214. *The Preparation of Hexafluoroniobates, Hexafluorotantalates, and Hexafluorobismuthates by Means of Bromine Trifluoride.*

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Niobium and tantalum, or their pentoxides, react with bromine trifluoride to give the *fluorobromonium hexafluoroniobate* and *hexafluorotantalate* [$(BrF_2)NbF_6$ and $(BrF_2)TaF_6$], which act as " acids " in bromine trifluoride and are neutralised by bromofluorides to give *hexafluoroniobates* $MNbF_6$ and *hexafluorotantalates* $MTaF_6$, respectively. Salts of *lithium, sodium, potassium,* rubidium, and cæsium were prepared in this way, but the *calcium* and *barium* salts always contained bromofluoride, the formation of which is believed to be due to solvolysis. Bismuth pentoxide containing 70% of quinquevalent bismuth reacted with bromine trifluoride to give *bismuth oxytrifluoride* containing bismuth trifluoride. Bismuth pentafluoride formed with bromine trifluoride the *fluorobromonium hexafluorobismuthate* [$(BrF_2)BiF_6$], which behaved as an " acid " in bromine trifluoride and reacted with silver bromofluoride, forming *silver hexafluorobismuthate.* The hexafluorobismuthates of sodium, potassium, and rubidium contained bromofluorides, probably owing to solvolysis in bromine trifluoride.

Little is known of the hexafluoroniobates and hexafluorotantalates. Ruff and Schiller (*Z. anorg. Chem.*, 1911, **72**, 329) showed that the anhydrous pentafluorides of niobium and tantalum formed only traces of complex fluorides with potassium fluoride, even at their boiling points. Balke and Smith (*J. Amer. Chem. Soc.*, 1908, **30**, 1637) prepared the double salts RbF,NbF_5 and CsF,NbF_5 by repeated recrystallisation of the compounds 2RbF,$NbOF_3$ and 2CsF,$NbOF_3$ from 35% hydrofluoric acid. Ant Wuorinen (*Suomen Kemistilehti*, B, 1940, 3) reported the formation of thallous hexafluoroniobate from thallous fluoride and a solution of niobium pentoxide in hydrofluoric acid. Hahn and Puetter (*Z. anorg. Chem.*, 1923, **127**, 153) isolated the free acid $HTaF_6$,$6H_2O$ and the ammonium salt, and Balke (*J. Amer. Chem. Soc.*, 1905, **27**, 1140) made lithium, sodium, and cæsium hexafluorotantalates from the alkali-metal carbonates, tantalum pentoxide, and hydrofluoric acid.

The use of bromine trifluoride as a reagent for preparing hexafluorophosphates, hexafluoroarsenates, hexafluoroantimonates, and hexafluorovanadates has already been described (Woolf and Emeléus, *J.*, 1949, 2865; 1950, 164; Emeléus and Gutmann, *J.*, 1949, 2979). It was expected that it would react with metallic niobium or tantalum and form the pentafluorides : in fact reaction with the metals occurred with incandescence and there was also a vigorous reaction with the pentoxides. In either case a clear solution remained from which, on evaporation of excess of bromine trifluoride in a vacuum, white or slightly yellow incrustations remained which contained bromine trifluoride and the metal pentafluoride in a 1 : 1 ratio. These products reacted much less violently with water or carbon tetrachloride than did bromine trifluoride. The compounds decomposed in a vacuum at 150—180° with volatilisation of a mixture of bromine trifluoride and the metal pentafluoride. Their formulation as the " acids " $(BrF_2)NbF_6$ and $(BrF_2)TaF_6$ (*fluorobromonium hexafluoroniobate* and *hexafluorotantalate*) is justified by the neutralisation reactions referred to below. It is probable that chlorine trifluoride, which is not known to form " acids " and " bases " as bromine trifluoride does, would yield the metal pentafluorides under the above conditions.

The reactions of the compounds $NbBrF_8$ and $TaBrF_8$ with potassium bromofluoride in bromine trifluoride solution yielded anhydrous *potassium hexafluoroniobate* and *hexafluorotantalate* by a neutralisation reaction (*e.g.*, $BrF_2^+NbF_6^- + K^+BrF_4^- \rightleftharpoons KNbF_6 + 2BrF_3$). When mixtures of niobium or tantalum with potassium chloride were treated with excess of bromine trifluoride the hexafluoro-complexes were again formed. In a similar way, by use of sodium carbonate, rubidium bromide, and cæsium bromide, anhydrous *sodium hexafluoroniobate*, rubidium hexafluoroniobate, and cæsium hexafluoroniobate were obtained as white crystalline non-hygroscopic solids. It is very likely that the last two compounds are identical with the double salts RbF,NbF_5 and CsF,NbF_5 described by Balke and Smith (*loc. cit.*). These reactions support the view that the bromofluorides of rubidium and cæsium exist in bromine trifluoride solution (Sharpe and Emeléus, *J.*, 1948, 2135). On the other hand it is also possible to prepare *lithium hexafluoroniobate* from lithium carbonate, niobium, and bromine trifluoride, but no other indications of the existence of lithium bromofluoride are known. Lithium, sodium, *rubidium*, and cæsium *hexafluorotantalates* were prepared similarly. The alkali hexafluoroniobates and hexafluorotantalates are but slightly soluble in hot or cold water. They are more stable than the hexafluorovanadates (Emeléus and Gutmann, *loc. cit.*). The lithium salt is readily hydrolysed by boiling water. All are soluble without decomposition in hydrofluoric acid.

Silver hexafluoroniobate and *hexafluorotantalate* were prepared by mixing silver and the appropriate metal in atomic proportions and adding bromine trifluoride, but the calcium and barium salts could not be prepared free from bromine. This is believed to be due to solvolysis which leads to contamination of the product by bromofluoride [*e.g.*, $Ba(NbF_6)_2 + 4BrF_3 \rightleftharpoons Ba(BrF_4)_2 + 2NbBrF_8$].

The last element of Group V for which fluoro-complexes might be expected is bismuth. Neither bismuth pentoxide nor bismuthates can be prepared in a pure state, but always contain considerable amounts of tervalent bismuth. Ruff (*Z. anorg. Chem.*, 1908, **57**, 220) obtained the compound $BiOF_3$,3KF and the corresponding sodium salt from the reaction of a mixture of bismuth pentoxide and alkali-metal fluoride with 60% hydrofluoric acid. The anhydrous oxytrifluoride, $BiOF_3$, was however unknown. The pentafluoride was prepared by von Wartenberg (*Z. anorg. Chem.*, 1940, **244**, 337). It was hydrolysed by hydrofluoric acid, whereas the oxytrifluoride is soluble (see below). Weinland and Lauenstein (*Z. anorg. Chem.*, 1899, **20**, 46) mentioned the formation of an unstable potassium fluorobismuthate or oxyfluorobismuthate, and it seems very likely that only the latter was obtained. Further unsucessful attempts to prepare hexafluorobismuthates were reported by Ant Wuorinen (*loc. cit.*).

Tervalent bismuth compounds are not converted into the pentafluoride by bromine trifluoride, probably because the trifluoride is insoluble in the reagent (Emeléus and Woolf, *J.*, 1950, 164). The pentoxide prepared according to Deichler (*Z. anorg. Chem.*, 1899, **20**, 81) contained only

70% of pentoxide and reacted readily with bromine trifluoride forming a white solid, which was shown by analysis to be a mixture of *bismuth oxytrifluoride* and trifluoride. It was readily hydrolysed by water or by acids, other than hydrofluoric acid, with precipitation of the chocolate-brown pentoxide.

Bismuth pentafluoride, prepared by fluorination of the trifluoride at 550° (von Wartenberg, *loc. cit.*), was sparingly soluble in bromine trifluoride (*ca.* 0·7 g./100 g.). After evaporation of the solvent *fluorobromonium hexafluorobismuthate*, $(BrF_2)BiF_6$, remained. This resembled the corresponding antimony, tin, gold, tantalum, and niobium "acids." It was a white hygroscopic solid, which decomposed appreciably in a vacuum at 70°. When a solution of this compound in bromine trifluoride was allowed to react with silver bromofluoride, the compound *silver hexafluorobismuthate* was formed. This was a white and slightly hygroscopic solid which was readily hydrolysed by water or by acids, other than hydrofluoric acid. Sodium, potassium, and rubidium hexafluorobismuthates could not be prepared free from bromofluorides, probably because of the ready solvolysis of these compounds. Attempts to prepare a barium salt were unsuccessful.

EXPERIMENTAL.

Reaction of Niobium and Tantalum with Bromine Trifluoride.—The two metals in the form of powder were suspended in bromine which was cooled in liquid air in a silica flask, and treated dropwise with a small excess of bromine trifluoride, with intermittent cooling to moderate the reaction. After a few minutes' refluxing to ensure complete reaction, excess of bromine trifluoride was pumped off at 30° in a vacuum. Fluorine in the products was determined by the Willard–Winter method (*Ind. Eng. Chem. Anal.*, 1933, **5**, 7), and niobium and tantalum were determined by dissolution of the product in dilute hydrochloric acid, precipitation with aqueous ammonia, and weighing as the ignited pentoxides. The alkali salts (see below) were determined as sulphates in the filtrates from the ammonia precipitations. Barium was removed from the barium salts by precipitation as sulphate before determining other elements. Calcium was determined by precipitation as calcium fluoride, and bromine as silver bromide after reduction with sulphurous acid.

The reaction of niobium pentoxide with bromine trifluoride was much less vigorous than that of niobium metal; in either case the hygroscopic yellow incrustation remaining after removal of excess of bromine trifluoride was rapidly decomposed by water with evolution of bromine and hydrogen fluoride. It reacted with carbon tetrachloride, but less vigorously than did bromine trifluoride (Found: Br, 24·8; Nb, 29·1; F, 46·8%; equiv., 322. $NbBrF_8$ requires Br, 24·6; Nb, 28·6; F, 46·8%; equiv., 325). The compound lost bromine trifluoride when heated, the thermal stability in a vacuum being shown by the following results obtained on heating a single sample at gradually increasing temperatures. Bromine trifluoride and the pentafluoride were pumped off continuously as formed and condensed.

Temperature	30°	50°	100°	120°	150°
Time of heating (hrs.)	6	6	1	1	1·5
Decomposed, %	0	7·2	14·5	47·7	91·6

Tantalum powder or pentoxide reacted similarly with bromine trifluoride, the *product* being very hygroscopic and reacting violently with water (Found: Ta, 44·0; Br, 18·7; F, 36·4%; equiv., 422. $TaBrF_8$ requires Ta, 43·9; Br, 19·4; F, 36·7%; equiv., 413). The thermal stability was greater than that of the niobium compound, as is shown by the following data for the decomposition in vacuum.

Temperature	40°	100°	120°	150°	175°	200°
Time of heating (hrs.)	6	1	1	1	1	1
Decomposed, %	0	5·4	8·1	19·3	43·7	71·7

Preparation of Hexafluoroniobates.—*Lithium hexafluoroniobate* was prepared by the reaction of excess of bromine trifluoride with an equimolecular mixture of lithium carbonate and niobium; with lithium chloride reaction was incomplete (Found: Nb, 43·4; F, 52·5%; equiv., 213. $LiNbF_6$ requires Nb, 43·6; F, 53·1%; equiv., 214). The lithium salt was a white non-hygroscopic solid easily hydrolysed by water. *Sodium hexafluoroniobate* was obtained by the reaction of excess of bromine trifluoride with a 1 : 1 mixture of sodium carbonate or fluoride and niobium (Found: Nb, 40·1; F, 48·2%; equiv., 226. $NaNbF_6$ requires Nb, 40·4; F, 49·6%; equiv., 230). The white solid was sparingly soluble in water, but dissolved readily in hydrofluoric acid. *Potassium hexafluoroniobate* was obtained similarly, using either potassium chloride or potassium fluoride. An alternative method was also used to show the occurrence of a neutralisation reaction. A solution of potassium bromofluoride in bromine trifluoride was added in the calculated proportion to a solution of fluorobromonium hexafluoroniobate ($NbBrF_8$) in bromine trifluoride. After removal of the solvent the hexafluoroniobate remained as a white non-hygroscopic solid which was stable in air, sparingly soluble in water, and soluble in hydrofluoric acid (Found: K, 15·0; Nb, 38·5; F, 46·7%; equiv., 251. $KNbF_6$ requires K, 15·8; Nb, 37·9; F, 46·3%; equiv., 246). When in the preparation by the first method niobium and potassium chloride were used in a 1 : 2 ratio, no heptafluoroniobate, but a 1 : 1 mixture of potassium hexafluoroniobate and bromofluoride, was formed (Found: K, 18·5; Nb, 20·9; F, 42·7; Br, 15·6%; equiv., 468. Calc. for $KNbF_6 + KBrF_4$: K, 17·7; Nb, 21·2; F, 43·0; Br, 18·2%; equiv., 441).

Rubidium hexafluoroniobate was prepared by using rubidium bromide, and was probably identical with the double salt RbF,NbF_5 obtained by Balke and Smith (*J. Amer. Chem. Soc.*, 1908, **30**, 1637). It was almost insoluble in water and dilute mineral acids, except hydrofluoric acid (Found: Rb, 28·5; Nb, 31·2; F, 39·2; Equiv., 295. Calc. for $RbNbF_6$: Rb, 29·3; Nb, 31·8; F, 38·9%; equiv., 293).

Cæsium hexafluoroniobate was obtained similarly using cæsium bromide (Found: Cs, 38·8; Nb, 29·0, 28·1; F, 33·7; equiv., 335. Calc. for $CsNbF_6$: Cs, 39·1; Nb, 27·4; F, 33·5%; equiv., 340). In the preparation of *silver hexafluoroniobate*, either silver or silver chloride was mixed with the calculated proportion of niobium metal or pentoxide, and allowed to react with an excess of bromine trifluoride. The pale yellow silver salt was soluble in water and in dilute acids (Found: Ag, 34·7; Nb, 28·9; F, 36·2%; equiv., 302. $AgNbF_6$ requires Ag, 34·2; Nb, 29·6; F, 36·2%; equiv., 315).

When calcium fluoride and niobium (1 : 1) were treated with excess of bromine trifluoride the product contained bromine, but less than would be expected for a 1 : 1 mixture of the hexafluoroniobate and bromofluoride. When this product was heated to 35° in a vacuum bromine trifluoride was evolved slowly. After 8 hours at 35° the product as calculated from the analysis contained calcium hexafluoroniobate, bromofluoride, and fluoride approximately in the ratio 1 : 0·45 : 0·55. When calcium fluoride and niobium were used in a 1 : 2 ratio for the preparation, partly solvolysed *calcium hexafluoroniobate* was formed [Found: Nb, 38·4; F, 50·1; Br, 2·9%; equiv., 480. $Ca(NbF_6)_2$ requires Nb, 41·0; F, 50·2%; equiv., 454]. Barium chloride and niobium (1 : 2) gave partly solvolysed *barium hexafluoroniobate* [Found: Ba, 21·9; Nb, 31·3; F, 43·5; Br, 4·8%; equiv., 644. 0·95 $Ba(NbF_6)_2$ + 0·1 $NbBrF_8$ + 0·05 $Ba(BrF_4)_2$ requires Ba, 21·6; Nb, 29·3; F, 44·7; Br, 4·4%; equiv., 638].

Preparation of Hexafluorotantalates.—Lithium hexafluorotantalate was prepared from lithium carbonate. It was stable in air, but was decomposed by water with separation of lithium fluoride (Found: Ta, 58·9; F, 38·4%; equiv., 319. Calc. for $LiTaF_6$: Ta, 60·0; F, 37·7%; equiv., 302). Quantitative formation of sodium hexafluorotantalate took place with sodium fluoride and tantalum powder (1 : 1) (Found: Na, 7·2; Ta, 56·9; F, 35·9%; equiv., 329. Calc. for $NaTaF_6$: Na, 7·2; Ta, 57·0; F, 35·8%; equiv., 318). *Potassium hexafluorotantalate* was readily formed by neutralisation of potassium bromofluoride with fluorobromonium hexafluorotantalate in bromine trifluoride. It was also obtained by the reaction of equimolecular amounts of potassium chloride and tantalum with bromine trifluoride (Found: K, 11·9; Ta, 53·4; F, 34·3%; equiv., 346. $KTaF_6$ requires K, 11·7; Ta, 54·2; F, 34·1%; equiv., 334).

Rubidium hexafluorotantalate was formed as a white non-hygroscopic solid by using rubidium bromide and tantalum. It was insoluble in dilute acids except hydrofluoric acid (Found: Rb, 21·9; Ta, 47·8; F, 30·3%; equiv., 375. $RbTaF_6$ requires Rb, 22·5; Ta, 47·5; F, 30·0%; equiv., 380). Cæsium hexafluorotantalate was prepared similarly (Found: Cs, 31·6; Ta, 42·0; F, 27·1%; equiv., 435. Calc. for $CsTaF_6$: Cs, 31·1; Ta, 42·3; F, 26·6%; equiv., 428). *Silver hexafluorotantalate* was obtained as a pale yellow solid from silver powder or silver chloride. Like the alkali salts, it was soluble in bromine trifluoride (Found: Ag, 26·5; Ta, 44·2; F, 28·8%; equiv., 407. $AgTaF_6$ requires Ag, 26·7; Ta, 45·0; F, 28·3%; equiv., 403).

Calcium fluoride was not completely converted into calcium hexafluorotantalate when mixed with tantalum in a 1 : 2 ratio and treated with bromine trifluoride. The product had the approximate composition $Ca(TaF_6)_2,0{\cdot}35BrF_3$ [Found: Ca, 6·1; Ta, 57·6; F, 35·3; Br, 2·1%; equiv., 622. Calc. for $Ca(TaF_6)_2$: Ca, 6·4; Ta, 57·3; F, 36·3%; equiv., 630). Similarly, the product from barium chloride was slightly solvolysed barium hexafluorotantalate, $Ba(TaF_6)_2,0{\cdot}09BrF_3$ (Found: Ba, 17·0; Ta, 47·0; F, 31·2; Br, 4·9%; equiv., 749. Calc. for $Ba(TaF_6)_2$: Ba, 18·9; Ta, 49·8; F, 31·3%; equiv., 727).

Formation of Bismuth Oxytrifluoride—Bismuth pentoxide was prepared by passing chlorine through a boiling suspension of bismuth trioxide in concentrated potassium hydroxide (Muir, *J.*, 1876, **29**, 144; Deichler, *Z. anorg. Chem.*, 1899, **20**, 81) (Found: Bi, 82·6; 2·77 g.-atoms of iodine ≡ 69·1% Bi^V. Calc. for Bi_2O_5: Bi, 83·9%; 4 g.-atoms of iodine). The oxide reacted vigorously with bromine trifluoride with precipitation of a mixture of $BiOF_3$, BiF_3, and some unchanged Bi_2O_3 (Found: Bi, 75·0; F, 20·8; 1·39 g. atoms of iodine ≡ 69·5% Bi^V; equiv., 273. Calc. for $BiOF_3$: Bi, 74·3; F, 20·2%; equiv., 282). Iodine titration gave reproducible results only in the absence of fluoride and thus was carried out after hydrolysis to bismuth pentoxide.

Preparation of Fluorobromonium Hexafluorobismuthate, $BiBrF_8$.—Bismuth trifluoride was precipitated by adding a solution of bismuth trioxide in acetic acid to a solution of sodium fluoride (Domange, *Compt. rend.*, 1941, **213**, 31). It was converted into the pentafluoride by fluorination at 500° (von Wartenberg, *Z. anorg. Chem.*, 1940, **244**, 337). The fluorination was done in a nickel boat in a nickel tube, the exit end of which was cooled in water to trap any pentafluoride which sublimed, and fitted with a standard ground joint. After the reaction the pentafluoride was transferred in a stream of dry nitrogen to a weighed nickel flask, fitted to the exit end of the reaction tube by the standard joint. The flask was stoppered and re-weighed, and a large excess of bromine trifluoride was added. A white hygroscopic *product* remained after excess of bromine trifluoride had been removed in a vacuum (Found: Bi, 49·1; F, 34·2; Br, 15·8%; equiv., 419. $BiBrF_8$ requires Bi, 47·4; F, 34·5; Br, 18·1%; equiv., 441). When this was heated in a vacuum bromine trifluoride was evolved and bismuth pentafluoride remained. The following data show the decomposition with successive periods of heating at gradually increasing temperatures.

Temperature	25°	50°	70°	100°	120°
Time of heating (hrs.)	5	1	1	1	1
Decomposed, %	16·0	23·9	51·1	83·2	100·0

Preparation of Silver Hexafluorobismuthate.—Fluorobromonium hexafluorobismuthate was prepared in bromine trifluoride solution and, while the nickel flask was cooled, the calculated quantity of silver was added. The mixture was warmed to complete the reaction and, after removal of excess solvent and heating of the residue for a short time in vacuum at 55°, the hygroscopic *silver* salt remained (Found: Ag, 24·6; Bi, 47·7; F, 25·7%; equiv., 435. $AgBiF_6$ requires Ag, 25·0; Bi, 48·5; F, 26·5%; equiv., 431). The compound was more stable than bismuth pentafluoride, in the hydrolysis of which some ozone was probably formed, leading to a low iodine value in the hydrolysate. Hydrolysis of the silver salt gave 95% of the calculated iodine value. The product of hydrolysis was a chocolate-brown precipitate which contained bismuth pentoxide. It was reduced by sulphur dioxide and dissolved in hydrofluoric acid.

Attempts to prepare alkali hexafluorobismuthates gave products containing considerable amounts of bromofluoride. Impure sodium hexafluorobismuthate was obtained from sodium carbonate (Found: Bi, 54·3; F, 32·5; Br, 6·3%; equiv., 390. Calc. for $NaBiF_6$: Bi, 60·3; F, 33·0%; equiv., 346). A mixture of bismuth pentafluoride and potassium chloride gave impure potassium hexafluorobismuthate, which was less solvolysed than the sodium salt (Found: Bi, 54·2; F, 32·5; Br, 2·5%; equiv., 405. Calc. for $KBiF_6$: Bi, 57·7; F, 31·4%; equiv., 362). In a similar way solvolysed rubidium hexafluorobismuthate was obtained from rubidium bromide (Found: Bi, 49·4; F, 28·2; Br, 1·8%; equiv., 444. Calc. for $RbBiF_6$: Bi, 51·2; F, 27·9%; equiv., 408).

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