regia, adding a liberal amount of strong hydrogen sulphide water, and, after gentle heating, adding some nitrate of silver solution, so that the sulphide of gold would be enclosed and protected by the sulphide of silver. The sulphides were filtered off, put into a porcelain crucible and the filter burned off carefully. The metallic sponge remaining was enclosed in a small cornucopia of sheet lead, more silver added and cupelled.

After trying various methods of gathering a little gold out of a solution containing much silver, I have come to prefer strong hydrogen sulphide water as it is a most excellent precipitant for the gold and the co-precipitated silver protects the gold in the subsequent operations, which are simplified for the sulphide precipitate over a chloride of silver precipitate. In practice a limited amount of the hydrogen sulphide water is added to the solution, which is allowed to stand, with occasional stirring, a day or two, before filtering.

It is a very easy matter to exhibit the solubility of finely divided gold in strong nitric acid. By alloying a small piece of gold with $2^1/_2$–3 times its weight of silver, and dissolving out the silver in diluted nitric acid the gold will be left in good condition for such a test. Five minutes' hard boiling in a few cubic centimeters of strong nitric acid, which may have been previously boiled if desired, will give a distinctly yellow solution, which may be further tested for gold.

The discussion of the application of these results to the question of gold bullion assaying is reserved for a future paper on the general subject of the accuracy of such assaying, but I would say that the practical conclusion of Hillebrand and Allen,[1] that the solubility of the gold in the parting acid in ordinary ore assaying is negligible, is undoubtedly sound, unless the ores be most unusually rich in gold, but the excessive boiling in nitric acid sometimes used by them in their tests might dissolve an appreciable amount of gold in very rich ores and even this drastic treatment is not entirely sure to remove all of the silver, unless more than three parts of silver to one of gold were present originally.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

HALIDE BASES OF TANTALUM.

BY WILLIAM H. CHAPIN.

Received January 17, 1910.

Preparation of a Lower Bromide of Tantalum from the Pentabromide.

While attempting to produce a lower bromide of tantalum by reduction of the pentabromide in hydrogen, Van Haagen[2] obtained a small

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[1] *Loc. cit.*

[2] Thesis, "Tantalum and Some of Its Halides," Univ. of Pa., 1909.

amount of a new green compound which he found to possess very remarkable properties. It dissolved in water without decomposition, and it suffered no change even when its solution was boiled or evaporated in the open. In the solid state it was perfectly stable in the air. Moreover it possessed remarkable tinctorial powers, a few milligrams being sufficient to color several hundred cubic centimeters of water a bright emerald-green. Also a piece of silk dipped in its solution afterwards possessed a delicate green color which was not removed by washing. With ammonia the compound gave a brown hydroxide, which on exposure to the air became white. What the structure of the new bromide was Van Haagen was not able to determine because of lack of time and material, but an analysis attempted on a very small sample pointed to something approaching a tribromide.

A few months later while engaged in the preparation of material for further investigation, we noticed the announcement of a new chloride of tantalum by Chabriè.[1] The properties of this compound, as described by its discoverer, corresponded in almost every detail with those of Van Haagen's bromide. The method of preparation, however, was entirely different, consisting essentially in the reduction of tantalum pentachloride in the dry way by means of sodium amalgam. Chabriè noted the crystalline form of his chloride, and also by means of the spectroscope proved its identity as a compound of tantalum. Owing to scarcity of material, however, he, too, gave but a single analysis; but from the results obtained believed himself justified in ascribing to the compound the formula $TaCl_2 2H_2O$.

A method being needed by which to prepare the bromide in larger quantity, Chabriè's announcement was welcome, and upon trial it was found that the method could be used with fair success. It finally was the only method used, although it was found to yield better results after slight modification. The following is an outline of the procedure: One part of tantalum pentabromide was mixed with four parts of 3 per cent. sodium amalgam, and the mixture quickly introduced into a combustion tube of hard glass. The air was then exhausted by means of a water pump, and the tube gradually heated, finally to redness. The reduction product was allowed to cool completely in a vacuum, and was then removed and thrown into water acidulated with hydrobromic acid. The by-products were filtered off, and the intensely green solution concentrated on the water bath until the acid present finally caused the compound to separate as a crystalline powder, leaving the supernatant liquid of a yellowish color. This powder was removed, washed with hydrobromic acid, and finally dried on a water bath.

The yield of the green bromide obtained by this method was always

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[1] *Compt. rend.*, 144, 804 (1907).

very slight, averaging only about 15 per cent. of the theory. Altogether 20 grams were obtained, and to do so 200 grams of the pentabromide were used. Just what this means can be appreciated by one who has made 200 grams of pure tantalum pentabromide. Fortunately the compound as first obtained was remarkably pure, and for that reason there was no necessity for repeated crystallizations and consequent loss of material.

The by-products mentioned above were important since they represented by far the larger part of the tantalum used. They seemed to consist of some lower oxide. While wet they were of a brown color, but upon drying became gray, and upon strong ignition they became pure white, and appeared then to be ordinary tantalum oxide. As will be shown later these by-products were turned to good account in establishing the identity of the bromide.

Some of the properties of this green bromide have already been mentioned, among them its high coloring power. As evidence of this it might be mentioned that a solution containing 1 gram per hundred cubic centimeters possessed such an intense color that a layer half an inch thick was perfectly opaque. Examined under the microscope the substance was found to consist of beautiful hexagonal crystals. No crystals over 0.25 mm. in diameter were ever seen, but they were often very brilliant, causing the powder to sparkle when placed in the sunlight. As ordinarily prepared the compound was black, but if ground down in a mortar it became dark green in color.

Identification of the Bromide as a Compound of Tantalum.

Although Chabriè had shown his chloride to be a tantalum compound it was not thought superfluous to obtain definite proof as to the identity of the new bromide. To this end the oxides mentioned above as "by-products" were collected and converted into the pentabromide. This was then reduced by means of sodium amalgam, producing a fresh yield of the green bromide, and of course more of the "by-products." The latter being collected, the process was repeated until finally the residue obtained was too small in amount to work with. If the bromide were not a tantalum compound the yield should have grown smaller each time the cycle was repeated, until finally a residue was obtained which would not respond to the reaction. No such diminution in the yield was noticed, however.

As further proof of the identity of the new bromide a portion was decomposed, and converted into the well-known double fluoride, K_2TaF_7. The product thus obtained possessed all the characteristic properties of this salt; and carefully conducted analyses failed to disclose any difference, as the following results will show:

K as K_2SO_4	Found 44.32,	Calculated	44.46 per cent.
Ta as Ta_2O_5	Found 56.40,	Calculated	56.32 per cent.

These results serve to confirm those mentioned in the last paragraph, and are to be accounted for only by assuming that we are here dealing with a tantalum compound.

Structure of the Bromide.

As has already been mentioned Chabriè regarded his compound as a dichloride, $TaCl_22H_2O$; and considering the close similarity of the two bodies there seemed no reason to doubt that the bromide would be found to possess an analogous structure, as represented by the formula $TaBr_22H_2O$. However, as the following example will show, the results of the analyses did not agree with this supposition:

	Found, per cent.	Calculated, for $TaBr_22H_2O$, per cent.
Ta	46.60	48.01
Br	48.06	42.44
H_2O	5.46	9.55
	100.12	100.00

The methods used for the analyses were very simple. The tantalum was precipitated from the boiling solution by means of ammonia, and subsequently ignited to the oxide Ta_2O_5. For the determination of the bromine one of two methods was employed: *first*, the filtrate from tantalum was acidified with nitric acid, and the bromine precipitated as silver bromide; or *second*, the filtrate from tantalum hydroxide was simply evaporated to dryness in a weighed porcelain crucible, and the residual ammonium bromide dried to constant weight in an oven at 100°. The results obtained by use of these two methods were surprisingly concordant, the maximum variation being less than 0.1 per cent. After the second method had been thoroughly tested it was given the preference, since its use permitted the application of a very simple check on the tantalum value. This consisted in the decomposition of the ammonium salt by means of nitric acid, and subsequent weighing of a very slight residue of oxide which had escaped the filter. It may be mentioned that this residue never in any case exceeded 0.2 mg. and in most cases was much less than this. The ammonium bromide could, of course, have been expelled simply by heating, but this procedure would almost certainly have caused the expulsion of the tantalum residue, either mechanically or otherwise. The values for tantalum as thus obtained were very concordant, the maximum variation in a series of five analyses being 0.1 per cent.

The percentage of water in the bromide was determined by mixing with litharge to retain the bromine, placing the mixture in a porcelain boat, and then heating in a combustion tube in a current of air, the water being collected in a calcium chloride tube. Three determinations made after this manner gave the following percentage: 5.40 per cent., 5.50 per cent., 5.50 per cent. or an average of 5.46 per cent. It was found impossible to determine the water without the use of the litharge, since the compound invariably broke down, giving off hydrobromic acid before all the water was expelled.

When, after repeated analyses, it was seen that the composition of the compound as first obtained did not correspond to that of dibromide it was thought that it might not be a single substance, but a mixture of two substances, for example the dibromide and the tribromide. With this in mind the whole stock of the bromide was recrystallized in such a way as to separate it into several fractions. In this way it was hoped to cause at least a partial separation of the different compounds if more than one were present. However, upon analyzing the different fractions, absolutely no difference could be detected, and the notion that the substance was not homogeneous had to be abandoned.

Accepting the results of the analysis as final, an empirical formula was calculated; thus, $Ta_6Br_{14}7H_2O$ for which the exact values would be:

	Per cent.
Ta	46.58
Br	48.01
H_2O	5.41
	100.00

Comparison of these values with those obtained from analysis will show a remarkably close agreement.

It scarcely seemed possible that all these fourteen atoms of bromine could exist in the same relation to the tantalum. The more likely possibility seemed to be the presence of a complex, in which a part of the bromine would be more loosely bound than the rest. To test this possibility the solution of a weighed amount of the bromide was treated with silver nitrate, the reaction being carried out in the cold to prevent decomposition. In two such determinations the percentages of bromine obtained were respectively 7.02 and 6.76, an average of 6.89. Now the total percentage of bromine corresponding to fourteen atoms was, as already shown, 48.06. Of this the above value is almost exactly one-seventh, and therefore corresponds to *two atoms*. To make the formula agree with the experimental data, then, it should be written $(Ta_6Br_{12})Br_27H_2O$. In water solution the molecule is undoubtedly divided into a positive complex ion and two negative bromine ions.

As further evidence of the nature of the bromide its molecular weight was determined both by boiling point and freezing point methods. For the boiling point method propyl alcohol (b. p. 99°) was chosen as the best available solvent. Using 1 gram of the salt in 16 grams of solvent the observed rise in two experiments was respectively 0.055 and 0.059°, corresponding to apparent molecular weights of 1800 and 1700, or an average of 1750. Now, an ordinary salt when dissolved in propyl alcohol in the proportion used in this experiment is dissociated to the extent of about 15 per cent. Allowing, then, for *15 per cent. dissociation*, an observed *molecular weight of 1750*, and *three ions* to the molecule, the true molecular weight may be calculated with a fair degree of certainty by use of the formula, $M = Mo(x(n - 1) + 1)$ where Mo = the observed molecular weight, x = the degree of dissociation, and n the number of ions per molecule, thus $M = 1750\ (0.15(3 - 1) + 1) = 2275$. The molecular weight calculated from the formula is 2332.

A freezing point determination, using water as the solvent, gave the following results: 1 gram of the salt in 16 grams of solvent gave a lowering of 0.162°, corresponding to an apparent molecular weight of 720, or about one-third the true molecular weight. This was exactly the result expected, since in water solution at the dilution here employed ordinary salts are almost completely dissociated.

Now, bringing together the facts stated in this section: Analysis has shown that the new green compound is not a dibromide, but that its different constituents are present in the proportions represented by the formula $Ta_6Br_{14}7H_2O$. The reaction with silver nitrate indicates that in water solution one-seventh of the bromine is in the ionic condition. This should be indicated by writing the formula $(Ta_6Br_{12})Br_27H_2O$. Molecular weight determinations by both freezing point and boiling point methods point to a molecule of approximately the same size as that indicated by the empirical formula. Hence it is believed that this is the true formula of the compound.

Replacement of the Ionized Bromine.

As would probably be expected it was found possible to replace the two ionized bromine atoms by other halogens, by hydroxyl, and by almost any acid radical. Replacement of bromine by hydroxyl was effected by treating a weighed amount of the salt (in solution) with just sufficient standard sodium hydroxide solution to complete the reaction:

$$(Ta_6Br_{12})Br_2 + 2NaOH = (Ta_6Br_{12})(OH)_2 + 2NaBr.$$

The hydroxide separated in crystalline form, and being only slightly soluble in water, left the solution nearly colorless. Analysis showed it to be $(Ta_6Br_{12})(OH)_210H_2O$. It was soluble in alcohol, insoluble in ether, consisted of thin hexagonal plates, and was stable in the air below 100°.

The replacement by chlorine could be brought about by dissolving the hydroxide in hydrochloric acid, but was most easily effected by simply evaporating a solution of the bromide with hydrochloric acid. The interesting point about this reaction was the fact that only two atoms of bromine were replaced, even when concentrated acid was used and the evaporation repeated four times. That the chlorine took the place of the ionized bromine was proved by the fact that treatment of the resulting mixed halide with silver nitrate or sulphate produced a precipitation of silver chloride containing no bromide. The formula of the compound, as shown by analysis, is $(Ta_6Br_{12})Cl_27H_2O$.

Replacement of bromine by iodine was effected by first preparing the hydroxide, and then dissolving this in hydriodic acid. Its formula is $(Ta_6Br_{12})I_27H_2O$.[1]

After following the bromide through these various transformations it becomes evident that a certain part of the molecule (Ta_6Br_{12}) acts like a single element or *base*, passing unchanged through a whole series of compounds. It is therefore proposed that this be given the name *bromotantalum*. The original compound $(Ta_6Br_{12})Br_27H_2O$ will then be called *bromotantalum bromide*, and the other compounds mentioned above will be respectively, *bromotantalum hydroxide, bromotantalum chloride*, and *bromotantalum iodide*.

Chabrie's Chloride.

As already mentioned the properties of Chabriè's chloride correspond very closely with those of the bromotantalum compounds. Even the crystalline form was identical. These facts made it seem highly probable that the formula should be $(Ta_6Cl_{12})Cl_27H_2O$ and not $TaCl_22H_2O$, as Chabriè writes it. Having only a very small amount of material to work with, which at the same time may not have been pure, he could easily have made such a mistake. Moreover, Chabriè determined the water in his compound by simply heating in an atmosphere of carbon dioxide, or at least he does not mention having used a retainer for the chlorine. This procedure would certainly not succeed in case of the bromide, and may account for a high value for water and a low value for chlorine.

To settle the matter we prepared the chloride according to Chabriè's method and, upon analysis, obtained the following values:

	Found, per cent.	Calculated for $(Ta_6Cl_{12})Cl_27H_2O$, per cent.
Ta	63.80	63.58
Cl	29.40	29.03
H_2O	7.20	7.37

Chabriè reports the following:

	Found, per cent.	Calculated from $TaCl_22H_2O$, per cent.
Ta	63.83	63.1
Cl	23.85	24.4
H_2O	12.22	12.5

It should be noted that his most reliable value—the value for tantalum,

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[1] For further details regarding these mixed compounds refer to the author's thesis "Halide Bases of Tantalum," Univ. of Pa., 1909.

—agrees much more closely with the complex formula than with the simple one, and the other values can be accounted for as mentioned above. His chloride is therefore without doubt the exact analogue of the bromotantalum bromide, and should be called "chlorotantalum chloride."

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METALLIC TITANIUM.

BY M. A. HUNTER.

Received January 19, 1910.

All the earliest attempts at the preparation of metallic titanium resulted for the most part in the production of the various nitrides which from their metallic appearance were always mistaken for the metal. Thus Wollaston[1] mistook the cyanonitride which is frequently found in the slag and metal from the blast furnace for the metal. Again Berzelius[2] reduced potassium titanifluoride with potassium and obtained a black powder which on polishing showed a metallic streak. This substance was insoluble in hydrofluoric but easily soluble in a mixture of hydrofluoric and hydrochloric acids and whatever it may have been it certainly was not metallic titanium, for titanium is immediately soluble in hydrofluoric acid. Rose[3] produced a dark blue or a black powder insoluble in hydrochloric acid from the compound $TiCl_4.4NH_3$ by heating alone or by reduction with metallic sodium. This material, which he considered to be metallic titanium, is now known to be Ti_3N_4.

Wöhler[4] and Wöhler and Deville[5] in their attempts at producing the metal succeeded in all cases in obtaining the nitrides. Up to this time no analysis of the material produced by the experimenters above mentioned appears to have been made. The confusion which existed in the earlier literature with regard to the pure metal titanium and its nitrides is therefore easily explained.

Nilson and Petersson[6] attempted to prepare metallic titanium by reducing $TiCl_4$ with sodium in an air-tight cylinder of solid steel. The metal was obtained in yellow scales (with frequently a bluish surface color) containing about 95 per cent. of titanium, the chief impurity being the monoxide of titanium.

Then Moissan[7] by reducing titanium dioxide at the extreme temperatures of his electric furnace produced a material containing 5 per cent. of carbon. On reheating this material with titanium dioxide, the amount of

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[1] *Phil. Trans.*, 17, 1823.

[2] *Pogg. Ann.*, 4, 3 (1825).

[3] *Ibid.*, 16, 57.

[4] *Compt. rend.*, 29, 505 (1849).

[5] *Ibid.*, 45, 480 (1857).

[6] *Z. physik. Chem.*, 1, 25 (1887).

[7] *Compt. rend.*, 120, 290 (1895).