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

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The reaction of $AlCl_3$ with Me_2E (E = S, Se or Te) or $^nBu_2E$ (E = Se or Te) in CH_2Cl_2 under rigorously anhydrous conditions gave the *pseudo*-tetrahedral complexes $[AlCl_3(R_2E)]$. The $[AlX_3(Me_2E)]$ (X = Br or I, E = S; X = Br, E = Te) were made from toluene solution since attempted syntheses in CH_2Cl_2 resulted in substantial chloride incorporation. The synthesis of $[(AlCl_3)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$, in which the ligand bridges two tetrahedral aluminium centres, and of the six-coordinate *trans*-$[AlX_2\{MeE(CH_2)_2EMe\}_2][AlX_4]$ (X = Cl or Br, E = S, and X = Cl, E = Se) and *cis*-$[AlI_2\{MeS(CH_2)_2SMe\}_2][AlI_4]$ are reported. The tripodal thioether forms $[AlCl_3\{MeC(CH_2SMe)_3\}]$, which is a chain polymer with κ^2-coordinated ligand and a tbp arrangement at Al(III). Chalcogenoether macrocycle complexes $[AlCl_3([9]aneS_3)]$, $[AlCl_2([14]aneS_4)][AlCl_4]$ and $[AlCl_2([16]aneSe_4)]$ $[AlCl_4]$ are also described. All complexes were characterised by microanalysis, IR and multinuclear NMR (^1H, ^{27}Al, ^{77}Se or ^{125}Te) spectroscopy as appropriate. In CH_2Cl_2 solution $[AlCl_3(Me_2S)]$ with added Me_2S forms $[AlCl_3(Me_2S)_2]$, and the $[AlX_2\{MeS(CH_2)_2SMe\}_2][AlX_4]$ exist as mixtures of *cis* and *trans* isomers which undergo rapid exchange at ambient temperatures. X-Ray crystal structures are reported for $[AlCl_3(Me_2Se]$, $[AlX_3(Me_2Te)]$ (X = Cl or Br), *trans*-$[AlCl_2\{MeE(CH_2)_2EMe\}_2][AlCl_4]$ (E = S or Se), *cis*-$[AlI_2\{MeS(CH_2)_2SMe\}_2][AlI_4]$, $[AlCl_3\{MeC(CH_2SMe)_3\}]$, and for the sulfonium salt $[Me_2SH][AlCl_4]$. 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 $[AlCl_3(^nBu_2E)]$ (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 $[AlCl_4]^-$ 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, AlF_3 is an inert polymer which forms few complexes.[3] Surprisingly little is known about AlX_3 adducts of chalcogenoethers, which are limited to early studies of adducts with Me_2S or Et_2S 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 coordinated to AlX_3 is the recently reported[8] $[AlCl_3(\text{thianthrene})]$, although there are a few $AlMe_3$ complexes with thiamacrocycles.[9] There are no reports of studies with telluroethers, and the single complex of a selenium ligand is $[AlCl_3(\text{selenoxan})]$, characterised only by microanalysis.[10]

Recent studies of gallium(III) halides GaX_3 (X = Cl, Br or I) with chalcogenoethers have established that most contain *pseudo*-tetrahedral gallium centres $[GaX_3L]$ (L = Me_2S, Me_2Se, Me_2Te, *etc.*) or dinuclear $[X_3Ga(\mu\text{-}L\text{–}L)GaX_3]$ (L–L = $RS(CH_2)_2SR$, $MeSe(CH_2)_2SeMe$, $MeTe(CH_2)_3TeMe$ *etc.*).[11–14] Higher coordination numbers are rare in the gallium systems, but found with the thia-macrocycle $[14]aneS_4$,‡ which binds *exodentate via* two sulfur centres, affording the chain polymer $[GaCl_3([14]aneS_4)]$ with a trigonal bipyramidal geometry.[15] The larger rings $[16]aneS_4$ and $[16]aneSe_4$ form octahedral cations

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† Electronic supplementary information (ESI) available: Structural data on $[o\text{-}C_6H_4CH_2Se(Me)CH_2][AlCl_4]$, $[AlCl_2([14]aneS_4)][AlCl_4]$ and $[^tBuTe(CH_2)_3Te(^tBu)\text{-}Te(CH_2)_3Te^tBu][AlCl_4]$. CCDC 966342–966353. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52991f

‡ $[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane, $[16]aneSe_4$ = 1,5,9,13-tetraselanacyclohexadecane, $[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane, $[9]aneS_3$ = 1,4,7-trithiacyclononane.

trans-[$GaCl_2$(macrocycle)][$GaCl_4$].[15] The larger indium centre forms 4-, 5- or 6-coordinate complexes of types [$InX_3(R_2E)$] (E = S, Se or Te), [$InX_3(R_2S)_2$], [$In_2X_6\{RE(CH_2)_2ER_2\}_2$], *trans*-[$InX_2\{RE(CH_2)_2ER_2\}_2$][$InX_4$],[11–16] *cis*-[$InCl_2${[14]ane$S_4$}][$InCl_4$] and *trans*-[$InCl_2${[16]ane$Se_4$}][$InCl_4$].[15,16]

We have recently reported that [$GaCl_3(^nBu_2E)$] (E = Se or Te) or [$GaCl_3\{\mu\text{-}^nBuE(CH_2)_nE^nBu)GaCl_3$] are effective single source precursors for low pressure chemical vapour deposition (LPCVD) of Ga_2E_3 thin films, and that preferential deposition occurs onto TiN in photolithographically patterned SiO_2/TiN substrates.[17] Here we report systematic studies of the reactions of AlX_3 (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 (AlX_3 (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 AlX_3, rigorously anhydrous solvents and ligands and exclusion of water at all stages of the manipulations. Trace water displaces the neutral ligands and also generates $[AlX_4]^-$ which are readily identified in the solids by their characteristic IR spectra ($[AlCl_4]^-$ t_2 = 498, $[AlBr_4]^-$ 394, $[AlI_4]^-$ 336 cm^{-1})[18] and in solution by ^{27}Al NMR spectroscopy (Table 1), where they have sharp characteristic resonances. 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 $AlCl_3$ are readily made in anhydrous CH_2Cl_2, use of this solvent for the $AlBr_3$ or AlI_3 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 $AlX_3/R_3PO/CH_2Cl_2$ systems. However, the pre-isolated pure [AlX_3L] (X = Br or I) react only slowly with CH_2Cl_2 (or CD_2Cl_2), which remains the NMR solvent of choice, as non-coordinating and useable down to 180 K. The reactivity of $AlCl_3$ in CH_2Cl_2 has been ascribed to the formation of the intermediate carbenium ion [CH_2Cl][$AlCl_4$],[8,20] and in previous studies of $GaCl_3$ complexes of thioethers we observed the formation of [*o*-$C_6H_4(SMeCH_2Cl)_2$][$GaCl_4$]$_2$ when [$(GaCl_3)_2\{\mu\text{-}o\text{-}C_6H_4(SMe)_2\}$] is allowed to stand in CH_2Cl_2 solution for several days.[13] Cleavage of C–Se or C–Te bonds is also observed, *e.g.* the formation of the selenonium cation in [*o*-$C_6H_4(CH_2)_2SeMe$]-[$GaCl_4$] from *o*-$C_6H_4(CH_2SeMe)_2$.[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.

[$AlX_3(R_2E)$] complexes

The reaction of $AlCl_3$ in CH_2Cl_2 or AlX_3 (X = Br or I) in toluene with Me_2S affords [$AlX_3(Me_2S)$] 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 Me_2S onto the appropriate AlX_3 at −196 °C, allowing the mixture to thaw, when the halide dissolves to give a clear solution, and then removing excess Me_2S *in vacuo*. The phase diagram of the $AlCl_3/Me_2S$ system[4] shows both [$AlCl_3(Me_2S)$] and [$AlCl_3(Me_2S)_2$], but on removing the volatiles *in vacuo* from a mixture of $AlCl_3$ and $3Me_2S$, only the 1 : 1 complex was isolated.

The IR spectrum of [$AlCl_3(Me_2S)$] shows features at 541 and 410 cm^{-1} assigned to the E and A_1 modes of the pyramidal $AlCl_3$ unit; both bands are quite broad and the E mode shows some evidence of further splitting. Similar observations were

Table 1 ^{27}Al NMR data[a]

Compound[b]	δ (^{27}Al), 298 K	δ (^{27}Al), 190 K	Comments
$[AlCl_4]^-$	103.5	103.6	$W_{1/2}$ ~ 5 Hz
$[AlBr_4]^-$	80.6	81.4	$W_{1/2}$ ~ 15 Hz
$[AlI_4]^-$	−23.0		$W_{1/2}$ ~ 25 Hz
[$AlCl_3(Me_2S)$]	111.6 $W_{1/2}$ ~ 310 Hz	111.2	73.8 with excess Me_2S (298 K)
[$AlBr_3(Me_2S)$]	81.2 $W_{1/2}$ ~ 250 Hz	81.6	No change with added Me_2S
[$AlI_3(Me_2S)$]	48.7 $W_{1/2}$ ~ 360 Hz	—	No change with added Me_2S
[$AlCl_3(Me_2Se)$]	110.5 $W_{1/2}$ ~ 300 Hz	110.1	No change with added Me_2Se
[$AlBr_3(Me_2Se)$]	99.7 $W_{1/2}$ ~ 170 Hz	—	
[$AlCl_3(Me_2Te)$]	105.9 $W_{1/2}$ ~ 310 Hz	103.4	
[$AlBr_3(Me_2Te)$]	92.6 $W_{1/2}$ ~ 320 Hz	—	Resonance lost on cooling
[$AlCl_3(^nBu_2Se)$]	109.9 $W_{1/2}$ ~ 490 Hz	—	
[$AlCl_3(^nBu_2Te)$]	92.6 $W_{1/2}$ ~ 555 Hz	—	
[$AlCl_2\{MeS(CH_2)_2SMe\}_2$][$AlCl_4$]	105.5, 37.4		
[$AlBr_2\{MeS(CH_2)_2SMe\}_2$][$AlBr_4$]	80.6	81.1	Only anion resonance seen
[$AlI_2\{MeS(CH_2)_2SMe\}_2$][$AlI_4$]	−23.0	−23.0	Only anion resonance seen
[$AlCl_2\{MeSe(CH_2)_2SeMe\}_2$][$AlCl_4$]	105.4	—	
[$(AlCl_3)_2\{C_6H_4(CH_2SEt)_2\}$]	111.3 $W_{1/2}$ ~ 900 Hz	—	

[a] Chemical shifts relative to $[Al(H_2O)_6]^{3+}$ in H_2O at pH = 1. [b] In CH_2Cl_2–CD_2Cl_2 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 [$AlCl_3(Me_2S)$] in CD_2Cl_2 (295 K) shows a singlet at δ = 2.53 which does not change significantly on cooling the solution to 190 K. Addition of aliquots of Me_2S 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 δ = 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_2S (δ = 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 δ = 111.6 is present in the spectrum of [$AlCl_3(Me_2S)$], which is little changed on cooling the solution to 190 K. However, addition of 1 mol. equivalent of Me_2S to the solution generates a new resonance at δ = 73.5 ($W_{1/2}$ = 650 Hz), and this resonance is unchanged upon addition of more Me_2S 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_2S in CH_2Cl_2 solution the 2 : 1 complex [$AlCl_3(Me_2S)_2$] forms; further addition of Me_2S does not produce any evidence for a 3 : 1 complex. As noted above, work-up of the solution results in decomposition to reform [$AlCl_3(Me_2S)$]. Five-coordination is established in the solid state with aluminium–phosphine complexes, *e.g.* [$AlI_3(PEt_3)_2$], which has a tbp geometry with axial phosphines.[22]

The complexes [$AlX_3(Me_2S)$] (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_2S in CH_2Cl_2 solution, no new resonances were evident in the ^{27}Al NMR spectra in the presence of a large excess of Me_2S, indicating that in these cases 2 : 1 complexes do not form.

The [$AlX_3(Me_2E)$] (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_2E to CH_2Cl_2 solutions of the appropriate [$AlX_3(Me_2E)$]. [$AlCl_3(Me_2Se)$] shows a ^{77}Se NMR chemical shift of δ = −11.3, which corresponds to a small low frequency coordination shift (Δ = −11.3); this can be compared with small high frequency coordination shifts observed in [$GaX_3(Me_2Se)$].[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 [$AlBr_3(Me_2Se)$] or ^{125}Te resonances from [$AlX_3(Me_2Te)$] 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_2E_2, Me_3E^+ or Me_2EX_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, [$AlCl_3(Me_2Se)$], [$AlCl_3(Me_2Te)$] and [$AlBr_3(Me_2Te)$] 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 [$AlX_3(Me_2Te)$] (X = Cl or Br) are the same within experimental error.

Storing a solution of [$AlCl_3(Me_2S)$] in CH_2Cl_2 in the refrigerator, produced a few small crystals which were identified as the sulfonium salt [Me_2SH][$AlCl_4$] (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,[25] the formation being promoted by "anhydrous" conditions and a large weakly coordinating

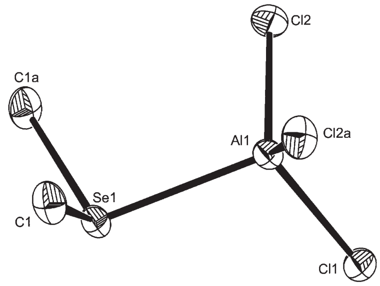

Fig. 1 The structure of [$AlCl_3(Me_2Se)$] showing the numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: *a* = *x*, *y*, 3/2 − *z*. Selected bond lengths (Å) and angles (°) Se1–Al1 = 2.486(2), Cl1–Al1 = 2.121(2), Cl2–Al1 = 2.1130(14), Cl2–Al1–Cl2a = 115.30(9), Cl2–Al1–Cl1 = 111.32(5), Cl2–Al1–Se1 = 106.47(5), Cl1–Al1–Se1 = 105.20(6).

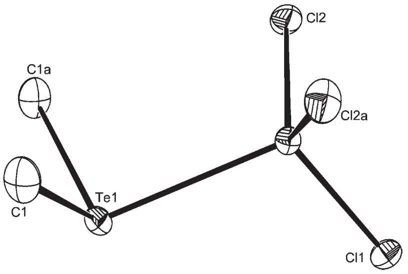

Fig. 2 The structure of [$AlCl_3(Me_2Te)$] showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: *a* = *x*, *y*, 1/2 − *z*. Selected bond lengths (Å) and angles (°): Al1–Cl2 = 2.1207(6), Al1–Cl1 = 2.1295(10), Al1–Te1 = 2.6871(9), Cl2–Al1–Cl2a = 115.20(4), Cl2–Al1–Cl1 = 111.14(3), Cl2–Al1–Te1 = 106.25(2), Cl1–Al1–Te1 = 106.21(3).

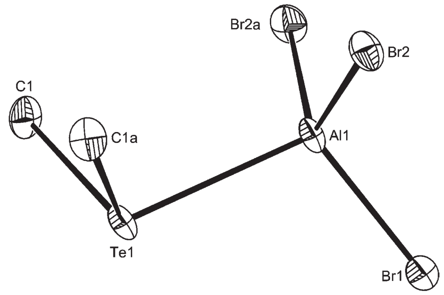

Fig. 3 The structure of $[AlBr_3(Me_2Te)]$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operation: $a = x, y, 3/2 - z$. Selected bond lengths (Å) and angles (°): Al1–Br1 = 2.286(3), Al1–Br2 = 2.287(2), Al1–Te1 = 2.692(4), Br1–Al1–Br2 = 111.19(9), Br2–Al1–Br2a = 114.01(15), Br1–Al1–Te1 = 106.34(12), Br2–Al1–Te1 = 106.80(9).

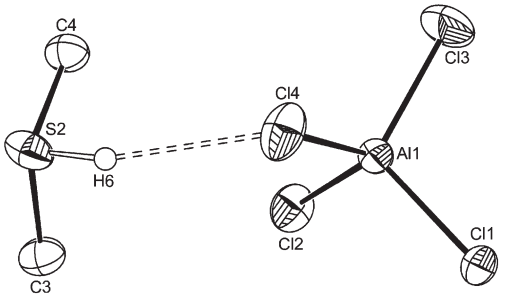

Fig. 4 The structure of $[Me_2SH][AlCl_4]$ showing the S2 centred cation and the H-bond (dashed bond) to an adjacent Cl atom. Ellipsoids are drawn at the 50% probability level and H atoms on C are not shown. The other crystallographically independent cation is similar. Selected bond lengths (Å): Al1–Cl3 = 2.1110(11), Al1–Cl4 = 2.1349(11), Al1–Cl2 = 2.1361(10), Al1–Cl1 = 2.1412(10), S2–H6 = 1.26(3), H6···Cl4 = 2.51(3).

anion. The S–H proton was identified in the difference map of residual electron density. A bulk sample of $[Me_2SH][AlCl_4]$ was obtained by saturating a dry CH_2Cl_2 solution of $[AlCl_3(Me_2S)]$ with HCl gas.

The *n*-butyl derivatives $[AlCl_3({}^nBu_2E)]$ (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 N_2 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 $[AlCl_3({}^nBu_2Te)]$ 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 $[{}^nBu_3Te]^+$, and this ion was also present in the ^{125}Te NMR spectrum (δ = 491).[13]

Complexes with bidentate ligands

By analogy with the corresponding GaX_3 adducts,[12] and considering the preference for four-coordination in $[AlX_3(R_2E)]$ adducts described above, it was expected that flexible dithioethers or diselenoethers (L–L) would produce complexes of the type $[X_3Al(\mu\text{-L–L})AlX_3]$. In fact this was only true for the bulky *o*-xylyl-backboned dithioether, $o\text{-}C_6H_4(CH_2SEt)_2$, which gave yellow crystals of $[(AlCl_3)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2SEt)_2\}]$. 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,[13] and serve as an example of this structure type (Fig. 5).

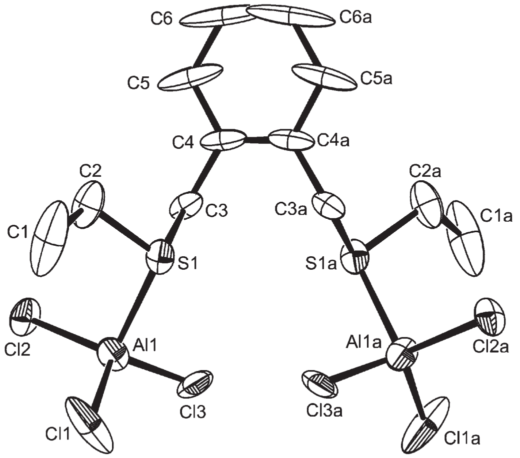

Fig. 5 The structure of $[(AlCl_3)_2\{o\text{-}C_6H_4(CH_2SEt)_2\}]$ showing the atom labelling scheme. The crystals had the properties of a modulated structure and the solution shown was derived from a smaller subcell. For this reason bond lengths and angles are less reliable than usual and not presented here.

The spectroscopic data are consistent with four-coordinate aluminium in solution. The corresponding diselenoether $o\text{-}C_6H_4(CH_2SeMe)_2$ was completely converted to the selenonium cation $[o\text{-}C_6H_4(CH_2)_2SeMe][AlCl_4]$ upon reaction with $AlCl_3$ in CH_2Cl_2 (see ESI†). The same selenonium cation is formed upon reaction of this ligand with $GaCl_3$ or $InCl_3$.[12,15]

Unexpectedly, reaction of AlX_3 with $MeE(CH_2)_2EMe$ (E = S or Se) failed to give $[X_3Al\{\mu\text{-}MeE(CH_2)_2EMe\}AlX_3]$, and the products had an $AlX_3 : MeE(CH_2)_2EMe$ 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, $[AlX_2\{MeE(CH_2)_2EMe\}_2][AlX_4]$ (X = Cl, E = S or Se; X = I, E = S). The structures of $[AlCl_2\{MeE(CH_2)_2EMe\}_2][AlCl_4]$ (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 DL conformation, the two crystals are not isomorphous and in the selenoether complex there are short contacts Se2···Se2′ (3.436 Å) and Se3···Se3″ (3.542 Å). These link Al2-centred cations into chains through Se2 (along the *a* direction)

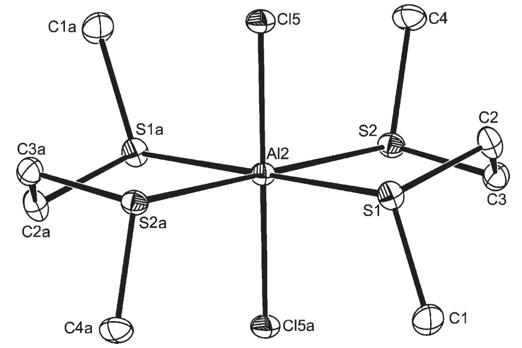

Fig. 6 The structure of a cation in *trans*-[AlCl$_2${MeS(CH$_2$)$_2$SMe}$_2$][AlCl$_4$] showing the numbering scheme for the centrosymmetric Al2 centred cation. Ellipsoids are drawn at the 50% probability level and H atoms are not shown for clarity. The other cation is similar. Symmetry operation: $a = 2 - x, -y, 1 - z$. Selected bond lengths (Å) and angles (°): Al2–Cl5 = 2.2131(10), Al2–S1 = 2.4595(11), Al2–S2 = 2.4809(10), S1–Al2–S2 = 87.92(4), S1–Al2–S2a = 92.08(4), Cl5–Al–S1a = 94.49(2), Cl5–Al2–S1 = 85.51(2), Cl5–Al2–S2a = 86.50(3), Cl5–Al2–S2 = 93.50(3).

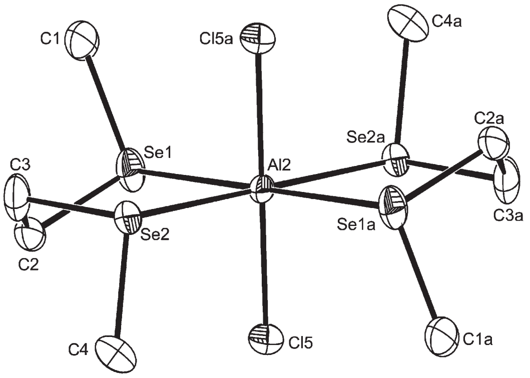

Fig. 7 The structure of a cation in *trans*-[AlCl$_2${MeSe(CH$_2$)$_2$SeMe}$_2$]-[AlCl$_4$] showing the numbering scheme for the centrosymmetric Al2 centred cation. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The other crystallographically independent cation is similar. Symmetry operation: $a = 1 - x, 1 - y, 1 - z$. Selected bond lengths (Å) and angles (°): Al2–Cl5 = 2.211(2), Al2–Se1 = 2.5950(13), Al2–Se2 = 2.6232(13), Se1–Al2–Se2 = 88.11(4), Se1–Al2–Se2a = 91.89(4), Cl5–Al2–Se1a = 94.50(6), Cl5–Al2–Se1 = 85.50(6), Cl5–Al2–Se2a = 86.51(6), Cl5–Al2–Se2 = 93.49(6).

and similarly, the Al3-centred cations are linked into chains through Se3 (again along the *a* direction) (Fig. 8).

The structure of the [AlI$_2${MeS(CH$_2$)$_2$SMe}$_2$][AlI$_4$] (Fig. 9) also contains a *pseudo*-octahedral cation, but this has a *cis*-geometry and with the dithioethers in the *meso* form. In *cis*-[AlI$_2${MeS(CH$_2$)$_2$SMe}$_2$]$^+$ the Al–S$_{trans\mathrm{I}}$ are longer by ~0.1 Å than Al–S$_{trans\mathrm{S}}$, but the Al–S$_{trans\mathrm{S}}$ distances are not significantly different to those in *trans*-[AlCl$_2$(MeSCH$_2$CH$_2$SMe)$_2$][AlCl$_4$].

The Nujol mull IR spectra for these salts all confirm the presence of [AlX$_4$]$^-$, 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 ^{27}Al resonances assignable to the [AlX$_4$]$^-$ (Table 1), but only [AlCl$_2${MeS(CH$_2$)$_2$SMe}$_2$][AlCl$_4$] shows a second resonance (δ ^{27}Al = 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 CD$_2$Cl$_2$ solution of [AlCl$_2${MeS(CH$_2$)$_2$SMe}$_2$][AlCl$_4$] shows singlet CH$_3$ (δ = 2.26) and CH$_2$ (δ = 3.08) resonances. On cooling to 223 K the spectrum shows three CH$_3$ resonances (δ = 2.26, 2.50, 2.66) and overlapping CH$_2$ resonances (δ = 3.08–3.31), which we tentatively assign to a mixture of *cis* and *trans* isomers of [AlCl$_2${MeS(CH$_2$)$_2$SMe}$_2$]$^+$, 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 [AlCl$_2${MeS(CH$_2$)$_2$SMe}]$^+$, 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 invertomers. The solutions decompose slowly on standing.

The *trans*-[AlCl$_2${MeSe(CH$_2$)$_2$SeMe}$_2$][AlCl$_4$] exhibits a singlet ^{77}Se NMR resonance at room temperature (δ = 95.5) which is a low frequency coordination shift (Δ = −25.5) and singlet CH$_3$ (δ = 2.36) and CH$_2$ (δ = 3.21) resonances in the ^{1}H NMR spectrum. Cooling the solution to 190 K produces little change in the ^{1}H NMR spectrum, although the ^{77}Se 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 CD$_3$CN solution resulted in displacement of the thio- or seleno-ethers by the nitrile.

Reaction of AlCl$_3$ with the ditelluroether ^{t}BuTe(CH$_2$)$_3$Te^{t}Bu produced a mixture of species resulting from ligand fragmentation. The ^{1}H NMR spectrum of the product showed multiple resonances for the *t*-butyl groups and the CH$_2$ units. Multiple signals were also observed in the ^{125}Te NMR spectrum, whilst the ^{27}Al NMR spectrum indicated the presence of [AlCl$_4$]$^-$. Very air sensitive, yellow crystals were isolated of one of the decomposition products, which proved to be [^{t}BuTe(CH$_2$)$_3$Te(^{t}Bu)Te(CH$_2$)$_3$Te^{t}Bu][AlCl$_4$], derived from fragmentation of the ditelluroether (see ESI†).

Polydentates and macrocycles

The reaction of the tripodal trithioether MeC(CH$_2$SMe)$_3$ with AlCl$_3$ in a 1 : 1 molar ratio in anhydrous CH$_2$Cl$_2$ gave colourless crystals whose structure (Fig. 10) showed a chain polymer with the ligand binding as a bridging bidentate with one uncoordinated –CH$_2$SMe 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 ^{1}H NMR spectrum shows single, sharp –CH$_2$, –SMe and –CMe resonances consistent with fast exchange. Attempts to isolate complexes with higher AlCl$_3$: tripod stoichiometries were unsuccessful. The [AlCl$_3${MeC(CH$_2$SMe)$_3$}] stoichiometry contrasts with the gallium complex

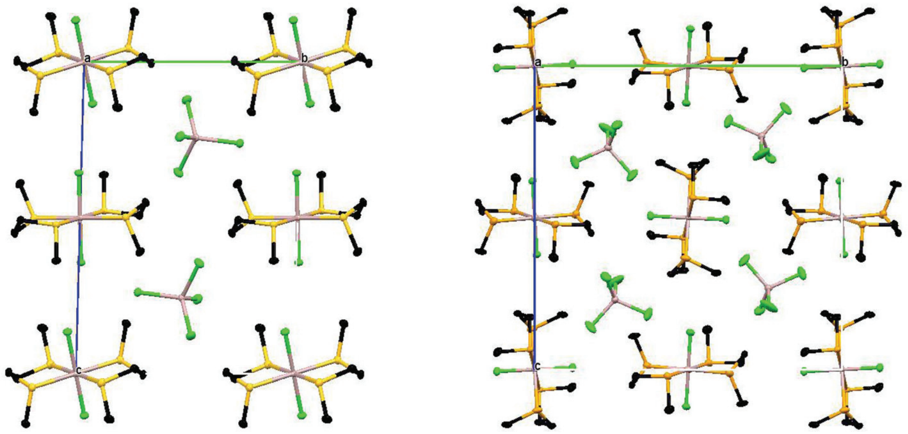

Fig. 8 View along the *a* axis of the packing diagrams of [$AlCl_2\{MeS(CH_2)_2SMe\}_2$][$AlCl_4$] (left) and [$AlCl_2\{MeSe(CH_2)_2SeMe\}_2$][$AlCl_4$] (right) showing the different molecular packing.

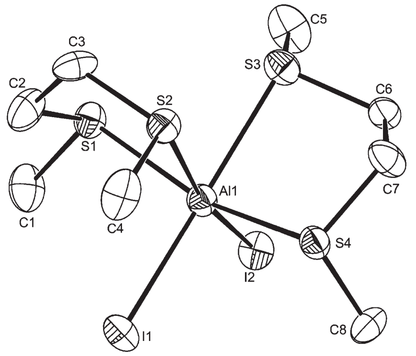

Fig. 9 The structure of the cation in *cis*-[$AlI_2\{MeS(CH_2)_2SMe\}_2$][$AlI_4$] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–S1 = 2.431(4), Al1–S4 = 2.448(4), Al1–S3 = 2.533(5), Al1–S2 = 2.546(5), Al1–I1 = 2.612(4), Al1–I2 = 2.635(4), I1 Al1–I2 = 97.30(13), S1–Al1–S3 = 84.84(15), S4–Al1–S3 = 83.28(14), S1–Al1–S2 = 83.46(15), S4–Al1–S2 = 79.24(14), S3–Al1–S2 = 76.13(15), S1–Al1–I1 = 99.17(14), S4–Al1–I1 = 89.96(14), S2–Al1–I1 = 93.69(14), S1–Al1–I2 = 94.43(13), S4–Al1–I2 = 101.02(15), S3–Al1–I2 = 92.95(14).

which was [$(GaCl_3)_3\{MeC(CH_2SMe)_3\}$], assumed to contain tetrahedral gallium coordination.[12]

The reaction of the small ring thia-macrocycle [9]aneS_3 with an equimolar amount of $AlCl_3$ in toluene gave a white powder, [$AlCl_3$([9]aneS_3)]. The complex is insoluble in CH_2Cl_2 and the macrocycle is displaced by coordinating solvents like MeCN, precluding solution measurements. Both gallium and indium form similarly intractable 1 : 1 complexes with this ligand,[11] and it seems likely that all three contain *fac*-octahedral structures. The larger macrocycles [14]aneS_4 and [16]aneSe_4 reacted with two molar equivalents of $AlCl_3$ in anhydrous CH_2Cl_2 to form insoluble white complexes. The analytical data supported a formulation [$AlCl_2$(macrocycle)][$AlCl_4$] (macrocycle = [14]aneS_4 and [16]aneSe_4) and the far IR spectra confirmed the presence of [$AlCl_4$]$^-$ anions. Poor quality crystals of [$AlCl_2$([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* $AlCl_2$ unit which serve to confirm the constitution (see ESI†). Although not isomorphous, the structure is similar to that of *cis*-[$InCl_2$([14]aneS_4)][$InCl_4$].[15] In contrast, gallium chloride forms an *exodentate* chain polymer [$GaCl_3$([14]aneS_4)] with trigonal bipyramidal coordination.[13] The larger ring [16]aneSe_4 forms *trans*-[MCl_2([16]aneSe_4)][MCl_4] (M = Ga or In)[13] and the aluminium complex probably has an analogous structure. The 16-membered ring macrocycle complexes were insoluble in CH_2Cl_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_2Se_3 and Ga_2Te_3,[17] several coordination complexes of $AlCl_3$ were synthesised as potential single source precursors to Al_2E_3 films. Ligands with ^{n}Bu substituents were selected as these had previously been shown to be more effective than ligands with Me substituents, probably because they have the β-hydride elimination route available.[17] [$AlCl_3(^nBu_2E)$] (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.[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 acid–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

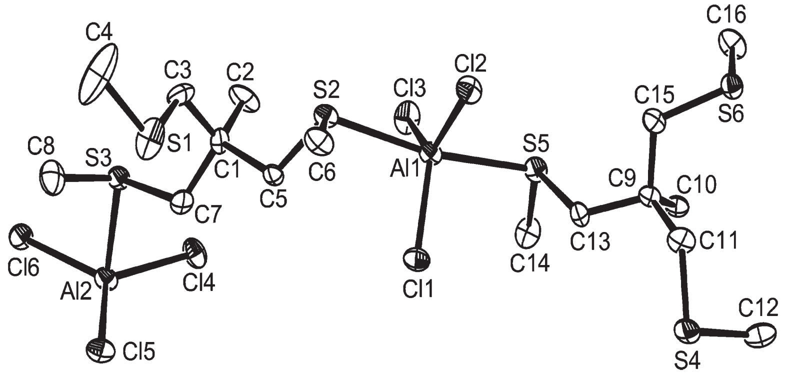

Fig. 10 The structure of the asymmetric unit in [$AlCl_3\{MeC(CH_2SMe)_3\}$] showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al1–Cl1 = 2.151(3), Al1–Cl2 = 2.152(3), Al1–Cl3 = 2.154(3), Al1–S5 = 2.473(3), Al1–S2 = 2.489(3), Al2–Cl5 = 2.158(3), Al2–Cl6 = 2.160(3), Al2–Cl4 = 2.169(3), Al2–S3 = 2.469(3), Al2–S6 = 2.488(3), Cl1–Al1–Cl2 = 117.05(12), Cl1–Al1–Cl3 = 118.80(13), Cl2–Al1–Cl3 = 124.15(13), Cl1–Al1–S5 = 94.98(11), Cl2–Al1–S5 = 88.33(11), Cl3–Al1–S5 = 86.31(10), Cl1–Al1–S2 = 95.32(11), Cl2–Al1–S2 = 89.27(11), Cl3–Al1–S2 = 86.49(10), S5–Al1–S2 = 169.38(11), Cl5–Al2–Cl6 = 117.44(13), Cl5–Al2–Cl4 = 119.86(12), Cl6–Al2–Cl4 = 122.70(12), Cl5–Al2–S3 = 94.48(10), Cl6–Al2–S3 = 89.38(11), Cl4–Al2–S3 = 86.84(11), Cl5–Al2–S6 = 90.27(10), Cl6–Al2–S6 = 92.63(10), Cl4–Al2–S6 = 86.71(11), S3–Al2–S6 = 173.30(12).

Lewis acidity falls $AlCl_3 > AlBr_3 > AlI_3$, and $AlCl_3 > AlBr_3 > GaCl_3 > GaBr_3$ (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_2Se 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 2.486(2) Å.

Our data also show the ready formation of six-coordinate cations with aluminium, $[AlX_2(L–L)_2]^+$, 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
$[AlCl_3(Me_2Se)]$	2.121(2), 2.113(1)	2.486(2)	4	This work
$[AlCl_3(Me_2Te)]$	2.1207(6), 2.1295(10)	2.6871(9)	4	This work
$[AlBr_3(Me_2Te)]$	2.286(3), 2.287(2)	2.692(4)	4	This work
trans-$[AlCl_2\{MeS(CH_2)_2SMe\}_2]^+$	2.2131(10)	2.4595(11), 2.4809(10)	6	This work
cis-$[AlI_2\{MeS(CH_2)_2SMe\}_2]^+$	2.612(4), 2.635(4)	2.431(4)–2.546(5)	6	This work
trans-$[AlCl_2\{MeSe(CH_2)_2SeMe\}_2]^+$	2.211(2)	2.5950(13), 2.6232(13)	6	This work
$[(GaI_3)_2\{MeS(CH_2)_2SMe\}_2]$	2.4997(7)–2.5316(7)	2.4048(12)	4	12
$[(GaCl_3)_2\{o\text{-}C_6H_4(CH_2SMe)_2\}]$	2.1478(14)–2.1650(15)	2.3573(15)	4	12
$[GaCl_3(Me_2Se)]$	2.1606(8), 2.1700(10)	2.4637(7)	4	12
$[GaI_3(Me_2Se)]$	2.5209(2)–2.5277(2)	2.479(2)	4	14
$[(GaCl_3)_2\{^nBuSe(CH_2)_2Se^nBu\}]$	2.149(2)–2.166(2)	2.468(1)	4	12
$[(GaCl_3)_2\{^tBuTe(CH_2)_3Te^tBu\}]$	2.158(3)–2.181(3)	2.6378(14), 2.6356(13)	4	17
trans-$[GaCl_2([16]aneS_4]^+$	2.276(3)–2.296(3)	2.482(4)–2.518(4)	6	13
trans-$[GaCl_2([16]aneSe_4]^+$	2.3058(11), 2.3220(12)	2.5906(7)–2.6106(8)	6	13
$[InBr_3(Me_2Se)]$	2.4901(12), 2.4981(7)	2.6455(11)	4	15
$[(InCl_3)_2(Me_2Se)_4]$	2.4243(1), 2.4457(1)[a]	2.7722(6), 2.7802(6)	6	14
trans-$[InCl_2(\{^iPrS(CH_2)_2S^iPr\}_2]^+$	2.4237(18), 2.393(18)	2.645(2)–2.696(2)	6	15
trans-$[InBr_2(\{^iPrS(CH_2)_2S^iPr\}_2]^+$	2.5775(5), 2.5918(5)	2.6518(10)–2.6901(11)	6	15
trans-$[InBr_2\{MeSe(CH_2)_2SeMe\}_2]^+$	2.6076(15), 2.6113(15)	2.7370(16)–2.7762(15)	6	15
trans-$[InCl_2([16]aneSe_4]^+$	2.475(2)	2.7189(10), 2.7394(11)	6	13

[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}. ^{1}H NMR spectra were recorded using a Bruker AV300 spectrometer. ^{77}Se{^{1}H}, ^{125}Te{^{1}H} and ^{27}Al NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external neat $SeMe_2$, $TeMe_2$ and aqueous $[Al(H_2O)_6]^{3+}$ at pH = 1, respectively. Microanalyses were undertaken by Medac Ltd or London Metropolitan University. Solvents were dried prior to use: toluene by distillation from sodium benzophenone ketyl, CH_2Cl_2 from CaH_2, and all preparations were undertaken using standard Schlenk techniques under a N_2 atmosphere. Anhydrous aluminium(III) halides (Aldrich or Strem) were used as received. SMe_2 and $SeMe_2$ (Aldrich) were stored over molecular sieves. Other thio-seleno- and telluroethers were made by literature methods[32–36] and stored under dinitrogen over molecular sieves.

$[AlCl_3(Me_2S)]$: Me_2S (0.09 g, 1.5 mmol) was added dropwise to a suspension of $AlCl_3$ (0.20 g, 1.5 mmol) in anhydrous CH_2Cl_2 (15 mL) with stirring to give a colourless solution. After 30 minutes, all solvent was removed *in vacuo* to give a colourless oil. Yield 0.26 g, 89%. Anal. Calcd for $C_2H_6AlCl_3S$: C, 12.3; H, 3.1. Found: C, 12.4; H, 3.1%. ^{1}H NMR ($CDCl_3$, 295 K): 2.53 (s). ^{27}Al NMR (CD_2Cl_2, 295 K): 111.6. IR (cm^{-1}): 541 (s), 410 (m). Raman (cm^{-1}): 404 (m) Al–Cl.

$[AlBr_3(Me_2S)]$: $AlBr_3$ (0.10 g, 0.37 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution and Me_2S (0.023 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 0.10 g, 79%. Anal. Calcd for $C_2H_6AlBr_3S$: C, 7.3; H, 1.8. Found: C, 6.4; H, 2.0%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.51 (s). ^{27}Al NMR (CD_2Cl_2, 295 K): 81.2; (185 K): 81.6. IR (cm^{-1}, Nujol): 392 (br) Al–Br.

$[AlI_3(Me_2S)]$: AlI_3 (0.20 g, 0.5 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution and Me_2S (0.03 g, 0.5 mmol) was added dropwise. After stirring for 15 minutes, all solvent was removed *in vacuo* to give a pale yellow solid. Yield 0.17 g, 75%. Anal. Calcd for $C_2H_6AlI_3S$: C, 5.1; H, 1.3. Found: C, 5.0; H, 1.3%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.44 (s). ^{27}Al NMR (CD_2Cl_2, 295 K): 48.7. IR (cm^{-1}, Nujol): 336 (br) Al–I.

$[Me_2SH][AlCl_4]$: Me_2S (0.09 g, 1.5 mmol) was added dropwise to a suspension of $AlCl_3$ (0.20 g, 1.5 mmol) in anhydrous CH_2Cl_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 *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 $C_2H_7AlCl_4S$: C, 10.4; H, 3.0. Found: C, 10.5; H, 2.9%. IR (cm^{-1}, Nujol): 2482 (br, w) SH, 488 (br), 467 (br), 395 (s) $[AlCl_4]^-$; the strong S–H⋯Cl–Al interactions causes extensive splitting of the t_2 Al–Cl stretching mode in the anion.

$[AlCl_3(Me_2Se)]$: Me_2Se (0.16 g, 1.5 mmol) was added dropwise to a suspension of $AlCl_3$ (0.2 g, 1.5 mmol) in anhydrous CH_2Cl_2 (15 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 colourless crystals. Yield 0.30 g, 82%. Anal. Calcd for $C_2H_6AlCl_3Se$: C, 9.9; H, 2.5. Found: C, 10.0; H, 2.6%. ^{1}H NMR ($CDCl_3$, 295 K): 2.92 (s); (283 K): 2.83 (s). ^{27}Al NMR ($CDCl_3$, 295 K): 110.5. ^{77}Se NMR ($CDCl_3$, 273 K): −11.3; (183 K): −14.0. IR (cm^{-1}, Nujol): 531 (s), 399 (m). Raman (cm^{-1}): 521 (w), 399 (s) Al–Cl.

$[AlBr_3(Me_2Se)]$: $AlBr_3$ (0.10 g, 0.37 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution and Me_2Se

(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 $C_2H_6AlBr_3Se$: C, 6.4; H, 1.6. Found: C, 6.1; H, 1.9%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.47 (s). ^{27}Al NMR (CD_2Cl_2, 295 K): 99.7. IR (cm^{-1}, Nujol): 446 (s), 397 (s) Al–Br.

[$AlCl_3(^n Bu_2Se)$]: A solution of $^n Bu_2Se$ (0.29 g, 1.5 mmol) in anhydrous CH_2Cl_2 (7 mL) was added dropwise to a suspension of $AlCl_3$ (0.20 g, 1.5 mmol) in anhydrous CH_2Cl_2 (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 $C_8H_{18}AlCl_3Se$: C, 29.4; H, 5.6. Found: C, 29.7; H, 5.8%. ^{1}H NMR (CD_2Cl_2, 295 K): 3.03 (t, [4H]), 1.82 (m, [4H]), 1.46 (m, [4H]), 0.97 (t, [6H]). ^{27}Al NMR (CD_2Cl_2, 295 K): 109.9. ^{77}Se NMR ($CDCl_3$, 295 K): 102.9. IR (cm^{-1}): 539 (s), 399 (m) Al–Cl.

[$AlCl_3(Me_2Te)$]: Me_2Te (0.12 g, 0.75 mmol) was added dropwise to a suspension of $AlCl_3$ (0.10 g, 0.75 mmol) in anhydrous CH_2Cl_2 (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 $C_2H_6AlCl_3Te$: C, 8.3; H, 2.1. Found: C, 8.6; H, 2.1%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.19 (s). ^{27}Al NMR (CD_2Cl_2, 295 K): 105.9. IR (cm^{-1}, Nujol): 491 (s), 395 (m) Al–Cl.

[$AlBr_3(Me_2Te)$]: $AlBr_3$ (0.10 g, 0.37 mmol) was dissolved in toluene (10 mL) to give a pale yellow solution. Me_2Te (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 $C_2H_6AlBr_3Te$: C, 5.7; H, 1.4. Found: C, 5.7; H, 1.8%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.66 (s). ^{27}Al NMR (CD_2Cl_2, 295 K): 92.6. IR (cm^{-1}, Nujol): 404 (m), 391 (m) Al–Br.

[$AlCl_3(^n Bu_2Te)$]: A solution of $^n Bu_2Te$ (0.18 g, 0.75 mmol) in anhydrous CH_2Cl_2 (7 mL) was added dropwise to a suspension of $AlCl_3$ (0.10 g, 0.75 mmol) in anhydrous CH_2Cl_2 (8 mL) with stirring to give a yellow solution. After 15 minutes, all solvent was removed *in vacuo* to yield a yellow oil. Yield 0.22 g, 78%. Anal. Calcd for $C_8H_{18}AlCl_3Te$: C, 25.6; H, 4.8. Found: C, 26.1; H, 5.1%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.95 (t, [4H]), 1.83 (m, [4H]), 1.43 (m, [4H]), 0.96 (t, [6H]). ^{27}Al NMR (CD_2Cl_2, 295 K): 106.8. IR (cm^{-1}): 495 (s), 395 (m) Al–Cl.

[$AlCl_2\{MeS(CH_2)_2SMe\}_2$][$AlCl_4$]: $MeS(CH_2)_2SMe$ (0.18 g, 1.5 mmol) was added dropwise to a suspension of $AlCl_3$ (0.20 g, 1.5 mmol) in anhydrous CH_2Cl_2 (15 mL) with stirring to give a colourless solution. After 30 minutes the volume of solvent was reduced *in vacuo* to ∼5 mL. A large quantity of white solid precipitated after storage at −18 °C for 24 hours. The solid was collected by filtration and dried *in vacuo*. Yield 0.26 g, 68%. Anal. Calcd for $C_8H_{20}Al_2Cl_6S_4$: C, 18.8; H, 3.9. Found: C, 18.3; H, 3.8%. ^{1}H NMR (CD_2Cl_2, 295 K): 3.07 (s, [4H]), 2.25 (s, [6H]). ^{27}Al NMR ($CDCl_3$, 295 K): 105.5, 37.4. IR (cm^{-1}, Nujol): 489 (s), 463 (s), 346 (w). Raman (cm^{-1}): 490 (w), 350 (s), 295 (s).

[$AlBr_2\{MeS(CH_2)_2SMe\}_2$][$AlBr_4$]: $MeS(CH_2)_2SMe$ (0.09 g, 0.75 mmol) was added dropwise to a pale yellow solution of $AlBr_3$ (0.20 g, 0.75 mmol) in toluene (15 mL) with stirring to give a colourless solution and a white precipitate. After 30 minutes the reaction mixture was filtered and the white solid dried *in vacuo*. Yield 0.21 g, 72%. Anal. Calcd for $C_8H_{20}Al_2Br_6S_4$: C, 12.3; H, 2.6. Found: C, 11.7; H, 2.9%. ^{1}H NMR (CD_2Cl_2, 295 K): 3.10 (s, [4H]), 2.26 (s, [6H]). ^{27}Al NMR (CD_2Cl_2, 295 K): 80.6. IR (cm^{-1}, Nujol): 405 (s, br), 355 (s, br).

[$AlI_2\{MeS(CH_2)_2SMe\}_2$][$AlI_4$]: $MeS(CH_2)_2SMe$ (0.06 g, 0.5 mmol) was added dropwise to a pale yellow solution of AlI_3 (0.20 g, 0.5 mmol) in toluene (15 mL) with stirring to give an orange solution and some pale yellow precipitate. After 30 minutes the reaction mixture was filtered and the pale yellow solid dried *in vacuo*. Crystals suitable for single crystal X-ray diffraction were obtained after storage of the filtrate at −18 °C for 48 hours. Yield 0.19 g, 74%. Anal. Calcd for $C_8H_{20}Al_2I_6S_4$: C, 9.1; H, 1.9. Found: C, 8.9; H, 3.3%. ^{1}H NMR (CD_2Cl_2, 295 K): 2.77 (s, [4H]), 2.17 (s, [6H]). ^{27}Al NMR (CD_2Cl_2, 295 K): −23.0. IR (cm^{-1}, Nujol): 338 (s), 304 (m).

[$AlCl_2\{MeSe(CH_2)_2SeMe\}_2$][$AlCl_4$]: $MeSe(CH_2)_2SeMe$ (0.16 g, 0.75 mmol) was added dropwise to a suspension of $AlCl_3$ (0.10 g, 0.75 mmol) in anhydrous CH_2Cl_2 (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 $C_8H_{20}Al_2Cl_6Se_4$: C, 13.8; H, 2.9. Found: C, 12.8; H, 2.7%. ^{1}H NMR ($CDCl_3$, 295 K): 3.21 (s, [4H]), 2.36 (s, [6H]). ^{27}Al NMR ($CDCl_3$, 295 K): 105.4. ^{77}Se NMR ($CDCl_3$, 295 K): 95.4. IR (cm^{-1}, Nujol): 488 (s), 442 (m).

[$AlCl_3\{MeC(CH_2SMe)_3\}$]: $MeC(CH_2SMe)_3$ (0.16 g, 0.75 mmol) was added dropwise to a suspension of $AlCl_3$ (0.10 g, 0.75 mmol) in anhydrous CH_2Cl_2 (10 mL) with stirring to give a colourless solution. After 30 minutes the volume of solvent was reduced *in vacuo* to ∼5 mL. Colourless crystals suitable for single crystal X-ray diffraction were obtained after storage at −18 °C for 48 hours. Yield 0.18 g, 70%. Anal. Calcd for $C_8H_{18}AlCl_3S_3\cdot 1/2CH_2Cl_2$: C, 26.4; H, 5.0. Found: C, 26.9; H, 4.9%. ^{1}H NMR ($CDCl_3$, 295 K): 2.76 (s, [6H]), 2.25 (s, [9H]), 1.16 (s, [3H]). IR (cm^{-1}, Nujol): 534 (s), 491 (s).

[$(AlCl_3)_2\{C_6H_4(CH_2SEt)_2\}$]: *o*-$C_6H_4(CH_2SEt)_2$ (0.17 g, 0.75 mmol) was added dropwise to a suspension of $AlCl_3$ (0.20 g, 1.5 mmol) in anhydrous CH_2Cl_2 (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 $C_{12}H_{18}Al_2Cl_6S_2$: C, 29.2; H, 3.7. Found: C, 29.3; H, 3.7%. ^{1}H NMR ($CDCl_3$, 295 K): 7.47 (m, [4H]), 4.37 (s, [4H]), 3.08 (q, [4H]), 1.49 (t, [6H]). ^{27}Al NMR ($CDCl_3$, 295 K): 111.3. IR (cm^{-1}, Nujol): 565–500 (vbr, s), 394 (s). Raman (cm^{-1}): 518 (m), 402 (m).

[$AlCl_3([9]aneS_3)$]: A solution of $[9]aneS_3$ (0.14 g, 0.75 mmol) in anhydrous toluene (10 mL) was added to a solution of $AlCl_3$ (0.10 g, 0.75 mmol) in anhydrous toluene (10 mL) with stirring to give a colourless solution and a large quantity of white precipitate. After 60 minutes, the precipitate was collected by filtration and dried *in vacuo*. Yield 0.16 g, 68%. Anal. Calcd for

$C_6H_{12}AlCl_3S_3$: C, 23.0; H, 3.9. Found: C, 23.1; H, 3.9%. IR (cm^{-1}, Nujol): 408 (s), 375 (m) Al–Cl.

[AlCl$_2$([14]aneS$_4$)][AlCl$_4$]: A solution of [14]aneS$_4$ (0.10 g, 0.37 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to a suspension of $AlCl_3$ (0.10 g, 0.75 mmol) in anhydrous CH_2Cl_2 (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 $C_{10}H_{20}Al_2Cl_6S_4$: C, 22.4; H, 3.8. Found: C, 22.6; H, 3.7%. IR (cm^{-1}, Nujol): 481 (br, s), 419 (m).

[AlCl$_2$([16]aneSe$_4$)][AlCl$_4$]: was made similarly from a solution of [16]aneSe$_4$ (0.18 g, 0.37 mmol) in anhydrous CH_2Cl_2 (10 mL) and $AlCl_3$ (0.1 g, 0.75 mmol) in anhydrous CH_2Cl_2 (10 mL). The precipitate was collected by filtration and dried *in vacuo*. Yield 0.20 g, 70%. Anal. Calcd for $C_{12}H_{24}Al_2Cl_6Se_4$: 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 (N_2 cryostream). Structure solution and refinement were straightforward,[37,38] except as

Table 3 Crystal data and structure refinement details[a]

Compound	[AlCl$_3$(Me$_2$Se)]	[AlCl$_3$(Me$_2$Te)]	[AlBr$_3$(Me$_2$Te)]	[AlCl$_2${MeS(CH$_2$)$_2$-SMe}$_2$] [AlCl$_4$]	[AlCl$_2${MeSe(CH$_2$)$_2$-SeMe}$_2$] [AlCl$_4$]
Formula	$C_2H_6AlCl_3Se$	$C_2H_6AlCl_3Te$	$C_2H_6AlBr_3Te$	$C_8H_{20}Al_2Cl_6S_4$	$C_8H_{20}Al_2Cl_6Se_4$
M	242.36	291.00	424.38	511.14	698.74
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbcm* (no. 57)	*Pbcm* (no. 57)	*Pbcm* (no. 57)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a [Å]	6.205(4)	6.248(1)	6.562(3)	6.708(5)	7.122(4)
b [Å]	12.603(8)	13.114(3)	13.400(5)	10.583(5)	17.744(8)
c [Å]	10.479(6)	10.514(2)	10.724(4)	15.383(5)	17.582(8)
α [°]	90	90	90	90.070(5)	90
β [°]	90	90	90	102.422(5)	93.169(8)
γ [°]	90	90	90	96.512(5)	90
U [Å^3]	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. reflns	4909	3839	8126	11 612	10 277
Unique reflns	1315	1312	1140	6072	5039
R_{int}	0.103	0.018	0.297	0.026	0.114
No. of params, restraints	38, 0	38, 0	38, 0	188, 0	188, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.055	0.018	0.065	0.046	0.077
R_1 [all data]	0.065	0.022	0.068	0.059	0.091
w$R_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.137	0.034	0.163	0.072	0.196
wR_2 [all data]	0.148	0.035	0.168	0.077	0.207

Compound	[AlI$_2${MeS(CH$_2$)$_2$SMe}$_2$] [AlI$_4$]	[{*o*-C$_6$H$_4$(CH$_2$SEt)$_2$}(AlCl$_3$)$_2$]	[AlCl$_3$(MeC(CH$_2$SMe)$_3$)]	[Me$_2$SH][AlCl$_4$]
Formula	$C_8H_{20}Al_2I_6S_4$	$C_{12}H_{18}Al_2Cl_6S_2$	$C_{16}H_{36}Al_2Cl_6S_6$	$C_2H_7AlCl_4S$
M	1059.84	493.04	687.47	231.92
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	14.825(3)	18.745(2)	16.131(7)	14.3783(7)
b [Å]	12.181(2)	10.810(10)	8.310(3)	10.9075(7)
c [Å]	15.150(4)	13.608(12)	24.976(11)	12.3742(5)
α [°]	90	90	90	90
β [°]	108.449(8)	125.779(1)	107.156(8)	90.260(3)
γ [°]	90	90	90	90
U [Å^3]	2595.3(10)	2237(3)	3199(2)	1940.64(17)
Z	4	4	4	8
μ(Mo Kα) [mm^{-1}]	7.563	1.026	0.991	1.443
Total no. reflns	24 085	8120	10 176	11 008
Unique reflns	5928	2199	4613	4432
R_{int}	0.152	0.041	0.133	0.035
No. of params, restraints	185, 0	100, 3	279, 0	153, 0
$R_1{}^b$ [$I_o > 2\sigma(I_o)$]	0.057	0.108	0.085	0.045
R_1 [all data]	0.135	0.121	0.103	0.055
w$R_2{}^b$ [$I_o > 2\sigma(I_o)$]	0.106	0.258	0.193	0.156
wR_2 [all data]	0.115	0.277	0.207	0.189

[a] Common items: temperature = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

detailed below, with H atoms bonded to C being placed in calculated positions using the default C–H distance. For $[AlCl_3\{MeC(CH_2SMe)_3\}]$ 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_{int} value, the data are of modest quality although the intensities seems satisfactory (80% exceed the Shelxl test, $I > 2\sigma(I)$). The structure that emerges from the analysis appears sound, with no unusual adp values or other causes for concern. For $[(AlCl_3)_2\{C_6H_4(CH_2SEt)_2\}]$ the diffraction pattern exhibits many additional reflections in the 100 projection. These are likely due to a modulation. In fact, the Ga analogue[13] 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.

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References

1 *Comprehensive organic synthesis*, ed. B. M. Tost, Pergamon, Oxford, 1991, *e.g.* H. Heaney, vol. 2, ch. 3 and G. O. Olah, R. Krishnamurti and G. K. Surya, vol. 4, ch. 1.8.

2 (*a*) *The chemistry of aluminium, gallium, indium and thallium*, ed. A. J. Downs, Blackie, London, 1993; (*b*) *The group 13 metals aluminium, gallium, indium and thallium*, ed. S. Aldridge and A. J. Downs, Wiley, NY, 2011; (*c*) G. H. Robinson, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2004, vol. 3, p. 347.

3 S. L. Benjamin, W. Levason and G. Reid, *Chem. Soc. Rev.*, 2013, **42**, 1460.

4 R. L. Richards and A. Thompson, *J. Chem. Soc. A*, 1967, 1248.

5 J. Lewis, J. R. Miller, R. L. Richards and A. Thompson, *J. Chem. Soc.*, 1965, 5850.

6 P. J. Ogren, L. Steenhoek, K. Greve and W. C. Hutton, *J. Inorg. Nucl. Chem.*, 1975, **37**, 293.

7 (*a*) L. A. Ganyushin, E. N. Guryanova, I. P. Romm and L. A. Lobanova, *Zh. Obshch. Khim.*, 1979, **49**, 2090; (*b*) L. A. Ganyushin, E. N. Guryanova and I. P. Romm, *Zh. Obshch. Khim.*, 1978, **48**, 2478; (*c*) I. P. Rom and E. N. Guryanova, *Zh. Obshch. Khim.*, 1968, **38**, 1927.

8 R. T. Tjahjanto, M. F. Peintinger, T. Bredow and J. Beck, *Eur. J. Inorg. Chem.*, 2012, 3625.

9 (*a*) G. H. Robinson and S. A. Sangokara, *J. Am. Chem. Soc.*, 1988, **110**, 1494; (*b*) G. H. Robinson and J. L. Atwood, *Organometallics*, 1987, **6**, 887.

10 K. L. Baker and G. W. A. Fowles, *J. Chem. Soc. A*, 1968, 801.

11 W. Levason, G. Reid and W. Zhang, *Dalton Trans.*, 2011, **40**, 8491.

12 C. Gurnani, M. Jura, W. Levason, R. Ratnani, G. Reid and M. Webster, *Dalton Trans.*, 2008, 6274.

13 K. George, M. Jura, W. Levason, M. E. Light, L. P. Ollivere and G. Reid, *Inorg. Chem.*, 2012, **51**, 2231.

14 S. Mishra, E. Jeanneau and S. Daniele, *Polyhedron*, 2010, **29**, 500.

15 C. Gurnani, M. Jura, W. Levason, R. Ratnani, G. Reid and M. Webster, *Dalton Trans.*, 2009, 1611.

16 (*a*) F. Fairbrother and N. Flitcroft, *J. Less-Common Met.*, 1962, **4**, 504; (*b*) C. A. Evans and M. J. Taylor, *J. Chem. Soc. A*, 1969, 1343.

17 K. George, C. H. de Groot, C. Gurnani, A. L. Hector, R. Huang, M. Jura, W. Levason and G. Reid, *Chem. Mater.*, 2013, **25**, 1829.

18 K. Nakamoto, *Infrared and Raman spectra of inorganic and coordination compounds*, 4th edn, Wiley, NY, 1986.

19 N. Burford, B. W. Royan, R. E. v. H. Spence and T. S. Cameron, *J. Chem. Soc., Dalton Trans.*, 1990, 1521.

20 H. Bock and U. Lechner-Knoblauch, *J. Organomet. Chem.*, 1985, **294**, 295.

21 J. Mason, *Multinuclear NMR*, Plenum, NY, 1987.

22 A. Ecker and H. Schnoeckel, *Z. Anorg. Allg. Chem.*, 1998, **624**, 813.

23 W. Levason, S. D. Orchard and G. Reid, *Coord. Chem. Rev.*, 2002, **225**, 159.

24 N. P. Luthra and J. D. Odon, in *The chemistry of organic selenium and tellurium compounds*, ed. S. Patai and Z. Rappoport, Wiley, NY, 1986, ch. 6, vol. 1.

25 M. Jura, W. Levason, G. Reid and M. Webster, *Dalton Trans.*, 2009, 7610.

26 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reeves, J. Eschevaria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832.

27 A. Y. Timoshkin, A. V. Suvorov, H. F. Bettinger and H. F. Schaefer III, *J. Am. Chem. Soc.*, 1999, **121**, 5687.

28 A. Ogawa and H. Fujimoto, *Inorg. Chem.*, 2002, **41**, 4888.

29 F. Bessac and G. Frenking, *Inorg. Chem.*, 2006, **45**, 6956.

30 A. Y. Timoshkin, M. Bodensteiner, T. N. Sevastianova, A. S. Lisovenko, E. I. Davydova, M. Scheer, C. Grassl and A. V. Butlak, *Inorg. Chem.*, 2012, **51**, 11602.

31 T. I. Madzhikov and G. A. Chmutova, *J. Phys. Chem. A*, 2013, **117**, 4011.

32 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J.-H. Gu, B. D. Johnston and B. M. Pinto, *J. Am. Chem. Soc.*, 1989, **111**, 6582.

33 T. Kemmitt and W. Levason, *Organometallics*, 1989, **8**, 1303.

34 W. Levason, M. Nirwan, R. Ratnani, G. Reid, N. Tsoureas and M. Webster, *Dalton Trans.*, 2007, 439.

35 D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray, D. M. Potter and G. L. Marshall, *J. Chem. Soc., Perkin Trans. 2*, 1984, 429.

36 N. Kuhn, P. Faupel and E. Zauder, *J. Organomet. Chem.*, 1986, **302**, C4.

37 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

38 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.