## X.—The Metallic Derivatives of Nitrogen Iodide and their Bearing on its Constitution.

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In the preceding paper, the author has given a definite proof of the constitution of nitrogen iodide, and has at the same time shown the uncertainty of much of the earlier work. For this reason, it appeared of interest to undertake a revision of the more important work on the derivatives of this compound, because, although a number of derivatives have been obtained by the action of metallic salts on nitrogen iodide or by the action of iodine on ammoniacal salt solutions, great uncertainty exists as to the composition of these substances. A review of this work has shown that both the methods of preparation and of analysis were very unsatisfactory.

The Copper Derivative.—Guyard (Compt. rend., 1884, 97, 526) ascribed the formula  $Cu_2I_2, 2NH_2I$  to the compound which he obtained by the action of a potassium iodide solution of iodine on copper ammonium sulphate. He did not, however, support this formula by any analytical data, nor did he give any description of his methods of analysis. Further investigations of the subject have rendered it probable that he deduced the above formula from estimations of the iodine only. He based its relationship to nitrogen iodide on the fact that on treatment with excess of ammonia the copper passed into solution with a simultaneous precipitation of nitrogen iodide.

It must, however, be remarked that the copper compound itself possesses no explosive properties whatever, a circumstance which at once renders Guyard's formula doubtful. The following investigation shows that the compound is a cuprosamine periodide. The compound is prepared by dropping a 20 per cent. solution of potassium iodide (100 c.c.) containing 5 grams of iodine into an aqueous solution containing a slight excess of cuprammonium sulphate in 1200 c.c. of water at the ordinary temperature. The compound separates in small,

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crystalline plates. Owing to its insolubility, it cannot be recrystallised from any solvent, and considerable care is therefore necessary for the production of the compound in a pure state. It was found necessary to devise special methods of analysis, and the following procedure was eventually selected as being most satisfactory. The compound was first warmed with dilute alkali and metallic aluminium for half an hour on the water-bath. This brought about complete precipitation of the copper. The precipitate was well washed with hot water, redissolved in a little hot nitric acid, and reprecipitated as cupric oxide and weighed.

After the removal of the copper, the filtrate was acidified in the cold with dilute sulphuric acid and treated with hydrogen peroxide and chloroform to extract the iodine. The chloroform solution was then titrated with standard thiosulphate solution. For the estimation of the nitrogen in this compound, Dumas' method was found to be the most satisfactory.

For comparison, the percentages required by a compound having the formula suggested by Guyard are given in the final column of the following table :

-	Found.		Cu <sub>2</sub> I <sub>2</sub> , (NH <sub>3</sub> ) <sub>5</sub> I <sub>4</sub> , H <sub>2</sub> C	Cu <sub>2</sub> I <sub>2</sub> ,2NH <sub>2</sub> I	
		·	requires	requires	
Copper	12.87	12.96	12.82	19.08	
Iodine	76.19	76.43	76.75	76.11	
Nitrogen	7.53	7.32	7.08	4.21	

The compound manifests the characteristics of a periodide in many ways. On heating, it evolves iodine vapour; by treatment with potassium iodide solution, the loosely combined iodine is removed quantitatively, and, on titrating this solution with sodium thiosulphate, the following results were obtained:

Loosely combined iodine found	51.20	51.12 p	er cent.
$Cu_2I_2(NH_3)_5I_4,H_2O$ requires		51.16	,,

The behaviour of the cuprosamine periodide towards ammonia, which was taken by Guyard to be indicative of its relationship to nitrogen iodide, must, however, be regarded as distinct evidence of its periodide character. According to the above formulation, the loosely combined iodine interacts with ammonia in a manner precisely similar to that in which potassium periodide acts on ammonia. It thus becomes evident that Guyard's formula for this compound is incorrect, and consequently that its existence is no support of the formula  $NH_2I$  for nitrogen iodide.

Cuprosamine Iodide,  $Cu_2I_2$ ,  $NH_3$ ,  $4H_2O$ .—When, in order to remove the loosely combined iodine, the above periodide is treated with potass-

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ium iodide—preferably by warming with a 25 per cent. solution—a green, crystalline residue is left, which, when thoroughly washed and dried, is obtained as an olive-green powder insoluble in water, but soluble in ammonia, forming a blue solution.

	Found.		$\mathrm{Cu}_{2}\mathrm{I}_{2},\mathrm{NH}_{3},\mathrm{4H}_{2}\mathrm{C}$	
			requires	
Copper	27.10	27.21	27.08	
Iodine	53.94	54.16	54.03	
Nitrogen	$3 \cdot 10$	3.05	2.98	

By the foregoing treatment, the cuprosamine periodide has therefore lost both iodine and ammonia.

The Silver Derivative.—It was shown by Szuhay (Ber., 1893, 26, 1933) that a silver compound could be obtained from nitrogen iodide which was in all probability a direct derivative of the latter. He prepared this silver compound by the addition of an ammoniacal solution of silver nitrate to nitrogen iodide suspended in water, and ascribed the formula  $AgNI_2$  to the product on the basis of determinations of the ratio of the elements to one another.

It is obvious, however, from Szubay's paper that insufficient precautions were taken for the production of a pure homogeneous compound; for, since the substance cannot be recrystallised, it is necessary to take extreme care to ensure absolute purity in the first instance. It is hardly to be expected that the conversion of one solid compound into another in this way will give rise to a pure derivative. The heterogeneous character of Szubay's product is shown by the following analysis of three different preparations carried out exactly as prescribed by him with the exception that the experiments were performed in the dark and at  $0^{\circ}$  in order to minimise the decomposition of the compounds.

	Analytical results (weight in grams).			Atomic proportions.		
	(1)	(2)	(3)	(1)	(2)	(3)
Nitrogen	0.05623 0.09469	0.04956 0.05479	0.05696	4.58	6.98	4.75
Iodine	0.5364	0.4197	0.5327	4.82	6.51	4.90

These numbers show that it is practically impossible to obtain a homogeneous product by Szuhay's method. The agreement of his analytical results with the formula  $AgN1_2$  must therefore have been accidental.

The weak point in Szuhay's procedure appeared to be that the purity of the compound depended on the complete conversion of one insoluble solid into another. This difficulty was overcome in the following manner. Twenty eight c.c. of a 5 per cent. solution of silver nitrate were added to 30 c.c. of 10 per cent. ammonia; the mixture was then cooled to  $0^{\circ}$  and treated with 6 c.c. of a 14 per cent. solution of iodine chloride (corresponding with 0.8 gram of iodine) also cooled to  $0^{\circ}$ . The black precipitate was washed by decantation in the dark.

On attempting to dry this silver derivative, it underwent decomposition with formation of silver iodide. In order to establish its composition, it therefore became necessary to determine the ratio of the elements present by working with the substance suspended in water.

The analytical methods used by Szuhay were examined and found to be open to criticism. He treated the precipitated compound with aluminium turnings in order to reduce the silver to the metallic condition and the nitrogen to ammonia. The ammonia was thereupon distilled off and estimated, the other elements being determined in the residue. He assumed that no loss of nitrogen would take place in this way. Trials of his method have shown, however, that the evolution of traces of nitrogen is practically unavoidable. After trying various methods, the following mode of procedure was found to give the most satisfactory results.

The compound suspended in water is first treated with sodium thiosulphate. The nitrogen is thus converted quantitatively into ammonia, which, after the addition of caustic soda, is distilled off and estimated. The residue is then treated with finely divided aluminium; the silver is thereby reduced to the metallic state and can be filtered off, dissolved in nitric acid, and estimated in the usual way. The iodine remains in solution as sodium iodide and can be readily estimated. The following analytical results were obtained in this way with four different preparations:

	Analytical results (weight in grams).				Atomic proportions.			s.
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Silver	0.1895	0.2141	0.1890	0.2105	1.00	1.00	1.00	1.00
Iodine	0.6753	0.7252		0.7437	3.03	2.88		3.01
Nitrogen		0.0260	0.0522	0.0549		2.02	2.14	2.01

The foregoing samples were prepared as follows :

Expts. 1 and 3.—22.8 c.c. of a 5 per cent. solution of silver nitrate were treated with just sufficient 10 per cent. ammonia to redissolve the precipitate, cooled to  $0^{\circ}$ , and 6 c.c. of a 14 per cent. solution of iodine chloride added.

Expt. 2.—22.8 c.c. of a 5 per cent. solution of silver nitrate were treated with 30 c.c. of 10 per cent. ammonia cooled to  $0^{\circ}$ , and 6 c.c. of a 14 per cent. solution of iodine chloride added.

Expt. 4.—This specimen was prepared from cyanogen iodide as described below.

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The ratio Ag:I:N is thus undoubtedly 1:3:2. The compound is therefore derived from nitrogen iodide by the replacement of one atom of hydrogen by silver, and possesses the formula  $NH_2AgNI_3$ .

The substance decomposes readily when left at the ordinary temperature, especially when exposed to light. In the dry state, it explodes on the slightest friction.

The Potassium Derivative.—Szuhay observed that the foregoing silver derivative dissolved readily in a solution of potassium cyanide, and that on subsequent addition of ammoniacal silver nitrate the original compound was regenerated. He did not, however, succeed in isolating any soluble derivative.

Regarded in the light of the above investigation, the potassium derivative would receive the formula  $NI_3NH_2K$ , and although a silver compound of this formula might well be formed it is very improbable that a direct derivative of potassamide would exist in aqueous solution. In order to gain some insight into the nature of the reaction, the effect of potassium cyanide solution on nitrogen iodide itself was first studied.

Action of Potassium Cyanide on Nitrogen Iodide.—It was observed by Millon, in 1839, that nitrogen iodide dissolves in potassium cyanide, but the products of the reaction have hitherto remained uninvestigated.

For the elucidation of the mechanism of the reaction, experiments were first made to ascertain the relative quantities of nitrogen iodide and potassium cyanide taking part therein. The nitrogen iodide was prepared by the addition of a standard solution of iodine chloride to From blank experiments carried out in a precisely dilute ammonia. similar manner with the same solutions, the yield of nitrogen iodide was found to be 97 per cent. of that calculated from the strength of the iodine chloride solution used. The amount of a standard solution of potassium cyanide necessary to dissolve a known amount of nitrogen iodide prepared as indicated above was then estimated. In this way, 10 c.c. of standard iodine chloride solution, corresponding with 0.385 gram of iodine, were converted into nitrogen iodide and titrated with a standard potassium cyanide (containing 0.01784 gram per c.c.). The volume required to cause complete solution of the nitrogen iodide was (1) 11.27, (2) 11.21, mean = 11.24 c.c.; that is, after correcting for the yield of nitrogen iodide, 1 atom of iodine corresponds with 1.034 molecule of potassium cyanide. Hence one molecule of nitrogen iodide (NH<sub>3</sub>:NI<sub>2</sub>) requires 3 molecules of potassium cyanide for its Experiments in which varying quantities of ammonia were solution. used showed that, provided the quantity present is sufficient to suppress the hydrolysis of the cyanide, excess of ammonia is without influence on the amount of potassium cyanide necessary for complete solution of the nitrogen iodide.

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For the investigation of the products of the reaction, a quantity of well washed nitrogen iodide was covered with a little ice-cold water, and then treated with a concentrated solution of potassium cyanide, also at  $0^{\circ}$ , until the black precipitate had disappeared. A white, insoluble residue remained, but this passed into solution on allowing the liquid to attain the ordinary temperature. A quantity of the white residue was collected at  $0^{\circ}$  and recrystallised from ether; it melted at  $146^{\circ}$  and its properties agreed with those of cyanogen iodide (m. p.  $146^{\circ}5^{\circ}$ ). The identity was confirmed by analysis:

0.1715 gave 13.6 c.c. moist nitrogen at  $18.5^{\circ}$  and 765 mm. N = 9.21. CNI requires N = 9.18 per cent.

A further quantity of this product was obtained by extracting the solution with ether. A portion of the solution which had not been thus extracted with ether was allowed to evaporate in a vacuum desiccator over concentrated sulphuric acid. Ammonia and cyanogen were evolved, the former in large quantities. As the solution became concentrated, crystals slowly separated; these were collected in four fractions and found to consist of the following salts:

lst Frac	tion.	KI = 75.0  pe	r cent.	$K_2CO_3 = 2$	23·8 per	cent.
2nd ,	,	KI = 91.9	,,	$K_2CO_3 =$	7.99	"
3rd ,	,	KI = 93.5	"			
4th ,	,	KI = 78.5	,,			

The fourth fraction contained, in addition, a quantity of potassium cyanate, which was identified by conversion into urea. With this object in view, the remainder was treated with ammonium sulphate and carefully evaporated to dryness. The residue was dissolved in a little water and a small quantity of 50 per cent. nitric acid added to the cold solution. The crystalline precipitate of urea nitrate which rapidly separated was collected, washed with water and alcohol to remove a small quantity of free iodine present, and further identified by means of the biuret test. The products thus isolated were ammonia, cyanogen, potassium iodide, potassium cyanate, and potassium carbonate.

It was shown above that each molecule of nitrogen iodide required 3 molecules of potassium cyanide for complete solution, thus:

 $3KCN + NH_3NI_3 + 3H_9O = 3CNI + 3KOH + 2NH_3$ 

The cyanogen iodide was partially isolated as such, but if left in solution it gradually interacted with the free potassium hydroxide. The other compounds isolated must be considered as products of this secondary decomposition. Cyanogen chloride is known to yield potassium cyanate when treated with caustic potash. Hence it is not surprising to find that cyanogen iodide behaves in a similar manner, yielding potassium cyanate and iodide. The potassium carbonate and ammonia found were evidently products of the hydrolysis of potassium cyanate.

As previously shown, the cyanogen iodide is present as an unstable, intermediate product, and is only isolated as a solid compound if the temperature is kept low and the solution sufficiently concentrated to prevent the iodide from dissolving and undergoing further decomposition.

Action of Potassium Cyanide on the Silver Compound.-The foregoing experiments show that the solubility of the silver compound in potassium cyanide is more likely to be due to the formation of cyanogen iodide than to any soluble potassium derivative of nitrogen iodide. Tn order to elucidate this point, a freshly prepared and carefully washed sample of the silver derivative was suspended in a little water and treated with four molecular proportions of potassium cyanide at  $0^{\circ}$ . A thick precipitate resulted, which, after filtration, proved to be very sparingly soluble in ether. The soluble portion consisted of cyanogen iodide (m. p. 146°) and the insoluble portion of silver iodide mixed with a small quantity of the cyanide. The aqueous solution yielded, on evaporation, the same compounds as those obtained when nitrogen iodide itself is treated with potassium cyanide, together with a small quantity of silver iodide which separated from solution during evaporation. The reaction is thus to be represented as follows :

 $NI_{a}NH_{2}Ag + 4KCN + 4H_{2}O = 3CNI + AgCN + 4KOH + 2NH_{a}$ 

As already indicated the production of potassium carbonate was evidently due to secondary reactions.

When the ice-cold solution of the silver derivative in potassium cyanide is allowed to attain the ordinary temperature, cyanogen is evolved, and the precipitate consists only of silver iodide. A second portion of the silver compound was therefore treated with a large excess of potassium cyanide. This increased the formation of cyanogen iodide considerably, upwards of 30 per cent. of the iodine being recovered as such. On acidifying the potassium cyanide solution, after extraction, 61.5 per cent. of the total iodine was recovered as silver iodide. It appears therefore that cyanogen iodide is not stable in presence of silver cyanide unless potassium cyanide is present in sufficient excess to prevent the precipitation of silver iodide.

It still remained, however, to explain the regeneration of the silver compound on the addition of ammoniacal silver nitrate. In order to elucidate this point, the action of cyanogen on ammonia and ammoniacal silver solutions was studied.

Experiment shows that cyanogen iodide does not precipitate nitrogen iodide from ammonia in the absence of silver. If, however, an ammoniacal solution of silver oxide, nitrate, or cyanide is added to cyanogen iodide, the silver compound is immediately precipitated.

Thus 22.8 c. c. of a 5 per cent. solution of silver nitrate were treated with 30 c.c. of 10 per cent. ammonia, cooled to  $0^{\circ}$ , and treated with 50 c.c. of a 2 per cent. solution of cyanogen iodide to which 2 c.c. of 30 per cent. ammonia had been previously added. The washed precipitate gave the following analytical results:

	Ag.	I.	N.
Weight in grams	 0.2105	0.7437	0.0549
Atomic proportions	 1.00	3.00	2.09

The mechanism of the regeneration of the silver compound is thus explained. Evidently cyanogen iodide reacts with ammonia, forming traces of nitrogen iodide, but the concentration does not reach the point at which the compound is precipitated. On the addition of silver solution, the more sparingly soluble silver compound at once separates out, and thus, by removing the nitrogen iodide from the sphere of action, admits of its further formation.

In conclusion, I wish to express my thanks to Mr. Smart for his assistance and to the Explosives Committee for permission to publish these results.

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