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Aluminum-Nitrogen Polymers by Condensation Reactions¹BY A. W. LAUBENGAYER, J. D. SMITH² AND GARRY G. EHRLICH

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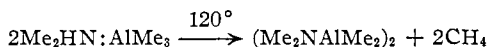
Amines react at low temperatures with aluminum alkyls or alkyl aluminum chlorides to form 1:1 addition compounds. When such addition compounds having N-H and Al-R bonding are pyrolyzed intermolecular condensation occurs, alkanes being evolved, and aluminum-nitrogen polymeric products are formed. By careful control of the conditions of pyrolysis the condensation can be resolved into a sequence of reactions, with successive production of amide aluminum polymers, imide aluminum polymers and finally aluminum nitride. The reactions and the properties of the products are accounted for by suggesting the stepwise building up of Al-N bonding at the expense of N-H and Al-R bonds, assuming that aluminum and nitrogen maintain tetrahedral coordination throughout the reaction sequence. No evidence has been found for π bonding in these aluminum-nitrogen materials.

Introduction

The formation of polymeric aluminum-nitrogen frameworks by the reactions of aluminum halides or organo-aluminum compounds with amines has been mentioned in the literature, but a systematic study of the reactions and the properties and structures of the products is needed to establish the basic chemistry of these systems.

The addition compounds $H_3N:Al(p\text{-tolyl})_3$ and $H_3N:Al(Ph)_3$ were described by Krause and Dittmar in 1930.³ The first was said to darken when heated above 120°, but no decomposition products were identified. About the same time Klemm, *et al.*,⁴ prepared and characterized a series of addition compounds between ammonia and the aluminum halides. The monomeric compound $H_3N:AlCl_3$ is, according to recent work,⁵ so thermally stable that it can be distilled at about 420° at atmospheric pressure "almost without decomposition."

Addition compounds containing both aluminum-alkyl and nitrogen-hydrogen bonds are much less stable and readily undergo condensation reactions, with the elimination of hydrocarbons. Thus, Davidson and Brown,⁶ in their study of the relative strength of bonding in adducts of aluminum trimethyl, reported the reaction



$(Me_2NAlMe_2)_2$ was shown by density measurements to be dimeric in the vapor phase and thermally stable up to 150°. Wiberg also studied this system, as reported later by Bähr.⁷ Wiberg also prepared $H_3N:Al(Me)_3$ and $MeH_2N:Al(Me)_3$ and found that these decomposed with loss of methane when heated. The reaction schemes proposed were However, Wiberg has not published the details of this work to fully support the proposed reactions.

(1) Presented at the Fall Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959. Extracted in part from thesis submitted by G. G. Ehrlich in partial satisfaction of the requirements for the Ph.D., September, 1959, Cornell University.

(2) N. S. F. Research Associate, 1958-1959. This author wishes to thank the United States Educational Commission in the U. K. for a Fulbright Travel Grant.

(3) E. Krause and P. Dittmar, *Ber.*, **63**, 2401 (1930).

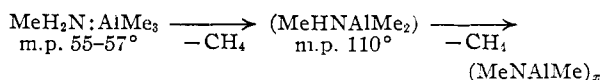
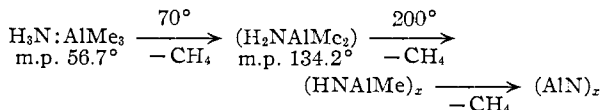
(4) W. Klemm and E. Tanke, *Z. anorg. u. allgem. Chem.*, **200**, 343 (1931); W. Klemm, E. Clausen and U. H. Jacobi, *ibid.*, **200**, 367 (1931).

(5) T. Renner, *ibid.*, **298**, 22 (1959).

(6) N. Davidson and H. C. Brown, *THIS JOURNAL*, **64**, 316 (1942).

(7) G. Bähr, *Fiat Review of German Science, 1939-1946*, **24**, Inorganic Chemistry, 155.

Of the compounds presumed to contain extended aluminum-nitrogen frameworks, $(HNAlMe)_x$ does



not seem to have been fully characterized and $(MeNAIME)_x$ is merely described as a glassy non-volatile material.

More work is needed on these interesting condensation reactions to elucidate the basic pattern of aluminum-nitrogen bonding possibilities. The aluminum-carbon bond is weaker than the aluminum-chlorine bond, and it is to be expected that more stable aluminum-nitrogen materials can be prepared from addition compounds in which the aluminum atom is bonded to chlorine or to some other electronegative group. We have undertaken a systematic investigation of such systems. The reaction of methylammonium chloride with aluminum triethyl and the related reaction of methylammonium chloride with diethyl aluminum chloride were chosen for study because the evolution of ethane provided a very convenient way to follow the course of the reactions quantitatively. The use of methylammonium chloride made it possible to determine whether carbon-nitrogen or carbon-aluminum bonds were being broken in the thermal decomposition and to study the replacement of alkyl groups on the aluminum by chlorine.

Experimental

Manipulative Methods.—All organo-aluminum compounds were handled either in a dry box with an atmosphere of Seaford grade nitrogen or in a glass vacuum line of conventional design. Oxygen and moisture were rigorously excluded. Aluminum triethyl and diethyl aluminum chloride were most conveniently transferred from one part of the vacuum line to another by condensing them in traps on one side of which a high vacuum was maintained, as recommended by Davidson and Brown.⁶ In this way attack on the silicone stopcock grease was kept negligible. Gases such as methylamine and ethane were manipulated and measured in the vacuum line.

Purification of Materials.—Methylamine, supplied by Matheson Co., was dried over sodium for 4 hr. (vapor pressure at -78.5°, 6.2 mm.; lit.⁸ 6.5 mm.).

Dimethylamine, Matheson "anhydrous," was dried over sodium for 18 hr. at 0° (vapor pressure at 0°, 563 mm.;

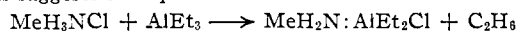
(8) J. G. Aston, C. W. Siller and G. H. Messerly, *THIS JOURNAL* **59**, 1743 (1937).

lit.⁹ 563 mm.). Methylammonium chloride from Eastman Organic Chemicals was recrystallized from 95% ethanol and dried for several days *in vacuo* (m.p. 228°; lit.¹⁰ 225–226). Triethyl aluminum from National Distillers' Products Corporation was distilled in a 50 cm. column containing a heated nichrome spiral. The fraction distilling between 112° and 114° (27 mm.) was used (lit.¹¹ 114° (27 mm.)). Diethyl aluminum chloride from the Ethyl Corporation was similarly distilled from excess dry sodium chloride to remove ethyl aluminum dichloride, and the fraction boiling between 106.5 and 108° (24.5 mm.) was selected. This melted sharply at -75.5° (lit.¹² b.p. 107° (24.5 mm.) and m.p. -74°).

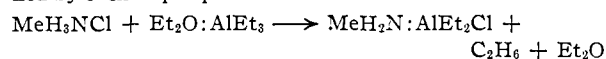
Analyses.—The compounds which were isolated were decomposed for analysis by hydrolysis, but it was necessary to vary the conditions according to the type of material dealt with. Aluminum alkyls and their amine addition compounds were sealed and weighed in fragile glass ampules which were then broken by a magnetic plunger inside the vacuum line. The sample was dissolved in toluene, cooled to -78° and treated with cold 95% aqueous ethanol in an apparatus like that described by Ziegler.¹³ All volatile material was then removed and the residue was dissolved in 2*N* H₂SO₄. Compounds with formula (R₂NAlX₂)_n, where R = Me or H and X = Cl or Et, and higher polymeric materials could be transferred under dry nitrogen to small tubes for weighing and then treated directly with dilute sulfuric acid. In all cases, any ethane that formed was collected, purified, identified by its vapor pressure at -129.7 and -111.6° (lit.¹⁴ 40 mm., 178 mm.), and its volume was measured in the vacuum line to give a quantitative estimate of the number of ethyl groups bonded to aluminum (alkyl groups bonded to nitrogen would not be hydrolyzed under the conditions employed).

Aliquots of the residual sulfuric acid solutions were used for the gravimetric determination of chlorine and aluminum (as the complex with 8-hydroxyquinoline) and for the semi-micro Kjeldahl determination of methylamine and dimethylamine.¹⁵

The Formation of Methylamine Diethyl Aluminum Chloride.—Finely powdered, dry MeH₂NCl (1.19 g., 17.65 mmoles) was added slowly from a rotating side arm to a solution of AlEt₃ (2.02 g., 17.7 mmoles) in 9 ml. of dry toluene at -78°. A gas was evolved immediately. This was removed and identified by its vapor pressure as ethane (16.8 mmoles). The reaction mixture was warmed to room temperature and, after removal of the toluene by pumping, 2.62 g. of a colorless liquid product, m.p. -11.5 ± 1°, remained. This suggests the equation

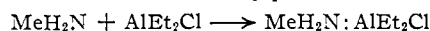


In another experiment aluminum triethyl etherate (easier to handle than aluminum triethyl) was used. Et₂O:AlEt₃ (1.35 g., 6.6 mmoles) did not react with MeH₂NCl (0.464 g., 6.9 mmoles) at -78°, but at -45° ethane and ether were formed. The ethane and ether were separated and identified by their vapor pressures.



An equally convenient route to MeH₂N:AlEt₂Cl was by the exothermic reaction between methylamine and diethyl aluminum chloride. Thus AlEt₂Cl (2.66 g., 22.1 mmoles) was transferred *in vacuo* to a 50 ml. round-bottomed reaction flask and MeH₂N (22.16 mmoles measured in the vacuum system) was added in small increments at -78°. The mixture was warmed to 0° after each addition of methylamine so that the solid product melted. The only product volatile under these conditions consisted of negligible traces

(0.03 mmole) of ethane, presumably from hydrolysis by traces of moisture inadvertently present.



This reaction also took place readily in toluene solution, and the toluene could be removed by pumping for several hours at room temperature. The product had a melting point and infrared spectrum identical with those of the adduct prepared by the interaction of methylammonium chloride and aluminum triethyl.

Attempts to prepare the pure adduct at room temperature were unsuccessful because the reaction is exothermic and some of the adduct underwent condensation to give a mixture of products.

Anal. Calcd. for MeH₂N:AlEt₂Cl: C₂H₅, 38.3; Al, 17.8; Cl, 23.4; MeH₂N, 20.5; mol. wt., 151.5. Found: C₂H₅ (as C₂H₆), 38.3; Al, 18.0; Cl, 23.3; MeH₂N, 20.5, 20.6; mol. wt. (cryoscopic in benzene), 155.

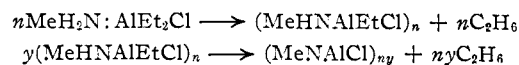
There was some evidence for the formation of a solid molecular addition compound containing a further equivalent of methylamine. Thus MeH₂N (5.67 mmoles) was mixed with diethyl aluminum chloride (0.206 g., 1.71 mmoles) at -78°, and the excess methylamine was condensed out, without pumping, at -196°. 3.5 mmoles of methylamine had been absorbed, and no further absorption occurred when the white solid product was allowed to stand in excess methylamine for 12 hr. at room temperature. When the solid then was pumped for several hours at 25°, 1.81 mmoles of methylamine was removed, leaving the liquid 1:1 addition compound. The 2:1 adduct has not been investigated further.

Properties of MeH₂N:AlEt₂Cl.—Methylamine diethyl aluminum chloride reacted rapidly but did not catch fire when exposed to traces of air or moisture. It was, however, thermally stable at room temperature in a sealed glass tube or under dry nitrogen. It is soluble in benzene, toluene and ether but insoluble in paraffin hydrocarbons. Cryoscopic measurements in a vacuum type cell¹⁶ showed the compound to be monomeric in benzene solution. It freezes at -11.5 ± 1° but has a great tendency to undercool. The adduct did not distil at 20° and 0.001 mm., but small quantities could be purified by very slow distillation at 48 to 50° onto a cold finger which was held at -196°.

Thermal Condensation Polymerization of MeH₂N:AlEt₂Cl.—Thermal decomposition of MeH₂N:AlEt₂Cl was not detectable below 50°, but above this temperature evolution of ethane became rapid. Ethane was the only gas evolved during the decomposition, and analysis of all of the residual products gave aluminum:chlorine:nitrogen:methyl mole

ratios of 1:1:1:1, indicating that the $\begin{matrix} \text{Cl} & \text{Me} \\ | & | \\ -\text{Al}- & \text{N}- \\ | & | \end{matrix}$ grouping

remained intact during the successive condensation polymerization reactions.



Separation of these steps and isolation of intermediates in the condensation was accomplished by careful control of temperature. Thus, when MeH₂N:AlEt₂Cl (4.60 g., 30.4 mmoles) was heated at 72 to 76°, ethane evolution (29.5 mmoles) almost ceased after 57 hr., and a glassy material (3.46 g.) with a composition corresponding to (MeHNAI(EtCl)_n remained. At 95° the reaction was more rapid, and from 27.0 mmoles of MeH₂N:AlEt₂Cl 26.5 mmoles of ethane was evolved during 9 hr.

Anal. Calcd. for (MeHNAI(EtCl)_n: C₂H₅, 23.9; Al, 22.2; Cl, 29.2; MeHN, 24.6; mol. wt., 121.5. Found: C₂H₅, 22.9; Al, 21.6; Cl, 28.7; MeHN (as MeH₂N), 24.5; mol. wt. (cryoscopic in benzene), 441, 445 ± 40.

The (MeHNAI(EtCl)_n glass crystallized slowly on standing for several days. The crystallinity was confirmed by the observation of appearance of extinction angles between crossed nicols and by powder X-ray diffraction (Table I). Attempts to recrystallize the solid from toluene solution were unsuccessful; when the solvent was removed the residue remained as a glass, which subsequently crystallized only very slowly. (MeHNAI(EtCl)_n was also soluble in car-

(9) J. G. Aston, M. L. Eidinoff and W. S. Forster, *THIS JOURNAL*, **61**, 1539 (1939).

(10) I. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, 1953, p. 294.

(11) A. W. Laubengayer and W. F. Gilliam, *THIS JOURNAL*, **63**, 477 (1941).

(12) Ethyl Corporation, Technical Data Sheet, August, 1958.

(13) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954).

(14) Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, Table 1k.

(15) A. Steyermark, "Quantitative Organic Microanalysis," Blakiston, Philadelphia, 1951.

(16) O. B. Billings, Thesis, Cornell University, 1942.

bon tetrachloride and benzene but not in *n*-pentane nor *n*-heptane. Addition of *n*-heptane to a toluene solution produced no crystallization. The compound reacted with acetone, alcohols and water but was not pyrophoric in air.

TABLE I

POWDER X-RAY DIFFRACTION DATA (CuK α RADIATION)

(MeHNAIEtCl) _n		(MeHNAIEtCl·MeNAICl) _n		Black product from pyrolysis of (MeNAICl) _n ^a	
<i>d</i> spacing	In-tensity	<i>d</i> spacing	In-tensity	<i>d</i> spacing	In-tensity
5.10	s	8.24	s	3.86	m
3.28	s	7.76	s	2.74	vs
3.02	s	7.37	s	2.24	w
2.60	m	4.34	s	1.95	m
2.40	w	3.79	s	1.74	w
2.16	s	3.22	m	1.59	s
1.96	m	3.03	m	1.38	w
1.79	m-s	2.81	w	1.30	w
1.64	w	2.59	m	1.23	w
1.58	w	2.35	m		
1.53	w				
1.45	vw				
1.35	vw				
1.31	vw				
1.27	vw				

^a (MeNAICl)_n gave only amorphous scattering.

Cryoscopic measurements of (MeHNAIEtCl)_n in 0.012 molal benzene solution gave values of 441, 445 (± 40) for the molecular weight, corresponding to a value of 3.6 for *n* in the formula. This and the observed reluctance of the material to crystallize may indicate a variable degree of association in solution and in the liquid phase, so that the molecules reorganize themselves only slowly into a crystal lattice in which, presumably, only one molecular species is present. Mass spectroscopic examination¹⁷ gave a spectrum which showed that the vapor consisted mainly of the dimer (MeHNAIEtCl)₂ definitely containing two chlorine atoms, with no indication of higher polymeric species.

Crystalline (MeHNAIEtCl)_n melted at 91° with decomposition to ethane and a white solid. By prolonged heating at 100 to 180° solid products with compositions intermediate between (MeHNAIEtCl)_n and (MeNAICl)_n could be obtained. These intermediates could be sublimed from the reaction flask to a water-cooled cold finger. The sublimate from the reaction vessel when MeH₂N:AlEt₂Cl was heated rapidly to 160° had a composition corresponding to (MeHNAIEtCl·MeNAICl)₂.

Anal. Calcd. for (MeHNAIEtCl·MeNAICl)₂: C₂H₆, 13.6; Al, 25.4; Cl, 33.3. Found: C₂H₆, 14.6; Al, 24.6; Cl, 33.8.

This white sublimate was insoluble in benzene so cryoscopic measurements could not be made, and an attempt to determine the molecular weight in the vapor in a mass spectrometer was unsuccessful because of rapid evolution of ethane. The sublimate was crystalline giving a well defined powder X-ray diffraction pattern (Table I), quite distinct from those of (MeHNAIEtCl)_n and (MeNAICl)_n; the latter never gave a crystalline pattern. Several other samples with compositions intermediate between (MeHNAIEtCl)_n and (MeNAICl)_n were prepared and analysed. These gave powder X-ray diffraction patterns which showed the lines of both (MeHNAIEtCl)_n and (MeHNAIEtCl·MeNAICl)₂.

Preparation and Properties of (MeNAICl)_n.—Prolonged heating of (MeHNAIEtCl)_n at 210 to 220° resulted in complete removal of ethane. Thus, when 0.765 g. of MeHNAIEtCl (6.3 *n* mmoles) was heated for 54 hr. at 212°, there was formed 6.25 mmoles of ethane and a white, non-volatile, solid (MeNAICl)_n, which was amorphous to X-rays and insoluble in benzene, carbon tetrachloride, pentane and heptane. These properties suggest that (MeNAICl)_n is highly polymeric.

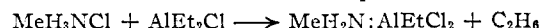
(17) The authors are grateful to Professor R. F. Porter for the mass spectroscopic studies reported in this paper.

Anal. Calcd. for (MeNAICl)_n: C₂H₆, 0.0; Al, 29.5; Cl, 38.8; MeN, 31.7. Found: C₂H₆, 0.0; Al, 29.9; Cl, 38.1; MeN, 31.6, 31.4.

(MeNAICl)_n reacted slowly with water and dissolved readily in dilute mineral acids or caustic alkalis. In one experiment (MeNAICl)_n (0.195 g. containing 2.13 mmoles of MeN) was transferred under nitrogen in a dry box to a 50 ml. flask and 1 ml. of water was distilled in. The mixture was warmed to room temperature and allowed to stand for one-half hour. There was no apparent gas evolution. All volatile material was pumped off and found to be water and methylamine (0.15 mmole MeH₂N estimated by titration with hydrochloric acid). It is possible, however, that the hydrolysis had gone to completion. In another experiment the solid residue from the hydrolysis of 0.201 g. of (MeNAICl)_n by 10 ml. of water was washed on a filter paper with cold water. After several washings the residue was dissolved in acid and found to contain no methylamine. This suggests that (MeNAICl)_n is completely hydrolyzed by cold water but that the resulting solution is not alkaline enough to give quantitative evolution of methylamine.

When 0.1247 g. of (MeNAICl)_n was heated in a sealed thick-walled Pyrex tube to 525° for 48 hr., the solid turned black. The tube was opened in the vacuum line and yielded a very small quantity of gas and a black refractory solid. Mass spectrographic analysis of the gas showed that it consisted of methane and hydrogen in about equal abundance. The black solid was only partially soluble in 2*N* H₂SO₄, chloride ions appearing in the resulting solution. Powder X-ray diffraction analysis of the black material gave a definite crystal pattern (Table I) which did not correspond to those given in the literature for the nitride, carbide or oxide of aluminum, nor for any other aluminum compound listed in the A.S.T.M. file. The very slow evolution of the small amounts of methane and hydrogen showed that nitrogen-carbon bonds were being ruptured, with presumably reorganization of the methyl fragments to give the two gases and some elementary carbon, thus accounting for the blackening. The bulk of the sample, originally amorphous to X-radiation, apparently slowly crystallized at 525°. The absence of CH₃Cl and HCl in the gas which formed indicated that even under this drastic heat treatment the aluminum-chlorine bonds persisted.

The Interaction of MeH₃Cl and AlEt₂Cl.—Methylammonium chloride did not react with diethyl aluminum chloride at -78°. However, when MeH₂NCl (2.04 g., 30.2 mmoles) was added slowly from a rotating side arm to an ice-cold solution of AlEt₂Cl (3.65 g., 30.2 mmoles) in 5 ml. of toluene, 29.0 mmoles of ethane was evolved smoothly. The absence of HCl in the gas was confirmed by washing it with standardized sodium hydroxide solution and back titrating. The results were consistent with the equation



Removal of the toluene gave the colorless liquid addition compound MeH₂N:AlEtCl₂ (m.p. 15°), which was recrystallized from toluene at -23° in an inert atmosphere to give a yield of 59%. This material also readily undercooled.

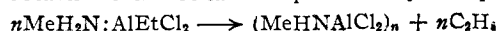
Anal. Calcd. for MeH₂N:AlEtCl₂: C₂H₆, 18.3; Al, 17.1; Cl, 44.9; MeH₂N, 19.6; mol. wt., 158. Found: C₂H₆, 18.2; Al, 16.8; Cl, 43.4; MeH₂N, 19.6, 19.2; mol. wt. (cryoscopic in 0.04 *m* benzene soln.), 168 \pm 9.

MeH₂N:AlEtCl₂ reacted very vigorously with water but slightly less rapidly with alcohols and acetone. It decomposed very rapidly in moist air but was not pyrophoric. It was soluble in benzene and toluene but not in paraffinic solvents. The cryoscopic data indicate that the adduct is monomeric in benzene.

Pyrolytic Condensation of Methylamine Ethyl Aluminum Dichloride.—MeH₂N:AlEtCl₂ did not distil at 20° (0.001 mm.). Thermal decomposition was very slow below 50°, but when 2.64 g. (16.7 mmoles) was heated at 127°, 16.6 mmoles of ethane was evolved during 35 hr. No HCl was detected in this gas. A colorless glass, which crystallized only very slowly on standing for several days, remained.

Anal. Calcd. for (MeHNAICl₂)_n: C₂H₆, 0.0; Al, 21.1; Cl, 55.5; MeNH, 23.4; mol. wt., 128. Found: C₂H₆, 0.0; Al, 21.0; Cl, 55.3; MeNH, 23.4, 23.5; mol. wt. (cryoscopic in benzene), 314 \pm 30.

The reaction therefore can be represented by the equation



(MeHNAI₂Cl)_n was soluble in toluene and benzene and cryoscopic measurements indicated a value of 2.4 ± 0.2 for n in benzene solution. Samples of the compound in small capillaries did not give sharp melting points, but all melted in the range 90 to 104°. In a high vacuum, however, the material sublimed without melting and without decomposition at approximately 170°. Mass spectrographic analysis with the sample at 100° gave a strong peak for mass 127, the mass of the monomer, with clear evidence for the presence of two chlorines per molecule. There was no evidence for particles of the dimer, but masses corresponding to AlCl₂⁺, AlCl²⁺ and HCl were recorded. Again, as in the case of the analogous material (MeHNAI₂EtCl)_n, (MeHNAI₂Cl)_n has a behavior which indicates a mixture of low polymeric species in the liquid phase and in solution, but it apparently vaporizes mainly as the monomer, with some fragmentation under the conditions prevailing in the mass spectrometer. In several sealed tube experiments no thermal decomposition was detected below 250°, and no formation of HCl or other highly volatile material was observed even when small samples of (MeHNAI₂Cl)_n were heated to 300° for 60 hr., although at 300° the sample became dark brown.

(MeHNAI₂Cl)_n is deliquescent and reacts vigorously with water to give an acidic solution. When 0.204 g. was treated with 1 ml. of water for 30 minutes at room temperature, and the volatile material then was distilled off, no methylamine was detected in the volatile material. The solid residue (0.212 g.) did not completely melt below 210°, and it gave an infrared spectrum consistent with the formation of methylammonium chloride and aluminum hydroxide. It is clear that hydrolysis took place, although the solution was not alkaline enough to liberate the methylamine formed.

The Interaction of Me₂HN and AlEt₂Cl.—In a typical experiment, diethyl aluminum chloride (5.82 g., 48.3 mmoles) was dissolved in 10 ml. of toluene, cooled to -78°, and dimethylamine (48.2 mmoles) was distilled into the reaction flask in small increments. When the addition of dimethylamine was complete, the mixture was warmed to 20° and 5 ml. of toluene was removed *in vacuo*. The remaining solution then was cooled to -78°, whereupon colorless needles of the addition compound crystallized out. These were filtered off under dry nitrogen at -78° and warmed to 20°, when a colorless liquid was obtained. Residual traces of toluene were removed by pumping at room temperature to give a 68% yield of the crystalline adduct.

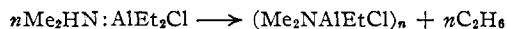
Anal. Calcd. for Me₂HN:AlEt₂Cl: C₂H₆, 35.0; Al, 16.3; Cl, 21.4; Me₂HN, 27.2; mol. wt., 165.5. Found: C₂H₆, 34.7; Al, 16.3; Cl, 21.3; Me₂HN, 26.9; mol. wt. (cryoscopic in benzene), 176, 179, ± 14.

Me₂HN:AlEt₂Cl melts at -6 to -5°. It has a vapor pressure of less than 0.2 mm. at 20° but could be distilled slowly in the vacuum line; it is thus noticeably more volatile than MeH₂N:AlEt₂Cl. In moist air reaction was very rapid.

Pyrolytic condensation of Me₂HN:AlEt₂Cl became detectable at 50° (16% in 16 hr.) but proceeded at a more convenient rate at 84 to 86°. Thus, when 5.39 g. (32.6 mmoles) was heated for 100 hr. at this temperature 29.7 mmoles of ethane was evolved. The solid residue was freed of undecomposed adduct by prolonged pumping at room temperature and finally was sublimed *in vacuo* at 52 to 60° to give well-formed colorless needles which melted at 80 to 81° under 100 mm. of nitrogen. The crystals were very sensitive to moisture.

Anal. Calcd. for (Me₂NAI₂EtCl)_n: C₂H₆, 21.4; Al, 19.9; Cl, 26.2. Found: C₂H₆, 21.9; Al, 20.3; Cl, 27.0.

The condensation reaction is therefore summarized by the equation



Mass spectrographic analysis of (Me₂NAI₂EtCl)_n gave a strong peak at mass 141, with evidence for two chlorine atoms per particle; Me₂NAI₂Cl₂ molecules would account for these data. A moderate peak at mass 242 with two chlorines per particle would appear to indicate some dimeric material. There was a weak peak for C₂H₆. Evidently considerable reorganization of (Me₂NAI₂EtCl)_n occurred in the mass spectroscopy.

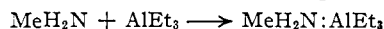
Infrared Spectra.—The infrared spectra of the new compounds prepared in this work were recorded on a Perkin Elmer 21 spectrometer using rock salt optics. Liquid addition compounds were examined as thin films (prepared in a

nitrogen atmosphere), and solids were made into mulls in Nujol or hexachlorobutadiene. These spectra were used to identify compounds prepared by different reactions and also for the detection of hydrolysis. The spectra of hydrolyzed products showed broad absorption in the region from 3500 to 2800 cm.⁻¹, whereas the unhydrolyzed products gave a series of sharply defined N-H and C-H stretching peaks. The absorption at 3210 to 3260 cm.⁻¹ and 1575 to 1585 cm.⁻¹, attributed to the N-H group, disappeared when (MeHNAI₂EtCl)_n was condensed to (MeNAI₂Cl)_n. No attempt was made to assign any peak as being due mainly to Al-N stretching. The principal absorption of aluminum nitride has been given¹⁸ recently as at 14.0 μ (714 cm.⁻¹), but this peak was so broad that an accurate value for the vibration frequency could not be obtained.

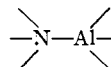
Discussion

Our experimental results, coupled with the data previously reported, establish a characteristic sequence of reactions which occur when amines or their hydrochlorides react with aluminum alkyls or alkyl aluminum chlorides. It becomes possible to suggest a simple structural pattern which apparently is typical for the proliferation of aluminum-nitrogen frameworks.

Amines associate readily at low temperatures with aluminum alkyls or alkyl aluminum chlorides to give 1:1 amine aluminum addition compounds. When an amine hydrochloride is used instead of the amine, chlorine replaces one of the alkyl groups on the aluminum and alkane is formed, together with a 1:1 amine adduct. For example

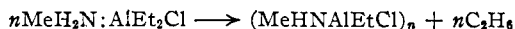


The 1:1 amine aluminum adducts are soluble in benzene (in which they are monomeric) and are liquids or low-melting solids. They have the structure

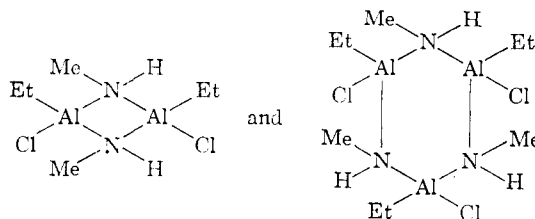


in which nitrogen and aluminum atoms have each achieved tetrahedral coordination by donation of an electron pair by nitrogen to aluminum to establish sp³ bonding. These adducts are noticeably less reactive than the parent aluminum alkyls but still react violently with water at room temperature, and they are pyrophoric in air.

When amine aluminum adducts which contain N-H and Al-R bonds are warmed they undergo intermolecular condensation, splitting out RH and leaving an amide compound of aluminum. Thus

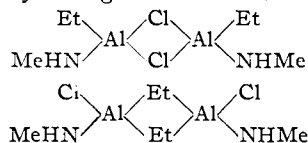


Presumably N-H and Al-R bonds are replaced by additional N-Al bonding to maintain tetrahedral coordination for the nitrogen and the aluminum atoms, setting up polymeric cyclic structures, such as



(18) E. G. Brame, J. L. Margrave and V. W. Meloche, *J. Inorg. Nuclear Chem.*, **5**, 48 (1957).

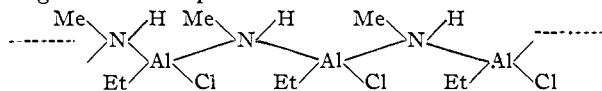
Such cyclic molecules of varying ring size are consistent with the molecular weight data and the solubility of these amide aluminum materials. We believe that nitrogen bridging to link together aluminum atoms is much more likely than chlorine-bridged or alkyl-bridged structures, such as



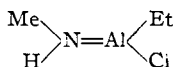
Similar amide aluminum compounds are obtained by condensation in the absence of chlorine or small alkyl groups. The arguments of Davidson and Brown,⁶ based on energy considerations, suggest that the nitrogen bridging is the most likely.

Of course, there is the possibility of *cis-trans* isomerism for such cyclic polymers. The difficulty encountered in obtaining crystallization of the amide aluminum compounds may well be due to there being not only a mixture of polymers of different ring size but also because there may be different isomers present.

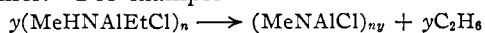
The possibility that the amide $(\text{MeHNAIEtCl})_n$ might have the puckered extended chain structure



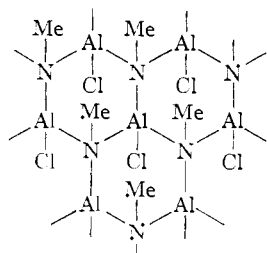
must also be considered, but the low molecular weight data would seem to rule this out. The double bonded monomeric structure also seems to be eliminated by the molecular weight data.



If the amide aluminum product of the first stage in the pyrolysis has both N-H and Al-R bonds, it readily undergoes a second step in the condensation when the temperature is raised, with evolution of more RH and formation of an imide aluminum polymer. For example

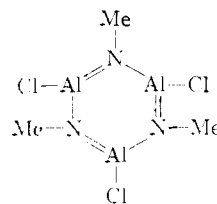


This is consistent with the notion that further intermolecular condensation is setting up more Al-N bonding at the expense of N-H and Al-R to give a crosslinked, high-polymeric framework of alternating aluminum and nitrogen atoms, such as



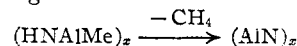
In this postulated structure each of the aluminum atoms is tetracoordinated to three nitrogen neighbors and one terminal group, and each nitrogen atom is tetracoordinated to three aluminum atoms and one terminal group. Such a continuous two or three dimensional aluminum-nitrogen framework is consistent with our observation of insolubility, non-volatility, amorphous structure and slow

rate of hydrolysis of $(\text{MeNAICl})_{ny}$. These characteristics are inconsistent with a six-membered ring structure, similar to that of borazine and benzene

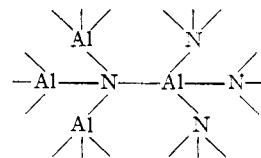


with some double bond resonance in the ring due to π bonding by the lone pair of electrons from the nitrogen and a coordination number of three for both aluminum and nitrogen.

Further condensation of the imide type of aluminum polymer would be expected if there are still N-H and Al-R groups present, as suggested in the report of Wiberg's work.⁷



Complete conversion of such a high polymer imide should be difficult, in view of the immobility of the polymer. This final step in the condensation will convert all the bonding to tetrahedral Al-N bonds to build up the three-dimensional wurtzite struc-



ture known for AlN.¹⁹ The high thermal stability and refractory nature of AlN attests the considerable strength of Al-N bonding. No graphitic modification of AlN has been reported. This supports the idea that conditions are not favorable for π bonding between aluminum and nitrogen. All of the data are consistent with the postulate that sp^3 bonding with tetrahedral coordination is always achieved in aluminum and nitrogen systems.

Aluminum amines, amides or imides which have only alkyl groups on the nitrogen or only chlorine on the aluminum do not undergo condensation polymerization readily. If they are heated sufficiently high some decomposition occurs slowly, apparently with the elimination of hydrocarbons and hydrogen rather than splitting out HCl or RCl.

Rapid heating of amine aluminum adducts produces considerable overlap of the successive stages of condensation and gives a mixture of products and materials intermediate in composition. The crystalline phase having the composition $(\text{MeHNAlEtCl} \cdot \text{MeNAICl})_x$, which was obtained by sublimation when $\text{MeH}_2\text{N}:\text{AlEt}_2\text{Cl}$ was heated rapidly to 160° , is an example of such an intermediate where a definite composition is associated with the building up of a stable crystal lattice.

Further work is under way to provide more information pertinent to the structures of the amides and imides of aluminum in an effort to fully substantiate the structures we have outlined.

Acknowledgments.—We wish to thank the National Science Foundation and the Standard Oil Company of Ohio for financial support for this research.

(19) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, 1950, p. 462.