Complexes of Organoaluminium Compounds. Part IX.[1] Crystal and Molecular Structure of Hepta-μ_3-methylimido-heptakis(methylaluminium) a Cage Compound in the Series of Oligomers $[R^1XYR^2]_n$ †

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The compound $(MeAlNMe)_7$ crystallises in space group $P2_1/c$ with a = 14.059(7), b = 14.407(8), c = 14.435(8) Å, β = 93.10(5)°, and Z = 4; the structure was solved by the symbolic addition method and least-squares refinement converged at R = 0.119 (1 179 reflections measured by diffractometer). The molecules have a cage structure with C_{3v} symmetry, in which each aluminium and each nitrogen atom is four-co-ordinate and bound to one methyl group and three atoms within the cage. Mean molecular dimensions are: Al–N 1.91(4), Al–C 1.98(7), N–C 1.56(6) Å; Al–N–Al 89(1) or 120(1)°, N–Al–N 90(2) or 110(2)°. C–Al–N angles range from 112 to 129°, and C–N–Al from 103 to 127°. The structure found is one of a related series shown by oligomeric molecules $(R^1XYR^2)_n$ (n = 1—8); a general discussion of these structures is given.

THERE are many well characterised compounds with empirical formulae R^1XYR^2 in which X and Y are pairs of main-group elements, either from Group 2 and Group 6, or from Group 3 and Group 5, and R^1, R^2 are alkyl or aryl groups. A few of these compounds are monomeric [2] in benzene solution, but the tendency of main-group elements to achieve co-ordination numbers >2 results in oligomeric or polymeric structures in most cases. Some of these (Table 1) are well established by spectroscopic or X-ray methods; others are inferred rather less certainly, particularly since most of the substances are very sensitive towards hydrolysis, from molecular-weight measurements in solution. In this paper, we describe an unusual heptameric species $(MeAlNMe)_7$ and discuss the relation between its cage structure and those shown by other oligomeric species $(R^1XYR^2)_n$. A preliminary account has been published.[3]

TABLE 1

Oligomeric compounds $(R^1XYR^2)_n$ [a]

n	
1	$MeHgOSiMe_3$, Pr^iHgOPr^i [b]
2	Bu^tBeOBu^t, $MeBeOCHPh_2$, $MeBeOCPh_3$,[c] $R^1BeOCH_2R^2$ (R^1 = Et or Bu^t, R^2 = Bu^t or Ph),[d] $MeCdOBu^t$, Bu^tZnOBu^t, $PhZnOCPh_3$,[e] ArBNAr (Ar = XC_6H_4, X = 2-Me,4-Me, 4-Cl, 4-MeO) [f]
3	$EtBeOCEt_3$, Bu^iBeOBu^i,[c] $Bu^iBeOCH_2Bu^t$,[d] $BuMgOPr^i$, $EtZnOCHPh_2$, $PhHgOR^2$ (R^2 = Me or Bu),[e] Borazenes R^1BNR^2 [g]
4	$MeBeOR^2$ (R^2 = Me, Et, Pr, Bu^t, CH_2Ph,[c] or $SiMe_3$ [g,h]), PhBeOMe,[c] $EtMgOR^2$ (R^2 = Pr^i or Bu^t), Pr^iMgOPr^i [e,i] $MeZnOR^2$ (R^2 = Me,[g,j] Bu^t, or $SiMe_3$ [e]), $EtZnOBu^t$,[g,k] $MeCdOR^2$ (R^2 = Me,[g] Et, Pr, Ph, or $SiMe_3$ [e]), $EtBeSR^2$ (R^2 = Et, Pr^i, or Bu^t), $MeBeSBu^t$,[c] $RMgSBu^t$ (R = Me or Et), $MeCdSBu^t$,[e] $RBNBu^i$ (R = Ph or halogen),[l,m] PhAlNPh,[g,n] PhAlNAr [Ar = 3-MeC_6H_4, 4-XC_6H_4 (X = Me, OMe, Cl or I)],[o] EtAlNPh,[p] $EtAlNBu^t$,[q] $HAlNBu^t$ [m,r,s]
5	$RZnSBu^t$ (R = Me,[g,t] or Et [e])
6	$MeCdSPr^i$,[e] $HAlNR^2$ [s] (R^2 = Pr^i,[g,u] Bu^s, Bu^i, or cyclo-C_6H_{11})
7	RAlNMe (R = Me [g] or Et [q]), $EtMgOPr^n$ [i]
8	$MeZnSPr^i$,[g,v] Pr^iMgOR^2 (R^2 = Me or Et)

[a] Unless stated otherwise, established by cryoscopic measurements in benzene. [b] Ref. 2. [c] G. E. Coates and G. L. Morgan, *Adv. Organometallic Chem.*, 1970, **9**, 195, and extensive refs. therein. [d] R. A. Anderson and G. E. Coates, *J.C.S. Dalton*, 1974, 1171. [e] B. J. Wakefield, *Adv. Inorg. Chem. and Radiochem.*, 1968, **11**, 341, which gives full refs. to original literature. [f] P. I. Paetzold, P. P. Habereder, and R. Müllbauer, *J. Organometallic Chem.*, 1967, **7**, 51. [g] Established by X-ray structure determination. [h] D. Mootz, A. Zinnius, and B. Böttcher, *Angew. Chem.*, 1969, **81**, 398. [i] G. E. Coates, J. A. Heslop, M. E. Redwood, and D. Ridley, *J. Chem. Soc.* (*A*), 1968, 1118. Values in the range 7–8.4 were found by cryoscopic measurements for those species described as octamers. [j] H. M. M. Shearer and C. B. Spencer, *Chem. Comm.*, 1966, 194. [k] Y. Matsui, K. Kamiya, M. Nishikawa, and Y. Tomiie, *Bull. Chem. Soc. Japan*, 1966, **39**, 1828. [l] H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 1965, 6421. [m] Established by mass spectrometric or other spectrometric methods. [n] Ref. 8. [o] J. Idris Jones and W. S. McDonald, *Proc. Chem. Soc.*, 1962, 366. [p] J. K. Gilbert and J. D. Smith *J. Chem. Soc.* (*A*), 1968, 233. [q] Ref. 5. [r] H. Nöth and P. Wolfgardt, personal communication. [s] S. Cucinella, T. Salvatori, C. Busetto, G. Perego, and A. Mazzei, *J. Organometallic Chem.*, 1974, **78**, 185. HAlNEt and $HAlNBu^t$ were obtained as mixtures of species with n = 6–9 [m]. [t] G. W. Adamson, H. M. M. Shearer, and C. B. Spencer, *Acta Cryst.*, 1966, **21**, A135. [u] Ref. 11. [v] G. W. Adamson and H. M. M. Shearer, *Chem. Comm.*, 1969, 897.

EXPERIMENTAL

N.M.R. Spectra.—The n.m.r. spectrum of MeAlNMe has been reported.[4] The spectrum of EtAlNMe [5] in benzene shows singlets (relative intensities in parentheses) at τ 7.06(1), 7.10(3) and 7.34(3) [N–CH_3], triplets centred at τ 8.33(1), 8.41(3), 8.54(3) [Al–CH_2CH_3], and quartets centred at τ 9.32(1), 9.47(3), and 9.57(3) [Al–CH_2CH_3]. Except for small changes in chemical shifts, the spectra in [$^2H_8$]-toluene show little variation between 60 and −40 °C, indicating that there is no interchange of alkyl groups on the n.m.r. time scale.

Crystal Data.—(*a*) $(EtAlNMe)_7$. $C_{21}H_{56}Al_7N_7$, M = 595.6, orthorhombic, a = 18.50, b = 34.94, c = 10.97 Å, Z = 8, D_c = 1.12 g cm^{-3}. Space group $Pbca$ from systematic absences: $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd.

(*b*) $(MeAlNMe)_7$. $C_{14}H_{42}Al_7N_7$, M = 497.4, monoclinic, a = 14.059(7), b = 14.407(8), c = 14.435(8) Å, β = 93.10(5)° U = 2 919 Å^3, Z = 4, D_c = 1.13 g cm^{-3}, $F(000)$ = 1 064. μ(Mo-K_α) = 2.7 cm^{-1}. Space group $P2_1/c$, from systematic absences: $0k0$ for k odd, and $h0l$ for l odd.

Crystallographic Measurements.—White needles of $[MeAlNMe]_7$, which reacted rapidly with traces of moist air, were recrystallised from heptane and sealed in thin-walled

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† No reprints available.

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[2] H. Schmidbaur and F. Schindler, *Angew. Chem.*, 1965, **77**, 865; G. A. Razuvaev, S. F. Zhil'tsov, Yu. A. Aleksandrov, and O. N. Druzhkov, *J. Gen. Chem. U.S.S.R.*, 1965, **35**, 1154.

[3] P. B. Hitchcock, G. M. McLaughlin, J. D. Smith, and K. M. Thomas, *J.C.S. Chem. Comm.*, 1973, 934.

[4] K. J. Alford, K. Gosling, and J. D. Smith, *J.C.S. Dalton*, 1972, 2203.

[5] K. Gosling, J. D. Smith, and D. H. W. Wharmby, *J. Chem. Soc.* (*A*), 1969, 1738.

capillaries. Preliminary rotation, Weissenberg, and precession photographs were used to find the space group and initial cell dimensions, which were later adjusted by the least-squares refinement of the angular settings of 12 reflections (mean θ 14°) determined on a Hilger and Watts Y 290 four-circle diffractometer by use of Mo-K_{α} radiation (β filter, $\lambda = 0.710\ 69$ Å). Intensity measurements were based on an ω—2θ scan routine, with checks for instrumental stability and crystal alignment every 40 reflections.

Of 3 356 crystallographically non-equivalent reflections having $1° \leqslant 2\theta \leqslant 42°$, 1 179 reflections having $I_0 \geqslant 3\sigma(I_0)$ were used in the subsequent structure analysis and refinement, with programs of ref. 6(*a*) and atomic scattering factors from ref. 6(*b*). Intensities were corrected for Lorentz and polarization effects but not for absorption.

Structure Solution and Refinement.—Initial attempts to solve the structure from a Patterson synthesis were unsuccessful.

Normalised structure factors $|E|$ were calculated from measured structure amplitudes and the statistical distribution was found closely to resemble the theoretical for the centric case. Reflection phases were generated by a symbolic-addition procedure, using all reflections with $|E| > 1.3$ and an acceptance probability of 0.98. This procedure gave the phases of 165 reflections which were used in an electron-density synthesis, and revealed the positions of all non-hydrogen atoms. A least-squares refinement with isotropic Debye factors minimising the function $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$ and $w = 1/[\sigma(F_o)]^2$, converged with $R = 0.119$, R' 0.137.

TABLE 2

Fractional atomic co-ordinates and thermal parameters, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	10^2U/Å^2
Al(1)	0.271 6(9)	−0.159 8(8)	0.221 3(9)	6.8(5)
Al(2)	0.239 0(9)	−0.029 8(9)	0.090 8(9)	7.6(5)
Al(3)	0.404 4(9)	−0.029 5(9)	0.192 4(8)	6.5(4)
Al(4)	0.305 5(8)	−0.010 5(9)	0.395 4(8)	6.4(4)
Al(5)	0.103 5(8)	−0.013 3(9)	0.269 2(8)	6.0(4)
Al(6)	0.264 3(9)	0.147 0(8)	0.234 5(9)	6.2(4)
Al(7)	0.167 1(9)	0.118 4(8)	0.384 2(9)	5.2(4)
N(1)	0.357 6(18)	−0.087 6(18)	0.301 6(19)	4.7(9)
N(2)	0.340 1(17)	−0.118 9(16)	0.119 6(18)	3.7(8)
N(3)	0.166 9(18)	−0.089 0(17)	0.183 2(18)	4.1(8)
N(4)	0.319 1(18)	0.064 4(18)	0.145 9(18)	5.0(8)
N(5)	0.301 4(19)	0.114 8(18)	0.352 1(18)	5.6(9)
N(6)	0.167 8(19)	−0.014 8(18)	0.384 4(18)	6.5(9)
N(7)	0.135 6(18)	0.114 9(19)	0.250 4(18)	5.6(9)
C(1)	0.257(3)	−0.293(2)	0.267(3)	8.5(14)
C(2)	0.185(3)	−0.005(3)	−0.027(3)	10.8(16)
C(3)	0.543(3)	0.001(3)	0.193(2)	6.8(12)
C(4)	0.358(2)	−0.033(2)	0.516(2)	7.0(13)
C(5)	−0.340(2)	−0.036(2)	0.275(2)	6.3(12)
C(6)	0.285(2)	0.282(2)	0.202(2)	6.6(12)
C(7)	0.115(3)	0.200(3)	0.480(3)	9.2(15)
C(8)	0.436(2)	−0.151(3)	0.335(2)	5.9(12)
C(9)	0.381(3)	−0.181(3)	0.044(3)	8.3(15)
C(10)	0.094(3)	−0.154(3)	0.122(3)	8.0(13)
C(11)	0.365(3)	0.116(3)	0.072(3)	6.3(13)
C(12)	0.383(3)	0.176(3)	0.409(3)	7.7(13)
C(13)	0.132(3)	−0.080(3)	0.466(3)	7.0(13)
C(14)	0.059(2)	0.171(2)	0.202(2)	5.4(11)

A final difference electron-density synthesis showed a maximum value of 0.96 eÅ^{-3} with 20 peaks > 0.8 eÅ^{-3}. Hydrogen-atom positions could not be located clearly. The maximum shift in positional and thermal parameters in the final cycle of refinement was 0.3σ, and mean shift 0.08σ. The error for an observation of unit weight was 3.2. An analysis of $|F_o|$ *vs.* $w\Delta^2$ showed the weighting scheme to be satisfactory. The data were considered insufficiently precise to warrant further refinement. Final atomic co-ordinates and thermal parameters are listed in Table 2, and observed and calculated structure factor amplitudes are given in Supplementary Publication No. SUP 21660 (11 pp., 1 microfiche).*

DISCUSSION

The solid consists of discrete molecules (Figure 1). Within each $(MeAlNMe)_7$ unit, aluminium and nitrogen atoms form a cage, with each nitrogen linked to one methyl group and three aluminium atoms, and each aluminium linked to three nitrogen atoms and one

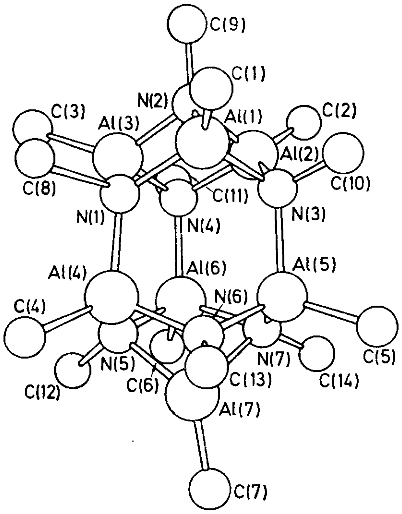

FIGURE 1 The molecule $(MeAlNMe)_7$

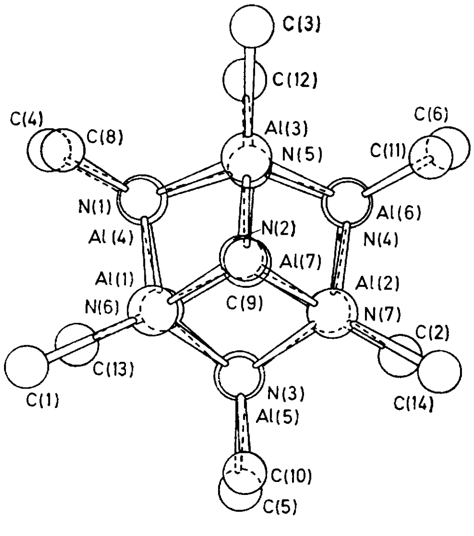

FIGURE 2 The molecule $(MeAlNMe)_7$ viewed along the C_3 axis

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[6] (*a*) '*X*-Ray '70' system of programmes, University of Maryland Technical Report; (*b*) D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

methyl group. All the methyl groups point outwards from the cage. Interatomic distances and valency angles are given in Table 3. No molecular symmetry is required by the space group, but displacements from the mean planes (i)—(iii) (Table 4 and Figure 2) show that the symmetry is, within the limits of the present determination, C_{3v}, with the three-fold axis through N(2) and Al(7).

TABLE 3

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Al(1)–N(1)	1.93(3)	Al(3)–C(3)	1.99(4)
Al(1)–N(2)	1.89(3)	Al(4)–C(4)	1.88(4)
Al(1)–N(3)	1.85(3)	Al(5)–C(5)	2.05(4)
Al(2)–N(2)	1.94(3)	Al(6)–C(6)	2.03(4)
Al(2)–N(3)	1.92(3)	Al(7)–C(7)	1.98(4)
Al(2)–N(4)	1.91(3)	N(1)–C(8)	1.50(5)
Al(3)–C(1)	1.93(3)	N(2)–C(9)	1.55(5)
Al(3)–N(2)	1.87(3)	N(3)–C(10)	1.61(5)
Al(3)–N(4)	1.91(3)	N(4)–C(11)	1.48(5)
Al(4)–N(1)	1.93(3)	N(5)–C(12)	1.63(5)
Al(4)–N(5)	1.91(3)	N(6)–C(13)	1.62(5)
Al(4)–N(6)	1.94(3)	N(7)–C(14)	1.50(4)
Al(5)–N(3)	1.91(3)	C(1)···C(8)	3.35(5)
Al(5)–N(6)	1.85(3)	C(2)···C(10)	3.34(5)
Al(5)–N(7)	1.92(3)	C(2)···C(11)	3.33(5)
Al(6)–N(4)	1.94(3)	C(3)···C(8)	3.40(5)
Al(6)–N(5)	1.81(3)	C(3)···C(11)	3.40(5)
Al(6)–N(7)	1.89(3)	C(4)···C(8)	3.35(5)
Al(7)–N(5)	1.97(3)	C(4)···C(13)	3.29(5)
Al(7)–N(6)	1.92(3)	C(5)···C(10)	3.44(5)
Al(7)–N(7)	1.96(3)	C(5)···C(14)	3.48(5)
Al(1)–C(1)	2.05(4)	C(6)···C(11)	3.28(5)
Al(2)–C(2)	1.85(4)		

(*b*) Angles

N(1)–Al(3)–N(2)	89.1(12)	Al(1)–N(1)–Al(3)	88.5(12)
N(2)–Al(1)–N(1)	88.2(12)	Al(3)–N(2)–Al(1)	91.7(10)
N(2)–Al(2)–N(3)	88.0(11)	Al(1)–N(2)–Al(2)	88.6(11)
N(3)–Al(1)–N(2)	91.6(12)	Al(2)–N(3)–Al(1)	90.6(10)
N(2)–Al(3)–N(4)	90.9(12)	Al(2)–N(2)–Al(3)	89.5(10)
N(4)–Al(2)–N(2)	88.4(11)	Al(3)–N(4)–Al(2)	89.3(11)
N(3)–Al(5)–N(6)	110.8(11)	Al(1)–N(3)–Al(5)	120.9(13)
N(6)–Al(4)–N(1)	109.8(12)	Al(5)–N(6)–Al(4)	120.8(13)
N(1)–Al(1)–N(3)	110.1(12)	Al(4)–N(1)–Al(1)	118.9(10)
N(1)–Al(4)–N(5)	108.7(12)	Al(2)–N(4)–Al(6)	117.7(10)
N(5)–Al(6)–N(4)	111.0(12)	Al(6)–N(7)–Al(5)	119.0(13)
N(4)–Al(3)–N(1)	111.1(12)	Al(5)–N(3)–Al(2)	118.8(12)
N(3)–Al(2)–N(4)	110.4(12)	Al(3)–N(1)–Al(4)	118.9(12)
N(4)–Al(6)–N(7)	110.3(12)	Al(4)–N(5)–Al(6)	123.5(11)
N(7)–Al(5)–N(3)	109.6(12)	Al(6)–N(4)–Al(3)	117.9(13)
N(5)–Al(4)–N(6)	89.5(13)	Al(5)–N(7)–Al(7)	85.9(16)
N(6)–Al(7)–N(5)	88.2(13)	Al(7)–N(6)–Al(5)	89.1(17)
N(7)–Al(7)–N(6)	88.6(13)	Al(4)–N(6)–Al(7)	88.4(16)
N(5)–Al(7)–N(7)	86.3(13)	Al(7)–N(5)–Al(4)	87.8(16)
N(7)–Al(6)–N(5)	93.0(14)	Al(6)–N(7)–Al(7)	86.9(17)
N(6)–Al(5)–N(7)	91.8(14)	Al(7)–N(5)–Al(6)	89.0(17)
C(1)–Al(1)–N(1)	112.5(14)	C(8)–N(1)–Al(1)	107.0(16)
C(1)–Al(1)–N(2)	127.5(14)	C(8)–N(1)–Al(4)	115.4(14)
C(1)–Al(1)–N(3)	121.3(14)	C(8)–N(1)–Al(3)	104.4(15)
C(2)–Al(2)–N(2)	125.4(15)	C(9)–N(2)–Al(1)	126.3(16)
C(2)–Al(2)–N(4)	116.6(15)	C(9)–N(2)–Al(3)	127.4(16)
C(2)–Al(2)–N(3)	121.1(15)	C(9)–N(2)–Al(2)	121.9(17)
C(3)–Al(3)–N(2)	126.7(14)	C(10)–N(3)–Al(1)	108.2(16)
C(3)–Al(3)–N(1)	117.8(14)	C(10)–N(3)–Al(2)	102.8(15)
C(3)–Al(3)–N(4)	116.2(14)	C(10)–N(3)–Al(5)	112.6(15)
C(4)–Al(4)–N(5)	118.2(14)	C(11)–N(4)–Al(2)	109.2(16)
C(4)–Al(4)–N(1)	113.8(13)	C(11)–N(4)–Al(6)	111.8(15)
C(4)–Al(4)–N(6)	114.3(14)	C(11)–N(4)–Al(3)	108.7(14)
C(5)–Al(5)–N(3)	115.6(14)	C(12)–N(5)–Al(4)	109.8(15)
C(5)–Al(5)–N(7)	113.5(14)	C(12)–N(5)–Al(7)	121.6(15)
C(5)–Al(5)–N(6)	113.2(15)	C(12)–N(5)–Al(6)	119.4(16)
C(6)–Al(6)–N(4)	111.8(14)	C(13)–N(6)–Al(4)	108.1(15)
C(6)–Al(6)–N(5)	115.2(17)	C(13)–N(6)–Al(5)	120.4(15)
C(6)–Al(6)–N(7)	114.2(16)	C(13)–N(6)–Al(7)	125.7(15)
C(7)–Al(7)–N(5)	125.1(15)	C(14)–N(7)–Al(5)	114.7(14)
C(7)–Al(7)–N(6)	126.4(15)	C(14)–N(7)–Al(6)	118.8(14)
C(7)–Al(7)–N(7)	129.1(15)	C(14)–N(7)–Al(7)	124.6(13)

TABLE 4

Displacements (Å) from mean planes

Plane (i): N(2),Al(2),N(7),Al(7),Al(4),N(1)
N(2) 0.003, Al(2) −0.006, N(7) 0.010, Al(7) −0.011, Al(4) 0.009, N(1) −0.006, C(9) −0.016, C(2) 0.036, C(14) −0.039, C(7) 0.042, C(4) −0.041, C(8) 0.031

Plane (ii): N(2),Al(1),N(6),Al(7),Al(6),N(4)
N(2) −0.021, Al(1) 0.015, N(6) −0.004, Al(7) 0.000, Al(6) −0.010, N(4) 0.019, C(9) 0.067, C(1) −0.152, C(13) −0.196, C(7) −0.113, C(6) −0.008, C(11) 0.037

Plane (iii): N(2),Al(3),N(5),Al(7),Al(5),N(3)
N(2) −0.004, Al(3) 0.000, N(5) 0.006, Al(7) −0.007, Al(5) 0.002, N(3) 0.002, C(9) 0.068, C(3) 0.003, C(12) −0.138, C(7) −0.073, C(5) 0.014, C(10) 0.136

Angles (°) between normals: (i)–(ii) 119.7, (i)–(iii) 61.0.

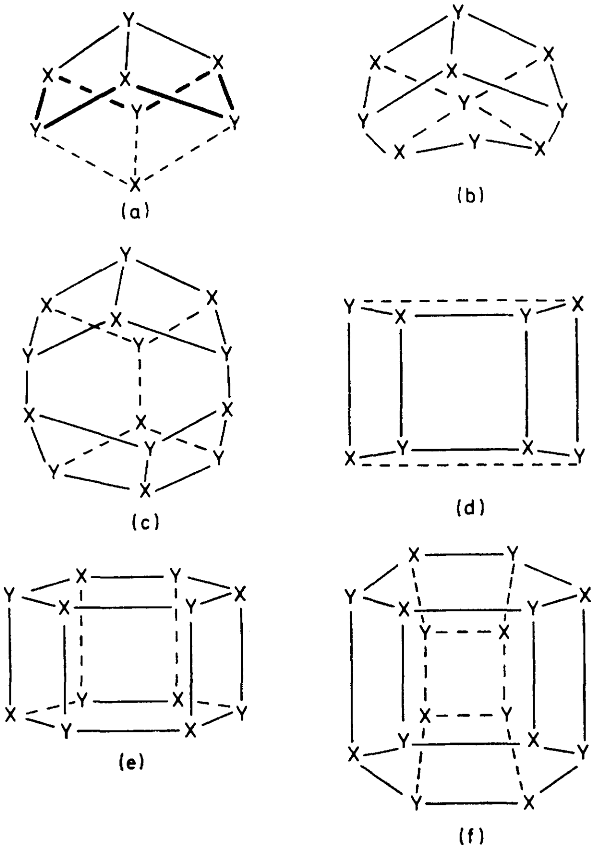

FIGURE 3 Cage structures $(R^1XYR^2)_n$ for (a) $n = 4$: cubane structure trigonally distorted by stretching bonds to one corner; (b) $n = 5$, as in $\mathrm{MeZnSBu^t}$; (c) $n = 7$, as in MeAlNMe; (d) $n = 4$: cubane structure with digonal distortion; (e) $n = 6$, as in $\mathrm{HAlNPr^i}$; and (f) $n = 8$, as in $\mathrm{MeZnSPr^i}$

The mean Al–N bond distance [1.91(4) Å] is comparable to those found in aluminium nitride (1.893 Å) [7] and $(\mathrm{PhAlNPh})_4$ [1.914(5) Å],[8] and shorter than in the com-

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pounds $(Me_2AlNMe_2)_2$ [1.958(5) Å],[9,10] and *cis*-$(Me_2AlNHMe)_3$ [1.940(11) Å].[10] In the cage compound $(HAlNPr^i)_6$[11] Al–N bond distances are 1.898(2) and 1.956(2) Å. Al–C [mean 1.98(7) Å] and N–C [mean 1.56(6) Å] distances are normal.

Bond angles at both aluminium and nitrogen in the four-membered rings are close to 90°. In six-membered rings $(AlN)_3$, the bond angles at nitrogen [mean 111.8(4)°] are greater than those at aluminium [mean 105.9(4)°], as has been found for six-membered rings which are not constrained in cages[10,12] and in the hexamer $(HAlNPr^i)_6$.[11] In the 'capped' ring formed by the atoms Al(1),N(1),Al(3),N(4),Al(2),N(3), the angles at nitrogen are less than those at aluminium, so the μ_3-bridging methylimido-group results in considerable deformation of this ring from the usual pattern. A similar situation arises in the capped six-membered ring of the cubane structure outlined heavily in Figure 3(a). Of the five six-membered rings within the cage, three [Al(1),N(3),Al(5),N(6),Al(4),N(1); Al(2),N(4),Al(6),N(7),Al(5),N(3); and Al(3),N(1),Al(4),N(5),Al(6),N(4)] are in the symmetrical boat conformation and two [Al(1),N(1),Al(3),N(4),Al(2),N(3) and Al(4),N(6),Al(5),N(7),Al(6),N(5)] are in the chair conformation. Various projections along aluminium–nitrogen bonds, showing dihedral angles, are given in Figure 4. Bonds from adjacent atoms are staggered only when the aluminium and nitrogen atoms belong to six-membered rings in the chair conformation [Figure 4(d) and (e)]. Several intramolecular C $\cdots$ C distances (Table 3) are <3.5 Å, showing that the molecule is crowded. In the open-ring compound *trans*-$(Me_2AlNHMe)_3$ methyl–methyl repulsions are relieved by distortion of the aluminium–nitrogen ring from a symmetrical to a twist-boat conformation.[10] This is not possible in the constrained rings in the $(MeAlNMe)_7$ cage.

The molecules are well separated, with no intermolecular C $\cdots$ C distance <3.5 Å. Since the lengths of the unit-cell axes are very nearly equal and the molecules are roughly spherical, it seems probable that the crystal packing is based on a close-packed arrangement. The centre of the reference molecule in the monoclinic unit cell is at approximately $\frac{1}{4},0,\frac{1}{4}$. With the symmetry-related molecules (at $\frac{1}{4},\frac{1}{2},\frac{3}{4}$; $\frac{3}{4},\frac{1}{2},\frac{1}{4}$; and $\frac{3}{4},0,\frac{3}{4}$), the array is approximately face-centered cubic and the molecules are oriented so that the molecular three-fold axes are along body diagonals of the face-centred cubic unit cell.

Mass spectra of the compounds RAlNMe (R = Me[4] or Et[5]) show strong peaks corresponding to the loss of one R group from the parent ions $(RAlNMe)_7^+$; there are also weak peaks due to the parent ions themselves. It seems that heptameric structures for both compounds are preserved both in solution and in the vapour. The octameric formulae previously reported[4,5] are clearly not correct.

It is of interest to inquire how the structure of the heptameric compound $(MeAlNMe)_7$ is related to those of other oligomeric species $(R^1XYR^2)_n$. For values of $n < 4$, where the $(XY)_n$ system is linear or planar, and for the compounds $(R^1BNR^2)_4$, which have open-ring rather than cage structures, it is necessary to postulate multiple bonding, if X and Y are to have complete octets. In compounds with $n \geqslant 4$, the X and Y atoms form cages, with four- or six-membered rings. Eight-membered rings are in principle possible, but they have not so far been established in cages of this kind. If the atoms X and Y have complete octets, the number of X–Y bonds in the cage oligomer $(R^1XYR^2)_n$ is $3n$ and, since each bond is shared between two rings, the numbers of four-membered rings p and six-membered rings q are related by $4p + 6q = 6n$. Further, the numbers of rings $p + q$, vertices $2n$, and bonds are related by

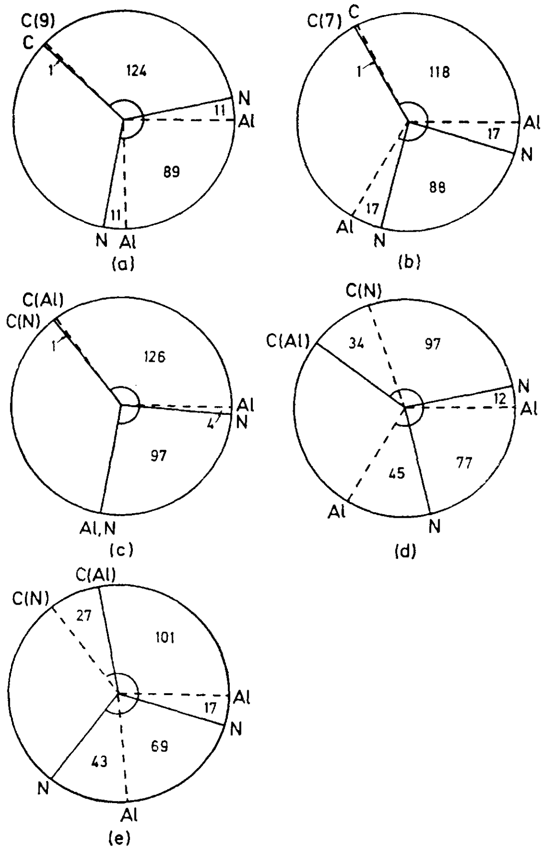

FIGURE 4 Projections along Al–N bonds, showing mean dihedral angles (°), averaged over the bonds related by the C_3 axis, for (a) Al(1)–N(2), Al(2)–N(2), and Al(3)–N(2); (b) Al(7)–N(5), Al(7)–N(6), and Al(7)–N(7); (c) Al(4)–N(1), Al(5)–N(3), and Al(6)–N(4); (d) Al(1)–N(1), Al(1)–N(3), Al(2)–N(3), Al(2)–N(4), Al(3)–N(4), and Al(3)–N(1); and (e) Al(4)–N(5), Al(4)–N(6), Al(5)–N(6), Al(5)–N(7), Al(6)–N(7), and Al(6)–N(5). For (d) and (e), the projections along half the bonds are the mirror images of those shown

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Euler's theorem, so that $p + q = n + 2$. Integral values of p and q which satisfy these conditions are given in Table 5. The compounds already established (*i.e.* with n = 4—8) form a related series, in which the geometrical relations are shown in more detail in Figure 3. Removal of one corner of the cubane, leaving a fragment $(R^1XYR^2)_3YR^2$ [Figure 3(a)], followed by the insertion of a fragment $(R^1X)_2YR^2$ yields the pentameric structure of $(MeZnSBu^t)_5$ [Figure 3(b)]. Combination of two fragments $(R^1XYR^2)_3YR^2$ and $(R^1XYR^2)_3R^1X$ yields the heptameric structure of $(MeAlNMe)_7$. Breaking two bonds of the cubane structure gives the fragment $(R^1XYR^2)_4$ [Figure 3(d)]. Insertion of a fragment $(R^1XYR^2)_2$ gives the hexameric structure of $(HAlNPr^i)_6$ [Figure 3(e)], and combination of two fragments of Figure 3(d) gives the octameric structure of the compound $(MeZnSPr^i)_8$ [Figure 3(f)]. It is possible to envisage other members of this series of oligomers. For example, another six-membered ring could be inserted in the structure of $(MeAlNMe)_7$, *e.g.* between the capping atom Al(7) and the ring Al(4),N(6),Al(5),N(7),Al(6),N(5). The molecule would have the formula $(R^1XYR^2)_{10}$ with 6 six-membered and 6 four-membered rings.

TABLE 5

Numbers of four-membered rings (p) and six-membered rings (q) in cage compounds $[R^2XYR^2]_n$

n	4	5	6	7	8
p	6	6	6	6	6
q	0	1	2	3	4

The factors which determine the values of n shown by particular oligomeric molecules $(R^1XYR^2)_n$ are presumably similar to those discussed earlier for the series of oligomers $(R^1{}_2XYR^2{}_2)_n$.[13] As n increases (Table 5), p/n (the number of four-membered rings per XY unit) decreases, and q/n (the number of six-membered rings per XY unit) increases. The thermodynamic driving force for the formation of oligomers with larger values of n from oligomers with smaller values of n is probably the relief of ring strain, or, in other words, the more favourable orbital overlap possible, as six-membered replace four-membered rings. This driving force must be sufficient to balance the unfavourable entropy contribution to the free energy of formation of oligomers with larger n from those with smaller n, and must also not be offset by steric hindrance between substituents R^1 and R^2. It is probable that, as for the compounds $(R^1{}_2AlNR^2{}_2)_n$, steric interactions between *N*-substituted groups are more important than those between *Al*-substituted groups. Thus the compounds (MeAlNMe) and (EtAlNMe) are heptameric, but the t-butylimido-derivatives $(EtAlNBu^t)$ and $(HAlNBu^t)$ and the compounds (PhAlNAr) (Table 1) are tetrameric. In magnesium–oxygen (isoelectronic with aluminium–nitrogen) cages, $(EtMgOPr^n)$ and (Pr^iMgOR^2) (R^2 = Me or Et) are hepta- or octameric, but $(EtMgOR^2)$ ($R^2 = Bu^t$ or Pr^i) and (Pr^iMgOPr^i) are tetrameric. Thus, although the higher oligomer is formed with a branched substituent R^1 at magnesium, branching in the substituent R^2 at oxygen leads to the lower oligomers. Steric interactions between substituents R^2 may account for the higher values of n shown by sulphur compounds, compared with corresponding oxygen derivatives.

The formation of oligomeric aluminium–nitrogen compounds requires careful control of the reaction conditions. Indeed, the compound (MeAlNMe) was first isolated as an involatile, glassy material.[14] The glassy forms of the compounds R^1AlNR^2 dissolve with difficulty in hydrocarbons and contrast strongly with the highly soluble crystalline forms. They are best made in reactions without solvents and are probably poly- rather than oligo-meric, with irregular cross-linked aluminium–nitrogen chains. Further work is necessary to elucidate the process whereby the trimeric precursors *cis*- and *trans*-$(Me_2AlNHMe)_3$ are converted into the heptameric compound $(MeAlNMe)_7$.

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