Approaching a cluster of aluminium(III) selenide: [Al$_4$Se$_5$(H)$_2$(NMe$_3$)$_4$]

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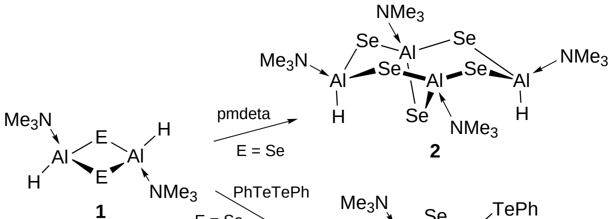
The reaction of *trans*-[{Me$_3$N(H)Al(μ-Se)}$_2$] with *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdeta) in toluene affords the tetranuclear, alane selenide cluster [Al$_4$Se$_5$(H)$_2$(NMe$_3$)$_4$] (structurally authenticated and *ab initio* modelled), and with PhTeTePh yields a mixed chalcogenide *trans*-[{Me$_3$N(PhTe)Al(μ-Se)}$_2$].

We recently showed that elemental selenium or tellurium react under mild conditions with the trimethylamine adduct of alane, [H$_3$AlNMe$_3$], in toluene affording the dimeric chalcogenidoalane, *trans*-[{Me$_3$N(H)Al(μ-E)}$_2$] (E = Se, Te) **1**, Scheme 1, with the elimination of hydrogen.[1] This new class of compounds can be regarded as tertiary-amine-stabilised adducts of the simplest selenido- and tellurido-aluminium(III) species, *viz* [{HAl(μ-E)}$_2$] (E = Se, Te) and should prove to have a rich chemistry. Instead of the adducts, base-free cubane structures are conceivable, [{HAl(μ$_3$-E)}$_4$], noting that organometallic analogues have been prepared, [{(η^5-C$_5$Me$_5$)Al(μ$_3$-E)}$_4$] (E = Se, Te)[2] and [{Bu^{t}Al(μ$_3$-S, Se or Te)}$_4$.[3] For our system, such cubane type structures are computed to be less stable than the solvated dimers.

In developing the chemistry of the adducts we report reactions of *trans*-[{Me$_3$N(H)Al(μ-Se)}$_2$] **1a** with (*i*) *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (pmdeta) and (*ii*) PhTeTePh. Reaction (*i*) was an attempt to gain access to a stabilised Lewis-base-saturated monomeric H–Al=Se complex by chelation of the metal centre. This was deemed a synthetic target on theoretical grounds. Rather, an unprecedented tetranuclear cluster formed, [Al$_4$Se$_5$(H)$_2$(NMe$_3$)$_4$] **2**, which approaches a stabilised cluster of aluminium(III) selenide. Reaction (*ii*) was successful in forming a mixed chalocogenide aluminium(III) species **3**, arising from metal hydride cleavage of the diorganoditelluride. This is related to the recently established facile cleavage of diorganoditellurides and diorganodiselenides by [H$_3$AlNMe$_3$] affording [(Me$_3$N)Al(ER)$_3$], (E = Se, Te, R = alkyl, aryl).[4]

Compounds **2** and **3** were prepared in toluene, Scheme 1.† While compound **2** is isolated in low yield, and crystallises over several weeks, its formation is reproducible. On mixing **1a** and pmdeta, a flocculant, insoluble, white precipitate was formed which is difficult to characterise: this product may be the ionic species [{(pmdeta)AlH$_2$}$^+$]$_2$Se^{2-}, and its formation would account for the change in Al : hydride : Se ratio from 1 : 1 : 1 in **1a** to 2 : 1 : 2.5 in **2**. It shows an IR band at 1789 cm^{-1} *cf.* 1822 cm^{-1} for [(pmdeta)AlH$_2$]$^+$AlH$_4$$^-$, a compound which has been structurally authenticated.[5] While the hydrides in **1** are resistant to further reaction with selenium or tellurium, reaction with a diorganoditelluride takes place, as demonstrated for **1a**, with elimination of hydrogen. Interestingly the integrity of the *trans*-isomer is maintained, whereas in the more complicated tetranuclear cluster this is lost with respect to the two residual hydrogens which are now in a *cis*-arrangement.



Scheme 1

Assignment of structure of the two compounds rests on X-ray diffraction studies.‡ Compound **2** crystallises as a toluene solvate with a single toluene and molecule of **2** as the asymmetric unit. The Al$_4$Se$_5$ metal core can be described as two six-membered rings, both in a boat conformation, sharing an Al$_2$Se plane and the molecule approximates to C_2 symmetry, with *cis*-hydrido groups, Fig. 1. Indeed, departure from a higher potential C_{2v} symmetry relates to puckering of the boat conformation of the two six-membered rings and angular distortion in Al$_3$Se$_4$ ring with angles subtended by Se(2,4) by two metal centres being more open at 98.6° (mean) relative to

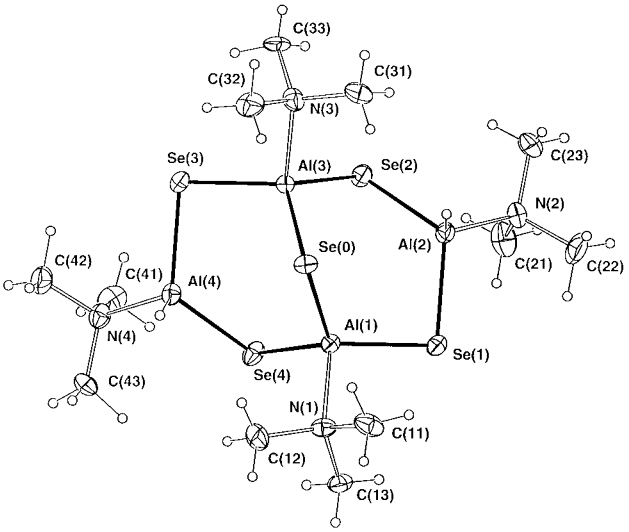


Fig. 1 Projection of [Al$_4$Se$_5$(H)$_2$(NMe$_3$)$_4$]. **2** Selected distances (Å) and angles (°): Se(0)–Al(1,3) 2.361(4), 2.354(4), Se(1)–Al(1,2) 2.345(3), 2.358(4), Se(2)–Al(2,3) 2.356(4), 2.334(4), Se(3)–Al(3,4) 2.345(3), 2.360(5), Se(4)–Al(1,4) 2.332(4), 2.355(3), Al(1,2,3,4)–N(1,2,3,4) 2.05(1), 2.00(1), 2.05(1), 1.98(1); Al(1)–Se(0)–Al(3) 94.6(1), Al(1)–Se(1)–Al(2) 92.2(1), Al(2)–Se(2)–Al(3) 98.7(1), Al(3)–Se(3)–Al(4) 91.5(1), Al(1)–Se(4)–Al(4) 98.5(1), Se(0)–Al(1)–Se(1,4), N(1) 115.7(2), 113.2(1), 103.2(3), Se(1)–Al(1)–Se(4), N(1) 115.6(2), 102.2(3), Se(4)–Al(1)–N(1) 104.7(3), Se(1)–Al(2)–Se(2), N(2) 115.7(2), 101.8(4), Se(2)–Al(2)–N(2) 101.0(3), Se(0)–Al(3)–Se(2,3), N(3) 114.6(1), 114.5(2), 103.9(4), Se(2)–Al(3)–Se(3), N(3) 113.9(2), 104.7(3), Se(3)–Al(3)–N(3) 103.3(3), Se(3)–Al(4)–Se(4), N(4) 116.5(2), 104.2(4), Se(4)–Al(4)–N(4) 100.0(3). Computed values for the same molecule with C_{2v} symmetry: Al(1)–N(1) 2.059, Al(2)–N(2) 2.086, Al(1)–Se(1,4) 2.431, Al(2)–Se(1,2) 2.445, Al(2)–H 1.600, Al(1)–Se(0) 2.437, Se(0)–Al(1)–N(1), Se(1,4) 103.49, 114.44, Se(1)–Al(1)–N(1), Se(4) 103.18, 115.78, N(1)–Al(1)–Se(4) 103.16, Se(1)–Al(2)–Se(2), N(2), H 119.33, 101.57, 115.27, Se(2)–Al(2)–N(2), H, 101.57, N(2)–Al(2)–H 98.90, Al(1)–Se(0)–Al(3) 99.75, Al(1)–Se(1)–Al(2) 111.99, Al(1)–Se(4)–Al(4) 111.99.

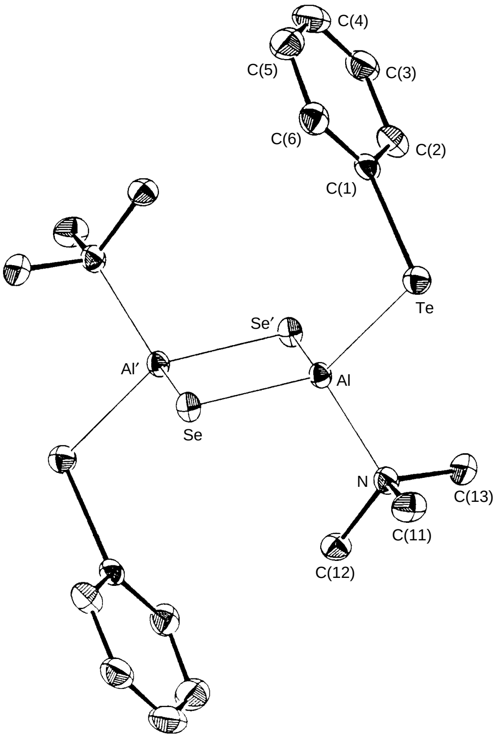


Fig. 2 Projection of *trans*-[{$Me_3N(PhTe)Al(\mu\text{-}Se)$}$_2$] **3**. Selected distances (Å) and angles (°): Te–Al, 2.610(2), Se–Al 2.359(2), Se–Al′ 2.347(2), Al–N 1.998(5); Al–Te–C(1), Al′ 94.6(1), 76.37(6), Te–Al–Se, N, Se′ 117.16(7), 102.1(1), 117.31(7), Se–Al–N, Se′ 107.2(2), 103.63(6), N–Al–Se′ 108.9(2)

those subtended by Se(1,3), 91.9° (mean). The corresponding angle at the unique selenium, Se(0), is intermediate at 94.6(1)°. All aluminium centres are four-coordinate. The bond distances around Al(1,3) which have the coordinated Lewis base NMe_3 are similar to those in [$(Me_3N)Al(SeEt)_3$], but the angles subtended by two seleniums are slightly more open at *ca.* 114.50, *cf.* 111.5(5), as are the Se–Al–N angles at *ca.* 113.4, *cf.* 87(1)°.[4] Similarly the bond distances around Al(2,4) are similar to those in *trans*-[{$Me_3N(H)Al(\mu\text{-}Se)$}$_2$] (and **3**, see below) with the Se–Al–Se angles more open, at *ca.* 116.0°, *cf.* 103.10(7)°,[1] as expected for a larger ring system. Molecules of **3** are centrosymmetric, as the *trans*-isomer, Fig. 2. The Al_2Se_2 core is very similar to that in *trans*-[{$Me_3N(H)Al(\mu\text{-}Se)$}$_2$].[1] The Te–Al distance at 2.610(2) Å is similar to that in [$(Me_3N)Al(TePh)_3$],[4] 2.589(2) Å.

An *ab initio* molecular-orbital calculation involving C_{2v} structure optimisation at the RHF/LanL2DZ level was undertaken on **2** giving reasonable correlation of structural parameters with experimental values, except for the angular distortions associated with C_2 rather than C_{2v} symmetry (Fig. 1).[6] Constraining the symmetry to C_{2v} was necessary for computational convenience. In order to estimate the energy change on production *via* hydrogenation, a similar calculation was performed under C_{2v} symmetry at the MP2/LanL2DZ level on the simpler analogous compound [$Al_4Se_5(H)_2(NH_3)_4$] and its hypothetical precursor [$Al_4Se_6(NH_3)_4$], the latter under T_d symmetry as shown in Fig. 3. The MP2/LanL2DZ energies (in E_h) of the reactants [$Al_4Se_6(NH_3)_4$] (−287.918 974 1) and H_2 (−1.143 905 1) in combination with those of the products [$Al_4Se_5(H)_2(NH_3)_4$] (−279.906 603 9) and H_2Se (−10.198 084 0) indicate that the formation of [$Al_4Se_5(H)_2(NH_3)_4$] *via* hydrogenation is exothermic by 654 kcal mol^{-1} (1 cal = 4.184 J). Thus the analogous reverse reaction of converting **2** to [$Al_4Se_6(NMe_3)_4$] on treatment with H_2Se is energetically unfavourable. However other sources of selenium, for example $Se(SiMe_3)_2$, may favour formation of [$Al_4Se_6(NMe_3)_4$], an area we are currently exploring.

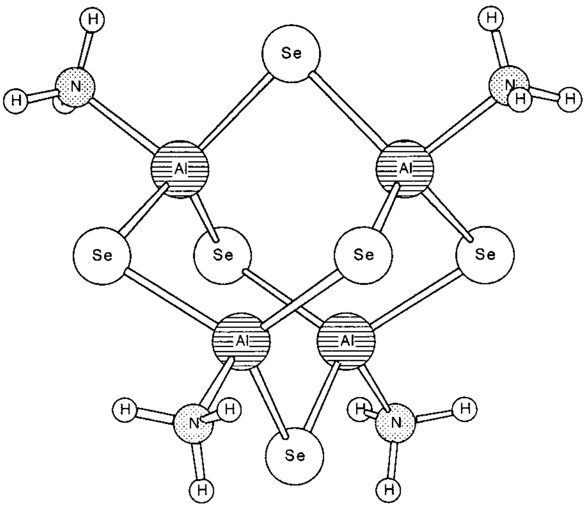


Fig. 3 Computed structure of [$Al_4(\mu\text{-}Se)_6(Me_3N)_4$] with T_d symmetry: Al–Se, N, 2.460, 2.059 Å; Se–Al–Se 116.16, Se–Al–N 101.46, Al–Se–Al 93.45°

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Footnotes and References

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† *Synthesis*: **2**: pmdeta (0.28 ml, 1.34 mmol) was added to a stirred solution of *trans*-[{$Me_3N(H)Al(\mu\text{-}Se)$}$_2$] (0.44 g, 1.32 mmol) in toluene at room temp. A white precipitate formed immediately and after 2 h the reaction mixture was filtered. Recrystallisation from toluene (*ca.* 40 ml) afforded colourless crystals (0.15 g, 20%). Mp (*in vacuo*); partial sublimation at 78–81 °C leaving a white powder which decomposes > 310 °C; IR ν_{Al-H} 1779 cm^{-1} (s). NMR: ^1H (300 MHz, C_6D_6, 25 °C) δ 2.10, 2.09 (NCH_3), ^{13}C (75.5 MHz, C_6D_6, 25 °C) δ 47.6, 47.5 (NCH_3). Anal. Found C, 23.11; H, 5.06; N, 6.58. Calc. for $C_{12}H_{38}Al_4N_4Se_5\cdot 0.5C_7H_8$: C, 23.65; H, 5.38; N, 7.12%.

3: PhTePh (0.65 g, 1.6 mmol) in toluene (10 ml) was added to *trans*-[{$Me_3N(H)Al(\mu\text{-}Se)$}$_2$] (0.53 g, 1.6 mmol) in toluene (20 ml) at room temp. with gas evolution. After 17 h the resulting orange solution was filtered, and volatiles removed *in vacuo*. Recrystallisation from toluene (*ca.* 15 ml) afforded orange crystals (0.48 g, 41%). Mp 145–147 °C (*in vacuo*). NMR: ^1H (200 MHz, C_6D_6, 25 °C) δ 8.17 (6 H, m, *o*-C_6H_5), 6.91 (4 H, m, *m*-, *p*-C_6H_5), 2.10 (18 H, s, NCH_3); ^{13}C (50.3 MHz, C_6D_6, 25 °C) δ 141.0 (*o*-C_6H_5), 129.1, 126.6 (*m*-, *p*-C_6H_5), 107.6 (*ipso*-C_6H_5), 47.1 (CH_3). Anal. Found C, 29.31; H, 4.03; N, 3.79. Calc. for $C_{18}H_{28}N_2Al_2Se_2Te_2$: C, 29.24; H, 3.82; N, 3.79%.

‡ *Crystallographic data* (CAD4 diffractometer, crystals mounted in a capillaries): **2**·C_6H_5Me: $C_{19}H_{46}Al_4N_4Se_5$, M = 833.3, orthorhombic, space group $Pna2_1$, a = 12.294(2), b = 27.769(5), c = 10.285(5) Å, U = 3511(2) Å^3, D_c (Z = 4) = 1.576 g cm^{-3}, $F(000)$ = 1640, μ_{Mo} = 53.3 cm^{-1}, specimen: 0.21 × 0.50 × 1.10 mm, $A^*_{min,max}$ = 3.15, 12.08, $2\theta_{max}$ = 50°, final R, R_w = 0.040, 0.038 (0.043, 0.041 other hand) N_o = 1934 'observed' [$(I > 3\sigma(I)$] reflections out of N = 3270 unique.

3: $C_{18}H_{28}Al_2N_2Se_2Te_2$, M = 739.5, monoclinic, space group $P2_1/n$, a = 6.746(4), b = 10.725(3), c = 17.529(7) Å, β = 90.57(4), U = 1268.3(9) Å^3, D_c (Z = 2) = 1.936 g cm^{-3}, $F(000)$ = 696, μ_{Mo} = 52.5 cm^{-1}, specimen: 0.35 × 0.20 × 0.22 mm, $A^*_{min,max}$ = 2.20, 3.59, $2\theta_{max}$ = 55°, final R, R_w = 0.033, 0.042, N_o = 2042 'observed' [$(I > 3\sigma(I)$] reflections out of N = 2915 unique. For both structures all H-atoms were included as invariants. CCDC 182/611.

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