LXXVII.—*Complex Nitrites of Bismuth.*

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THE author has been unable to find a description of any nitrites of bismuth, although such compounds evidently exist, for on adding powdered bismuth nitrate to a strong solution of an alkali nitrite an orange liquid is formed, and nitrous fumes are evolved. When a large amount of the bismuth salt has been added, the colour of the solution is deep orange, with a purplish reflex. This liquid rapidly absorbs oxygen from the air, its surface becoming covered with a white film of basic bismuth nitrate.

A similar solution may also be obtained by mixing the powdered salts with acetone; the resulting orange liquid, on evaporation in absence of air, leaves a yellow, crystalline mass. If potassium nitrite is used instead of the sodium salt, needle-shaped crystals are formed on evaporation, but in either case they rapidly decompose. Various attempts were made to isolate a more stable crystalline derivative from the orange solutions, but the only successful method was to pour the liquid, obtained by adding bismuth nitrate to saturated aqueous sodium nitrite into an aqueous solution of ammonium nitrate saturated at 0°. A yellow, crystalline, and very unstable substance is precipitated, which is described in the sequel.

a. *Bismuth Sodium Ammonium Nitrite.*

A more stable compound is obtained by dissolving powdered bismuth nitrate in a saturated solution of ammonium nitrate at 0°,

and then gradually pouring this liquid into an ice-cold, nearly saturated solution of sodium nitrite, slightly acidified with nitrous fumes. The best proportions are 10 grams of bismuth nitrate, 15 grams of ammonium nitrate, and 15 grams of sodium nitrite; but these numbers may be varied considerably.

The liquid must be at once poured off and the precipitate drained on a porous tile. It is then pressed several times between filter paper to remove adherent liquid, and the drying is completed by compressing the substance between pieces of porous plate in a desiccator kept at 0° . It is essential to dry the product in this manner, otherwise decomposition takes place.

Bismuth sodium ammonium nitrite, $\text{Bi}(\text{NO}_2)_3 \cdot 2\text{NH}_4\text{NO}_2 \cdot \text{NaNO}_2$, is a bright yellow substance which crystallises in octahedra, and possesses a slight green fluorescence. It decomposes slowly at 0° , more rapidly at the ordinary temperature, evolving nitric oxide and leaving a moist white mass which contains no nitrite. If some of the substance is touched at any point with a hot wire, decomposition rapidly occurs throughout, and the resulting white mass is found to be free from nitrite. The substance detonates feebly on being struck.

ANALYSIS.

Found.

Preparation.	Bi.	Na.	NH_4 .	NO_2 per cent.
(1)	38.9; 39.1	4.54	6.30	49.7
(2)	39.5	4.48	6.25	49.8

Calculated.

38.25	4.24	6.64	50.87
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The methods of analysis are described later (p. 765). The slight deficits in the ammonium and nitrite are probably due to interaction between these constituents.

b. *Bismuth Potassium Nitrite.*

The most stable of these compounds is obtained by passing nitrous fumes into a suspension of bismuth hydroxide in concentrated potassium nitrite solution until white particles can no longer be seen in the orange precipitate. The product should be dried quickly, as when moist it absorbs oxygen.

Bismuth potassium nitrite, $\text{Bi}(\text{NO}_2)_3 \cdot 3\text{KNO}_2 \cdot \text{H}_2\text{O}$, is an orange, crystalline, and slightly fluorescent substance. Like the other compounds described, it is immediately hydrolysed by water; but,

unlike them, it is stable at the ordinary temperature, and does not detonate when struck.

ANALYSIS.

Preparation.	<i>Found.</i>			
	Bi.	K.	NO ₂ .	Water by difference per cent.
(1)	34.1	19.09	44.3	2.5
(2)	33.8	19.06	44.2	2.8
(3)	—	—	44.6	—

Calculated.

33.5	18.96	44.6	2.9
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The formulæ of these two compounds resemble those of many complex nitrites of other elements in having an atom of the monad metal for each valency of the polyvalent metal, as, for instance, $\text{Co}(\text{NO}_2)_3, 3\text{NaNO}_2, \text{H}_2\text{O}$ and $\text{Co}(\text{NO}_2)_2, 2\text{KNO}_2, \text{H}_2\text{O}$.

c. Other Complex Bismuth Nitrites.

The compound obtained by mixing bismuth nitrate with sodium nitrite and adding the mixture to ammonium nitrate (p. 761) is both more complex and less stable than those already described. It may be obtained by mixing 15 or 20 grams of powdered bismuth nitrate with a saturated aqueous solution of 15 grams of sodium nitrite. The resulting orange liquid is then filtered, preferably in absence of air, although instead of excluding air it is sufficient to filter the liquid quickly by suction. As soon as the filtrate becomes clear, it is allowed to drop slowly into saturated ammonium nitrate solution, kept at 0°. The supernatant liquid is rapidly poured off, and the yellow precipitate carefully dried, first with filter paper and then in a desiccator at 0° (p. 762); it is advantageous to replace the air in the desiccator by nitrogen.

The substance thus obtained, which is most probably

forms small, canary-yellow crystals, possessing a green fluorescence; it gradually decomposes, even at 0°, becoming white and evolving nitric oxide. If the salt is kept in a bottle, the decomposition is rapid, and the residue becomes moist, owing to the water produced from the ammonium nitrite, but in a desiccator the decomposition is slower, because of the removal of the water as it is formed. The decomposition is complex, as in addition to the resolution of the ammonium nitrite into nitrogen and water, and the liberation of nitric oxide from the bismuth nitrite, there is further a gradual absorption of oxygen.

The substance detonates feebly when struck, and is decomposed throughout when touched by a hot wire. It thus resembles bismuth sodium ammonium nitrite, from which it may be regarded as being derived by the replacement of a molecule of ammonium nitrite by ammonium nitrate and the addition of a molecule of sodium nitrate.

On account of the unusual character of the foregoing formula numerous analyses were made on specimens prepared under various conditions. The proportion of bismuth nitrate to sodium nitrite was varied between 3:5 and 5:3 by weight, and the ammonium nitrate was, in some cases, added to the mixture of bismuth nitrate and sodium nitrite; but the analyses showed no parallel variations. When the substance was precipitated fractionally, the variations were also small and irregular, and this renders it unlikely that the substance could be a mixture of two or more salts precipitated together; the composition of a precipitate would in such case change as the concentration of the dissolved salts altered.

ANALYSIS.

Found (mean).

	Bi.	Na.	NH ₄ .	NO ₂ .	NO ₃ per cent.
	32.6	3.59	8.32	34.3	19.0
Number of determinations of each constituent.....	(5)	(5)	(8)	(15)	(5)

Calculated.

32.5	3.60	8.46	36.0	19.4
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The numbers are fairly concordant except for the nitrite; the bismuth and sodium showed a very constant ratio. The ammonium and nitrite are low, probably in part on account of some action between them. The bismuth is not present as a basic salt, for the acids are equivalent to the bases; in this the compound differs from the nitrate-nitrites of lead, which are all basic.

The tendency of these compound bismuth nitrites to oxidise is not entirely due to hydrolysis into bismuth hydroxide and nitrous acid, followed by decomposition of the latter. The orange liquid, obtained by mixing bismuth nitrate and sodium nitrite, became coated with a white film immediately it came into contact with the air, and direct measurement proved that such a solution absorbed oxygen much more quickly than it evolved nitric oxide.

In addition to the above compounds, some other salts were prepared: an orange tetramethylammonium salt; a black triple nitrite of bismuth, copper, and ammonium; and a yellow com-

pound, apparently a double nitrite of bismuth and cinchonine. A light yellow solution is obtained by passing nitrous fumes into water containing bismuth hydroxide in suspension, and also by adding the hydroxide and a little water to the blue liquid obtained by condensing nitrous fumes. These solutions probably contain bismuth nitrite, but it was not found possible to prepare this substance in the solid state.

The slight fluorescence possessed by these salts suggested that they might be susceptible to radium, or to the cathode rays; but in neither case was any perceptible effect produced.

Methods of Analysis.

The bismuth was estimated as oxide or sulphide, and the sodium and potassium as sulphates. To estimate the ammonium, about 0.5 gram of the solution was weighed in a small tube, which was then dropped into cold caustic soda solution, the ammonia being then distilled into *N*/10 acid. If the substance is first added to water there is a slight loss of ammonia.

As the substance was decomposed immediately by water with evolution of nitrous fumes, and ammonium was present, it was found impossible to obtain concordant values for the nitrite, except by the following method. About 0.1 gram of the substance was weighed in a small tube; this was dropped into a 500 c.c. bottle, almost full of ice-cold acidified water, to which about one and a half times the calculated quantity of *N*/10 permanganate had been added. After a few minutes the excess of permanganate was estimated by ferrous sulphate. Control analyses were made on pure sodium nitrite and mixtures of sodium nitrite, ammonium nitrate, and bismuth nitrate; the method gave good results, whilst departures from this mode of procedure gave high and discordant values.

The nitrate was determined by difference, the total nitrogen in about 0.2 gram of the substance being converted into ammonia by reduction with aluminium and sodium hydroxide. Simultaneous determinations of the ammonium and nitrite were made on the same specimen, so that the nitrogen present as NO_3 was given by the difference. Three treatments with aluminium were usually necessary before all the nitrate and nitrite were reduced.

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