitable for single crystal X-ray diffraction were obtained after storage of the filtrate at ~18 °C for 24 hours. Yield 82%. Anal. Calcd for C₄H₆AlCl₃S: C, 10.4; H, 3.0. Found: C, 10.5; H, 2.9%. IR (cm⁻¹, Nujol): 2482 (br, w), 488 (br), 467 (br), 395 (s) [AlCl₃]; the strong S⋯H⋯Cl-Al interactions cause extensive splitting of the t₂ Al−Cl stretching mode in the anion.
(0.04 g, 0.37 mmol) was added dropwise when the solution became colourless. After stirring for 15 minutes, all solvent was removed in vacuo to give a white solid. Yield 0.11 g, 80%. Anal. Calcd for C2H6AlBr3Se: C, 6.4; H, 1.6. Found: C, 6.1; H, 1.9%. 1H NMR (CD2Cl2, 295 K): 2.47 (s). 27Al NMR (CD2Cl2, 295 K): 99.7. IR (cm−1, Nujol): 446 (s), 397 (s) Al–Br.

[AlCl3(Bu2Se)]: A solution of Bu2Se (0.29 g, 1.5 mmol) in anhydrous CH2Cl2 (7 mL) was added dropwise to a suspension of AlCl3 (0.20 g, 1.5 mmol) in anhydrous CH2Cl2 (8 mL) with stirring to give a colourless solution. After 30 minutes, all solvent was removed in vacuo to yield a pale yellow oil. Yield 0.36 g, 73%. Anal. Calcd for C3H18AlCl3Se: C, 29.4; H, 5.6. Found: C, 29.7; H, 5.8%. 1H NMR (CD2Cl2, 295 K): 3.03 (t, [4H]), 1.82 (m, [4H]), 1.46 (m, [4H]), 0.97 (t, [6H]). 27Al NMR (CD2Cl2, 295 K): 106.8. IR (cm−1): 338 (s), 3648 (w). 350 (s), 295 (s). 295 (s).

[AlCl3(Me2Te)]: Me2Te (0.12 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.10 g, 0.75 mmol) in anhydrous CH2Cl2 (10 mL) with stirring to give a colourless solution. After 30 minutes, the volume of solvent was reduced in vacuo to ~5 mL. Storage at −18 °C for 24 hours produced yellow crystals. Yield 0.135 g, 62%. Anal. Calcd for C8H18AlCl3S3·1/2CH2Cl2: C, 26.4; H, 5.0. Found: C, 26.9; H, 5.1%. 1H NMR (CDCl3, 295 K): 2.47 (s). 27Al NMR (CDCl3, 295 K): 3.10 (s, [4H]), 2.26 (s, [6H]). 404 (m), 391 (m) Al–Cl.

[AlBr3(Me2Te)]: AlBr3 (0.10 g, 0.37 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution. Me2Te (0.06 g, 0.37 mmol) was added dropwise to give a paler yellow solution. After stirring for 15 minutes, all solvent was removed in vacuo to give a yellow solid. Yield: 0.11 g, 68%. Anal. Calcd for C8H20Al2Br6S4: C, 12.3; H, 2.6. Found: C, 12.8; H, 2.7%. 1H NMR (CDCl3, 295 K): 2.76 (s, [6H]), 2.25 (s, [9H]), 1.43 (m, [4H]), 0.96 (t, [6H]). 27Al NMR (CDCl3, 295 K): 108.3. IR (cm−1): 495 (s), 395 (s) Al–Br.

[AlCl3(MeSe(CH2)2SMe)]: MeSe(CH2)2SMe (0.16 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.10 g, 0.75 mmol) in anhydrous CH2Cl2 (10 mL) with stirring to give a yellow solution. After 30 minutes the volume of solvent was reduced in vacuo to ~5 mL. Storage of the solution at −18 °C for 48 hours produced yellow crystals. Yield 0.18 g, 69%. Anal. Calcd for C8H20Al2Cl6Se4: C, 13.8; H, 2.9. Found: C, 12.8; H, 2.7%. 1H NMR (CDCl3, 295 K): 2.19 (s). 27Al NMR (CDCl3, 295 K): 109.9. 77Se NMR (CDCl3, 295 K): 102.9. IR (cm−1): 539 (s), 399 (m) Al–Cl.

[AlCl3(Me2S):]: AlCl3 (0.10 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.10 g, 0.75 mmol) in anhydrous CH2Cl2 (8 mL) with stirring to give a colourless solution. After 30 minutes, the volume of solvent was reduced in vacuo to ~5 mL. Storage at −18 °C for 24 hours produced yellow crystals. Yield 0.11 g, 59%. Anal. Calcd for C8H20Al2Cl6Cl2S: C, 29.3; H, 3.7. Found: C, 29.3; H, 3.7%. 1H NMR (CDCl3, 295 K): 7.47 (m, [4H]), 4.37 (s, [4H]), 3.08 (q, [4H]), 1.49 (t, [6H]). 27Al NMR (CDCl3, 295 K): 111.3. IR (cm−1, Nujol): 565–500 (vbr, s), 394 (s). Raman (cm−1): 518 (m), 402 (m).

[AlCl3([AlI2{MeS(CH2)2SMe}2]): AlI2{MeS(CH2)2SMe}2 (0.17 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.10 g, 0.75 mmol) in anhydrous CH2Cl2 (10 mL) with stirring to give a yellow solution. After 30 minutes the volume of solvent was reduced in vacuo to ~5 mL. Storage of the solution at −18 °C for 24 hours produced colourless crystals. Yield 0.18 g, 69%. Anal. Calcd for C8H20Al2I6Se4: C, 9.1; H, 1.9. Found: C, 9.0; H, 1.9%. 1H NMR (CDCl3, 295 K): 2.36 (s, [6H]), 2.17 (s, [6H]). 27Al NMR (CDCl3, 295 K): 23.0. IR (cm−1, Nujol): 338 (s), 304 (m).

[AlCl3([AlCl3){[AlCl3]}2]: AlCl3 (0.20 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.20 g, 0.75 mmol) in anhydrous toluene (15 mL) with stirring to give a yellow solution. After 30 minutes the volume of solvent was reduced in vacuo to ~5 mL. Storage of the solution at −18 °C for 48 hours produced yellow crystals. Yield 0.18 g, 70%. Anal. Calcd for C8H18Al2Cl6S3·1/2CH2Cl2: C, 26.9; H, 5.1%. 1H NMR (CDCl3, 295 K): 2.95 (t, [4H]), 1.83 (m, [4H]), 1.43 (m, [4H]), 0.96 (t, [6H]). 27Al NMR (CDCl3, 295 K): 92.6. IR (cm−1): 495 (s), 395 (s) Al–Cl.

[AlCl3(Me2S):]: AlCl3 (0.10 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.10 g, 0.75 mmol) in anhydrous CH2Cl2 (8 mL) with stirring to give a colourless solution. After 30 minutes, the volume of solvent was reduced in vacuo to ~5 mL. Storage at −18 °C for 48 hours. Yield 0.18 g, 70%. Anal. Calcd for C8H18Al2Cl6S2·1/2CH2Cl2: C, 29.2; H, 3.7. Found: C, 29.2; H, 3.7%. 1H NMR (CDCl3, 295 K): 4.9 (s, [4H]), 3.54 (s, [4H]), 3.08 (q, [4H]), 1.49 (t, [6H]). 27Al NMR (CDCl3, 295 K): 111.3. IR (cm−1, Nujol): 565–500 (vbr, s), 394 (s). Raman (cm−1): 518 (m), 402 (m).

[AlCl3([AlSe(CH2)2SMe]2): AlCl3 (0.10 g, 0.75 mmol) was added dropwise to a suspension of AlCl3 (0.20 g, 1.5 mmol) in anhydrous CH2Cl2 (15 mL) with stirring to give a yellow solution. After 30 minutes the volume of solvent was reduced in vacuo to ~5 mL. Storage of the solution at −18 °C for 24 hours produced yellow crystals. Yield 0.22 g, 60%. Anal. Calcd for C8H20Al2Cl6Se4: C, 13.8; H, 2.9. Found: C, 13.8; H, 2.9%. 1H NMR (CDCl3, 295 K): 4.98 (s, [4H]), 3.54 (s, [4H]), 3.08 (q, [4H]), 1.49 (t, [6H]). 27Al NMR (CDCl3, 295 K): 108.3. IR (cm−1, Nujol): 488 (s), 442 (m).
C₆H₁₂AlCl₃S₃: C, 23.0; H, 3.9. Found: C, 23.1; H, 3.9%. IR (cm⁻¹, Nujol): 408 (s), 375 (m) Al–Cl.

[AlCl₃][14]aneSe₄][AlCl₃]: A solution of [14]aneSe₄ (0.10 g, 0.37 mmol) in anhydrous CH₂Cl₂ (10 mL) was added to a suspension of AlCl₃ (0.10 g, 0.75 mmol) in anhydrous CH₂Cl₂ (10 mL) with stirring to give a colourless solution. After approximately 5 minutes a large quantity of white precipitate formed. After 60 minutes, the precipitate was collected by filtration and dried in vacuo. Yield 0.14 g, 70%. Anal. Calcd for C₁₀H₂₀Al₂Cl₆S₄: C, 22.4; H, 3.8. Found: C, 22.6; H, 3.7%. IR (cm⁻¹): 3646, 3617, 3592, 2354, 1654, 1531, 1384, 1352, 1073 (s), 955 (m), 762 (s), 690 (s), 558 (s).

X-Ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 3. 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 (100 µm focus) with the crystal held at 100 K (N₂ cryostream). Structure solution and refinement were straightforward, except as noted.

Table 3 Crystal data and structure refinement details

| Compound | [AlCl₃][Me₂Se] | [AlCl₃][Me₂Te] | [AlBr₃][Me₂Te] | [AlCl₃][Me₄S(CH₃)₂SMe] | [AlCl₃][Me₄S(CH₃)₂SeMe] |
|----------|----------------|----------------|----------------|------------------------|------------------------|
| Formula  | C₆H₁₂AlCl₃Se  | C₆H₁₂AlCl₃Te  | C₆H₁₂AlBr₃Te  | C₆H₁₄Cl₄Se₄             | C₆H₁₄Cl₄Se₆           |
| M        | 242.36         | 291.00         | 424.38         | 511.14                 | 698.74                 |
| Space group | Pbcm (no. 57) | Pbcm (no. 57) | Pbcm (no. 57) | Pbcm (no. 57) | Pbcm (no. 57) |
| a [Å]    | 6.205 (4)      | 13.114 (3)    | 13.400 (4)    | 10.724 (4)             | 10.907 (5)             |
| b [Å]    | 12.603 (8)     | 10.512 (4)    | 13.003 (4)    | 10.907 (5)             | 10.907 (5)             |
| c [Å]    | 15.150 (4)     | 13.608 (12)   | 24.976 (11)   | 12.374 (5)             | 17.582 (8)             |
| u [Å³]   | 819.6 (8)      | 861.4 (3)     | 943.0 (6)     | 1059.2 (10)            | 2218.5 (18)            |
| Z        | 4              | 4              | 4              | 2                      | 4                      |
| µ(Mo Kα) [mm⁻¹] | 5.564 | 4.388 | 15.870 | 1.276 | 7.405 |
| Total no. refns | 4909 | 3839 | 8126 | 11.612 | 10.277 |
| Unique refns | 1315 | 1312 | 1140 | 6072 | 5039 |
| R₁ | 0.103 | 0.018 | 0.297 | 0.026 | 0.114 |
| No. of params, restraints | 38, 0 | 38, 0 | 38, 0 | 188, 0 | 188, 0 |
| R₁ | 0.055 | 0.018 | 0.065 | 0.046 | 0.077 |
| R₁ | 0.065 | 0.022 | 0.068 | 0.059 | 0.091 |
| wR₂ | 0.137 | 0.034 | 0.163 | 0.072 | 0.196 |
| wR₂ | 0.148 | 0.035 | 0.168 | 0.077 | 0.207 |

| Compound | [AlCl₃][Me₄S(CH₃)₂SMe] | [AlCl₃][Me₄S(CH₃)₂SeMe] | [Me₅SH][AlCl₃] |
|----------|------------------------|------------------------|---------------|
| Formula  | C₆H₁₂AlCl₃S₄           | C₆H₁₂AlCl₃S₄           | C₆H₁₂AlCl₃S₄ |
| M        | 205.84                 | 205.84                 | 205.84        |
| Space group | Monoclinic             | Monoclinic             | Monoclinic |
| a [Å]    | 14.825 (3)             | 14.825 (3)             | 14.825 (3)    |
| b [Å]    | 12.182 (1)             | 12.182 (1)             | 12.182 (1)    |
| c [Å]    | 15.150 (4)             | 15.150 (4)             | 15.150 (4)    |
| u [Å³]   | 493.04                 | 493.04                 | 493.04        |
| Z        | 4                      | 4                      | 4             |
| µ(Mo Kα) [mm⁻¹] | 7.563 | 1.026 | 0.991 | 1.443 |
| Total no. refns | 24085 | 8120 | 10.176 | 11.008 |
| Unique refns | 5928 | 2199 | 4613 | 4432 |
| R₁ | 0.152 | 0.041 | 0.133 | 0.035 |
| No. of params, restraints | 185, 0 | 100, 3 | 278, 0 | 153, 0 |
| R₁ | 0.057 | 0.108 | 0.085 | 0.045 |
| R₁ | 0.135 | 0.121 | 0.103 | 0.055 |
| wR₂ | 0.106 | 0.258 | 0.193 | 0.156 |
| wR₂ | 0.115 | 0.277 | 0.207 | 0.189 |

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

R = Σ|Fo| - |Fc|/Σ|Fo|; wR = [Σw(Fo² - Fc²)]/ΣwFo². 

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detailed below, with H atoms bonded to C being placed in calculated positions using the default C–H distance. For [AlCl₃(MeC(CH₂SMe)₃)] the data were collected using the Rigaku automated routines which normally gives close to 100% of the data out to 2θ of 55°. For reasons that are not clear this did not happen in this case and it proved difficult to obtain more suitable crystals for a re-collection. Judged by the high R_merge value, the data are of modest quality although the intensities seems satisfactory (80% exceed the Shelx test, I > 2σ(I)). The structure that emerges from the analysis appears sound, with no unusual adp values or other causes for concern. For [[AlCl₃]₂C₆H₄(CH₂SEt)₂] the diffraction pattern exhibits many additional reflections in the 100 projection. These are likely due to a modulation. In fact, the Ga analogue exhibits the same behaviour and in that case it was clear this did not happen in this case and it proved difficult to

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