

# Synthesis and structure of an anionic aluminium–nitrogen compound containing a ladder-shaped core

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An X-ray crystallographic study of the aluminium–nitrogen compound  $C_{52}H_{78}Al_4Li_2N_4$  showed it to possess a ladder-shaped  $(AlN)_4$  core. The mesityl ligands of the inner nitrogen atoms are each metallated by one of their neighbouring aluminium atoms, while on the outer negative charge is localised. The reported structure is the first tetrameric anionic  $Al-N$  compound.

During the last decades molecules containing  $Al-N$  bonds have been extensively investigated. Monomers were prepared by Sheldrick and Sheldrick<sup>1</sup> and by Power and co-workers.<sup>2</sup> The structurally characterised di- and tri-meric aminoalanes carrying substituents such as H, aryl and alkyl, respectively, have been synthesized mostly by elimination reactions.<sup>3</sup> Aminoalanes are generally the starting materials for the preparation of iminoalanes, which can adopt a multitude of different geometries in the solid state, namely rings,<sup>4,5</sup> chains,<sup>6</sup> cubes and more complex cages.<sup>7,8</sup>

Most of the compounds containing  $Al-N$  bonds are neutral; only a small number of them are positively charged.<sup>8,9</sup> Anionic complexes which are known mono- and di-meric species are generally of interest with regard to multiple bonding between the aluminium and the nitrogen atoms.<sup>5,10,11</sup> Herein, we report on the synthesis and crystal structure of the first tetrameric anionic  $Al-N$  compound.

## Results and Discussion

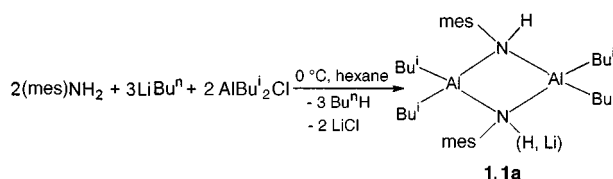
### Preparation, characterisation and crystallography

**$[Bu^i_2AlN(H)(mes)]_2$  **1** and  $Bu^i_2AlN(Li)(mes)AlBu^i_2N(H)(mes)$  **1a**.** The obtained product (Scheme 1) is a mixture of compound **1** and its monolithiated species **1a**, that could not be separated by crystallisation. However, **1** was described in 1993 by Robinson and co-workers.<sup>12</sup> The proton NMR spectrum shows two N–H peaks ( $\delta$  4.08 and 4.01, respectively). In **1a** the methyl protons of the isobutyl groups are not equivalent and appear as two doublets ( $\delta$  1.06 and 0.79, respectively) while the analogous protons of **1** give one signal ( $\delta$  0.94).

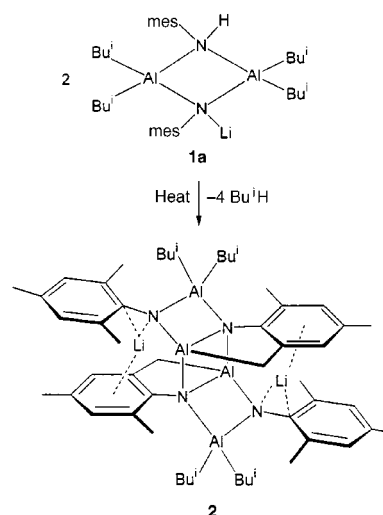
**$C_{52}H_{78}Al_4Li_2N_4$  **2**.** The mixture of compounds **1** and **1a** was heated in an oil-bath (Scheme 2). After the liquid melted, it started foaming. Gas elimination could be observed using a bubbler. Finally small cubic crystals were obtained. On exposure to air they turned from colourless to yellow. At 245 °C the crystals decompose by gas elimination.

In the <sup>1</sup>H NMR spectrum the N–H resonances are no longer observed and moreover in the IR spectrum no N–H vibrations are found. The protons of the methylene group that resulted from the metallation are diastereotopic and occur as two doublets with a coupling constant of <sup>2</sup>J(HH) = 6.1 Hz.

The crystal structure of compound **2** is shown in Fig. 1. Selected bond distances and angles are reported in Table 1. The four Al atoms and the four N atoms forming the core of the compound are arranged in a ladder-like structure, with the Al and the N atoms at the opposite corners of the three condensed



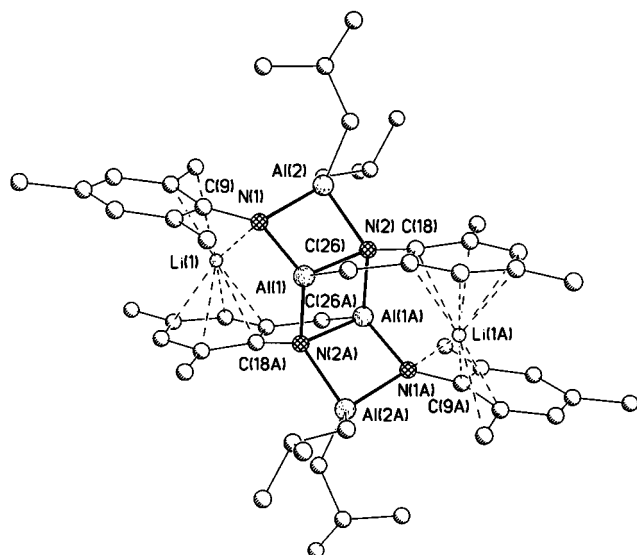
**Scheme 1** Formation of the mixture of  $[Bu^i_2AlN(H)(mes)]_2$  **1** and  $Bu^i_2AlN(Li)(mes)AlBu^i_2N(H)(mes)$  **1a** (mes = 2,4,6-trimethylphenyl)



**Scheme 2** Formation of  $C_{52}H_{78}Al_4Li_2N_4$  **2**

four-membered rings. The molecule lies on a centre of inversion and therefore while the two symmetry related four-membered rings at both ends of the 'ladder' show a deviation from planarity of 0.1 Å, the central one is perfectly planar. The angle between the mean plane of one of the external four-membered rings and the plane of the central one is 61.4°. Although this type of arrangement has been previously observed in the case of  $[AlMe_2]_2[C_{12}H_{28}N_6][AlMe_2]_2$ ,<sup>6</sup> the analogies are limited to the ladder-like geometry of the  $Al-N$  core, as the structure we report in this paper is ionic and furthermore not stabilised by chelating ligands.

The two outermost Al atoms co-ordinate two disordered isobutyl groups each, the ratio between the major and the minor component being 7:3 for both isobutyl ligands. Of the four 2,4,6-trimethylphenyl groups bound to the N atoms, two show an orthometallation due to C–H activation with the two remaining Al atoms  $[Al(1)-C(26)$  1.981(4) Å]. All the Al atoms



**Fig. 1** Crystal structure of  $C_{52}H_{78}Al_4Li_2N_4$  **2**. Hydrogen atoms and disordered components of the isobutyl groups have been omitted for clarity

**Table 1** Selected bond lengths (Å) and angles (°) for compound **2**

Al(1)–N(1)	1.857(3)	N(1)···Li(1)	2.066(7)
Al(1)–N(2)	1.976(3)	Li(1A)···C(18)	2.313(7)
Al(2)–N(1)	1.948(3)	Li(1A)···C(19)	2.408(8)
Al(2)–N(2)	1.969(3)	Li(1A)···C(20)	2.415(8)
Al(1)–N(2A)	1.916(3)	Li(1A)···C(21)	2.430(7)
Al(1)–C(26)	1.981(4)	Li(1A)···C(22)	2.381(7)
		Li(1A)···C(23)	2.338(7)
Al(1)···Al(1A)	2.674(2)	Li(1A)···C(9)	2.186(7)
Al(1)···Al(2)	2.715(2)	Li(1A)···C(10)	2.283(7)
N(1)–Al(1)–N(2)	91.0(1)	Al(1)–N(2)–Al(2)	87.0(1)
N(1)–Al(2)–N(2)	88.6(1)	N(2)–Al(1)–N(2A)	93.2(1)
Al(1)–N(1)–Al(2)	91.0(1)	Al(1)–N(2)–Al(1A)	86.8(1)

in the structure are thus four-co-ordinated, with a tetrahedral arrangement of the surrounding atoms. The Al···Al distance between the two external four-membered rings is 2.715(2) Å, while it is 2.674(2) Å in the central one. The orthometallation of mesityl substituents by aluminium has been previously observed only in the case of  $[(C_5Me_5)Al(\mu-NHC_6H_2Me_2-4,6-CH_2-2)]_2$  prepared in our research group (Al···CH<sub>2</sub> 1.988 Å). In comparison to the supermesityl ( $C_6H_2Bu_3-2,4,6$ ) derivatives,<sup>12,13</sup> the bond lengths of the aluminium–carbon bridge in mesityl compounds are slightly longer.

The negative charge preferentially localised on the two N atoms at the two extreme ends of the 'ladder' is neutralised by the close proximity of the two lithium ions at the two sides of the Al–N core. The Li···N distance is 2.066(7) Å and therefore 0.03 Å longer than in comparable compounds.<sup>2,10</sup> Shorter and longer bonds are found in complexes with one or more co-ordinated tetrahydrofuran molecules. Each Li atom is also  $\eta^6$  co-ordinated to the aromatic ring involved in the orthometallation [Li···C (orthometallated ring) in the range 2.313(7) to 2.430(7) Å] and shows shorter contacts with two of the C atoms of the non-metallated ring [Li···C(9) 2.186(7) Å and Li···C(10) 2.283(7) Å]. These distances are quite comparable to other Li···C  $\pi$  bonds (in the range of 2.22 Å to 2.57 Å).<sup>2,14,15</sup> The angle between the planes of the two aromatic rings co-ordinating each Li atom is 12.0°.

In summary the results demonstrate quite nicely a 'frozen' intermediate on the pathway of an aminoalane to an iminoalane. The isolation of compound **2** was possible due to the lithiation of reactive protons and the C–H activation by aluminium.

## Experimental

### Crystal structure determination of complex **2**

**Crystal data.**  $C_{52}H_{78}Al_4Li_2N_4$ ,  $M = 880.98$ , monoclinic, space group  $C2/c$ ,  $a = 20.762(9)$ ,  $b = 14.344(9)$ ,  $c = 20.303(9)$  Å,  $\beta = 120.38(4)^\circ$ ,  $U = 5216(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.122$  g cm<sup>-3</sup>,  $F(000) = 1904$ , colourless crystals, dimensions 1.00 × 0.70 × 0.40 mm,  $\mu(Mo-K\alpha) = 0.126$  mm<sup>-1</sup>.

**Data collection and processing.** Intensity data were collected by the  $\omega$ -2 $\theta$  scan method at 153(2) K on a Siemens AED2 four-circle diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and according to the learnt-profile method.<sup>16</sup> Of the 5416 reflections measured ( $3.6 \leq \theta \leq 25^\circ$ ) 4503 were unique (merging  $R = 0.022$ ) and all were used in the refinement. Three standard reflections showed no significant variations in intensity during data collection.

**Structure analysis and refinement.** The structure was solved by direct methods (SHELXS 90)<sup>17</sup> and refined against  $F^2$  by means of the full-matrix least-squares technique using SHELXL 93.<sup>18</sup> The weighting scheme  $w^{-1} = \sigma^2(F_o^2) + (0.0480P)^2 + 29.4951P$  with  $P = (F_o^2 + 2F_c^2)/3$  was applied in the final cycles of the refinement. The converged residuals were  $R1 = 0.067$  for reflections with  $I > 2\sigma(I)$ , and  $wR2 = 0.179$  for all data. A final Fourier-difference map showed no electron density  $>0.537$  and  $<-0.298$  e Å<sup>-3</sup>. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located in positions riding on the corresponding C atoms (C–H 0.96 and 0.93 Å for the sp<sup>3</sup> and sp<sup>2</sup> carbons, respectively).

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### General

Owing to the extreme water and air sensitivity of the compounds, oxygen and moisture were excluded during all procedures. The <sup>1</sup>H NMR data were recorded on a Bruker AM 200 FT NMR spectrometer, IR data on a Bio-Rad Digilab FTS 7 spectrometer and mass spectral data on a Finnigan MAT 95 and on a Varian MAT CH5 spectrometer. Elemental analyses were done by the Analytical Laboratory of the institute. The commercially available LiBu<sup>n</sup> was used without further purification, (mes)NH<sub>2</sub> was dried over CaH<sub>2</sub> and distilled under nitrogen.

### Synthesis

**[Bu<sub>2</sub>AlN(H)(mes)]<sub>2</sub> **1** and Bu<sub>2</sub>AlN(Li)(mes)AlBu<sub>2</sub>N(H)(mes) **1a**.** *n*-Butyllithium (9.4 cm<sup>3</sup>, 15 mmol in hexane) was added dropwise to a solution of (mes)NH<sub>2</sub> (1.4 cm<sup>3</sup>, 10 mmol) in hexane (60 cm<sup>3</sup>) at 0 °C. The compound AlBu<sub>2</sub>Cl (1.95 cm<sup>3</sup>, 10 mmol) was added *via* syringe. After warming to room temperature the mixture was allowed to stir for 4 h and then LiCl was filtered off. Removal of solvent afforded a pale yellow solid **1**, **1a** (1.3 g, 95%), m.p. (mixture **1**, **1a**) 143 °C (uncorrected);  $\tilde{\nu}_{max}/cm^{-1}$  (Nujol) 3256m (NH), 1766vw, 1733w, 1142s, 1066s, 854s, 839s, 667s and 510s;  $\delta_H$ (200 MHz, C<sub>6</sub>D<sub>6</sub>, SiMe<sub>4</sub>) 6.69 (s, aromatic H), 4.08 and 4.01 (s, NH), 2.47 and 2.43 (s, *o*-CH<sub>3</sub>), 2.06 (s, *p*-CH<sub>3</sub>), 1.97 (m, CH of Bu<sup>n</sup>), 1.06, 0.94 and 0.79 (d, CH<sub>3</sub> of Bu<sup>n</sup>) and 0.68 to 0.32 (m, AlCH<sub>2</sub>);  $\delta_{Li}$ (155.5 MHz, C<sub>6</sub>D<sub>6</sub>, LiCl) 1.36 (br s,  $W_1 = 225$  Hz);  $m/z$  534 ( $M_{1a} - Li - CH_3$ ) and 275 ( $\frac{1}{2} M_1$ ).

**C<sub>52</sub>H<sub>78</sub>Al<sub>4</sub>Li<sub>2</sub>N<sub>4</sub> **2**.** The solvent-free mixture of **1**, **1a** (1.0 g, 1.8 mmol) was heated in an oil-bath (180 °C). When gas elimination ceased the yellow, glassy solid was allowed to cool to room temperature. Recrystallisation from hexane gave extreme air- and moisture-sensitive crystals of compound **2** (44 mg, 5.5%), m.p. 245 °C (decomp., uncorrected) (Found: C, 71.0; H, 8.8; N, 6.1.  $C_{52}H_{78}Al_4Li_2N_4$  requires C, 70.9; H, 8.9; N, 6.4%).  $\tilde{\nu}_{max}/cm^{-1}$  (Nujol) 1745w, 1615m, 1295s, 1232s, 1196s, 1167s, 1142s, 1065s, 876s, 861s, 825s and 688vs;  $\delta_H$ (200 MHz, C<sub>6</sub>D<sub>6</sub>, SiMe<sub>4</sub>) 7.00 (s, aromatic H of metallated mesityl), 6.64 (s, aro-

matic H of mes), 5.98 (s, aromatic H of metallated mes), 2.27 (s, *o*-CH<sub>3</sub> of mes), 2.03 (s, *o*-CH<sub>3</sub> of metallated mes), 1.80 [m, <sup>3</sup>J(HH) 6.5, CH of Bu<sup>†</sup>], 1.60 (s, *p*-CH<sub>3</sub>), 1.46, 1.39, 0.83 and 0.77 [d, <sup>3</sup>J(HH) 6.5, CH<sub>3</sub> of Bu<sup>†</sup>], 0.61 to 0.54 [2 d, <sup>2</sup>J(HH) 6.1, *o*-CH<sub>2</sub>Al of metallated mes] and 0.10 to -0.10 [4 d, <sup>3</sup>J(HH) 6.5 Hz, AlCH<sub>2</sub> of Bu<sup>†</sup>]; *m/z* 880 (*M*<sup>+</sup>) and 824 (*M* - C<sub>4</sub>H<sub>8</sub>).

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