

A tetranuclear aluminium hydrazide derivative with a ladder-type structure

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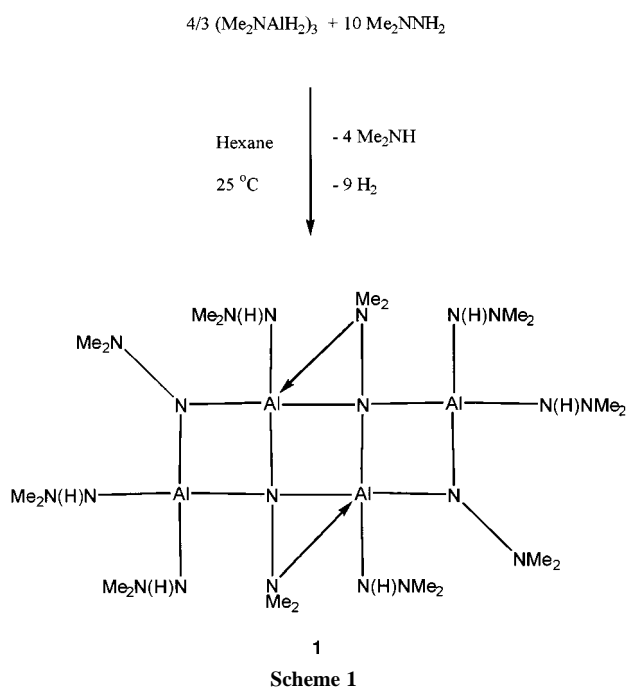
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The reaction of $(\text{Me}_2\text{NAlH}_2)_3$ with excess H_2NNMe_2 affords $[\text{Al}_4(\text{NHNMe}_2)_6(\text{NNMe}_2)_4]$; the compound possesses an Al_4N_4 ladder-shaped core.

The renewed interest in group 13 hydrazides can be attributed to two driving forces. Firstly, since hydrazide ligands are potentially multi-functional they can promote the formation of novel rings, cages, and polymers featuring group 13–nitrogen linkages. Secondly, group 13 hydrazides could play an important role as precursors to group 13 nitrides. The most successful current approach to the deposition of such nitrides involves the thermal reaction of the respective metal alkyl with ammonia.¹ Unfortunately, the requisite reaction temperatures are somewhat high (>900 °C) and lower thermal budgets are desirable to obviate such problems as thermal stresses and stoichiometry losses in the resulting films. Hydrazine² and dimethylhydrazine³ have been suggested as alternative, lower temperature nitrogen delivery sources thus rendering the investigation of group 13 hydrazides an attractive proposition.

Despite being known since 1961,⁴ structural information on aluminium hydrazides is confined to that of the dimer, $[\text{Me}_2\text{Al}\{\mu\text{-N}(\text{H})\text{NMe}_2\}]_2$.⁵ Moreover, it was only in 1995 that $[\text{Et}_2\text{Ga}\{\mu\text{-N}(\text{H})\text{NPh}_2\}]_2$, the first gallium hydrazide, was prepared.⁶ More recent interest has focused on the construction of cage and ring structures from group 13 hydrazides, two important examples of which are $[\text{MeGaN}(\text{H})\text{NPh}]_4$ ⁷ and an octa-aluminium analogue of a calix[4]pyrrole which features four five-membered AlN_3C rings connected by Me_2Al bridges.⁸ Herein, we describe the synthesis and structural assay of a novel tetra-aluminium hydrazide derivative that possesses a ladder-type core.⁹ A further distinguishing feature of the present work is that the replacement of a trialkylalane by $(\text{Me}_2\text{NAlH}_2)_3$ ¹⁰ as the aluminium source results in lower reaction temperatures.



The reaction of $(\text{Me}_2\text{NAlH}_2)_3$ with an excess of 1,1-dimethylhydrazine in hexane solution at 25 °C is exothermic and results in the evolution of hydrogen and dimethylamine (Scheme 1). Following filtration of the reaction mixture, cooling of the filtrate to –20 °C resulted in the formation of colourless crystals of **1**.[†] Mass spectroscopic assay indicated a composition of $\text{C}_{20}\text{H}_{67}\text{Al}_4\text{N}_{20}$ for **1** (HRMS: calc. for $(\text{M} + \text{H})^+$, 695.512; found, 695.513) and this was in accord with combustion analysis data. Unfortunately, it was not possible to deduce the structure of **1** using ^1H , ^{13}C , and ^{27}Al NMR data[†] at this stage, hence an X-ray diffraction experiment became necessary.[‡]

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (for an asymmetric unit of formula $[\text{Al}_2\{\text{NHNMe}_2\}_3\{\text{NNMe}_2\}_2]$). The crystalline state comprises an array of tetranuclear molecules. $[\text{Al}_4\{\text{NHNMe}_2\}_6\{\text{NNMe}_2\}_4]$ and there are no unusually short intermolecular contacts. As illustrated in Fig. 1, the Al_4N_4 skeleton of **1** adopts a ladder-type arrangement that consists of three fused four-membered Al_2N_2 rings. The

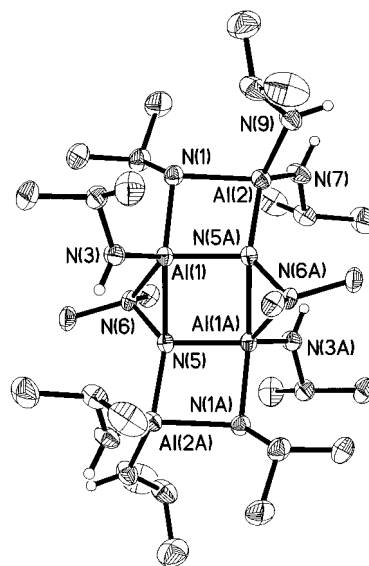


Fig. 1 Molecular structure of **1** showing the atom numbering scheme. Some hydrogen atoms have been eliminated for clarity. Selected bond distances (Å) and angles (°): Al(1)–N(5) 2.091(3), Al(1)–N(5A) 1.877(2), Al(1)–N(6) 1.957(2), N(5)–N(6) 1.488(3), Al(1)–N(3) 1.787(3), Al(1)–N(1) 1.959(3), Al(2)–N(1) 1.973(2), N(1)–N(2) 1.467(3), Al(2)–N(5A) 1.860(2), N(5A)–Al(1)–N(5) 89.43(10), N(3)–Al(1)–N(5A) 128.09(12), N(1)–Al(1)–N(5) 142.17(10), N(6)–Al(1)–Al(1A) 74.08(8), N(1)–Al(1)–N(3) 107.29(11), N(3)–Al(1)–N(6) 110.90(11), N(5A)–Al(1)–N(6) 113.73(10), N(5A)–Al(1)–N(1) 83.09(10), N(6)–Al(1)–N(1) 107.68(10), N(3)–Al(1)–N(5) 106.43(11), N(6)–Al(1)–N(5) 42.97(9), N(3)–Al(1)–Al(1A) 128.29(10), N(5A)–Al(1)–Al(1A) 47.77(8), N(1)–Al(1)–Al(1A) 120.32(8), N(5)–Al(1)–Al(1A) 41.67(6), N(3)–Al(1)–Al(2) 128.06(9), N(5A)–Al(1)–Al(2) 39.70(8), N(6)–Al(1)–Al(2) 118.41(8), N(1)–Al(1)–Al(2) 43.39(7), N(5)–Al(1)–Al(2) 120.18(7), Al(1A)–Al(1)–Al(2) 81.99(4), N(6)–N(5)–Al(2A) 132.2(2), N(6)–N(5)–Al(1A) 122.9(2), Al(2A)–N(5)–Al(1A) 100.16(11), N(6)–N(5)–Al(1) 63.72(13), Al(2A)–N(5)–Al(1) 141.68(13), Al(1A)–N(5)–Al(1) 90.57(10), N(7)–Al(2)–N(9) 105.46(13), N(7)–Al(2)–N(5A) 116.80(12), N(9)–Al(2)–N(5A) 122.14(12), N(7)–Al(2)–N(1) 121.93(12), N(9)–Al(2)–N(1) 106.76(12), N(5A)–Al(2)–N(1) 83.14(10).

central such ring, which resides on a crystallographic inversion centre, is essentially rectangular with bond angles of 89.43(10) and 90.57(10)° at aluminium and nitrogen, respectively, and a difference of *ca.* 0.2 Å in the Al–N bond distances. In turn, the central Al₂N₂ moiety is flanked on either side by a fused three-membered AlN₂ ring formed by N → Al dative bonding from hydrazide lone pairs. As a consequence, the coordination numbers of Al(1) and Al(1A) are both five. In a formal sense, there are four Al–N σ-bonds (Al(1)–N(5) 2.091(3) Å; Al(1)–N(5A) 1.877(2) Å; Al(1)–N(3) 1.787(2) Å, Al(1)–N(1) 1.959(3) Å and one N → Al dative bond (Al(1)–N(6) 1.957(2) Å) at each aluminium centre. The average Al–N bond distance of 1.934(3) Å is close to that reported for [Me₂Al{μ-N(H)NMe₂}]₂ (1.955(3) Å), the only aluminium hydrazide structurally characterized previously.⁵ The bond angles within the AlN₅ coordination sphere range from 42.97(9)° (N(5)–Al(1)–N(6)) to 142.17(10)° (N(1)–Al(1)–N(5)); at best, the geometry can be described as highly distorted trigonal bipyramidal. Not unexpectedly, the geometries at N(5) and N(5A) show a marked departure from the ideal tetrahedral angle and range from 63.72(13)° for Al(1)–N(5)–N(6) to 132.2(2)° for Al(2A)–N(5)–N(6). The outer four-membered Al₂N₂ rings are somewhat rhomboid; however, there is a wide scatter in the Al–N bond distances and intra-ring angles (Fig. 1 caption). The average Al–N bond distance of 1.917(3) Å for the outer Al₂N₂ rings is shorter than that for the inner ring (1.934(3) Å). The geometries at Al(2) and N(1) are distorted tetrahedral and pyramidal, respectively. Overall, the geometry of the Al₄N₄ core of **1** is somewhat similar to that reported¹¹ for a lithium salt of composition C₅₂H₇₈Al₄Li₂N₄.

Ex post facto, the NMR data for **1** can be interpreted satisfactorily and indicate the integrity of the ladder-type structure in solution. Thus, two aluminium environments are evident in the ²⁷Al NMR spectrum and the methyl groups on N(6) and N(6A) are anisochronous. The observation of four, rather than three, N(H)NMe₂ environments may be due to the presence of rotational isomers.

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Notes and references

† *Experimental procedures:* **1**: An excess of Me₂NNH₂ (4.0 ml, 3.12 g, 53 mmol) was added dropwise *via* syringe to a stirred solution of (H₂AlNMe₂)₃¹⁰ (1.0 g, 4.6 mmol) in hexane (75 ml) at 25 °C. After stirring for 1 h, an initial precipitate of white powdery **1** was isolated by filtration (0.5 g, 21%). The clear, colourless filtrate was stored at –20 °C resulting in a second crop of **1** (0.65 g, 27%) as X-ray quality crystals that were used for

the acquisition of spectroscopic and analytical data. In subsequent experiments, total yields as high as 66% have been obtained. Mp 192–193 °C. HRMS: calc. for C₂₀H₆₇Al₄N₂₀ [*i.e.* (M + H)⁺] 695.512; found, 695.513. ¹H NMR (300.15 MHz, C₆D₆) δ 1.72 (s, 2H, H–N), 1.75 (s, 2H, H–N), 2.50 (s, 12H, C1, C2/C5, C6), 2.56 (s, 24H, C7, C8, C9, C10), 2.58 (s, 12H, C1, C2/C5, C6), 2.90 (s, 6H, C3/C4), 3.04 (s, 6H, C3/C4), 3.08 (s, 2H, H–N), 3.66 (s, 2H, H–N). ¹³C {¹H} NMR (75.14 MHz, C₆H₆) δ 51.29 (C3/C4), 52.98 (C1, C2/C5, C6), 53.20 (C3/C4), 54.66 (C1, C2/C5, C6), 55.28 (C7, C8, C9, C10). ²⁷Al NMR (78.21 MHz, C₆D₆) δ 62.7 (br); 96.7 (br). Anal. Calc. for C₂₀H₆₆Al₄N₂₀: C, 34.51; H, 9.63. Found: C, 33.78; H, 9.33%.

‡ *Crystal data:* **1**: C₂₀H₆₆Al₄N₂₀, *M* = 694.88, triclinic, space group *P* $\bar{1}$, *a* = 9.1066(3), *b* = 10.8316(7), *c* = 11.8213(8) Å; α = 69.101(3), β = 70.496(4), γ = 78.967(4)°, *U* = 1023.36(10) Å³, *Z* = 2, *D_c* = 1.127 g cm^{–3}, *T* = 213(2) K, μ = 0.154 mm^{–1}, *wR*₂ = 0.1275 (4139 independent reflections), *R* = 0.0566 (*I* > 2σ(*I*)). CCDC 182/1334. See <http://www.rsc.org/suppdata/cc/1999/1645/> for crystallographic files in .cif format.

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