412. *Gallium. Part V.*

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The only complex fluorides of gallium so far described are those of the alkali metals. The present paper describes the preparation and properties of complex *gallifluorides* of *manganese, cobalt, nickel, copper, zinc,* and *cadmium,* all of which are of the type $[M(H_2O)_6][GaF_5,H_2O]$. Complexes of *barium* ($Ba_3[GaF_6]_2,H_2O$), *strontium* ($3SrF_2,GaF_3,3H_2O$), *silver* ($Ag_3[GaF_6],10H_2O$), and *thallium* ($Tl_2[GaF_5,H_2O]$) are also described. Although the alkali and alkaline-earth metal complexes are insoluble in water, those of the heavy metals described are soluble and crystallise from aqueous solution.

The author (this vol., p. 1046) has already described some complex fluorides of gallium and the alkali metals, all of which may be represented as compounds of co-ordination number six, *viz.*, $Li_3[GaF_6]$, $Na_3[GaF_6]$, $(NH_4)_3[GaF_6]$, $K_2[GaF_5,H_2O]$, $Rb[GaF_4,2H_2O]$, and $Cs[GaF_4,2H_2O]$. These are the only complex fluorides of gallium so far described.

Other tervalent metals form complexes with the fluorides of bivalent metals and, as a rule, they are of the general type $M''F_2,M'''F_3,7H_2O$, or, more correctly, $M''[M'''F_5,H_2O],6H_2O$. For instance, Weinland and Köppen (*Z. anorg. Chem.*, 1899, **22**, 266) described complex fluorides of tervalent iron and aluminium with nickel, cobalt, zinc, cadmium, and bivalent iron; Petersen (*J. pr. Chem.*, 1889, **40**, 47, 60) described complexes of tervalent vanadium and chromium with nickel and cobalt, and Piccini and Giorgis (*Gazzetta*, 1892, **22**, I, 90) those of vanadium with zinc and cadmium. Gallium is now shown to form similar *complex fluorides* with bivalent *manganese, cobalt, nickel, copper, zinc,* and *cadmium.* It is noteworthy that, although the copper gallifluoride now described is $Cu[GaF_5,H_2O],6H_2O$, which has a bivalent anion, the corresponding copper complexes with iron and aluminium are of the type $[Cu(H_2O)_6]_3[MF_6]_2$, having a tervalent anion (Weinland, Lang, and Fikentscher, *Z. anorg. Chem.*, 1926, **150**, 51), and the complex with chromium is $[Cu(H_2O)_4][CrF_5,H_2O]$ (Higley, *J. Amer. Chem. Soc.*, 1904, **26**, 630).

Barium and strontium also form complexes with gallium fluoride. The *barium* compound, $3BaF_2,2GaF_3,H_2O$ or $Ba_3[GaF_6]_2,H_2O$, is the analogue of the complex barium ferrifluoride described by Nielsen (*Z. anorg. Chem.*, 1936, **227**, 423). The *strontium* complex fluoride, however, is not of this type, but $3SrF_2,GaF_3,3H_2O$, for which the structure $[SrF,H_2O]_3[GaF_6]$ is suggested.

Of the univalent metals silver and thallium, the former gives rise to only a few complex fluorides. Christensen (*J. pr. Chem.*, 1887, **35**, 169) has prepared $AgF,MnF_3,4H_2O$, and Weinland, Lang, and Fikentscher (*loc. cit.*) have recently prepared $[Ag(H_2O)_2][FeF_5,H_2O]$. With gallium fluoride, silver forms the *complex* $Ag_3[GaF_6],10H_2O$. Univalent thallium shows a strong resemblance to the alkali metals and forms similar complexes; *e.g.*, Ephraim and Barteczko (*Z. anorg. Chem.*, 1909, **61**, 238) have described compounds of iron, aluminium, and chromium of the type $Tl_3[MF_6]$, and Weinland, Lang, and Fikentscher (*loc. cit.*) have recently prepared $Tl_2[FeF_5,H_2O],2H_2O$. With gallium fluoride, thallium yields the *analogue* of potassium gallifluoride, *viz.*, $Tl_2[GaF_5,H_2O]$.

EXPERIMENTAL.

Methods of Analysis.—In all the preparations described herein, fluorine was determined by precipitation as lead chlorofluoride, followed by volumetric estimation of chlorine in the precipitate (Hillebrand and Lundell, "Applied Inorganic Analysis," p. 605). For the determination of the metals, fluorine was first removed by evaporation with concentrated sulphuric acid and, when the second metal did not interfere with the method, gallium was precipitated as the tannin complex; when this was not possible, cupferron was used (Moser and Brukl, *Monatsh.*, 1928, **50**, 657; 1929, **51**, 73). For the thallium compound, ammonia was used so that thallium could subsequently be precipitated as chromate.

Manganese Gallifluoride, $[Mn(H_2O)_6][GaF_5,H_2O]$.—For this and all the following preparations hydrated gallium fluoride, $GaF_3,3H_2O$, was used; it was made from pure gallium as already described by the author (*loc. cit.*). All operations were carried out in platinum vessels.

Manganese carbonate contains higher oxides of manganese, which give brown solutions in hydrofluoric acid, and these again give brownish crystals when evaporated with gallium fluoride. The above compound was prepared in the pure state as follows: manganese carbonate (1·5 g.) was dissolved in dilute hydrochloric acid, and the solution evaporated to dryness in order to decompose compounds of ter- and quadri-valent manganese. The residue was dissolved in water and transferred to a platinum basin. Gallium fluoride (2 g.) and dilute hydrofluoric acid were then added, and the solution evaporated to dryness; evaporation with hydrofluoric acid was repeated three times. Finally, the residue was dissolved in 30 c.c. of hot dilute hydrofluoric acid, and the solution allowed to cool. Clear, colourless crystals separated on standing. They were washed with ice-cold water, and dried in the air to constant weight, forming white clusters with a faint pink tinge.

In analysing the *compound*, gallium was precipitated with cupferron, after boiling with sulphur dioxide; and the manganese was determined in the filtrate by the bismuthate method, the excess of cupferron being first destroyed with nitric and sulphuric acids in a Kjeldahl flask (Found: Mn, 15·8; Ga, 20·2; F, 27·2. $[Mn(H_2O)_6][GaF_5,H_2O]$ requires Mn, 15·9; Ga, 20·2; F, 27·5%). When heated at 110°, it loses $5H_2O$ (Found: loss at 110°, 26·1. Calc. for $5H_2O$: 26·0%). It does not lose hydrogen fluoride at this temperature, but during 7 hours at 230° it loses 40% in weight, and the residue contains only 70% of the fluorine in the original substance. It evidently decomposes into manganese fluoride and gallium oxide, and the following five complex salts behave similarly.

The crystals consist of pyramids, which probably belong to the orthorhombic system. In convergent light they show a biaxial negative figure with a very small axial angle (the sign was determined by means of a Berek compensator, and checked with a quartz wedge); n 1·45, $D_{20^\circ}^{20^\circ}$ 2·216. The substance is quite stable in air, and very soluble in water.

Cobalt Gallifluoride, $[Co(H_2O)_6][GaF_5,H_2O]$.—Cobalt carbonate (0·64 g.) was dissolved in 30 c.c. of dilute hydrofluoric acid, and gallium fluoride (1 g.) added to the hot solution. Tiny pink crystals appeared immediately. The solution was cooled, and the crystals separated. The mother-liquor was then evaporated slowly in the air to about 2 c.c., whereupon a second crop of crystals, identical with the first, was obtained. The total yield (1·8 g.) was nearly theoretical. The crystals were dried in the air.

Gallium was determined in these crystals by means of cupferron (tannin gave high results, the oxide being contaminated with cobalt oxide) and cobalt was precipitated from the filtrate with hydrogen sulphide and converted into sulphate (Found: Co, 16·8; Ga, 19·9; F, 27·0. $[Co(H_2O)_6][GaF_5,H_2O]$ requires Co, 16·9; Ga, 19·9; F, 27·2%).

The *gallifluoride* forms pale pink crystals, the majority of which appear to be rhombs; prisms terminated by a pyramid also occur. In convergent light they show a biaxial negative figure with a small axial angle, which suggests that they belong to the monoclinic system but have pseudo-hexagonal form; n 1·45, $D_{20^\circ}^{20^\circ}$ 2·347. It is quite stable in air, but loses $5H_2O$ at 110°, giving a light mauve mass (Found: loss at 110°, 25·8. Calc. for $5H_2O$: 25·7%). It is only sparingly soluble in water, but dissolves readily in acids with decomposition.

Nickel Gallifluoride, $[Ni(H_2O)_6][GaF_5,H_2O]$.—This was made in exactly the same manner as the cobalt complex from gallium fluoride (1 g.) and an equivalent amount of nickel carbonate, the nickel content of which had been determined. It crystallised readily from 20 c.c. of hot dilute hydrofluoric acid; yield, 1·7 g. Gallium was determined in the air-dried material by precipitation with cupferron; nickel was estimated in the filtrate by dimethylglyoxime (Found: Ni, 16·9; Ga, 19·8; F, 27·4. $[Ni(H_2O)_6][GaF_5,H_2O]$ requires Ni, 16·8; Ga, 19·9; F, 27·2%). *Nickel gallifluoride* forms pale green crystals which appear to be rhombs; in convergent light they are biaxial negative with a small axial angle, which again suggests the monoclinic system with a pseudo-hexagonal form; *n* 1·45, $D_{20^\circ}^{20^\circ}$ 2·454. It is stable in air but loses $5H_2O$ at 110° (Found: loss at 110°, 25·7. Calc. for $5H_2O$: 25·8%). The dehydrated material forms yellowish crystals, which turn green again in air. It is only sparingly soluble in water.

Copper Gallifluoride, $[Cu(H_2O)_6][GaF_5,H_2O]$.—Copper oxide (0·66 g.) and gallium fluoride (1·5 g.) were dissolved in 20 c.c. of hot dilute hydrofluoric acid. On cooling, the liquid set to a mass of microscopic crystals. These were redissolved in 50 c.c. of hot dilute hydrofluoric acid, and the solution allowed to evaporate slowly in the air. The pale blue crystalline powder was centrifuged, washed with cold water, and dried in the air; yield, 2·6 g. Copper was determined electrolytically, and gallium was recovered as the tannin complex and weighed as oxide (Found: Cu, 18·0; Ga, 19·8; F, 26·5. $[Cu(H_2O)_6][GaF_5,H_2O]$ requires Cu, 18·0; Ga, 19·7; F, 26·8%). The *gallifluoride* forms a pale blue crystalline powder, but the crystals are too small for accurate characterisation. The forms suggest the monoclinic system; *n* 1·45, $D_{20^\circ}^{20^\circ}$ 2·202. The salt is sparingly soluble in water, but dissolves, with decomposition, in acids. It is stable in air but loses $5H_2O$ at 110° (Found: loss at 110°, 25·6. Calc. for $5H_2O$: 25·4%).

Zinc Gallifluoride, $[Zn(H_2O)_6][GaF_5,H_2O]$.—This complex salt was made by dissolving molecular proportions of zinc oxide (1·04 g.) and gallium fluoride (2·32 g.) in hydrofluoric acid and evaporating the liquid to a syrupy consistency. The liquid crystallised slowly. The crystals were washed quickly with small quantities of ice-cold water and dried in the air to constant weight. During drying, they smelled strongly of hydrogen fluoride and lost their transparent appearance; it is possible that the freshly crystallised material contains co-ordinated hydrogen fluoride which is replaced by water on standing in air. The cadmium salt behaves in the same way.

In analysing the *substance*, gallium was precipitated by tannin, a double precipitation being necessary, and zinc was recovered as sulphide and converted into sulphate (Found: Zn, 18·3; Ga, 19·7; F, 27·0. $[Zn(H_2O)_6][GaF_5,H_2O]$ requires Zn, 18·4; Ga, 19·6; F, 26·7%). Like the manganese complex, it forms colourless pyramids, which probably belong to the orthorhombic system; in convergent light they show a biaxial negative figure with a small axial angle; *n* 1·45, $D_{20^\circ}^{20^\circ}$ 2·335. It is very soluble in water. In air it is stable, and even over phosphoric oxide it undergoes no loss in weight in 3 weeks; but it readily loses $5H_2O$ at 110° (Found: loss at 110°, 25·6. Calc. for $5H_2O$: 25·3%. Found, in dehydrated product: Zn, 24·7; Ga, 26·0; F, 35·6. $Zn[GaF_5,H_2O],H_2O$ requires Zn, 24·6; Ga, 26·2; F, 35·7%).

Cadmium Gallifluoride, $[Cd(H_2O)_6][GaF_5,H_2O]$.—This was made from cadmium oxide (2·2 g.) and gallium fluoride (3·1 g.) as for the zinc salt. The concentrated solution on standing gave clear, colourless crystals, which on drying in the air formed a white, crystalline mass. In analysing this substance, cadmium was first separated by double precipitation of the sulphide and gallium was then precipitated with tannin (Found: Cd, 27·9; Ga, 17·2; F, 23·9. $[Cd(H_2O)_6][GaF_5,H_2O]$ requires Cd, 27·8; Ga, 17·3; F, 23·7%). It was not possible to get good crystals for identification, but it is certain that they do not belong to the isometric system; *n* 1·45, $D_{20^\circ}^{20^\circ}$ 2·778. It is very soluble in water and is stable in air, but loses $5H_2O$ at 110° (Found: loss at 110°, 22·2. Calc. for $5H_2O$: 22·3%).

Barium Gallifluoride, $Ba_3[GaF_6]_2,H_2O$ or $3BaF_2,2GaF_3,H_2O$.—Nielsen (*loc. cit.*) made the corresponding ferric complex by adding freshly prepared barium carbonate to a solution of ferric fluoride. The gallium compound was made by adding, in small quantities at a time, freshly made barium carbonate (from 2 g. of barium chloride) to a solution of gallium fluoride (1 g.) in 100 c.c. of hot dilute hydrofluoric acid. A heavy, white precipitate was formed immediately. The liquid was boiled well, and the solid filtered off, washed, and dried in the air; yield, 2·0 g. (Found: Ba, 51·7; Ga, 17·3; F, 28·5. $Ba_3[GaF_6]_2,H_2O$ requires Ba, 51·7; Ga, 17·5; F, 28·6%). The *gallifluoride* is a sub-microscopic powder, practically insoluble in water; $D_{20^\circ}^{20^\circ}$ 4·063. It loses $\frac{1}{2}H_2O$ at 110°, and the other $\frac{1}{2}H_2O$ at 230°; at a dull red heat it decomposes completely into barium fluoride and gallium oxide.

Strontium Gallifluoride, $3SrF_2,GaF_3,3H_2O$.—This *substance* was obtained as a semi-gelatinous but heavy precipitate by adding strontium carbonate to a hot solution of gallium fluoride in hydrofluoric acid. The same material was produced whether 1, 2, or 3 mols. of strontium carbonate were used per mol. of gallium fluoride. On drying in air, it forms a sub-microscopic powder, almost insoluble in water (Found: Sr, 46·6; Ga, 12·5; F, 30·7. $3SrF_2,GaF_3,3H_2O$ requires Sr, 47·1; Ga, 12·5; F, 30·7%). It loses all its water at 220°, and at a low red heat it decomposes into strontium fluoride and gallium oxide.

Thallous Gallifluoride, $Tl_2[GaF_5,H_2O]$.—Although the corresponding $K_2[GaF_5,H_2O]$ is very sparingly soluble in water, the *thallium* salt is moderately soluble and crystallises well. It was made by dissolving thallous carbonate (1·57 g.) and gallium fluoride (0·6 g.) in 30 c.c. of dilute hydrofluoric acid, and evaporating the solution to 10 c.c. (Found: Tl, 68·5; Ga, 11·7; F, 16·0. $Tl_2[GaF_5,H_2O]$ requires Tl, 69·1; Ga, 11·8; F, 16·1%). It forms clear transparent prisms and pyramids, which show a biaxial negative figure and appear to belong to the monoclinic or orthorhombic system; n 1·645; $D_{20^\circ}^{20^\circ}$ 6·440. It is quite stable in air and also when heated at 110°.

Silver Gallifluoride, $Ag_3[GaF_6],10H_2O$.—This substance is very sensitive to light and all operations had therefore to be carried out in the dark, in which the crystals retain their transparency indefinitely. Moreover, as the substance is exceedingly soluble and difficult to crystallise, considerable difficulty was experienced in making a pure specimen. This was finally accomplished as follows: silver carbonate (7·9 g.), prepared in the dark from pure silver nitrate, was dissolved in 20 c.c. of hydrofluoric acid, and gallium fluoride (3·46 g.) added. The liquid was filtered from the small amount of metallic silver which had separated, and 2 vols. of alcohol were added. The liquid separated into two layers, and the lower, aqueous layer crystallised spontaneously. The crystals were separated, redissolved in 15 c.c. of water, and the liquid was filtered and fractionally precipitated by adding alcohol. The lower layer obtained after adding 2 c.c. of alcohol contained a small excess of gallium fluoride; the upper, alcoholic layer was decanted, and to it were added another 2 c.c. of alcohol and the liquid was covered and left undisturbed. In the course of a few days, large, clear crystals separated from the lower layer. These were extracted, washed with alcohol, and dried in a current of dry air. A further crop of crystals was obtained by adding more alcohol to the remaining liquid (Found: Ag, 46·9; Ga, 10·2; F, 16·7. $Ag_3[GaF_6],10H_2O$ requires Ag, 47·1; Ga, 10·1; F, 16·6%).

Silver gallifluoride forms large clear tabular crystals, biaxial negative and probably monoclinic or orthorhombic; n 1·493, $D_{20^\circ}^{20^\circ}$ 2·90. The crystals undergo no change in weight and are not deliquescent, though they have a moist feel. They become anhydrous when kept over phosphoric oxide and also when heated at 110°.

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