Complexes of Organoaluminium Compounds. Part II.[1] Ammonia, Aniline, and Diphenylamine Complexes of Ethylaluminium Chlorides

By **J. K. Gilbert** and **J. D. Smith**, Chemical Laboratory, University of Sussex, Brighton BN1 9QJ

Reactions and conductivities in liquid ammonia suggest that the adduct $Et_2AlCl,2NH_3$ has the structure $[Et_2Al(NH_3)_2]^+Cl^-$. Triethylaluminium forms a liquid adduct $Et_3Al,2NH_3$ and gives a solution of low conductivity in liquid ammonia. Aniline complexes of ethylaluminium chlorides lose ethane on heating, with the formation of the derivatives $(R_2AlNHPh)_2$ and $(RAlNPh)_4$ (R = Et or Cl), and diphenylamine complexes give derivatives $(R_2AlNPh_2)_2$. When these react with compounds HX (X = Cl, NH_2, or NMe_2), aluminium–nitrogen bonds are attacked before aluminium–carbon bonds. Amido-derivatives of aluminium are discussed.

EARLIER [1] it was suggested that the adduct $Et_2AlCl,2NH_3$ from diethylaluminium chloride with an excess of ammonia had the structure $[Et_2Al(NH_3)_2]^+Cl^-$. This Paper describes experiments to test this assumption, and the preparation of some related compounds. Pyrolyses of ammonia [1] and methylamine [2] complexes of ethylaluminium chlorides give ethane and derivatives with aluminium–nitrogen frameworks. The preparation and reactions of aniline and diphenylamine complexes are considered here: methylamine and dimethylamine derivatives will be described later.[3]

EXPERIMENTAL

Oxygen and moisture were excluded from all reactions. Ethylenediamine was refluxed over sodium and distilled. Aniline was distilled from potassium hydroxide: di- and tri-phenylamine were twice sublimed before use.

Liquid Ammonia Solutions of Diethylaluminium Chloride.—(a) *Physical measurements.* Samples of diethylaluminium chloride were sealed in fragile capillaries and broken under liquid ammonia. Conductivities (Figure) at −40° measured in a standard 30 ml. evacuable cell (cell constant 0·2774) on a Pye 11700 conductance bridge, were reproducible, but it was not possible to obtain results at sufficiently low concentrations for extrapolation to infinite dilution, *e.g.*, by use of the methods of Fuoss.[4] Molecular weights from vapour-pressure measurements [5] were as in Table 1.

TABLE 1

c^a	0·32	0·49	0·72	0·82	1·08	1·18
M^b	83	82	105	131	138	146

[a] Concn. in formula units/kg. NH_3. [b] $Et_2AlCl,2NH_3$: *M*, 154·5.

(b) *Reaction with potassium salts.* Potassium iodide (4·68 g., 28·2 mmoles) was added to diethylaluminium chloride (3·40 g., 28·2 mmoles) in liquid ammonia (50 ml.) at −78°. The white precipitate, which was filtered off, washed with 4 × 20 ml. ammonia, and dried under reduced pressure, was potassium chloride (27 mmoles, 96%), identified by its *X*-ray powder photograph and analysis (Found: Cl, 47·4. Calc. for KCl: Cl, 47·5%). The washings and filtrate were evaporated, leaving the *adduct* $Et_2AlI,2NH_3$ [Found: Et, 22·2; Al, 10·4; I, 50·8%; *M* (v.p. depression of 0·52m soln.), 173. $C_4H_{16}AlIN_2$ requires Et, 23·6; Al, 10·9; I, 51·6%; *M*, 246]. Similarly, from diethylaluminium chloride and potassium thiocyanate in liquid ammonia, KCl (94%) was obtained but we could not purify the ammonia-soluble product. From diethylaluminium chloride and potassium borohydride the products were KCl (89%) and the *adduct* $Et_2Al(BH_4),2NH_3$ (Found: Et, 42·4; Al, 20·1. $C_2H_{20}AlBN_2$ requires Et, 43·4; Al, 21·1%), which was insoluble in organic solvents and decomposed slowly above *ca.* 35° before melting. The adducts $Me_2AlCl,2NH_3$ (Found: Al, 21·1; Cl, 28·0; NH_3, 26·8. Calc. for $C_2H_{12}AlClN_2$: Al, 21·3; Cl, 28·0; NH_3, 26·9%) and $Me_2AlI,2NH_3$ (Found: Al, 12·1; I, 16·1; NH_3, 15·5. Calc. for $C_2H_{12}AlIN_2$: Al, 12·4; I, 16·3; NH_3, 15·6%) were made similarly.

(c) *Reaction with ethylenediamine* (*en*). Ammonia (36·3 mmoles) was condensed into diethylaluminium chloride (2·18 g., 18·1 mmoles) in toluene (20 ml.) at −78° and ethylenediamine (3·91 g., 65 mmoles) in toluene (15 ml.) added with stirring at 0°. During 3 hr. at room temperature, ammonia (36·0 mmoles) was collected, and the white precipitate of *diethylaluminium chloride–2-ethylenediamine* (4·1 g., 17·0 mmoles) was filtered off, washed with 6 × 10 ml. toluene, and freed from solvent under reduced pressure (Found: Et, 23·8; Al, 11·2; Cl, 14·3. $Et_2AlCl,2en$ requires Et, 24·2; Al, 11·2; Cl, 14·7%).

Triethylaluminium–ammonia.— A pressure–composition study at −78° showed that triethylaluminium absorbed 2 mol. of ammonia at this temperature to give a liquid adduct. Conductivity and vapour-pressure measurements on solutions of triethylaluminium in liquid ammonia were made in the same way as for solutions of diethylaluminium chloride (Found: at concn. 0·41 formula unit/kg. NH_3: *M*, 149; at concn. 0·82 formula unit/kg. NH_3: *M*, 148. Calc. for $Et_3Al,2NH_3$: *M*, 148). It was not possible to make the adduct $Et_2AlCl,2NH_3$ either by treating Et_3Al,NH_3 with ammonium chloride at 20°, or by the reaction between $Et_3Al,2NH_3$ and HCl at −78°. The reactions were complicated.

Adducts of Ethylenediamine.—The adducts $(Et_2AlCl)_2,en$, Et_2AlCl,en, $Et_2AlCl,2en$, and $EtAlCl_2,2en$ were made by the interaction of the stoicheiometric quantities of the components in toluene below 0°. Analytical data are given in Table 2. The bisdiamine adducts $Et_2AlCl,2en$ and $EtAlCl_2,2en$ dissolved in, and could be recovered unchanged from, liquid ammonia. Conductivity data are shown in the Figure. In neither case was potassium chloride precipitated when potassium iodide was added to liquid ammonia

---

[1] Part I, M. Cohen, J. K. Gilbert, and J. D. Smith, *J. Chem. Soc.*, 1965, 1092.

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

[3] K. Gosling, J. D. Smith, and D. Wharmby, unpublished work.

[4] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 476; R. M. Fuoss, *ibid.*, 1935, **57**, 488.

[5] R. W. Parry, G. Kodama, and D. R. Schultz, *J. Amer. Chem. Soc.*, 1958, **80**, 24; WADC Technical Report 56-318, 1956, p. 85.

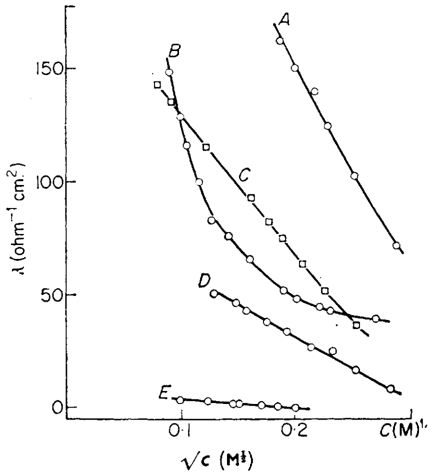
solutions. Triethylaluminium gave only a 1 : 1 adduct, even with excess of ethylenediamine [n.m.r. in cyclohexane: CH_2(en) 7·26; NH_2(broad) 7·9; CH_3(Et) 8·99; CH_2(Et) 10·27 τ. $J(CH_2-CH_3) = 7·8$ c./sec.]: this decomposed slowly at room temperature and more quickly at 50° giving one equiv. of ethane. A second mol. of ethane was liberated above 130° leaving a *solid* $[EtAl(NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH)]_x$, which was soluble and polymeric in benzene (Found: Et, 24·9; Al, 23·5%; *M*, 1950. $C_4H_{11}AlN_2$ requires Et, 25·5; Al, 23·7%; *M*, 114).

TABLE 2

Ethylenediamine adducts of ethylaluminium chlorides

	Found/calc.				
	Et (%)	Al (%)	Cl (%)	*M*	
Et_3Al,en	48·1/50·0	15·3/15·5	—	180/174 [a]	*b*
$(Et_2AlCl)_2$en	38·1/38·8	17·8/17·9	23·5/23·5	291/301 [a]	*b*
Et_2AlCl,en	32·3/32·5	15·0/15·1	19·3/19·8	—	*c*
Et_2AlCl,2en	23·2/24·2	10·9/11·2	14·6/14·7	235/240 [d]	*c*
$EtAlCl_2$,2en	11·0/11·7	10·6/10·9	28·3/28·7	—	*c*

[a] Cryoscopically in benzene. [b] Liquid adduct, soluble in organic solvents. [c] Solid adduct, insoluble in organic solvents. [d] From vapour-pressure depression.[5]



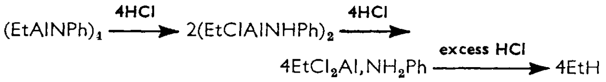
Plot of equivalent conductivity (λ) against square-root of concentration (*c*)

A $Et_2AlI,2NH_3$
B $Et_2AlCl,2NH_3$
C $EtAlCl_2$,2en
D Et_2AlCl,2en
E $Et_3Al,2NH_3$

Derivatives from Aniline and Triethylaluminium.—When aniline (15·5 mmoles) in toluene (20 ml.) was added to triethylaluminium (1·78 g., 15·5 mmoles) in toluene (15 ml.) at −78°, ethane was evolved immediately, and 15·2 mmoles were collected as the solution warmed to 0° during 2 hr. After concentration, *di-μ-anilidobisdiethylaluminium*, m. p. 58°, crystallised slowly [Found: Et, 31·9; Al, 15·2%; *M*, 355. $(Et_2AlNHPh)_2$ requires Et, 32·8; Al, 15·2%; *M*, 354]. A sample (3·31 g., 9·4 mmoles) of $(Et_2AlNHPh)_2$ was stable below 90°, but after 12 hr. at 150° gave ethane (18·6 mmoles) and an amorphous solid which was insoluble in organic solvents, but which at 250°/10^{-3} mm. yielded an off-white crystalline *sublimate* [Found: Et, 19·1; Al, 18·1%; *M*, 589. $(EtAlNPh)_4$ requires Et, 19·9; Al, 18·5%; *M*, 588].

Reactions of $(EtAlNPh)_4$.—(a) *With hydrogen chloride.* Dry HCl was distilled into a solution of $(EtAlNPh)_4$ in toluene (15 ml.) at 0°, and the products (see below) identified by analysis, m. p., molecular weight, and *X*-ray powder photographs. The stepwise reaction sequence of Scheme 1 was confirmed: no ethane was evolved until more than 8 equiv. of HCl were added.

Scheme 1



$$(EtAlNPh)_4 \xrightarrow{4HCl} 2(EtClAlNHPh)_2 \xrightarrow{4HCl} 4EtCl_2Al,NH_2Ph \xrightarrow{\text{excess HCl}} 4EtH$$

(b) *With ammonia.* Ammonia (15·6 mmoles) was condensed into a stirred solution of $(EtAlNPh)_4$ (1·14 g.; 7·8 mmoles) in toluene (40 ml.) at 0°. The white amorphous precipitate of *diamidoethylaluminium* which formed slowly during 3 hr. was filtered off and washed with toluene, and the solvent was removed under reduced pressure [Found: Et, 32·4; Al, 30·4. $EtAl(NH_2)_2$ requires Et, 33·0; Al, 30·6%]. The filtrate was treated with dry HCl and the precipitate of anilinium chloride washed with ether and dried (7·0 mmoles, m. p. 198°, lit.,[6] 198°).

Derivatives from Aniline and Diethylaluminium Chloride.—A solution of aniline (43·4 mmoles) and diethylaluminium chloride (5·22 g., 43·4 mmoles) in toluene (20 ml.) was stable below 0° but slowly gave ethane at room temperature. After 2 hr. at 57° ethane (42·5 mmoles) was collected and, after removal of solvent, there remained a glassy *solid* which slowly crystallised, m. p. 58—61° [Found: Et, 15·2; Al, 14·6; Cl, 19·1%; *M*, 369. $(EtClAlNHPh)_2$ requires Et, 15·8; Al, 14·7; Cl, 19·3%; *M*, 367]. A sample of $(EtClAlNHPh)_2$ gave one equiv. of ethane (per monomer unit) after 14 hr. at 162° and an amorphous white *solid* which was insoluble in organic solvents (Found: Al, 17·6; Cl, 23·0. ClAlNPh requires Al, 17·6; Cl, 23·1%). It sublimed with difficulty (and some decomposition) at *ca.* 300°/10^{-3} mm. and the sublimate, which analysed correctly for AlClNPh, appeared to be crystalline (powder pattern). The crystalline form was precipitated when diethylaluminium chloride (48·1 mmoles) and aniline (48·1 mmoles) in tetralin (25 ml.) were heated under reflux (207°) for 14 hr.; the darkening of the solution may indicate some attack on the solvent. In a number of similar experiments, only the glassy form was obtained: the production of the crystalline form seems to depend critically on concentration, time of refluxing, etc. The crystalline form was so insoluble that satisfactory cryoscopic measurements could not be made, but a molecular weight of 760 ± 150 was estimated by a differential Swietoslavski ebulliometer[7] [$(ClAlNPh)_4$ requires *M*, 614]. The compound was insufficiently volatile for a determination of its mass spectrum by the facilities at present available.

Reactions of $(ClAlNPh)_4$.—(a) *With ammonia.* Ammonia was condensed on a stirred suspension of $(ClAlNPh)_4$ in toluene at 0°. After several hours, the white solid was filtered off, washed with 4 × 50 ml. toluene, dried, and analysed. Aniline was recovered from the filtrate by treatment with hydrogen chloride. Results of several experiments appear in Table 3. All the amido-derivatives obtained were apparently amorphous to *X*-rays and between crossed nicols, and insoluble in hydrocarbon solvents, ether, and tetrahydrofuran. The compound

---

[6] 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1965.

[7] A. Weissberger, ed., 'Physical Methods of Organic Chemistry,' Interscience, London, 1959, vol. 1, p. 377.

TABLE 3

Reaction of $(ClAlNPh)_4$ with ammonia

$(ClAlNPh)_4$ taken (mmole)	6·25	4·26	4·1
NH_3 taken/recovered (mmole)	124·9/51·0	34·1/—	16·4/—
Mmole NH_3 absorbed per mmole ClAlNPh	11·8	8·0	4·0
$PhNH_3Cl$ recovered (mmole)	21·1	15·5	—
Product	$ClAl(NH_2)_2,NH_3$	$ClAl(NH_2)_2$	$ClAl(NH_2)(NHPh)$
Found/calc.			
Al (%)	24·1/24·2	29·7/29·9	15·7/15·8
Cl (%)	31·7/31·8	37·4/37·5	20·6/20·8

$ClAl(NH_2)_2,NH_3$ was also insoluble in liquid ammonia. On heating it lost ammonia reversibly, and the dissociation pressure obeyed the equation log p(mm.) = $-2841/T + 10{\cdot}1$. Hence ΔH for the reaction $ClAl(NH_2)_2,NH_3 \rightleftharpoons ClAl(NH_2)_2 + NH_3$ is 13·0 kcal./mole.

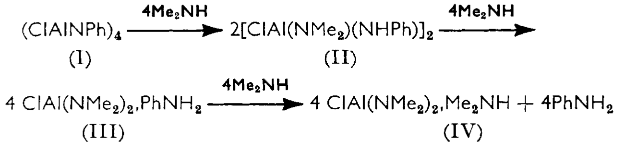
(b) *With dimethylamine.* The interaction of $(ClAlNPh)_4$ and dimethylamine was studied similarly, but the products were soluble in toluene, and crystalline. The details (Table 4) indicate Scheme 2.

TABLE 4

Reaction of $(ClAlNPh)_4$ with dimethylamine

$(ClAlNPh)_4$ taken (mmole)		3·2	3·25	3·6	3·3
Me_2NH taken (mmole)		6·4	13·0	28·6	39·7
$PhNH_3Cl$ recovered (mmole)		—	—	—	11·1
Product		(I) + (II)	(II)	(III)	(IV)
Found/calc.	Al (%)	15·1/15·3	13·4/13·5	11·0/11·1	16·1/16·3
	Cl (%)	20·2/20·2	17·3/17·4	14·4/14·6	21·1/21·4
	M	452/469	409/397	240/243	168/165
M. p.			92—94°	72—73	132—134

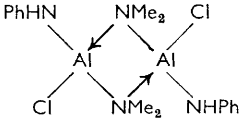
Scheme 2



$$\underset{(I)}{(ClAlNPh)_4} \xrightarrow{4Me_2NH} \underset{(II)}{2[ClAl(NMe_2)(NHPh)]_2} \xrightarrow{4Me_2NH}$$

$$\underset{(III)}{4\ ClAl(NMe_2)_2,PhNH_2} \xrightarrow{4Me_2NH} \underset{(IV)}{4\ ClAl(NMe_2)_2,Me_2NH} + 4PhNH_2$$

The dimethylamine thus adds successively across the Al–N bonds of $(ClAlNMe)_4$ giving the complex (III), and then displaces the weaker base aniline. The molecular weight of the material obtained from a 1 : 2 mixture of (I) and Me_2NH showed that half the molecules of (I) had reacted. There was no evidence for the formation of an intermediate $(ClAlNPh)_4,2Me_2NH$ (M, 694). The structure of (II) remains uncertain, since the four-membered Al–N ring may have NMe_2 or NHPh bridges. It has been suggested[8] that terminal and bridging NR_2 groups can be distinguished by tensimetric titrations with boron trichloride. Only terminal groups react rapidly. A tensimetric titration of a small sample of (II) in decane at 20° showed a sharp discontinuity when two moles of BCl_3 per mole of (II) had been added. In another experiment, the white solid from two equivs. of BCl_3 and one of (II) in pentane was filtered off, washed with pentane, sublimed, and shown to be $(Cl_2AlNMe_2)_2$, m. p. 148° (lit.,[8] 150°) (Found: Al, 18·8; Cl, 49·6. Calc.for $C_2H_6AlCl_2N$: Al, 19·0; Cl, 50·0%). An unstable solid with composition $PhHNBCl_2$[9] (Found: Cl, 38·9. Calc. for $C_6H_6BCl_2N$: Cl, 40·8%) was isolated from the filtrate. This suggests that the structure of (II) is as shown.



(II)

The possibility of a rearrangement during the reaction with BCl_3 cannot at present be ruled out, though n.m.r. measurements show[10] that bridging and terminal NR_2 groups in $[Al(NR_2)_3]_2$ interchange more slowly than alkyl groups in $[AlR_3]_2$. The relative bridging strengths of various $>NR_2$ groups in Al–N compounds are being studied.

Aniline and Diphenylamine Derivatives of Ethylaluminium Dichloride.—The crystalline adducts of aniline and di- and tri-phenylamine with ethylaluminium dichloride (Table 5) were obtained by mixing solutions containing equivalent quantities of the components at −78°, and removing the solvent at room temperature. On heating to 120°, the aniline and diphenylamine adducts gave an equivalent of ethane and the crystalline, sublimable derivatives $(Cl_2AlNHPh)_2$ and $(Cl_2AlNPh_2)_2$. The triphenylamine adduct dissociated in a vacuum at room temperature.

TABLE 5

Derivatives of ethylaluminium dichloride

		Found/calc.			
	M. p.	Et (%)	Al (%)	Cl (%)	M
$EtAlCl_2,PhNH_2$	57—59°	13·1/13·2	12·1/12·3	32·0/32·2	226/220
$EtAlCl_2,Ph_2NH$	118	9·6/9·8	9·0/9·1	23·9/23·9	291/296
$AlCl_3,PhNH_2$[a]	89—91	—	11·6/11·9	46·7/47·0	229/226
$(Cl_2AlNHPh)_2$	170	—	14·0/14·2	37·2/37·3	382/380
$(Cl_2AlNPh_2)_2$	138	—	10·0/10·1	26·5/26·7	524/532

[a] From $PhNH_3Cl$ and $EtAlCl_2$ at 20°.

The compound $(Cl_2AlNPh_2)_2$ (3·17 g., 5·95 mmoles) in toluene (50 ml.) at 0° absorbed 58·9 mmoles of ammonia. The white *precipitate* was filtered off, washed with 6 × 20 ml. of toluene, and dried in a vacuum (Found: Al, 14·7; Cl, 38·8. $Cl_2AlNH_2,4NH_3$ requires Al, 14·8; Cl, 38·9%). Diphenylamine (11·1 mmoles) was recovered from the filtrate and washings. This indicates reaction (1). Compound

$$(Cl_2AlNPh_2)_2 + 10NH_3 \longrightarrow \underset{(V)}{2Cl_2Al(NH_2),4NH_3} + 2Ph_2NH \quad (1)$$

(V) lost one mol. of ammonia reversibly on heating and the dissociation pressure measured between 58 and 127° obeyed the equation log p(mm.) = $2004/T + 7{\cdot}52$ whence ΔH for the reaction $Cl_2AlNH_2,4NH_3 \longrightarrow Cl_2AlNH_2,3NH_3$ (VI) + NH_3 is 9·75 kcal./mmole. The ammonia *complex* (VI) (Found: Al, 16·1; Cl, 42·8. $AlCl_2NH_2,3NH_3$ requires Al, 16·4; Cl, 43·0%) could be obtained by heating (V) under reduced pressure at 120°. When (VI) was heated above 160°, aluminium trichloride–ammonia,[11] identified by its analysis and X-ray powder photograph, sublimed. This is in accord with the observation[1] that uncomplexed Cl_2AlNH_2 decomposes similarly at this temperature.

DISCUSSION

Ammonia Complexes.—The molecular weight of the adduct $Et_2AlCl,2NH_3$ (VII), as determined by the

---

[8] J. K. Ruff, *J. Amer. Chem. Soc.*, 1961, **83**, 2835.

[9] W. Gerrard and E. F. Mooney, *J. Chem. Soc.*, 1960, 4028.

[10] E. P. Schram, *Inorg. Chem.*, 1966, **5**, 1291.

[11] W. Klemm and E. Tanke, *Z. anorg. Chem.*, 1931, **200**, 343; W. Klemm, E. Clausen, and H. Jacobi, *ibid.*, p. 367.

depression of the vapour pressure of liquid ammonia solutions, was concentration-dependent, falling with increased dilution. This suggests dissociation at low concentrations. The conductivities of liquid ammonia solutions (equivalent conductivity at concentration 0·01M, $\lambda_{100} = 130$ ohm^{-1} cm.^{2}) are in the range expected for 1 : 1 electrolytes (cf. KCl [12] 117; KBr [12] 160 ohm^{-1} cm.^{2}) and much larger than values for non-electrolytes (cf. $MeCONH_2$ [13] <1 ohm^{-1} cm.^{2}). Molecular-weight and conductivity measurements thus suggest an ionic structure such as $[Et_2Al(NH_3)_2]^+Cl^-$ (VIII) or $[NH_4]^+[Et_2AlClNH_2{}^-]$ (IX) rather than one with pentaco-ordinate aluminium or one in which the second molecule of ammonia is held weakly in the solid, but dissociated in solution. The infrared spectra of (VII) and related compounds show peaks characteristic of co-ordinated ammonia [14] rather than $NH_4{}^+$: this is evidence against structure (IX). The rapid and quantitative precipitation of potassium chloride by liquid ammonia solutions of potassium salts suggests metathetical reactions involving structure (VIII), *e.g.*, (2). It is noteworthy that in the reaction with potassium borohydride, hydrogen is evolved only slowly. This is evidence against structure (IX) since ammonium borohydride is

$$[Et_2Al(NH_3)_2]^+Cl^- + KX \longrightarrow [Et_2Al(NH_3)_2]^+X^- + KCl\downarrow \quad (X{=}I,CNS,BH_4) \qquad (2)$$

known [15] to decompose to hydrogen and ammonia–borane. $[Et_2Al(NH_3)_2]^+Cl^-$ is thus analogous to 'borazylammonium' [16] salts and $[Me_2Ga(NH_3)_2]^+Cl^-$,[17] which also undergoes metathetical reactions of the type described. Diethylaluminium chloride–pyridine has been reported to be a good conductor in nitrobenzene and the structure $[Et_2Al2py]^+[Et_2AlCl_2]^-$ has been suggested.[18]

In order to compare the aluminium and gallium compounds more closely, the methylaluminium derivative $Me_2AlCl,2NH_3$ was made. This had properties like those of the ethyl analogue, but was not isomorphous with $[Me_2Ga(NH_3)_2]Cl$. The aluminium compounds were very much more reactive than the gallium compound towards moisture and oxygen, so reactions in aqueous solution were ruled out. The aluminium compounds were, however, more stable than the gallium complexes in the absence of moisture and air. Thus $[Me_2Al(NH_3)_2]Cl$ was unchanged after six months in a sealed tube whereas $[Me_2Ga(NH_3)_2]Cl$ was completely converted into ammonium chloride and $(Me_2GaNH_2)_2$.[17] This is in accord with the generalisation that gallium– and boron–chlorine bonds are ammonolysed more readily than aluminium–chlorine bonds.[19]

The bis-ammonia complexes of dialkyl-aluminium and -gallium chlorides also behave differently towards ethylenediamine. Thus, whereas $[Me_2Ga(NH_3)_2]Cl$ gives the compound [Me_2Ga en]Cl which shows ionic reactions in aqueous solution, $[Et_2Al(NH_3)_2]Cl$ reacts with 2 mol. of ethylenediamine to give an adduct Et_2AlCl,2en. This observation prompted a brief investigation of ethylenediamine adducts. The compounds Et_2AlCl,2en and $EtAlCl_2$,2en were soluble in liquid ammonia to give conducting solutions, but potassium chloride was not precipitated on addition of potassium iodide solution. The adducts may have structures such as $[Et_2Al\ en_4]^+[Et_2AlCl_2]^-$. Structures with $[NH_4]^+$ or $[NH_2(CH_2)_2NH_3]^+$ ions seem less likely from the infrared spectra. 2 : 1 Complexes between trimethylaluminium and bidentate ligands have recently been described.[20] Diethylaluminium chloride forms a liquid adduct $(Et_2AlCl)_2$,en which is soluble and monomeric in benzene, but on standing this slowly gives solid Et_2AlCl,2en and diethylaluminium chloride (3). Apparently Et_2AlCl,en

$$4(Et_2AlCl)_2,en \longrightarrow 2Et_2AlCl,2en + 3(Et_2AlCl)_2 \qquad (3)$$

is not formed. Material with this composition can be obtained by interaction of the stoicheiometric quantities of diethylaluminium chloride and ethylenediamine, but it is amorphous and insoluble both in organic solvents and in liquid ammonia. This suggests a structure with $Al{-}NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2{-}Al$ bridges between penta- or hexa-co-ordinate aluminium atoms. The formation of Et_2AlCl,2en both directly and from $Et_2AlCl,2NH_2$ remains puzzling.

Triethylaluminium is freely soluble in liquid ammonia without evolution of ethane, and vapour-pressure measurements indicate formation of a monomeric adduct. The conductivity ($\lambda_{100} = 4{\cdot}5$ ohm^{-1} cm.^{2}) is about that found for many non-ionised substances.[13] The adduct $Et_3Al,2NH_3$, detected in a pressure–composition study, may be an example of a compound with a pentaco-ordinate aluminium atom, but data on liquid ammonia solutions are equally consistent with the presence of molecules of Et_3Al,NH_3. Since complexed and solvating ammonia molecules are probably exchanging rapidly,[21] the distinction between $Et_3Al,2NH_3$ and Et_3Al,NH_3 in liquid ammonia is of little significance. The adduct Et_3Al,en is monomeric in benzene and all the methylene protons are shown to be equivalent by nuclear magnetic resonance. This may imply rapid inter- or intra-molecular exchange between unidentate ethylenediamine molecules,[22] or a pentaco-ordinate aluminium atom: measurements at low temperatures would be of interest here.

---

[12] V. F. Hnizda and C. A. Kraus, *J. Amer. Chem. Soc.*, 1949, **71**, 1565.

[13] F. A. Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 2162.

[14] J. Fujita, K. Nakamoto, and M. Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3295; R. J. H. Clark and C. S. Williams, *J. Chem. Soc.* (*A*), 1966, 1425.

[15] S. G. Shore and R. W. Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 8.

[16] H. Nöth and H. Beyer, *Chem. Ber.*, 1960, **93**, 1078; H. Nöth, H. Beyer, and H.-J. Vetter, *ibid.*, 1964, **97**, 110.

[17] D. F. Shriver and R. W. Parry, *Inorg. Chem.*, 1962, **1**, 835.

[18] H. Lehmkuhl, quoted in R. Köster and P. Binger, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 263, 283.

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

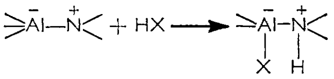
[20] K. M. Thiele, H. K. Muller, and W. Brüser. *Z. anorg. Chem.*, 1966, **345**, 194; K.-H. Thiele and W. Brüser, *ibid.*, 1966, **348**, 179.

[21] T. Mole, *Austral. J. Chem.*, 1963, **16**, 801; A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Comm.*, 1966, 89.

[22] T. Mole, *Chem. and Ind.*, 1964, 281.

Aniline Derivatives.—Aniline adducts of ethylaluminium chlorides are similar to the corresponding methylamine and ammonia adducts, except that they lose ethane more readily and the phenylammonium compound corresponding to $[MeNH_3]^+[EtAlCl_3]^-$ [23] is unstable at room temperature. These differences reflect the increased acidity of protons in aromatic compared with aliphatic amines. Ethane elimination proceeds stepwise and gives isolable crystalline intermediates, *e.g.*, $Et_2Al{\cdot}NHPh$, $EtClAl{\cdot}NHPh$, $Cl_2Al{\cdot}NHPh$, which are dimeric in freezing benzene. The corresponding methylamine derivatives have values of n as follows: $Et_2Al{\cdot}NHMe$[3] 3·0; $EtClAl{\cdot}NHMe$[2] 3·6; $Cl_2Al{\cdot}NHMe$[2] 2·4. Steric hindrance, less in the dimer than in the trimer,[24] may be important in determining the molecular complexity of the aniline derivatives; this point is receiving attention. The infrared spectra of the aniline derivatives show bands characteristic of the NHPh group: the single N–H stretching frequency decreases as ethyl groups attached to aluminium are replaced by chlorines, *e.g.*, $Et_2Al{\cdot}NHPh$ 3240, $EtClAl{\cdot}NHPh$ 3200, $Cl_2Al{\cdot}NHPh$ 3140 cm.$^{-1}$.

The isolation of the tetrameric derivatives $(RAlNPh)_4$ has made possible a preliminary study of the reactions of molecules with Al–N frameworks. The compounds HX (X = Cl, NMe_2, or NH_2) readily attack Al–N bonds at room temperature according to the equation (4). Except in complexes R_3Al,NR_3, this reaction takes precedence over reaction of HX with Al–C bonds and is likely to be useful for the preparation of new aluminium–nitrogen derivatives.



$$\geqslant\overset{-}{Al}-\overset{+}{N}\!< + HX \longrightarrow \geqslant\underset{X}{\overset{-}{Al}}-\underset{H}{\overset{+}{N}}\!< \qquad (4)$$

Amido-derivatives of Aluminium.— Tris(amido)aluminium, $Al(NH_2)_3$, loses ammonia at room temperature.[25] Bis(amido)-derivatives, *e.g.*, $EtAl(NH_2)_2$, $ClAl(NH_2)_2$, which are more stable, are readily obtained by treating $(EtAlNPh)_4$ or $(ClAlNPh)_4$ with excess of ammonia, but it has not proved possible to recrystallise them because of their extreme insolublity in organic solvents. It is likely that their structures consist of cross-linked $\geqslant Al-NH_2 \longrightarrow Al\leqslant$ units. They do not form adducts with aniline but $ClAl(NH_2)_2$ forms a 1 : 1 adduct with the more basic ammonia. The value of 13·0 kcal./mole for ΔH of the reaction $ClAl(NH_2)_2,NH_3 \longrightarrow ClAl(NH_2)_2 + NH_3$ suggests that Al–N rather than hydrogen bonds are broken in the dissociation.

Monoamido-derivatives Et_2AlNH_2 (trimeric in benzene), $EtClAlNH_2$ and Cl_2AlNH_2 were obtained earlier.[1] The last compound can also be made by the reaction of ammonia with $(Cl_2AlNPh_2)_2$ from which the weakly basic diphenylamine is readily displaced. With excess of ammonia, an adduct $Cl_2Al(NH_2),4NH_3$ is obtained: this loses one mol. of ammonia reversibly below 150°: ΔH for this dissociation is comparable with that for the higher ammonia adducts of aluminium halides.[11] The N–H infrared stretching frequencies of the adducts with co-ordinated ammonia are broadened and shifted to low frequencies, suggesting that hydrogen bonds are important in the solid.

This research was supported by the Air Force Materials Laboratory, Research and Technology Division AFSC, through the European Office of Aerospace Research, Department of the Air Force. We thank Shell Chemical Company for gifts of aluminium alkyls.

[7/596 *Received, May* 15*th*, 1967]

---

[23] J. D. Smith, *J. Chem. Soc.*, 1962, 4734.

[24] O. T. Beachley and G. E. Coates, *J. Chem. Soc.*, 1965, 3241.

[25] E. Wiberg and A. May, *Z. Naturforsch.*, 1955, **10b**, 231.