397. *Hydrazine. Part III.* The Hydrazinium Salts of Complex Fluoro-Acids of Tin, Antimony, and Bismuth.*

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

Hydrazinium fluoro-salts of tin, antimony, and bismuth have been made (cf. chlorostannates; Pugh and Stephen, *J.*, 1952, 4138; 1953, 354), but those of arsenic could not be obtained. There is evidence that ketazinium fluoro-salts exist in solution, but it has not been possible to crystallise them.

COMPLEX fluorides of the hydrazinium ion described in the literature include the fluoro-silicate and -titanate (Ebler and Schott, *J. pr. Chem.*, 1910, **81**, 552), -aluminate (Weinland, Lang, and Fikentscher, *Z. anorg. Chem.*, 1925, **150**, 47), -borate (Funk and Binder, *ibid.*, 1926, **159**, 121), -beryllate (Ray, *ibid.*, 1931, **201**, 289), and -germanate (Dennis, Staneslow, and Forgeng, *J. Amer. Chem. Soc.*, 1933, **55**, 4392). No such compounds of tin, antimony, or bismuth have been described, though these metals are known to form anionic complex fluorides with both uni- and bi-valent cations (Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., London, 1927, Vol. VII, p. 422; 1929, Vol. IX, pp. 465, 659).

Chlorostannates of hydrazine, and of some of its condensation products with ketones, have been described (Pugh and Stephen, *locc. cit.*), and the present paper records the results of attempts to make similar fluoro-salts of tin, arsenic, antimony, and bismuth. The compounds described are hydrazinium hydrogen tetrafluorostannite, hydrazinium hexafluoroantimonate, hydrazinium hydrogen pentafluoroantimonite, hydrazinium hydrogen pentafluorobismuthite, and dihydrazinium hexafluorostannate. They were made by crystallisation of the mixed component fluorides from aqueous solutions, though better results were obtained from aqueous acetone in some cases. The fluoro-bismuthite, however, was made by prolonged digestion of bismuth trifluoride with hydrazine dihydrofluoride solution. Attempts to crystallise fluoroarsenites were unsuccessful, for though arsenious oxide dissolves readily in warm solutions of hydrazine dihydrofluoride the only solid recovered by evaporation at room temperature was the latter component. The fluoroarsenite ion, if it exists in solution, is too unstable, and arsenic volatilises completely as the trifluoride.

It is significant that, although crystallisation of the mixed chlorides of hydrazine and tin from aqueous acetone (*idem, loc. cit.*) yields dimethylketazinium chlorostannate (and further work, yet unpublished, has shown that similar chloroantimonites and chlorobismuthites can be prepared), yet crystallisation of the mixed fluorides, under the same conditions, yields the unchanged hydrazinium complex salt. There is, however, some evidence, *e.g.*, liberation of heat, that condensation does take place when the mixed fluoride solutions are treated with acetone, and it is possible that ketazinium fluoro-salts do exist in solution. They do not, however, separate in the solid phase.

EXPERIMENTAL

Analytical Methods.—Metals were determined by weighing the oxides after repeated evaporation with nitric acid and ignition; fluoride was determined, after removal of the metal as sulphide, by titration with thorium nitrate (Rowley and Churchill, *Ind. Eng. Chem. Anal.*,

* The papers, *J.*, 1952, 4138, and *J.*, 1953, 354, are considered as Parts I and II, respectively.

1937, **9**, 551); hydrazine was determined by titration with iodate (Andrews's method). In the fluoro-stannites and -antimonites, the anions of which also consume iodate, a total iodate titre was determined on one sample, and then a second iodate titre, determined on another sample after removal of the metal as sulphide, gave the hydrazine titre alone; this procedure provided a check on the results for both hydrazine and metal.

Dihydrazinium Hexafluorostannate.—Stannic chloride pentahydrate (12 g.) was dissolved in hot distilled water, and ammonia solution was added until the mixture was alkaline to methyl-orange. The stannic hydroxide was filtered off, washed with hot water until free from chloride, and dissolved in a small excess of 40% hydrofluoric acid. Other methods of making stannic fluoride solutions, *e.g.*, evaporation of stannic chloride with hydrofluoric acid, were tedious. The solution was then treated with hydrazine hydrate (12 c.c.; 28%), previously made acid with hydrofluoric acid, and evaporated to crystallisation. The first crop of crystals was contaminated with hydrazine dihydrofluoride, but subsequent crops were reasonably pure. Recrystallisation from acetone–water (4 : 1) by slow evaporation gave large flat plates, d_{22}^{22} 2·57, m. p. 194—196° (decomp.) [Found: N_2H_4, 21·3; F, 37·9; Sn, 39·8. $(N_2H_5)_2SnF_6$ requires N_2H_4, 21·4; F, 38·2; Sn, 39·8%]. The *salt* is non-hygroscopic, yet it attacks glass. It decomposes with effervescence when heated above its m. p., the vapours smelling strongly of hydrazine. It is insoluble in ether, ethanol, acetone, chloroform, benzene, or light petroleum, but freely soluble in water, yielding clear solutions which do not immediately afford a precipitate with hydrogen sulphide: precipitation is complete only after repeated filtration and re-saturation in hot solution. Stannic hydroxide is, however, completely precipitated by ammonia. Much heat is evolved when concentrated solutions are mixed with acetone but the salt is recovered unchanged on cooling or on evaporation; it has not been possible to prepare ketazinium and hydrazonium fluorostannates analogous to the chlorostannates previously described (*idem, loc. cit.*).

The crystals are monoclinic. They are generally flat quadrangular (010) plates with angles of 75° and 105°, often elongated parallel to *c* and showing (100) with prism and other faces. No pronounced cleavage. Lamellar twinning common. Optically negative, negative elongation. $\widehat{Xc} = 20°$. $2V^{\alpha}(D) = 17\frac{1}{2}°$. Dispersion of the optic axes is extreme, with red > violet, giving rise to incomplete extinction and abnormal interference colours in white light. n_D: α 1·442, β 1·451, γ 1·453, γ − α 0·011.

Hydrazinium Hydrogen Tetrafluorostannite.—Freshly precipitated stannous hydroxide, made from stannous chloride dihydrate (11·3 g.) by precipitation with ammonia as described above for stannic hydroxide, was dissolved in a solution of hydrofluoric acid (10 g.; 40%) and hydrazine hydrate (13 g.; 28%). Rapid evaporation on the water-bath yielded needles which, after drying on paper and then *in vacuo*, had d_{23}^{23} 3·09, m. p. 117—118° (Found: N_2H_4, 13·9; F, 33·0; Sn, 51·8. $N_2H_5,HSnF_4$ requires N_2H_4, 14·0; F, 33·2; Sn, 51·9%). The *salt* is non-deliquescent and is not unduly oxidised by air when dry. Its solutions in water, however, are rapidly oxidised, so the preparation and crystallisation must be carried out as expeditiously as possible. Continued exposure of acid solutions yielded crystals of pure dihydrazinium hexafluorostannate. Like the latter, it is insoluble in the common organic solvents.

The crystals belong to the orthorhombic system. They are colourless, elongated pinacoidal plates with pronounced cleavages parallel to the elongation direction. The optic axial plane is parallel to the elongation direction, with $Bx^{\circ}(\alpha)$ emerging normal to the plane of the plates. Elongation positive. Optically negative. $2V^{\alpha}(D) = 65°$. Dispersion strong, red > violet. n_D: α 1·570, β 1·633, γ 1·647. Birefringence high; γ − α 0·077.

Hydrazinium Hexafluoroantimonate.—Antimony pentachloride (16 g.) was added slowly to water (200 c.c.) at 0° and the hydrated antimony pentoxide, after being washed free from chloride, was dissolved in hydrofluoric acid (20 g.; 40%) containing hydrazine hydrate (10 g.; 28%). The liquid was concentrated to about half bulk on the water-bath and was then kept for several days over solid sodium hydroxide. At no stage was there any evidence, *e.g.*, evolution of nitrogen, of oxidation–reduction. The large dense crystals were dried on filters and *in vacuo* (Found: N_2H_4, 11·2; Sb, 42·6. $N_2H_5SbF_6,H_2O$ requires N_2H_4, 11·2; Sb, 42·5%). The determination of antimony in this *salt* was troublesome. Precipitation with hydrogen sulphide, even after preliminary boiling with sodium hydroxide, was slow and incomplete; reduction in boiling solution with sulphurous acid, with zinc, or with aluminium, was also slow and incomplete after an hour. The methods finally adopted involved the removal of fluoride either by evaporation to fumes with sulphuric acid, or by repeated evaporation with nitric acid. In the former procedure, the antimony was subsequently reduced with sulphurous acid and

titrated with standard permanganate (Pugh, *J.*, 1933, 1); in the latter, the residue was ignited and weighed as antimony tetroxide. The two methods gave identical results.

The salt is deliquescent and exceedingly soluble in water but insoluble in common organic solvents. It dissolves partially in its water of crystallisation at 50° and dissolution (or melting) is complete at 75°.

The crystals, probably orthorhombic, are colourless, pinacoidal plates with no pronounced cleavage. Optically negative. $2V^{\alpha}(D) = 57°$. Dispersion strong, red < violet. n_D: α 1·423, β 1·436, γ 1·445.

Hydrazinium Hydrogen Pentafluoroantimonite.—Antimony trioxide (6 g.) was dissolved in hydrofluoric acid (6 g.; 40%), and the solution was treated with hydrazine hydrate (6 c.c.; 28%) previously neutralised with hydrofluoric acid. The complex separated on cooling and the liquid yielded a further crop on concentration. Recrystallisation from water or from aqueous acetone yielded needles, with d_{26}^{26} 3·15 and m. p. 94—95° (Found: N_2H_4, 12·7; F, 37·7; Sb, 48·7. $N_2H_5HSbF_5$ requires N_2H_4, 12·8; F, 37·9; Sb, 48·6%). The *salt* is non-hygroscopic but is freely soluble in water, forming clear and stable solutions. This complex anion is not as stable as the hexafluoroantimonate ion, its solutions being readily and completely decomposed by hydrogen sulphide. The salt is insoluble in the organic solvents quoted earlier.

The crystals are monoclinic; (010) pinacoids elongated parallel to *c* and often terminated by domes or pyramids. The optic axial plane is parallel to (010). $\widehat{Xc} = 20°$. Elongation negative; optically negative. $2V^{\alpha}(D) = 21°$. Dispersion strong, red > violet, giving abnormal interference tints near the extinction position for white light. n_D: α 1·540, β 1·588, γ 1·595. Birefringence high: γ − α 0·055.

Hydrazinium Hydrogen Pentafluorobismuthite.—Bismuth trioxide (5 g.) was dissolved in the minimum amount of dilute nitric acid, and hydrofluoric acid added until precipitation was complete. The bismuth fluoride, after being washed with water to remove nitric acid, was digested on the water-bath for an hour with hydrazine dihydrofluoride (2 g.), and the insoluble product was washed, dried, ground well, and re-digested in the same way. Repetition of this process yielded a crystalline powder of constant composition and d_{26}^{26} 4·43 (Found: N_2H_4, 9·4; F, 28·3; Bi, 62·0. $N_2H_5,HBiF_5$ requires N_2H_4, 9·5; F, 28·1; Bi, 61·8%). Although this *complex* is almost insoluble in water, all attempts to make it by precipitation from bismuth salt solutions with hydrazine fluoride–hydrofluoric acid solutions yielded mixtures of the complex and bismuth trifluoride. Similar mixtures were obtained when freshly precipitated bismuth hydroxide was added as a slurry to solutions of hydrazine fluoride in excess of hydrofluoric acid. Long digestion of these mixtures was necessary to effect complete recrystallisation of the fluoride in the form of the complex.

The salt decomposes when heated, without melting, yielding a white sublimate, vapours of hydrofluoric acid, and a black residue of metallic bismuth. It is soluble in acids and insoluble in organic solvents.

The crystals are orthorhombic or monoclinic, being minute, colourless scales with six-sided outline and perfect cleavage parallel to the surface. Optically positive. $2V^{\gamma} = 72°$ (calc.). The plates give centred, or near-centred optic normal figures, suggesting orthorhombic symmetry. n_D: α 1·603, β 1·615, γ 1·638. γ − α 0·035.

Attempts to Prepare Hydrazinium Fluoroarsenite.—Arsenious oxide (6 g.) dissolved readily in a mixture of hydrofluoric acid (15 g.; 33%) and hydrazine hydrate (12 g.; 28%), the liquid smelling strongly of arsenic trifluoride. However, hydrazine dihydrofluoride (4 g.) separated on cooling, the crystals being contaminated with arsenious oxide (Found: N_2H_4, 43·0; F, 51·0; As, 2·1. Calc. for $N_2H_6F_2$: N_2H_4, 44·5; F, 52·9%). Evaporation at room temperature yielded further crystals of similar composition, and neighbouring objects became coated with arsenious oxide dust. The whole of the hydrazine used originally was recovered as dihydrofluoride, but only a small fraction of the arsenic was recovered. Arsenic trifluoride evidently volatilised, and was hydrolysed in moist air. H. von Helmolt (*Z. anorg. Chem.*, 1893, **3**, 115) found that arsenious oxide dissolved in ammonium fluoride solutions, and he was likewise unable to prepare ammonium fluoroarsenite.

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