193. *Complexes of Organoaluminium Compounds. Part I. Ammonia Complexes of Ethylaluminium Chlorides.*

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Ethylaluminium dichloride forms complexes with one, two, five, and eight moles of ammonia per mole of aluminium and diethylaluminium chloride complexes with one and two moles of ammonia. There is no ammonolysis of aluminium–chlorine bonds. On heating, the complexes lose ethane and aluminium trichloride–ammonia, with the formation of aluminium–nitrogen polymers.

Aluminium trialkyls give ammonia adducts which decompose [1,2] at room temperature forming hydrocarbons and compounds $(R_2AlNH_2)_x$ ($x = 2$ or 3), but the trihalides form

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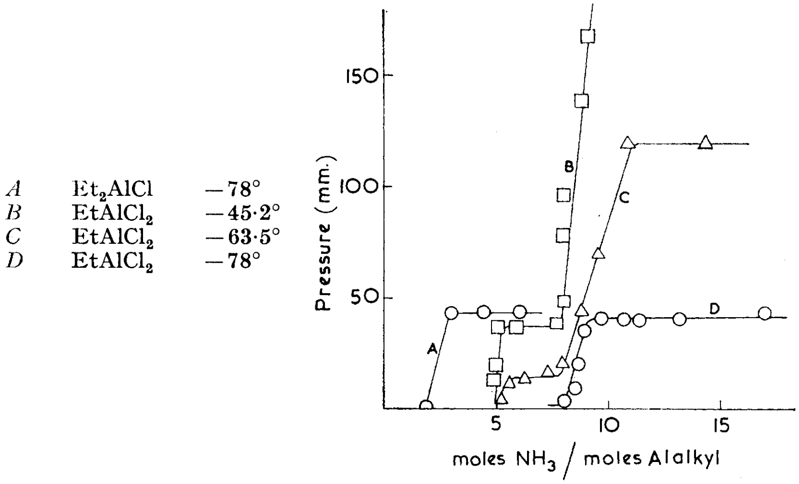
[1] G. Bahr, F.I.A.T. Review of German Science, 1939—1946, Inorganic Chemistry, Part II, p. 155.
[2] K. Ziegler and H. Gellert, *Annalen*, 1960, **629**, 20.

complicated series of readily isolated complexes.[3] We now describe ammonia complexes of ethylaluminium dichloride and diethylaluminium chloride.

The aluminium-carbon bond in ethylaluminium dichloride was not cleaved by excess of ammonia below room temperature, and pressure-composition studies [4] showed (Figure) the formation of the complexes $EtAlCl_2,8NH_3$ and $EtAlCl_2,5NH_3$. The latter remained when excess of ammonia was removed at room temperature. It decomposed reversibly between 30 and 70° to ammonia and a lower adduct, but side reactions involving elimination of ethane prevented the determination of accurate equilibrium pressures and the detection of adducts with less than five mols. of ammonia per aluminium. Powder photographs of solid products with compositions ranging from $EtAlCl_2,NH_3$ to $EtAlCl_2,5NH_3$, prepared by the interaction of ethylaluminium dichloride in toluene and the stoicheiometric quantities of ammonia, showed that the complexes $EtAlCl_2,NH_3$, $EtAlCl_2,2NH_3$, and $EtAlCl_2,5NH_3$ were probably distinct. Ammonium chloride lines were absent from all photographs, and peaks characteristic of ammonium chloride [5] were absent from the infrared spectra of all adducts. Formation of ammonia complexes does not therefore involve ammonolysis of aluminium-chlorine bonds. Ethylaluminium dichloride-ammonia was soluble in benzene and toluene and did not dissolve in paraffinic hydrocarbons, but no solvent could be found for $EtAlCl_2,2NH_3$ or $EtAlCl_2,5NH_3$. All the adducts were rapidly decomposed by water, alcohols, and acetone with quantitative evolution of ethane.



Between 70 and 150° the ammonia adducts of ethylaluminium dichloride gave amidoaluminium dichloride, of empirical formula $AlCl_2NH_2$. This white material was insoluble in most organic solvents and in liquid ammonia, and its molecular weight could not be found. On distillation it yielded aluminium trichloride-ammonia, and an off-white solid which appeared to be a highly crosslinked polymeric substance analogous to the final products in the condensations of amine addition compounds of aluminium alkyls.[6,7]

$$2n(AlCl_2NH_2)_x \rightleftharpoons nxAlCl_3NH_3 + (AlClNH)_{xn}$$

The equilibrium is probably shifted to the right by the removal of the volatile addition

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[3] W. Klemm and E. Tanke, *Z. anorg. Chem.*, 1931, **200**, 343; W. Klemm, E. Clausen, and H. Jacobi, *ibid.*, p. 367; G. W. Watt and J. H. Braun, *J. Amer. Chem. Soc.*, 1956, **78**, 5494.

[4] G. W. Fowles and D. Nicholls, *Quart. Rev.*, 1962, **16**, 19.

[5] F. A. Miller and C. H. Wilkins, *Analyt. Chem.*, 1952, **24**, 1253; J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295.

[6] A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, *J. Amer. Chem. Soc.*, 1961, **83**, 542.

[7] A. W. Laubengayer, K. Wade, and G. Lengnick, *Inorg. Chem.*, 1962, **1**, 632.

compound. Above 400°, NH_4AlCl_4 [8] and hydrogen chloride were detected as volatile degradation products of amidoaluminium dichloride. Elimination of hydrogen chloride from the AlClNH system, noticed by Renner,[9] seems to be easier than elimination of RCl from polymers containing the AlClNR system (R = alkyl [6] or aryl [7]).

Diethylaluminium chloride-1-ammonia was formed from stoicheiometric quantities of the components without evolution of ethane. On heating it gave $(EtAlClNH_2)_n$ and, at higher temperatures, $(AlClNH)_x$. With an excess of ammonia, diethylaluminium chloride gave a white solid product of composition $Et_2AlCl,2NH_3$, insoluble in hydrocarbons and ether but soluble in liquid ammonia. The shape of the pressure–composition curve for the diethylaluminium chloride–ammonia system and the X-ray powder photograph, infrared spectrum and solubility characteristics of $Et_2AlCl,2NH_3$ all indicated that it was not a 1 : 1 mixture of ammonium chloride and $(Et_2AlNH_2)_3$ from ammonolysis. A molecular weight determination by the depression of the vapour pressure of liquid ammonia solution indicated extensive dissociation, and the adduct may have the structure $[Et_2Al(NH_3)_2]^+Cl^-$ analogous to that of dimethylgallium chloride-2-ammonia.[10]

EXPERIMENTAL

General methods have been described.[6,11] Triethylaluminium and diethylaluminium chloride were distilled before use and ethylaluminium dichloride was recrystallised from pentane or heptane. Molecular weights were measured cryoscopically in benzene using a thermistor as the temperature-sensing device.[12]

Ethylaluminium Dichloride–Ammonia Adducts.—(a) *Pressure-composition studies.* The results (Figure) were obtained by the standard procedure.[3] The dissociation pressures of $EtAlCl_2,8NH_3$ at the three temperatures studied (−78°/2·5 mm.; −63·5°/14 mm.; −45·2°/38 mm.) gave ΔH for the reaction $EtAlCl_2,8NH_3 \longrightarrow EtAlCl_2,5NH_3 + 3NH_3$ as $2{\cdot}2 \pm 0{\cdot}5$ kcal./mole of complex, and it is probable that the readily dissociated ammonia molecules are held weakly by hydrogen bonds. In several experiments, excess of ammonia was removed and absorbed in standard acid, and any ethane collected in the vacuum system. In every case the ethane formed was less than ½% of that corresponding to complete decomposition: thus the aluminium–carbon bond is not cleaved by excess of ammonia below room temperature.

(b) *Preparation of* $EtAlCl_2,NH_3$. A slight deficiency of ammonia (16 mmoles) was bled through a partially open tap into a solution of ethylaluminium dichloride (2·16 g., 16·7 mmoles) in dry toluene (20 ml.) at −78°. The mixture was agitated with a magnetic stirrer until absorption of ammonia was complete and then warmed to room temperature. After separation from a trace of white solid the solution was concentrated and cooled to −78° when white crystals of *ethylaluminium dichloride-ammonia* separated (Found: Et, 19·9; Al, 18·8; Cl, 49·4; NH_3, 11·9. $EtAlCl_2,NH_3$ requires Et, 20·2; Al, 18·7; Cl, 49·3; NH_3, 11·8%). An alternative preparation was from diethylaluminium chloride. Thus well-dried ammonium chloride (1·09 g., 20·5 mmoles) was added slowly to diethylaluminium chloride (2·47 g., 20·5 mmoles) in toluene at −78°. As the mixture warmed to room temperature, ethane (19·6 mmoles, 96%), identified by its vapour pressure, was collected, and ethylaluminium dichloride–ammonia isolated from the solution as above. The adduct melted at 66—67° and sublimed at 10^{-3} mm. on a cold finger. Although the sublimate had an X-ray diffraction pattern and analysis identical with those of the pure 1 : 1 adduct, some decomposition occurred during sublimation with the formation of ethane and a less volatile residue.

(c) *Higher ammonia adducts.* These were prepared similarly in toluene except that the products were precipitated before absorption of ammonia was complete. In each case the suspension was stirred until the required amount of ammonia was taken up, usually during 5—10 hr., and the solvent was removed by pumping. The composition of the residue was

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[8] J. Kendall, E. D. Crittenden, and H. K. Miller, *J. Amer. Chem. Soc.*, 1923, **45**, 963.
[9] T. Renner, *Z. anorg. Chem.*, 1959, **298**, 22.
[10] D. F. Shriver and R. W. Parry, *Inorg. Chem.*, 1962, **1**, 835.
[11] J. D. Smith, *J.*, 1962, 4734.
[12] K. Letton, W. McCorkindale, and A. C. Syme, *Chem. and Ind.*, 1963, 776.

checked by analysis to make sure that no decomposition, *e.g.*, accidental hydrolysis or cleavage of aluminium–ethyl bonds, had occurred.

	Found (%)				Calc. (%)			
	Et	Al	Cl	NH_3	Et	Al	Cl	NH_3
$EtAlCl_2,2NH_3$	17·5	16·9	44·2	21·0	18·0	16·7	44·1	21·1
$EtAlCl_2,3NH_3$	16·0	15·3	40·0	28·5	16·3	15·1	39·9	28·7
$EtAlCl_2,4NH_3$	14·5	14·0	36·6	34·5	14·9	13·9	36·3	34·9
$EtAlCl_2,5NH_3$	13·6	12·7	33·5	40·0	13·7	12·7	33·4	40·1

X-Ray powder photographs were recorded with Debye–Scherrer cameras of 5·75 or 11·48 cm. diameter using Copper-K_α radiation, Lindemann glass capillaries being filled in the drybox. Materials corresponding to $EtAlCl_2,NH_3$, $EtAlCl_2,2NH_3$, and $EtAlCl_2,5NH_3$, gave distinct powder patterns, but samples with compositions $EtAlCl_2$, $3NH_3$, and $EtAlCl_2,4NH_3$ gave no new lines and were probably mixtures of other adducts. Ammonium chloride lines were obtained only when samples were exposed to moist air during manipulation. Ethylaluminium dichloride–2-ammonia and –5-ammonia were insoluble in benzene, toluene, pentane, ether, acetonitrile, nitrobenzene, tetrahydrofuran, and dioxan. $EtAlCl_2,5NH_3$ was slightly soluble with decomposition in dimethyl sulphoxide and was insoluble in liquid ammonia.

Thermal Decompositions.—(a) *Below* 70°. When $EtAlCl_2,5NH_3$ (1·19 g., 5·62 mmoles) was heated for 8 hr. at 62° only 3% decomposed to ethane. The remainder gave ammonia and a lower adduct which reabsorbed ammonia on cooling. In a similar experiment, a white *sublimate* of $EtAlCl_2,8NH_3$ was collected on a cold finger at −78° (Found: Et, 10·8; Al, 10·3; Cl, 27·1; NH_3, 51·5. $EtAlCl_2,8NH_3$ requires Et, 11·0; Al, 10·3, Cl, 27·0; NH_3, 51·7%). This gave a diffraction pattern different from those of the other ammonia adducts of ethylaluminium dichloride, and lost ammonia on standing at room temperature for several hours. If the cold finger was cooled with tap water instead of acetone–solid carbon dioxide the $EtAlCl_2,5NH_3$ was collected as a sublimate.

(b) *Amidoaluminium dichloride.* Ethylaluminium dichloride–ammonia (1·68 g., 11·7 mmoles) was heated gradually in an atmosphere of 600 mm. of nitrogen from room temperature to 125°, and maintained at that temperature for 15 hr. Ethane was condensed as it formed, so that the pressure in the apparatus was constant, and at the end of the experiment 10·5 mmoles (90%) had been collected. The white residue of *amidoaluminium dichloride* (Found: Al, 23·5; Cl, 61·8; NH_2, 14·2. $AlCl_2NH_2$ requires Al, 23·7; Cl, 62·3; NH_2, 14·1%) was apparently amorphous, as it did not give a powder pattern. It was insoluble in benzene, toluene, ether, pentane, nitrobenzene, tetrahydrofuran, and liquid ammonia.

(c) *Reorganisation of amidoaluminium dichloride.* Amidoaluminium dichloride (11·02 g., 8·95 mmoles) was distilled in a microdistillation unit attached to the vacuum system. The distillate, b. p. 148°/0·003 mm., m. p. 125—126°, was apparently aluminium trichloride–ammonia (lit.,[9,13] m. p. 125°) (Found: Cl, 70·6; Al, 18·0; NH_3, 12·2. Calc. for $AlCl_3NH_3$: Cl, 70·8; Al, 17·9; NH_3, 11·3%). The infrared spectrum and *X*-ray powder photograph were identical with those of an authentic sample of $AlCl_3,NH_3$ prepared from aluminium trichloride and ammonia. The residue was amorphous to *X*-rays and was hydrolysed only slowly by water. These properties suggest a crosslinked polymer [Found: Al, 28·8; Cl, 46·6. $(AlClNH)_x$ requires Al, 34·8; Cl, 45·8%]. Some deviation from the ideal composition corresponding to AlClNH is to be expected owing to incorporation of $>AlCl_2$ and $>NH_2$ groups.

(d) *Decomposition at higher temperatures.* From $AlCl_2NH_2$ (0·567 g.) at 500° was obtained a white sublimate (0·243 g.) which appeared to be a mixture of aluminium trichloride–ammonia and ammonium tetrachloroaluminate, identified by powder photographs and analysis (Found: Al, 16·5; Cl, 72·6. Calc. for $AlCl_3,NH_3$: Al, 17·9; Cl, 70·8. Calc. for NH_4AlCl_4: Al, 14·5; Cl, 75·0%). In another experiment, amidoaluminium dichloride (0·45 g.) at 850° gave hydrogen chloride (1·28 mmoles by titration) and a residue which had a composition $Al_{10}N_{6\cdot5}Cl$.

Diethylaluminium Chloride–Ammonia Adducts.—These were prepared in the same way as the ethylaluminium dichloride compounds. Thus diethylaluminium chloride (1·93 g., 16·1 mmoles) and ammonia (16·1 mmoles) gave *diethylaluminium chloride–ammonia*, m. p. −11 to

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[13] J. Goubeau and H. Siebert, *Z. anorg. Chem.*, 1947, **254**, 126; H. Gerding and H. Houtgraaf, *Rec. Trav. chim.*, 1955, **74**, 15.

$-10°$ (Found: Et, 42·1; Al, 19·5; Cl, 25·1; NH_3, 12·2. Et_2AlCl,NH_3 requires Et, 42·2; Al, 19·6; Cl 25·8; NH_3, 12·4%). This colourless liquid, which decomposed slowly at room temperature with evolution of ethane, was best manipulated in toluene solution. It was insoluble in methylcyclohexane. From diethylaluminium chloride (3·21 g., 26·6 mmoles) in toluene (40 ml.) and ammonia (57·4 mmoles) 53·4 mmoles of ammonia were absorbed. The white precipitate of *diethylaluminium chloride–2-ammonia* was washed with toluene and dried *in vacuo* (Found: Et, 37·5; Al, 17·4; Cl, 22·8; NH_3, 20·0. $Et_2AlCl,2NH_3$ requires Et, 37·6; Al, 17·4; Cl, 22·9; NH_3, 22·0%). It was stable at room temperature in dry nitrogen and insoluble in hydrocarbon solvents, ether, dioxan, tetrahydrofuran, and " diglyme " but soluble with very slow decomposition in dimethyl sulphoxide. Its molecular weight was measured by the lowering of the vapour pressure of a 0·49-molal solution in liquid ammonia (Found: *M*, 80, 79; $Et_2AlCl,2NH_3$ requires *M*, 154·5). The procedure was similar to that of Parry *et al.*[14] and the apparatus was checked using urea as solute.

Diethylaluminium chloride–ammonia (3·03 g., 22·0 mmoles), heated for 50 hr. at 65°, gave ethane (21·8 mmoles) and a glassy *solid*, soluble in toluene and ether (Found: Et, 26·6; Al, 24·8; Cl, 32·0; NH_2, 13·7. $EtAlClNH_2$ requires Et, 27·0; Al, 25·1, Cl, 33·0; NH_2, 14·9%). A second sample of diethylaluminium chloride–ammonia (3·85 g., 28·0 mmoles) was heated for 4 hr. at 125° and gave ethane (53·0 mmoles) and a white *residue* which was amorphous to *X*-rays (Found: Et, 4·6; Al, 33·9; Cl, 42·0, NH, 19·2. AlClNH requires Al, 34·8; Cl, 45·8; NH 19·4%). Complete elimination of ethane was achieved at higher temperatures (*e.g.*, after 20 hr. at 425°), but under the last conditions a white sublimate was obtained in high vacuum and this was identified by its powder photograph and analysis as aluminium trichloride–ammonia. This shows that $(AlClNH)_x$ like $AlCl_2NH_2$ undergoes reorganisation reactions at high temperatures with the elimination of the volatile and very stable addition compound.

$$(AlClNH)_{3+x} \longrightarrow AlCl_3NH_3 + 2AlN,xAlClNH$$

Preparation of Amidodiethylaluminium.—A solution of triethylaluminium–ammonia was made by carefully admitting ammonia (26·1 mmoles) to triethylaluminium (2·98 g., 26·1 mmoles) in toluene (10 ml.) at $-78°$. On warming slowly to room temperature, ethane (25·7 mmoles) was evolved and the colourless liquid remaining after removal of solvent was *amidodiethylaluminium*, m. p. $-57°$ (Found: Et, 57·3; Al, 26·7; NH_3, 15·8. Et_2AlNH_2 requires Et, 57·4; Al, 26·8; NH_3, 15·8). Amidodiethylaluminium was freely soluble in benzene in which it was apparently trimeric (Found for 0·20-molal solution: *M*, 299. $[Et_2AlNH_2]_3$ requires *M*, 303). It was decomposed rapidly by alcohols and water. On heating to 140° it gave polymeric $(EtAlNH)_x$ (Found: Et, 38·6; Al, 36·8; NH, 20·4. EtAlNH requires Et, 40·9; Al, 38·0; NH, 21·1%) which was insoluble in organic solvents and amorphous to *X*-rays.

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[14] R. W. Parry, G. Kodama, and D. R. Schultz, *J. Amer. Chem. Soc.*, 1958, **80**, 24.