Complexes of Organoaluminium Compounds. Part 10.[1] Crystal and Molecular Structures of the Cage Compounds Bis-μ-methylamido-hexa-μ$_3$-methylimido-bis(dimethylaluminium)-hexakis(methylaluminium) and Bis-μ-methylamido-hexa-μ$_3$-methylimido-bis(dimethylgallium)-hexakis-(methylgallium) †

By **Saeid Amirkhalili, Peter B. Hitchcock,** and **J. David Smith,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The adduct $AlMe_3 \cdot NH_2Me$ decomposes at 215 °C to give the cage compound $(MeAlNMe)_8$ besides the well established $(MeAlNMe)_7$. The intermediate $(Me_2AlNHMe)_2(MeAlNMe)_6$ (1), isolated from reactions at lower temperatures, has been characterised by spectroscopic and *X*-ray methods. Crystals are orthorhombic (space group *Abam*) with a = 15.389(2), b = 19.747(4), c = 11.613(1) Å, and Z = 4. The structure has been solved by sharpened Patterson and Fourier methods and least-squares refinement converged at R = 0.087 (927 reflections measured by diffractometer). The molecules have cage structures, apparently with C_{2h} symmetry, with each nitrogen and each aluminium four-co-ordinate and methyl groups pointing outwards. Mean molecular parameters are: Al–N 1.910(6), Al–C 1.97(2), N–C 1.52(2) Å; N–Al–N 91.3(3) or 106.7(10), Al–N–Al 88.4(3) or 115.6(10), N–Al–C 113.5(6), Al–N–C 111.4(11), C–Al–C 109(1)°. The gallium analogue $(Me_2GaNHMe)_2(MeGaNMe)_6$ (2), obtained similarly, crystallises in space group $P\bar{1}$ with a = 9.670(2), b = 9.905(2), c = 11.156(3) Å, α = 98.24(2), β = 108.23(2), γ = 115.57(1)°, and Z = 1. The structure has been solved by direct methods and refined to R = 0.05 for 2 143 reflections collected by diffractometer. The molecular structure is almost the same as that of the aluminium compound and mean bond lengths and angles are: Ga–N 1.970(4), Ga–C 1.986(4), N–C 1.49(2) Å; N–Ga–N 89.8(2) or 106.8(10), Ga–N–Ga 89.8(3) or 115(1), Ga–N–C 111.4(9), N–Ga–C 113.1(7), C–Ga–C 113.2(10)°. The Me_2ENHMe (E = Al or Ga) fragments of both structures are disordered and two isomers, one with C_2 (*cis*) and the other with C_i symmetry (*trans*), apparently crystallise together. The *cis* and *trans* isomers may be detected in n.m.r. spectra of solutions of the compounds in hydrocarbons.

THE reaction between trimethylaluminium and methylamine yields the cyclic trimers *cis*- and *trans*-$(Me_2AlNHMe)_3$,[2,3] and, at higher temperatures, the cage compound $(MeAlNMe)_7$ [1] [equation (1)]. Other oligomers, *e.g.* $(PhAlNPh)_4$,[4] $(HAlNPr^i)_n$ (n = 4 or 6),[5,6] $(HAlNPr^n)_n$ (n = 6 or 8),[7] $(HAlNBu^t)_4$,[8] and $(MeAlNPr^i)_n$ (n = 4 or 6),[6,9] have been made by similar reactions.

$$21AlMe_3 + 21NH_2Me \xrightarrow[70\,^\circ C]{-21\,CH_4} 7(Me_2AlNHMe)_3 \xrightarrow[215\,^\circ C]{-21\,CH_4} 3(MeAlNMe)_7 \quad (1)$$

The transformation of the amido-compounds $(Me_2AlNHMe)_3$ into imido-compounds, *e.g.* $(MeAlNMe)_7$, necessarily involves intermediates of general formula $(Me_2AlNHMe)_m(MeAlNMe)_n$ which must be characterised in order to understand the process of cage formation. In this paper we describe the isolation and crystal structure of the compound $(Me_2AlNHMe)_2(MeAlNMe)_6$ and some preliminary experiments to show how this is converted into the oligomers $(MeAlNMe)_7$ and the hitherto uncharacterised $(MeAlNMe)_8$. As part of an attempt to replace the cage atoms in imidoaluminium compounds by those of other Group 3 or Group 5 elements, we have obtained the gallium compound $(Me_2GaNHMe)_2(MeGaNMe)_6$. This suggests that the chemistry of Ga–N cages may well be similar to that of the well explored Al–N analogues.

EXPERIMENTAL

Air and moisture were excluded as far as possible from all reactions. Hydrogen-1 n.m.r. spectra of solutions in C_6D_6 were obtained using a Perkin-Elmer R32 90 MHz instrument; chemical shifts (relative intensities in parentheses) are measured from the benzene peak assumed to be at τ 2.85. Carbon-13 n.m.r. spectra were recorded using a JEOL PFT-100 spectrometer at 25.15 MHz, with C_6D_6 or $[^2H_8]$toluene as internal standards; chemical shifts given are relative to $SiMe_4$. Signals from $AlCH_3$ groups were broad and could not always be observed. Mass spectra were obtained with an A.E.I. MS 30 instrument using direct insertion.

The Octamer $(MeAlNMe)_8$.—Hydrogen-1 n.m.r. spectra of a sample of $(MeAlNMe)_7$, obtained by the procedure described previously,[2] showed the presence of an impurity. By careful fractional sublimation [2] at 10^{-3} Torr ‡ it was possible to separate the heptamer, subliming at 105—115 °C [n.m.r.: ^1H, τ 7.35(1), 7.52(3), 7.69(3), 10.45(1), 10.47(3), and 10.55(3); ^{13}C, −32.7(1), −31.5(3), −30.2(3) (NCH_3); 16.9 (br) $(AlCH_3)$], from the *octamer*, subliming 115—125 °C [Found: C, 34.1; H, 8.5; N, 19.4%; *M* (mass spectrometric) 568. $C_{16}H_{48}Al_8N_8$ requires C, 33.8; H, 8.5; N, 19.7%; *M* 568. N.m.r.; ^1H, τ 7.55(1), 7.59(1), and 10.49 (2, br); ^{13}C, −34.0(1) and −31.7(1)].

Both the heptamer and octamer in toluene were separately heated in n.m.r. tubes at 210 °C for 48 h. The solutions became slightly yellow and the peaks slightly broader but there was no evidence for conversion of one oligomer into the other.

The Compound $(Me_2AlNHMe)_2(MeAlNMe)_6$ (1).—The adduct $AlMe_3 \cdot NH_2Me$ (5.51 g) in toluene (50 cm^3) was heated for 16 h at 175 °C in a stainless-steel autoclave. Methane was blown off, and the white *plates*, subliming at 135—145 °C at 10^{-3} Torr, obtained when the solution was concentrated, were recrystallised twice from toluene (Found: C, 36.1; H, 9.35; N, 18.6. $C_{18}H_{56}Al_8N_8$ requires C, 36.0;

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† No reprints available.

‡ Throughout this paper: 1 Torr = (101 325/760) Pa.

H, 9.4; N, 18.7%). The mass spectrum (relative intensities in parentheses) of a carefully sublimed sample showed strong peaks at *m/e* 585.290 8 (100), corresponding to loss of methyl from the parent ion ($^{12}C_{17}{}^{1}H_{53}{}^{27}Al_{8}{}^{14}N_{8}$ requires *m/e* 585.291 6), and 498(40) [$(Me_2AlNHMe)(MeAlNMe)_6 - Me]^+$. The ^1H n.m.r. spectrum showed peaks at τ 7.59(6), 7.66(6), 7.86(3), 7.89(3), 8.04d(6) [NCH_3, *J*(HNCH) 6.5 Hz]; 9.85(2) (br) (NH); 10.44(6), 10.51(12), 10.58(6), and 10.73(6) ($AlCH_3$). The peak at τ 10.51 was resolved into two in [$^2H_8$]toluene. When the sample was irradiated at the frequency of the NH resonance the doublet at τ 8.04 collapsed to a singlet, but the other peaks in the spectrum were unchanged. There was also no significant change when the temperature of the sample was varied between −40 and 100 °C. Carbon-13 n.m.r. spectrum: −32.9(4), −30.6(2), −17.9(2) [*J*(CH) 136—137 Hz, NCH_3]; and *ca.* 9 (vbr) ($AlCH_3$). The compound $(Me_2AlNHMe)_2(MeAlNMe)_6$ is undoubtedly the same as that isolated earlier,[2] but then wrongly identified as $(Me_2AlNHMe)_3(MeAlNMe)_4$.

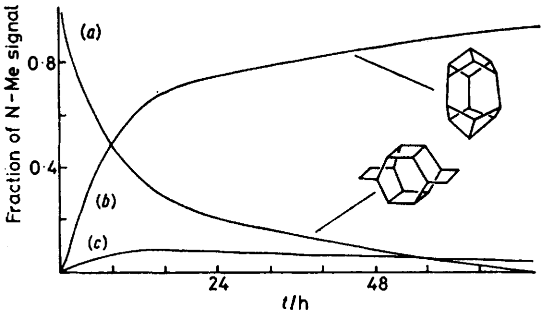

FIGURE 1 Fraction of *N*-methyl n.m.r. signal attributed to (*a*) compound (1), (*b*) $(MeAlNMe)_7$, and (*c*) an unidentified intermediate in toluene at 213 °C

Mass spectra show that there are several other products, possibly with $(AlN)_9$ or $(AlN)_{10}$ frameworks, in the mother liquor from recrystallisation, but these have not yet been isolated analytically pure.

A sample of compound (1) in [$^2H_8$]toluene was heated in an n.m.r. tube at 213 ± 1 °C, and the spectra recorded after various times (Figure 1). Complete resolution of all components was not achieved at 90 MHz, but it is clear that as compound (1) disappeared [curve (*a*)] the main new peaks [curve (*b*)] could be assigned to the heptamer $(MeAlNMe)_7$. Only trace amounts of octamer were formed. A new intermediate with peaks at τ 7.25, 7.48, and 9.93 reached a maximum concentration after 14 h [curve (*c*)] and then slowly disappeared on further heating. Experiments are in progress to identify and, if possible, isolate this compound.

The Compound $(Me_2GaNHMe)_2(MeGaNMe)_6$ (2).—Trimethylgallium (0.132 g, 1.11 mmol), toluene (10 cm³), and methylamine (1.11 mmol) were heated in a sealed ampoule at 210 °C for 15 h. Methane (2.12 mmol) was collected by a Sprengle pump and white *crystals* subliming at 145—155 °C at 10^{-3} Torr were obtained by concentrating the clear colourless solution (Found: C, 23.0; H, 6.2; N, 11.3%. $C_{18}H_{56}Ga_8N_8$ requires C, 22.9; H, 6.0; N, 11.9%). Hydrogen-1 n.m.r. spectrum: τ 7.46(6), 7.61(6), 7.73, and 7.76, incompletely resolved (6); 8.01 d(6) [NCH_3, *J*(HNCH) 7.0 Hz], 9.80(2) (NH); 10.08(6), 10.13(6), 10.23(6), 10.29(6), and 10.39(6) ($GaCH_3$). On irradiation at the frequency of the NH resonance the doublet at τ 8.01 became a singlet. The mass spectrum (relative intensities in parentheses) showed peaks with an isotope pattern indicating eight Ga atoms centred on *m/e* 926.831(10) [$^{12}C_{17}{}^{1}H_{53}{}^{69}Ga_{5}{}^{71}Ga_{3}{}^{14}N_{8}$ (parent − Me) requires 926.841] and peaks characteristic of seven Ga atoms centred on *m/e* 798(100) [$(Me_2GaNHMe)(MeGaNMe)_6 - Me]^+$. The conditions under which the crystalline product (2) may be isolated have not been fully explored, but they seem to be rather circumscribed. Thus, at higher concentrations insoluble (possibly polymeric) materials were obtained and some decomposition to metal was observed when $GaMe_3{\cdot}NH_2Me$ was heated for 15 h at 240 °C.

Crystal Data.—(*a*) (1) $C_{18}H_{56}Al_8N_8$, $M = 600.5$, Orthorhombic, $a = 15.389(2)$, $b = 19.747(4)$, $c = 11.613(1)$ Å, $U = 3\,529.0$ Å³, $Z = 4$, $D_c = 1.13$ g cm^{-3}, $F(000) = 1\,296$, $\mu(\text{Mo-}K_\alpha) = 2.6$ cm^{-1}, space group *Aba*2 or *Abam* (a non-standard setting of *Cmca*) from systematic absences *hkl* with $k + l = 2n + 1$, 0*kl* with $k = 2n + 1$, and *h*0*l* with $h = 2n + 1$.

(*b*) (2) $C_{18}H_{56}Ga_8N_8$, $M = 942.5$, Triclinic, $a = 9.670(2)$, $b = 9.905(2)$, $c = 11.156(3)$ Å, $\alpha = 98.23(2)$, $\beta = 108.23(2)$, $\gamma = 115.57(1)°$, $U = 865.8$ Å³, $Z = 1$, $D_c = 1.81$ g cm^{-3}, $F(000) = 468$, $\mu(\text{Mo-}K_\alpha) = 64.7$ cm^{-1}, space group $P\bar{1}$.

Crystallographic Measurements.—Both compounds crystallised in thin plates, *ca.* 0.5 × 0.5 × 0.1 mm, which were sealed in vacuum in thin-walled Lindemann glass capillaries. Space groups were found from Weissenberg and precession photographs and further data were collected on a Hilger and Watts Y290 four-circle diffractometer. Accurate cell parameters were estimated from setting angles for 12 reflections. Intensities for unique reflections with $2 < \theta < 25°$ were measured by an ω—2θ step scan, using Mo-K_α radiation (λ 0.710 69 Å) with a graphite-crystal monochromator. Three reference reflections, remeasured after every 100 reflections, showed no significant alteration. Data from compound (1), with higher mosaic spread and little from high-angle reflections, were of poorer quality than those from (2). Corrections were made for Lorentz and polarisation effects. For compound (1) no correction was made for absorption; data with $I < 2\sigma(I)$ were rejected, leaving 927 reflections for the structural analysis out of 1 963 measured. For compound (2) 3 472 reflections were measured, 2 143 having $I > 3\sigma(I)$.

Structure Solution and Refinement.—Initial data processing employed University of Sussex computer programs, using the SHEL-X program system of G. M. Sheldrick for structure solution and refinement, with atomic scattering factors from ref. 10.

(*a*) *Compound* (1). Positions of the aluminium and nitrogen atoms were derived from a sharpened Patterson map and carbon atoms were found from a subsequent Fourier map. The structure, initially refined in space group *Aba*2, with only a two-fold rotation axis imposed on the cage structure, with anisotropic temperature factors, and with a weighting scheme $w = 2.392/[\sigma^2(F) + 0.000\,1F^2]$, converged at $R = 0.081$, $R' = 0.079$ with a maximum shift-to-error of 0.27. No peaks of electron density >1.0 e Å^{-3} were found on a difference map. The resulting model appeared to have planar geometry at N(2) (Figure 2) with a very short N(2)–C(2) bond and thermal vibration ellipsoids of both atoms elongated perpendicular to the bond. In addition the Al–C bond lengths to the two methyl groups on Al(2), which were strongly correlated, were significantly different to a chemically unreasonable extent. For these reasons it was suspected that the correct space group might be *Abam* in which the atoms N(1), C(1), Al(2), N(2), C(2), Al(3), and C(31) are precisely coplanar, implying that N(2) and C(2) are disordered across the mirror plane. Refinement in *Abam* with anisotropic temperature factors and a weighting scheme $w = 1/[\sigma^2(F) + 0.009\ 34F^2]$ converged at $R = 0.087$, $R' = 0.135$, with a maximum shift-to-error of 0.21. Again no peaks of electron density >1.0 e Å^{-3} were found on the difference map. This latter refinement in *Abam* is preferred, in spite of the marginally significant increase in *R*, because of the chemically unreasonable bond lengths observed in *Aba*2. The difference between the two refinements is small. Final atom co-ordinates are shown in Table 1. No attempt was made to locate hydrogen atoms since the data were not of sufficient quality.

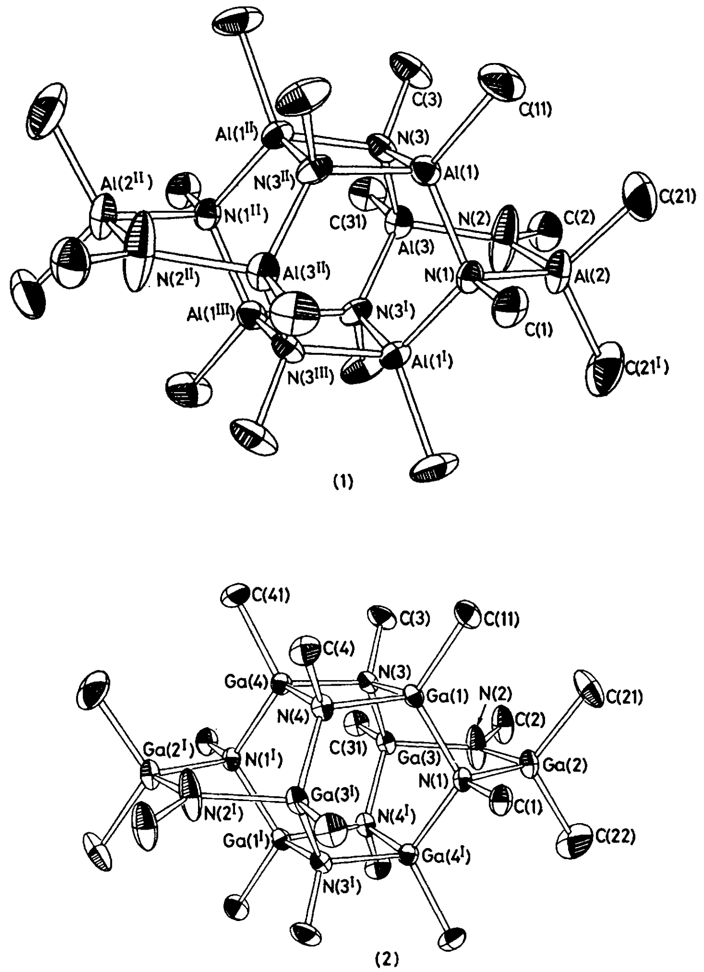

FIGURE 2 The molecules (1) and (2)

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses, for compound (1)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Al(1)	608(1)	487(1)	−1 377(2)
Al(2)	645(3)	1 868(2)	0
Al(3)	−1 109(2)	914(2)	0
N(1)	982(5)	909(4)	0
N(2)	−600(9)	1 795(6)	0
N(3)	−0 646(4)	482(3)	−1 289(5)
C(1)	1 977(8)	917(7)	0
C(2)	−1 083(11)	2 402(7)	0
C(3)	−1 087(6)	786(6)	−2 389(9)
C(11)	1 136(7)	829(7)	−2 840(9)
C(21)	1 006(12)	2 351(6)	−1 340(14)
C(31)	−2 412(8)	989(7)	0

TABLE 2

Fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses, for compound (2)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ga(1)	1 873(1)	254(1)	−747(1)
Ga(2)	−889(2)	−2 815(1)	−3 339(1)
Ga(3)	−1 847(1)	−64(1)	−2 240(1)
Ga(4)	1 501(1)	2 555(1)	654(1)
N(1)	238(9)	−2 006(9)	−1 341(8)
N(2)	2 120(20)	1 673(18)	3 731(10)
N(3)	575(10)	1 325(9)	−1 248(8)
N(4)	2 620(9)	1 341(9)	1 168(8)
C(1)	1 155(15)	−2 891(13)	−912(12)
C(2)	2 804(23)	1 677(21)	5 046(12)
C(3)	1 166(19)	2 379(16)	−2 053(14)
C(4)	4 502(13)	2 413(14)	1 904(13)
C(11)	3 781(15)	836(16)	−1 275(15)
C(21)	−2 666(28)	−5 068(19)	−4 059(19)
C(22)	784(24)	−2 301(27)	−4 148(16)
C(31)	3 156(16)	−934(15)	2 981(13)
C(41)	2 994(17)	4 864(13)	1 014(16)
H(11)	1 918	−2 559	139
H(12)	1 946	−2 692	−1 446
H(13)	196	−4 128	−1 282
H(31)	2 516	3 025	−1 466
H(32)	684	3 176	−1 994
H(33)	889	1 867	−3 080
H(41)	5 151	1 769	2 152
H(42)	4 788	3 251	2 806
H(43)	4 912	3 039	1 252
H(111)	3 368	310	−2 330
H(112)	4 557	421	−717
H(113)	4 506	2 109	−1 001
H(211)	−2 933	−5 524	−5 094
H(212)	−3 830	−5 561	−3 936
H(213)	−1 827	−5 392	−3 449
H(221)	988	−1 200	−4 326
H(222)	319	−3 195	−5 079
H(223)	1 961	−2 133	−3 459
H(311)	2 930	−1 773	3 519
H(312)	4 481	−43	3 435
H(313)	2 796	−1 542	1 955
H(411)	3 954	5 135	1 983
H(412)	2 806	5 839	968
H(413)	3 391	4 584	251

(*b*) *Compound* (2). The choice of the centrosymmetrical space group $P\bar{1}$ was confirmed by the subsequent successful refinement. The structure was solved by the direct-methods program in the SHEL-X system. From the *E* map obtained, four gallium atoms were located (*R* 0.20) and from the next Fourier map the positions of all the nitrogen and carbon atoms were deduced (*R* 0.10). After correction for absorption, refinement continued smoothly to *R* 0.07. Hydrogen atoms were visible on a difference map and were included at idealised positions, except those on N(2) and C(2) (Figure 2). With a weighting scheme $w = 1.06/[\sigma^2(F) + 0.004\ 3F^2]$, refinement was continued until the shift-to-error ratio was $\leqslant 0.15$ with $R = 0.057$, $R' = 0.079$. The largest peaks in the final difference map were at 0.57 e Å^{-3}. Final atomic positions are given in Table 2.

Observed and calculated structure-factor amplitudes and thermal parameters for both structures are given in Supplementary Publication No. SUP 22501 (22 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

DISCUSSION

The structures of compounds (1) and (2) are similar. Both show discrete molecules (Figure 2) based on E–N (E = Al or Ga) cages in which both E and N are four-co-ordinate, and from which methyl groups point outwards. Interatomic distances and valency angles are given in Tables 3 and 4. For compound (1) the space group requires C_{2h} symmetry: for (2) the crystallographically required molecular symmetry is only C_i but calculated displacements from mean planes (i) and (ii) (Table 4) show that the distortion from C_{2h} is small. The mean * Al–N bond distance in (1) [1.910(6) Å] is similar to that in related cage structures.[1,4-7] Some individual bond distances differ significantly from the mean. Bonds adjacent to four-membered rings are

TABLE 3

Intramolecular distances (Å) and angles (°), with estimated standard deviations in parentheses, and displacements from mean planes (Å) for compound (1)

(*a*) Distances

Al(1)–N(1)	1.893(5)	Al(1)–C(11)	2.001(11)
Al(1)–N(3)	1.932(6)	Al(2)–C(21)	1.908(15)
Al(1)–N(3$^{\mathrm{II}}$)	1.917(6)	Al(3)–C(31)	2.010(13)
Al(2)–N(1)	1.963(9)	N(1)–C(1)	1.532(14)
Al(2)–N(2)	1.922(14)	N(2)–C(2)	1.412(19)
Al(3)–N(2)	1.909(13)	N(3)–C(3)	1.567(12)
Al(3)–N(3)	1.864(6)	Al(1) · · · Al(1$^{\mathrm{II}}$)	2.683(3)
		N(3) · · · N(3$^{\mathrm{II}}$)	2.752(9)

(*b*) Angles

Al(1)–N(1)–Al(2)	110.2(3)	N(1)–Al(1)–N(3)	105.1(3)
Al(1)–N(1)–Al(1$^{\mathrm{I}}$)	115.3(4)	N(1)–Al(1)–N(3$^{\mathrm{II}}$)	112.6(3)
Al(1)–N(3)–Al(1$^{\mathrm{II}}$)	88.4(3)	N(1)–Al(2)–N(2)	101.0(4)
Al(1)–N(3)–Al(3)	114.9(3)	N(3)–Al(3)–N(3$^{\mathrm{I}}$)	106.8(3)
Al(2)–N(2)–Al(3)	118.5(6)	N(2)–Al(3)–N(3)	105.1(3)
Al(3)–N(3)–Al(1$^{\mathrm{II}}$)	120.7(3)	N(3)–Al(1)–N(3$^{\mathrm{II}}$)	91.3(3)
Al(1)–N(1)–C(1)	107.9(4)	N(1)–Al(1)–C(11)	116.5(4)
Al(1)–N(3)–C(3)	112.8(5)	N(1)–Al(2)–C(21)	113.9(4)
Al(1)–N(3$^{\mathrm{II}}$)–C(3$^{\mathrm{II}}$)	110.6(5)	N(2)–Al(2)–C(21)	109.1(6)
Al(2)–N(1)–C(1)	104.7(7)	N(2)–Al(3)–C(31)	110.0(6)
Al(2)–N(2)–C(2)	117.5(10)	N(3)–Al(1)–C(11)	116.9(4)
Al(3)–N(2)–C(2)	124.0(10)	N(3)–Al(3)–C(31)	114.5(3)
Al(3)–N(3)–C(3)	108.3(5)	N(3)–Al(1$^{\mathrm{II}}$)–C(11$^{\mathrm{II}}$)	111.7(4)
C(21)–Al(2)–C(21$^{\mathrm{I}}$)	109.3(6)		

(*c*) Displacements (Å) from mean planes

Plane (i): Al(1), Al(1$^{\mathrm{II}}$), N(3), N(3$^{\mathrm{II}}$)
[Al(1) −0.051, Al(1$^{\mathrm{II}}$) −0.051, N(3) 0.051, N(3$^{\mathrm{II}}$) 0.051]

Plane (ii): Al(1$^{\mathrm{I}}$), Al(1$^{\mathrm{II}}$), N(3), N(3$^{\mathrm{III}}$), C(11$^{\mathrm{I}}$), C(11$^{\mathrm{II}}$), C(3), C(3$^{\mathrm{III}}$)
[Al(1$^{\mathrm{I}}$) −0.069, N(3) −0.056, C(11$^{\mathrm{II}}$) 0.035, C(3) 0.030]

Plane (iii): Al(1), Al(1$^{\mathrm{III}}$), N(3$^{\mathrm{I}}$), N(3$^{\mathrm{II}}$), C(11), C(11$^{\mathrm{III}}$), C(3$^{\mathrm{I}}$), C(3$^{\mathrm{II}}$)
[Al(1) 0.121, N(3) 0.074, C(11) −0.062, C(3) −0.041]

Plane (iv): Al(1), Al(1$^{\mathrm{I}}$), Al(1$^{\mathrm{II}}$), Al(1$^{\mathrm{III}}$), N(1), N(1$^{\mathrm{II}}$), C(11), C(11$^{\mathrm{I}}$), C(11$^{\mathrm{II}}$), C(11$^{\mathrm{III}}$), C(1), C(1$^{\mathrm{II}}$)
[Al(1) 0.138, Al(1$^{\mathrm{I}}$) −0.138, N(1) 0.409, C(11) 0.135, C(11$^{\mathrm{II}}$) −0.135, C(1) −0.561]

Plane (v): Al(3), Al(3$^{\mathrm{II}}$), N(3), N(3$^{\mathrm{I}}$), N(3$^{\mathrm{II}}$), N(3$^{\mathrm{III}}$), C(3), C(3$^{\mathrm{I}}$), C(3$^{\mathrm{II}}$), C(3$^{\mathrm{III}}$), C(31), C(31$^{\mathrm{II}}$)
[Al(3) 0.433, N(3) 0.172, N(3$^{\mathrm{II}}$) −0.172, C(3) 0.250, C(3$^{\mathrm{II}}$) −0.250, C(31) −0.643]

Angles (°) between normals: (i)—(ii) 60.1, (i)—(iii) 61.4, (iv)—(v) 76.4

Symmetry: I, $x, y, -z$; II $-x, -y, z$; III $-x, -y, -z$

TABLE 4

Intramolecular distances (Å) and angles (°), with estimated standard deviations in parentheses, and displacements from mean planes for compound (2)

(*a*) Distances

Ga(1)–N(1)	1.953(7)	Ga(1)–C(11)	1.987(17)
Ga(1)–N(3)	1.973(11)	Ga(2)–C(21)	2.006(24)
Ga(1)–N(4)	1.987(8)	Ga(2)–C(22)	1.972(15)
Ga(2)–N(1)	2.003(8)	Ga(3)–C(31)	1.980(17)
Ga(2)–N(2)	1.966(22)	Ga(4)–C(41)	1.986(11)
Ga(3)–N(2)	1.995(16)	N(1)–C(1)	1.520(19)
Ga(3)–N(3)	1.940(7)	N(2)–C(2)	1.407(19)
Ga(3)–N(4$^{\mathrm{I}}$)	1.940(9)	N(3)–C(3)	1.516(19)
Ga(4)–N(3)	1.979(8)	N(4)–C(4)	1.503(11)
Ga(4)–N(4)	1.969(10)	Ga(1) · · · Ga(4)	2.794(1)
Ga(4)–N(1$^{\mathrm{I}}$)	1.961(10)	N(3) · · · N(4)	2.793(12)

(*b*) Angles

Ga(1)–N(1)–Ga(2)	109.0(4)	N(1)–Ga(1)–N(3)	106.9(3)
Ga(1)–N(1)–Ga(4$^{\mathrm{I}}$)	114.6(5)	N(1)–Ga(1)–N(4)	113.3(3)
Ga(1)–N(3)–Ga(4)	89.9(3)	N(1)–Ga(2)–N(2)	102.0(4)
Ga(1)–N(3)–Ga(3)	115.3(4)	N(2)–Ga(3)–N(3)	104.8(6)
Ga(1)–N(4)–Ga(4)	89.8(3)	N(2)–Ga(3)–N(4$^{\mathrm{I}}$)	101.2(5)
Ga(1)–N(4)–Ga(3$^{\mathrm{I}}$)	118.2(3)	N(3)–Ga(1)–N(4)	89.7(4)
Ga(2)–N(1)–Ga(4$^{\mathrm{I}}$)	108.9(3)	N(3)–Ga(3)–N(4$^{\mathrm{I}}$)	106.9(4)
Ga(2)–N(2)–Ga(3)	119.5(5)	N(3)–Ga(4)–N(4)	90.0(4)
Ga(3)–N(3)–Ga(4)	119.3(5)	N(3)–Ga(4)–N(1$^{\mathrm{I}}$)	112.5(3)
Ga(4)–N(4)–Ga(3$^{\mathrm{I}}$)	115.4(4)	N(4)–Ga(4)–N(1$^{\mathrm{I}}$)	106.9(4)
		C(21)–Ga(2)–C(22)	113.2(10)
Ga(1)–N(1)–C(1)	109.5(5)		
Ga(1)–N(3)–C(3)	112.8(9)	N(1)–Ga(1)–C(11)	115.7(5)
Ga(1)–N(4)–C(4)	113.2(8)	N(1)–Ga(2)–C(21)	112.2(5)
Ga(2)–N(1)–C(1)	106.7(6)	N(1)–Ga(2)–C(22)	112.8(6)
Ga(2)–N(2)–C(2)	119.1(15)	N(1$^{\mathrm{I}}$)–Ga(4)–C(41)	116.2(6)
Ga(3)–N(2)–C(2)	119.0(15)	N(2)–Ga(2)–C(21)	111.1(9)
Ga(3)–N(3)–C(3)	106.9(6)	N(2)–Ga(2)–C(22)	104.6(8)
Ga(3$^{\mathrm{I}}$)–N(4)–C(4)	108.1(7)	N(2)–Ga(3)–C(31)	109.3(6)
Ga(4)–N(3)–C(3)	111.8(6)	N(3)–Ga(1)–C(11)	115.4(5)
Ga(4)–N(4)–C(4)	111.0(7)	N(3)–Ga(3)–C(31)	116.5(4)
Ga(4$^{\mathrm{I}}$)–N(1)–C(1)	107.6(7)	N(3)–Ga(4)–C(41)	111.5(6)
		N(4$^{\mathrm{I}}$)–Ga(3)–C(31)	116.3(5)
		N(4)–Ga(4)–C(41)	116.7(5)
		N(4)–Ga(1)–C(11)	112.7(4)

(*c*) Displacements (Å) from mean planes

Plane (i): Ga(2), Ga(2$^{\mathrm{I}}$), Ga(3), Ga(3$^{\mathrm{I}}$), N(1), N(1$^{\mathrm{I}}$), N(2), N(2$^{\mathrm{I}}$), C(2), C(2$^{\mathrm{I}}$), C(31), C(31$^{\mathrm{I}}$), C(1), C(1$^{\mathrm{I}}$)
[Ga(2) −0.019, Ga(3) −0.028, N(1) −0.003, N(2) 0.107, C(1) −0.222, C(2) −0.137, C(31) 0.047]

Plane (ii): Ga(1), Ga(4), N(3), N(4)
[Ga(1) 0.044, Ga(4) 0.044, N(3) −0.044, N(4) −0.044]

Plane (iii): Ga(4), Ga(4$^{\mathrm{I}}$), N(4), N(4$^{\mathrm{I}}$), C(4), C(4$^{\mathrm{I}}$), C(41), C(41$^{\mathrm{I}}$)
[Ga(4) 0.131, N(4) 0.045, C(4) −0.026, C(41) −0.068]

Plane (iv): Ga(1), Ga(1$^{\mathrm{I}}$), N(3), N(3$^{\mathrm{I}}$), C(11), C(11$^{\mathrm{I}}$), C(3), C(3$^{\mathrm{I}}$)
[Ga(1) −0.111, N(3) −0.053, C(11) 0.058, C(3) 0.029]

Plane (v): Ga(1), Ga(1$^{\mathrm{I}}$), N(4), N(4$^{\mathrm{I}}$), C(11), C(11$^{\mathrm{I}}$), C(4), C(4$^{\mathrm{I}}$)
[Ga(1) −0.002, N(4) 0.003, C(11) 0.001, C(4) −0.002]

Plane (vi): Ga(4), Ga(4$^{\mathrm{I}}$), N(3), N(3$^{\mathrm{I}}$), C(41), C(41$^{\mathrm{I}}$), C(3), C(3$^{\mathrm{I}}$)
[Ga(4) −0.005, N(3) 0.006, C(41) 0.003, C(3) −0.004]

Plane (vii): Ga(1), Ga(1$^{\mathrm{I}}$), Ga(4), Ga(4$^{\mathrm{I}}$), N(1), N(1$^{\mathrm{I}}$), C(11), C(11$^{\mathrm{I}}$), C(41), C(41$^{\mathrm{I}}$)
[Ga(1) 0.008, Ga(4) 0.023, N(1) −0.146, C(11) 0.070, C(41) −0.085]

Plane (viii): Ga(3), Ga(3$^{\mathrm{I}}$), N(3), N(3$^{\mathrm{I}}$), N(4), N(4$^{\mathrm{I}}$), C(3), C(3$^{\mathrm{I}}$), C(4), C(4$^{\mathrm{I}}$)
[Ga(3) −0.044, N(3) 0.004, N(4) −0.029, C(3) 0.021, C(4) −0.010]

Angles (°) between normals: (i)—(ii) 0.9, (ii)—(iii) 60.7, (ii)—(iv) 61.2, (ii)—(v) 64.8, (ii)—(vi) 63.3, (ii)—(vii) 88.9, (i)—(viii) 89.5, (vii)—(viii) 89.4

Symmetry: I $\bar{x}, \bar{y}, \bar{z}$.

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* Standard deviations (σ) of mean molecular parameters x for the whole cage have been calculated from n individual measurements x_i by $\sigma^2 = \sum_i^n (x_i - x)^2/n(n-1)$.

systematically short; presumably this reflects the greater *s* character of the exocyclic bonds balancing the greater *p* character of bonds in the ring. As in $(MeAlNMe)_7$[1] and $(HAlNPr^n)_8$,[7] the mean length of the three Al–N cage bonds to any one nitrogen or aluminium is close to the mean for the whole cage. Aluminium–carbon [mean 1.97(2) Å] and N–C [mean 1.52(2) Å] distances are normal, but the apparent C–Al–C angle (109°) is smaller than in most other dimethylaluminium derivatives.[3]

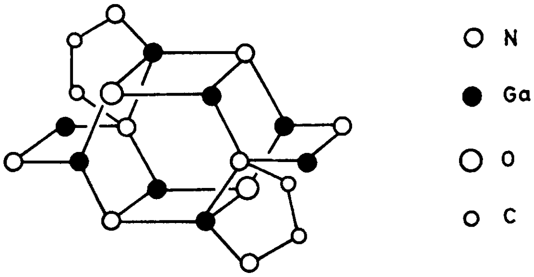

FIGURE 3 Cage structure of compound (3), with exocyclic atoms omitted

Bond angles within the Al–N cage also follow the established pattern. Thus in the four-membered rings Al–N–Al angles [mean 88.4(3)°] are slightly smaller than N–Al–N angles [mean 91.3(3)], but in six-membered rings Al–N–Al [mean 115.6(10)°] are greater than N–Al–N angles [mean 106.7(10)°]. The atoms of the four-membered rings are almost coplanar [Table 3, plane (i)] and all the six-membered rings are in the boat conformation so that bonds to carbon from adjacent aluminium and nitrogen atoms are eclipsed [Table 3, planes (ii) and (iii)].

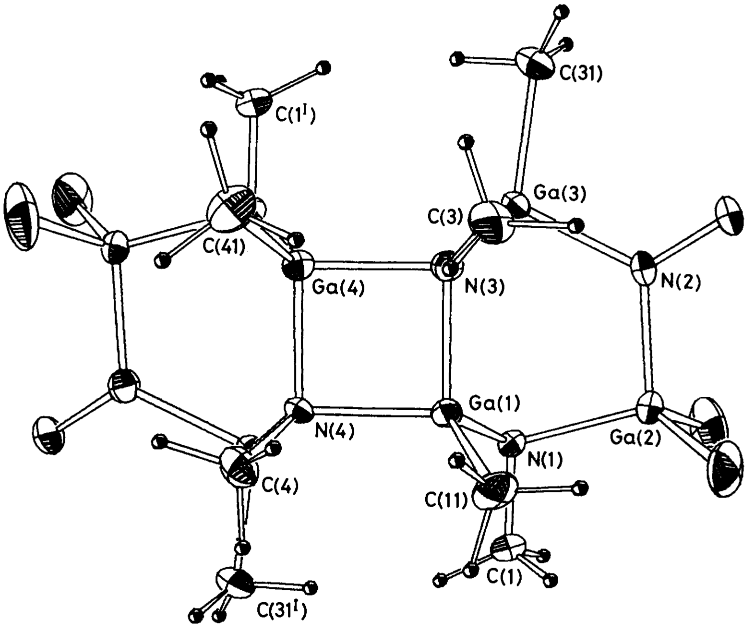

FIGURE 4 Partial structure of molecule (2), showing positions of hydrogen atoms

The only compound in the literature comparable to (2) appears to be $(GaH)_6(GaH_2)_2(\mu_3\text{-}O)_2(\mu_3\text{-}NCH_2CH_2NMe_2)_4(\mu\text{-}NHCH_2CH_2NMe_2)_2$ (3), made accidentally from *NN*-dimethylethylenediamine and gallane–trimethylamine in the presence of water vapour.[11] This has the cage structure shown in Figure 3. The mean Ga–N distance in (2) [1.970(4) Å] is very similar to that in (3) [1.972(3) Å], and close to that in other compounds in which the environment around gallium is approximately tetrahedral [some Ga atoms in (3) are five-co-ordinate]. Some of the Ga–N distances within the cage of (2) differ significantly from the mean, but variations in bond lengths are less than in compound (1). The shortest Ga–N bonds are again those adjacent to four-membered rings. The mean Ga–C distance [1.986(4) Å] is similar to that found in other organogallium compounds[12,13] and the mean N–C distance [1.49(2) Å] is comparable to that in compound (1). Bond angles in the four-membered rings are close to 90°; in the six-membered rings, Ga–N–Ga angles [mean 115(1)°] are greater than N–Ga–N angles [mean 106.8(10)°], as has been found in $[(CH_2)_2NGaH_2]_3$,[13] in which the $(GaN)_3$ rings have the chair conformation. The six-membered rings in (2), like those in (1), are in the boat conformation, with bonds to carbon from adjacent Ga and N atoms being eclipsed. [See, for example, Table 4, planes (iii)—(vi).] Carbon atoms C(11) and C(41) are closer to the plane defined by Ga(1), N(1), and Ga(4) and atoms C(3) and C(4) are closer to the plane defined by Ga(3), N(3), and N(4) [Table 4, planes (vii) and (viii)] than are the corresponding carbon atoms to the diagonal planes in (1) [Table 3, planes (iv) and (v)]. The triclinic cell of (2) and the orthorhombic cell of (1) are simply related. Compound (2) has the smaller molecular volume [866 compared with 882 Å^3 for (1)]. There are no obviously short intermolecular contacts in either compound, but hydrogen atoms within each molecule are crowded. Some of those located in (2) are shown in Figure 4.

For both compounds (1) and (2), thermal parameters associated with atoms of the Me_2ENHMe bridges ($E = Al$ or Ga) are large and anisotropic, as is indicated by the vibrational ellipsoids of Figure 2. This suggests that these molecular fragments are disordered. The atom N(2) has a flattened tetrahedral co-ordination because of non-bonded contacts between the C(2) methyl group and adjacent methyl groups, *e.g.* on N(3). Both orientations of this flattened tetrahedron (Figure 5) appear to be superimposed. The short N(2)–C(2) distance is an artefact of the disorder. Since there are two Me_2ENHMe groups per molecule a kind of *cis–trans* isomerism is possible. In the *cis* isomer the two Me_2ENHMe groups are related by a C_2 axis and the N(2)–C(2) bonds of the two methylamido-groups point on the same side of the molecular plane. In the *trans* isomer the Me_2ENHMe groups are related by a centre of symmetry and the two N(2)–C(2) bonds point on opposite sides of the molecular plane.

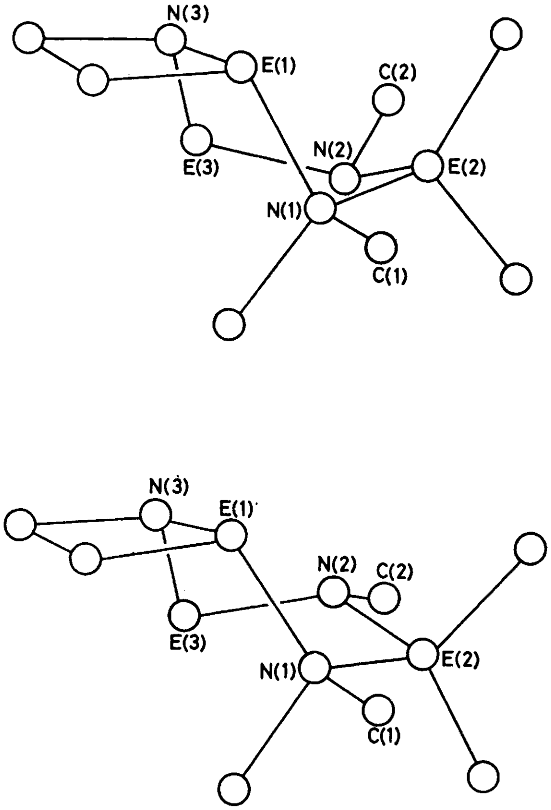

FIGURE 5 Partial structures of molecules (1) and (2), showing alternative configurations of Me_2ENHMe groups ($E = Al$ or Ga)

If the space group of (1) is correctly assigned as *Abam* the atoms N(2) are equally distributed above and below the mean plane with the average position of N(2) in the plane; C(2) is similarly distributed on either side of the plane, but since the elongation of the thermal ellipsoid is less than that of N(2) the displacement of C(2) from the plane appears to be less. Movement of N(2) from one side of the mean plane to the other causes a rotation of Al(2) so that the two attached carbon atoms have ellipsoids elongated perpendicular to the Al(2)–C(2) bonds. The crystallographic results imply that, in the crystal: (*i*) molecules of the *cis* isomer are orientated so that the N(2)–C(2) bonds point randomly on either side of the mean molecular plane; (*ii*) molecules of the *trans* isomer are similarly disordered; or (*iii*) equal amounts of *cis* and *trans* isomers crystallise together. If the correct space group of (1) is *Aba*2 the implication is that there is an imbalance of *cis* and *trans* isomers or that one orientation of the *cis* isomers is preferred. A similar argument applies to the gallium compound (2). The ellipsoid of C(2) in (2) is more elongated (Figure 2) than that in (1) suggesting that C(2) is displaced further from the mean plane in (2) than in (1). The distortion of the compound (2) from C_{2h} symmetry involves downward displacements of N(3) and Ga(3) by *ca.* 0.03 Å, and upward displacement of Ga(1) and N(2); C(2) is displaced downwards by *ca.* 0.14 Å. The structural determination is, however, insufficiently precise to show whether the distortion implies an imbalance between C_i and C_2 isomers in the crystal. Crystallographic disorder has been observed in several other studies on compounds with aluminium–nitrogen cages.[4-6]

Further evidence for *cis* and *trans* isomers of compounds (1) and (2) may be obtained from n.m.r. spectra. A compound with C_{2h} symmetry would give three signals in the N–Me region, with relative intensity 2 : 1 : 1, corresponding to atoms C(3), C(1), and C(2). Three such peaks are observed in the ^{13}C spectrum of (1), although the peak of highest intensity shows further structure at higher resolution. The 90-MHz ^1H spectra of both (1) and (2) are, however, more complicated, and further splitting of signals in the N–Me region is seen at 300 MHz. The additional peaks, beyond those expected for molecules with C_{2h} symmetry, do not arise from spin coupling between *N*-methyl protons and the proton attached directly to nitrogen in the amido-group, since they are unchanged by irradiation at the N–H frequency. Each of the *cis*-(C_2) or *trans*-(C_i) isomers is expected to give peaks in the *N*-methyl region with relative intensity 1 : 1 : 1 : 1d (d = doublet). The spectrum observed at 300 MHz, which shows peaks with intensity 1 : 1 : 2 : 1 : 1d : 1d, could arise from overlap of two such patterns. The N–H region shows two overlapping quartets. The Al–Me or Ga–Me regions are, however, not so clear, and signals for the *cis* and *trans* isomers are incompletely resolved. The isomers remain distinct on the n.m.r. time scale up to 100 °C, but it is impossible to tell whether they are formed upon dissolution by transient opening of the Me_2ENHMe bridge [*cf.* $(Me_2AlNHMe)_3$ [3]] or whether the two isomers are already present in the solid. The small chemical-shift differences between isomers and the possible formation of mixed crystals indicate the close similarity, resulting from the flattening of the co-ordination tetrahedron at N(2), between C_2 and C_i molecules.

It would be interesting to know more about the role of compound (1) as a precursor to the oligomers (Me-

AlNMe)$_n$ (n = 7 or 8). The ^{1}H and ^{13}C n.m.r. spectra of the octamer, which show two peaks of equal intensity in the N–Me region, suggest that the cage has structure (4) with S_4 symmetry (Figure 6) as has the compound (HAlNPr^n)$_8$. It is not clear, however, how the octamer is formed. The main product on heating (1) is the heptamer (MeAlNMe)$_7$, but formation of this seems to involve extensive rearrangement of the Al–N framework (see Figure 1). It may be significant that the only strong peak in the mass spectrum of compound (1), besides that corresponding to [$C_{17}H_{53}Al_8N_8$]$^+$ (P – Me) is from the Al_7N_7 fragment [$C_{14}H_{43}Al_7N_7$]$^+$. Compound (1) does not appear to be a precursor of the octamer. Since (MeAlNMe)$_7$ and (MeAlNMe)$_8$ are interconverted only slowly at *ca.* 200 °C, the proportions of heptamer and octamer formed from (Me$_2$AlNHMe)$_3$ in any one experiment may depend on kinetic factors in the early stages of the pyrolysis. The precursor of the octamer may well be an isomer of (1) with the cage structure (5) (Figure 6). As suggested earlier,[8] this could easily give octamer by intramolecular elimination.

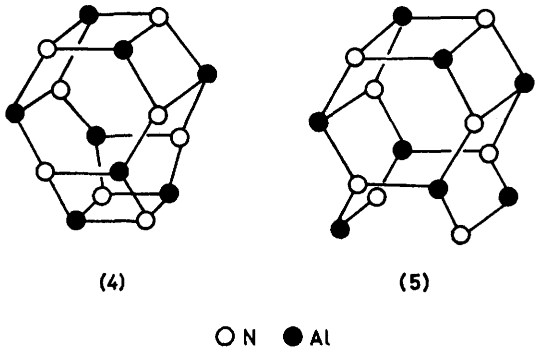
(4) (5)

FIGURE 6 Cage structures of (MeAlNMe)$_8$ (4) and its possible precursor (5). Exocyclic atoms are omitted

Mass spectra of impure samples of the gallium compound (2) show peaks which may be assigned to compounds (Me$_2$GaNHMe)$_2$(MeGaNMe)$_{6-n}$ (MeGaO)$_n$. These are almost certainly formed by accidental admission of moisture to the reaction mixture and probably have cage structures like that of Figure 3 (without the ethylenediamine bridges). It seems likely that a variety of compounds based on Ga–N and O–Ga–N frameworks may be accessible.

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