

219. *Complex Fluorides of Gallium and the Alkali Metals.*

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THE formation of stable complex compounds is a characteristic of elements of weak electropositiveness. The tendency to co-ordinate, however, diminishes as the electropositiveness of the central atom increases. So, although boron and aluminium form stable complex

fluorides, the other members of the group should form them with increasing difficulty. Of these other members, little is known. One complex gallium fluoride, $3\text{NH}_4\text{F}\cdot\text{GaF}_3$ (Hannebohn and Klemm, *Z. anorg. Chem.*, 1936, **229**, 341), and one complex indium fluoride, $3\text{NH}_4\text{F}\cdot\text{InF}_3$ (Huysse, *Z. anal. Chem.*, 1900, **39**, 9) have been described. Thallic fluoride has apparently not been prepared, but Gewecke (*Annalen*, 1909, **366**, 217) isolated $\text{KF}\cdot 2\text{TlF}_3$. As expected, however, this is unstable, being decomposed by water into thallic hydroxide and hydrofluoric acid.

It is here shown that gallium forms complex fluorides with all the alkali-metal fluorides. The series is of interest, for it clearly shows, for a single element, the effect of the atomic volume of the co-ordinated molecules on the number of such molecules co-ordinated. The compounds now described are: $3\text{LiF}\cdot\text{GaF}_3$; $3\text{NaF}\cdot\text{GaF}_3$; $3\text{NH}_4\text{F}\cdot\text{GaF}_3$; $2\text{KF}\cdot\text{GaF}_3\cdot\text{H}_2\text{O}$; $\text{RbF}\cdot\text{GaF}_3\cdot 2\text{H}_2\text{O}$; and $\text{CsF}\cdot\text{GaF}_3\cdot 2\text{H}_2\text{O}$. They are all sparingly soluble in water, and are precipitated when solutions of their components are mixed. They form semi-gelatinous but dense precipitates, which on drying yield fine white powders. The potassium and the ammonium compound crystallise well, but the others form microcrystalline powders too irregular in shape to be characterised.

EXPERIMENTAL.

The gallium was obtained from germanite by a method shortly to be described. It was believed to be spectroscopically pure, since its spectrum showed no lines which could be definitely attributed to any other element.

Methods of Analysis.—Estimations of gallium and alkali metal were always made on the same weighed sample, which was first heated to fuming with sulphuric acid in a small platinum crucible in order to remove hydrogen fluoride. From the clear acid extract of the residue, gallium hydroxide was precipitated with ammonia at the neutral point to methyl-red, paper pulp being added to facilitate filtration, and the precipitate was washed with a dilute solution of ammonium nitrate, charred, and ignited to the oxide. The alkali metal was weighed as sulphate after evaporation of the filtrate and ignition of the residue. In this way concordant results were always obtained, but estimations attempted without previous removal of hydrogen fluoride gave low and variable values.

The fluoride content was determined in a separate sample by precipitation as lead chloride, followed by volumetric estimation of chlorine in the precipitate (Hillebrand and Lundell, "Applied Inorganic Analysis," p. 605). The method gave good results.

Preparation of Gallium Fluoride, $\text{GaF}_3\cdot 3\text{H}_2\text{O}$.—Ignited gallium oxide is insoluble in hydrofluoric acid. Johnson and Parsons (*J. Physical Chem.*, 1932, **36**, 2591), however, prepared gallium fluoride in two ways: (a) by dissolving the metal in 40% hydrofluoric acid, (b) by dissolving gallium hydroxide in dilute hydrofluoric acid. The first method is very slow, for even in contact with platinum no more than 2 g. of the metal will dissolve in a day. The second method involves the solution of the metal and the precipitation and washing of the hydroxide. A more convenient method consists in evaporating the nitrate solution with hydrofluoric acid. Nitric acid is the best solvent for the metal. 5 G. of gallium metal were dissolved in concentrated nitric acid in a flask heated on the water-bath. The syrupy liquid was transferred to a platinum basin, evaporated with hydrofluoric acid, and the evaporation repeated three times with small amounts of hydrofluoric acid. The residue was finally dried on the water-bath to a fine white powder (Found: Ga, 38.4; F, 31.45. Calc.: Ga, 38.6; F, 31.5%); yield, 12.90 g. (Calc. for $\text{GaF}_3\cdot 3\text{H}_2\text{O}$, 12.96 g.).

Sodium Gallifluoride, $3\text{NaF}\cdot\text{GaF}_3$.—Theoretical quantities of hydrated gallium fluoride (3.614 g.) and of pure anhydrous sodium carbonate (3.18 g.) were dissolved separately in about 40 c.c. of dilute hydrofluoric acid, and the solutions mixed. A gelatinous but heavy precipitate appeared. The liquid was evaporated on the water-bath to about 10 c.c., cooled, and decanted. The residue was washed by decantation with cold water and finally by centrifuging, and dried in the air (Found: Na, 26.7; Ga, 27.7; F, 45.2. $3\text{NaF}\cdot\text{GaF}_3$ requires Na, 27.3; Ga, 27.6; F, 45.1%); yield, 4.9 g. (Calc.: 5.05 g.). *Sodium gallifluoride* is a fine white powder which remains unchanged on long standing in air. In crystallising slowly from water, it forms clusters of tiny crystals, which, however, are too indefinite in outline to be classified.

Ammonium Gallifluoride, $3\text{NH}_4\text{F}\cdot\text{GaF}_3$.—The existence of this complex salt (Hannebohn and Klemm, *loc. cit.*) is now confirmed. It may be made by substituting ammonium fluoride for sodium fluoride in the foregoing preparation (Found: NH_4 , 22.75; Ga, 29.2; F, 48.2. Calc.:

NH_4 , 22.7; Ga, 29.3; F, 48.0%). This compound is evidently more soluble than the sodium compound, for the yield obtained was poorer and the product was definitely crystalline. It recrystallises well in small but well-formed octahedra. It is stable in air at the ordinary temperature, and decomposes on heating in moist air with loss of ammonium fluoride and hydrogen fluoride. The loss in weight of 0.44 g. at 380° was 0.18 g., and the residue (Found : Ga, 56.0; F, 26.6%) was evidently a mixture of fluoride and oxide.

Lithium Gallifluoride, $3\text{LiF}\cdot\text{GaF}_3$.—Lithium carbonate (0.60 g.), dissolved in about 200 c.c. of hot dilute hydrofluoric acid, and a solution of gallium fluoride (1.00 g.) were mixed. A slight turbidity appeared, and the liquid was evaporated to dryness. After standing for some time with about 30 c.c. of hot dilute hydrofluoric acid, the granular residue was washed well and dried in the air to constant weight; yield, 1.05 g. (Found : Li, 10.3; Ga, 33.5; F, 55.4. $3\text{LiF}\cdot\text{GaF}_3$ requires Li, 10.2; Ga, 34.1; F, 55.7%). *Lithium gallifluoride* is a snow-white micro-crystalline powder. Attempts to define the form of the crystals by slow crystallisation on a glass slide were unsuccessful.

Potassium Gallifluoride, $2\text{KF}\cdot\text{GaF}_3\cdot\text{H}_2\text{O}$.—This was prepared from solutions of gallium fluoride (3 g.) and an excess of potassium fluoride obtained from pure anhydrous potassium carbonate (4 g.). The liquid was evaporated to about 20 c.c., cooled, and decanted. The gelatinous heavy residue was washed by decantation and several times by centrifuging, and finally dried in the air; yield, 4.3 g. (Found : K, 29.7; Ga, 26.6; F, 36.5. $2\text{KF}\cdot\text{GaF}_3\cdot\text{H}_2\text{O}$ requires K, 30.0; Ga, 26.7; F, 36.4%). The crystals consist of what appear to be rhombs with an occasional swallow-tail twin. They are anisotropic and extinction is not always parallel. They are probably monoclinic. They are stable at 110° , but at 230° they lose $1\text{H}_2\text{O}$ (Loss : 7.0. Calc. : 6.9%). The anhydrous salt so formed underwent no change in weight on standing in air for 10 days.

Rubidium Gallifluoride, $\text{RbF}\cdot\text{GaF}_3\cdot 2\text{H}_2\text{O}$.—Gallium fluoride (1.0 g.) and rubidium chloride (0.66 g.) were dissolved separately in dilute hydrofluoric acid and mixed. The solution was evaporated on the water-bath, more hydrofluoric acid added, and the solution again taken to dryness. The residue was extracted and well washed with water (5 c.c. at a time), and dried at 110° (Found : Rb, 31.8; Ga, 26.2; F, 28.0. $\text{RbF}\cdot\text{GaF}_3\cdot 2\text{H}_2\text{O}$ requires Rb, 32.0; Ga, 26.1; F, 28.4%). The crystals lose $2\text{H}_2\text{O}$ (Loss : 13.5. Calc. : 13.5%) at 230° , and the anhydrous salt on standing in air reabsorbs half of this water in 2 days. Thereafter there is no appreciable change in the course of 10 days.

Cæsium Gallifluoride, $\text{CsF}\cdot\text{GaF}_3\cdot 2\text{H}_2\text{O}$.—This complex salt was made from gallium fluoride (1 g.) and cæsium chloride (2 g.) in the same manner as the rubidium analogue. It was dried at 110° (Found : Cs, 42.0; Ga, 22.25; F, 24.2. $\text{CsF}\cdot\text{GaF}_3\cdot 2\text{H}_2\text{O}$ requires Cs, 42.25; Ga, 22.15; F, 24.15%). All the water is lost at 230° , but half of it is recovered rapidly in air, and there is a subsequent slow increase in weight, 80% of the loss at 230° being recovered in 12 days. Both the rubidium and the cæsium compound are snow-white powders, definitely crystalline, but too irregular to be characterised.