505. *Hydrazine. Part V.* Complex Halides of Aluminium and Hydrazine.*

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(*With Notes on the Optical Properties of the Crystals.* By H. C. G. VINCENT.)

Hydrazinium hexachloro- and hexabromo-aluminates are described. These compounds are unique, being the only known compounds in which aluminium is 6-covalent with chlorine and bromine. Attempts to make similar compounds of some ketazines and hydrazones were not successful. The reported existence of anhydrous hydrazinium hydrogen pentafluoroaluminate is confirmed, no other complex fluoride having been obtained. Corresponding iodoaluminates could not be isolated.

HÜCKEL ("Structural Chemistry of Inorganic Compounds," translated by Long, Elsevier Publ. Co., Amsterdam, 1950, Vol. I, p. 168, footnote) states, without giving references, that compounds of the type $M^I_3AlCl_6$ exist and contain $[AlCl_6]^{3-}$ ions; Sidgwick ("The Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, Vol. I, p. 435) maintains that only fluorine gives aluminium a covalency of more than 4. The original

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* Part IV, preceding paper.

literature contains, to our knowledge, only one reference to the preparation of compounds of the above type, Baud (*Ann. Chim. Phys.*, 1904, **1**, 8) claiming to have isolated both sodium and potassium hexachloroaluminate. However, the existence of these compounds was not confirmed by the later work of Kendall, Crittenden, and Miller (*J. Amer. Chem. Soc.*, 1923, **45**, 963) who, by an extensive thermal analysis of 41 systems, established the identity of 53 compounds, all of the general type $x\text{AlX}_3,y\text{M}^{n+}\text{X}_n$ (X = Cl or Br); in the individual formulations, y never exceeds x, and in the majority, $y = x$ or $0{\cdot}5x$ (*i.e.*, $\text{M}^{\text{I}}[\text{AlX}_4]$, $\text{M}^{\text{II}}[\text{AlX}_4]_2$). It is probable, then, that aluminium is 4-covalent in all of them, and it has not hitherto been clearly established that aluminium can be 6-covalent in such compounds. It is well known to be 6-covalent in complex fluorides, and also in aluminium chloride (Ketelaar, Macgillavry, and Renes, *Rec. Trav. chim.*, 1947, **66**, 501).

The preparation of hexachloro- and hexabromo-aluminates of hydrazine, described below, shows clearly for the first time that aluminium can be 6-covalent towards chlorine and bromine in complex salts. The compounds are typically salt-like and probably contain discrete $[\text{AlCl}_6]^{3-}$ and $[\text{AlBr}_6]^{3-}$ ions in the crystal lattice. Another new feature is that they were isolated as hydrates from aqueous solution. All the chloro- and bromoaluminates previously described were obtained either by fusion methods (Baud, *loc. cit.*; Kendall *et al.*, *loc. cit.*; Friedman and Taube, *J. Amer. Chem. Soc.*, 1950, **72**, 2236), or from non-aqueous solutions (Friedman *et al.*, *loc. cit.*; Jakubson, *Ber. Inst. Chem. Acad. Wiss., Ukraine*, 1940, **7**, 13, 17; Plotnikov and Gorenbein, *J. Gen. Chem., U.S.S.R.*, 1935, **5**, 1108), and statements that such compounds cannot be isolated from aqueous media are found in authoritative texts (Sidgwick, *op. cit.*; Moeller, " Inorganic Chemistry," J. Wiley and Sons, Inc., New York, 1952, p. 766).

It is possible that previous failure to prepare such compounds is due, not to the inability of the aluminium atom to co-ordinate six chlorine, or even bromine, ions, but, in part at least, to solubility relations. The simple hydrazine halides are very soluble in water, like the aluminium halides. Our own attempts to crystallise ammonium hexabromoaluminate, by the method used for the hydrazine salt, failed, because the less soluble ammonium bromide fractionated out. It may well be that similar attempts using other very soluble halides (lithium, magnesium, calcium, zinc) would be successful.

A pentafluoroaluminate of hydrazine, but of somewhat variable composition, has been described by Weinland, Lang, and Fikentscher (*Z. anorg. Chem.*, 1926, **150**, 47) as a non-crystalline powder. A few other pentafluoroaluminates are known, but some of them are hydrated and probably contain $[\text{AlF}_5 \longleftarrow \text{H}_2\text{O}]^{2-}$ ions. It seemed desirable, therefore, to characterise the hydrazine salt more fully, and to determine whether it exists in a hydrated form. The only complex fluoride that could be obtained, however, was the anhydrous salt, described by the above authors, but it was obtained as a pure, crystalline product whose optical properties have been studied.

While mixtures of the tin halides with hydrazine halides have been shown (*J.*, 1953, 354, 1934) to react with ketones to form crystalline halogeno-stannates and -stannites of dimethyl ketazine and of some hydrazones, similar compounds were not obtained with aluminium chloride. One possible reason is the well-known catalytic activity of aluminium chloride in promoting the condensation of hydrazine and acetone to 3 : 5 : 5-trimethylpyrazoline. It was also not possible to isolate iodoaluminates of hydrazine, which is not surprising when only two iodoaluminates, NaAlI_4 and KAlI_4, are reported in the literature (Weber, *Pogg. Ann.*, 1857, **101**, 465; **103**, 259).

Experimental

Trihydrazinium Hexachloroaluminate Hexahydrate.—Approximately molar proportions of aluminium chloride and hydrazine monohydrochloride were dissolved in the minimum amount of water, and the concentrated solution was evaporated slowly over sulphuric acid and solid sodium hydroxide, yielding colourless rhombs or prisms which, dried on paper and *in vacuo*, had d_{17}^{17} 1·55 [Found: N_2H_4, 21·2; Cl, 47·4; Al, 6·0. $(\text{N}_2\text{H}_5)_3\text{AlCl}_6,6\text{H}_2\text{O}$ requires N_2H_4, 21·4; Cl, 47·5; Al, 6·0%]. When larger proportions of hydrazine hydrochloride were used (*e.g.*, 3 : 1 mol. ratio, theoretically required), hydrazine dihydrochloride separated first and it was necessary to resort to fractional crystallisation.

Trihydrazinium hexachloroaluminate hexahydrate undergoes partial melting, probably partial solution in its own water of hydration, at 142°, the melt clearing at 194—196°. At 20° the salt is stable, undergoing no loss in weight when kept over sulphuric acid for several days, but at 100° in air it loses both water and hydrogen chloride, leaving a mixture of hydrazine hydrochloride and hydrated aluminium oxide. It is very soluble in water and deliquescent, but it is insoluble in ether, alcohol, benzene, chloroform, carbon tetrachloride, and light petroleum.

The crystals are trigonal, stout prisms, often highly modified, or appear to be perfect rhombohedra, sometimes with small prism faces. There is no cleavage. Prismatic crystals are length positive. Optically positive. Refractive indices (D) : $\omega = 1{\cdot}564$; $\varepsilon = 1{\cdot}588$.

Trihydrazinium Hexabromoaluminate Hexahydrate.—Quantities of hydrazine monohydrobromide and aluminium bromide (mol. ratio, 3 : 1), when crystallised together from aqueous solution, yielded clear, transparent prisms of pure *trihydrazinium hexabromoaluminate hexahydrate*, d_{17}^{17} 2·25 [Found : N_2H_4, 13·3; Br, 67·3; Al, 3·8. $(N_2H_5)_3AlBr_6,6H_2O$ requires N_2H_4, 13·4; Br, 67·3; Al, 3·8%]. When less than 3 mols. of hydrazine bromide were used per mol. of aluminium bromide, the same product was obtained, but it was always contaminated with aluminium bromide.

Like the chloroaluminate, it decomposes and dissolves partly in its water of crystallisation at 150°, forming a clear melt at 192°. It is quite stable at 20°, undergoing no loss in weight in the course of several days over sulphuric acid. It is very soluble in water, and deliquescent; it loses both water and hydrogen bromide when heated in air. The crystals are stout modified prisms, blades, or often rhomb-shaped plates. Cleavage is absent. $2V(\gamma) = 0°$ or near 0°. Optically positive. The plates give symmetrical extinction, an off-centred figure, and the shorter diagonal yields the γ index. Extinction on the blades is often oblique. The crystals may be trigonal but are probably monoclinic. Because of their extreme sensitiveness to moisture, optical measurements were difficult to make. Refractive index (D): $\omega = 1{\cdot}634$ (approx.). Birefringence low.

The complex ions in both these salts are considerably broken down in aqueous solution, the molecular conductivity at finite dilution reaching values which are characteristic of salts of the type AB_3 at infinite dilution. The molecular conductivities, μ, at 25° of the chloroaluminate (*A*) and bromoaluminate (*B*) at different dilutions (v l.) are :

v	5	25	50	125	500	625	3125
μ (*A*)	375	517	—	615	—	695	765
μ (*B*)	480	—	610	—	735	—	—

Hydrazinium Hydrogen Pentafluoroaluminate.—Solutions of aluminium fluoride, made from freshly precipitated aluminium hydroxide, and hydrazine dihydrofluoride were mixed, and the precipitate was filtered off, washed, and dried for several hours *in vacuo* over sulphuric acid. The fluorine was estimated by Willard's method (*Ind. Eng. Chem. Anal.*, 1936, **5**, 7) (Found : N_2H_4, 20·4; F, 60·6; Al, 17·4. Calc. for $N_2H_5,HAlF_5$: N_2H_4, 20·5; F, 60·9; Al, 17·4%). Varying the proportions of hydrazine fluoride and aluminium fluoride, temperature of precipitation, concentration of the reagents, and the period of digestion, had no effect on the composition. Variable results were obtained, however, when metallic aluminium (reagent grade, which was not completely soluble in hydrofluoric acid) was used as source of aluminium fluoride.

The salt is only sparingly soluble in water. The crystals are monoclinic, being colourless, much elongated plates and needles, too minute to yield exact optical data. The extinction angle is 25°, and the crystals are length slow. Refractive index for β is approximately 1·43; birefringence is fairly low.

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