Self-assembling polymeric mixed donor (O/N) *N*-ethylmorpholine adducts of alane (AlH_3)

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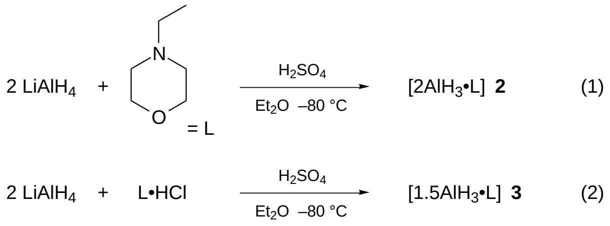
The 2 : 3 and 1 : 2 stoichiometric reactions of *N*-ethyl morpholine with the Et_2O adduct of AlH_3, prepared from $LiAlH_4$ and H_2SO_4 in Et_2O at −80 °C, afford alane-rich hydride-bridged polymers exhibiting a range of bonding modes of Lewis bases to AlH_3 including unprecedented mono Al···H hydride bridging.

Lewis-base adducts of alane (AlH_3) are important precursors in CVD production of thin films.[1] The stability of such compounds and hence ease of decomposition is often determined by the nature of the Lewis bases present. Attempts at rationalising the stability of such complexes has led to a great deal of solid-state structural information on N-amine and P-phosphine stabilised adducts, for example $AlH_3\cdot 2$quinuclidine, $AlH_3\cdot 2NMe_3$ and $AlH_3\cdot PBu^t_3$ which are monomeric five- or four-coordinate species, dimeric $[AlH_3\cdot NMe_2(CH_2Ph)]_2$ with weak hydride bridging and thus five-coordinate metal centres, and polymeric $[AlH_3\cdot tmen]_\infty$ and $[AlH_3\cdot Pr^i_2PCH_2CH_2PPr^i_2]_\infty$ which have polydentate ligands associated with five-coordinate metal centres.[2] In contrast the only structurally authenticated alane derivatives involving Lewis bases donating through an O atom are $AlH_3\cdot 2thf$, $[AlH_2(\mu\text{-}H\cdot thf]_2$[3] and the mixed-donor complex $[AlH_3\cdot N\text{-methylmorpholine}]_\infty$ **1**.[4] Such complexes are important since they give insight into the possible decomposition processes for alane and gallane (GaH_3), Lewis-base adducts in the presence of air and/or moisture where simple O-complexation at the metal centre is likely to be the primary process for decomposition, as well as how such adducts bind to oxidised silica surfaces.[5]

Herein, we report the synthesis and crystal structures of two alane adducts of *N*-ethylmorpholine (L): namely $[2AlH_3\cdot L]_\infty$ **2** and $[1.5AlH_3\cdot L]_\infty$ **3**. The compounds spontaneously self-assemble into one- or two-dimensional polymeric structures with head-to-head hydride bridging and/or two O-donating groups to the same metal centre. This has implications for building even more complex systems for polydentate donor ligands in general. In addition, a new structural type for alane has been established, and overall both structures taken together summarise the structural variety found for all other characterised Lewis base adducts of alane and gallane.

Complexes **2** and **3** were prepared as shown in reactions (1) and (2).[†] In reaction (1) the *N*-ethylmorpholine is added immediately on cooling to −80 °C an Et_2O solution of alane preformed from sulfuric acid (98%) and an Et_2O solution of $LiAlH_4$. In reaction (2) the hydrochloride salt of the morpholine is present together with the $LiAlH_4$ in Et_2O prior to the addition of the sulfuric acid. The use of the hydrochloride salt in reaction (2) is important in finely controlling the stoichiometry of the reaction. Therefore an L : $AlH_3\cdot xEt_2O$ ratio of 1 : 2 for **2** and 1 : 1.5 for **3** is ensured. Colourless crystals of both **2** and **3** are obtained at −30 °C from an Et_2O solution, although the colourless rhomboidal crystals of **3** were also obtained from *in vacuo* sublimation. Both sets of crystals are stable at room temperature with **2** melting with gas evolution *in vacuo* at 66–67 °C and finally decomposing to metal at *ca*. 137 °C, and **3** decomposing > 150 °C.



Due to the quadrupolar ^{27}Al nucleus the only meaningful information from the NMR studies was the relative chemical shifts of the AlH_3 protons, giving a relatively broad singlet, and the protons and ^{13}C in the complexed *N*-ethylmorpholine.

The solid-state structures of **2** and **3** are shown in Figs. 1 and 2 respectively.[‡] Both structures are polymeric crystallising in the space group $P\bar{1}$, albeit showing significant differences: **2** forms a polymeric chain due to the linking of discrete N and O bound AlH_3 units *via* hydride bridging, while this is also a feature of **3** there are several other important additional features which give rise to a two-dimensional net-like structure. The repeating unit in **3** consists of four L moieties and two lots of three different types of AlH_3 units giving in total three different trigonal-bipyramidal Al environments. One Al centre behaves in a similar fashion to that as seen in **2**. However the two other

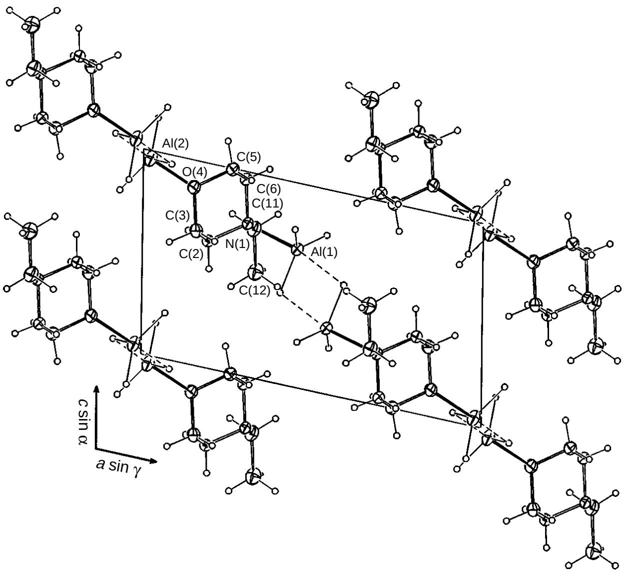


Fig. 1 Crystal structure of **2** showing 20% ellipsoids; selected distances (Å) (bridging hydride distances in italics) and angles (°): Al(1)–N(1) 2.133(3), Al(2)–O(4) 1.993(3), 3[Al(1)–H] *1.56(3)*, 1.48(2), 1.47(2), 3[Al(2)–H] 1.54(3), 1.49(3), *1.56(3)*, Al(1)···H(01a) 2.11(3), Al(2)···H(02c) 1.93(3); N(1)–Al(1)–Al(1′) 138.95(8), O(4)–Al(2)–Al(2″) 136.46(9), Al(1)–N(1)–C(11) 107.4(2), Al(1)–N(1)–C(6) 110.3(2), 3[N(1)–Al(1)–H] 95(1), 94(1), 101(1); 3[H–Al(1)–H], 122(2), 113(1), 120(1). 3[O(4)–Al(2)–H], 94(1), 94(1), 94(1); 3[H–Al(2)–H] 128(2), 116(2), 114(2)

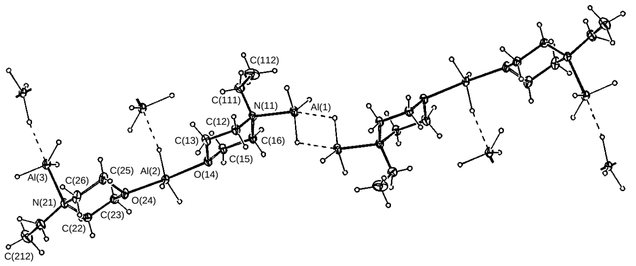


Fig. 2 Crystal structure of **3** showing 20% ellipsoids; selected distances (Å) (bridging hydride distances in italics) and angles (°): Al(1)–N(11) 2.099(3), Al(2)–O(14), 2.172(3), Al(2)–O(24) 2.034(3), Al(3)–N(21) 2.182(3), 3[Al(1)–H] 1.49(5), *1.46*(*4*), 1.46(3); 3[Al(2)–H] *1.43*(*4*), 1.49(3), 1.55(4); 3[Al(3)–H] 1.32(5), 1.49(6), 1.58(6); Al(1)···H(01b) 2.13(3), Al(3)···H(02a) 2.29(4); Al(1)–N(11)–C(16) 109.0(2), Al(1)–N(11)–C(111) 111.6(3), O(14)–Al(2)–O(24) 174.7(1), Al(2)–O(14)–C(13) 110.7(2), Al(2)–O(24)–C(23) 120.8(2), Al(3)–N(21)–C(22) 114.8(2), Al(3)–N(21)–C(211) 108.3(3), 3[N–Al(1)–H] 95(2), 93(1), 102(1); 3[O(14)–Al(2)–H] 84(2), 88(1), 90(2); 3[O(24)–Al(2)–H] 94(2), 89(1), 95(2); 3[N(21)–Al(3)–H] 104(2), 99(2), 84(2)

Al centres which are both five-coordinate help form the two-dimensional structure through the formation of single Al–H hydride bridging, which is unprecedented for alane species. The Al which is bound by two O atoms contributes a $H^{\delta-}$ while it is the N-bound Al centre which provides the electropositive metal centre, thus achieving five-coordination. It is interesting that the polymer **1**, which is formed from the 1 : 1 reaction of $LiAlH_4$ with the hydrochloride salt of *N*-methylmorpholine (L′·HCl) gives a simpler asymmetric unit in compliance with the stoichiometry of the reaction; repeating AlH_3·L′ with each five-coordinate Al centre bound by both O and N from different morpholine moieties and with no intermolecular hydride bridging and with the donor ligands arranged head-to-tail rather than head-to-head as seen in **2** and **3**. In complete contrast the 1 : 1 L′ adduct of trimethylaluminium shows no Al–O bonding although it is observed in the 2 : 1 adduct which forms a monomer.

The reaction of AlH_3 in Et_2O with 4-(2-chloroethyl)morpholine hydrochloride affords the *N*-ethylmorpholine adduct, $[(AlH_3)(AlClH_2)\cdot L]_\infty$ **4**, which exhibits another variation in the polymeric framework, containing features of both **2** and **3**.†‡ Essentially it has the same hydrogen-bonded backbone as **2** but the cross-linking features of **3** with the close electrostatic interactions being between the bis O-bound Al (on which hydride/chloride exchange has occurred between the AlH_3 and NCH_2CH_2Cl units) and Cl instead of Al···H.

The variety in structural motifs contained within **2** and **3** are clearly seen from an analysis of the bond lengths and angles. In **2** the Al–O bonds are relatively short, 1.993(3) Å, in comparison to the longer bonds of 2.172 and 2.034 Å in **3** and 2.19(2) Å in **1** reflecting the lower covalent interactions at the Al centre {*cf.* also the mono [1.967(2) Å] and bis [av. 2.066(3) Å] thf adducts of alane cited above}. In **3** the O–Al–O bond angle bisecting the trigonal-planar AlH_3 unit is almost linear at 174.7(1)°. The intermolecular $Al_2\cdots H_2$ distances of 2.11(3) and 1.93(3) Å in **2** and 2.13(3) Å in **3** are significantly longer than those within the AlH_3 units, 1.47(2)–1.58(6) Å. The N–Al···H–Al polymer linking bonds in **3** are longer again at 2.29(3) Å. All the Al–N distances are comparable with those found in related amine–alane adducts.

The use of ethereal solutions of alane by-passes the typical, and as yet unfavourable, ligand substitution reactions with $AlH_3\cdot NMe_3$ for forming exclusively O-donor ligand bound complexes. It also allows for the possibility of determining the relative stability of the Lewis-base O-donating species in comparison with their amine or phosphine stabilised analogues.

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Footnotes

† **2**. The Et_2O complex of AlH_3 was generated *in situ* at −80 °C from the reaction of $LiAlH_4$ (0.46 g, 12 mmol) with H_2SO_4 (98%, 0.59 g, 6.12 mmol) in Et_2O (30 ml). Almost immediately *N*-ethylmorpholine (0.69 g, 6 mmol) was added dropwise while the reaction mixture was stirred. This was then allowed to warm slowly to room temp. and stirred for a further 2 h. The white suspension was filtered leaving a clear Et_2O solution from which rhomboidal colourless crystals were obtained at −30 °C (1.4 g, 73%). Alternatively a white powder can be formed on quick removal of Et_2O from the clear solution and sublimed *in vacuo* to give the same rhomboidal crystals. Melting with gas evolution at 66–67 °C, further gas evolution from 94 °C until decomposition to metal at *ca.* 137 °C. ^1H NMR (300 MHz, 25 °C, C_6D_6) δ 4.14 (s, AlH), 3.62 (m, OCH_2), 2.15 (m, NCH_2), 0.87 (t, CH_3), ^{13}C NMR (75.5 MHz, 25 °C, C_6D_6) δ 63.16, 54.84, 52.87, 8.81. Anal. required (found) C, 41.14 (41.48); H, 10.93 (10.98); N, 8.00 (8.13)%.

3. H_2SO_4 (98%, 0.38 g, 3.90 mmol) was added dropwise to a stirred reaction mixture of *N*-ethylmorpholine hydrochloride (L·HCl) (0.61 g, 4 mmol) and $LiAlH_4$ (0.30 g, 8 mmol) in Et_2O (25 ml) at −80 °C. This was allowed to stir and warm slowly to room temp. at which point it was stirred for a further 2 h. The white suspension was filtered and the clear Et_2O solution cooled to −30 °C at which temperature fine colourless crystals of **3** were obtained (0.43 g, 62%); decomp. >151 °C, ^1H NMR (300 MHz, 25 °C, C_6D_6) δ 4.15 (s, AlH), 3.65 (m, OCH_2), 2.20 (m, NCH_2), 0.85 (t, CH_3), ^{13}C NMR (75.5 MHz, 25 °C, C_6D_6) δ 63.25, 54.77, 52.91, 8.91. Anal: required (found) C 44.99 (41.88), H 11.01 (11.06), N 8.74 (8.51)%.

4. This was prepared from the reaction of 2 equiv. of $LiAlH_4$ and 1 equiv. of 4-(2-chloroethyl)morpholine hydrochloride in Et_2O at −80 °C. Large colourless crystals were grown from the filtered clear ether solution at 4 °C, mp 123 °C.

‡ *Crystal structure determinations* (CAD4 diffractometer, crystals mounted in capillaries): **2**. $C_6H_{19}Al_2NO$, M = 175.2, triclinic, space group $P\bar{1}$, a = 11.941(6), b = 7.021(3), c = 6.963(3) Å, α = 101.68(3), β = 98.29(4), γ = 103.27(4)°, U = 544.1 Å^3. D_c (Z = 2) = 1.069 g cm^{-3}, $F(000)$ = 192. μ_{Mo} = 2.2 cm^{-1}, specimen: 0.27 × 0.18 × 0.15 mm, $A^*_{min,\,max}$ = 1.03, 1.04. $2\theta_{max}$ = 50°, final R, R_w = 0.044, 0.042. N_0 = 1301 'observed' $[I > 3\sigma(I)]$ reflections out of N = 1905 unique.

3. $C_{12}H_{35}Al_3N_2O_2$, M = 320.4. Triclinic, space group $P\bar{1}$, a = 15.388(4), b = 10.233(5), c = 6.676(3) Å, α = 73.15(4), β = 77.95(4), γ = 81.62(4)°, U = 980 Å^3, D_c (Z = 2) = 1.086 g cm^{-3}, $F(000)$ = 352. μ_{Mo} = 1.9 cm^{-1}, specimen: 0.50 × 0.49 × 0.48 mm (no correction), $2\theta_{max}$ = 55°, final R, R_w = 0.049, 0.051, N = 2625, N_0 = 1868.

4. $C_{12}H_{34}Al_3ClO_2N_2$, M = 354.8 triclinic, space group $P\bar{1}$, a = 12.964(7), b = 12.447(6), c = 6.887(2) Å, α = 83.54(3), β = 77.30(4), γ = 71.06(4)°. U = 1003 Å^3, D_c (Z = 2) = 1.18 g cm^{-3}, $F(000)$ = 384. μ_{Mo} = 3.2 cm^{-1}, specimen: 0.55 × 0.50 × 0.40 mm (no correction), $2\theta_{max}$ = 50°, final R, R_w = 0.055, 0.062. N = 3512, N_0 = 2655. Refinement abnormalities, including a significant difference map residue, were modelled in terms of disorder of Cl(1) to either side of Al(3), populations of Cl(1,1′) being (x, $1 - x$) x = 0.840(3). Hydrogen atoms were refined in $(x, y, z, U_{iso})_H$ leaving an effectively featureless final difference map (max. residue 0.45 e Å^{-3}). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/327.

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