DALTON

Preparation and structures of some new pyrrolidinido- and piperidinido-alanes and -aluminates

Mbolatiana M. Andrianarison, Miles C. Ellerby, Ian B. Gorrell, Peter B. Hitchcock, J. David Smith * and David R. Stanley

School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK

Alane and lithium tetrahydroaluminate each reacted with an excess of pyrrolidine or piperidine in tetrahydrofuran (thf) to give the new dinuclear compounds $\{Al[\overline{N(CH_2)_nC}H_2]_3\}_2$ [n = 3 (from pyrrolidine) **1** or 4 (from piperidine) **2**] and $L_2Li[\mu\text{-}\overline{N(CH_2)_nC}H_2]_2Al[\overline{N(CH_2)_nC}H_2]_2$ [n = 3, L = thf **3** or $H\overline{N(CH_2)_3C}H_2$ **4**; n = 4, L = thf **5**]. The compounds were characterised by elemental analysis, multinuclear NMR spectroscopy, mass spectrometry and, for **1**, **4** and **5**, X-ray crystallography. In **1**, which contains an Al_2N_2 ring, average distances are Al–N(terminal) 1.797(2) and Al–N(bridging) 1.963(2) Å. Exocyclic N–Al–N angles are in the range 112.6–114.4°, the endocyclic N–Al–N angle is 86.69(9)° and Al–N–Al is 93.31(9)°. The sums of the angles at the terminal nitrogens are close to 360°. In **4**, which contains an LiN_2Al ring, distances are Al–N(terminal) 1.824(8), Al–N(bridging) 1.880(7), Li–N(terminal) 2.035(20) and Li–N(bridging) 2.149(20) Å. The sums of the angles at terminal nitrogens are 349.1 and 355.4°. Ring angles are N–Al–N 100.0(3), Al–N–Li 82.0(4) and N–Li–N 84.2(5)°. In **5** average distances are Al–N(terminal) 1.828(3), Al–N(bridging) 1.895(3), Li–O 1.987(6) Å and Li–N(bridging) 2.135(6) Å. The sums of the angles at terminal nitrogens are 358.1 and 357.4°. Ring angles are N–Al–N 100.69(13), Al–N–Li 84.0(2) and N–Li–N 86.2(2)°. Exchange between bridging and terminal amido groups is slow on the NMR time-scale at 250 MHz in **1** and **2** but fast in **3**–**5**. Separate signals for axial and equatorial protons are observed from cooled samples of **2** and **5**.

Recent work on amido derivatives of aluminium and gallium has focussed on compounds bearing substituents at the carbon atom adjacent to nitrogen.[1–3] The aim has been to isolate compounds in which association by nitrogen bridges is curtailed.[4–6] There has been much less work on unsubstituted pyrrolidinido and piperidinido derivatives and the emphasis in many early studies was on compounds containing Al–H bonds. Very few of these were isolated in crystalline form and structures were deduced from spectroscopic and relative-molar-mass measurements.[7–9] Mono-, bis-, and tris-(dimethylamido)-alane[10,11] and bis(tetrahydrofuran)lithium tetrakis(dimethylamido)aluminate[12] have been fully characterised but, as far as we are aware, there have been no crystallographic studies on corresponding pyrrolidinido and piperidinido derivatives. We have recently been able to obtain pure samples of several pyrrolidinido and piperidinido derivatives without ring substituents and have taken advantage of improved techniques for X-ray diffraction and NMR studies to obtain detailed structural information.

Results and discussion

Bis(μ-pyrrolidinido)tetrakis(pyrrolidinido)dialuminium $Al_2(NC_4H_8)_6$ 1

Solid $(Me_3N{\cdot}AlH_3)_2$, or a solution of alane in tetrahydrofuran (thf), reacted with an excess of pyrrolidine to give compound **1** in good yield [equation (1), L = thf or NMe_3, n = 3]. The

$$2L{\cdot}AlH_3 + 6H\overline{N(CH_2)_nC}H_2 \longrightarrow Al_2[\overline{N(CH_2)_nC}H_2]_6 + 2L \quad (1)$$

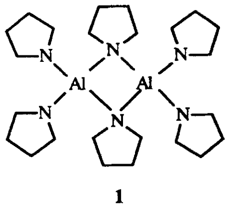
product was isolated as colourless crystals and shown to be dimeric in the gas phase (from the mass spectrum), in solution (from ^1H and ^{13}C NMR spectra) and in the solid state by X-ray crystallography (Fig. 1 and Table 1).

The molecule of compound **1**, like that of $Al_2(NMe_2)_6$,[10,11] possesses an inversion centre with both aluminium atoms

Table 1 Intramolecular distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **1**

Al–N(1)	1.958(2)	Al–N(1′)	1.967(2)
Al–N(2)	1.800(2)	Al–N(3)	1.793(2)
N(1)–C(1)	1.494(3)	N(1)–C(4)	1.500(3)
N(2)–C(5)	1.465(3)	N(2)–C(8)	1.459(3)
N(3)–C(9)	1.457(3)	N(3)–C(12)	1.459(3)
C(1)–C(2)	1.528(4)	C(2)–C(3)	1.526(4)
C(3)–C(4)	1.531(4)	C(5)–C(6)	1.514(4)
C(6)–C(7)	1.512(4)	C(7)–C(8)	1.526(4)
C(9)–C(10)	1.519(4)	C(10)–C(11)	1.521(4)
C(11)–C(12)	1.514(4)		
N(1)–Al–N(1′)	86.69(9)	N(1)–Al–N(2)	114.16(9)
N(1)–Al–N(3)	113.4(1)	N(1′)–Al–N(2)	114.43(9)
N(1′)–Al–N(3)	113.19(9)	N(2)–Al–N(3)	112.6(1)
Al–N(1)–Al′	93.31(9)	Al–N(1)–C(1)	119.6(2)
Al–N(1)–C(4)	112.4(1)	Al′–N(1)–C(1)	117.9(1)
Al′–N(1)–C(4)	113.3(1)	C(1)–N(1)–C(4)	101.1(2)
Al–N(2)–C(5)	122.0(2)	Al–N(2)–C(8)	131.5(2)
C(5)–N(2)–C(8)	106.3(2)	Al–N(3)–C(9)	125.5(2)
Al–N(3)–C(12)	130.3(2)	C(9)–N(3)–C(12)	104.1(2)
N(1)–C(1)–C(2)	104.5(2)	C(1)–C(2)–C(3)	104.3(2)
C(2)–C(3)–C(4)	105.2(2)	N(1)–C(4)–C(3)	105.6(2)
N(2)–C(5)–C(6)	105.0(2)	C(5)–C(6)–C(7)	102.7(2)
C(6)–C(7)–C(8)	105.5(2)	N(2)–C(8)–C(7)	107.2(2)
N(3)–C(9)–C(10)	106.3(2)	C(9)–C(10)–C(11)	105.8(2)
C(10)–C(11)–C(12)	103.5(2)	N(3)–C(12)–C(11)	105.8(2)

Symmetry element: ′ $-x, -y, -z$.



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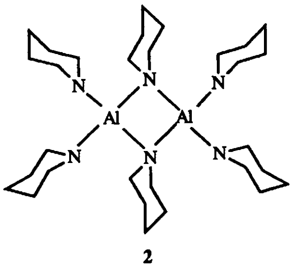

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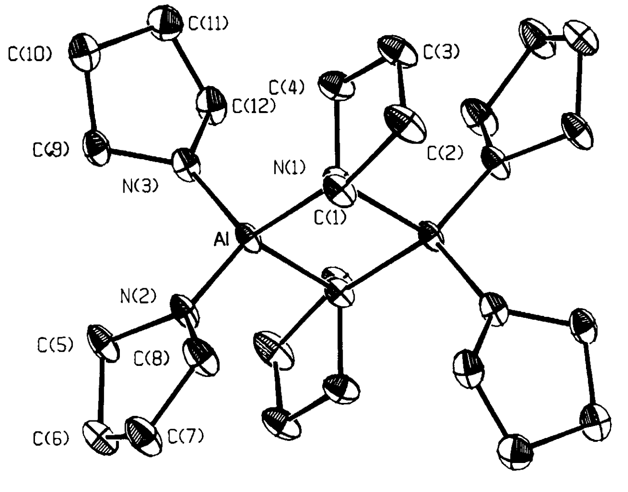
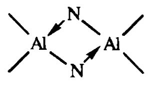


Fig. 1 Molecular structure of $Al_2(NC_4H_8)_6$ **1**



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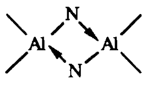


II

showing distorted-tetrahedral co-ordination. The Al_2N_2 ring is planar, as is the geometry at the terminal nitrogen atoms [sum of angles: at N(2), 359.8°; at N(3), 359.9°]. The average Al–N bond lengths are 1.797(2) (terminal N) and 1.963(2) Å (bridging N). The N–C bond lengths in the bridging ligands are 1.497(3) Å whereas those in the terminal pyrrolidinide groups are 1.460(2) Å, reflecting the change from sp^3 to sp^2 hybridisation at nitrogen. The angle between the NC_2 planes in the two terminal pyrrolidinide groups on each aluminium atom is 78.5°; to get maximum electronic delocalisation in the NAlN system the NC_2 fragments should be coplanar. The Al $\cdots$ Al distance is 2.860 Å. A planar configuration at nitrogen together with a bond length for Al–N(terminal) less than the sum of the covalent radii for aluminium (1.30 Å)[4] and nitrogen (0.70 Å)[4] has previously been taken as evidence for Al–N p_π–p_π bonding.[13] However, more recent work, taking bond polarity into account,[14] suggests that the σ bond between four-co-ordinate aluminium and three-co-ordinate nitrogen should be about 1.81 Å, in good agreement with the value obtained in this work. The endocyclic Al–N bonds can be viewed in terms of two canonical forms, **I** and **II**, each with two normal and two dative Al–N bonds.[14] If the Al←N dative bond length is 2.08 Å,[14] a 1 : 1 normal/dative bond length should be 1.945 Å, again in agreement with the value obtained in this study.

The ^1H and ^{13}C NMR spectra of compound **1**, like those of $Al_2(NMe_2)_6$, show distinct signals for bridging and terminal groups in both toluene and thf solution. The ^1H signals move closer together as the temperature is raised to 90 °C, probably indicating more rapid bridge–terminal exchange. The peaks show no splitting as the temperature is lowered to −90 °C.

Bis(μ-piperidinido)tetrakis(piperidinido)dialuminium $Al_2(NC_5H_{10})_6$ 2

Piperidine reacted with solid $(Me_3N{\cdot}AlH_3)_2$, or a solution of alane in thf, to give compound **2** [equation (1), L = thf or NMe_3, $n = 4$]. Again the mass spectrum and ^1H and ^{13}C NMR data suggested that the molecules were dimeric. Crystals suitable for an accurate X-ray analysis could not be obtained but an incomplete structure determination confirmed that the compound was dimeric in the solid state. The triplet at δ 3.04 in the NMR spectrum of a solution in $C_6D_5CD_3$, and the quintets at δ 1.51 and 1.72 are assigned, respectively, to the α, β and γ methylene protons of the terminal piperidinide groups. The splitting patterns suggest that these piperidinide rings are inverting rapidly on the NMR time-scale.

In contrast, six signals are observed for the bridging piperidinide groups, indicating that the rings are fixed in the chair conformation. A detailed analysis of the complex ten-spin system is not attempted here but the multiplets are assigned on the basis of their chemical shifts and intensities. The signals at δ 2.28 and 2.89 are assigned to the α-methylene protons, those at δ 0.65 and 1.14 to the β-, and the signals at δ 0.84 and 1.43 to the γ-methylene protons. The signals are slightly broader than those due to the terminal piperidinide groups. The doublet at δ 2.89 is assigned to the equatorial protons with a typical geminal coupling constant of *ca.* 13 Hz.[15,16] The signal at δ 2.28 must therefore be assigned to the axial protons. It is expected to be a doublet of doublets of doublets with two coupling constants of *ca.* 8–14 and one of *ca.* 4 Hz. The observed signal is consistent with this but the peaks are so broad, perhaps because of ring inversion or long-range coupling to γ-protons, that accurate coupling constants cannot be measured at 250 MHz. From a sample at 85 °C a triplet was observed for the bridging α-methylene protons showing that at this temperature the bridging as well as the terminal rings were inverting rapidly on the NMR time-scale. Further, the chemical shifts of bridging and terminal α-methylene groups had become closer indicating that the rate of bridge–terminal exchange had increased also. At 250 MHz peaks from bridging and terminal groups were still distinct at 100 °C but the exchange process resulted in broad signals.

The ^1H and ^{13}C NMR spectra of compound **2** were also recorded from samples in $[^2H_8]$thf, but they were less easy to interpret than spectra from samples in toluene because of overlap of signals from bridging and terminal β- and γ-protons. At room temperature signals from α-protons of bridging piperidinide groups were broader than those from samples in toluene perhaps indicating that the rates of ring inversion and for bridge–terminal exchange were increased by co-ordination of donor solvent at Al. The spectra became clearer below −10 °C when the triplet assigned to the α-protons of the rapidly inverting terminal piperidinide groups at room temperature became a broad singlet as the rate of inversion decreased, and the fine structure on the signals from the α-protons of the bridging groups became sharper. At −30 °C the terminal signal had broadened further and the bridging signals showed well resolved axial and equatorial coupling. Below −50 ± 2 °C the signals from axial and equatorial protons of terminal piperidinide groups separated. The rate constant k_e and free energy of activation $\Delta G^\ddagger$ for the exchange process were calculated[15] as 342.7 s^{-1} and 43.2 kJ mol^{-1}. At −70 °C the spectra were dominated by the poorly resolved signals for the terminal axial and equatorial protons.

The ^1H NMR spectra of compound **2** in toluene with a large excess of piperidine showed, besides signals ascribed to free base, just three well resolved signals: a triplet and two quintets assigned respectively to α-, β- and γ-protons of the amido compound. Under these circumstances there appeared to be both rapid ring inversion and no distinction between bridge and terminal piperidinide groups. The simplest interpretation is that the dimeric structure had been broken [equation (2)].

$$\mathrm{Al_2[\overline{N(CH_2)_4CH_2}]_6 + 2\overline{CH_2(CH_2)_4NH} \longrightarrow 2\{\overline{CH_2(CH_2)_4HN}\}Al[\overline{N(CH_2)_4CH_2}]_3} \quad (2)$$

Bis(tetrahydrofuran)lithium tetrakis(pyrrolidinido)aluminate $(thf)_2LiAl(NC_4H_8)_4$ 3 and bis(pyrrolidine)lithium tetrakis(pyrrolidinido)aluminate $(C_4H_8NH)_2LiAl(NC_4H_8)_4$ 4

The reaction of pyrrolidine with $LiAlH_4$ in thf in either a 6 : 1 or 4 : 1 molar ratio gave a solution which showed six ^1H NMR signals. These could be divided into two groups, (a) at δ 3.4, 2.3,

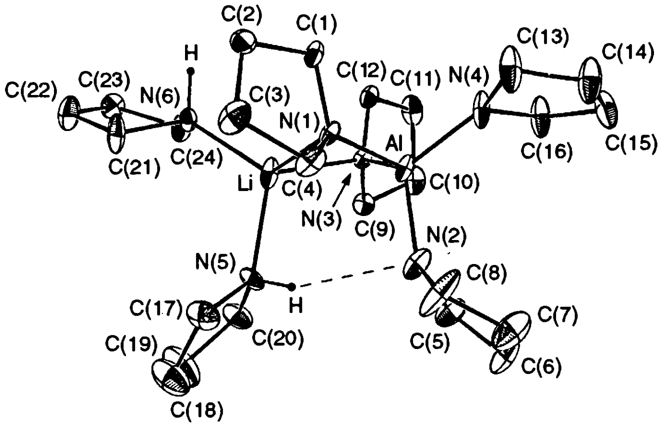
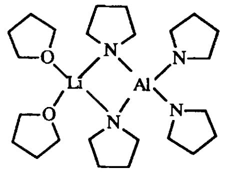


Fig. 2 Molecular structure of $(C_4H_8NH)_2LiAl(NC_4H_8)_4$ **4**



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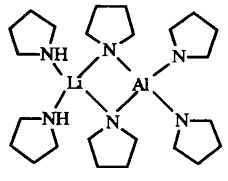

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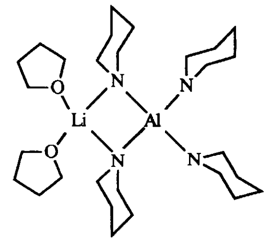
Table 2 Intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for compound **4**

Al–Li	2.648(13)	Al–N(1)	1.888(7)
Al–N(2)	1.828(9)	Al–N(3)	1.871(6)
Al–N(4)	1.820(8)	Li–N(1)	2.147(14)
Li–N(3)	2.15(2)	Li–N(5)	2.04(2)
Li–N(6)	2.03(2)		
N–C mean	1.462(10)	C–C mean	1.476(13)
N(1)–Al–N(2)	108.2(3)	N(1)–Al–N(3)	100.0(3)
N(1)–Al–N(4)	109.1(3)	N(2)–Al–N(3)	108.0(3)
N(2)–Al–N(4)	117.9(4)	N(3)–Al–N(4)	112.0(3)
Al–Li–N(1)	44.9(3)	Al–Li–N(3)	44.4(3)
Al–Li–N(5)	99.2(6)	Al–Li–N(6)	145.8(9)
N(1)–Li–N(3)	84.2(5)	N(1)–Li–N(5)	108.0(7)
N(1)–Li–N(6)	120.4(8)	N(3)–Li–N(5)	109.4(8)
N(3)–Li–N(6)	115.8(8)	N(5)–Li–N(6)	115.0(7)
Al–N(1)–Li	81.7(4)	Al–N(1)–C(1)	120.8(5)
Al–N(1)–C(4)	124.6(6)	Li–N(1)–C(1)	106.1(7)
Li–N(1)–C(4)	117.5(7)	C(1)–N(1)–C(4)	103.7(6)
Al–N(2)–C(5)	127.2(6)	Al–N(2)–C(8)	118.8(7)
C(5)–N(2)–C(8)	103.1(8)	Al–N(3)–Li	82.2(4)
Al–N(3)–C(9)	127.9(5)	Al–N(3)–C(12)	117.5(5)
Li–N(3)–C(9)	110.0(6)	Li–N(3)–C(12)	116.6(7)
C(9)–N(3)–C(12)	102.1(6)	Al–N(4)–C(13)	126.4(6)
Al–N(4)–C(16)	124.6(6)	C(13)–N(4)–C(16)	104.4(7)
Li–N(5)–C(17)	123.8(7)	Li–N(5)–C(20)	117.8(7)
Li–N(6)–C(24)	115.5(6)	C(17)–N(5)–C(20)	105.4(7)
C(21)–N(6)–C(24)	103.4(6)	Li–N(6)–C(21)	117.7(7)
N–C–C mean	107.3(7)	C–C–C mean	105.9(7)

1.3 and 1.2 and (b) at δ 3.2 and 1.7 such that the total intensities of the signals (a) was always equal to half that of signals (b). Within group (a) the signals at δ 2.3 and 1.2 were stronger relative to those at δ 3.4 and 1.3 the higher the concentration of pyrrolidine. These results suggest that the former signals can be assigned to compound **4** and the latter to **3**. The signals in group (b) are assigned to rapidly exchanging bridging and terminal pyrrolidinide groups. The crystalline solid isolated from the solution appeared to be a mixture of **3** and **4** and the presence of co-ordinated pyrrolidine was shown by the presence of an IR band at 3130 cm^{-1}.

The preparation of compound **3** in the absence of **4** was achieved by slow addition of pyrrolidine to lithium aluminium hydride solution. A pure sample of **4** was obtained after the mixture of **3** and **4** was crystallised from toluene with a little added pyrrolidine. Crystals of **3** suitable for X-ray analysis could not be obtained, but the crystal structure of **4** was determined. The molecule is shown in Fig. 2, bond distances and angles in Table 2.



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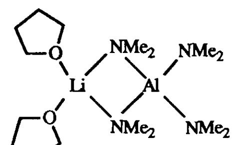

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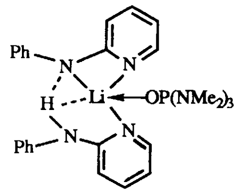

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The structure contains a non-planar Li(μ-N)$_2$Al ring with two bridging pyrrolidinide groups. The angle between the LiN$_2$ and AlN$_2$ planes is 142°. Compound **4** can be considered as a solvated lithium cation bound to a tetrahedral $[Al(NC_4H_8)_4]^-$ anion, similiar in this respect to the known compound $(thf)_2LiAl(NMe_2)_4$ **6**, the structure of which has been determined.[12] Molecular parameters are compared in Table 3. The average Li–N (pyrrolidine) distance, 2.04(2) Å, is probably not significantly different from the Li–N (piperidine) distance in $(C_5H_{10}NLi{\cdot}HNC_5H_{10})_4$, 2.158(25) Å,[17] and the Li–N (isopropylamine) distance in $(Ph_2NLi{\cdot}HNPr^i{}_2)_2$, 2.109(15) Å.[18]

The structure of compound **4** reveals an intramolecular hydrogen bond between N(5) and N(2) [N(5) ··· N(2) 3.20(1) Å]. This is weak, as shown by the N(2) ··· H distance [2.45(6) Å], which is much greater than that [2.11(6) Å] in **7**.[19] The atoms Li, Al, N(2), H and N(5) in **4** are essentially coplanar with the N(5)–H ··· N(2) angle 159(7)°. The angles at Li and Al are considerably distorted from the tetrahedral value. The rings containing N(5) and N(2) lean towards each other so that the N(5)–H vector points towards N(2).

The ^{1}H NMR spectra from samples in both toluene and thf indicate that the terminal and bridging pyrrolidinide groups in compounds **3** and **4** are exchanging rapidly on the NMR timescale. Since complete dissociation into ions is unlikely in toluene it is probable that exchange occurs by breaking of one Li–N bond and rotation about the other. Low-temperature spectra show that the signals for the ligands (thf and C_4H_8NH) move downfield by *ca.* 0.35 ppm as the sample is cooled to −80 °C. The mass spectra of both **3** and **4** only show peaks assignable to **1** presumably indicating decomposition at the probe temperature (*ca.* 300 °C).

Bis(tetrahydrofuran)lithium tetrakis(piperidinido)aluminate $(thf)_2LiAl(NC_5H_{10})_4$ 5

The reaction of $LiAlH_4$ with a six-fold excess of piperidine in thf gave compound **5**. Crystals were obtained from toluene solution and the structure was determined by X-ray diffraction (see Fig. 3 and Table 4). The structure is similar to those of **4** and **6** and is based on a LiN$_2$Al ring with bridging piperidinide groups. The ring is more nearly planar than that in **4** but similar to that in **6** (Table 4). The average Al–N(terminal) and Al–N(bridging), Li–N and Li–O distances are similar to those in **4** and **6**. The sums of the angles at N(1) and N(2) in the terminal piperidinido groups and at O(1) and O(2) in **5** and **6** are

Table 3 Mean bond lengths (Å) and angles (°) involving aluminium, lithium and nitrogen

	$Al_2(NMe_2)_6$[a]	$Al_2(NMe_2)_4H_2$[a]	$Al_2(NC_4H_8)_6$	
Al–N(terminal)	1.814(2)	1.814(2)	1.797(2)	
Al–N(bridging)	1.970(2)	1.966(2)	1.963(2)	
N–Al–N ring	88.1(1)	87.7(1)	86.7(1)	
Al–N–Al ring	91.9(1)	92.3(1)	93.3(1)	
N–Al–N exocyclic	114.4(1)	—	112.6(1)	
		4	**5**	**6**[b]
Al–N(terminal)		1.824(8)	1.828(3)	1.845(4)
Al–N(bridging)		1.880(9)	1.895(3)	1.911(4)
Li–N		2.15(2)	2.135(6)	2.135(6)
Li–O		2.04(2)[c]	1.987(6)	1.995(10)
N–Al–N ring		100.0(3)	100.7(1)	98.5(2)
N–Li–N ring		84.2(5)	86.2(2)	85.1(3)
N–Al–N exocyclic		117.9(4)	117.7(1)	112.7(2)
Li–N–Al		82.0(4)	84.0(2)	85.5(3)
Li • • • Al		2.648(13)	2.703(6)	—
Sum of ring angles		348.1	355.0	354.7
Sum of angles at N(terminal)		349.1, 355.4	357.4, 358.1	355.3, 359.9
Sum of angles at O		—	359	359
		—	360	360

[a] Refs. 10 and 11. [b] Ref. 12. [c] Li–N.

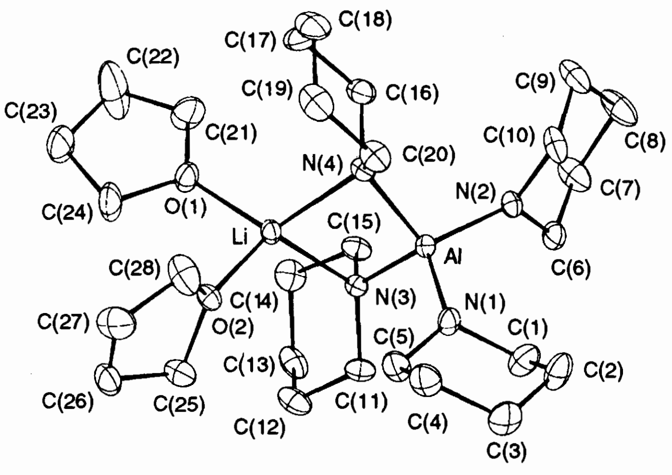

Fig. 3 Molecular structure of $(thf)_2LiAl(NC_5H_{10})_4$ **5**

consistent with sp^2 hybridisation at nitrogen and oxygen. The terminal nitrogen atoms in **4** appear to be more pyramidal than those in **5** and **6** but it is not clear from the present data whether this is significant. Similar deviations from planarity have been noted elsewhere.[5]

The ^1H NMR spectra showed two signals for the co-ordinated thf and three for the α-, β- and γ-methylene groups of the rapidly exchanging piperidinide groups. On cooling the sample the signal due to the α-methylene protons split into two broad signals of equal intensity at δ 2.75 and 3.20 and assigned to the axial and equatorial protons respectively. The signals coalesced at −48 °C giving a rate constant for the exchange process of 230.8 s^{-1} and a free energy of activation of 44.4 kJ mol^{-1}. The values in **2** and **5** are slightly greater than that for free piperidine, *viz.* 39.9 kJ mol^{-1};[15] the activation energy is thus increased by attachment of the piperidinide group to aluminium which is itself contained in a ring.

Even when $LiAlH_4$ was treated with a very large excess of piperidine there was no spectroscopic evidence for the presence of co-ordinated piperidine in the crystalline product. The contrast with the pyrrolidinido analogue is attributed to the greater steric effect of the α-methylene group of a six- compared with that of a five-membered ring. Similar effects have been noted previously in boron chemistry.[20] The mass spectrum of **5** is dominated by peaks due to **2** (*cf.* **3** and **4**) with peaks assignable to $LiAl(NC_5H_{10})_4$ also present.

Conclusion

Alane reacts with an excess of pyrrolidine or piperidine in thf to give fully substituted amidoalanes which are dimeric both in the solid state and in solution. There is no evidence for substantial π bonding in these species. Pyrrolidine reacts with $LiAlH_4$ in thf to give either $(thf)_2LiAl(NC_4H_8)_4$ or $(C_4H_8NH)_2LiAl(NC_4H_8)_4$ depending on the conditions. In contrast, piperidine gives only the thf-substituted analogue $(thf)_2LiAl(NC_5H_{10})_4$.

The tendency of amido groups to form bridges between pairs of aluminium atoms or between lithium and aluminium atoms is confirmed by X-ray crystallographic studies. Several generalisations may be made. In dimeric amidoalanes the Al–N(terminal) bond lengths are consistently 1.80–1.82 Å and the Al–N(bridging) lengths 1.95–1.97 Å. The lengths of the Al–N(terminal) bonds are close to those in monomeric amidoaluminium compounds which are 1.82–1.89 Å depending on steric and ionic effects.[4] The difference between bridging and terminal Al–N bond lengths is less in compounds **4**–**6** than in the hexaamidodialuminiums. This, together with the fact that the Li–N bond lengths are at the upper end of the range found in a wide variety of amido compounds,[21] suggests that these lithium tetrakis(amido)aluminates are best viewed as ion pairs rather than bridged dinuclear lithium–aluminium complexes. Other consistent features are that the exocyclic NAlN angles are wider than tetrahedral as is usual in dimeric aluminium compounds Al_2X_6, and that the bonds at exocyclic nitrogen atoms are approximately planar.

Bridging and terminal groups in hexaamidodialuminium molecules exchange slowly on the NMR time-scale. Bridging groups appear to be more rigid than terminal groups and distinct signals for axial and equatorial protons in terminal groups can be detected in 250 MHz spectra only when samples are cooled below room temperature. Exchange between bridging and terminal groups in lithium tetrakis(amido)aluminates is more rapid than that in hexaamidodialuminiums and in compound **5** the bridge–terminal exchange of piperidinide groups is more rapid than ring inversion. One or more of the Li–N bonds in the ion pairs found in the solid are thus readily broken in solution consistent with X-ray evidence that nitrogen is more strongly bound to aluminium than to lithium.

The isolation of pure crystalline tetrakis(pyrrolidinide)aluminates is made difficult by the similarity between pyrrolidine and thf. Molecules containing ether and amine bases cocrystallise. Pure $L_2Li[\mu\text{-}\overline{N(CH_2)_3CH_2}]_2Al[\overline{N(CH_2)_3CH_2}]_2$ compounds

Table 4 Bond lengths (Å) and angles (°) for compound **5**

Al–N(2)	1.824(3)	Al–N(1)	1.832(3)
Al–N(4)	1.893(3)	Al–N(3)	1.897(3)
Al···Li	2.703(6)	Li–O(2)	1.985(6)
Li–O(1)	1.988(6)	Li–N(3)	2.129(6)
Li–N(4)	2.141(6)		
N–C mean	1.460(4)	O–C mean	1.430(5)
C–C mean (thf)	1.464(6)	C–C mean ($C_5H_{10}N$)	1.515(5)
N(2)–Al–N(1)	111.71(14)	N(2)–Al–N(4)	111.49(13)
N(1)–Al–N(4)	110.06(14)	N(2)–Al–N(3)	112.19(13)
N(1)–Al–N(3)	110.19(14)	N(4)–Al–N(3)	100.69(13)
O(2)–Li–O(1)	98.1(3)	O(2)–Li–N(3)	118.6(3)
O(1)–Li–N(3)	118.4(3)	O(2)–Li–N(4)	115.9(3)
O(1)–Li–N(4)	121.4(3)	N(3)–Li–N(4)	86.2(2)
C(24)–O(1)–C(21)	108.4(3)	C(24)–O(1)–Li	121.0(3)
C(21)–O(1)–Li	130.4(3)	C(25)–O(2)–C(28)	107.1(3)
C(25)–O(2)–Li	128.2(3)	C(28)–O(2)–Li	124.7(3)
C(5)–N(1)–C(1)	110.1(3)	C(5)–N(1)–Al	127.6(2)
C(1)–N(1)–Al	119.7(2)	C(10)–N(2)–C(6)	109.8(3)
C(10)–N(2)–Al	122.5(2)	C(6)–N(2)–Al	126.0(2)
C(15)–N(3)–C(11)	108.3(3)	C(15)–N(3)–Al	117.6(2)
C(11)–N(3)–Al	114.9(2)	C(15)–N(3)–Li	108.0(3)
C(11)–N(3)–Li	122.6(3)	Al–N(3)–Li	84.2(2)
C(20)–N(4)–C(16)	108.1(3)	C(20)–N(4)–Al	116.0(2)
C(16)–N(4)–Al	116.3(2)	C(20)–N(4)–Li	127.2(3)
C(16)–N(4)–Li	103.9(3)	Al–N(4)–Li	83.9(2)
N–C–C mean	113.0(3)	C–C–C mean (NC_5H_{10})	110.3(3)
O–C–C mean	107.0(4)	C–C–C mean	106.6(4)

can be obtained only by extremely careful control of the experimental conditions.

Experimental

All air- and moisture-sensitive compounds were handled using conventional Schlenk-tube techniques under an atmosphere of dry argon. Piperidine and pyrrolidine were dried over KOH, then over sodium, and distilled. Solutions of alane in tetrahydrofuran were obtained as described previously.[22] Toluene was dried by refluxing over sodium, followed by distillation. Tetrahydrofuran was dried by refluxing over sodium–benzophenone, followed by distillation. The NMR spectra were recorded on Bruker WM 360 (^1H only) or AC 250 instruments, mass spectra on a Fisons VG Autospec [electron impact (EI) at 70 eV ($\approx 1.12 \times 10^{-17}$ J)] and IR spectra on a Perkin-Elmer 1720 FT spectrometer. Melting points were determined on samples in sealed capillaries using a Gallenkamp electrothermal apparatus.

For analysis hydridic hydrogen was determined by decomposing samples in thf (2 cm^3) with 1 mol dm^{-3} H_2SO_4 and measuring evolved hydrogen with a Sprengel pump.[23] Aluminium was determined as the quinolin-8-olate,[24] lithium by flame photometry and nitrogen by the Markham semimicro Kjeldahl procedure.[25]

Preparations

$Al_2(NC_4H_8)_6$ 1. Pyrrolidine (30.4 g, 0.43 mol) was added slowly to solid $(Me_3N \cdot AlH_3)_2$ (4.4 g, 0.025 mol) at −10 °C. The mixture was stirred overnight and the excess of pyrrolidine removed under vacuum to leave a pale yellow residue. This was crystallised from toluene (5 cm^3) to give colourless crystals of compound **1** (6.2 g, 56%), m.p. 104 °C (Found: Al, 11.4; N, 17.7. $C_{24}H_{48}Al_2N_6$ requires Al, 11.4; N, 17.7%); $\tilde{\nu}_{max}/cm^{-1}$ 2675m, 1344s, 1300ms, 1246m, 1109s, 1045s, 992s, 910s, 876m and 832m; $\delta_H(C_6D_5CD_3)$ 1.45 (8 H, m, μ-CH_2), 1.61 (16 H, m, CH_2), 2.91 (8 H, m, μ-NCH_2) and 3.10 (16 H, m, NCH_2); $\delta_C(C_6D_5CD_3)$, 25.4 (μ-CH_2), 27.2 (CH_2), 49.7 (μ-NCH_2) and 50.0 (NCH_2); $\delta_{Al}(C_6D_5CD_3)$ 111 ($\Delta\nu_{\frac{1}{2}}$ = 1967 Hz); *m*/*z* 474 (4, *M*), 404 (6, *M* − C_4H_8N), 334 (29, *M* − $2C_4H_8N$), 264 (25, *M* − $3C_4H_8N$), 237 [6, $Al(NC_4H_8)_3$], 194 (6, *M* − 4 C_4H_8N), 167 [14, $Al(NC_4H_8)_2$], 97 [14, $Al(NC_4H_8)$] and 70 (100%, C_4H_8N).

$Al_2(NC_5H_{10})_6$ 2. A solution of piperidine (1.45 g, 17.2 mmol) in thf (10 cm^3) was added dropwise to a stirred solution of AlH_3 (3 mmol) in thf (5 cm^3) at room temperature. Gas was evolved and the mixture was stirred for 5 h before the solvent was removed to leave a sticky solid. This was washed with light petroleum (b.p. 40–60 °C) (2 × 1 cm^3) then dissolved in toluene (2 cm^3) and kept at −30 °C for 12 h to give colourless crystals of compound **2** (0.47 g, 57%), m.p. 110 °C (Found: Al, 9.7; N, 15.1. $C_{30}H_{60}Al_2N_6$ requires Al, 9.7; N, 15.05%); $\tilde{\nu}_{max}/cm^{-1}$ 2729m, 2678m, 1344w, 1333w, 1316s, 1274m, 1201s, 1116s, 1077w, 1041s, 995w, 936s, 870m, 851m, 826w, 808w, 741m and 667s; $\delta_H(C_6D_5CD_3)$ 0.65 (4 H, m, μ-β-CH), 0.84 (2 H, m, μ-γ-CH), 1.14 (4 H, m, μ-β-CH), 1.43 (2 H, m, μ-γ-CH), 1.51 (16 H, qnt, β-CH_2), 1.72 (8 H, qnt, γ-CH_2), 2.28 (4 H, m, μ-α-CH_{ax}), 2.89 [4 H, d, μ-α-CH_{eq}, $^2J_{(HaxHeq)}$ = *ca.* 13] and 3.04 (16 H, t, α-CH_2, ^3J = 5.10 Hz); $\delta_C(C_6D_5CD_3)$ 26.1 (μ-β-C), 26.6 (μ-γ-C), 27.3 (γ-C), 30.0 (β-C), 46.4 (μ-α-C) and 50.1 (α-C); $\delta_{Al}(C_6D_5CD_3)$ 108 ($\Delta\nu_{\frac{1}{2}}$ = 2742 Hz); *m*/*z* 559 (51, *M* + 1), 474 (32, *M* − $C_5H_{10}N$), 390 (17, *M* − 2 $C_5H_{10}N$), 306 (15, *M* − 3 $C_5H_{10}N$), 279 [4, $Al(C_5H_{10}N)_3$], 222 (1, *M* − 4 $C_5H_{10}N$), 195 [29, $Al(C_5H_{10}N)_2$], 111 [35, $Al(C_5H_{10}N)$] and 84 (100%, $C_5H_{10}N$).

$(C_4H_8O)_2LiAl(NC_4H_8)_4$ 3. A solution of pyrrolidine (0.88 cm^3, 10.5 mmol) in thf (10 cm^3) was added dropwise (over *ca.* 30 min) to a well stirred suspension of $LiAlH_4$ (0.1 g, 2.6 mmol) in thf (10 cm^3) at room temperature. After evolution of hydrogen had ceased the mixture was stirred for 2 h then filtered to give a clear, colourless solution. This was concentrated to *ca.* 2 cm^3 and kept at −30 °C for 16 h to to give transparent crystals of compound **3** (0.45 g, 38%), m.p. 95 °C (Found: Al, 5.1; Li, 1.5; N, 12.2. $C_{24}H_{48}AlLiN_4O_2$ requires Al, 5.9; Li, 1.5; N, 12.2%); $\tilde{\nu}_{max}/cm^{-1}$ 2722s, 2681 (sh), 2581m, 2428m, 1359s, 1329w, 1305m, 1256m, 1220w, 1168s, 1103m, 1045w, 998s, 973s, 941w, 900m, 841s, 810m, 529w and 460m; $\delta_H(C_6D_5CD_3)$ 1.31 (8 H, m, OCH_2CH_2), 1.71 (16 H, m, NCH_2CH_2), 3.18 (16 H, m, NCH_2CH_2) and 3.36 (8 H, m, OCH_2CH_2); $\delta_C(C_6D_5CD_3)$ 25.6

Table 5 Fractional atomic coordinates for compound **1**

Atom	*x*	*y*	*z*
Al	0.137 71(7)	0.028 41(5)	0.054 36(8)
N(1)	−0.047 7(2)	0.030 3(1)	0.121 5(2)
N(2)	0.209 5(2)	0.142 3(1)	0.028 1(2)
N(3)	0.258 8(2)	−0.047 1(1)	0.157 1(2)
C(1)	−0.106 4(3)	0.120 4(2)	0.167 7(3)
C(2)	−0.232 8(3)	0.092 0(2)	0.242 9(3)
C(3)	−0.192 8(3)	−0.002 7(2)	0.309 2(3)
C(4)	−0.054 4(3)	−0.028 3(2)	0.253 0(3)
C(5)	0.357 9(3)	0.156 2(2)	0.013 3(3)
C(6)	0.361 1(3)	0.230 4(2)	−0.101 0(3)
C(7)	0.242 3(3)	0.293 9(2)	−0.071 6(3)
C(8)	0.143 0(3)	0.233 2(2)	0.004 0(3)
C(9)	0.385 5(3)	−0.017 3(2)	0.244 5(3)
C(10)	0.399 2(3)	−0.079 2(2)	0.376 6(3)
C(11)	0.298 9(3)	−0.160 0(2)	0.341 5(3)
C(12)	0.252 1(3)	−0.147 2(2)	0.183 5(3)

$(\mathrm{OCH_2}\mathit{C}\mathrm{H_2})$, 27.5 $(\mathrm{NCH_2}\mathit{C}\mathrm{H_2})$, 50.3 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2})$ and 68.2 $(\mathrm{O}\mathit{C}\mathrm{H_2CH_2})$; $\delta_{Li}(C_6D_5CD_3)$ −0.19; $\delta_{Al}(C_6D_5CD_3)$ 106.9 ($\Delta\nu_{\frac{1}{2}}$ = 392 Hz); *m*/*z* 474 (5), 404 (15), 334 (60), 264 (67), 237 (19), 194 (4), 167 (58), 97 (20) and 70 (66%).

$(C_4H_8NH)_2LiAl(NC_4H_8)_4$ 4. A solution of pyrrolidine (1.3 cm³, 15.6 mmol) in thf (10 cm³) was added dropwise (over *ca.* 10 min) to a well stirred suspension of $LiAlH_4$ (0.1 g, 2.6 mmol) in thf (10 cm³) at room temperature. After hydrogen evolution had ceased the mixture was stirred for 2 h and then filtered to give a colourless solution. The solvent was removed to give a white solid which was dissolved in a mixture of toluene (5 cm³) and pyrrolidine (*ca.* 0.1 cm³). The solution was then kept at −30 °C for 16 h to give crystals of compound **4** (0.54 g, 45%), m.p. 112 °C (Found: C, 61.9; H, 10.8; N, 17.7. $C_{24}H_{50}AlLiN_6$ requires C, 63.1; H, 11.0; N, 18.4%); $\tilde{\nu}_{max}/cm^{-1}$ 3130m, 2740 (sh), 2674 (sh), 2623 (sh), 1341s, 1283w, 1261w, 1207w, 1170w, 1085s, 1035s, 963s, 892s and 805w; $\delta_H(C_6D_5CD_3)$ 1.22 (8 H, m, $\mathrm{HNCH_2C}\mathit{H}_2$), 1.69 (16 H, m, $\mathrm{NCH_2C}\mathit{H}_2$), 2.15 (8 H, m, $\mathrm{HNC}\mathit{H}_2\mathrm{CH_2}$) and 3.18 (16 H, m, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2}$); $\delta_C(C_6D_5CD_3)$ 25.8 $(\mathrm{HNCH_2}\mathit{C}\mathrm{H_2})$, 27.5 $(\mathrm{NCH_2}\mathit{C}\mathrm{H_2})$, 47.2 $(\mathrm{HN}\mathit{C}\mathrm{H_2CH_2})$ and 50.6 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2})$; $\delta_{Li}(C_6D_5CD_3)$ 0.13; $\delta_{Al}(C_6D_5CD_3)$ 106.0 ($\Delta\nu_{\frac{1}{2}}$ = 489 Hz); *m*/*z* 474 (2), 404 (8), 334 (11), 264 (10), 237 (3), 194 (2), 167 (16), 97 (8) and 70 (84%).

$(C_4H_8O)_2LiAl(NC_5H_{10})_4$ 5. A solution of piperidine (1.56 cm³, 15.8 mmol) in thf (10 cm³) was added slowly to a well stirred suspension of $LiAlH_4$ (0.1 g, 2.6 mmol) in thf (10 cm³) at room temperature. Hydrogen was evolved and the mixture was stirred for 2 h, then filtered to give a colourless solution. The solvent was removed to give a sticky solid which was dissolved in toluene (2 cm³) and kept at −30 °C for 14 h to give crystals of compound **5** (0.49 g, 36%), m.p. 123 °C (Found: Al, 5.3; Li, 1.35; N, 10.9. $C_{28}H_{56}AlLiN_4O_2$ requires Al, 5.25; Li, 1.35; N, 10.9%); $\tilde{\nu}_{max}/cm^{-1}$ 2720 (sh), 2672 (sh), 1347m, 1310m, 1272w, 1253w, 1202m, 1191m, 1153m, 1117s, 1100s, 1041s, 1029s, 956w, 935s, 896s, 864w, 851w, 820w, 808w and 650w; $\delta_H(C_6D_5CD_3)$ 1.30 (8 H, m, $\mathrm{OCH_2C}\mathit{H}_2$), 1.50 (16 H, m, $\mathrm{NCH_2C}\mathit{H}_2\mathrm{CH_2}$), 1.70 (8 H, m, $\mathrm{NCH_2CH_2C}\mathit{H}_2$), 3.07 (16 H, m, $\mathrm{NC}\mathit{H}_2\mathrm{CH_2CH_2}$) and 3.40 (8 H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2}$); $\delta_C(C_6D_5CD_3)$ 25.5 $(\mathrm{OCH_2}\mathit{C}\mathrm{H_2})$, 27.3 $(\mathrm{NCH_2CH_2}\mathit{C}\mathrm{H_2})$, 30.0 $(\mathrm{NCH_2}\text{-}\mathit{C}\mathrm{H_2CH_2})$, 50.6 $(\mathrm{N}\mathit{C}\mathrm{H_2CH_2CH_2})$ and 68.5 $(\mathrm{O}\mathit{C}\mathrm{H_2CH_2})$; $\delta_{Li}(C_6D_5CD_3)$ −0.26; $\delta_{Al}(C_6D_5CD_3)$ 104.2 ($\Delta\nu_{\frac{1}{2}}$ = 718 Hz); *m*/*z* 558 (15), 474 (80), 390 (18), 370 (32), 306 (17), 286 (21), 274 (40), 202 (30), 195 (46), 111 (30) and 84 (89%).

Table 6 Fractional atomic coordinates for compound **4**

Atom	*x*	*y*	*z*
Al	0.0640(2)	0.1923(2)	0.1975(2)
Li	0.0783(11)	0.1981(12)	0.0119(9)
N(1)	0.1962(5)	0.1692(4)	0.1334(4)
N(2)	0.0594(5)	0.3000(5)	0.2174(5)
N(3)	−0.0535(5)	0.1665(4)	0.1025(4)
N(4)	0.0626(5)	0.1269(6)	0.3002(4)
N(5)	0.0796(5)	0.3192(4)	−0.0057(5)
N(6)	0.0792(5)	0.1338(4)	−0.1100(4)
C(1)	0.2322(7)	0.0878(6)	0.1201(6)
C(2)	0.3401(8)	0.0913(6)	0.0649(6)
C(3)	0.3789(8)	0.1766(7)	0.0742(7)
C(4)	0.3056(7)	0.2134(6)	0.1461(6)
C(5)	−0.0411(8)	0.3476(7)	0.2399(7)
C(6)	−0.0089(8)	0.3959(7)	0.3217(7)
C(7)	0.1102(9)	0.3736(8)	0.3550(8)
C(8)	0.1549(8)	0.3373(8)	0.2737(8)
C(9)	−0.1594(7)	0.2105(6)	0.0749(6)
C(10)	−0.2533(7)	0.1701(7)	0.1250(6)
C(11)	−0.2181(8)	0.0838(7)	0.1281(6)
C(12)	−0.0934(7)	0.0850(6)	0.0975(6)
C(13)	0.1640(8)	0.0983(8)	0.3602(6)
C(14)	0.1410(8)	0.1095(9)	0.4572(6)
C(15)	0.0165(9)	0.1233(8)	0.4580(6)
C(16)	−0.0323(7)	0.1216(8)	0.3603(6)
C(17)	0.1826(8)	0.3649(7)	−0.0306(8)
C(18)	0.1420(10)	0.4309(8)	−0.0879(9)
C(19)	0.0257(10)	0.4167(9)	−0.1221(9)
C(20)	−0.0207(8)	0.3561(6)	−0.0610(7)
C(21)	0.1582(8)	0.1597(7)	−0.1799(6)
C(22)	0.1144(9)	0.1282(8)	−0.2733(6)
C(23)	−0.0099(8)	0.1020(6)	−0.2663(6)
C(24)	−0.0348(7)	0.1265(7)	−0.1672(6)

Table 7 Atomic coordinates (× 10⁴) for compound **5**

Atom	*x*	*y*	*z*
Al	1040.4(9)	1416.1(7)	2215.5(5)
Li	2791(5)	2083(4)	3299(3)
O(1)	3159(2)	3055(2)	4004(1)
O(2)	4390(2)	1439(2)	3590(1)
N(1)	1628(3)	387(2)	1922(2)
N(2)	−513(2)	1676(2)	1695(1)
N(3)	1082(2)	1389(2)	3225(1)
N(4)	2192(2)	2324(2)	2164(1)
C(1)	745(4)	−255(3)	1535(2)
C(2)	1203(4)	−660(3)	921(2)
C(3)	2470(4)	−1089(3)	1176(2)
C(4)	3388(4)	−441(3)	1608(2)
C(5)	2825(4)	−19(3)	2196(2)
C(6)	−1684(3)	1348(3)	1830(2)
C(7)	−2663(3)	2050(3)	1793(2)
C(8)	−2861(4)	2517(4)	1063(2)
C(9)	−1610(4)	2822(3)	909(2)
C(10)	−707(3)	2065(3)	985(2)
C(11)	1025(4)	514(2)	3531(2)
C(12)	1305(4)	506(3)	4354(2)
C(13)	414(4)	1087(3)	4647(2)
C(14)	450(4)	1991(3)	4333(2)
C(15)	202(3)	1952(2)	3505(2)
C(16)	1690(3)	3217(2)	2130(2)
C(17)	2690(4)	3909(3)	2222(3)
C(18)	3464(4)	3813(3)	1639(3)
C(19)	3975(4)	2899(3)	1652(2)
C(20)	2939(3)	2235(3)	1601(2)
C(21)	2445(4)	3832(3)	4084(3)
C(22)	3173(7)	4342(4)	4606(4)
C(23)	4271(5)	3877(3)	4968(3)
C(24)	4207(5)	3024(3)	4586(3)
C(25)	4687(4)	764(3)	4116(2)
C(26)	6055(4)	833(3)	4421(2)
C(27)	6575(4)	1258(3)	3840(3)
C(28)	5480(4)	1587(4)	3298(2)

Crystallography

Crystal data. $C_{24}H_{48}Al_2N_6$ **1**, *M* = 474.7, monoclinic, space group $P2_1/c$ (no. 14), *a* = 9.634(4), *b* = 14.339(6), *c* = 9.387(7) Å, β = 96.33(5)°, *U* = 1289 Å³, λ = 0.710 69 Å, *Z* = 2, D_c = 1.15 g cm⁻³, *F*(000) = 494. Colourless, air-sensitive blocks, piece cut to 0.4 × 0.4 × 0.4 mm, μ(Mo-Kα) = 0.97 cm^{-1}, T = 173 K.

$C_{24}H_{50}AlLiN_6$ **4**, M = 456.6, monoclinic, space group $P2_1/n$, a = 11.563(6), b = 16.753(5), c = 14.145(4) Å, β = 95.34(3)°, U = 2728 Å^3, λ = 0.710 69 Å, Z = 4, D_c = 1.11 g cm^{-3}, F(000) = 1008. Colourless, air-sensitive blocks, 0.3 × 0.3 × 0.2 mm, μ(Mo-Kα) = 0.9 cm^{-1}, T = 173 K.

$C_{28}H_{56}AlLiN_4O_2$ **5**, M = 514.7, monoclinic, space group $P2_1/c$, a = 10.915(4), b = 15.358(4), c = 18.872(7) Å, β = 101.61(3)°, U = 3099 Å^3, λ = 0.710 73 Å, Z = 4, D_c = 1.10 g cm^{-3}, F(000) = 1136. Colourless, air-sensitive blocks, 0.3 × 0.3 × 0.2 mm, μ(Mo-Kα) = 0.09 mm^{-1}, T = 173 K.

Data collection and processing. CAD4 diffractometer, θ–2θ scan mode, Mo-Kα radiation, $2 < \theta < 25°$. For **1**, 2368 unique reflections giving 1927 with $|F^2| > 2\sigma(F^2)$, no absorption or decay correction; **4**, 4961, 1841 as for **1**. **5**, 5428, 3374, as for **1**.

Structure analysis and refinement. Direct methods (SHELXS 86).[26] Full matrix least-squares refinement on F using Enraf-Nonius MOLEN[27] programs and data with $|F^2| > 2\sigma(F^2)$ for compounds **1** and **4**, and on F^2 using SHELXL 93[28] with all reflections for **5**, with non-hydrogen atoms anisotropic. Hydrogen atoms: **1**, refined isotropically; **4**, hydrogens on N(5) and N(6) refined, rest fixed, calculated with $U_{iso} = 1.3U_{eq}$ for parent atom; **5** included in riding mode with $U_{iso} = 1.2U_{eq}$ for parent atom. $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$, $w = \sigma^{-2}(F)$ for **1** and **4**; for **5** the weighting scheme was defined by the program. Final R and R' values: 0.057 and 0.067 for **1**, 0.103 and 0.093 for **4**. For **5**, $I > 2\sigma(I)$; $R1 = 0.068$, $wR2 = 0.147$; all data, $R1 = 0.122$, $wR2 = 0.185$. $R = R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2\Sigma|F_o|^4)]^{\frac{1}{2}}$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Fractional atomic coordinates are shown in Tables 5–7.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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