352. *Aluminium Halide Complexes with Pyridine, Trimethylamine, and Triethylamine. Part I.*

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The following 1 : 1 complexes of aluminium halides and nitrogen bases have been prepared: C_5H_5N,AlX_3, NMe_3,AlX_3, where $X = Cl, Br, I$, and also $NEt_3,AlCl_3$. For a given base the melting point of a complex seems to depend but little on whether X is Cl, Br, or I, in agreement with earlier work on the NH_3 complexes.

The side reactions which occur with triethylamine and aluminium bromide and iodide are briefly discussed.

The co-ordinate link $R \rightarrow AlX_3$ formed between a donor molecule R and a half-molecule of aluminium halide is of great interest for the theory of Friedel–Crafts catalysis. Previous work from this laboratory has been concerned to estimate the strength of this link in a number of cases by measurements of the heat of mixing of the two components in the presence of an inert diluent (Dilke and Eley, *J.*, 1949, 2601; Dilke, Eley, and Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 261). We now propose a more direct approach to the bond energy through the heat of hydrolysis of the complex, and for this purpose have investigated the preparation of the crystalline 1 : 1 complexes. In this paper we describe the method finally adopted, and its successful application in seven instances. The tertiary amines have been chosen as donor molecules because of the known tendency of primary and secondary amines and ethers to give side reactions.

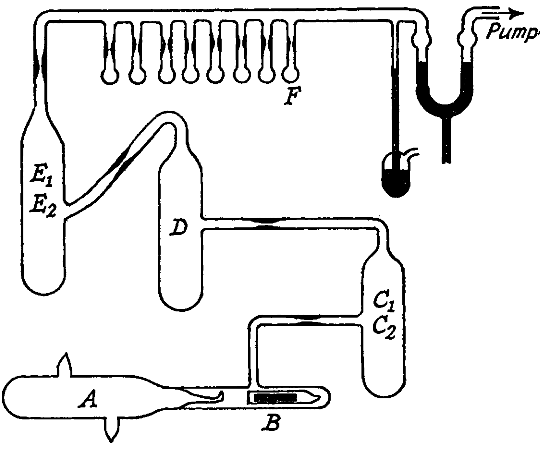
Experimental

Preparative Method.—In accordance with earlier work (*e.g.*, Muller and Bauer, *Z. anorg. Chem.*, 1926, **156**, 69), we found that complexes crystallised from solution contained many molecules of the donor molecule, and sometimes solvent molecules, and were often of indefinite composition. Being primarily interested in 1 : 1 complexes, we finally evolved the following method, which we describe for the specific case of pyridine and aluminium chloride. The preparation throughout was conducted in an all-glass apparatus (see fig.), capable of evacuation to 10^{-6} mm. of Hg, mercury cut-offs being used in place of greased taps wherever necessary. Tube *A* contained pure aluminium chloride which, after the seal had been broken with the magnetic hammer *B* enclosed in glass, was sublimed successively through tubes C_1 and C_2 (only one shown in the diagram), and a third time into the reaction vessel *D*, where it formed a film on the walls of the vessel. After each sublimation the residue-vessel was sealed off and removed. The reaction tube *D* was then cooled in ice and the necessary amount of pyridine condensed into it, from a storage bulb beyond the mercury cut-off and not shown in the diagram.

After ½ hour's contact with the aluminium chloride, excess of pyridine was distilled back into its storage vessel by cooling the latter in liquid oxygen. The complex was then connected to the pumps and heated to near its b. p., until, on raising the cut-off, no increase in pressure occurred. At this stage the complex was distilled twice through vessels E_1 and E_2 (only one shown), and finally sealed off in ampoules *F*, of a size suitable for subsequent calorimetric and dipole work.

Additional Measurements.—M. p.s of the complexes were all determined in the sealed ampoule and are " corrected." The aluminium chloride–pyridine complex was further investigated: the pressure–temperature relation of a known amount was taken in a glass vessel attached to a glass-spiral pressure gauge, the whole being kept at a temperature uniform to within 3°; and a freezing-point depression measurement was made in an evacuated apparatus with magnetic stirring.

Analysis.—An ampoule of complex was broken under sodium hydroxide solution, the amine liberated distilled into excess of standard acid, and its amount determined by a back-titration, the hydrogen ion being determined potentiometrically (quinhydrone electrode). The residual solution was divided into aliquot portions. Chloride ion was determined in one half by Volhard's method, and aluminium in the other half gravimetrically with 8-hydroxyquinoline. Bromide and iodine ions were determined with silver nitrate and eosin adsorption indicator.



Materials.—*Aluminium chloride.* Commercial aluminium chloride was mixed with aluminium turnings and resublimed in a stream of dry hydrogen chloride, the iron chlorides thus being reduced to iron (Gratzianskii, *Ukrain. Chem. J.*, 1934, **9**, 432). The white product was then resublimed in dry nitrogen to remove adsorbed hydrogen chloride. Analysis showed it to be 99·6±1% pure, and no iron was detectable by thiocyanate. However, it was still found necessary to resublime this material seven times *in vacuo*, the last 10% being rejected each time, before all the aluminium chloride could be sublimed without leaving an ash-like residue. We attribute the effect to slightly hydrated aluminium chlorides, which sublime with the anhydrous material, afterwards decomposing into alumina and hydrogen chloride.

To overcome this difficulty, aluminium chloride was synthesised directly from the elements. Chlorine from a cylinder was diluted with nitrogen, dried (P_2O_5), and passed over heated aluminium turnings that had previously been carefully dried. The aluminium chloride, as first formed, was tinged yellow by ferric chloride, which was removed as the product passed over further aluminium in the reaction tube. The product was sublimed into a tube fitted with a " breakable joint " and sealed off under dry nitrogen. This tube could subsequently be attached to the vacuum apparatus (tube *A*).

Aluminium bromide and iodide. These were prepared by a modification of the above procedure, as described by Eley and King (*Trans. Faraday Soc.*, 1951, **47**, 1287).

Pyridine. B.D.H. " AnalaR " product was dried over potassium hydroxide and distilled; it had b. p. 115°.

Tri-methyl- and -ethyl-amine. B.D.H. trimethylamine was distilled off potassium hydroxide in a vacuum apparatus, then off freshly sublimed phosphoric oxide into the storage vessel. This process is reported to remove primary and secondary amines (Brown, Bartholmay, and Taylor, *J. Amer. Chem. Soc.*, 1944, **66**, 435); the base had v. p. at 0° = 680 mm., agreeing with Simon and Huter's value (*Z. Elektrochem.*, 1935, **41**, 28). Triethylamine was treated in the same way to give a product of b. p. 89°.

The Complexes.—The formula given is the monomeric formula, which, in actual fact, probably holds for the molecule of complex in the crystalline state (cf. following discussion).

Aluminium Chloride–Pyridine.—This is a colourless crystalline *substance*, m. p. 118°±0·2° (Found: Al, 12·8; Cl, 50·5; C_5H_5N, 36·8. $C_5H_5N,AlCl_3$ requires Al, 12·7; Cl, 50·1; C_5H_5N, 37·2%).

Vapour density. 0·2796 G. of complex was sealed in a reaction vessel of volume 968·2 ml. The vessel was heated and pressure readings were taken up to 300°, at which temperature a slow side-reaction was detectable, rendering further heating undesirable. It seems very likely, by comparison with $NH_3,AlCl_3$, b. p. 422°, that we had not reached the b. p. of the complex. Therefore the significance of the apparent molecular weight value in Table 1 is that the gaseous complex is probably monomeric (*M* 212), but that some liquid was still present.

Molecular weight in benzene. 0·4799 G. of complex, dissolved in 35·21 g. of benzene, gave a f. p. depression of 0·183°, corresponding to *M* 380; *i.e.*, degree of association of monomer (*M* 212) into dimer = 0·88.

TABLE 1. *Apparent molecular weight of gaseous* $C_5H_5N,AlCl_3$.*

Temp.	230·3°	237·5°	258·5°	263·0°	270·0°	276·5°	288·5°	301·0°
Apparent *M*	801	788	507	453	466	384	317	284

* Calculated on the assumption that all the 0·2796 g. of complex is gaseous.

Molecular weight in nitrobenzene. Three experiments were made in a conventional apparatus, it being found that, unlike the case with benzene as solvent, the rate of water absorption was not sufficient to cause appreciable hydrolysis during the time concerned. Approximately 1% solutions were examined, and the molecular weights obtained were 240, 250, and 220.

Aluminium Chloride–Trimethylamine.—Trimethylamine was condensed on a film of aluminium chloride at −80° and reaction appeared to occur immediately. The complex is a colourless crystalline substance, m. p. 156·4°±0·2° (Found: Al, 14·1; C, 55·6; NMe_3, 30·3. Calc. for $NMe_3,AlCl_3$: Al, 14·0; Cl, 55·3; NMe_3, 30·7%).

Aluminium Chloride–Triethylamine.—The *complex*, when isolated, was slightly discoloured; it had m. p. 121·6—122·1° (Found: Al, 10·6; Cl, 46·9; NEt_3, 44·7. $NEt_3,AlCl_3$ requires Al, 11·5; Cl, 45·4; NEt_3, 43·1%). On prolonged heating above 300° the complex decomposed to give a fluorescent liquid.

Aluminium Bromide–Pyridine.—This *complex*, m. p. 115—117° (Found: Al, 7·5; Br, 70·1; C_5H_5N, 22·9. $C_5H_5N,AlBr_3$ requires Al, 7·8; Br, 69·4; C_5H_5N, 22·7%), and the *trimethylamine* analogue, m. p. 156·9°±0·2° (Found: Al, 8·5; Br, 73·4; NMe, 18·1. $NMe_3,AlBr_3$ requires Al, 8·3; Br, 73·6; NMe_3, 18·1%), were isolated as colourless crystals.

Aluminium Bromide–Triethylamine.—A side reaction occurred with the evolution of some gas, not condensable at a pressure of 25 mm. in a liquid-oxygen bath. The product was a liquid, with some tarry matter.

Aluminium Iodide–Pyridine.—This *complex*, m. p. 110·5—112° (Found: Al, 5·6; I, 78·3; C_5H_5N, 16·6. C_5H_5N,AlI_3 requires Al, 5·55; I, 78·2; C_5H_5N, 16·25%), and the *trimethylamine* analogue, m. p. 156·4°±0·2° (Found: Al, 5·7; I, 81·7; NMe_3, 12·8. NMe_3,AlI_3 requires Al, 5·8; I, 81·5; NMe_3, 12·7%), were also colourless crystals.

Aluminium Iodide–Triethylamine.—Evolution of some permanent gas occurred, and the only product was a tarry residue.

DISCUSSION

Melting Points.—In Table 2 are collected melting-point data for the complexes, together with published data on the $NH_3 \rightarrow AlX_3$ complexes (Klemm and Tanke, *Z. anorg. Chem.*, 1931, **200**, 343) and the simple halides Al_2X_6 (Fischer and Rahlfs, *ibid.*, 1932, **205**, 37).

TABLE 2. *Melting points of* AlX_3 *complexes.*

	Halide		
Ligand	$AlCl_3$	$AlBr_3$	AlI_3
" AlX_3 "	193°	97°	191°
C_5H_5N	118	115—117	110·5—112
NEt_3	121·6—122·1	—	—
NMe_3	156·4	156·9	156·4
NH_3	125	124	126

The peculiar behaviour over the series Al_2Cl_6, Al_2Br_6, Al_2I_6 has been attributed to the presence of an ionic lattice in Al_2Cl_6, whereas the other two halides have a molecular lattice (Fischer and Rahlfs, *loc. cit.*; Fischer, *ibid.*, 1931, **200**, 332). *X*-Ray and other work supports this view (Al_2Cl_6, Ketelaar, MacGillavry, and Renes, *Rec. Trav. chim.*, 1947, **66**, 501; Al_2Br_6, Gerding and Smit, *Z. physikal. Chem.*, 1941, *B*, **50**, 171; Renes and MacGillavry, *Rec. Trav. chim.*, 1945, **64**, 375). All the $NH_3 \rightarrow AlX_3$ complexes probably have molecular lattices (Klemm, Clausen, and Jacobi, *Z. anorg. Chem.*, 1931, **200**, 367) and this seems very likely to be so for the complexes we have prepared. We might then have expected a rise in melting point with molecular weight over any given series, X = Cl to I, for example, for C_5H_5N,AlX_3. It is rather striking that the melting point stays nearly constant over this series in all cases. The melting point T_m is given by the ratio of $\Delta H/\Delta S$, where ΔH is the heat-content change and ΔS the entropy change on melting. It may be that the expected increase in ΔH arising from increased van der Waals forces through the series X = Cl to I is somehow offset by a decrease in the ease with which the molecules pack into the lattice, ΔH remaining constant. If ΔS also remained constant, then T would stay constant. Alternatively, ΔH may show the expected increase but be offset by an increase in ΔS, but we cannot take the matter further without a determination of ΔH.

The Monomeric Formula.—The results on $C_5H_5N,AlCl_3$ suggest a considerable association into dimer in the gas phase and in benzene, but in nitrobenzene the substance is probably monomeric. The data on heats of mixing (Dilke, Eley, and Sheppard, *loc. cit.*) make it very unlikely that nitrobenzene will displace pyridine from the dissolved complex. The view that $C_5H_5N,AlCl_3$ is monomeric in nitrobenzene and does not undergo a displacement by the solvent, is supported by the work of Van Dyke and Crawford (*J. Amer. Chem. Soc.*, 1951, **73**, 2022). It seems very likely that the association in benzene and the gas phase is a dipolar association. This would agree with the high dipole moments, *ca.* 7 D, which might be expected from Nespital's results on $C_2H_5\cdot NH_2,AlCl_3$ and other complexes (*Z. physikal. Chem.*, 1932, *B*, **16**, 153). Ulich's freezing-point measurements (*ibid.*, Bodenstein Festband, 1931, 423) on aluminium chloride complexes in benzene (amine complexes were not investigated) established a partial association into dimers, which decreased as the solution was diluted, again suggesting dipolar association. Klemm, Clausen, and Jacobi (*loc. cit.*) found a monomeric formula for gaseous $NH_3,AlCl_3$, but in their case, the complex was so stable that its vapour density could be taken at a temperature above 390°. Our results would suggest that $C_5H_5N,AlCl_3$ would be monomeric in the gas at this temperature.

Dissociation of the Complexes.—In contrast to the result in Table 1, C_5H_5N,BF_3 has been investigated up to 356° without side reactions occurring (van der Meulen and Heller, *J. Amer. Chem. Soc.*, 1932, **54**, 4404). At 356° the complex was 56% dissociated into its components, and a bond energy for $N \rightarrow B$ of 50·6 kcal. was calculated. The bond energy of $C_5H_5N,AlCl_3$, in the light of the results in Table 1, which may be taken to imply no dissociation at 300°, is probably at least this. An estimate of 56·6 kcal. has been made from the heats of mixing of the components (cf. Dilke, Eley, and Sheppard, *loc. cit.*—figure revised in the light of more recent work by Mr. D. J. A. Dear). The successful dissociation of the boron trifluoride compounds depends (*a*) on their low boiling points and (*b*) on the relatively low catalytic activity of the boron trifluoride on the side reactions of the organic base.

Chemical Stability.—The NEt_3,AlX_3 complexes are unstable, entering into some side reaction, increasingly over the series Cl < Br < I. This series may be the order of the strength of the $N \rightarrow Al$ bond; thus, from heats of mixing by Mr. Dear we estimate for $C_5H_5N \rightarrow AlX_3$, 56·6, 71, and 77·1 kcal. for X = Cl, Br, and I, respectively. The order Cl < I < Br is found for the velocity of the Gattermann–Koch reaction, where I lies intermediately, possibly because of decomposition of the iodide (Dilke and Eley, *J.*, 1949, 2613).

Without further work, the nature of the side reaction must remain obscure. Nosaki (*J. Amer. Chem. Soc.*, 1942, **64**, 2920) has investigated the effect of heating the di-*n*-butylamine–aluminium chloride complex. At 190° a marked redistribution of alkyl groups occurs to give complexes of the primary and tertiary bases. This reaction is almost negligible with $NHEt_2,AlCl_3$. Above 200° with the *n*-butylamine complex he noted a slow side reaction to give high-boiling products, which he suggested might be an alkylation of the alkyl group of the tertiary amine. This is possibly what happened with our triethylamine complexes at *ca.* 300°.

In preliminary work on a monobutylamine complex, $C_4H_9\cdot NH_2,AlCl_3$, we attributed the indefinite composition and variable melting point of our products to the presence of alkyl-migration side reactions of the Nozaki type. However, it seems likely that the side reaction is negligible with the ethylamine and methylamine derivatives. Nespital (*loc. cit.*, p. 168) has isolated $C_2H_5{\cdot}NH_2,AlCl_3$, m. p. 63°, by distillation at 230°. Goubeau and Siebert (*Z. anorg. Chem.*, 1950, **261**, 63) prepared complexes of mono-, di-, and tri-methylamine with aluminium chloride but did not note any marked side reactions. They stated, however, that the last complex was not quite pure, and in fact its m. p. was 22° below that recorded by us.

We are attempting to apply this method to the preparation of ferric chloride complexes.

We gratefully acknowledge the award of a D.S.I.R. maintenance grant (to H. W.).

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[*Received, January* 14*th*, 1952.]