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

Kathryn George,a Marek Jura,b William Levasont,⁎ Mark E. Lichta and Gillian Reida

The reaction of AlCl3 with Me2E (E = S, Se or Te) or nBu2E (E = Se or Te) in CH2Cl2 under rigorously anhydrous conditions gave the pseudo-tetrahedral complexes [AlCl3(R2E)]. The [AlX3(Me2E)] (X = Br or I, E = S; X = Br, E = Te) were made from toluene solution since attempted syntheses in CH2Cl2 resulted in substantial chloride incorporation. The synthesis of [AlCl3(μ-Ch2H4(CH2SEt)2)] and of the six-coordinate trans-[AlX2(MeE(CH2)2EMe)2][AlX4] (X = Cl or Br, E = S, and X = Cl, E = Se) and cis-[AlX2(MeS(CH2)2SMethylene)][AlX4] are reported. The tripodal thioether forms [AlCl3(MeC(CH2SMethylene)2)], which is a chain polymer with κ3-coordinated ligand and a ttp arrangement at Al(III). Chalcogenoether 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(Me2S)] with added Me2S forms [AlCl3(Me2S)2], and the [AlX2{MeS(CH2)2SMethylene}2][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(μ-MeSe)] (X = Cl or Br), trans-[AlCl2(MeE(CH2)2EMe)2][AlCl4] (E = S or Se), cis-[AlX2(MeS(CH2)2SMethylene)]AlCl4, [AlCl3(MeC(CH2SMethylene)3)] and for the sulfonium salt [Me2SH][AlCl4]. The aluminium halide chalcogenoether chemistry is compared with the corresponding gallium and indium systems, and the relative Lewis acidities of the metals discussed. Attempts to use [AlCl3(nBu2E)] (E = Se or Te) as LPCVD reagents to form aluminium chalcogenide films were unsuccessful.

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 combination with [AlCl4]− anions. Aluminium bromide and iodide promote similar chemistry and have some niche applications. 1 The strong Lewis acidity of these three halides has resulted in the characterisation of very many adducts, mostly with N- or O-centres in solvents or donor ligands.2 In contrast, AlF3 is an inert polymer which forms few complexes.3 Surprisingly little is known about AlX3 adducts of chalcogenoethers, which are limited to early studies of adducts with Me2S or Et2S that reported phase diagrams, IR and 1H NMR spectra,4,6 and several studies of solution enthalpies.7 The only crystallographically characterised example of a neutral thioether co-ordinated to AlX3 is the recently reported [AlCl3(thianthrene)], although there are a few AlMe3 complexes with thiamicrocycles.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 = RS-, Me2S, Me2Se, Me2Te, etc.) or dinuclear [X2Ga(μ-L)-GaX2] (L = RS-, Me2S, Me2Se), etc.11 Higher coordination numbers are rare in the gallium systems, but found with the thia-macrocycle [14]aneS4,† which binds exodentate via two sulphur centres, affording the chain polymer [GaCl3([14]aneS4)] with a trigonal bipyramidal geometry.12 The larger rings [16]aneS4 and [16]aneSe4 form octahedral cations

†[14]aneS4 = 1,4,8,11-tetraethiacyclotetradecane, [16]aneSe4 = 1,5,9,13-tetraselana-cyclohexadecane, [16]aneS4 = 1,5,9,13-tetraethiacyclohexadecane, [9]aneS = 1,4,7-trithiacyclononane.

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Electronic supplementary information (ESI) available: Structural data on [AlCl3([9]aneS3)], [AlCl3([14]aneS4)][AlCl4] and [Bu2Te(CH2)7TeBu][AlCl4]. CCDC 966342. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52991f
trans-[GaCl2(macrocycle)][GaCl4]. The larger indium centre forms 4-, 5- or 6-coordinate complexes of types [InXn(R2E)] (E = S, Se or Te), [InX6(RE(CH2)2ER2)], [InX6(RE2)] or trans-[InX2(RE(CH2)2ER2)] 11−16 cis-[InCl2(14-aneS4)][InCl4] and trans-[InCl2(16-aneSe4)][InCl4] 15,16

We have recently reported that [GaCl2(Bu2E)] (E = S or Te) or [GaCl2(Bu2E)] is effective single source precursors for low pressure chemical vapour deposition (LPCVD) of Ga2E 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- or telluro-ethers requires anhydrous AlX3, rigorously anhydrous solvents and ligands and exclusion of water at all stages of the manipulations. Trace water displaces the neutral ligands and also generates [AlX3]− which are readily identified in the solids by their characteristic IR spectra ([AlCl4]− t2 = 498, [AlBr4]− 394, [AlI4]− 336 cm−1)18 and in solution by 27Al NMR spectroscopy (Table 1), where they have sharp characteristic resonances. The moisture sensitivity of the halides and the formation of the selenonium cation in [o-C6H4(SMeCH2Cl)2][GaCl4] when [GaCl4]− is allowed to stand in CH2Cl2 solution is much slower at low temperatures, permitting growth of X-ray quality crystals overnight at −18 °C.

Table 1 27Al NMR data

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<th>Compound</th>
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<th>δ (27Al, 190 K)</th>
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*a Chemical shifts relative to [Al(H2O)6]3+ in H2O at pH = 1. b In CH2Cl2–CD2Cl2 solution at temperature specified.

[AlX3(R2E)] complexes

The reaction of AlCl3 in CH2Cl2 or AlX3 (X = Br or I) in toluene with Me2S affords [AlCl3(Me2S)] in high yield. The chloro-complex is an oil at room temperature, the others crystalline solids. The complexes can also be made by condensing excess Me2S onto the appropriate AlX3 at −196 °C, allowing the mixture to thaw, when the halide dissolves to give a clear solution, and then removing excess Me2S in vacuo. The phase diagram of the AlCl3/Me2S system4 shows both [AlCl3(Me2S)] and [AlCl3(Me2S)2], but on removing the volatiles in vacuo from a mixture of AlCl3 and 3Me2S, only the 1:1 complex was isolated.

The IR spectrum of [AlCl3(Me2S)] shows features at 541 and 410 cm−1 assigned to the E and A1 modes of the pyramidal AlCl3 unit; both bands are quite broad and the E mode shows some evidence of further splitting. Similar observations were...
The complexes $[\text{AlX}_3(\text{Me}_2E)]$ (X = Br or I) are generally similar to the chloride complex, and exhibit progressively lower frequency shifts in the $^{27}\text{Al}$ NMR spectra as the halogen becomes heavier (Table 1). However, the $^1\text{H}$ NMR spectra show fast exchange with added Me$_2$S in CH$_2$Cl$_2$ solution, and no new resonances were evident in the $^{27}\text{Al}$ 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 $[\text{AlX}_3(\text{Me}_2E)]$ (X = Cl, Br, E = Se or Te) were obtained in high yields and their $^1\text{H}$ NMR and IR spectroscopic properties are similar to those of the thioether analogues. The $^{27}\text{Al}$ 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 $[\text{AlX}_3(\text{Me}_2E)]$. $[\text{AlCl}_3(\text{Me}_2Se)]$ shows a $^{77}\text{Se}$ 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 $[\text{GaX}_3(\text{Me}_2Se)]$. Although high frequency coordination shifts are seen in most transition metal selenoether (and tellueroether) complexes, in p-block complexes both high and low frequency shifts are seen in different systems, and the causes are not understood.

We were unable to observe a $^{77}\text{Se}$ NMR resonance from $[\text{AlBr}_3(\text{Me}_2Se)]$ or $^{125}\text{Te}$ resonances from $[\text{AlX}_3(\text{Me}_2Te)]$ over the temperature range 295–190 K, presumably due to fast exchange. The solutions of the selenoether and tellueroether 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 $^{77}\text{Se}$ and $^{125}\text{Te}$ chemical shifts to concentration, solvent etc. 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, $[\text{AlCl}_3(\text{Me}_2Se)]$, $[\text{AlCl}_3(\text{Me}_2Te)]$ and $[\text{AlBr}_3(\text{Me}_2Te)]$ 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 $[\text{AlX}_3(\text{Me}_2Te)]$ (X = Cl or Br) are the same within experimental error.

Storing a solution of $[\text{AlCl}_3(\text{Me}_2S)]$ in CH$_2$Cl$_2$ in the refrigerator, produced a few small crystals which were identified as the sulfonium salt $[\text{Me}_2\text{SH}]\,[\text{AlCl}_4]$ (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, the formation being promoted by “anhydrous” conditions and a large weakly coordinating

Fig. 1 The structure of $[\text{AlCl}_3(\text{Me}_2Se)]$ showing the 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 (°): Se1–Al1 = 2.486(2), Cl1–Al1 = 2.121(2), C12–Al1 = 2.1130(14), C12–Al1–C12a = 115.30(9), C12–Al1–C11 = 111.32(5), C12–Al1–Se1 = 106.47(5), C11–Al1–Se1 = 105.20(6).

Fig. 2 The structure of $[\text{AlCl}_3(\text{Me}_2Te)]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = x, y, 1/2 - z$. Selected bond lengths (Å) and angles (°): Al1–C12 = 2.1207(6), Al1–C11 = 2.1295(10), Al1–Te1 = 2.6873(19), C12–Al1–C12a = 115.23(4), C12–Al1–C11 = 111.14(5), C12–Al1–Te1 = 106.25(2), C11–Al1–Te1 = 106.21(3).
Fig. 3 The structure of [AlBr₃(Me₂Te)] 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 (°): Al1−Br1 = 2.286(3), Al1−Br2 = 2.287(2), Al1−Te1 = 2.692(4), Br1−Al1−Br2 = 111.19(9), Br2−Al1−Br2a = 114.01(15), Br1−Al1−Te1 = 106.34(12), Br2−Al1−Te1 = 106.80(9).

Fig. 4 The structure of [Me₂SH][AlCl₄] showing the S₂ 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 residual electron density. A bulk sample of [Me₂SH][AlCl₄] was obtained by saturating a dry CH₂Cl₂ solution of [AlCl₃(Me₂S)] with HCl gas.

The n-butyl derivatives [AlCl₃(“Bu₂E)] (E = Se, Te) were also synthesised as potential single source precursors for LPCVD as discussed below. Their characterisation data matched well with that of the equivalent methyl substituted complexes. The telluroether complexes are not stable when stored at room temperature over a period of days to weeks, even in an N₂ filled glove box. They gradually become darker and a quantity of black solid (elemental Te) forms. Samples can be stored at −18 °C for a few weeks with minimal decomposition. A sample of [AlCl₃(“Bu₂Te)] that had been stored in the glove box for several weeks and had visibly decomposed was analysed by ESI+ mass spectrometry, which showed the presence of (“Bu₂Te)⁺, and this ion was also present in the ¹²⁵Te NMR spectrum (δ = 491).¹³

Complexes with bidentate ligands

By analogy with the corresponding GaX₃ adducts,¹² and considering the preference for four-coordination in [AlX₂(R₂E)] adducts described above, it was expected that flexible dithioethers or diselenoethers (L−L) would produce complexes of the type [X₃Al(μ-L-L)AlX₃]⁻. In fact this was only true for the bulky o-xylyl-backboned dithioether, o-C₆H₄(CH₂SMe)₂, which gave yellow crystals of [[AlCl₃]₂[μ-o-C₆H₄(CH₂SMe)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(m) analogue,¹³ 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 o-C₆H₄(CH₂SeEt)₂ was completely converted to the selenonium cation [o-C₆H₄(CH₂SeEt)₂]⁺ upon reaction with AlCl₃ in CH₂Cl₂ (see ESI†). The same selenonium cation is formed upon reaction of this ligand with GaCl₃ or InCl₃.¹²,¹⁵

Unexpectedly, reaction of AlX₃ with MeE(CH₂)₂EMe (E = S or Se) failed to give [X₃Al(μ-MeE(CH₂)₂EMe)AlX₃] and the products had an AlX₂: MeE(CH₂)₂EMe 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, [AlX₂(MeE(CH₂)₂EMe)]₂[AlX₄] (X = Cl, E = S or Se; X = I, E = S). The structures of [AlCl₃(MeE(CH₂)₂EMe)]₂[AlCl₄] (Fig. 6 and 7) reveal centrosymmetric cations (trans isomer) with identical d(Al−Cl), which are as expected longer than in the four-coordinate complexes. The d(Al−S) and d(Al−Se) differ by ~0.14 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 chalcogenoether in the di conformation, the two crystals are not isomorphous and in the selenoether complex there are short contacts Se₂−…Se’ (3.436 Å) and Se₃−…Se” (3.542 Å). These link Al₂-centred cations into chains through Se2 (along the a direction)
[AlCl₄] shows a second resonance (δ²⁷Al = 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 [AlCl₃(MeS(CH₂)₂SMe)]⁺, 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 [AlCl₃(MeS-(CH₂)₂SMe)]⁺, being present. At 183 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 invertomers. The solutions decompose slowly on standing.

The trans-[AlCl₃(MeSe(CH₂)₂SeMe)]₂[AlCl₄] exhibits a singlet ⁷⁷Se NMR resonance at room temperature (δ = 95.5) which is a low frequency coordination shift (Δδ = −25.3) and singlet CH₂ (δ = 2.36) and CH₃ (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 CD₂CN solution resulted in displacement of the thio- or seleno-ethers by the nitrile.

Reaction of AlCl₃ with the ditelluroether ⁴⁴BuTe(CH₂)₃Te⁴⁴Bu produced a mixture of species resulting from ligand fragmentation. The ¹H NMR spectrum of the product showed multiple resonances for the t-butyl 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 [⁴⁴BuTe(CH₂)₃Te⁻(⁴⁴Bu)Te(CH₃)₃Te⁴⁴Bu][AlCl₄], derived from fragmentation of the ditelluroether (see ESIF).

**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 –CH₃SMe 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 : tripod stoichiometries were unsuccessful. The [AlCl₃(MeC-(CH₂SMe)₃)] stoichiometry contrasts with the gallium complex and similarly, the Al₃-centred cations are linked into chains through Se3 (again along the a direction) (Fig. 8). The structure of the [Al₃(MeS(CH₂)₂SMe)]⁴⁺ [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-[Al₃(MeS(CH₂)₂SMe)]⁴⁺ 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-[AlCl₃(MeSCH₂CH₂SMe)]₂[AlCl₄].

The Nujol mull IR spectra for these salts all confirm the presence of [AlX₄]⁻, 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 [AlX₄]⁻ (Table 1), but only [AlCl₃(MeS(CH₂)₂SMe)]²⁻.
form similarly intractable 1 : 1 complexes with this ligand,\(^\text{11}\) precluding solution measurements. Both gallium and indium macrocycle is displaced by coordinating solvents like MeCN, aneS\(_4\) and [16]aneSe\(_4\) and the far IR spectra confirmed the presence of [AlCl\(_4\)]\(^-\) anions. Poor quality crystals of [AlCl\(_4\)([14]aneS\(_4\)]AlCl\(_4\)] were obtained from the filtrate from the reaction solution and the structure shows the cation with endodentate macrocycle and a cis AlCl\(_4\) unit which serve to confirm the constitution (see ESI†). Although not isomorphous, the structure is similar to that of cis-[InCl\(_2\)([14]aneSe\(_4\)]InCl\(_4\)].\(^\text{15}\) In contrast, gallium chloride forms an exodentate chain polymer [GaCl\(_3\)([14]aneS\(_4\])] with trigonal bipyramidal coordination.\(^\text{13}\) The larger ring [16]aneSe\(_4\) forms trans-[MCl\(_2\)([16]aneSe\(_4\)]- [MCl\(_4\)] (M = Ga or In)\(^\text{13}\) and the aluminium complex probably has an analogous structure. The 16-membered ring macrocycle complexes were insoluble in CH\(_2\)Cl\(_2\) and the macrocycle was displaced by stronger donor solvents.

**LPCVD investigation**

Following previous success in using neutral chalcogenoether adducts of GaCl\(_3\) to deposit thin films of crystalline Ga\(_2\)Se\(_3\) and Ga\(_2\)Te\(_3\),\(^\text{17}\) several coordination complexes of AlCl\(_3\) were synthesised as potential single source precursors to Al\(_2\)E\(_3\) films. Ligands with \(^\text{\textsuperscript{\textbf{t}}}\)Bu substituents were selected as these had previously been shown to be more effective than ligands with Me substituents, probably because they have the \(\beta\)-hydride elimination route available.\(^\text{17}\) [AlCl\(_3\)(\(^\text{\textsuperscript{\textbf{t}}}\)Bu\(_3\)E)] (E = Se, Te) were synthesised as yellow oils as described above. LPCVD using both complexes was attempted at temperatures between 723 and 873 K, using the CVD equipment described previously.\(^\text{13}\) In all cases the precursor evaporated cleanly, having changed colour to dark brown during the evaporation. There was no deposition on the substrates and some elemental selenium or tellurium was deposited on the tube at the exit of the furnace. We conclude that these reagents are unsuitable for LPCVD under these conditions.

**Comparisons of Lewis acid behaviour of Al, Ga and In towards chalcogenoethers**

There has been much recent interest in exploring Group 13 Lewis–Lewis base adducts both by modelling and experiment. The modelling work has mostly focussed on boron and aluminium complexes with O- or N-donor ligands, with trends sometimes extrapolated to gallium. The conclusions of these studies, although sometimes disputed in detail, were that
Lewis acidity falls AlCl₃ > AlBr₃ > AlI₃, and AlCl₃ > AlBr₃ > GaCl₃ > GaBr₃ (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 bond lengths in comparable complexes of Al and Ga are also 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 study31 suggested that whilst Ga and In halide complexes of Me₂Se 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 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 2.486(2) Å.

Our data also show the ready formation of six-coordinate cations with aluminium, [AlX₂(L₂)+], 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 GaX₃ and InX₃. The aluminium complexes are extremely moisture sensitive, and complexes with selenium or telluroligands are prone to slow E–C bond cleavage in solution. Nonetheless, the formation and structural characterisation of telluroether complexes of the hard AX₃ 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.
Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm\(^{-1}\). \(\text{\textsuperscript{1}}\text{H}\) NMR spectra were recorded using a Bruker AV300 spectrometer. \(\text{\textsuperscript{77}}\text{Se}\{\text{\textsuperscript{1}}\text{H}\}\), \(\text{\textsuperscript{125}}\text{Te}\{\text{\textsuperscript{1}}\text{H}\}\) and \(\text{\textsuperscript{27}}\text{Al}\) NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external neat \(\text{SeMe}_{2}\), \(\text{TeMe}_{2}\) and aequous \([\text{AlH}_{2}\text{O}_{4}]^{-}\) at pH = 1, respectively. Microanalyses were undertaken by Medac Ltd or London Metropolitan University. Solvents were dried prior to use: toluene by distillation preparations were undertaken using standard Schlenk techniques under a \(N_{2}\) atmosphere. Anhydrous aluminium(III) halides (Aldrich or Strem) were used as received. \(\text{SeMe}_{2}\) and \(\text{TeMe}_{2}\) (Aldrich) were stored over molecular sieves. Other thio- and telluroethers were made by literature methods and stored under dinitrogen over molecular sieves.

\(\text{[AlCl}_{3}\{\text{Me}_{3}\text{Se}\}\}^{+}\): \(\text{Me}_{3}\text{Se}\) (0.09 g, 1.5 mmol) was added dropwise to a suspension of \(\text{AlCl}_{3}\) (0.2 g, 1.5 mmol) in anhydrous \(\text{CH}_{2}\text{Cl}_{2}\) (15 mL) with stirring to give a colourless solution. After 30 minutes, all solvent was removed \(\text{in vacuo}\) to give a colourless oil. Yield 0.26 g, 89%. Anal. Calcd for \(\text{C}_{2}\text{H}_{6}\text{AlCl}_{3}\text{Se}\): C, 9.9; H, 2.9. Found: C, 9.8; H, 3.1.

\(\text{[AlBr}_{3}\{\text{Me}_{3}\text{Se}\}\}^{+}\): \(\text{AlBr}_{3}\) (0.1 g, 0.37 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution and \(\text{Me}_{3}\text{Se}\) (0.023 g, 0.37 mmol) was added dropwise when the solution became colourless. After stirring for 15 minutes, all solvent was removed \(\text{in vacuo}\) to give a white solid. Yield 0.10 g, 79%. Anal. Calcd for \(\text{C}_{2}\text{H}_{6}\text{AlBr}_{3}\text{Se}\): C, 7.3; H, 1.8. Found: C, 6.4; H, 2.0.

\(\text{[AlI}_{3}\{\text{Me}_{2}\text{S}\}\}^{+}\): \(\text{AlI}_{3}\) (0.20 g, 0.5 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution and \(\text{Me}_{2}\text{S}\) (0.03 g, 0.5 mmol) was added dropwise. After stirring for 15 minutes, all solvent was removed \(\text{in vacuo}\) to give a pale yellow solid. Yield 0.17 g, 75%. Anal. Calcd for \(\text{C}_{2}\text{H}_{6}\text{AlI}_{3}\text{Se}\): C, 10.4; H, 2.6%. Found: C, 10.0; H, 2.6. 1H NMR (CDCl\(_3\), 295 K): \(\delta 2.44\) (s).

\(\text{[AlI}_{3}\{\text{Me}_{3}\text{Te}\}\}^{+}\): \(\text{AlI}_{3}\) (0.2 g, 1.5 mmol) was dissolved in CH\(_2\)Cl\(_2\) (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 \(\text{in vacuo}\). 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 \(\text{C}_{2}\text{H}_{6}\text{AlI}_{3}\text{Te}\): C, 10.4; H, 3.0. Found: C, 10.5; H, 2.9.

\(\text{[AlCl}_{3}\{\text{Me}_{3}\text{Se}\}\}^{+}\): \(\text{AlCl}_{3}\) (0.2 g, 1.5 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution and \(\text{Me}_{3}\text{Se}\). After stirring for 15 minutes, all solvent was removed \(\text{in vacuo}\) to give a pale yellow solid. Yield 0.10 g, 79%.

}\[\text{[AlCl}_{3}\{\text{Me}_{3}\text{Se}\}\}^{+}\] is a terminal M-X.

\begin{table}[h]
\centering
\caption{Structural data on Group 16 ligand adducts of Al, Ga and In halides}
\begin{tabular}{|c|c|c|c|}
\hline
Compound & M-XÅ & M-EÅ & Coordination number of M \\
\hline
\([\text{AlCl}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.121(2), 2.113(1) & 2.486(2) & 4 \\
\([\text{AlCl}_{3}\{\text{Me}_{3}\text{Te}\}\}]^{+} & 2.1207(6), 2.1295(10) & 2.6871(9) & 4 \\
\([\text{AlBr}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.286(3), 2.287(2) & 2.692(4) & 4 \\
\([\text{GaCl}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.191(2) & 2.5950(13), 2.6232(13) & 4 \\
\([\text{GaCl}_{3}\{\text{Me}_{3}\text{Te}\}\}]^{+} & 2.4907(7), 2.5316(7) & 2.4048(12) & 4 \\
\([\text{GaI}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.1575(14), 2.1650(15) & 2.3573(15) & 4 \\
\([\text{GaI}_{3}\{\text{Me}_{3}\text{Te}\}\}]^{+} & 2.1606(8), 2.1700(10) & 2.4637(7) & 4 \\
\([\text{GaI}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.5290(2) & 2.5277(2) & 4.14 \\
\([\text{InCl}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.1492(2) & 2.166(2) & 4 \\
\([\text{InCl}_{3}\{\text{Me}_{3}\text{Te}\}\}]^{+} & 2.158(3), 2.181(3) & 2.6378(14), 2.6356(13) & 4 \\
\([\text{InCl}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.276(3), 2.296(3) & 2.482(4), 2.518(4) & 4 \\
\([\text{InBr}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.3038(11), 2.3202(12) & 2.5906(7), 2.6106(8) & 4 \\
\([\text{InBr}_{3}\{\text{Me}_{3}\text{Te}\}\}]^{+} & 2.4901(12), 2.4981(7) & 2.6455(11) & 4 \\
\([\text{InBr}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.4243(1), 2.4457(1) & 2.7722(6), 2.7802(6) & 4 \\
\([\text{InCl}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.4237(18), 2.393(18) & 2.645(2), 2.696(2) & 4 \\
\([\text{InBr}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.5775(5), 2.5918(5) & 2.6518(10), 2.690(11) & 4 \\
\([\text{InBr}_{3}\{\text{Me}_{3}\text{Te}\}\}]^{+} & 2.6076(15), 2.6113(15) & 2.7370(16), 2.7762(16) & 4 \\
\([\text{InBr}_{3}\{\text{Me}_{3}\text{Se}\}\}]^{+} & 2.475(2) & 2.7199(10), 2.7394(11) & 4 \\
\hline
\end{tabular}
\end{table}
Found: C, 29.7; H, 5.8%. 1H NMR (CD2Cl2, 295 K): 3.03 (t, 4H), 1.83 (m, 4H), 2.66 (s). 27Al NMR (CD2Cl2, 295 K): 92.6. IR (cm−1): 404 (m), 391 (m) Al–Cl.

[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 (7 mL) with stirring to give a pale yellow solution. After 15 minutes, all solvent was removed in vacuo to yield a pale yellow oil. Yield 0.26 g, 78%. Anal. Calcd for C8H18AlCl3Te: C, 12.3; H, 2.1. Found: C, 12.8; H, 2.7%. 1H NMR (CDCl3, 295 K): 3.21 (s, 4H), 1.83 (m, 4H), 2.25 (s, 9H). IR (cm−1): 495 (s), 395 (s) Al–Cl.

[AlCl3(Me2Te)][AlCl4]: Me2Te (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 pale yellow solution. After 30 minutes the volume of solvent was reduced in vacuo to ~5 mL. Storage at −18 °C for 48 hours produced colourless crystals. Yield 0.18 g, 69%. Anal. Calcd for C8H20Al2Cl6S4: C, 12.3; H, 2.6. Found: C, 11.7; H, 2.1%. 1H NMR (CD2Cl2, 295 K): 9.0 (s, 4H), 3.95 (s, 4H), 2.66 (s, 4H). 27Al NMR (CD2Cl2, 295 K): 105.4. IR (cm−1): 489 (w), 350 (s), 295 (s).
C₆H₁₂AlCl₃S₄: 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][AlCl₄]: 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 C₁₂H₂₄Al₂Cl₆Se₄: C, 19.2; H, 3.2. Found: C, 19.0; H, 3.1%. IR (cm⁻¹): 483 (s), 434 (br).

**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

![Table 3 Crystal data and structure refinement details](image)

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<tr>
<th>Compound</th>
<th>[AlCl₃(Me₅Se)]⁻</th>
<th>[AlCl₃(Me₅Te)]⁻</th>
<th>[AlBr₃(Me₅Te)]⁻</th>
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<th>[AlCl₃(AlCl₄)]⁻</th>
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<td>C₆H₁₂AlBr₃Te</td>
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* Common items: temperature = 100 K; wavelength (Mo-Kα) = 0.71073 Å; θ(max) = 27.5°. b R₁ = Σ||Fᵩ|| – |Fᵩ||/Σ|Fᵩ||; wR₂ = [Σ|wFᵩ² – Fᵩ|²]/ΣwFᵩ².  

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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 Rint value, the data are of modest quality although the intensities seems satisfactory (80% exceed the Shelxl 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]2(C6H4(CH2SEt)2]] the diffraction pattern exhibits many additional reflections in the 100 projection. These are likely due to a modulation. In fact, the Ga analogue13 exhibits the same behaviour and in that case it was possible to index the modulated cell. As with the Ga analogue, the data were indexed on a strong sub-cell making refinement of the basic structure possible; however, the ignored reflections result in unrealistic thermal parameters for many of the atoms. For both of these structures therefore, detailed comparisons of the geometric parameters require caution.

Acknowledgements

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