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XVII. *On a new Metal, found in crude Platina.* *By* William Hyde Wollaston, *M.D. F.R.S.*

Read June 24, 1804.

Notwithstanding I was aware that M. Descotils had ascribed the red colour of certain precipitates and salts of platina, to the presence of a new metal; and although Mr. Tennant had obligingly communicated to me his discovery of the same substance, as well as of a second new metal, in the shining powder that remains undissolved from the ore of platina; yet I was led to suppose that the more soluble parts of this mineral might be deserving of further examination, as the fluid which remains after the precipitation of platina by sal ammoniac, presents appearances which I could not ascribe to either of those bodies, or to any other known substance.

My inquiries having terminated more successfully than I had expected, I design in the present Memoir to prove the existence, and to examine the properties, of another metal, hitherto unknown, which may not improperly be distinguished by the name of *Rhodium*, from the rose-colour of a dilute solution of the salts containing it.

I shall also take the same opportunity of stating the result of various experiments, which have convinced me, that the metallic substance which was last year offered for sale by the name of Palladium, is contained (though in very small proportion) in the ore of platina.

The colour of the solution that remains after the precipitation of platina, varies, not only according to its state of dilution, but also according to the strength and proportions of the nitric and muriatic acids employed. This colour, though principally owing to the quantity of iron contained in it, arises also in part from a small quantity of the ammoniaco-muriate of platina, that necessarily remains dissolved, and from other metals contained in still smaller proportions.

(A. 1.) To recover the remaining platina, as well as to separate the other metals that are present from the iron, I have in some experiments employed zinc, in others iron, for their precipitation. The former appears preferable; but, when the latter has been used, the precipitate may immediately be freed from the iron that adheres to it, by muriatic acid, without the loss of any of those metals which are at present the subject of inquiry.

(A 2.) Having in one instance dissolved such a precipitate in nitro-muriatic acid, and precipitated the platina by sal ammoniac, I suffered the remaining fluid to evaporate without heat; and obtained a mixture of various crystals, very different from each other in form and colour. From these, I selected for examination some that were of a deep red colour, partly in thin plates adhering to the sides of the vessel, and partly in the form of square prisms having a rectangular termination.

(A 3.) A portion of these crystals being heated in a small tube, yielded sal ammoniac by sublimation, and left a black residuum, which, by greater heat, acquired a brilliant metallic whiteness, but could not be fused under the blowpipe. Having obtained this substance from a distinctly crystallized salt, I was inclined to consider it as a simple metal; and, as I found it to be wholly insoluble in nitro-muriatic acid, I judged it not to be platina.

(A 4.) The crystals also, instead of being nearly insoluble, like the ammoniaco-muriate of platina, were dissolved in a small quantity of water, and gave a rose-coloured solution. Upon mixing this with a solution of platina, the ammonia was transferred by superior affinity to the latter, forming an ammoniaco-muriate of platina; and the precipitate was of a yellow colour. Consequently, the metal contained in the salt, was neither platina nor that which gives the red colour to the salts of platina.

It would be useless to detail my first unsuccessful experiments, made upon the properties of this metal, in hopes of discovering means by which its separation from platina might be effected; I shall therefore confine myself to the following process, which appears to be the most direct for procuring rhodium in a state of purity. In the same process also palladium is obtained, so as to afford a presumption, that it is rather a natural simple body, than any artificial compound.

(B 1.) Since the platina to be procured in this country, generally contains small scales of gold intermixed, as well as a portion of the mercury which the Spaniards employ for the separation of the gold, the platina used for my experiments, after being by mechanical means freed, as far as possible, from all visible impurities, was exposed to a red heat, for the purpose of expelling the mercury. It was then digested for some time in a small quantity of dilute nitro-muriatic acid, and frequently shaken, till the whole of the gold was dissolved, together with any impurities that might superficially adhere to the grains of platina.

(B 2.) Of the ore thus prepared, nearly 2½ ounces were then dissolved in nitro-muriatic acid, (diluted for the purpose of leaving as much as possible of the shining powder,) and the whole suffered to remain in a moderate sand heat, till completely saturated.

(B 3.) Such a portion of this solution was then taken for analysis, as corresponded to 1000 grains of the prepared ore. An ounce of sal ammoniac was next dissolved in hot water, and used for the precipitation of the platina. The precipitate obtained was of a yellow colour, and, upon being heated, yielded 815 grains of purified platina.

(B 4.) The water used for washing this precipitate having been added to the solution poured from it, a piece of clean zinc was immersed in it, and suffered to remain, till there appeared to be no further action upon the zinc. The iron contained in the ore (to the amount of 14 or 15 *per cent.)* remained in solution. The other metals had subsided, in the form of a black powder, which I estimated between 40 and 50 grains; but, as there was no occasion to weigh it with accuracy, I thought it better not to dry this precipitate, for, if it be heated, the rhodium is in danger of being rendered insoluble.

(B 5.) As I had previously ascertained that this precipitate would contain platina, rhodium, the substance called palladium, copper, and lead, the two last metals were first dissolved in very dilute nitric acid, aided by a gentle heat. The remainder, after being washed, was digested in dilute nitro-muriatic acid, which dissolved the greater part, but left as much as 4½ grains undissolved.*

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* It was presumed that this residuum consisted principally of the metal called by Mr. TENNANT Iridium; but, as it was accidentally mislaid, and was not examined, it might also contain a portion of rhodium.

(B 6.) To the solution were added 20 grains of common salt; and, when the whole had been evaporated to dryness with a very gentle heat, the residuum, which I had found, from prior experiments, would consist of the soda-muriates of platina, of palladium, and of rhodium, was washed repeatedly with small quantities of alcohol, till it came off nearly colourless. There remained a triple salt of rhodium, which by these means is freed from all metallic impurities.

(C 1.) This salt, having been dissolved in a small quantity of hot water, and let to stand 12 hours, formed rhomboidal crystals, of which the acute angle was about 75°.

(C 2.) It was then again dissolved in water, and divided into two equal portions. Of these, one was decomposed by a piece of zinc, and the other examined by the following reagents.

(C 3.) Sal ammoniac occasioned no precipitation; but, when a solution of platina was added to the mixture, a precipitate was immediately formed, and the colour of this precipitate was yellow; which again proves that the metal contained in this salt, is neither platina itself nor that which gives the red colour to its precipitates.

(C 4.) Prussiate of potash occasioned no precipitation, as it would have done, if the solution had contained palladium.

(C 5.) Hydro-sulphuret of ammonia, which would have precipitated either platina or palladium, caused no precipitation of this metal.

(C 6.) The carbonates of potash, of soda, or of ammonia, occasioned no precipitation; but the pure alkalis precipitated a yellow oxide, soluble by excess of alkali, and also soluble in every acid that I have tried.

(D 1.) The solution of this oxide in muriatic acid, upon being evaporated, did not crystallize; the residuum was soluble in alcohol, and of a rose colour. Sal ammoniac, nitre, or common salt, caused no precipitation from the muriatic solution; but formed triple salts, which were not soluble in alcohol.

(D 2.) The solution in nitric acid also did not crystallize. A drop of this solution, being placed upon pure silver, occasioned no stain. On the surface of mercury a metallic film was precipitated, but did not appear to amalgamate. The metal was also precipitated by copper and other metals, as might be presumed, from the usual order of their affinities for acids.

(E 1.) The precipitate obtained by zinc (C 2.) from the remaining half of the salt, appeared in the form of a black powder, weighing, when thoroughly dried, nearly 2 grains, corresponding to about 4 grains in the 1000 of ore dissolved.

(E 2.) When exposed to heat, this powder continued black; with borax, it acquired a white metallic lustre, but appeared infusible by any degree of heat.

(E 3.) With arsenic, however, it is, like platina, rendered fusible; and, like palladium, it may also be fused by means of sulphur. The arsenic, or the sulphur, may be expelled from it by a continuance of the heat; but the metallic button obtained does not become malleable, as either of the preceding metals would be rendered by similar treatment.

(E 4.) It unites readily with all metals that have been tried, excepting mercury; and, with gold or silver it forms very malleable alloys, that are not oxidated by a high degree of heat, but become incrusted with a black oxide, when very slowly cooled.

(E 5.) When 4 parts of gold are united with 1 of rhodium, although the alloy may assume a rounded form under the blowpipe, yet it seems to be more in the state of an amalgam than in complete fusion.

(E 6.) When 6 parts of gold are alloyed with 1 of rhodium, the compound may be perfectly fused, but requires far more heat than fine gold. There is no circumstance in which rhodium differs more from platina, than in the colour of this alloy, which might be taken for fine gold, by any one who is not very much accustomed to discriminate the different qualities of gold. On the contrary, the colour of an alloy containing the same proportion of platina, differs but little from that of platina. This was originally observed by Dr. LEWIS. "The colour was still so "dull and pale, that the compound (5 to 1) could scarcely be "judged by the eye to contain any gold."*

I find that palladium resembles platina, in this property of destroying the colour of a large quantity of gold. When 1 part of palladium is united to 6 of gold, the alloy is nearly white.

(E 7.) When I endeavoured to dissolve an alloy of silver or of gold with rhodium, the rhodium remained untouched by either nitric or nitro-muriatic acids; and, when rhodium had been fused with arsenic or with sulphur, or when merely heated by itself, it was reduced to the same state of insolubility. But, when 1 part of rhodium had been fused with 3 parts of bismuth, of copper, or of lead, each of these alloys could be dissolved completely, in a mixture of 2 parts, by measure, of muriatic acid, with 1 of nitric. With the two former metals, the proportion of the acids to each other seemed not to be of so much consequence as with lead; but the lead appeared on another account preferable, as it was most easily separated, when reduced to an insoluble muriate by evaporation. The muriate of rhodium had then the same colour

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* LEWIS's Philosophical Commerce of Arts, p. 526.

and properties, as when formed from the yellow oxide precipitated from the original salt. (D 1.)

(E 8.) The specific gravity of rhodium, as far as could be ascertained by trial on so small quantities, seemed to exceed 11. That of an alloy consisting of 1 part rhodium and about 2 parts lead, was 11,3; which is so nearly that of lead itself, that each part of this compound may be considered as having about the same specific gravity.

F. As it was expected that the alcohol employed for washing the salt of rhodium (B 6.) would contain the soda-muriates of platina and of palladium, the platina was first precipitated by sal ammoniac. This precipitate was of a deep red colour; and, when it had been heated, to expel the sal ammoniac, the platina which remained was of a dark gray colour.

(G 1.) To the remaining solution, after it had been diluted to prevent any further precipitation of platina, I added prussiate of potash, which instantly occasioned a very copious precipitate, of a deep orange-colour at first, but changing afterwards to a dirty bottle-green, which I ascribed to iron contained in the prussiate.

(G 2.) This precipitate, when dry, weighed 12½ grains. After it had been heated, it left a metallic residuum, in small grains, of a gray colour, weighing nearly 7 grains. A small portion of it being heated with borax, communicated a dark brown colour to the borax, as from iron, and acquired a bright metallic lustre, but could not be fused under the blowpipe. With sulphur, however, it fused immediately into a round globule, which, by floating upon mercury, appeared of less specific gravity than that metal.

(G 3.) The whole quantity was then treated in the same manner, and purified by cupellation with borax, till it cooled with a bright surface. From the globule the sulphur was expelled, by exposure to the extremity of the flame; and it became spongy and malleable, weighing in this state very nearly 5 grains.

(G 4.) A portion of this metal was dissolved in strong nitrous acid, was precipitated by green sulphate of iron, and, in other respects, possessed all the properties ascribed to the palladium offered for sale, in the printed paper that accompanied it, as well as others since noticed by Mr. CHENEVIX.

(G 5.) In its precipitation by prussiates, it differs most essentially from platina; and consequently is by no means difficult to be distinguished, or separated from it.

(G 6.) The action of muriate of tin upon the solutions of these metals, is also totally different. A dilute solution of platina, is thereby changed from a pale yellow to a transparent blood-red. A solution of palladium, on the contrary, usually becomes opaque, by the formation of a brown or black precipitate; but, if mixed in such proportion as to remain transparent, it changes to a beautiful emerald-green.

(G 7.) In the formation of triple salts with the alkalis, as observed by Mr. CHENEVIX, palladium may be said to resemble platina; but the salts thus formed are far more soluble than the corresponding salts of platina, and differ entirely, in the colour and form of the crystals.

(G 8.) The soda-muriate of palladium is a deliquescent salt; that of platina, on the contrary, forms permanent crystals.

(G 9.) The triple salts of platina, with either muriate of ammonia or of potash, form octaedral crystals of a yellow colour, that are very sparingly soluble in water. The corresponding salts of palladium, likewise resemble each other in every respect. The crystals are very soluble in water, but insoluble in alcohol; their form is that of a four-sided prism, and they each present a curious contrast of colour, that certainly is not observable in any known salt of platina.

(G 10.) Although the solution is of a deep red, the crystals are of a bright green when viewed transversely. In the direction of their axes, however, the colour is the same as that of the solution; but, on account of its extreme intensity, it is with difficulty distinguished in fragments that exceed $\frac{1}{100}$ of an inch in thickness. One consequence of this colour is nevertheless very observable; namely, that in viewing any crystal obliquely, it appears of a dull brown, that arises from a mixture of the red and green.*

The characters of palladium that have been enumerated, undoubtedly belong to none of the simple substances that we are

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* The change of colour above described, though certainly uncommon, is nevertheless not peculiar to the salts of palladium, but may be seen also in some kinds of tourmalin. Among those which come to us from Ceylon, some are transparent; and one variety is of a deep red in the direction of its axis, but of a yellowish-green when viewed transversely. There is also a corresponding, but opposite contrast of colours, that has been observed by MÜLLER, and described by BERGMANN, in some of the Tyrolese tourmalins. The general aspect of these stones is black, and apparently opaque. Some, however, of which the fracture is vitreous, are found to transmit a yellowish-red light when viewed transversely, but in the direction of their axis the colour is a dull bottle-green.

In each of these tourmalins, as well as in the salts of palladium, the colour in the direction of the axis, is at least 10 times more intense than in the transverse direction. A thin lamina, cut from the end of a Tyrolese tourmalin for this purpose, transmitted no visible light, till it was reduced to $\frac{1}{50}$ of an inch in thickness; and, when less than $\frac{1}{100}$ of an inch, it was not more transparent than another portion of the same crystal seen transversely, $\frac{1}{10}$ of an inch in thickness.

acquainted with; and no experiment that I have made, has tended to confirm the suspicion of its being a compound, consisting of any known ingredients. The experiments above related, show evidently, that the ore of platina contains a very small quantity of palladium; and it is not unlikely that this may have been a constituent part of some of the compounds obtained by Mr. CHENEVIX, and may have misled him, by some properties which he would consequently observe, into the supposition that he had formed palladium.

It is not, however, without having repeatedly endeavoured to imitate his experiments, that I have ventured to dissent from such authority. I made many attempts to unite pure platina with mercury, by solution, and by amalgamation; but without success, in any one instance.

From a solution of platina, carefully neutralized, as Mr. CHENEVIX directs, with red oxide of mercury, and mixed with a solution of green sulphate of iron, I indeed obtained such a precipitate of metallic flakes as he describes; but, upon examination of these flakes, they yielded mercury by distillation; and the remainder consisted of platina combined with a portion of iron, but had not any properties which I could suppose owing to the presence of palladium.

Upon comparing the specific gravity of this substance, which was said to be, at most, 11,8, with that of mercury or of platina, I was always strongly inclined to doubt the possibility of its being composed of these metals. I could recollect no one instance, in which the specific gravity of any compound is less than that of its lightest ingredient, and could not, without careful examination, admit the supposition, that mercury could be rendered lighter by intimate union with platina. It now appears fully confirmed that this persuasion, arising from uniform experience, was well founded; for, if we consider the difficulty of producing even an imperfect imitation of palladium, the failure of all attempts to resolve it into any known metals, the facility of separating it from any mixed solution of those which it has been supposed to contain, as well as the number and distinctness of its characteristic properties, I think we must class it with those bodies which we have most reason to consider as simple metals.