Complexes of Organoaluminium Compounds. Part VII.[1] Preparation and Spectra of *cis*- and *trans*-Cyclotri-μ-methylamido-tris(dimethylaluminium) and Some Related Compounds

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Trimethylaluminium–methylamine decomposes at 50 °C with evolution of methane to give *cis*- and *trans*-cyclotri-μ-methylamido-tris(dimethylaluminium), $(\mathrm{Me_2AlNHMe})_3$, which may be separated by fractional sublimation. The solid isomers are stable in vacuum for long periods but readily interconvert in organic solvents. N.m.r., vibrational, and mass spectra are reported. Above 150 °C, the compounds decompose with formation of products, including $(\mathrm{MeAlNMe})_8$, the molecules of which are presumed to be based on condensed aluminium–nitrogen frameworks.

THE reaction between trimethylaluminium and a stoicheiometric quantity of methylamine was first studied by Wiberg,[2] who showed that the donor–acceptor complex formed at low temperatures decomposed at *ca.* 55 °C to give methane and white needles of empirical formula $\mathrm{Me_2AlNHMe}$. These released further methane above 110 °C with formation of an involatile, glassy solid, presumed to be polymeric. No information was given about the molecular complexities or the structures of the condensation products, and so we thought that more detailed examination of these materials would be worthwhile.

$$nm\mathrm{Me_3Al,NH_2Me} \xrightarrow{55^\circ} m(\mathrm{Me_2AlNHMe})_n + mn\mathrm{CH_4} \xrightarrow{110^\circ} (\mathrm{MeAlNMe})_{mn} + 2mn\mathrm{CH_4} \qquad (1)$$

We quickly confirmed the reported stoicheiometry [Equation (1)], but the n.m.r. spectrum of a solution in benzene of the needles $\mathrm{Me_2AlNHMe}$, obtained after recrystallisation from hexane, suggested the presence of more than one molecular species in solution. We therefore heated a sample of the adduct $\mathrm{Me_3Al,NH_2Me}$ in toluene to 70 °C for several hours, and, after removal of solvent, carefully sublimed the product in vacuum. Two crystalline substances were obtained. Both analysed correctly for $\mathrm{Me_2AlNHMe}$, both showed molecular weights in freezing benzene corresponding to trimeric species, and both gave the same i.r. and n.m.r. spectra in solution. The more volatile substance (2) formed block-like crystals, which grew till they were several mm across, during some weeks at 20 °C in evacuated sealed ampoules, but, whenever these crystals were manipulated under nitrogen, bundles of fine needles, which appeared to be the less volatile substance, (1) grew from the surface. The nitrogen used in the preparative work thus appeared to contain an impurity which catalysed the transformation of the more to the less volatile substance. Needles of the less volatile substance could be manipulated in a nitrogen-filled dry-box and sublimed without apparent change. Single crystals were studied by *X*-ray methods and the cyclic molecules of the two substances were shown to differ in the configuration of the substituents at one nitrogen.[1] The substances are thus stereoisomers, (1) and (2).[3]

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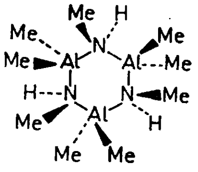
[1] Part VI, G. M. McLaughlin, G. A. Sim, and J. D. Smith, preceding paper.

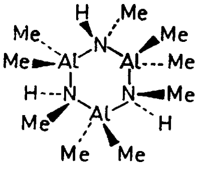
[2] Work described by G. Bähr, F.I.A.T. Review of German Science, 1939—1945, Inorganic Chemistry Part II, p. 159.

[3] K. Gosling, G. M. McLaughlin, G. A. Sim, and J. D. Smith, *Chem. Comm.*, 1970, 1617.

In the solid, molecules (1) adopt a chair conformation, with all *N*-methyl substituents equatorial. The molecules (2) adopt skew-boat conformations, (2a) and (2b),

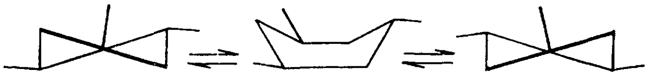


(1)
cis-



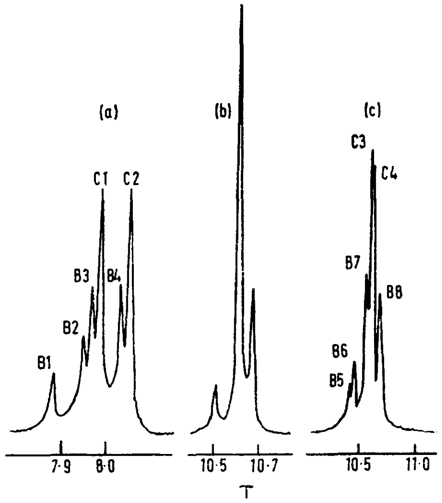
(2)
trans-

which arise by small distortions of the symmetrical boat (2c), in which all *N*-methyl groups point outwards from the ring (*Al*-methyl groups are omitted from these structures. See Figure 2 of ref. 1).



(2a) (2c) (2b)

Triethylaluminium and methylamine react similarly to give ethane and two compounds (Et$_2$AlNHMe)$_3$ which can be separated by distillation.[4] It is probable that the two fractions so obtained are *cis*- and *trans*-isomers analogous to the dimethylaluminium compounds. The liquid (Me$_2$AlNHEt)$_3$ was also made. The *cis*- and *trans*-isomers were not obtained by distillation but n.m.r. spectra suggested that more than one molecular species was present in solution. Stereoisomers of borazanes (H$_2$BNHR)$_n$ [5] and gallazanes (H$_2$GaNHR)$_n$ [6,7] have been characterised.



The n.m.r. spectrum of (Me$_2$AlNHMe)$_3$ in C$_6$D$_5$CD$_3$ at −30°; (a) *N*-methyl, (b) *Al*-methyl, and (c) *Al*-methyl region in the presence of an excess of methylamine

N.m.r. Spectra.—The spectrum obtained from a solution of *cis*-(Me$_2$AlNHMe)$_3$ in C$_6$D$_5$CD$_3$ is shown in the Figure. The resonance at *ca.* τ 8 (relative to trimethylsilane), attributed to protons of methyl groups attached to nitrogen, consists of three doublets, each with separation 6·7 Hz. There is a broad, weak and featureless signal at *ca.* τ 9·7, assigned to protons attached directly to nitrogen. Irradiation in the region of this signal leads to the collapse of the doublets at lower field into a single resonance with the same structure (one weak and two stronger peaks) as before. The signal at τ 10·6, (b), attributed to protons of methyl groups attached to aluminium, consists of three peaks; at high resolution, the central peak is split into a closely spaced (3 Hz at 100 MHz) unsymmetrical doublet. The shape of the high-field resonance is unaffected by irradiation at the frequency of the *N*-Me protons, so long-range coupling between *N*-Me and *Al*-Me protons is ruled out. The n.m.r. spectra changed remarkably little over the temperature range from −65 to +65 °C, apart from small variations in peak heights. The peaks became more widely separated at lower temperatures, perhaps owing to more anisotropic solvation. Similar, but not identical, spectra were reported[6] from the compounds (Me$_2$GaNHMe)$_3$.

It is clear that the spectrum (Figure) cannot arise solely from the molecules of the *cis*-isomer originally present in the solid. These molecules have three equivalent *N*-methyl substituents, which would give a doublet in the low-field region of the n.m.r. spectrum, by coupling to adjacent protons, and two sets (axial and equatorial) of three equivalent *Al*-methyl substituents, which would give two equally intense signals at high field. The axial and equatorial *Al*-methyl protons do not become equivalent, like the axial and equatorial protons of cyclohexane, by rapid changes in ring conformation, since the two exocyclic groups attached to each nitrogen are different. Some of the molecules in the *cis*-isomer (1) must therefore have changed before the spectrum was recorded. In an attempt to obtain spectra of the separate isomers, each uncontaminated by other molecular species, a sample was sublimed in apparatus to which n.m.r. tubes were connected. The separated fractions were washed into the n.m.r. tubes with freshly distilled C$_6$D$_5$CD$_3$, and the sealed tubes were immediately cooled to −40 °C while spectra were recorded. Very similar spectra were obtained from the two isomers, suggesting that an equilibrium mixture is established in aromatic solvents within a few minutes at 20 °C.

The n.m.r. spectra may be understood, if it is assumed that the molecular species in solution are the *cis*- and *trans*-isomers, (1) and (2), which interconvert slowly on the n.m.r. time scale. Full assignment of the high-field (*Al*-methyl) part of the spectrum is not obvious because peaks due to the two isomers overlap. Similar spectra were obtained from solutions in dimethyl ether and dichloromethane, but

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

[5] D. F. Gaines and R. Schaeffer, *J. Amer. Chem. Soc.*, 1963, **85**, 395; M. P. Brown, R. W. Heseltine, and L. H. Sutcliffe, *J. Chem. Soc.* (*A*), 1968, 612.

[6] A. Storr, *J. Chem. Soc.* (*A*), 1968, 2605.

[7] A. Storr and A. D. Penland, *J. Chem. Soc.* (*A*), 1971, 1237.

more features were apparent on spectra in trimethylamine. The high-field region [Figure (c)] from a solution in $C_6D_5CD_3$–methylamine at −30 °C shows six clearly resolved peaks: peaks B5—8 may be assigned to the *trans*-isomer and peaks C3 and 4 to the *cis*-isomer. In benzene and toluene, peaks B6 and 7 and peaks C3 and 4 are incompletely resolved within the largest high-field peak [Figure (b)]. There is also some evidence that in toluene at 40 °C the *N*-hydrogen resonance is incompletely resolved from the *Al*-methyl peak B5. In principle, it should be possible to find the ratio of the concentrations of *trans*- and *cis*-isomers, *K*, from the areas under the n.m.r. peaks. In practice, there are difficulties because the peaks are not completely resolved, but areas may be checked for mutual consistency by comparison of the *N*-methyl spectra at 60 and 100 MHz. Approximate values of the equilibrium constant, *K*, at various temperatures, *T*, are given in Table 1; spectra at lower temperatures were not used because the peaks were broad and because there was uncertainty about whether equilibrium was attained. From a plot of *K vs.* $1/T$, the following were derived for the reaction *cis*-$(Me_2AlNHMe)_3 \rightarrow$ *trans*-$(Me_2AlNHMe)_3$ in toluene: ΔH, 6 kJ mol^{-1}; ΔS 26 J K^{-1} mol^{-1}. The value of *K* found at 20 °C is <3, the value for random configurations of *N*-methyl substituents. The enthalpy difference between the chair and boat forms of the $(AlN)_3$ ring is less than that (*ca.* 25 kJ mol^{-1}) between chair and boat forms of cyclohexane rings.[8] The value found for ΔS is greater than that for the conversion of *cis*- to *trans*-1,3,5-trimethylcyclohexane,[9] which is close to the value ($\mathbf{R}\ln 3$), derived from the ratio of the rotational partition functions. The greater entropy difference between *cis*- and *trans*-$(Me_2AlNHMe)_3$ may perhaps be attributed to solvation effects and to greater vibrational entropy in the flexible *trans*-isomer, with contributions from low-frequency Al–N bending modes. A similar difference in entropy was found for *cis*- and *trans*-1,3-di-t-butylcyclohexane which show, respectively chair and boat conformations in solution.[8]

TABLE 1

The ratio of concentrations of *trans*- and *cis*-$(Me_2AlNHMe)_3$ at various temperatures, *T*, in $C_6D_5CD_3$

T/°C	27	6	−8	−16	−23	−30	−40
[*trans*-]/[*cis*-], *K*	1·9	1·6	1·5	1·4	1·1	1·0	0·95

The slight variation of the n.m.r. spectra over a wide temperature range is evidence against the alternative postulate that the trimeric molecules of the solid give molecules of various complexities in solution. Different oligomers would give different translational entropies, and the proportions would change markedly with temperature.

N.m.r. spectra correspond to the average of the various conformations which the molecules may adopt in solution. Since steric hindrance is more serious between *N*- than between *Al*-methyl axial substituents,[1,3] the predominant conformation of the *cis*-isomer in solution is almost certainly that found in the solid, with all *N*-methyl substituents equatorial. The small difference in chemical shifts between axial and equatorial *Al*-methyl substituents (C3, 4), compared with shifts between axial and equatorial *C*-methyl protons in cyclohexane derivatives (*e.g.* 0·14 p.p.m. in *trans*-1,3,5-trimethylcyclohexane[10]), probably results from the longer Al–N and Al–Al distances compared with C–C distances in cyclohexane [Al–N 1·95, Al–Al 3·40, and N–N 3·01 Å; compare C(1)–C(2) 1·54, C(1)–C(3) 2·50 Å in C_6H_{12}]. For the more flexible *trans*-isomer, a variety of boat forms is accessible by pseudo-rotations, but, if the *N*-methyl substituents avoid 'bowsprit' positions, the most probable conformations are (2a) and (2b). Chemical shifts between protons of methyl substituents on the same aluminium atom, which point on opposite sides of the ring are appreciably greater for the boat than for the chair conformation (compare, *e.g.*, B5, 6; C3, 4). The reasons for this are not obvious and a complete account of chemical shifts must include solvent as well as intramolecular interactions. Attempts to distinguish conformations in solution from chemical shifts seem to be unreliable; considerable solvent effects have been noticed recently in similar systems.[11]

The n.m.r. spectra of both[4] compounds $(Et_2AlNHMe)_3$ in cyclopentane or benzene provide similar evidence for the formation of a mixture of *cis*- and *trans*-isomers. The *N*-methyl part of the spectrum consists of three doublets (*J* 6·5 Hz) with similar chemical shifts relative to the solvent peak; the absorption due to the β-protons of the *Al*-ethyl groups also consists of three overlapping triplets. The signal due to the α-protons of the *Al*-ethyl groups is broad and complex: this complexity arises not only because of inequivalence between *Al*-ethyl groups, but also because of magnetic inequivalence between α-protons of each ethyl group.[4] It was not possible accurately to determine the proportions of the isomers, because there was too much overlap between peaks, but a rough estimate from the *N*-methyl signal in cyclopentane at 30 °C indicated *ca.* 30% of the *trans*-isomer. The spectra of the neat liquids were less well resolved than spectra from solutions.

The spectrum of $(Me_2AlNHEt)_3$ in toluene at 30 °C shows two triplets, with relative intensities 3·6 : 1, assigned to the β-protons of the *N*-ethyl group. The *Al*-methyl region is dominated by two closely spaced equally intense peaks, but, on either side, there are distinct shoulders with relative intensity 2 : 1. This spectrum suggests that the dominant species in solution is the *cis*-isomer, having the symmetrical chair conformation with all *N*-ethyl groups equivalent and equatorial, and with two kinds (axial and equatorial) of *Al*-methyl

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[8] N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, 1960, **82**, 2393.

[9] C. J. Egan and W. C. Buss, *J. Phys. Chem.*, 1959, **63**, 1887.

[10] A. Segre and J. I. Musher, *J. Amer. Chem. Soc.*, 1967, **89**, 706.

[11] K. Gosling, A. L. Bhuiyan, and K. R. Mooney, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 913.

group. The proportion of the *trans*-isomer is probably <20%.

Transaminations between amidoaluminium compounds and excess of amines are known [4] to proceed easily at or below 20 °C. The spectra of $(Me_2AlNHMe)_3$ in methylamine at −25 °C show that exchange between uncombined and combined methylamine [equation (2)] is

$$(Me_2AlNHMe)_3 + Me^*NH_2 \longrightarrow (Me_2AlNHMe)_2(Me_2AlNHMe^*) + MeNH_2 \quad (2)$$

slow on the n.m.r. time-scale. At 30 °C, however, most of the structure of both the *N*- and *Al*-methyl resonances is lost, and single, but not quite symmetrical, peaks, corresponding to an average for uncombined and combined amine, are obtained. The rapid exchange between free and combined amine probably involves ring-opening reactions which convert one isomer of $(Me_2AlNHMe)_3$ into the other.

Vibrational Spectra.—I.r. spectra of *cis*- and *trans*-$(Me_2AlNHMe)_3$, as Nujol mulls, showed no significant difference. Raman spectra from samples in sealed ampoules were different (Table 2), particularly in the region 300—600 cm^{-1}, but a quantitative comparison of intensities could not be made. The more volatile *trans*-isomer, after being set aside at 20 °C for some days, formed large well-developed crystals which gave a better spectrum than the needles of the *cis*-isomer. Spectra of solutions were all weak, because of the low solubility of the aluminium compounds, but the peaks which were observed corresponded with those of the symmetrical *cis*-isomer. In view of the n.m.r. evidence, it must be assumed that these are more intense than the peaks of the *trans*-compound. Most of the bands at wavenumbers >600 cm^{-1} can be assigned by comparisons with similar compounds. The strong bands at 505 cm^{-1} in the *trans*- and at 579 and 460 cm^{-1} in the *cis*-compound are probably associated mainly with stretching vibrations of the $(AlN)_3$ rings, but considerable interactions between vibrations of the same symmetry are expected. From the rather poor polarisation data from solution spectra, the bands at 579 and 460 cm^{-1} can be associated, respectively, with e and a_1 vibrations expected for a molecule with C_{3v} symmetry.

TABLE 2

Vibrational spectra (cm^{-1}) of *cis*- and *trans*-$(R_2AlNHMe)_3$ [a]

(*a*) $(Me_2AlNHMe)_3$

I.r.	Soln. in CH_2Cl_2: 3340m, 3320sh, 3290m, 3280sh, 2940s, 2910s, 2830m, 1605m, 1460m, 1330w, 1195s, 1140w, 1048m, 1000m, 975s, 950m, 800—700vs,vb, 610s, 585sh,m, 550vw, 495vw, 470vw
Raman	*cis*-Isomer (solid): 1184w, 986w, 961w, 685m, 612m, 579s, 460vs, 305m, 293s, 203m, 176s, 136s
	trans-Isomer (solid): 1196m, 1052w, 732vw, 688w, 662w, 602s, 505vs, 477w, 328s, 289m, 208m, 194sh, 164m, 144m
	Soln. in C_5H_{10}: 594p, 564d, 432p, 298d, 277p

(*b*) $(Et_2AlNHMe)_3$

I.r.	*cis*-Isomer: 3313vw, 3268m, 2988m-s, 2938vs, 2904vs, 2867vs, 2798m, 2732w, 1468m, 1410m, 1378w, 1330m, 1232m, 1197m, 1143m, 1108w, 1065m, 1045m, 1027m, 975vs, 953s, 937s, 905s, 833m, 807m, 654vs, 627vs,b, 470w,b
	trans-Isomer: 3312m,[b] 3271vw, 660vs,b, 630vs,b, 552m, 478m
Raman	*cis*-Isomer: 3262w,p, 2930s,d, 2897s,d, 2863s,d, 2823w,p, 2793m,p, 2727w,p, 1470m,d, 1431m,d, 1407m,d, 1379w,d, 1327w,d, 1306w,d, 1230w,d, 1198s,d, 1143vw, 1092w,p, 1023w,d, 993s,d, 960m,d, 906w, 872w,p, 627m,d, 554s,p, 528sh,d, 477s,p, 424vs,p, 376m,d, 298m,p, 257w, 190m,p, 114m
	trans-Isomer: 3312w,[b] 636m,d, 563m,p, 478vs,p, 457m,d, 378s,p, 273m,p, 189m,d, 109m,d

[a] s = Strong, m = medium, w = weak, v = very, sh = shoulder, b = broad, p = polarised, d = depolarised. [b] Between 3000 and 600 cm^{-1} the spectra of the *cis*- and *trans*-isomers were very similar.

The i.r. and Raman spectra of the compounds $(Et_2AlNHMe)_3$, isolated previously, differ significantly in the NH stretching region, 3250—3350 cm^{-1}, and below 500 cm^{-1}. The Raman spectrum of the more volatile compound is dominated by a strong peak at 478 cm^{-1}. The spectrum of the less volatile compound has two strong absorptions at 554 and 424 cm^{-1}. The low-frequency regions of the spectra of the compounds $(Me_2AlNHMe)_3$ and $(Et_2AlNHMe)_3$ are thus superficially similar.

Mass Spectra.—The mass spectrum from a sample of *trans*-$(Me_2AlNHMe)_3$ confirms the presence of trimeric species in the vapour. Strong peaks arise also from dimeric species and there is a metastable peak corresponding to the elimination of monomer. As with other organoaluminium compounds,[4,12] the parent ion is not observed and the strongest peaks in the spectrum correspond to loss of methyl from the trimer and dimer ions. Accurate mass measurements (Table 3) and metastable peaks showed that the predominant fragmentation was by loss of methyl from the trimer and dimer ions, giving the strongest peaks in the spectrum, followed by a series of hydrogen abstractions with elimination of methane or methylamine. Elimination

TABLE 3

Mass spectrum of $(Me_2AlNHMe)_3$

m/e	Intensity [a]	Assignment	Deviation from calc./p.p.m.	Metastable peaks	*m**
247	12				
246·16480	100	$Me_5Al_3N_3H_3Me_3^+$	−1·2		
230·13177	14	$Me_4Al_3N_3H_2Me_3^+$	−9·0	246—16	215
215·12330	24	$Me_5Al_3N_2HMe_2^+$	+6·0	246—31	187·9
199·09313	8	$Me_4Al_3N_2Me_2^+$	+7·6	230—31	172·3
174	18				
160	8				
159·10128	82	$Me_3Al_2N_2H_2Me_2^+$	−5·8	246—87	102·8
143·07106	40	$Me_2Al_2N_2HMe_2^+$	+0·8	159—16	128·6
128	10	$Me_3Al_2NMe^+$		159—31	103·0
114	17				

[a] As % strongest peak. [b] Other strong peaks at *m/e* 86, 72, 58, and 43.

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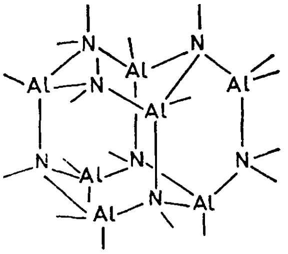
[12] D. B. Chambers, G. E. Coates, F. Glockling, and M. Weston, *J. Chem. Soc.* (*A*), 1969, 1712; J. Tanaka and S. R. Smith, *Inorg. Chem.*, 1969, **8**, 265.

of hydrogen or ethane was observed in the mass spectrum of $(Et_2AlNHMe)_2$, but, in this compound, fragmentation by elimination of ethylene (not available for methylaluminium compounds) was more important.[4] The mass spectrum of *cis*-$(Me_2AlNHMe)_3$ was similar to that of the *trans*-isomer, except that ions from the fragmentation of the dimer were more intense than those from the trimer. This is probably simply a consequence of the higher inlet and source temperatures required to obtain a spectrum of the less volatile compound. Ions from the trimer could not be observed in the mass spectrum of $(Me_2AlNHEt)_3$. The strongest peak resulted from loss of methyl from the dimer: subsequent eliminations of methane, ethylamine and $MeCH{:}NH$ were also apparent.

Thermal Decomposition of $(Me_2AlNHMe)_3$.—Although the solid of empirical formula MeAlNMe, obtained by Wiberg[2] was involatile and glassy, we obtained crystalline products by effecting the reaction in organic solvents. These products, with composition $(Me_2AlNHMe)_x(MeAlNMe)_y$ were extremely sensitive towards oxidation, were very soluble in benzene and toluene, and could be sublimed in vacuum. Determination of x and y in the molecular formulae by chemical analyses was difficult, and cryoscopic determinations of high molecular weights were rather uncertain. Cage-like structures, based on aluminium–nitrogen frameworks, with methyl groups pointing outwards, would be consistent with the high solubility of these substances. Two crystalline materials were characterised. For the first, the formula $(Me_2AlNHMe)_3(MeAlNMe)_4$ seems best to fit the available data, including the n.m.r. spectrum, which is consistent with the presence of 7, or 8 but not 6 *N*-methyl groups and 10 *Al*-methyl groups. An N–H vibration frequency at 3247 cm^{-1} shows in the i.r. spectrum: (3) represents a possible structure for the Al–N cage.



(3)

The second crystalline material has no N–H band in the i.r. spectrum, and seems to be the octamer $(MeAlNMe)_8$ analogous to the ethylaluminium compound reported previously.[4] The n.m.r. spectrum, which shows three *N*-methyl peaks (relative intensities 1 : 4 : 3) and three *Al*-methyl peaks (relative intensities 2 : 3 : 3) is not consistent with a structure of symmetry $\bar{4}$, like that found for the compound $(MeZnSPr^i)_8$.[13] Single-crystal data for $(MeAlNMe)_8$ have been collected but attempts to solve the structure by both Patterson syntheses and direct methods have so far been unsuccessful.[14]

EXPERIMENTAL

Air and moisture were excluded as rigorously as possible from all reactions. Trimethylaluminium was manipulated in a vacuum line with mercury float valves. Methylamine was dried with sodium, and solvents with sodium or with lithium aluminium hydride. Solutions were manipulated in Schlenk tubes or in a dry-box filled with nitrogen from which oxygen was removed by a BASF copper catalyst. Compounds were analysed by hydrolysing small samples with 2N-sulphuric acid, and collecting the methane evolved in a Toepler pump. This estimated only methyl groups attached to aluminium. Aluminium and amine contents of the aqueous hydrolysate were determined separately. Molecular weights were measured cryoscopically in benzene.

N.m.r. spectra were recorded on Varian HA 100 or A 60 or Perkin-Elmer R 10 spectrometers, i.r. spectra on Perkin-Elmer 237 or 337 spectrometers, Raman spectra on a Codberg PH 1 instrument by use of a helium–neon laser. Mass spectra were obtained at 70 eV on an AEI MS 9 instrument.

Reactions between Trimethylaluminium and Methylamine. (a) *Below* 0 °C. No attempt was made to characterise the adduct formed exothermically from trimethylaluminium and methylamine below 0 °C. It sublimed in vacuum at 40—50 °C and was freely soluble in toluene, but less so in hexane.

(b) *Between* 0 *and* 100 °C. When the adduct from Me_3Al (1·30 g, 18·1 mmol) and methylamine (18·1 mmol) was warmed to 70 °C for 4 h, methane (18·1 mmol) was evolved. The white residue was sublimed at 10^{-3} mmHg up a tube 30 cm × 20 mm, surrounded by a tightly fitting copper sleeve of which the bottom 5 cm were heated to 85 °C. This gave as the more volatile fraction, block-like crystals of trans-*cyclo-tri-μ-methylamido-tris*(*dimethylaluminium*), m.p. 109—111 °C [Found: Me, 35·0; Al, 31·7; MeNH, 34·4%; *M*, 263. $(Me_2AlNHMe)_3$ requires Me, 34·5; Al, 31·0; MeNH, 34·5%; *M*, 261] and, as the less volatile fraction, needles of the cis-*isomer*, m.p. 113—114 °C [Found: Me, 34·8; Al, 30·7%; *M*, 267]. Both isomers were soluble in hydrocarbon solvents and dichloromethane; the *cis*-isomer was the less soluble in hexane at 0—30 °C and was obtained in recrystallisations.

(c) *Above* 100 °C. In several experiments, samples of the adduct Me_3Al,NH_2Me in xylene or tetralin were heated to 150°. Methane was evolved, but crystallisable products could not be obtained from the dark brown solutions. When Me_3Al,NH_2Me (12·7 mmol) in toluene (10 ml) was heated for 24 h at 180 °C in a sealed tube, methane (22·6 mmol) was evolved. The product, which was very soluble in toluene, was obtained as a white solid, m.p. 262—265 °C after five recrystallisations from heptane [Found: Me, 28·6; Al, 34·7%; *M*, 489. $(Me_2AlNHMe)_3(MeAlNMe)_4$ requires Me, 27·8; Al, 34·7%, *M*, 545]. I.r. spectrum (mull): 3247w, 3028w, 3005w, 2960vs, 2920vs, 2895vs, 2816m, 1459s, 1365s, 1335w, 1277b,m, 1207m, 1130m, 1074w, 1052w, 993s, 976s, 951s, 930m, 758s, 740s, 712b,s, 674s, 643m, 604m, and 580m cm^{-1}; n.m.r. spectrum in benzene (intensities in parentheses): τ 7·53 (1·5), 7·59 (1·5), 7·78 (1),

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[13] G. W. Adamson and H. M. M. Shearer, *Chem. Comm.*, 1969, 897.

[14] G. M. McLaughlin, G. A. Sim, and J. D. Smith, unpublished results.

7·82 (1), 7·91 (1), 8·02 (1), 10·37 (2), 10·44 (4), 10·50 (2), and 10·66 (2); *Al*-Me to *N*-Me (by integration), 1·3—1·5. In another experiment, Me_3Al,NH_2Me (146 mmol) in toluene (25 ml) was heated at 215 °C for 27 h in a stainless-steel autoclave with a glass liner. The methane was blown off and the brown residue after removal of solvent was crystallised repeatedly from heptane, yielding white *needles* [Found: Me, 21·3; Al, 37·4%; *M*, 585. $(MeAlNMe)_8$ requires Me, 21·2; Al, 38·0; *M*, 568]. I.r. spectrum (mull): 3084w, 3030w, 2932vs, 2910vs, 2890vs, 2872sh,s, 2807vs, 1550vw, 1462s, 1424m, 1275m,b, 1200vs, 1140m, 1117s, 1089m, 1050vs, 1033sh,s, 1020sh, s, 975sh, s, 950vs, 860m, 777sh,s, 760vs,b, 685vs,b, 583m, 550s, and 488m cm^{-1}; n.m.r. spectrum in benzene (relative intensities in parentheses): τ 7·17 (1), 7·34 (4), 7·51 (3), 10·31 (2), 10·33 (3), and 10·41 (3). The compound sublimed slowly in vacuum at 180 °C.

Reaction between Trimethylaluminium and Ethylamine.—When Me_3Al (2·26 g, 31·4 mmol) and ethylamine (1·41 g, 31·4 mmol) were condensed together, an adduct, liquid at 20 °C, was formed by an exothermic reaction. After heating to 70 °C for 6 h, methane (31·2 mmol) was collected and the residue was distilled. Only one fraction, b.p. 72—73 °C, at 10 mmHg was obtained [Found: Me, 29·9; Al, 25·2; EtNH, 43·1%; *M*, 308. $(Me_2AlNHEt)_3$ requires Me, 29·7; Al, 26·7; EtNH, 43·6%; *M*, 303]; i.r. spectrum: 3280m, 2970vs, 2930vs, 2890s, 2830m, 1600w, 1485m, 1465m, 1395s, 1385m, 1350w, 1265m, 1205vs, 1120m, 1080s, 1070s, 1055s, 1040m, 900m, 875m, 860m, 830m, and 695vs cm^{-1}; mass spectrum (relative intensity in parentheses): *m/e* 188 (10), 187 (100) $Me_3Al_2N_2H_2Et_2^+$, 171 (15) $Me_2Al_2N_2HEt^+$, 143 (7), 142 (6), 129 (8), 100 (15), 86 (12), and 84 (8).

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