Cationic Aluminium Hydrides: $[H_2AlL]^+[AlH_4]^-$, L = *N,N,N′N″,N″*-Pentamethyldiethylenetriamine and 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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Reaction of H_3AlNMe_3 with *N,N,N′,N″,N″*- pentamethyldiethylenetriamine (pmdien) in diethyl ether or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4cyclam) in tetrahydrofuran yields $[H_2Al(pmdien)]^+[AlH_4]^-$, which possesses a trigonal bipyramidal cation with the hydrides in the trigonal plane [Al–N′ 2.158(7), Al–N,N″ 2.01(1), Al–H 1.62 Å] or $[H_2Al(Me_4\ cyclam)]^+[AlH_4]$, where the metal centre in the cation is *trans*-octahedral [Al–N(mean) 2.13, Al–H 1.60, 1.64 Å].

Tertiary amine adducts of alane are of interest as hydride sources for hydroalumination of unsaturated substrates,[1] formation of derivatives of other metal complexes,[2] and as precursors for chemical vapour deposition of aluminium metal,[3,4] and have attracted theoretical studies,[5] as has alane itself.[6] Despite this there is little structural information on such compounds, being available for monomeric H_3AlNMe_3, **1a** (gas phase),[7] $H_3AlNBu^n_3$, **1b**,[8] and $H_3Al(NMe_3)_2$, **2**,[9] weakly associated $[\{LH_2Al(\mu\text{-}H)\}_2]$, **3**,[5] and polymeric H_3Al-(tmen) (tmen = *N,N,N′,N′*-tetramethylethylenediamine), **4**.[10]

We show that cationic structures are possible using higher polydentate tertiary amine ligands. Features of the work include the synthesis and characterisation of (*i*) $[H_2Al(pmdien)]^+[AlH_4]^-$, **5** (pmdien = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine), and (*ii*) $[H_2Al(Me_4cyclam)]^+[AlH_4]^-$, **6** ($Me_4$cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) which represent the first structurally authenticated cationic aluminium hydrides, and the first examples of tertiary amine adducts of alane incorporating chelate ring systems; the related tmen complex has a polymeric structure, **4**, with the amine bridging metal centres.[10] Interestingly, cationic aluminium alkyls are accessible using crown ethers and *N*-functionalised alkyls,[11] and Me_4cyclam yields a 1:4 adduct with $AlMe_3$ with all the metal centres four-coordinate, rather than a cationic species.[12]

Synthesis of **5** and **6** are shown in Scheme 1.† Treatment of H_3AlNMe_3 with pmdien in diethyl ether or Me_4cyclam in tetrahydrofuran (THF) gave exclusively alane–Lewis base complexes, as white solids which were recrystallised from THF. These complexes have much higher temperatures for the onset of degradation to aluminium and hydrogen (>182,

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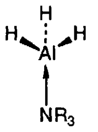
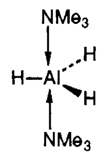
† *Compound* **5**: A solution of *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (1.20 g, 6.9 mmol) in OEt_2 (20 ml) was added over 30 min to a stirred solution of H_3AlMe_3 (0.61 g, 6.9 mmol)[18] in OEt_2 (50 ml) at 0 °C. The resulting white suspension was stirred for 2 h at room temp. after which solvent was removed *in vacuo* to yield an oily white solid. This was washed with hexane (30 ml), then recrystallised from THF (120 ml) as colourless prisms (0.59 g, 73% yield). M.p. 172–173 °C (decomp. > 182 °C); ^1H NMR (250 MHz, $[^2H_8]$THF, 25 °C, Me_4Si): δ 2.35 (s, 15H, CH_3) 2.64, 2.75 (s, 2 × 4H, CH_2) 3.09 (br, 6H, AlH); ^{13}C NMR: δ 42.3 (Me) 47.1 (4 × Me) 55.9, 57.8 (2 × CH_2); ^{27}Al NMR: δ 102.0 (AlH_4); IR: ν/cm^{-1} 1660, 1822 (br, Al–H).

Compound **6**: To a solution of H_3AlNMe_3 (0.20 g, 2.25 mmol) in OEt_2 (50 ml) at 80 °C was added Me_4cyclam (0.26 g, 1.0 mmol) in OEt_2 (20 ml) over 30 min. A white precipitate rapidly formed which was collected after 2 h at room temp., washed with hexane (30 ml), and recrystallised from THF (20 ml) as colourless plates (0.23 g, 73% yield). M.p. 243–246 °C (decomp.); ^{13}C CP MAS TOSS NMR (75.4 MHz, 3800 Hz) δ 18.3 (br, $CH_2\mathit{CH_2}CH_2$) 43.5 (br, Me) 53.2 (br, $N\mathit{CH_2}CH_2CH_2$) 58.1 (br, $N\mathit{CH_2CH_2}N$); ^{27}Al CP MAS NMR: δ 96.2 (AlH_4^-) IR: ν/cm^{-1} 1660, 1740 (br, Al–H).



1a; R = Me
1b; R = Bu^n



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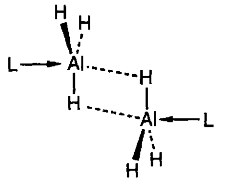
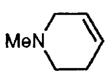
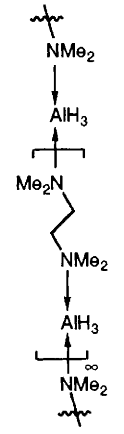


3 L = NMe$_3$, NMe$_2$CH$_2$Ph,





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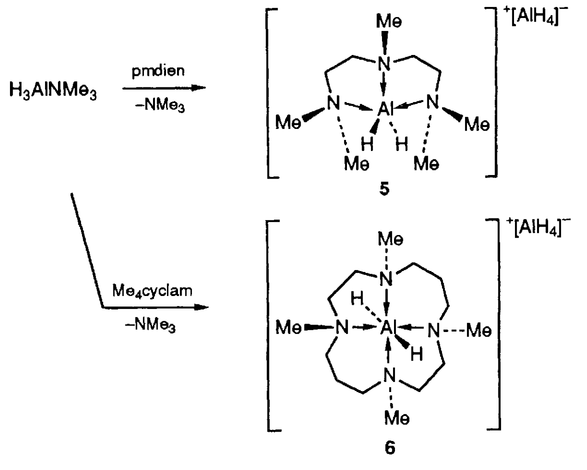

Scheme 1

>243 °C) than monodentate tertiary amine derivatives of alane, including H$_3$AlNMe$_3$ (decomp. > 100 °C),[3] and also the bidentate tmen derivative, **4** (decomp. *ca.* 146 °C). Thus progressively increasing the number of tertiary amine sites results in higher thermal stability of 'alane'. In contrast, the polydentate tertiary amines tmen and pmdien destabilise gallane relative to monodentate tertiary amines.[13] This relates to the preference of aluminium in alane to adopt a coordination number greater than four, even *via* hydride bridges, **3**, whereas gallium in gallane forms four-coordiante species. For example, even though tmen forms a 1 : 1 adduct with gallane it decomposes *in vacuo* to the gallane rich species with two four-coordinate gallium centres, *viz* [(H$_3$Ga)$_2$(tmen)].[13]

Results of the X-ray structure determinations of **5** and **6**‡ are presented in Fig. 1. In **5** the cation has 2*mm* crystallographically symmetry so that it is disordered over two orientations with one half the cation the asymmetric unit; in **6** the cation lies on a mirror plane, so it is also disordered. The trigonal bipyramidal aluminium centre of the cation in **5** has the pendant N-centres of pmdien in apical positions, Al–N, 2.158(7) Å, *cf.* 2.01(1) Å for the unique nitrogen. The *trans*-octahedral metal centres in **6** have more uniform Al–N distances, 2.11(2)–2.15(2) Å and are close to the average

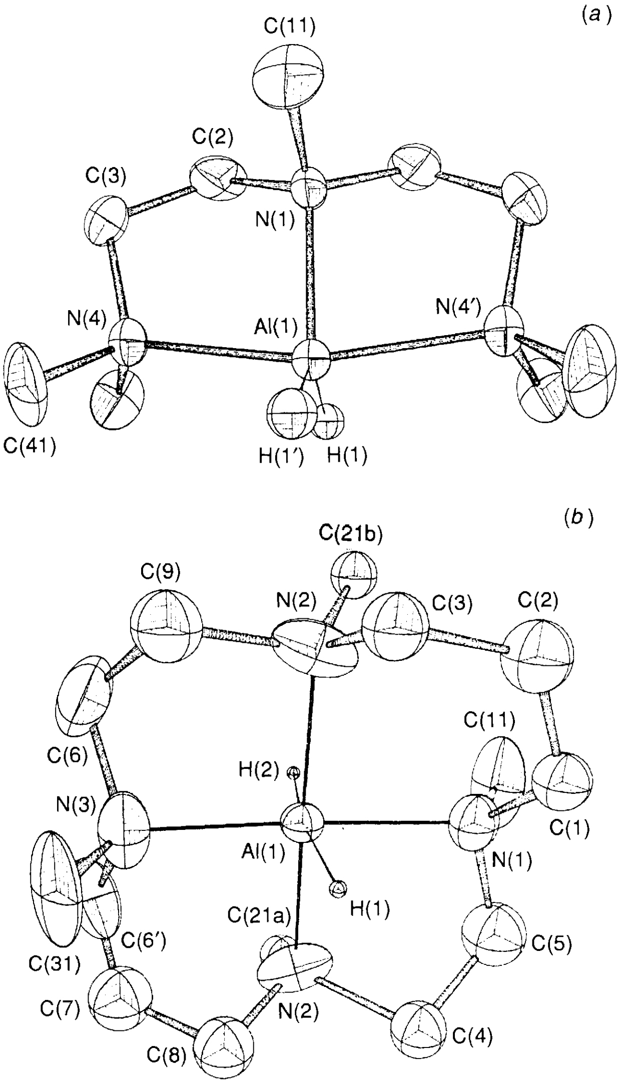

Fig. 1 Projections of (*a*) [H$_2$Al(pmdien)]$^+$[AlH$_4$]$^-$, **5**, and (*b*) [H$_2$Al(Me$_4$cyclam)]$^+$[AlH$_4$]$^-$, **6** with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms shown. Selected bond distances (Å) and angles (°): **5** Al(1)–N(1) 2.01(1), Al(1)–N(4) 2.158(7), Al(1)–H(1) 1.62, Al(2)–H(2) 1.82; N(1)–Al(1)–N(4) 83.0(2), N(1)–Al(1)–H(1) 114.0, N(4)–Al(1)–N(4)' 166.1(2), N(4)–Al(1)–H(1) 92.8, H(1)–Al–H(1)' 132: **6** Al(1)–N(1, 2, 3) 2.15(2), 2.12(1), 2.11(2), Al(1)–H(1, 2) 1.64, 1.60; N(1, 2, 3)–Al(1)–H(1) 84, 90, 90, N(1, 2, 3)–Al(1)–H(2) 87, 90, 99, H(1)–Al(1)–H(2) 171, N(1)–Al(1)–N(2, 3), 89.2(5), 173.8(8), N(2)–Al(2)–N(3), 90.8(5), N(2)–Al(1)–N(2)' 178.6(5).

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‡ *Crystal structure determinations*: (T = 296 K; Enraf-Nonius CAD4 diffractometer, crystals mounted in capillaries, Cu-Kα λ = 1.5418 Å): Compound **5**, C$_9$H$_{29}$Al$_2$N$_3$, M = 233.2, tetragonal, space group $P\bar{4}2_1m$, a = 10.730(4), c = 7.020(4) Å, U = 808 Å^3, F(000) = 266; Z = 2, D_c = 0.96 g cm^{-3}, μ(Cu-Kα) = 14.3 cm^{-1}, A*0.91–0.99 specimen 0.3 × 0.3 × 0.4 mm, 597 unique reflections, 538 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 110°.

Compound **6**: C$_{14}$H$_{38}$Al$_2$N$_4$, M = 316.5, orthorhombic, space group *Pnma*, a = 11.641(1), b = 18.248(2), c = 9.590(1) Å, U = 2037 Å^3, F(000) = 704; Z = 4, D_c = 1.04 g cm^{-3}, μ(Cu-Kα) = 12.6 cm^{-1}, A* 0.88–0.99, specimen 0.1 × 0.2 × 0.35 mm, 872 unique reflections, 514 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 110°.

The structures were solved by the heavy-atom method, **5** and direct methods, **6**, and refined by full-matrix least-squares refinement using SHELX programmes. Methylene carbon atoms, C-2 and C-3, and the unique methyl carbon, C-11, in **5** are disordered with one of two 50% occupancy sets shown in Fig. 1(*a*); carbon atoms in **6** are disordered across a mirror containing C-11, C-3, N-1, N-3 and H-12, the only one of two 50% occupancy sets is shown in Fig. 1(*b*). For **5** hydrogen atoms attached to Al were located and included as invariants (cation) or refined in *x,y,z* (anion); hydrogens attached to carbon were not included. For **6** only hydrogen atoms attached to the cationic metal centre were lcoated from difference maps and included as invariants. Unit weights were used and the final residuals were R = 0.071, 0.087, R_w = 0.083, 0.084, **5** and **6**, respectively. Both structures were initially solved in lower symmetry space groups, to the same agreement factors but with correlation problems. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Al–N distance in **5**. The conformation of the Me$_4$cyclam ring defines the *R, S, R, R/S, R, S, S* diastereoisomer which has precedence in transition metal chemistry,[14] but overall the other diastereoisomers are more common. The Al–H distances with both cations are unexceptional.[5,7,8,15] Hydrogen atoms for the anion in **6** were not located, in accordance with the high thermal parameters of the metal centre and its special position symmetry $\bar{1}$ requiring a disordered $[AlH_4]^-$ entity. In contrast, the anion in **5** has $\bar{4}$ symmetry with hydrides located in difference maps; well defined tetrahedral $[AlH_4]^-$ have previously been structurally authenticated.[16]

The detection of a single sharp ^{27}Al NMR signal at δ 102.0 for **5** in THF is consistent with the presence of $[AlH_4]^-$ species in solution; the absence of a signal assignable for the cation is not unusual for quadrupolar aluminium in an unsymmetric electric field. The low solubility of **6** in various solvents precluded solution NMR studies on this compound, although a single signal for ^{27}Al CP MAS NMR, δ 96.2, is consistent with $[AlH_4]^-$ in the solid state.[17]

We thank the Australian Research Council and the Department of Industry, Technology and Commerce (Australia) for support of this work.

Received, 5th July 1991; Com. 1/03398K

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