XV. *Contributions to the Chemical History of Palladium and Platinum.*
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NOTWITHSTANDING the attention which has been paid to the properties of the noble metals by the chemists who have made their compounds an object of study, their history is yet very far from the state of completeness, to which so many departments of inorganic chemistry have recently been brought. The researches hitherto made have had for their objects generally, either the more direct or certain extraction of the metal from the state of combination in which it naturally exists, or the examination of some few compounds, which were remarkable for their beauty or facility of production, or important from their applications. But the general history of these metals has as yet been but imperfectly studied, as may be seen by reference to the meagre account of their salts and other compounds, which even the most extended systematic works present. It is my object in this and in some subsequent papers, to examine specially into the composition and properties of the compounds of palladium, platinum, and gold, and to endeavour to ascertain how far they agree, and in what they differ, as to the laws of combination to which these compounds are subjected. As this paper may be considered but as the commencement of this work, the general bearings of which may change according to the progress of our knowledge, I shall not attempt to give to it any systematic form, or to arrange the bodies to be described in any order or classification, except that all the compounds of the same metal will in each memoir be described together.

It is my duty, at this moment, to express my sincere gratitude and thanks to the Council of the Royal Society, which most kindly placed in my hands, for the purposes of these investigations, a portion of the palladium that had been bequeathed to the Society by its illustrious discoverer, to be used in the advancement of science. Should the results I have obtained, in endeavouring to extend and render more accurate our knowledge of the compounds of that remarkable metal, appear such as to justify that appropriation, for which when made I feel I had little claim, I shall be fully rewarded for the time and labour they have required, and use my best efforts to extend them by subsequent researches.

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Section I.—Palladium Compounds.

Oxides of Palladium.

It has been long established that palladium combines with oxygen, at least in two proportions, forming the *protoxide*, which is the basis of its ordinary salts, and the *deutoxide*, which appears to be analogous to the deutoxide of platinum, and to react in many cases as an acid. To this last body I have not hitherto directed much attention, but some properties of the protoxide which I have noticed appear not unworthy of being described.

The protoxide of palladium is best prepared by the decomposition of the protochloride, by means of a solution of carbonate of soda in excess. The precipitate which first forms is light-coloured, but it soon becomes darker, carbonic acid gas is disengaged, and finally an ochrey brown powder falls, which, by drying, becomes dark brown. The precipitation is in this case by no means perfect, the liquor is coloured yellow by traces of the metal dissolved, and the precipitate retains with obstinacy traces of the alkali, from which, however, it may be freed by washing.

When this substance is heated, it first evolves water and then oxygen, leaving a black powder, to the nature of which I shall recur. By a very high temperature (full white heat) it is totally reduced to the metallic state.

The analyses of this hydrated oxide when first performed led to very irreconcileable results, owing to two circumstances,—1st, that the oxide of palladium is by no means so easily reduced to the metallic state by the mere agency of heat as has been supposed; and 2nd, that although the precipitation of the hydrated oxide is accompanied with the disengagement of much carbonic acid, yet the precipitate always contains some traces of that acid; it effervesces very distinctly when dissolved in dilute muriatic acid, and is in fact a highly basic carbonate of palladium, rather than a true hydrated protoxide. The following details of the experiments made as to its composition, will place these circumstances in evidence.

A. 53·524 grains of a specimen which had been carefully washed until the liquors ceased to react alkaline, were gently heated over the flame of a spirit-lamp, until no more traces of water were evolved. The residue, a jet black powder, of anhydrous oxide, weighed 45·224 grains, or 84·49 per cent., having lost 15·51, apparently only water.

B. 41·102 grains of another portion, similarly treated, gave a dry residue of 34·512 grains, or 83·96 per cent. This was then heated to full redness, and when cold weighed 31·779 grains, or 77·32 per cent.

C. 72·481 grains of a specimen prepared at another time gave, when dried until the last traces of water had been driven off, a black powder weighing 61·241 grains, or 84·49 per cent., and at exposure to a red heat was reduced to 56·131 grains, or 77·45 per cent.

D. 56·578 grains of a different specimen gave when dried 48·306 grains, or 85·38

per cent., having lost 14·62 of water. By a red heat it gave off oxygen, and was reduced to 44·846 grains, or 79·43 per cent.

These results placed together for comparison give,—

	A.	B.	C.	D.
Expelled by a moderate heat . .	15·51	16·04	15·51	14·62
Expelled by a red heat	} 84·49	6·64	7·04	5·95
Residual black powder		77·32	77·45	79·43

The material (6 to 7 per cent.) expelled by a red heat is oxygen gas, but I found, by trials conducted after the above results were obtained, that neither is all the material expelled by a moderate heat merely water, nor is the residual black powder metallic palladium.

E. To determine the nature of the black powder which remains after the moderate ignition of the oxide, 51·346 grains of it were introduced into a tube of Bohemian glass, and heated in a current of dry hydrogen gas ; it became of itself brightly red-hot, water was abundantly, almost explosively formed, and the powder assumed at once a gray metallic aspect. It then weighed 47·165 grains, or 91·85 per cent.

F. To control this result another portion of the black powder, obtained from a different portion of oxide, was heated in the same way in hydrogen gas. From 46·300 grains there remained 42·952 grains of metal, or 92·72 per cent.

The quantity of oxygen thus shown to be combined with the metal in this black powder is almost exactly half that which the protoxide should contain. It must therefore be considered as *suboxide of palladium*, at least provided it be not a mixture of metal and protoxide, which shall be discussed further on. I shall here only compare the experimental results with those given by the formula $Pd_2 Cl$ for its composition.

	Theory.		Experiment.	
$Pd_2 =$	106·6	93·02	91·85	92·72
$O =$	8·0	6·98	8·15	7·28
	114·6	100·00	100·00	100·00

The mean quantity of black suboxide obtained by the moderate ignition of the hydrated oxide as already found, is 78·07, and this is shown by the latter experiments to contain 72·60 of metal ; excluding therefore for the moment, the question whether anything but water is first driven off, we find that the oxide of palladium may be obtained anhydrous, that by gentle ignition it abandons one-half of its oxygen and leaves a black powder, *suboxide*, which may be totally reduced to the metallic state by violent ignition or by hydrogen gas, at incipient redness.

The mean quantity of suboxide furnished from 100 of dry protoxide, in the above described three analyses, may be thus compared with theory :—

	Theory.		Experiment.—Mean of B, C, D.	
$Pd_2 O =$	114·6	93·47	78·07	92·27
$O =$	8·0	6·53	6·54	7·73
	122·6	100·00	84·61	100·00

The analysis D alone gives a result much more closely approximating to theory: by it there is

$$Pd_2 O \quad 79\cdot43, \text{ or } 93\cdot03$$
$$O \quad 5\cdot95, \text{ or } 6\cdot97$$
$$\overline{85\cdot38} \quad \overline{100\cdot00}$$

As there were many circumstances which led me to consider it unlikely that the 15·42, the mean quantity of material expelled from the hydrated oxide by a moderate heat, could be entirely water, I determined the real quantity of water present in the following manner. The substance was placed in a tube of Bohemian glass, which at one end was put in connection with an apparatus evolving dry hydrogen gas, and at the other extremity was adapted to a tube containing recently fused chloride of calcium. When the apparatus had been completely filled with hydrogen, the tube containing the oxide of palladium was heated by means of charcoal. Water was evolved and the metal reduced. The current of gas was continued until all water had been carried into the chloride of calcium tube, and the weights were then determined. It was found that from 45·687 grains of the hydrated oxide, there were obtained 33·532 grains of metal, and 11·298 grains of water, giving 73·95 for the former, and 24·74 for the latter per cent., but of this 24·74, there were formed 12·49 by means of 11·10 of oxygen which had been combined with the metal, and the water of hydration amounted therefore to but 12·25 per cent.

The difference between the total volatile matter and the water (3·17 per cent.), may be certainly considered as carbonic acid, from the circumstances under which the substance is prepared, and from the fact that it in all cases effervesces slightly when dissolved in muriatic acid.

We may sum up, therefore, the composition of this true basic carbonate of palladium as follows :—

	Last Experiment.	Mean of A, B, C, D.
Palladium . .	73·95	72·60
Oxygen . . .	10·63	11·98
Water	12·25 ⎫	15·42
Carbonic acid .	3·17 ⎭	
	$\overline{100\cdot00}$	$\overline{100\cdot00}$

The formula deducible from these results is $10\,.\,Pd\,O + C\,O_2 + 10\,.\,H\,O$, which gives the following numerical result :—

Ten atoms of palladium	533·0	73·52
Ten atoms of oxygen	80·0	11·04
Ten atoms of water	90·0	12·41
One atom of carbonic acid . . .	22·0	3·03
	$\overline{725\cdot0}$	$\overline{100\cdot00}$

It is not impossible but this body may be in reality a mixture of a less basic carbonate, with the true hydrated oxide, but I consider that the remarkable constancy of composition, indicated by so many specimens, prepared at different times, giving results so closely coinciding, argues very strongly in favour of its definite nature. It occurred to me also that the content in carbonic acid might arise from the presence of carbonate of soda, but I satisfied myself that although it is very difficult to obtain specimens which do not after ignition yield traces of alkali, yet it is never present in such quantity as could give the above results, when the freshly precipitated substance has been properly washed.

The properties of the suboxide of palladium, now first definitely found, are not very distinct. The existence of this suboxide had been long suspected, especially from the fact, that by heating to dull redness in contact with air, metallic palladium becomes coloured blue or green on the surface, which colours are removed by violent ignition. BERZELIUS found, however, that this colouring was not attended with any increase of weight, which arises, however, from the minute quantity of oxide formed, the colours being those of thin plates; but there can be now no doubt but that formation of suboxide does so occur. That the black powder which is left by the dull ignition of the basic carbonate is really a definite compound, is strongly supported by the fact of the accuracy with which the decomposition stops at its formation, and by the analogy of the subchloride, to be hereafter described, it gains additional force. Yet I have not been able to combine in any way this suboxide with acids. By contact with them, it gives an ordinary salt of the protoxide and metal. It is possible, however, that in future trials I may be more successful.

It is known that by the addition of a caustic fixed alkali to a salt of palladium a precipitate is obtained, which redissolves in a great excess of the alkali. The precipitate is in this case a basic salt, not the hydrated oxide, and always contains traces of the alkali, from which it is with difficulty freed by washing. The soluble alkaline compound cannot be obtained in a definite form by any process that I have as yet tried. By evaporation to dryness, the oxide separates anhydrous, and retaining a small quantity of alkali.

When the basic carbonate of palladium (hydrated oxide) is diffused through water of ammonia, it partially dissolves, giving a brown powder and a yellow-coloured liquor, which when evaporated dries down to a bright yellow deliquescent mass. When heated, this decomposes with slight deflagration and copious disengagement of gas, leaving metallic palladium. The brown powder also contains ammonia, and when heated gives it off with water, and the metal is reduced. I can, however, at present only indicate the existence of these two bodies, as the analytical results which I have obtained respecting them are too discordant to admit of my assigning any definite formulæ for their constitution. The soluble compound I conceive to arise from the ammonia acting on the carbonate, as it does on any other palladium salt, and the insoluble to be the product of the ammonia on the oxide which is present in excess. I reserve these bodies, therefore, as objects of future study.

Chlorides of Palladium.

The properties of the ordinary protochloride of palladium have been for the most part so fully described by those chemists that have previously occupied themselves with the study of this metal, that I shall notice it but briefly. From a strong solution, it crystallizes in prismatic needles which are very deliquescent. These crystals were found to contain two atoms of water of crystallization, which they lose by a gentle heat.

The action of a high temperature on protochloride of palladium developes some facts of considerable interest. It is not so reduced to the metallic state unless by very violent ignition, but just at a red heat it melts and begins to evolve chlorine, which continues until it has parted with one-half of that which it contains. The liquefied mass which remains is a true subchloride, which is not further acted upon, unless the heat be very much increased.

The following numerical results will render this decomposition evident:—

A. 29·881 grains of the crystallized protochloride being carefully dried as long as they gave off any traces of watery vapour were found to have lost 5·247 grains, or 17·56 per cent.

The dried mass was heated until it had completely fused. It was then dull red. In this state it was found to weigh 22·055 grains, having given off 2·577 grains of chlorine, or 8·63 per cent.

This was next kept melted at a bright red heat until it appeared to cease giving off any gas. It then weighed 19·632 grains, having lost in addition 2·423 grains, or 8·11 per cent. of chlorine.

This residue was now fully ignited with some carbonate of ammonia, until the metallic palladium remaining appeared to be quite pure; this then weighed 14·554 grains, or 48·71 per cent., the quantity of chlorine abandoned in this final stage having been 5·078 grains, or 16·99 per cent.

The quantity of palladium and the total quantity of chlorine and water, show that the salt in its crystalline condition has the formula $Pd\,Cl + 2\,H\,O$, by which we have

	Theory.		Experiment.
Palladium . .	53·3	49·95	48·71
Chlorine . .	35·4	33·18	33·73
Water . . .	18·0	16·87	17·56
	106·7	100·00	100·00

The relation between the proportions of chlorine which were evolved at the different periods, were as 8·11, 8·63, and 16·99. I do not attach much importance to the two first being so nearly equal, but to the fact that the quantity which was not expelled by the heat was sensibly equal to half the total quantity in the salt.

B. 58·919 grains of dried protochloride were heated in a porcelain crucible to full redness, until it fused without any disengagement of gas. The residual subchloride weighed 47·782 grains, or 81·13 per cent.

C. 138·397 grains were fused in a porcelain crucible and kept at a full red heat until all effervescence from loss of chlorine ceased. When cold it weighed 110·185 grains, equivalent to 80·41 per cent.

These results fully prove that the loss of chlorine which the protochloride undergoes when kept for some time fused at a full red heat, is perfectly definite; and also that the loss represents one-half of the chlorine which the salt contains. Thus,

$$\text{by theory } Pd_2 = 106\cdot6 \text{ produce } Pd_2 = 106\cdot6$$
$$Cl_2 = 70\cdot8 \text{ produce } Cl = 35\cdot4$$
$$\overline{177\cdot4} \qquad \overline{142\cdot0}$$

or 80·05 per cent. The substance formed is a true subchloride analogous to calomel, or to subchloride of copper, and its formula is $Pd_2\,Cl$.

The fused mass obtained by the methods now described, is of a deep red brown colour, and highly crystalline in structure. Its powder is light red. It deliquesces rapidly, and becomes dark-coloured from the separation of metallic palladium and the formation of protochloride. This change is effected almost instantly by contact with water, or solutions of sal-ammoniac, or iodide of potassium, also by water of ammonia. It is, however, not all decomposed; the quantity of metallic palladium which separates, I have found to be but from one-fifth to one-sixth of that which the subchloride contained. The liquor formed contains, therefore, both the subchloride and the protochloride dissolved together. The action of reagents on this liquor, however, does not differ materially from that produced with solutions of the protochloride. The liquor is much darker coloured than a solution of protochloride of the same strength should be, and is rendered turbid by dilution with more water. The first action of ammonia appears to be, the formation of a white compound, which is however almost instantly broken up into the pinkish ammonia-protochloride, and metallic palladium.

In the double salts formed by the protochloride of palladium with the chlorides of the alkaline metals, I have found the similarity of constitution so usual between the compounds of ammonium and potassium to be violated. The double chloride of palladium and potassium has been fully shown by BERZELIUS to have the formula $Pd \cdot Cl + K \cdot Cl$, and not to contain any water of crystallization; but the double chloride of palladium and ammonium retains an atom of water when crystallized. I examined a quantity of this salt which had formed long rectangular prisms of an olive colour with a rich bronze lustre. They were quite free from any foreign impurities. When heated, they yielded water, muriatic acid, sal-ammoniac, and left metallic palladium.

By a very cautious application of heat the water may be completely expelled. From many experiments its quantity was found to be from 5·52 to 5·95 per cent.,

and the residual palladium was ascertained to be from 35·56 to 35·27 in 100 of the crystals. These numbers indicate the formula $Pd\,Cl + N\,H_4.Cl + H\,O$, which gives

$$
\begin{aligned}
Pd &= 53\cdot3 & 35\cdot28 \\
Cl_2 &= 70\cdot8 & 46\cdot86 \\
N\,H_4 &= 18\cdot0 & 11\cdot91 \\
&= 9\cdot0 & 5\cdot95 \\
\hline
& 151\cdot1 & 100\cdot00
\end{aligned}
$$

If the salt were anhydrous it should yield 37·51 per cent. of metal.

It is only in consequence of its differing from the potassium salt that I deem this body worthy of notice here.

Of the Oxychloride of Palladium.

When a solution of chloride of palladium is partially precipitated by means of a solution of potash or of soda, care being taken that the metallic chloride shall still be present in considerable excess, a dark brown powder is obtained, which is a definite oxychloride of palladium.

When dried in a stove at a temperature of 150°, its properties are as follows:—if it be heated, it gives off water, and at a full red heat chlorine and oxygen, leaving behind a mixture of subchloride, suboxide, and metal. It dissolves in dilute acids, giving a mixture of protochloride and an ordinary palladium salt of the acid used.

Its analysis was conducted as follows :—

A. 40·639 grains fused with carbonate of soda and the saline mass dissolved in water left 28·508 grains of palladium, purely metallic, being equal to 69·80 per cent.

The solution acidulated by nitric acid and precipitated by nitrate of silver, gave 18·103 grains of chloride of silver, or 44·55 per cent., containing 10·99 of chlorine.

B. 67·543 grains of another specimen were heated over a spirit-lamp as long as any watery vapour came off, but not so high as to expel any traces of chlorine or oxygen. The dry mass which remained weighed 59·977 grains, being 88·62 per cent. The loss of water had thus been 11·38 per cent.

This dry residue was then vividly ignited and a lump of carbonate of ammonia introduced to favour the separation of the chlorine. The metallic palladium which remained weighed 47·442 grains, or 70·25 per cent.

These results lead to the formula $Pd\,Cl + 3\,Pd\,O + 4\,H\,O$, which gives,—

	Theory.		Experiment A.	Experiment B.
$4\,Pd = 213\cdot2$	69·10		69·80	70·25
$3\,O = 24\cdot0$	7·77			
$Cl = 35\cdot4$	11·47		10·99	
$4\,H\,O = 36\cdot0$	11·66			11·38
308·6	100·00			

It is therefore quite analogous to the ordinary oxychloride of copper.

Of the Ammonia-chlorides of Palladium.

It is well known that on adding water of ammonia to a solution of chloride of palladium, a pink-coloured precipitate is produced, which by boiling dissolves, giving a brownish yellow liquor, from which on cooling a crystalline yellow substance separates. These two bodies have the same per cent. composition, expressed by the formula Pd Cl + N H_3. Of this I need not detail any evidence, as it has been fully established by the labours of BERZELIUS, and quite recently by the experiments of FEHLING.

By means of an excess of ammonia, the pink red precipitate which first forms may be totally redissolved, giving a colourless solution, from which by evaporation, a salt is deposited on cooling, in colourless rectangular prisms. The existence of this salt has been long known, and as its analysis has been recently published by FEHLING, I need not detail any of my own experimental results, which fully coincide with his. The formula of this body is Pd Cl + 2 N H_3 + H O, or rationally, according to the principles I have elsewhere laid down for the copper salts, N H_4 . Cl + Pd O . N H_3. When gently heated it evolves water and ammonia, and leaves the yellow substance Pd Cl + N H_3. The same decomposition may be effected by evaporating its solution to dryness, in which case the yellow salt generally crystallizes in cubes. Were it not hazardous to draw any inference with regard to the isomorphism of bodies belonging to the regular system, I should notice this fact as illustrative of the equivalency of Pd Cl . N H_3 with K. By a very cautious application of heat to the colourless crystallized salt, some water may be expelled before the ammonia begins to come off, but I have never succeeded in rendering it quite anhydrous. It however partially assumes the formula N H_4 . Cl + Pd . N H_2, to which we shall find the ammonia-sulphate of palladium to present an equivalent.

By the action of solutions of caustic potash on solutions of these ammonia-chlorides of palladium, a variety of products are formed, according to the proportions employed and the circumstances of temperature. For the complete investigation of these bodies I have not yet accumulated materials, but the results which have been already obtained are not without interest as indicative of the analogies of palladium to other metals whose laws of combination are better known. I shall consequently describe those substances I have as yet examined, although I intend to resume and extend their investigation before long.

A. When the pink-red precipitate is boiled with a large quantity of water it dissolves, and on cooling but little of the isomeric yellow salt crystallizes out. On adding to the brownish yellow liquor so obtained a solution of caustic potash not in excess, a yellowish precipitate falls, which by boiling becomes brown red, and distinctly crystalline. If the pink red substance (Pd Cl + N H_3) be dissolved in the hot water without much boiling, there is generally no precipitate on adding the caustic potash, and the solution is merely yellow, not brownish coloured. It appears necessary that, by the boiling, partial decomposition should occur, and some ammonia be ex-

pelled to bring the liquor to the state suitable for the action of the caustic potash. This may also be effected by adding to the solution of the ammonia-chloride some solution of protochloride of palladium, so as to have in solution apparently a substance containing Pd Cl + Pd Cl . N H$_3$, which is not known in the solid form.

The yellow precipitate which first falls is the ordinary crystalline body PdCl + NH$_3$, but by boiling in the liquor from which it has separated, its nature is completely changed. The properties of the crystalline brown red substance then produced are, that it dissolves readily in muriatic acid, and gives by heat, sal-ammoniac, nitrogen and water, and leaves metallic palladium. Its composition was determined by analysis to be as follows :—

I. 14·601 grains having been ignited to perfect fusion with carbonate of soda, gave, when the saline material was dissolved in water, 8·072 grains of palladium, or 55·28 per cent.

The solution acidulated with nitric acid and precipitated by nitrate of silver, gave 14·802 grains of chloride of silver, equivalent to 101·4 per cent., containing 25·03 of chlorine.

II. 7·964 grains of substance gave, by the method pursued in similar instances, 3·3907 cubic inches of nitrogen, at standard temperature and pressure. These weigh 1·080 grains, equal to 13·64 per cent.

III. 9·231 grains of substance having been mixed with dry carbonate of soda, were introduced into a tube of Bohemian glass, and some pieces of platina foil being interposed, about four inches of the tube in front of the mixture were filled with oxide of copper. To this apparatus was adapted a tube containing recently fused chloride of calcium, and the whole being disposed and heated exactly as for an organic analysis, it yielded 3·212 grains of water, being 34·78 per cent., containing 3·85 of hydrogen.

After this operation, the tube being cut by a file, that portion of it which contained the saline mass was digested with dilute nitric acid, and the metallic palladium collected on a filter. It weighed 5·170 grains, or 56·02 per cent.

The solution treated in the usual way gave 9·337 of chloride of silver, or 101·2 per cent., containing 24·92 of chlorine.

The summary of these results is

	I.	II.	III.
Palladium	55·28		56·02
Nitrogen		13·64	
Hydrogen			3·85
Chlorine	25·03		24·92

The deficiency in the sum of the preceding results being counted as oxygen, these numbers lead to the formula Pd$_3$ Cl$_2$ O N$_3$ H$_9$, which gives

3 . Pd =	159·9	55·20
2 . Cl =	70·8	24·44
O =	8·0	2·76
9 . H =	9·0	3·10
3 . N =	42·0	14·50
	289·7	100·00

This body may be considered as a compound of ammonia-chloride with ammonia-oxide of palladium, thus 2 (Pd Cl . N H$_3$) + Pd O . N H$_3$, and its origin explained, by an atom of potash producing with three atoms of ammonia-chloride, it and chloride of potassium, for 3 (Pd Cl . N H$_3$) and K O give Pd$_3$ Cl$_2$ O N$_3$ H$_9$ and K Cl. I shall, however, return to the notice of its rational constitution when the next substance has been described.

B. When the same kind of palladium liquid from which the brown red substance last noticed is prepared, is heated with an excess of solution of caustic potash in the cold, a whitish powder falls, which on drying, even by a very gentle heat, becomes dark olive-coloured. If it be boiled its colour changes to yellow, and is then found to be identical with the yellow crystalline body (Pd Cl . N H$_3$) which makes its appearance under such various circumstances. This olive-coloured substance when heated evolves water and vapours of sal-ammoniac, leaving metallic palladium. Its analysis gave the following results :—

12·224 grains gave, by fusion with carbonate of soda and decomposition by nitrate of silver, in the usual manner, 8·242 grains of metallic palladium, equivalent to 67·43 per cent., and 5·939 grains of chloride of silver, being 48·48 per cent., containing 11·96 per cent. of chlorine.

12·113 grains, heated with oxide of copper as for an organic analysis, gave 2·423 of water, being 20·03 per cent., containing 2·22 per cent. of hydrogen.

Hence the formula expressing the composition of this body appears to be Pd$_4$ Cl N O$_6$ H$_6$, the numbers being

	Theory.		Experiment.
Pd$_4$ = 213·2	67·34		67.43
Cl = 35·4	11·18		11·96
N = 14·0	4·43 ⎫		18·39
O$_6$ = 48·0	15·16 ⎭		
H$_6$ = 6·0	1·89		2·22
	316·6	100·00	100·00

I regret very much that the quantity of this substance at my disposal did not allow me to make a distinct nitrogen determination at the time of the above analyses, and the difficulty of procuring either this or the preceding (A. red brown) body quite free from the crystalline yellow substance being very great, I have not had a subsequent opportunity. I shall however return to it, although I consider the arguments which might be brought forward in favour of the formula just now given to be very decisive for its reception: indeed no other formula that can reasonably explain the circumstances of the production of this body agrees with the numerical results of its analysis.

This empirical formula assumes more interest when rationally expressed: it becomes $Pd\,Cl + 3\,Pd\,O + N\,H_3 + 3\,H\,O$. It therefore consists of the ordinary oxychloride, with an atom of ammonia in place of one atom of its water of hydration, or it may be written $Pd\,Cl\,.\,N\,H_3 + 3\,(Pd\,O\,.\,H\,O)$, being a compound of ammonia-chloride and hydrated oxide. But it is more consonant to analogy to consider it as containing a metallic amidide, and its formula is then written $Pd\,Cl + 2\,.\,Pd\,O + Pd\,.\,N\,H_2 + 4\,H\,O$. It is thus the perfect analogue to the yellow powder produced by the action of water on the white precipitate of mercury, except that like all the copper and palladium bodies, it is hydrated, whilst the corresponding mercurial compounds are anhydrous. Such I consider to be the real constitution of this olive powder, and by our knowledge of its existence we are enabled to view the other ammonia-chlorides of palladium more intimately than previously had been possible. Thus the change of the pink ammonia-chloride to the yellow must, as I conceive, be attended with an alteration in the mode of combination of its elements. The pink body is formed only by the direct union of ammonia with chloride of palladium. It appears to be truly and simply $Pd\,Cl + N\,H_3$; but the yellow crystalline substance is produced only by processes in which the palladium has certainly passed, at least in a great degree, from union with chlorine, and has combined with oxygen or amidogene. It is hence most probable that the yellow substance cannot also be simply $Pd\,Cl + N\,H_3$. The arrangement of its elements may be expressed by the formula $H\,Cl + Pd\,.\,N\,H_2$, or else there may exist for palladium a compound analogous to the mercurial white precipitate, its formula being $Pd\,Cl + Pd\,N\,H_2$, and this combined with sal-ammoniac may form the yellow substance, precisely as the true white precipitate $(Hg\,Cl + Hg\,.\,Ad)$ by union with sal-ammoniac forms WÖHLER's white precipitate, the composition of which, as I have elsewhere shown, is expressed by the simple formula $Hg\,Cl + N\,H_3$.

C. By boiling a solution of the colourless crystalline ammonia-chloride of palladium $(Pd\,Cl + 2\,N\,H_3 + H\,O)$ with caustic potash in excess, for a long time, an olive-green powder falls, which when heated deflagrates like loose gunpowder. A quantity of it which I had prepared for analysis and incautiously heated, was thus lost, and I can therefore merely indicate the existence of this body, and defer the exact account of it to a future time.

In the memoir already often alluded to, FEHLING has noticed that, on dissolving the pink ammonia-chloride in boiling water, a small quantity of a brown powder is sometimes left undissolved, and on analysing it (determining only the content of metal and chlorine), he deduced that it had the formula $Pd_3\,Cl + 3\,N\,H_3$. He remarks, however, that the origin of a body having that formula, is under the circumstances incomprehensible; it indeed assumes the existence of a peculiar chloride of palladium for which there is no other evidence whatsoever. I have on two occasions

examined this trace of brown matter, and found its composition variable, and that it contains oxygen, as it evolves water when heated. It is most probable that the ammonia-chloride is partially decomposed by water into the olive body (B.) and sal-ammoniac, thus 4 ($Pd . Cl . N H_3$) and $2 . H O$ give $Pd_4 Cl O_2 N H_2$ and $3 . N H_4 Cl$, and that this olive substance (hydrated) combines with a certain quantity of ammonia-chloride, undecomposed, or is more probably but mixed with it. The formula $Pd_9 Cl_3 N_3 H_{15} O_{12} = Pd . Cl . N H_3 + 2 (Pd_4 Cl N H_6 O_6)$ gives very accurately the result obtained by FEHLING.

It may be remarked, however, that another and very interesting formula expresses the composition of FEHLING's substance. It is this: $Pd_3 Cl N_2 H_6 O_2$, or rationally, $Pd Cl + 2 . Pd N H_2 + 2 Aq.$ This gives

		Theory.		FEHLING.
Pd_3 . . .	159·9	65·18		64·18
Cl . . .	35·4	14·43		14·85
$2 N H_3$ . .	34·0 ⎫		20·39	20·97
O_2 . . .	16·0 ⎭			
	245·3	100·00		100·00

It should then be an oxychloride of palladium united to ammonia, or a hydrated chloramidide of palladium, analogous in constitution to the very peculiar oxychloride of copper, $Cu Cl + 2 Cu O$, which I have elsewhere described.

The observations I have had occasion to make respecting the iodides and cyanide of palladium, and the bodies derivable from them, agree perfectly with those obtained by FEHLING, and published in the memoir to which I have so often had occasion to refer, on the relation of the haloid compounds of palladium to ammonia, inserted in LIEBIG's 'Annalen der Chemie und Pharmacie.' I deem it hence unnecessary to notice any of those results in detail, as they already have been placed before the public.

Of the Sulphates of Palladium.

The sulphate of palladium is best prepared by dissolving the metal in a mixture of sulphuric acid and nitric acid, the former being in excess, and evaporating the deep brown red liquor so obtained to the consistence of a syrup. On cooling, it crystallizes, though very confusedly, and only when so concentrated as to become almost completely solid.

In this state it tastes sour and metallic. It is reddish brown coloured, very soluble in water, and in damp air deliquescent. It contains water of crystallization. Its composition was determined as follows:—

45·286 grains of the crystalline mass, dried between folds of bibulous paper, were heated cautiously as long as any traces of moisture were given off. The residual mass weighed 38·124 grains, or 84·19 per cent., having lost 15·81 per cent. of water.

Of the material so dried, 32·043 grains were fused with carbonate of soda, and the mass having been boiled with water, the palladium was collected on a filter and ignited. It was purely metallic, and weighed 16·653 grains, being 51·97 per cent. of the dry, or 43·75 per cent. of the hydrated salt.

The liquor filtered from the metallic palladium was acidulated by muriatic acid, and precipitated by nitrate of barytes. It gave 37·492 grains of sulphate of barytes, containing 12·997 grains of sulphuric acid, equivalent to 40·17 per cent. of the dry, and to 33·82 per cent. of the hydrated salt.

These results give therefore for the

	Dry Salt.	Hydrated Salt.
Water		15·81
Sulphuric acid .	40·17	33·82
Palladium . . .	51·97	43·75
Oxygen and loss .	7·86	6·62
	100·00	100·00

The formula $PdO . SO_3 + 2 . HO$ gives

	Dry Salt.	Hydrated Salt.
Water		15·08
Sulphuric acid .	39·54	33·58
Palladium . . .	52·56	44·64
Oxygen	7·90	6·70
	100·00	100·00

When the dried sulphate of palladium is exposed to the air it rapidly re-acquires water to the extent of one equivalent, without becoming sensibly damp. This quantity was determined several times; the proportion being that 100 parts of the dry salt regained nine to ten parts of water, forming therewith a greenish olive powder. If the air be very damp, it subsequently deliquesces completely. By this property the sulphate of palladium appears to ally itself with the sulphates of copper, magnesia, &c., but it differs widely from them in others. Thus it is decomposed by water, and I could not succeed in forming any double salts by bringing it into contact with the alkaline sulphates. Its analogue here would appear to be the sulphate of mercury.

Basic Sulphate of Palladium.

When a strong solution of sulphate of palladium is mixed with much water it is decomposed; a deep brown powder is separated, and the liquid becomes very acid. By the addition of free sulphuric acid this action of water may be prevented; but on neutralizing this excess of acid by an alkali, even ammonia, a brown powder separates, which is found on analysis to be identical with the former.

The following analyses were made of specimens of this salt, prepared under various circumstances.

A. Prepared by dilution with water.

39·467 grains were heated over a spirit lamp cautiously until all water had been given off. The dry mass, which had become much darker in colour, weighed 35·994 grains, or 91·2 per cent., having lost 8·80 of water.

The dry powder was fused with carbonate of soda, and the metallic palladium collected precisely as described in the preceding article. It weighed 29·215 grains, or 73·68 per cent.

By the addition of nitrate of barytes the sulphuric acid was determined; it amounted to 2·408 grains, or 6·11 per cent.

B. Prepared by the addition of potash.

The method of analysis was precisely as in the foregoing instance.

23·645 grains of material gave when dried 21·670 grains, or 91·64 per cent., having lost 8·36 of water.

This residue gave 17·379 grains of palladium, being 73·49 per cent.; and then 4·569 grains of sulphate of barytes, being 19·36 per cent., containing 6·65 of sulphuric acid.

C. A portion of the same specimen having been exposed to the air for some time was analysed.

27·443 grains gave when dried 23·722 grains, or 86·45 per cent., having lost 13·55 of water.

This residue was ignited with carbonate of ammonia. It left 19·215 grains of metallic palladium, equivalent to 70·02 per cent.

This basic salt had, therefore, by exposure to the air, regained a quantity of water of which it had been deprived by the high temperature of the stove in which the drying of the precipitates had been effected.

D. Prepared by ammonia, not added in excess, and dried at about 150° FAHR.

I. 47·072 grains of material gave, by a temperature near, but still below, redness in the dark, 40·361 grains of dry substance, being 85·74 per cent. It had thus lost 14·26 of water.

By fusion with carbonate of soda, and treatment in the usual manner, were obtained 32·444 grains of metallic palladium, and 9·800 grains of sulphate of barytes. These weights indicate 68·91 per cent. of metal, and 7·15 of sulphuric acid.

II. 24·780 grains of this specimen were heated until all water was given off; it then weighed 21·159 grains, having lost 14·58 per cent. The dry salt was then exposed to a damp atmosphere for twenty-four hours; it did not increase very sensibly in weight. This basic sulphate has, therefore, no power to reassume the hydrated condition, having once been fully dried.

This dry material was fused with carbonate of soda, and the metal and sulphuric acid determined by the usual methods. It gave 16·977 grains of palladium, or 69·47 per cent., and 4·275 grains of sulphate of barytes, indicating 6·94 of sulphuric acid per cent.

The analyses A. B. and C. would tend to show that this salt may exist in two degrees of hydration, but I rather think that the difference is not important, for in heating the other specimens I could not trace any distinct term at which an interruption to the evolution of the water occurred. In the first examples, the specimens had been dried in the stove at a temperature which would have probably rendered them quite anhydrous, had they been exposed to its influence for a much longer time.

I shall exhibit the results of all the analyses as follows :—

	A. by Water.	B. by Potash.
Water	8·80	8·36
Sulphuric acid .	6·11	6·65
Palladium . . .	73·68	73·49
Oxygen and loss .	11·41	11·50
	100·00	100·00

	C. by Potash.	D. I.	D. II. by Ammonia.
Water	13·55	14·26	14·58
Palladium . . .	70·02	68·91	68·53
Sulphuric acid . .	} 16·43	7·15	6·94
Oxygen and loss .		9·68	9·95
	100·00	100·00	100·00

It is thus abundantly evident that there exists but the one basic sulphate of palladium which may be prepared by the action of water or of any alkali upon the sulphate, and the analyses given indicate that the dry salt has the formula $SO_3 + 8\,PdO$, from the per cent. composition of which none of the results found vary much, whilst the mean of all coincides completely with it. Thus,

	Theory.		Mean of analyses abstracting water.
8 Pd . =	426·4	80·38	80·72
8 O =	64·0	12·06	11·42
SO_3 =	40·1	7·56	7·86
	530·5	100·00	100·00

The two hydrated states of this salt are accurately expressed by the formulæ

$$SO_3 + 8\,.\,PdO + 6\,HO,\ \text{and}\ SO_3 + 8\,.\,PdO + 10\,HO,$$
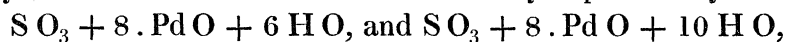
which give in numbers,

8 Pd	=	426·4	72·96	8 Pd	= 426·4	68·72
8 O	=	64·0	10·95	8 O	= 64·0	10·32
SO_3	=	40·1	6·85	SO_3	= 40·1	6·47
6 . HO	=	54·0	9·24	10 . HO	= 90·0	14·49
		584·5	100·00		620·5	100·00

Of the Ammonia-sulphates of Palladium.

On adding water of ammonia to a solution of sulphate of palladium, no ammonia-cal compound is at first obtained, but merely the basic compound already described. When, however, the ammonia is added in excess, the basic salt redissolves, and a colourless liquor is produced, from which the ammonia-sulphate may be obtained crystallized, by cautious evaporation and cooling.

This salt is best obtained by taking a strong solution of the neutral sulphate, and passing into it a stream of ammoniacal gas until the brown precipitate which first appears is totally redissolved ; then filtering, if necessary, and setting aside to cool slowly. It then forms rectangular prisms, often of considerable size and of a beautiful pearly lustre.

When this salt is very gently heated, it gives off water, and the crystals become opake, but without losing their form or whiteness. Ammonia is next evolved, and the salt changes into a yellow powder, which, when more strongly heated, fuses, evolves sulphite of ammonia, ammonia, nitrogen, and water, and leaves metallic palladium.

A very finely crystallized specimen was analysed as follows :—

A. 25·987 grains decomposed by very full ignition gave 9·414 grains of palladium, or 36·24 per cent.

B. 48·677 grains dried at a very moderate heat as long as any water was evolved, but without any loss of ammonia, and remaining quite white, then weighed 45·672 grains, having lost 6·19 per cent. of water.

17·039 grains of this dry material gave by bright ignition 6·591 grains of palladium, which is 38·68 per cent. for the dry, and 36·28 for the hydrated salt.

C. 28·462 grains of the crystals were fused with carbonate of soda and the mass treated with boiling water. The metallic palladium which remained weighed 10·340 grains, or 36·50 per cent.

The alkaline liquor acidulated by nitric acid and treated with nitrate of barytes, gave 22·827 grains of sulphate of barytes, indicating 27·67 per cent. of sulphuric acid.

These results may be thus exhibited.

	Hydrated Salt.			Dry Salt.
	A.	B.	C.	
Water		6·19		
Sulphuric acid . .			27·67	29·49
Palladium . . .	36·24	36·28	36·50	38·68

These results abundantly show that the formula of this salt is, when crystallized, $SO_3 + PdO + 2NH_3 + HO$, which gives

$$
\begin{array}{llr}
SO_3 = & 40 \cdot 1 & 27 \cdot 75 \\
Pd = & 53 \cdot 3 & 36 \cdot 95 \\
O = & 8 \cdot 0 & 5 \cdot 54 \\
2 \cdot NH_3 = & 34 \cdot 0 & 23 \cdot 53 \\
HO = & 9 \cdot 0 & 6 \cdot 23 \\
\hline
& 144 \cdot 4 & 100 \cdot 00
\end{array}
$$

I have shown elsewhere* that the sulphates of this class must be considered as consisting of an ordinary ammoniacal salt united to a metallic oxide combined with ammonia, or to a true metallic amidide. Of these two states, the ammoniacal sulphates of copper and of silver afford examples, the former having the formula $SO_3 . NH_4O + CuO . NH_3$, whilst that of the latter is $SO_3 . NH_4O + Ag . NH_2$. The salt of palladium, at present in question, affords an excellent instance of the passage from the one to the other state, for as the crystals lose their water by a gentle heat, and the quantity of it amounts to exactly an equivalent, the formula of the dried salt becomes $SO_3 . NH_4O + Pd . NH_2$, and there is hence good ground for the opinion that the atom of water is really present as such in the hydrated salt, and that in this, and also in the corresponding salts of nickel, cobalt, copper, and zinc, the metal is truly combined with amidogene. The formula is then to be written for this, as for all such salts, $SO_3 . NH_4O + Pd . Ad + Aq$.

There exists another ammonia-sulphate of palladium, which may be formed by the action of a moderate heat upon that already described, until it is totally converted into a yellow powder, or it may be produced by adding sulphuric acid to a strong solution of the preceding salt, or by boiling such solution for a long time. It then precipitates as a yellow crystalline powder, which dissolves easily in boiling, but very sparingly in cold water. By a strong heat it is decomposed into water, and gaseous products, sulphite of ammonia, and metallic palladium.

It was analysed by fusion with carbonate of soda, treatment of the residue with water and determination of the sulphuric acid, as sulphate of barytes. From 27·103 grains there were thus obtained 12·128 grains of metal, or 44·70 per cent., and 26·886 grains of sulphate of barytes, or 99·8 per cent., containing 34·40 of acid.

The formula deducible from these numbers is $SO_3 . PdO + NH_3$. Thus there is

		Theory.		Experiment.
Sulphuric acid	.	40·1	33·87	34·30
Palladium . .	.	53·3	45·02	44·70
Oxygen . . .	.	8·0	6·75 ⎱	21·00
Ammonia . .	.	17·0	14·36 ⎰	
		118·4	100·00	100·00

On adding muriatic acid to a solution of the white ammonia-sulphate, it is not this salt which separates, but the yellow ammonia-chloride already noticed.

Of the Nitrates of Palladium.

It has been long known that palladium dissolves in nitric acid without any evolution of nitric oxide gas unless heat be applied. On evaporating the olive-brown

* Transactions of the Royal Irish Academy, vol. xix. p. 77.

solution so obtained, it becomes more reddish, and if set aside when of a sirupy consistence, and allowed to cool slowly, the nitrate of palladium crystallizes in long rhombic needles, which are, however, so deliquescent that I found it impossible to determine with accuracy the quantity of water of crystallization which they contain. In general, the solution of this salt dries down to a mass with scarcely any trace of crystalline structure.

If a solution of nitrate of palladium be diluted with much water, a dark brown powder falls, which is a basic nitrate. It may be generated also by adding solution of potash, or water of ammonia in small quantity, to a solution of the metallic salt. This basic nitrate, when heated, evolves water, and then red fumes of nitrous acid; leaving oxide or suboxide of palladium, according to the temperature to which the material may have been finally exposed.

The following analyses will show that the basic nitrate, as prepared by different methods, is really of uniform constitution.

A. Basic nitrate prepared by water of ammonia.

60·808 grains of this specimen were placed in a tube of Bohemian glass, about twelve inches long, and in front of this, but completely separated by some rolled pieces of platinum foil, the tube was filled for a space of about four inches, with clean finely-divided metallic copper, as reduced from the oxide by hydrogen gas. To each end of the tube was attached a bulb-tube, containing recently fused chloride of calcium, and that next the metallic copper was placed, by a caoutchouc connecter, in communication with a vessel of water, by the flowing out of which a current of air might be established through the apparatus, precisely as is effected in the process proposed by LIEBIG for drying organic substances previous to analysis. The long tube containing the palladium salt and the metallic copper being placed in a charcoal furnace, that portion containing the copper was heated to redness, and then, whilst by the flowing out of the water a stream of air was brought through the tube, a gentle heat was applied to the basic nitrate of palladium. Water and red fumes were given off, which latter were reduced to the state of nitrogen or nitrous oxide by contact with the ignited metallic copper. The current of air, which had been accurately dried by passing through the first chloride of calcium tube, carried these products forwards. The water was collected by the chloride of calcium tube into which it passed, whilst the gases mixing with the general current of the air passed into the vessel from which the water flowed.

As soon as the palladium salt had been feebly ignited, the process was interrupted, and the tube allowed to cool. It was then so cut by a file, as that the residual oxide of palladium could be removed without any sensible loss. It weighed 44·620 grains, or 73·15 per cent. The chloride of calcium tube in which the water had been collected, was weighed before and after the operation. The increase of weight was 7·208 grains, indicating 11·85 per cent. of water.

In order to verify the degree of oxidation and determine the quantity of metal in

the residual oxide, the 44·620 grains were ignited in a current of hydrogen gas, and the water so formed was collected in a chloride of calcium tube. It weighed 6·251 grains, or 10·28 per cent., containing 9·14 of oxygen, and the remaining metallic palladium weighed 38·927 grains, corresponding to 64·01 per cent.

B. Basic nitrate produced by water.

I. 29·665 grains of the brown precipitate, formed by diluting a strong solution of nitrate of palladium with a large quantity of water, gave, by very gentle ignition, a black residue of oxide weighing 21·747, or 73·31 per cent., and by vivid ignition 18·939, or 64·36 per cent. of pure metallic palladium.

II. 12·858 grains were mixed with copper filings, and more clean metallic copper being placed in front, the tube was heated in the same manner and with the same arrangement of apparatus as already described in A. The water collected in the chloride of calcium tube weighed 1·420, corresponding to 11·20 per cent.

III. 17·239 grains were mixed with copper turnings, and placed at the bottom of a tube of Bohemian glass, which was then filled with clean freshly-reduced metallic copper. The tube was about nine inches long. From it passed to the pneumatic trough a bent tube, of which the extremity opened, above the level of the water, under a narrow graduated jar, so adjusted as that it should rise as gas passed into it. The pure metallic copper having been first fully ignited, heat was applied to the extremity of the tube, and the nitric acid of the salt was so completely deoxidized by the red-hot copper, that the gas which passed over contained no sensible trace of nitric oxide. When the operation was concluded the apparatus was allowed to cool, and the proper correction being made for the change of temperature which had taken place in the air of the room during the experiment, the volume of the gas collected in the graduated jar was considered to represent the quantity of nitrogen which the substance contained. After the proper corrections for temperature, pressure, and moisture, it measured 2·319 cubic inches, weighing 0·7452 grains, or 4·31 per cent.

By this method the composition of the basic nitrate of palladium is found to be

	A. By Ammonia.	B. By Water.		
		I.	II.	III.
Palladium	64·01	64·36		
Oxygen combined with metal	9·14	8·95		
Water	11·85		11·20	
Nitrogen				4·31

These results lead to the simple formula $N O_5 + 4 Pd O + 4 H O$, which gives

4 Pd =	213·2	63·61		4 . Pd O =	245·2	73·15
4 O =	32·0	9·54		N O_5 =	54·0	14·91
N =	14·0	4·17		4 H O =	36·0	11·94
O_5 =	40·0	11·94				
4 H O =	36·0	10·74			335·2	100·00
	335·2	100·00				

Ammonia-nitrates of Palladium.

A. When a solution of nitrate of palladium is heated with a considerable excess of water of ammonia, or when ammoniacal gas is passed into the solution, a colourless liquor is ultimately obtained, the precipitate which first forms being perfectly redissolved. By careful evaporation, this solution deposits a pure white salt in rhombic crystals (prisms or plates), of a brilliant pearly lustre. When heated, this salt fuses, and deflagrates violently with a brilliant white flame, depositing metallic palladium, and evolving water and nitrogen gas. The existence of this salt and its property of so exploding has been long known, and its composition only remained to be determined by me.

I. 20·696 grains of this salt in good crystals were mixed with powdered glass, and placed in a tube : in front of the mixture was put oxide of copper, and in front of that again clean metallic copper, in thin turnings. The latter part of the tube having been heated to redness, heat was applied to the part of the tube containing the mixture, and the gas and watery vapour brought into contact with the oxide and metallic copper. The water was collected in a chloride of calcium tube, the last portions being obtained by breaking open the far extremity of the analysis tube which had been formed to a point for the purpose, and drawing by the mouth a current of air through the apparatus: the quantity of water was 8·180, or 39·53 per cent., containing 4·39 of hydrogen.

II. 16·036 grains were mixed with powdered glass, and heated in a platinum crucible, at first gently, until all volatile products had been expelled, but then to dull redness. The weight of the glass used being known, it was found that there remained of metallic palladium 5·725, or 35·71 per cent.

III. 16·237 grains being mixed with powdered glass and placed in a tube with oxide of copper and metallic copper as in the last experiment, but from which a narrow tube passed to a graduated jar in the water-pneumatic trough, the decomposition was effected, and the volume of the nitrogen gas evolved determined as already noticed in the analysis of the basic nitrate. It measured 14·7075 cubic inches, weighing 4·7149 grains, equivalent to 29·04 per cent.

The composition of this salt is, therefore,

$$\left.\begin{array}{lr}\text{Palladium} & 35\text{·}71 \\ \text{Nitrogen} & 29\text{·}04 \\ \text{Hydrogen} & 4\text{·}39 \\ \text{Oxygen (by loss)} & 30\text{·}86\end{array}\right\}100\text{·}00$$

The formula $N O_5 + Pd O + 2 . N H_3$, exactly agrees with these results, giving

Pd = 53·3	35·70	Pd O = 61·3	41·09
N_3 = 42·0	28·13	N O$_5$ = 54·0	36·12
O_6 = 48·0	32·15	2 . N H$_3$ = 34·0	22·79
H_6 = 6·0	4·02		
149·3	100·00	149·3	100·00

The rational formula of this salt is, therefore, $NO_5 . NH_4O + Pd . NH_2$, and it is completely analogous in constitution to the corresponding ammoniacal nitrate of copper.

B. If the quantity of ammonia added to the solution of nitrate of palladium be not sufficient to redissolve all of the brown basic nitrate which is first formed, a deep yellow liquor is produced, which deposits on standing, or by moderate concentration, small yellow crystals, whose form appears to be rhombic-octohedral. When heated, these crystals deflagrate, producing water and nitrogen gas with copious fumes of nitrous acid, and some clouds of nitrate of ammonia. The residue after ignition is metallic palladium.

The analysis of this body was conducted as follows :—

I. 6·065 grains were ignited in a tube of Bohemian glass, and the volatile products having been conducted over red-hot metallic copper to decompose any red fumes, were passed through a tube containing chloride of calcium, which collected water amounting to 1·219 grains, or 20·10 per cent., corresponding to 2·23 of hydrogen in 100·00.

The tube being cut the residual palladium was found to weigh 2·623 grains, or 43·6 per cent.

II. 5·016 grains ignited in a platinum crucible gave 2·285, or 45·54 per cent. of metal.

III. 5·571 grains gave when treated exactly in the manner described in the preceding salt, nitrogen gas, which after correction measured 4·211 cubic inches, weighing 1·355 grain, or 24·10 per cent. The decomposition did not appear to proceed so regularly, nor to give so pure gas as in other cases.

From these experiments this compound appears to contain in 100 parts,

Palladium	43·60	45·54
Nitrogen.	24·10	
Hydrogen	2·23	
Oxygen (by loss) . . .	30·07	
	100·00	

The formula to which these numbers lead is very anomalous. It is $NO_5 + Pd . NH_2$, which gives

One atom palladium . .	53·3	43·23
Two atoms nitrogen . .	28·0	22·71
Two atoms hydrogen . .	2·0	1·62
Five atoms oxygen . . .	40·0	32·44
	123·3	100·00

If this formula were perfectly established it would constitute the first example of a direct combination of a metallic amidide with an acid. The only other supposition at all possible is, that it may contain the elements of an atom of water; the formula

should then become N O_5+ Pd O . N H_3, and correspond to the yellow crystalline form of the ammonia-chloride Pd . Cl + N H_3, or the yellow ammonia-sulphate, S O_3 . Pd O + N H_3. Adopting this formula, the composition of the salt should have been

One atom palladium	. .	53·3	40·29
Two atoms nitrogen	. .	28·0	21·16
Three atoms hydrogen	.	3·0	2·27
Six atoms oxygen	. . .	48·0	36·28
		132·3	100·00

And with this the hydrogen and nitrogen determinations might be considered as perfectly agreeing. However, from the irregular way in which this salt is decomposed I attach little value to the nitrogen result, and, on the other hand, the quantity of palladium found exceeds that given by the formula as last written, too much to be accounted for by any error of experiment, as the crystals analysed were very pure. I hence consider that although the formula N O_5 + Pd O . N H_3 agrees best with our received ideas, and with the analogies of other compounds, yet the former, N O_5 + Pd . N H_2, is more strictly deducible from the analytical results, and deserves at least provisional adoption until an opportunity presents itself of obtaining more decisive results, for I have found that this substance is not formed in all cases when its elements are brought together. I have procured it crystallized and sufficiently pure for analysis but twice, and then only in such small quantity as limited my power of experiment, as has been already seen.

Double Oxalate of Palladium and Ammonia.

This salt, which may be formed by adding oxalic acid to a solution of any colourless ammonia-salt of palladium, or by dissolving the freshly-precipitated hydrated oxide, or basic carbonate in a solution of binoxalate of ammonium, crystallizes in very beautiful bronze-yellow rhombic prisms, which are of two kinds, differing in the quantity of water of crystallization which they contain. I shall describe them as being, the one form in short prisms, the other in needles.

The short prismatic salt gave on analysis the following results :—

31·225 grains gave, when very gently heated until the evolution of watery vapour ceased, 27·624 of dry salt, being 88·43 per cent.

This dry substance being then ignited there remained 9·429 grains of metallic palladium, or 30·20 per cent.

A quantity of the salt having been mixed with oxide of copper and introduced into a tube of German glass, with clean metallic copper in front, it was burned as for an organic analysis, and the relative volumes of nitrogen and carbonic acid in the gaseous mixture, which came over, were determined in the usual way. This relation varied very much in the different tubes full of gas, showing that the constituents of

the salt were not uniformly acted on by the heat, but the relation of the total volume of nitrogen to the total volume of carbonic acid was very exactly 1 : 4.

These results show that the formula of this salt is $Pd \cdot O \cdot C_2 O_3 + N H_4 O \cdot C_2 O_3 + 2 Aq$, giving

		Theory.	Experiment.
Pd =	53·3	30·06	30·20
$2 \cdot C_2 O_4$ =	88·0	49·64 ⎫	
$N H_4$ =	18·0	10·15 ⎭	58·23
$2 \cdot Aq$ =	18·0	10·15	11·57
	177·3	100·00	100·00

The salt crystallizing in long needles, gives, when dried, about 70 per cent. of dried salt, having lost 30 per cent. of water. By ignition it yields from 23 to 23·26 of metallic palladium. These numbers point out that it contains eight atoms of water of crystallization, from which the numbers should be 31·13 of water, and 23·04 of metal.

Section II.—Platinum Compounds.
Protoxychloride of Platinum.

During experiments conducted for the purpose of preparing sulphate of the deut-oxide of platinum, and the results of which I shall on another occasion more specially describe, I had occasion to remark the formation of the substance now in question, and to determine its properties and composition. The bichloride of platinum being boiled with strong sulphuric acid in a retort, nearly to dryness, much muriatic acid gas is driven off, and on washing out the residue with water, a black powder remains undissolved, which may be collected on a filter. It is anhydrous. At a red heat it evolves oxygen and chlorine, leaving metallic platinum. In solution of potash it appears to dissolve. By ammonia it is converted into a fulminating substance, of which the analysis is not yet completed. By muriatic acid it is converted into the ordinary protochloride of platinum.

Its analysis was effected as follows :—

29·402 grains were perfectly fused with an excess of carbonate of soda. When the saline matter was dissolved out with water, metallic platinum remained which weighed 25·620 grains, or 87·14 per cent. The solution having been precipitated by nitrate of silver, after being acidulated by nitric acid, gave 8·995 of chloride of silver, or 30·55 per cent., containing 7·54 of chlorine.

These results lead to the formula $Pt \, Cl + 3 \, Pt \, O$, which gives

		Theory.	Experiment.
Pt_4 =	395·2	86·94	87·14
Cl =	35·4	7·78	7·54
O_3 =	24·0	5·28	5·32
	454·6	100·00	100·00

The material which is dissolved off from this black powder is by no means a pure sulphate of platinum. It contains also bichloride, the decomposition of which appears to have a definite limit regarding sulphuric acid.

Action of Ammonia on Biniodide of Platinum.

When the biniodide of platinum is digested in water of ammonia, either cold or hot, it becomes gradually changed to a bright cinnabar red powder, which is insoluble in water. This powder may also be formed by adding water of ammonia to a solution of the double iodide of platinum and potassium. The liquor becomes nearly colourless, and the red substance precipitates.

On heating this body it gives off ammonia with fumes of iodine and of hydriodate of ammonia: water also separates. It may, however, be exposed to a temperature of 350° FAHR. without losing water, which does not escape until complete decomposition has commenced.

The analysis of this body was effected as follows :—

32·490 grains were fused with carbonate of soda, and the residual mass digested in water. The platinum which remained behind weighed 12·472, or 38·01 per cent.

The alkaline solution being rendered acid by acetic acid, was decomposed by nitrate of silver. The iodide of silver, being collected, dried and weighed, was 29·295 grains, or 89·8 per cent., containing 48·37 of iodine.

47·226 grains, ignited with oxide of copper in the manner already described, gave 9·215 cubic inches of dry nitrogen, equivalent to 6·26 per cent. in weight.

44·468 grains, ignited with oxide of copper, gave 4·584 of water, equivalent to 1·15 of hydrogen per cent.

These results lead directly to the formula $Pt\,I\,N\,H_4\,O_2$. or $Pt\,O_2 + N\,H_4\,.\,I$., for which the numbers are

		Theory.	Experiment.
$Pt =$	98·8	38·12	38·01
$O_2 =$	16·0	6·17	6·21
$N =$	14·0	5·44	6·26
$H_4 =$	4·0	1·54	1·15
$I =$	126·3	48·73	48·37
	259·1	100·00	100·00

The hydrogen being found below the quantity assigned by theory, I endeavoured to ascertain whether a portion of it could be eliminated as water, and I exposed a quantity of the substance to a current of dry air at 300° FAHR. until all traces of water ceased to pass. The quantity of water which escaped was 1·95 per cent. If this were not hygrometric, the formula of the dry substance should be $Pt\,I_2 + Pt\,O_2 + 2\,.\,N\,H_3$. and the hydrogen should be 1·20 per cent., nearly what was furnished by analysis. The specimen analysed for hydrogen was probably so dried.

It is interesting to find here the form assumed by the ammoniacal compounds of quicksilver, but still hydrated, and so rendered much more complex. It is curious also to recognise in the two hydrated states of this red platinum body, the analogues to the two formulæ assigned to the mercurial white precipitate before its true constitution was known. Thus $Pt\,O_2 + N\,H_4\,.\,I\,.$ corresponds to the formula $Hg\,O_2 + N\,H_4\,.\,Cl$ given by MITSCHERLICH, and $Pt\,I_2 + Pt\,O_2 + 2\,.\,N\,H_3$ is equivalent to that suggested by Mr. RICHARD PHILLIPS, $Hg\,Cl_2 + Hg\,O_2 + 2\,.\,N\,H_3$. I do not believe, however, that the perfectly anhydrous condition of white precipitate can be given to this platinum body.

On the Action of Ammonia on the Perchloride of Platinum.

A. When a dilute solution of perchloride of platinum is added to water of ammonia, also dilute, a pale yellowish precipitate is produced, insoluble in cold water, but decomposed by boiling water, or even by much washing; the double chloride of platinum and ammonia being dissolved out, and the colour of the residue becoming much less yellow.

When this powder is heated it gives out sal-ammoniac, chlorine, nitrogen, and leaves metallic platinum. No trace of water appears: it hence does not contain oxygen as a constituent. With muriatic acid it is changed into the common double chloride of platinum and ammonium.

This substance was analysed as follows :—

21·098 grains were carefully mixed with an excess of carbonate of soda, and ignited until the mixture was completely fused. The saline matter was then dissolved out with distilled water, and the metallic platinum remaining being collected and ignited, weighed 10·881 grains, = 51·6 per cent.

The solution having been acidulated by nitric acid was precipitated by nitrate of silver, the chloride of silver produced was collected and fused, it then weighed 18·521, equivalent to 38·8 of chlorine per cent.

45·332 grains of another quantity, treated in a precisely similar way, gave 23·614 of platinum, = 52·1 per cent., and 70·151 of chloride of silver, equivalent to 38·20 of chlorine per cent.

These results indicate for the composition of this substance the very simple formula $Pt\,Cl_2 + N\,H_3$, which gives the numbers

		Theory.		Experiment.	
One atom of platinum	= 98·8	52·38		51·6	52·10
Two atoms of chlorine	= 70·8	37·94		38·8	38·20
One atom of ammonia	= 17·1	9·68		9·6	9·70
	186·7	100·00		100·0	100·00

From the circumstance of no water being produced when this body is decomposed by heat, and the relation between the chlorine and platinum showing that these con-

stituents are directly combined, the loss must necessarily be nitrogen and hydrogen in the proportions to form ammonia. This constituent, therefore, was not directly estimated; the analyses showing that the brownish yellow powder consists of an equivalent of perchloride of platinum united to an equivalent of ammonia.

This substance is not by any means always formed by the action of water of ammonia upon a solution of chloride of platinum; on the contrary, it is difficult to obtain it unless by using both solutions very weak, and by having the platinum quite free from muriatic acid in excess. In the great majority of cases, this first product is either rendered impure by the passage of a portion into the second stage of the reaction, or else by the precipitation of the double chloride of platinum and ammonium which is generated at the same time. With moderately weak solutions, the platinum being in excess, and avoiding too much washing of the precipitate, the substance may generally be obtained pure.

B. When the solutions of chloride of platinum and ammonia are boiled together, the precipitate rapidly assumes a remarkable fawn colour. In this state it is insoluble in water. It dissolves in muriatic acid, producing a yellow liquor. When heated, it gives off chlorine and muriatic acid gases, water, a trace of sal-ammoniac, and leaves metallic platinum.

The analysis of this body was effected as follows :—

I. 27·999 grains ignited with an excess of carbonate of soda, gave by the same mode of treatment as that described in paragraph A, 12·332 of platinum, being 44·24 per cent., and 47·365 of chloride of silver, equivalent to 41·94 in 100.

For the determination of the hydrogen and nitrogen, the same methods were employed as in the analyses of organic bodies, and the details of which need not be inserted.

20·064 grains burned with oxide of copper, gave 19·386 of water, or 2·17 per cent. of hydrogen.

20·049 grains of substance produced 4·29 cubic inches of dry pure nitrogen, equivalent at standard temperature and pressure to 1·420 grain, or 7·09 per cent.

II. Another quantity of substance prepared at a different time and at a much lower temperature, gave the following result :—

23·599 grains ignited with carbonate of soda, gave by treatment with nitric acid and nitrate of silver 40·223 chloride of silver, equivalent to 41·20 of chlorine per cent., and left 10·507 of platinum, equal to 44·47 in 100.

The hydrogen being determined, as in the former case, there was obtained from 24·925 grains of substance 5·170 of water, equivalent to 2·30 of hydrogen per cent.

In this instance the nitrogen was not determined. The formula to which these results lead is very remarkable, and will hereafter give origin to some observations; for

the present I shall only put it forward in a purely empirical form, as follows: $Pt_2 Cl_5 H_{11} N_2 O_4$, which gives the following numbers:—

Two atoms of platinum	= 197·6	44·35
Five atoms of chlorine	= 177·0	39·72
Two atoms of nitrogen	= 28·2	6·28
Eleven atoms of hydrogen =	11·0	2·47
Four atoms of oxygen	= 32·0	7·18
	445·8	100·00

III. The substance used in analysis No. 1. was again boiled for a short time in water of ammonia, but without allowing the colour to become perceptibly altered, it was then dried at a temperature of 120°, and analysed.

14·462 grains of substance gave, by the usual treatment, 6·467 of metallic platinum, equivalent to 44·72 per cent., and 23·799 of chloride of silver, equivalent to 40·61 of chlorine.

24·139 grains of substance burned with oxide of copper gave 4·799 of water, or 2·21 of hydrogen per cent. 27·968 gave, by the usual method, 5·602 cubic inches of pure dry nitrogen, weighing at standard temperature and pressures 1·7961 grain, and hence equivalent to 6·44 per cent.

The experimental results are hence as follows:—

	I.	II.	III.
Platinum	44·24	44·47	44·72
Chlorine	41·94	41·20	40·61
Nitrogen	7·09		6·44
Hydrogen	2·17	2·30	2·21
Oxygen	4·56		6·92
	100·00		100·00

It is very remarkable that in all these results the chlorine appears to be a little (about 1 per cent.) above the theoretical number; this is perhaps due to the presence of traces of the double chloride of platinum and ammonium, which, from its sparing solubility, if once formed is very difficult to be removed, and is not changed, except when the accompanying bodies are also decomposed. The composition of this substance is, however, evidently the same, although prepared under varied circumstances; and it may also be produced, even in the cold, by allowing chloride of platinum to remain in contact with an excess of water of ammonia for a considerable time.

When this substance is heated to about 250° or 300° it abandons some water, but no ammonia. The quantity of water thus given off, was found to be 2·57 per cent. By the loss of one equivalent it should be 2 per cent., and hence probably the perfectly dried substance has the composition of $Pt_2 Cl_5 N_2 H_{10} O_3$.

The formula of this body presents a remarkable relation, which may be at the pre-

sent moment noticed. It may be considered as the ordinary double chloride of ammonium and platinum, Pt Cl + N H Cl, united to a compound of chloride of platinum and oxide of ammonium, and then two atoms of water added. Thus

$$\left.\begin{array}{l} Pt . Cl_2 + N H_4 Cl \\ Pt . Cl_2 + N H_4 O \end{array}\right\} + 2 Aq = Pt_2 Cl_5 N_2 H_{10} O_3.$$
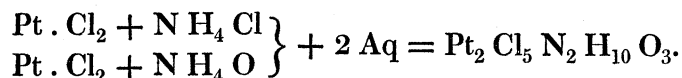
Whether this be its true constitution will be discussed in the sequel.

It may be also composed of the chloride of platinum and ammonium united to the body described in paragraph A. and to water. Thus

$$\left.\begin{array}{l} Pt Cl_2 + N H_4 Cl . \\ Pt Cl_2 + N H_3 \\ \qquad H_4 O_4 \end{array}\right\} = Pt_2 Cl_5 N_2 H_{11} O_4.$$
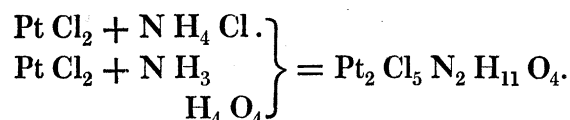
This is a more likely supposition than the former.

C. When the fawn-coloured substance last described is continually boiled in water of ammonia, it ultimately dissolves, but it may be observed to become dark brown before it disappears. This brown substance dissolves almost as soon as formed, and hence it is difficult to obtain a quantity of it for analysis; even a large quantity of chloride of platinum yielding by the action of ammonia only traces of it. This brown powder is not acted on by boiling water. With muriatic acid, it partly dissolves, giving a yellow liquor, and is partly converted into a white powder, sparingly soluble in water.

When heated it gives off sal-ammoniac, water and nitrogen, and metallic platinum remains. To determine the composition of this substance the same methods of analysis were used as in the former cases.

21·608 grains ignited with carbonate of soda, gave 13·455 of platinum, or 61·80 per cent., and then 9·939 of chloride of silver, corresponding to 11·35 of chlorine in 100.

23·799 grains gave, by ignition with oxide of copper, 7·085 of water, indicating 3·31 per cent. of hydrogen.

14·663 grains gave 6·2247 cubic inches of pure nitrogen reduced to 30 inches barometer and 32° FAHR., indicating 13·50 per cent. in weight.

The formula to which this analysis leads is remarkable; it is $Pt_2 Cl N_3 H_{10} O_4$, which gives the following numerical results :—

Two equivalents of platinum .	197·6	62·28	61·80
One equivalent of chlorine . .	35·4	11·16	11·35
Three equivalents of nitrogen .	42·3	13·33	13·50
Ten equivalents of hydrogen .	10·0	3·15	3·31
Four equivalents of oxygen . .	32·0	10·08	10·04
	317·3	100·00	100·00

The specimen employed in the above analysis had been dried at a temperature of 310°, and had lost a quantity of water which it retains when dried at lower temperatures; the quantity of water thus loosely combined was found to be three equivalents.

When we look to the constitution of the formula just described, we may probably consider the chlorine to exist as sal-ammoniac, and then combined with an ammonia oxide of platinum, such as is found really to exist; thus the formula may become

$$2 (Pt O_2 + N H_3) + Cl N H_4.$$

It also obviously bears a remarkable relation to the constitution of the fawn-coloured substance, four equivalents of muriatic acid being removed from the latter, and being replaced by one equivalent of ammonia and one of water.

D. When the action of the water of ammonia is still longer continued, this brown matter dissolves and a perfectly colourless liquor is obtained, from which nothing separates by cooling. If, however, a quantity of spirit of wine be added, a copious white, or pale-yellowish white precipitate is produced. This, on drying, aggregates into a mass like coarse meal, which when powdered is nearly quite white.

This substance is not insoluble in water, and dissolves readily in water of ammonia: its solution gives with the oxalic and muriatic acids copious white precipitates, and it dissolves in sulphuric and nitric acids, giving crystalline compounds; when heated it evolves water, ammonia, nitrogen and sal-ammoniac, and leaves metallic platinum.

Its analysis was conducted in the usual manner.

I. 25·357 grains gave 13·043 of platinum, or 50·94 per cent., and yielded by subsequent treatment 18·552 of chloride of silver, corresponding to 18·03 of chlorine in 100.

24·838 grains gave 9·089 of water, equivalent to 3·91 of hydrogen in 100.

22·102 grains gave 10·1259 cubic inches of pure nitrogen at 30 inches barometer and 32° FAHR., equivalent to 14·69 per cent.

II. Another quantity prepared at a different time and of a rather more decidedly yellowish shade than the former was also analysed.

11·406 grains ignited gave 5·741 of platinum, or 50·34 per cent. An accident prevented the determination of the chlorine on that quantity.

17·256 grains, ignited with oxide of copper, gave 6·002 of water, indicating 4·05 per cent. of hydrogen. The residue was treated with nitric acid and nitrate of silver, and gave 12·889 of chloride of silver, equivalent to 18·26 of chlorine in 100.

The experimental results are therefore

	I.	II.
Platinum . . .	50·94	50·34
Chlorine . . .	18·03	18·26
Hydrogen . .	3·91	4·05
Nitrogen . . .	14·69	} 27·35
Oxygen	12·43	
	100·00	100·00

The formula deducible from these analyses is $Pt\ Cl\ N_2\ H_8\ O_3$. From this the numerical results should be as follows :—

One equivalent of platinum	=	98·8	50·83
One equivalent of chlorine	=	35·4	18·21
Two equivalents of nitrogen	=	28·2	14·51
Eight equivalents of hydrogen	=	8·0	4·11
Three equivalents of oxygen	=	24·0	12·34
		194·4	100·00

By the application of a gentle heat, some water, apparently of hydration, may be separated from the substance, it however does not exceed one equivalent; when dry, therefore, it probably consists of $Pt\ Cl\ N_2\ H_7\ O_2$.

The relation between this formula and that of the brown substance last described, is exceedingly remarkable, for the above may be considered as consisting of $(Pt\ O_2 + N\ H_3) + Cl\ N\ H_4$, when dry differing from the brown substance in containing twice as much sal-ammoniac; and this relation is supported by the circumstance that by prolonged digestion in a solution of sal-ammoniac, the brown substance may be converted into this white substance.

This body becomes remarkably of interest, inasmuch as the compounds which it forms with acids are found to be identical with the interesting class of salts recently described by Gros, and that this substance is indeed the compound base which Gros considers to be united with the acids in the bodies which he described. The formula which he assigns to the base he hypothetically assumed was $Pt\ Cl\ N_2\ H_6\ O$, identical with that of the substance just described, with the exception of 2 aq, the separation of which is rendered difficult by the facility with which the body is decomposed. I shall hereafter have occasion to notice the influence which our thus finding Gros's base in the present series must exercise on the views which he put forward, but for the present I shall pass to the additional experimental matter.

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E. If, in place of precipitating the ammoniacal solution in the cold by alcohol, it be boiled violently so as to expel all the excess of ammonia, a quantity of the body last described falls down mixed with another of a pale brick-red colour. To obtain this last pure, the solution must be evaporated rapidly with ebullition to perfect dryness. If then any particles of white or yellow still remain, the mass must be mixed up with more water and again boiled until ultimately a pale brick-red, or a lively flesh-red powder remains behind.

The liquor obtained by washing contains much sal-ammoniac.

This powder when heated gives off water, sal-ammoniac and ammonia, and leaves metallic platinum. Boiled in water of ammonia it regenerates Gros's base. When boiled in muriatic acid it produces a yellow solution and a white powder, and by boiling in a solution of sal-ammoniac the muriatic salt of Gros's base.

It was analysed as follows :—

19·077 grains, ignited with carbonate of soda, gave 9·569 of metallic platinum, or 50·11 per cent., and then 22·627 of chloride of silver, equivalent to 29·35 of chlorine in 100.

21·963 grains gave, by ignition with oxide of copper, 6·745 of water, indicating 3·41 of hydrogen per cent.

Another portion dried at a higher temperature and similarly treated, gave 3·34 of hydrogen in 100.

33·478 grains gave 14·8295 cubic inches of pure nitrogen at 30 barometer and 32° FAHR., amounting to 14·21 per cent.

The formula to which this analysis points is $Pt_2 Cl_3 N_4 H_{13} O_2$, from which the numbers follow :—

Two equivalents of platinum . .	197·6	50·77
Three equivalents of chlorine. .	106·2	27·29
Four equivalents of nitrogen . .	56·4	14·49
Thirteen equivalents of hydrogen	13·0	3·34
Two equivalents of oxygen . .	16·0	4·11
	389·2	100·00

The relation of this substance to that last described is easily to be seen; it consists in the union of one equivalent of muriatic acid to two equivalents of GROS's base. It would, indeed, upon the principles of that chemist, stand in the singular position of an oxychloride of his compound radical, for it is evident that $(Pt\ Cl\ N_2\ H_6)\ O + (Pt\ Cl\ N_2\ H_6)\ Cl = Pt_2\ Cl_3\ N_4\ H_{12}\ O + 2$ aq. Evidently the manner of formation of this substance is the expulsion of ammonia from GROS's base by the temperature of ebullition and the subsequent combination of the sal-ammoniac of the liquor with the body so evolved. Thus $Pt_2\ Cl_2\ N_4\ H_{12}\ O_2$ losing $N\ H_3$ becomes $Pt_2\ Cl_2\ N_3\ H_9\ O_2$, and by the addition of $N\ H_4\ Cl$ forms the body in question, $Pt_2\ Cl_3\ N_4\ H_{13}\ O_2$.

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I have not hitherto stopped to consider the precise manner in which these several bodies are derived from each other, or from the chloride of platinum, and in order to see more clearly their natural relations, it is necessary to make the change already noticed in the commencement of this paper. Ammonia being amidide of hydrogen, and nothing occurring in the chain of reactions now studied to disturb its constitution, I shall for the future look upon the nitrogen as existing in the state of amidogene, and the formulæ already described become then as follows :—

A. $Pt\ Cl_2\ N\ H_3 \qquad = Pt\ Cl_2 + Ad\ H$.
B. $Pt_2\ Cl_5\ N_2\ H_{11}\ O_4 = Pt_2\ Cl_5\ Ad_2\ H_7\ O_4$
C. $Pt_2\ Cl\ N_3\ H_{10}\ O_4 \ = Pt_2\ Cl\ Ad_3\ H_4\ O_4$
D. $Pt\ Cl\ N_2\ H_8\ O_3 \quad = Pt\ Cl\ Ad_2\ H_4\ O_3$
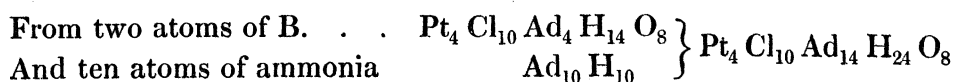E. $Pt_2\ Cl_3\ N_4\ H_{13}\ O_2 = Pt_2\ Cl_3\ Ad_4\ H_5\ O_2$.

If we were disposed to consider that the principle which was found so remarkably displayed in the instance of the mercurial compounds held with platinum, and that in those instances where oxygen was present it should be looked upon as existing in the state of water, we might find here numerous additions to the class of metallic amidides; thus the body C. should become, doubling the formula above written, $Pt\,Cl_2 + 3\,Pt\,Ad_2 + 8\,H\,O$, and similarly with the others. But it is exceedingly difficult to say when $Pt\,O_2$ and $2\,Ad\,H$ act on one another, whether they unite directly, or whether they mutually decompose, forming $Pt\,Ad_2$ and $2\,H\,O$, which then unite; this difficulty exists in all cases where the water cannot be separated without the substance being completely decomposed. I would postpone for the moment the consideration of this point, and for the time at least look upon the hydrogen as being equally essential with the platinum as a constituent of these bodies.

The formation of the first substance described requires no remark. I find that the same body may be produced by the action of dry ammoniacal gas upon chloride of platinum. There is absorbed about 11 or 12 per cent., indicating one equivalent, $Pt\,Cl_2 + Ad\,H$; but if the current of gas be continued a white powder is obtained, formed by the union of two equivalents of ammonia to one of platinum, and which is identical with the muriatic salt of GROS, of which the formula may be simply written $Pt\,Cl_2 + 2\,Ad\,H$.
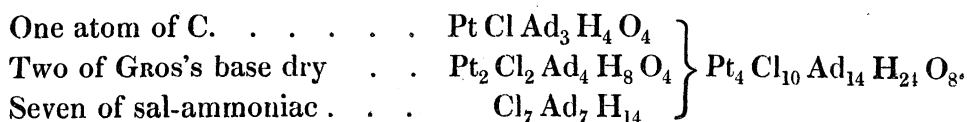
It is evident that the body B. cannot be produced directly from the perchloride of platinum, as that does not contain the quantity of chlorine necessary for its constitution, and indeed, if we examine the ammoniacal liquor from the first commencement of the formation of the fawn-coloured substance, it will yield the body D. on the addition of alcohol. I consider therefore these two bodies as being of simultaneous origin, there being formed from

$$3\,Pt\,Cl_2 \text{ with } 4\,Ad\,H \text{ and } 7\,H\,O$$
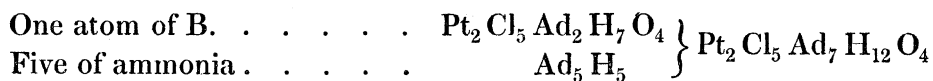$$Pt_2\,Cl_5\,Ad_2\,H_7\,O_4 \text{ and } Pt\,Cl\,Ad_2\,H_4\,O_3.$$
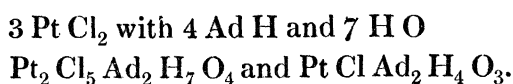
From the fawn-coloured substance B., the brown body C. may be simply formed, four equivalents of muriatic acid being removed, and one of ammonia given in their place. This is not equivalent substitution, but it still shows the origin of the body. If, however, the fawn-coloured substance all passed through the brown condition, the quantity of this last generated should, I consider, be much greater than it actually is found to be, and hence I am inclined to consider that

From two atoms of B. . .	$Pt_4\,Cl_{10}\,Ad_4\,H_{14}\,O_8$	$\Big\}\ Pt_4\,Cl_{10}\,Ad_{14}\,H_{24}\,O_8$
And ten atoms of ammonia	$Ad_{10}\,H_{10}$	

there are formed

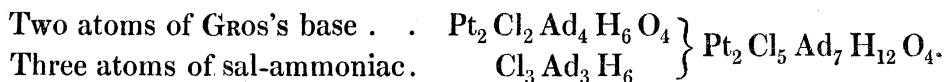|		
One atom of C.	$Pt\,Cl\,Ad_3\,H_4\,O_4$	
Two of GROS's base dry . .	$Pt_2\,Cl_2\,Ad_4\,H_8\,O_4$	$\Big\}\ Pt_4\,Cl_{10}\,Ad_{14}\,H_{24}\,O_8.$
Seven of sal-ammoniac . . .	$Cl_7\,Ad_7\,H_{14}$	

One source of the origin of the body D. (GROS's base) is thus explained, but it may be produced directly from the fawn-coloured substance as follows :—

$$\left.\begin{array}{l}\text{One atom of B.} \quad\quad Pt_2 Cl_5 Ad_2 H_7 O_4 \\ \text{Five of ammonia.} \quad\quad\quad\quad\quad Ad_5 H_5\end{array}\right\} Pt_2 Cl_5 Ad_7 H_{12} O_4$$

One atom of B. . . . . . $Pt_2 Cl_5 Ad_2 H_7 O_4$
Five of ammonia . . . . . $Ad_5 H_5$ $\Big\} Pt_2 Cl_5 Ad_7 H_{12} O_4$

produce

Two atoms of GROS's base . . $Pt_2 Cl_2 Ad_4 H_6 O_4$
Three atoms of sal-ammoniac . $Cl_3 Ad_3 H_6$ $\Big\} Pt_2 Cl_5 Ad_7 H_{12} O_4.$

In this case no brown substance (C.) should be formed.

The origin of the body E. from GROS's base has been already noticed.