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# V.—Observations upon the Deportment of Diplatosamine with Cyanogen.

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The peculiar deportment exhibited by aniline, toluidine, and several other volatile organic bases, when exposed to the action of cyanogen, rendered it desirable to investigate the behaviour of some of the fixed bases in the same direction. At the request of Dr. Hofmann, and with his supervision, I have undertaken some experiments on this subject, the results of which I beg to communicate to the Chemical Society.

The substance on which I have worked is the remarkable alkaloid discovered by Reiset, obtained by the action of ammonia upon the green salt of Magnus, long known under the name of Reiset's first platinum-base, for which, more recently, the shorter name of diplatosamine has been proposed.

On passing a stream of cyanogen through a moderately concentrated solution of diplatosamine, free from carbonic acid, the gas is slowly absorbed, and after some time a yellowish-white crystalline substance is deposited, which continues to form until the solution changes colour from the partial decomposition of the cyanogen, at which point it is desirable to suspend the operation.

This substance is soluble to a slight extent in cold, but much more readily in boiling water, from which it may be recrystallised without It then appears as a mass of minute colourless crystals, difficulty. which under the microscope exhibit the form of hexagonal plates, and frequently arrange themselves in regular stellar groups. It is, however, difficult to obtain them without a yellow tinge, from traces of decomposed cyanogen, which obstinately adhere even after three crys-When heated in the air, the substance spontaneously tallisations. takes fire, and smoulders like tinder, leaving as sole residue a light It freely evolves ammonia when heated in a sponge of platinum. dry test-tube; but the presence of cyanogen could not be detected by the usual test of potassa, proto-sesquioxide of iron and hydrochloric acid.

On analysis this substance gave the following numbers :

I. 0.3465 grm. of substance, dried at 100°, left on ignition

	0.2410	,,	" platinum.
II.	0.4002	,,	" substance gave
	0.2780	,,	,, platinum.
III.	0.4588	,,	,, substance, when burnt with soda-lime, yielded
	1.4700	,,	,, ammonio-chloride of platinum, equivalent to
	0.0922	,,	"nitrogen.
IV.	0.3957	,,	" substance yielded
	1.2775	,,	,, ammonio-chloride of platinum, equal to
	0.0801	,,	" nitrogen.

These numbers correspond to the following percentages:

			Ι.	· 11.	111.	IV.
Platinum			69.55	69.41		
Nitrogen	•	•			20.09	20.24

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and also to the formula

Pt NH<sub>3</sub> Cy,

as is exhibited in the annexed table :

							$\mathbf{T}\mathbf{h}$	eory.	Experimental mean.
1	equiv.	of	Platinum				98.68	69.64	69.48
2	,,	,,	Nitrogen		•		28.00	19.78	20.16
3	,,	,,	Hydrogen		•		3.00	2.12	
2	"	,,	Carbon	•	•	•	12.00	8.46	
						•	141.68	100.00	

These analyses show that the action of cyanogen upon diplatosamine, far from being analogous to that on aniline, toluidine, &c., (which, as is well known, combine directly with the gas,) gives rise to the same compound which Reiset obtained by saturating the base with hydrocyanic acid, and which he considered as the cyanide of his second series, viz., as the hydrocyanate of platosamine, or as the cyanide of platosammonium.

 $\frac{H_2}{Pt} \Big\} N$  . HCy, or  $\frac{H_3}{Pt} \Big\} N$  . Cy.

I have carefully compared the substance prepared by the action of cyanogen, with that obtained by Reiset's method, and find them identical in all respects.

It may be mentioned here, that a very convenient method of obtaining the compound in considerable quantity, consists in adding cyanide of potassium to the chloride of diplatosammonium (the direct product of the action of an excess of ammonia upon protochloride of platinum). By this process the tedious operation of isolating the base is avoided; the precipitate requires only two or three crystallisations to remove the soluble chloride of potassium.

The formation of the cyanide by the action of cyanogen upon a solution of diplatosamine is readily intelligible.

The mother-liquor of the crystals was found to contain a considerable quantity of carbonate of ammonia, and, moreover, the carbonate of diplatosamine. This compound was identified by conversion into the sulphate and analysis of the latter.

It is evident that the first action consists in a decomposition of water, the elements of which unite with cyanogen, producing hydrocyanic and cyanic acids; the former giving rise to the crystalline cyanide, ammonia, and water,

 $PtH_6 N_2 O . HO + HCy = PtH_3 N . Cy + NH_3 + 2 HO;$ 

the latter inducing the transient formation of cyanate of diplatosamine, which, by assimilation of the elements of water, is immediately converted into the carbonate of this alkaloid and carbonate of ammonia.

## $Pt H_6 N_2 O, Cy O + 4 HO = Pt H_6 N_2 O, CO_2 + NH_4 O CO_2$ .

As the general deportment of the salt, Pt H<sub>3</sub> N Cy, seemed to be somewhat anomalous, and in many respects different from that of an ordinary evanide (the usual tests failing altogether to indicate the presence of cyanogen), I have studied the behaviour of this compound with various reagents, in order if possible to obtain new data by which to elucidate its constitution. The cyanide in question is soluble in potassa without decomposition. It imitates in this respect the deportment of cyanide of silver. It is also soluble without change in hydrochloric acid, although the crystals deposited from the solution assume a somewhat different shape and a yellow colour.\* It may be recrystallised without decomposition also from dilute sulphuric acid. Concentrated sulphuric and nitric acids, however, decompose it : but the products of these reactions have not been farther examined.

The action of nitrate of silver upon the cyanide is very remarkable, and appears to throw much light upon the true nature of this substance.

When nitrate of silver is added to an aqueous solution of the cyanogen-compound, a copious, white, and curdy precipitate immediately falls, in outward appearance resembling cyanide of silver, and, like the latter salt, soluble in ammonia. On evaporating the solution, filtered off from the precipitate at a gentle heat, a crop of beautiful crystals made their appearance, which lost their transparency on carrying the evaporation to dryness. On raising the temperature beyond this point, they suddenly took fire, and left a residue of pure platinum. In the conception of the substance being cyanide of platosammonium,

\* The substances crystallised from potassa (I.) and from hydrochloric acid (II.) were identified by analysis.

I.	0.4065	grm.	of	substance	gave
	0.2830	**	"	platinum.	
II.	0.4685	,,	"	substance	gave
	0.3250	"	,,	platinum.	

The experimental and theoretical percentages are-

		Theory.	Exper	Mean of experiments.	
			/	·	-
Platinum		69·64	69.61	69.37	69.49

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I was inclined to consider these needles as the nitrate of platosamine, when the reactions would have been represented by the equation,

$$Pt H_3 N \cdot Cy + Ag NO_6 = Pt H_3 N \cdot NO_6 + Ag Cy.$$

In order to verify this equation, the needles were subjected to analysis, when the following results were obtained :

I.	0.5030	grm.	of	this salt gave	
	0.2525	,,	,,	platinum.	
II.	0.3930	,,	,,	from another	preparation
	0.1960	,,	,,	platinum.	

These numbers, far from agreeing with the formula of the nitrate of platosamine, exhibit on the contrary a close accordance with the theoretical values required by the composition of the nitrate of Reiset's first compound, as may be seen by the following comparison:

	The	Experiment.			
	·	<i>۸</i>	<u>_</u>		
	$Pt H_3 N, NO_6$	$Pt H_6 N_2 NO_6$	г.	п.	
Platinum	. 5 <sup>*</sup> 5.53	50·68	50.19	49.87	

As the determination of nitrogen in the nitrate presented some difficulties, to vary the analysis and furnish a means of corroboration, a solution of the cyanide was precipitated with sulphate of silver, the filtrate evaporated, and the platinum determined in the sulphate thus obtained—

> 0.4080 grm. of substance gave 0.2215 ,, ,, platinum.

This result perfectly corroborates the inference drawn from the former analysis, namely, that the action of nitrate of silver upon the cyanide under examination gives rise to the formation of a salt, not of platosamine, but of diplatosamine (Reiset's first base). For the sake of comparison I subjoin the theoretical percentage of the salt :

			Theory.	Experiment.
Platinum .			54.61	54.22

The unexpected results obtained in the examination of the soluble compound produced by the action of the silver-salt upon the cyanide, compelled me more carefully to investigate the white precipitate, which hitherto I had regarded as cyanide of silver. I found at once that this precipitate is by no means cyanide of silver, but that it contains platinum as one of its constituents.

The quantitative analysis of this white compound presented, how-

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ever, some difficulty, from the extreme tenacity with which the cyanogen holds the combined metals. No constant results could be obtained by fusing with carbonate of soda and potassa, ignition with soda lime, or the combined action of nitric acid and chlorate of potassa. The analysis, however, succeeded without difficulty, when the salt under examination was dissolved in strong ammonia, and immediately precipitated with sulphide of ammonium, when pure sulphide of silver is thrown down, the whole of the platinum remaining in solution. This solution, when evaporated, yielded at first beautiful iridescent crystals, which subsequently left pure metallic platinum on ignition.

In this manner the following results were obtained :

0.6019 g	rm. of	substance gave
0.2884	,, ,,	sulphide of silver, equal to
0.2511	,, <b>,</b> ,	metallic silver, and
0.2302	,, ,,	platinum.
0.4555*	,, ,,	substance gave
0.1745	,, ,,	platinum.
	0.6019 g 0.2884 0.2511 0.2305 0.4555* 0.1745	0.6019 grm. of 0.2884 ,, ,, 0.2511 ,, ,, 0.2305 ,, ,, 0.4555* ,, ,, 0.1745 ,, ,,

These numbers correspond to the following percentages :

		Ι.	11.
Platinum		38·29	38·30
Silver .		4 <b>1·7</b> 1	

and prove that the white precipitate is nothing but platino-cyanide of silver,

as is exhibited in the following comparison of the experimental results with the values required by theory.

									The	ory.	Mean of	experiments.
21	equiv. "	of ,,	Cyanoge Platinun	en n	•	•		•	52·00 98·68	20·1 38·1	5 0	38.29
1	" "	,, ,,	Platino- silver	су	7an:	· ide	of	· }	258·68	41·7 100·0	6 - 0	41.71

This conclusion was fully borne out by the deportment of the silversalt with reagents, when compared with that of the platino-cyanide, obtained by the usual method.

Detailing the analysis of this substance, I have mentioned that on treating the ammoniacal solution of the cyanide with hydrosulphuric

\* The silver was lost.

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acid, iridescent needles are obtained. These needles are the corresponding platino-cyanide of ammonium. A similar result was found when the silver-salt was treated with potassa, with which on ebullition it gave a heavy black precipitate containing all the silver, and a colourless solution which yielded long needles of a purple hue by These crystals change to a reflected, and yellow by transmitted light. deep yellow when heated, and then fuse to a mass of carbon and The aqueous solution of this compound gives first a bright platinum. orange precipitate with the nitrate of the suboxide of mercury, which speedily changes to a cobalt-blue on increasing the quantity of the It need scarcely be mentioned that this deportment, in mercury-salt. all respects, agrees with that of the platino-cyanide of potassium described by Gmelin, which moreover was satisfactorily proved by direct comparison of the two salts.

The formation of platino-cyanide of silver from the cyanide which forms the subject of the present communication, fully explains the simultaneous production of a salt of Reiset's first base. The reaction is expressed by the following equation:

# 2 Pt H<sub>3</sub> N. Cy + Ag NO<sub>6</sub> = Pt H<sub>6</sub> N<sub>2</sub>. NO<sub>6</sub> + Ag. PtCy<sub>2</sub>.

To obtain a quantitative control of the correctness of this equation, a weighed portion of the cyanide was decomposed by nitrate of silver. The precipitated salt was carefully dried upon a weighed filter, and the quantity obtained compared with the amount required by theory.

I.	0.2398	grm.	of	salt produced
	0.2175	,,	"	platino-cyanide of silver.
II.	0.5935	,,	,,	another specimen gave
	0.5425	"	,,	platino-cyanide of silver.

The quantity required by theory, and obtained by experiment, reduced to 100 parts, is as follows :

Theory.	Exper	iment.	
	Ι.	11.	
91.29	90.70	<b>91·40</b>	

The facts observed in the study of the crystalline compound which is formed by the action of hydrocyanic acid, or cyanogen, upon the oxide of diplatosammonium, suggests a mode of viewing the constitution of this substance which is different from that hitherto adopted.

If, with M. Reiset, we consider this compound as the cyanide of platosammonium, we are forced to admit that this substance owes its origin to a very singular play of affinity, inasmuch as the influence of

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hydrocyanic acid on the oxide of diplatosammonium gives rise to the cyanide of platosammonium, whilst on the other hand a metallic solution reconverts this compound into a salt of the original base.

It appeared much simpler to regard the compound in question as a salt of the base from which it is derived, viz., as a platino-cyanide of diplatosammonium, which is isomeric with the cyanide of platosammonium.

2 Pt 
$$H_3$$
 N . Cy = Pt  $H_6$  N<sub>2</sub> . Pt Cy<sub>2</sub>.

This formula explains equally well the formation of the substance by the action of hydrocyanic acid upon the oxide of diplatosammonium:

## $2Pt H_6 N_2 O + 4 H Cy = Pt H_6 N_2 \cdot Pt Cy_2 + 2 N H_4 Cy + 2 HO$ ,

but the interpretation of its behaviour with silver-salts becomes infinitely simpler, as the whole change is reduced to a case of ordinary double decomposition.

Pt $H_6 N_2$ . Pt $Cy_2 +$	Ag $NO_6 =$	Pt H <sub>6</sub> N <sub>2</sub> . NO <sub>6</sub> -	+ Ag Pt $Cy_2$ .
Platino-cyanide of diplatosammonium	Nitrate of silver.	Nitrate of diplatosammonium.	Platino-cyanide of silver.

To test the accuracy of this view experimentally, I prepared a quantity of hydroplatino-cyanic acid, by treating the mercury-salt with hydrosulphuric acid. On saturating this acid with the oxide of diplatosammonium, I obtained at once a colourless crystalline substance, which could not be distinguished from the cyanide previously described, either by appearance or behaviour with reagents.

The same salt may be more conveniently procured, by adding platino-cyanide of potassium to the chloride of diplatosammonium.

On recrystallising and drying at 100°,

0.2084 grm. of substance gave on ignition 0.1446 ,, ,, platinum,

in accordance with the formula

the calculated and experimental numbers in 100 parts being,

			Theory.	Experiment.
Platinum	•		69.64	<b>69·34</b>

On reference to Reiset's excellent paper upon the platino-bases, it does not appear that he attempted the construction of the cyanide of platosammonium, by directly operating upon a salt of the correspond-

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ing base, considering, doubtless, that the substance would prove itself identical with that previously described by him.

As a last step, it appeared desirable to try the preparation of the true cyanide of platosammonium, as it was not improbable that a compound might be thus obtained, similar in composition, but differing in its molecular arrangement, and consequently presenting some possible discrepancies in its chemical and physical properties.

Accordingly, I digested a few grammes of the chloride of platosammonium with an excess of cyanide of silver; the decanted liquid was found to yield, on concentration, fine and regular needles of a paleyellow colour. These crystals proved to be much more soluble in water and ammonia, than the platino-cyanide of diplatosammonium, from which they also materially differed in their deportment with reagents.

0.4695 grm. of substance gave 0.3256 ,, ,, platinum,

which agrees with the formula

Pt H<sub>3</sub>N, Cy,

the numerical percentages being

		Theory.	Experiment
Platinum	•	69.64	69.35

Hence, it is evident that there are two substances of the same composition, the one, by the mode of formation and behaviour with reagents, proved to be a salt of a platinum-base with a platinum-acid, (platino-cyanide of diplatosammonium), the other, as far as we can judge from the method of preparation, the true cyanide of platosammonium.

The latter substance appears to call for closer attention than I have been able to bestow upon it; but I hope at a future time to have the honour of laying the results of an extended examination before the Chemical Society.