Hydrazine. Part VII. Some Halogeno-antimonites and -bismuthites of Hydrazine.*

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The following new complexes have been prepared by crystallisation, from aqueous solutions, of mixtures of antimony or bismuth halide and the corresponding hydrazine halide:† $(N_2H_5)_2SbCl_5$; $(N_2H_5)_2BiCl_5$; $N_2H_5HBiCl_5,2H_2O$; $N_2H_5BiCl_4$; $(N_2H_5)_{11}Sb_2Br_{17}$; $(N_2H_5)_{10}Sb_3Br_{19}$; $(N_2H_5)_2SbBr_5$; $(N_2H_5)_3Sb_2Br_9$; $(N_2H_5)_4BiBr_7$; $(N_2H_5)_3BiBr_6$; $(N_2H_5)_6HBi_3Br_{16},10H_2O$; $N_2H_5HBiBr_5,4H_2O$; $(N_2H_5)_3Bi_2Br_9$; $(N_2H_5)_3SbI_6$; $N_2H_5SbI_4,3H_2O$; $(N_2H_5)_3BiI_6$; $(N_2H_5)_5Bi_3I_{14},6H_2O$; $(N_2H_5)_6HBi_4I_{19},10H_2O$. The chloro-complexes are colourless, the bromo- yellow, and the iodo- red; they are very soluble in water, forming colourless, yellow, or red solutions which are decomposed on dilution, giving insoluble basic antimony or bismuth halides.

ANTIMONY and bismuth seem to form a great variety of complex halides, ranging in composition from the simpler ones, *e.g.*, $NaSbI_4$, K_2SbCl_5, and K_3BiCl_6, to highly complex ones, *e.g.*, $(NH_4)_7Sb_3Br_{16}$ and $(NH_4)_3Sb_4I_{15},9H_2O$ (Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans Green and Co., London, 1929, Vol. IX, pp. 479, 496, 502, 666, 672, 676). Some highly complex iodoantimonites of some ketazines have recently been reported in Part VI (*loc. cit.*). However, the only complex halides of these metals with the hydrazinium cation, so far described, are the fluoro-salts (Part III, *loc. cit.*), and the hexachloroantimonite and the hexachlorobismuthite prepared by Ferratini (*Gazzetta*, 1912, **42**, 138) by boiling the metal chlorides in alcoholic solution with solid hydrazine hydrochloride.

The present paper confirms the individualities of these two chloro-salts (which, however, have now been obtained from aqueous solutions) and also describes a number of other complex antimonites and bismuthites which are no less remarkable for their variety and complexity. The new compounds are formulated in the summary. These salts were all made by crystallisation from aqueous solution, though better results were obtained from aqueous-alcoholic solution in a few cases; but no claim is made that the above is an exhaustive list of all possible compounds. The experimental details given later show that the composition of the solid phase, at room temperature, depends not only on the weight ratio of the component simple salts but also on the concentration of free halogen acid. Phase-rule studies would no doubt establish the existence of other compounds in these series.

The chloro-salts are colourless, the bromo-salts yellow, and the iodo-salts red. They are all exceedingly soluble in water, and deliquescent; most of them dissolve in a fraction of their own weight of water, forming colourless, yellow, or red solutions, which are decomposed on dilution, with separation of insoluble basic salts. They are insoluble in light petroleum, benzene, carbon tetrachloride, chloroform, ether, and alcohol (except the iodo-salts which are soluble in alcohol), but they dissolve readily in acetone–water, forming the corresponding salts of dimethylketazine (Part VI, *loc. cit.*).

EXPERIMENTAL

The methods of analysis used have been described in Part VI (*loc. cit.*). In this section complexes are named for convenience as salts of complex ions without prejudice as to the actual existence of the complex ions implied.

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* Parts III, VI, *J.*, 1953, 1934, 3445.

† These formulæ are given for simplicity, but with full realisation that some of the compounds, at least, may be double salts or lattice compounds rather than complex ions. Only structure investigations can determine the exact co-ordination number of the metals in the compounds.

General Method of Preparation.—The chloro- and bromo-salts were prepared from antimony and bismuth trioxides and hydrazine hydrate as source materials. Solutions of the metal oxides in concentrated hydrochloric, or hydrobromic, acid were treated with the appropriate quantities of hydrazine hydrochloride, or hydrobromide, solution, prepared by neutralising hydrazine hydrate (60%) with concentrated acid (methyl-orange indicator). Crystallisation was at room temperature, by slow evaporation in air or, sometimes, over desiccating agents. In some cases, indicated below, the metal halide solution was evaporated to dryness, or as near dryness as possible, to remove excess of acid, before the hydrazine salt solution was added. It was from solutions which had not been so evaporated that the acid salts described separated.

The iodo-salts were prepared by dissolving antimony tri-iodide and bismuth iodide in warm solutions of hydrazine hydriodide, but addition of free hydrioidic acid was found necessary when the formal ratio was less than 3 : 1.

Whenever any of the mixed solutions were boiled, separation of metallic antimony or bismuth occurred, with evolution of nitrogen; however, it was always possible to concentrate the solutions on the water-bath, because reduction was seldom noticeable at this temperature; cold solutions generally remained stable indefinitely.

In the various preparations described, the term " formal ratio " means the number of formula weights of hydrazine salt per formula weight of metal halide.

The Chloroantimonites.—(a) *Trihydrazinium hexachloroantimonite.* Hydrazine monohydrochloride and antimony trichloride, formal ratio 3 : 1, were dissolved in half their combined weight of water. The solution effervesced slowly (nitrogen) and deposited antimony during several hours. However, rapid evaporation under reduced pressure yielded colourless, silky needles, m. p. 138—140°, free from metallic antimony (dried *in vacuo*; H_2SO_4) [Found: N_2H_4, 21·9; Cl, 49·0; Sb, 27·9. Calc. for $(N_2H_5)_3SbCl_6$: N_2H_4, 22·1; Cl, 49·1; Sb, 28·1%]. A less pure product was obtained by boiling under reflux for 4 hr. a chloroform solution of antimony trichloride, in large excess, with solid hydrazine monohydrochloride. The latter slowly changed its form and appearance, and the yield was nearly quantitative.

(b) *Dihydrazinium pentachloroantimonite.* Antimony trichloride dissolved in a concentrated solution of hydrazine dihydrochloride (formal ratio 2 : 1), but slow evaporation of the solution led to continuous separation of hydrazine dihydrochloride. The *pentachloro*-salt was made from a mixture of the above salts (formal ratio 1 : 1) by evaporation with hydrochloric acid, on the water-bath, to a syrupy consistency, the syrup then being shaken with its own volume of ethanol. (Hydrazine dihydrochloride again separated but redissolved as evaporation proceeded.) The mixture slowly separated into two phases, and the lower phase yielded colourless needles at 0° [Found, on crystals dried *in vacuo*: N_2H_4, 17·5; Cl, 48·5; Sb, 33·2. $(N_2H_5)_2SbCl_5$ requires N_2H_4, 17·5; Cl, 48·5; Sb, 33·4%].

The Chlorobismuthites.—(a) *Trihydrazinium hexachlorobismuthite.* Hot concentrated solutions of hydrazine dihydrochloride dissolve bismuth trioxide, and a solution of the mixed chlorides, formal ratio 3 : 1, was made in this way. Evaporation over desiccating agents then yielded the hexachlorobismuthite as long, flat prisms and plates, often with domed ends [Found, on material dried *in vacuo*: N_2H_4, 18·4; Cl, 40·8; Bi, 40·2. Calc. for $(N_2H_5)_3BiCl_6$: N_2H_4, 18·4; Cl, 40·9; Bi, 40·1%]. (The same compound was precipitated from the mother-liquors by addition of ethanol). The crystals melt partially at 210° but there is evidence of slow decomposition (gas evolution) at temperatures as low as 120°; gas evolution is vigorous at the m. p.

(b) *Dihydrazinium pentachlorobismuthite.* This *chlorobismuthite* was obtained as fine colourless needles from a highly concentrated, acid-free, solution of the mixed chlorides, formal ratio 2 : 1 (prepared by evaporating bismuth oxide with excess of hydrochloric acid to complete dryness, and dissolving the acid-free chloride in hydrazine monohydrochloride solution) [Found, on material dried *in vacuo*: N_2H_4, 14·1; Cl, 39·2; Bi, 46·3. $(N_2H_5)_2BiCl_5$ requires N_2H_4, 14·2; Cl, 39·2; Bi, 46·2%]. This salt also shows signs of decomposition at temperatures below its m. p. (190—195°) and it decomposes actively over the melting range.

(c) *Hydrazinium hydrogen pentachlorobismuthite and* (d) *hydrazinium tetrachlorobismuthite.* These two salts were obtained by crystallisation of mixtures, formal ratio 2 : 1, containing free hydrochloric acid. The first crops consisted of colourless needles, or plates with domed ends, of the acid pentachlorobismuthite as a *dihydrate* [Found: N_2H_4, 7·2; Cl, 38·9; Bi, 46·2. $N_2H_5HBiCl_5,2H_2O$ requires N_2H_4, 7·0; Cl, 39·0; Bi, 45·8%]. The middle fractions were mixtures of this salt and the *tetrachlorobismuthite*, which in turn was the sole constituent of the tail fractions (colourless needles) [Found: N_2H_4, 7·9; Cl, 37·0; Bi, 54·6. $N_2H_5BiCl_4$ requires N_2H_4, 8·3; Cl, 37·0; Bi, 54·5%].

The Bromoantimonites.—(a) *Undecahydrazinium heptadecabromodiantimonite.* A mixed solution of hydrazine hydrobromide and antimony tribromide (formal ratio 3 : 1) was used, the solution of antimony oxide in hydrobromic acid having been evaporated to near-dryness on the water-bath before addition of the hydrazine salt solution. The mixed warm solution was then treated with an equal volume of methanol, and yellow, granular crystals of the *heptadecabromo-salt* separated [Found: N_2H_4, 18·2; Br, 69·4; Sb, 12·4. $(N_2H_5)_{11}Sb_2Br_{17}$ requires N_2H_4, 18·3; Br, 69·2; Sb, 12·4%]. The crystals melt partially at 165°, clearing at 186°, but there is considerable gas evolution at intermediate temperatures, and decomposition is vigorous at 186°. Crystallisation of similar mixtures from hydrobromic acid solutions (without preliminary evaporation) yielded mixtures of the above salt and the nonabromodiantimonite described below under (d).

(b) *Decahydrazinium nonadecabromotriantimonite.* Mixtures, of formal ratio 3 : 1, crystallised from aqueous solution free from excess of hydrobromic acid, yielded a number of products. The first fractions consisted essentially of the heptadecabromo-salt (a); the middle fractions approximated closely in composition to trihydrazinium hexabromoantimonite, but this salt was not obtained pure; the last fractions consisted of long, slender, yellow needles of *decahydrazinium nonadecabromotriantimonite* [Found: N_2H_4, 14·4; Br, 68·4; Sb, 16·5. $(N_2H_5)_{10}Sb_3Br_{19}$ requires N_2H_4, 14·4; Br, 68·6; Sb, 16·5%].

(c) *Dihydrazinium pentabromoantimonite.* The earlier fractions obtained by crystallising mixtures of formal ratio 2 : 1, containing the minimum of hydrobromic acid, consisted of granular yellow crystals of the *pentabromoantimonite* [Found: N_2H_4, 10·7; Br, 67·5; Sb, 20·4. $(N_2H_5)_2SbBr_5$ requires N_2H_4, 10·9; Br, 68·0; Sb, 20·7%].

(d) *Trihydrazinium nonabromodiantimonite.* The middle fractions obtained in the immediately preceding preparation (c) consisted of the pure *nonabromodiantimonite,* but this salt was obtained more easily from a mixture of formal ratio 1 : 1, prepared by evaporating antimony oxide with hydrobromic acid to near-dryness and adding a concentrated solution of hydrazine monohydrobromide. It separated as yellow blades and plates which are not deliquescent in dry weather [Found: N_2H_4, 8·9; Br, 67·6; Sb, 22·9. $(N_2H_5)_3Sb_2Br_9$ requires N_2H_4, 9·0; Br, 67·7; Sb, 22·9%].

The Bromobismuthites.—(a) *Tetrahydrazinium heptabromobismuthite.* Concentrated solutions of mixtures of hydrazine and bismuth bromides, formal ratio 3 : 1, which are free from hydrobromic acid, undergo slow decomposition, even when cold. They become dark and deposit bismuth slowly. The first two crystal fractions obtained by evaporating such solutions over calcium chloride were essentially the *heptabromobismuthite,* as yellow needles and laths, contaminated with bismuth inclusions [Found: N_2H_4, 13·8; Br, 61·3; Bi, 24·3. $(N_2H_5)_4BiBr_7$ requires N_2H_4, 14·2; Br, 62·2; Bi, 23·2%].

(b) *Trihydrazinium hexabromobismuthite.* Following the above crops of the heptabromo-salt, there appeared several crops of yellow rhomboidal bars or needles of the *hexabromobismuthite.* However, this salt was obtained more easily, in better yields, and without separation of bismuth by treating a similar mixture (formal ratio 3 : 1), containing free hydrobromic acid, with its own volume of ethanol, and cooling it to 0° [Found: N_2H_4, 12·2; Br, 60·8; Bi, 26·5. $(N_2H_5)_3BiBr_6$ requires N_2H_4, 12·2; Br, 61·0; Bi, 26·6%]. The salt does not melt; it decomposes actively at 215° (approx.).

(c) *Hexahydrazinium hydrogen hexadecabromotribismuthite.* This salt separated as the *decahydrate,* in large, tetragonal, yellow prisms, or flat oblong tablets, from mixed solutions of hydrazine and bismuth bromides (formal ratio 2 : 1), which were free from hydrobromic acid [Found: N_2H_4, 8·5; Br, 56·1; Bi, 27·5; H_2O, 8·0. $(N_2H_5)_6HBi_3Br_{16},10H_2O$ requires N_2H_4, 8·4; Br, 56·0; Bi, 27·4; H_2O, 7·9%]. The hydrated salt dissolves partially in its water of hydration at 48°, and completely at 80°. It loses its water of hydration very readily, desiccation *in vacuo* over sulphuric acid at 20° yielding the anhydrous *salt* [Found: N_2H_4, 9·1; Br, 61·0; Bi, 29·6. $(N_2H_5)_6HBi_3Br_{16}$ requires N_2H_4, 9·1; Br, 61·0; Bi, 29·7%].

(d) *Trihydrazinium nonabromodibismuthite.* Mixed solutions of the simple salts, of formal ratio 1·5 : 1 and free from hydrobromic acid, yielded the pure *nonabromodibismuthite* as yellow needles and prisms [Found, on material dried *in vacuo*: N_2H_4, 7·7; Br, 58·3; Bi, 33·6. $(N_2H_5)_3Bi_2Br_9$ requires N_2H_4, 7·8; Br, 58·2; Bi, 33·8%].

(e) *Hydrazinium hydrogen pentabromobismuthite.* The pure *tetrahydrate* of this salt was obtained in the later fractions which separated from mixtures (formal ratio 1 : 1) dissolved in hydrobromic acid [Found: N_2H_4, 4·5; Br, 55·8; Bi, 29·1. $N_2H_5HBiBr_5,4H_2O$ requires N_2H_4, 4·5; Br, 55·9; Bi, 29·2%]. [The earlier fractions were mixtures of this salt and the nonabromodibismuthite (d).] It forms yellow needles and prisms which are very deliquescent, and lose water rapidly (approx. 4 mols.) over sulphuric acid. This initial rapid loss is followed by a slower loss of hydrogen bromide.

The Iodoantimonites.—(a) *Trihydrazinium hexaiodoantimonite.* Antimony tri-iodide dissolved completely in aqueous solutions of hydrazine hydriodide, provided the formal ratio was 3 : 1, and the dark red solutions yielded scarlet needles and prisms of the *hexaiodoantimonite* [Found: N_2H_4, 9·8; I, 77·8; Sb, 12·4. $(N_2H_5)_3SbI_6$ requires N_2H_4, 9·8; I, 77·5; Sb, 12·4%].

(b) *Hydrazinium tetraiodoantimonite.* Antimony tri-iodide was dissolved in hot aqueous hydrazine hydriodide solution (formal ratio 1 : 1) with the aid of the minimum amount of hydriodic acid, the red solution depositing dark red, almost black, octahedra of the tetraiodoantimonite as *trihydrate* (Found: N_2H_4, 4·4; I, 71·5; Sb, 17·0; H_2O, 7·8. $N_2H_5SbI_4,3H_2O$ requires N_2H_4, 4·5; I, 71·0; Sb, 17·0; H_2O, 7·5%). The *anhydrous* salt was obtained as a maroon powder by desiccating the above hydrate over sulphuric acid (Found: N_2H_4, 4·7; I, 77·0; Sb, 18·4. $N_2H_5SbI_4$ requires N_2H_4, 4·8; I, 76·6; Sb, 18·4%).

The Iodobismuthites.—(a) *Trihydrazinium hexaiodobismuthite.* The dark red aqueous solutions containing hydrazine hydriodide and bismuth iodide (formal ratio 3 : 1) yielded scarlet needles and tetragonal prisms of the *hexaiodobismuthite*, m. p. 182° (decomp. with vigorous gas evolution) [Found: N_2H_4, 9·0; I, 71·2; Bi, 19·7. $(N_2H_5)_3BiI_6$ requires N_2H_4, 9·0; I, 71·2; Bi, 19·6%].

(b) *Pentahydrazinium tetradecaiodotribismuthite.* Mixtures of the simple iodides of formal ratio 2 : 1 and 1·5 : 1, containing the minimum of free hydriodic acid for complete solution, did not yield the expected pentaiodo-salt or the iodo-analogues of the bromo-salts (see above) obtained from similar mixtures; instead, they yielded pentahydrazinium tetradecaiodotribismuthite as the *hexahydrate*, ruby-red needles and elongated prisms and plates [Found: N_2H_4, 5·9; I, 66·3; Bi, 23·4; H_2O, 4·3. $(N_2H_5)_5Bi_3I_{14},6H_2O$ requires N_2H_4, 6·0; I, 66·5; Bi, 23·4; H_2O, 4·1%]. The hydrated salt loses its water of crystallisation readily over sulphuric acid, yielding black lustrous crystals of the *anhydrous* salt [Found: N_2H_4, 6·2; I, 69·3; Bi, 24·4. $(N_2H_5)_5Bi_3I_{14}$ requires N_2H_4, 6·2; I, 69·2; Bi, 24·4%].

(c) *Hexahydrazinium hydrogen nonadecaiodotetrabismuthite.* Mixtures of formal ratio 1 : 1 in hydriodic acid solution yielded the *decahydrate* of this salt as dark red needles, m. p. 75° [Found: N_2H_4, 5·2; I, 65·8; Bi, 22·8; H_2O, 6·0. $(N_2H_5)_6HBi_4I_{19},10H_2O$ requires N_2H_4, 5·2; I, 66·0; Bi, 22·8; H_2O, 5·9%]. It loses its water of crystallisation when kept over sulphuric acid, but there is a slight loss of hydrogen iodide at the same time.

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