monds at the point of impact, with which it is hoped that many of the difficulties with which we have had to contend will disappear.

STANFORD UNIVERSITY, CAL.,
June 5, 1913.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

HALIDE BASES OF COLUMBIUM.

BY HERBERT S. HARNED.

Received July 23, 1913.

In 1907 Chabriè[1] reported a lower hydrated chloride of tantalum to which he gave the formula $TaCl_2.2H_2O$. He obtained this substance by heating tantalum pentachloride with sodium amalgam in a tube of hard glass, which was sealed at one end and evacuated by means of a suction pump.

In 1908, Van Haagen,[2] working with the halides of tantalum and their products of reduction, got, by passing tantalum pentabromide through a red hot tube in a current of hydrogen, a greenish black substance which was soluble in water to an intense emerald-green solution. Every attempt to produce by this method a sufficient quantity of material for investigation proved of no avail.

During the winter of 1908–1909, Chapin[3] continued this work. He used the Chabriè method of reduction on tantalum pentabromide. The reaction mass was boiled with water containing a little hydrobromic acid. An intense emerald-green solution similar to that described by Van Haagen was obtained and, on evaporation, black crystals separated. These were filtered off and dried. When ground to a powder, this substance had a green color. It was very soluble in water, the solution possessing a remarkable coloring power (1 gram in 100 cc. of water giving such an intense coloration that a layer half an inch thick was opaque). Ammonia water precipitated a brown hydroxide from this solution.

Chapin carried out a number of analyses which showed that this compound possessed a composition represented by the formula $(Ta_6Br_{12})Br_2H_2O$. Molecular-weight determinations by both the freezing- and boiling-point methods also indicated this constitution. Only one-seventh of the bromine acted as ion. The tantalum seemed to be present in a complex cation.

From this compound Chapin prepared an interesting series of derivatives.

He also made Chabriè's chloride from tantalum pentachloride and proved that it was $(Ta_6Cl_{12})Cl_2.7H_2O$.

The object of the present investigation was to find out whether these

---

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

[2] Thesis, University of Pennsylvania, 1908.

[3] THIS JOURNAL, 32, 323 (1910).

compounds were peculiar to tantalum or whether it was possible to obtain similar derivatives with columbium. The Chabriè reaction was used.

The details of the method and the form of apparatus employed are given accurately in Chapin's paper, so it will not be necessary to describe them here. It seemed desirable to investigate a little more closely the temperature conditions. To this end, 10 grams of columbium pentachloride were mixed with 70 grams of 3% sodium amalgam and allowed to react at a temperature just high enough to cause the reaction to propagate itself entirely through the mixture. On treating the reaction mass with water a brownish black oxide was obtained and a brown solution which quickly decomposed, giving more of the brown oxide. On repeating this experiment and on heating the first product of the reaction to a red heat for a period of one hour, then allowing to cool to room temperature without breaking the vacuum, and finally boiling the mass with water, an intense olive-green solution was obtained, and, at the same time, a precipitate of the brown oxide. Two reactions seemed to take place here: first, at lower temperatures, the columbium pentachloride was reduced to a chloride which was easily decomposed to the dark brown oxide on the addition of water; secondly, this chloride, at higher temperatures, was partially converted into the substance which gave the green solution. The olive-green colored liquid was stable and promised to be very similar to the emerald-green solution obtained by Chapin. One hundred and fifty grams of columbium pentachloride were reduced by this method, the most satisfactory temperature used being just sufficient to collapse the Jena tube. The substance which gave the olive-green colored solution was only soluble in boiling water and a large quantity was needed for its complete solution. The hot liquid was filtered from the brown oxide and evaporated after the addition of a small quantity of hydrochloric acid. Small, black, shiny crystals separated; these were filtered off and recrystallized. The crystals obtained from this second crystallization were perfectly homogeneous and, since they dissolved with so much difficulty in water, it was thought that a high degree of purity must have been reached. They were filtered upon a Monroe crucible and dried in an air bath at 80° to constant weight. From 150 grams of columbium pentachloride only 6 grams of this stable lower chloride were obtained.

It could be heated to 100° without decomposition. The crystals were so small that the crystallin form could not be observed with the naked eye. When powdered, the substance was olive-green in color. It was insoluble in cold water but soluble in boiling water. On addition of ammonia water to this solution, little or no decomposition took place, and, even after long-continued boiling with ammonia, it was not completely decomposed. Chapin's bromide was completely decomposed by this reagent. Concentrated nitric acid decomposed a boiling solution of this compound, giving first a brown coloration, and finally a separation of columbic hydroxide. The compound was completely soluble in concentrated alkalies, yielding a dark brownish green colored solution.

Since the chloride was not easily decomposed by boiling ammonia water, the following method of analysis was adopted: The chloride was dissolved in boiling water and concentrated nitric acid was added to the boiling liquid until complete decomposition took place. This required about one minute. An excess of ammonia water was then added and the solution again boiled for a few minutes. The columbic hydroxide, thus completely precipitated, was filtered off, washed with boiling water, ignited and weighed. Ammonium carbonate and nitrate solutions cannot be used in washing columbic hydroxide precipitated in this manner, because they dissolve quite a considerable quantity of it. On washing the precipitate with boiling water, a small quantity of the hydroxide invariably dissolved, forming a colloidal solution. This was boiled with a little more nitric acid and again precipitated with ammonia, filtered off, ignited and weighed. The filtrate from the columbic hydroxide was acidified with nitric acid and the chlorine was precipitated in the usual way with silver nitrate, filtered onto a gooch and weighed. The following results were obtained, corresponding to a body of the composition: $(Cb_6Cl_{12})Cl_2.7H_2O$, analogous to $(Ta_6Br_{12})Br_2.7H_2O$:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5 gram	0.1349	0.1353	Cb	47.25	47.38
AgCl	0.3395	0.3394	Cl	41.99	41.98

It was thought that it would be well to determin the columbium in this compound by two methods entirely different from the above. (1) To ignite a weighed sample with nitric acid and obtain columbic oxide directly. (2) To decompose the substance with concentrated sulfuric acid, heat to fumes, dilute with water and boil, filter off the precipitated columbic hydroxide, wash with boiling water until free from sulfuric acid, and finally ignite to the oxide and weigh. The following results were obtained:

Weight of sample, 0.2000 gram.

		Found.	Calc.		Found. Per cent.	Calc. Per cent.
Method 1	Cb_2O_5	0.1342	0.1353	Cb	47.00	47.38
Method 2	Cb_2O_5	0.1349	......	Cb	47.25	...

The determination of the ionized chlorine by the gravimetric method would necessitate the precipitation of silver chloride from a cold solution not containing nitric acid, for, if nitric acid be present, decomposition of the complex cation would likely occur. If a hot solution be used, a high chlorine result was to be expected, due to the secondary dissociation of the complex radical. Chapin found, in the case of $(Ta_6Br_{12})Br_2.7H_2O$, that dilution affected the result considerably. Since 0.2 gram of the chloride of columbium required at least 100 cc. of water for its solution, high results were to be feared. It was concluded to titrate the ionized chlorine with a 0.1 *N* silver nitrate solution, using a silver concentration cell.[1] The e. m. f. of the cell remains nearly constant as long as chlorine ions are present in the solution. After all the chloride ions have been removed, the e. m. f. rises rapidly, due to the rapid increase of silver ions in the solution. The apparatus used was identical with that described by Hildebrand and Harned[2] in their paper on the determination of magnesium by means of the hydrogen electrode with the single exception that a silver-coated platinum electrode was employed in place of the hydrogen electrode.

The determination of the ionized chlorine in the chloride was carried out as follows: 0.2 gram sample was dissolved in 150–200 cc. water and the solution was allowed to cool to room temperature. The silver electrode and calomel electrode were then placed in the solution. Leakage of the solution of potassium chloride in the calomel electrode into the columbium solution was found to occur. To prevent this, a solution of potassium nitrate, free from chlorides, was drawn up into the side arm of the calomel electrode. This proved entirely satisfactory. 0.1 *N* silver nitrate was then added, 0.2 cc. at a time, and a reading of the e. m. f. of the cell taken after each addition. 3.9 cc. of 0.1 *N* silver nitrate were used to titrate the ionized chlorine,

Weight of sample, 0.2000 gram.

	Found.	Calc. (one-seventh total chlorine).
Grams of ionized Cl	0.0138	0.0120

which would mean that one-seventh of the total chlorine in this compound was ionized in solution. This was exactly analogous to the behavior of Chapin's bromide.

The contents of the cell were then washed into another beaker, the silver and calomel electrodes were washed and the columbium and total chlorine were determined by the method outlined above, namely, decomposition by means of concentrated nitric acid and ammonia water. The following results were obtained:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5	0.1358	0.1353	Cb	47.55	47.38
AgCl	0.3396	0.3394	Cl	42.00	41.98

To determin the water in this compound, the chloride was intimately mixed with about 10 times its volume of ignited lead oxide and heated to

---

[1] Behrend, *Z. physik. Chem.*, 11, 426 (1893).

[2] Hildebrand and Harned, Vol. I, 8th International Congress of Applied Chemistry.

300° C. in a current of dry air. The water was carried over into a calcium chloride tube and weighed. The following results were obtained:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
1. H_2O.........	0.0224	0.0213	H_2O..........	11.2	10.64
2. H_2O.........	0.0218	0.0213	H_2O..........	10.9	10.64

They show conclusively that the compound is analogous to $(Ta_6Br_{12})Br_2.7H_2O$ and that its formula is probably $(Cb_6Cl_{12})Cl_2.7H_2O$.

Chapin gave to his compound the name "bromo-tantalum bromide" and to the complex cation the name "bromo-tantalum." The other compounds he called by the corresponding names, *e. g.*, bromo-tantalum hydroxide, bromo-tantalum chloride. The same nomenclature has been adopted here and the chloride will be referred to as chloro-columbium chloride.

One gram of the latter was dissolved in as little water as possible and the solution allowed to cool to room temperature. Just enough 0.1 *N* sodium hydroxide was added to replace the two ionized chlorine atoms with hydroxyl groups. On standing, a black microcrystalline body separated. This was filtered upon a Munroe crucible, washed with cold water and then with ether. It was dried in a desiccator over calcium chloride. One gram of chloro-columbium chloride yielded 0.6 gram of this supposed chloro-columbium hydroxide.

It was insoluble in water but soluble in both acids and alkalies. The acid solutions were olive-green in color and probably contained the corresponding salts (*e. g.*, chloro-columbium nitrate, chloro-columbium sulfate). The alkalin solution was dark brownish green in color and probably contained $(Cb_6Cl_{12})(ONa)_2$ aq., but attempts to isolate anything from this solution, stable enough to analyze, proved fruitless.

To analyze this hydroxide, the weighed substance was washed into a beaker and about 100 cc. of water were added. The solution was brought to boiling, concentrated nitric acid was added and the boiling continued until the nitrate, which was first formed, was completely decomposed and oxidized. The solution was made ammoniacal and the analysis was continued in precisely the same manner as described under chloro-columbium chloride. The results seemed to indicate the formula $(Cb_6Cl_{12})(OH)_2.8H_2O$, as shown by the following:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5........	0.1379	0.1376	Cb........	48.28	48.15
AgCl........	0.2998	0.2956	Cl.........	37.08	36.56

The chlorine results were not very satisfactory. Therefore, another one-gram sample of chloro-columbium chloride was converted to the hydroxide by the method outlined above. Its analysis gave the following:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5........	0.1380	0.1367	Cb........	48.32	48.15
AgCl........	0.2968	0.2956	Cl.........	36.70	36.56

The water was determined as with chloro-columbium chloride, only in this case it was necessary to raise the temperature of the tube higher in order to drive off the last traces.

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Fer cent.
H_2O...........	0.0275	0.0278	H_2O........	13.75	13.90

This analysis corresponds very closely to that calculated from the formula $(Cb_6Cl_{12})(OH)_2.8H_2O$.

	Calc. Per cent.	Found. Per cent.
Cb_6...............................	48.15	48.32
Cl_{12}..............................	36.56	36.70
9 H_2O............................	13.90	13.75
O (by difference)....................	1.39	1.23

Two-tenths of a gram of chloro-columbium hydroxide were weighed out in a platinum crucible and then dissolved in dilute hydrobromic acid. This solution was evaporated to dryness on a water bath and the crucible and its contents reweighed. It was to be expected that the bromide would have an analogous constitution to the chloride and therefore be $(Cb_6Cl_{12})Br_2.7H_2O$. The theoretical increase in weight calculated from the ratio

$$(Cb_6Cl_{12})(OH)_2.8H_2O \quad \text{to} \quad (Cb_6Cl_{12})Br_2.7H_2O$$

equaled 0.0185 gram. The observed increase in weight was 0.0186 gram. This is confirmation of both the formula of the hydroxide and bromide. The bromide was similar in appearance to the chloride but differed by the fact that it dissolved in a small quantity of cold water. Ammonia water precipitated from the solution of the bromide small, shiny crystals, probably the hydroxide, but no decomposition took place. The analysis of the bromide was carried out by the same method as that used for the analysis of the chloride and hydroxide. The following results were obtained and agree closely with those calculated from the formula $(Cb_6Cl_{12})Br_2.7H_2O$:

Weight of sample, 0.2186 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5..........	0.1377	0.1375	Cb	44.11	44.07
AgCl + AgBr..	0.3621	0.3602	Cl + Br....	46.25	46.03

A water determination of the bromide was not made.

The Investigation of the Alkalin Solution of Chloro-Columbium Chloride.

Koppel,[1] in a paper on "The Constitution of the Halogen Compounds of Bivalent Molybdenum," mentions the series of compounds prepared by Chapin and their similarity to the molybdenum compounds. Since $(Mo_3Cl_4)Cl_2.6H_2O$ is soluble in concentrated alkalies and since double salts of the type $(Mo_3Cl_4)Cl_2.2KCl.2H_2O$ are precipitated from these solutions by concentrated acids, the question is naturally raised as to the constitution of the alkalin solution of chloro-columbium chloride and whether double salts can be formed by the addition of strong acids to this solution. Chapin had mentioned that bromo-tantalum hydroxide was soluble in concentrated alkalis and that the solution probably contained $(Ta_6Br_{12})(ONa)_2$ aq. He went no further than this point with the investigation of the alkalin solution.

It has been mentioned that both chloro-columbium chloride and hydroxide were soluble in concentrated alkalis, giving a dark brownish green solution. On evaporating this solution in a vacuum, no substance of a homogeneous nature separated. On the addition of a large quantity of concentrated hydrochloric acid, a brown powder was precipitated.

It appeared perfectly homogeneous. When ground in a mortar, the color of the powder was brown and was distinctly different from the olive-green color of chloro-columbium chloride. It was soluble with greater difficulty in boiling water than chloro-columbium chloride and its solution at first appeared a yellowish green but changed, on boiling, to an olive-green. From this olive-green solution, chloro-columbium chloride could be obtained by evaporation, after the addition of a little hydrochloric acid.

The brown compound was analyzed by the same method as was adopted with chloro-columbium chloride and hydroxide. There was a possibility that this substance contained potassium and was a double salt. To determin whether this was true, the filtrate from the silver chloride precipitate, which contained the excess of silver nitrate, was boiled with hydrochloric acid and the precipitated silver chloride was filtered off. The filtrate was evaporated to dryness, heated until the ammonium salts were driven off, and the weight of the residue was obtained. This amounted to only 0.3 mg., showing that the brown compound was not a double salt. The following analyses were obtained and agree very closely with the values calculated from $Cb_6Cl_{14}.9H_2O$.

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5	0.1285	0.1313	Cb	45.00	45.98
AgCl	0.3321	0.3293	Cl	41.08	40.74

---

[1] Koppel, *Z. anorg. Chem.*, 77.

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5..........	0.1317	0.1313	Cb........	46.10	45.98
AgCl..........	0.3314	0.3293	Cl.........	40.99	40.74

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5..........	0.1314	0.1313	Cb........	46.00	45.98
AgCl..........	0.3322	0.3293	Cl.........	41.08	40.74

A water determination was made by the method previously used and the following result obtained:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
H_2O...........	0.0280	0.0266	H_2O..........	14.0	13.28

As the brown chloride was converted upon solution into the green chloride, an ionized chlorine determination was not made.

These figures seemed to show that the brown compound had the formula $Cb_6Cl_{14}.9H_2O$. If the difference between the brown chloride and the green chloride was due only to two molecules of water of crystallization, simple heating of the brown chloride to 100° should give the green chloride and the loss in weight should indicate the completeness of the reaction. Therefore, 0.2 gram of the brown chloride was heated to 100° but, at this temperature, it decomposed, giving off a white powder which coated the inside of the crucible. At the same time, no change from the brown to the green chloride was noticed. On the other hand, the action of boiling water or the action of water at room temperature for a long period of time (a week) gave an olive-green solution, from which the green compound could be precipitated by evaporation with dilute hydrochloric acid. These experiments would indicate that there was a constitutional difference between the brown and the olive-green chlorides.

Since the action of water converts the brown into the green compound, it was thought that, if the solution of the green compound be precipitated by concentrated hydrochloric acid, the brown compound would be obtained. A powder was found to be precipitated by concentrated hydrochloric acid, but when this was dried and ground in a mortar, it gave the same olive-green color as $(Cb_6Cl_{12})Cl_2.7H_2O$ and on analysis proved to be this compound:

Weight of sample, 0.2000 gram.

	Found.	Calc.		Found. Per cent.	Calc. Per cent.
Cb_2O_5........	0.1340	0.1353	Cb..........	46.92	47.38
AgCl........	0.3394	0.3394	Cl...........	41.98	41.98

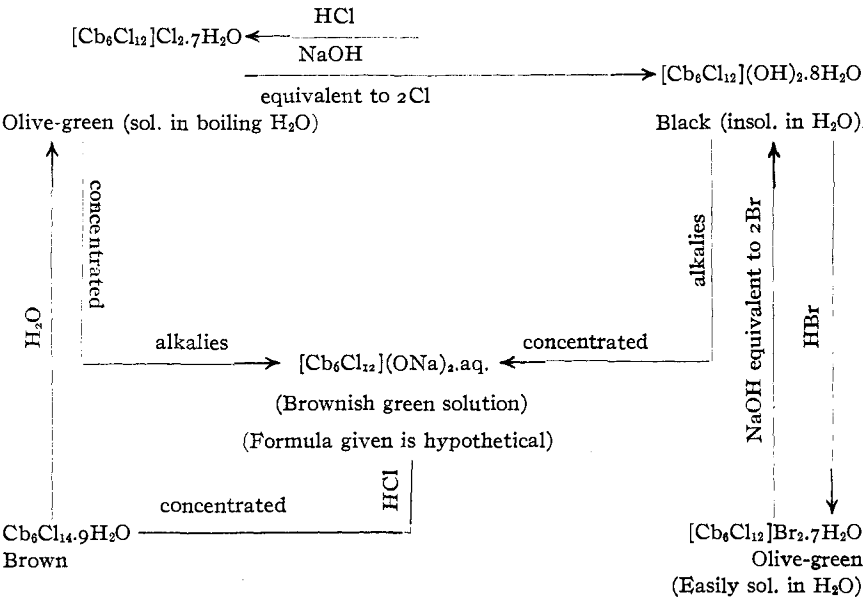
The fact that the brown compound could be prepared from the alkalin solution, but not from the solution of $(Cb_6Cl_{12})Cl_2.7H_2O$ in water, afforded additional evidence that there was a constitutional difference between the brown and the green chlorides.

The present investigation had to end at this point because the material had been exhausted and lack of time prevented the preparation of more.

Summary.

1. Columbium furnishes the compound represented by the formula $(Cb_6Cl_{12})Cl_2.7H_2O$, exactly analogous to the bromide of tantalum prepared by Chapin.

2. The following table gives the most important characteristics and relations of the members of this group of derivatives:



UNIVERSITY OF PENNSYLVANIA.

THE HYDROTHERMAL FORMATION OF SILICATES, A REVIEW.

By GEORGE W. MOREY AND PAUL NIGGLI.

Received July 23, 1913.

The study of the conditions of mineral formation and stability has been carried on principally by two different methods, the fusion method and the hydrothermal method. By far the greater number of syntheses have been made by the fusion method, in open vessels at high temperatures, the minerals obtained being those which will separate from dry melts. In the hydrothermal method the components are subjected to the action of water, at temperatures generally near, though often considerably above, the critical temperature of water (ca. 370°), in closed bombs, and therefore under the corresponding high pressures developed by such solu-