

CONCERNING CERTAIN COMPOUNDS OF CHROMIUM.

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Received March 21, 1904.

THE compounds of chromium have been known for a long time and have been noted for the number of erroneous opinions that have prevailed in reference to their composition and constitution. A green chloride was first prepared by Peligot,¹ and assigned the formula $\text{CrCl}_3, 6\text{H}_2\text{O}$. Discovering, as he thought, that only two-thirds of its chlorine was precipitable, in the cold, by silver nitrate, he assigned to it the constitutional formula $\text{CrOCl}_2, 2\text{HCl}, 5\text{H}_2\text{O}$. A little later, Löwel² obtained, by double decomposition between violet chromic sulphate solution and barium chloride solution, a second chloride in which all the chlorine was precipitable in the cold by silver nitrate.

In 1885 Godefroy³ demonstrated the existence of two other chromium chlorides. The first was obtained by keeping a saturated solution of the ordinary green salt for some days in a vacuum below $+6^\circ$. This salt was found to have the composition represented by the formula $\text{CrCl}_3, 10\text{H}_2\text{O}$. To the second salt, which was obtained by drying the ordinary salt in a vacuum over sulphuric acid, he assigned the formula $\text{CrCl}_3, 4\text{H}_2\text{O}$. Still later Recoura⁴ succeeded in preparing, by an improved method, the green chloride of Peligot. He also crystallized a violet chloride which had been obtained only in solution by Löwel and found it to be isomeric with the ordinary green salt. Speransky investigated these salts with reference to their conductivity and showed that a solution of a violet salt possessed a much greater conductivity than that of a green salt of the same concentration, while Marechetti proved that something of the same difference existed between their effect in lowering the freezing-point of water.

Up to this time much of the chemistry of these compounds remained obscure. Their molecular weights were not accurately known, that of the ordinary green salt having been given values, fluctuating between 200 and 300. Even the chemical composition of both the violet and the green salt was in dispute, since to each were assigned the formulas $\text{CrCl}_3, 6\text{H}_2\text{O}$ and $\text{CrCl}_3, 6\frac{1}{2}\text{H}_2\text{O}$.

¹ *Compt. rend.*, 19, 738.

² *Ann. chim. phys.*, [3], 14, 246.

³ *Compt. rend.*, 100, 105.

⁴ *Ibid.*, 102, 515.

In 1900 there appeared the beautiful work of Gubser¹ in which these salts were subjected to a careful and thorough investigation. They were prepared, in some cases, by new and improved methods and were examined with a view of determining their electrical conductivity, their molecular weight, and their chemical behavior.

The molecular conductivity of the violet chloride at 0° was found to be constant at 174.7, showing that no further dissociation took place in the case of this salt; on the other hand, the conductivity of the green chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, and its two derivatives, $\text{CrCl}_3 \cdot 10\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$, were found to be widely different from the preceding, but to agree closely among themselves, as is shown by the following table:

	$\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.	$\text{CrCl}_3 \cdot 10\text{H}_2\text{O}$.	$\text{CrCl}_3 \cdot 4\text{H}_2\text{O}$.
μ 125	50	49	50.5

As the corresponding value for potassium chloride under the same conditions of dilution and temperature is 74, it is clear that the molecule of each of the green chlorides, at the moment of solution, consists of only two ions. However, the conductivity of each of these green solutions was found not to be constant, but to continually increase, tending after some days at 0° to become equal to the corresponding value for the violet chloride (174 approximately). The results of conductivity experiments at 25° were in harmony with those just given; that of the violet salt was found to be constant at 274; on the other hand, the conductivities of the three green salts were much lower at first, rapidly rising in each case, to values which closely approximated that found for the violet salt.

The determination of the molecular weight by the Beckmann method gave results which were entirely in harmony with the preceding. The values were: For the violet chloride 76.3

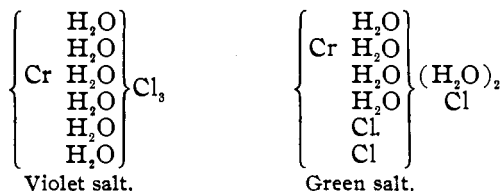
$\left(\frac{266.57}{4} = 66.6, \text{ calculated}\right)$; for the ordinary green chloride 126

$\left(\frac{266.57}{2} = 133.28, \text{ calculated}\right)$.

The chemical examination of these salts also yielded interesting results. The violet and the ordinary green salts were found to

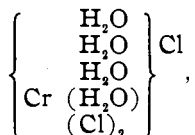
¹ Inaugural Dissertation, Zürich.

contain 6 molecules of water instead of 6.5 molecules, as claimed by Recoura. All the chlorine in the violet chloride was found to be precipitable at once by silver nitrate in the cold, while only *one-third* of the chlorine of each of the green salts was thus precipitable. Here again was the most complete confirmation of the results obtained from the study of the electrical conductivity, *viz.*, that the molecule of the violet salt has three chlorine ions, while those of the three green chlorides have, immediately after solution, only one each. Furthermore, it showed that Peligot was in error in stating that two-thirds of the chlorine in the ordinary green chloride is precipitable by soluble silver salts in the cold. The formulas of the four salts are then written in accordance with Werner's theory as follows:

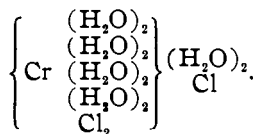


The fact that the 2 molecules of water, and no more, can be removed from this salt by drying in a vacuum over sulphuric acid, is an additional reason for writing the formula in this manner.

To the salt, obtained from the ordinary green salt, as just indicated, there was assigned the formula

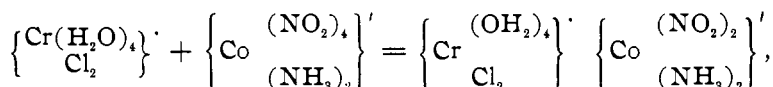


and to the salt with 10 molecules of water the formula



Further study showed that the ordinary green chloride differs from the violet in this respect also, that the former yields a com-

pound when treated with a solution of the ammonium salt of tetranitritodiaminecobalt nitrite,



while the violet chloride yields no such salt.

Gubser also showed that the violet sulphate of chromium, $\text{Cr}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$, could be prepared from the solution of the violet chloride by direct precipitation with concentrated sulphuric acid, while this reaction could be obtained with the green salt only after the solution had been allowed to stand for some time, or had been boiled and cooled.

On taking up this research at this point several matters presented themselves for investigation:

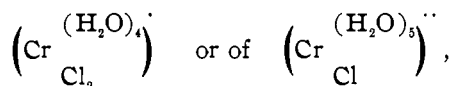
(1) The behavior of the green and the violet chlorides, respectively, toward chlorplatinic acid.

(2) The nature of the change produced in violet chromium chloride on standing or on heating.

(3) The possibility of preparing a violet chloride of chromium having doubled water molecules, $\text{Cr}((\text{H}_2\text{O})_2)_6\text{Cl}_3$.

(4) The heat of solution of the green chlorides with 4 and 10 molecules of water respectively.

It is a well-known fact that the hydrates of the metallic salts form double salts with various acids. These compounds, with the chromium chlorides can, theoretically, be derivatives of either of two forms.



or of either of these with one or more doubled molecules of water in the complex. An example of the first class is the tetranitritodiaminecobalt compound of Gubser, previously alluded to. Derivatives of the second form given above were not known previous to the beginning of this work.

Preparation of the Green Chromic Chloride according to Gubser.—A mixture of 100 grams of chromic anhydride and 400 cc. concentrated hydrochloric acid is boiled for an hour with a reflux condenser; the solution is then concentrated for one and a half

hours on a water-bath, while a rapid current of hydrogen chloride is passed through the solution. The heating is now discontinued and the current of gas kept up as long as bubbles of gas can be forced through the solution. Then the preparation is allowed to stand for from six to eight hours. The resulting mass is now rubbed with a little water, if necessary, and filtered as dry as possible by means of the pump; the crystals thus obtained are dissolved in an equal weight of water, filtered and saturated with hydrogen chloride in the cold. The resulting green crystals are filtered out and dried for from one to two days over sulphuric acid. The last traces of hydrogen chloride are removed by thorough washing with dry acetone, after which the crystals are air-dried for the removal of acetone. The green chloride and chlorplatinic acid were dissolved in water in molecular proportions, 4 grams of the former to 7 grams of the latter, the solution filtered, and placed in a desiccator over phosphorus pentoxide. There soon separated thin rhombic plates, very soluble in water and in alcohol, nearly insoluble in acetone. These were filtered out, washed in acetone and dried on porous plates over sulphuric acid. (It was found out later that the substance could be readily obtained by simple evaporation of the mixture, mentioned above, on a water-bath.)

Analysis:

0.375 gram, fused with sodium carbonate and potassium nitrate and precipitated with silver nitrate gave 0.5601 gram of silver chloride containing 0.1387 gram of chlorine equal to 36.99 per cent. total chlorine.

0.5126 gram gave 0.7659 gram silver chloride = 37.05 per cent. chlorine.

0.2897 gram gave 0.085 gram platinum = 29.34 per cent.

0.479 gram gave 0.1406 gram platinum = 29.35 per cent.

0.479 gram gave 0.0532 gram chromic oxide = 0.03638 gram chromium, or 7.6 per cent.

0.2897 gram gave 0.0338 gram chromic oxide = 0.02305 gram chromium, or 7.95 per cent.

	Calculated for $\text{Cr}[(\text{H}_2\text{O})_6]\text{PtCl}_6$.	Found.	
Chromium	7.82	7.6	7.95
Platinum.....	28.82	29.34	29.35
Chlorine	36.7	36.99	37.05

To determine the relation of the chlorine atom and of the chlorplatinate group to the molecule, a test was made of the action of silver nitrate solution on a solution of the salt. The resulting precipitate was silver chlorplatinate, mixed with a trace of silver chloride. The salt then, at the moment of going into solution, consists apparently of two ions, a PtCl_6 group and a complex cation, which contains the chlorine atom; the latter becomes active only as it gradually becomes dissociated. To settle this point, precipitation reactions were carried out at 0° , according to the method of Peligot and Cubser. The determination of precipitable chlorine was made as follows:

About 0.3 gram of the double salt was weighed out. One gram of silver nitrate was dissolved in 20 cc. of water in a small Erlenmeyer flask, 10 drops of concentrated nitric acid were added, and the solution cooled to 0° . At the same time the distilled water flask was immersed in a freezing-mixture and a portion of the water frozen. The substance was now washed into the silver nitrate with this water, the flask stoppered, shaken vigorously for a few seconds, and filtered. The filtration was made by the use of a hardened filter, and as rapidly as possible to avoid contamination of the chlorplatinate of silver by silver chloride produced as a result of dissociation of chlorine from the complex. The residue of silver chlorplatinate was washed well with cold water containing a few drops of nitric acid, then with pure water, dried at 110°C . and weighed. The filtrate, which was at first clear, soon contained a precipitate of silver chloride, while no further precipitation of chlorplatinate took place. The filtrate was warmed to complete the precipitation of silver chloride, in which the chlorine was determined in the usual manner. The results were as follows:

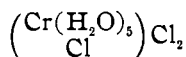
	Calculated for ($\frac{((\text{H}_2\text{O})_2)_5}{\text{Cl}}$) PtCl_6 .	Found.	
Precipitable chlorine.....	10.48	10.55	10.04

Titration according to the method of Peligot: A solution of silver nitrate was made up containing 0.00577 gram of silver per cubic centimeter and therefore equivalent to 0.00190 gram of chlorine per cubic centimeter. A weighed quantity of double salt was dissolved in a small amount of ice-cold water, a calculated volume of the silver nitrate solution quickly run in from a burette.

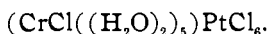
the solution shaken vigorously, and a few drops quickly filtered out and tested with a drop of silver nitrate solution. If the solution remains clear it is proof of the fact that the silver salt, added at first, was more than sufficient to precipitate all of the PtCl_3 ions and chlorine ions present at the moment of addition. If, on the other hand, a precipitate is produced in the test solution, it is proof that too little silver solution has been added from the burette. By a series of tests, the correct number can be approached from each side and the correct value determined. The results are given in the following table:

Salt. Gram.	Vol. AgNO_3 cc.	Corresponding weight Cl.	Per cent. Cl.	Filt. + drop of AgNO_3 .
0.1644	9.5	0.01807	10.99	Remained clear.
0.1821	9.5	0.01807	9.92	Ppt. of Ag_2PtCl_6 .
0.1443	8.1	0.01541	10.79	Immediate ppt. of AgCl .
Calculated precipitable chlorine, 10.48				

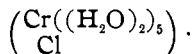
The salt then is a derivative of a hypothetical chromic chloride of the formula



with doubled water molecules in the complex, and its formula is



We have here the first member of a new series of chromium compounds containing the radical



Preparation of Violet Chromic Chloride (Recour's Method as Modified by Gubser).—Fifty grams of pure green chromic chloride are dissolved in 50 grams of water and boiled with inverted condenser for half an hour to convert it, as far as possible, into the violet salt. It is then cooled quickly to a point a little below 0° and maintained at that temperature while a current of hydrochloric acid gas is passed through it to saturation; the current of gas is continued for fifteen minutes longer, and then the flask is allowed to stand for some time in pounded ice. After the precipitate has settled, the clear liquid is poured off, the solid

matter washed out with a cold saturated hydrochloric acid solution, filtered as dry as possible by means of the pump, and placed on porous plates over sulphuric acid; it is then washed with dry acetone to remove green chloride, and spread on porous plates to free it from acetone. The crystals are now dissolved in 20 cc. of water, filtered, and reprecipitated with hydrochloric acid gas, the solution being meanwhile kept cool with cold water. The precipitation is completed at 0° . The crystals are now filtered out, washed well with dry acetone and dried on porous plates over sulphuric acid. This method is long and tedious, requiring, at certain points, a very careful regulation of temperature; furthermore, the yield is not very satisfactory. In looking about for a violet chromium compound which could be used as the original substance in a shorter process, attention was directed to chrome alum, and it was decided to try the action of hydrogen chloride gas upon this compound, in the hope that the violet chloride could be directly precipitated. Accordingly, 10 grams of alum were dissolved in 55 grams of water and 5 cc. of hydrochloric acid, and saturated with hydrogen chloride at $+10^{\circ}$ to 15° . The result was 4 grams of chloride containing a trace of potassium chloride and sulphate. This was dissolved in 6 cc. of water and reprecipitated at $+10^{\circ}$. The salt was washed with dry acetone and dried over sulphuric acid; weight, 3 grams, or 60 per cent. of the theoretical. The crystals were very large and perfect in form and were apparently pure. The analysis gave 19.35 per cent. Cl. Calculated, 19.51 per cent.

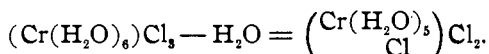
This experiment was repeated with double the amount of alum and yielded 7 grams of pure violet chloride or 66 per cent. of the theoretical. Since, however, the volume of solution to be saturated with hydrogen chloride was rather large, experiments were made to ascertain the solubility of chrome alum in hydrochloric acid with a view of minimizing the labor of saturating the solution, while keeping the volume about the same as in the preceding experiments and thus avoiding the precipitation of alkali chloride and sulphate. It was found that 20 grams of alum dissolved in 80 cc. of concentrated hydrochloric acid and 20 cc. of water.

Accordingly, the preparation was modified as follows: 250 grams of chrom-alum were dissolved in a well-cooled mixture

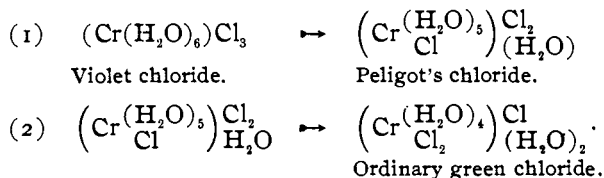
of 1000 cc. of concentrated hydrochloric acid and 250 cc. of water, the solution was filtered and saturated with hydrogen chloride at $+10^{\circ}$ to 15° . The solution was now nearly colorless. The crystals, washed and dried in the usual manner, weighed 115 grams. They contained only a little potassium chloride and sulphate. The crystals were dissolved in 175 cc. of water and reprecipitated at 10° . The resulting salt weighed 90 grams, or 66 per cent. of the theoretical. While thus the improved process gives no better yield than the one previously tried, there is a very great saving of time. This method is believed to be a great improvement over that of Recoura.

The Action of Heat on Violet Chromium Chloride.—Gubser has noted that this salt, on standing, gradually becomes green. The only investigation that seems to have been carried out on this subject is that of this same worker who found that this salt, when heated to 100° , undergoes rapid and complete decomposition.

It was at first attempted to expel a molecule of water from the salt with a view of ascertaining the character of the salt formed; it seemed possible in this way to produce a salt having two chlorine ions:



However, as the salt, when heated at such a temperature as to lose water, seemed to suffer a marked change superficially, this method was finally abandoned and it was decided to heat the salt at such a temperature that little water would be lost, but that an exchange would, if possible, take place between the chlorine ions and the molecules of water in the complex. Theoretically, this substitution could proceed in two stages:



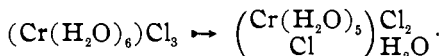
(1) In order to determine the nature of the change 2.56 grams of the violet chloride were heated at about 70° for four hours.

Analyses for chlorine, precipitable at 0° , gave 29.06 and 27.7 per cent. The differences in results are due to the different rates of filtration and the resulting variation in the amount of dissociation of chlorine from the complex.

Calculated for $\left(\text{Cr}(\text{H}_2\text{O})_3\right)\text{Cl}_2\text{H}_2\text{O}$, 26.6 per cent.; for $\left(\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2\right)\text{Cl}(\text{H}_2\text{O})_2$, 13.3 per cent.

(2) Two and nine-tenth grams of violet chloride were heated at 70° for four hours. Analysis for chlorine, precipitable at 0° , gave 26.8 per cent.

Apparently, then, there had been a transformation of the violet chloride into a green chloride having only one atom of chlorine in the complex, consequently with two-thirds of its chlorine immediately precipitable by soluble silver salts in the cold.



It was possible, however, that the transformation of violet into green salt had been superficial, and that the substance analyzed was not homogeneous, but a mixture of violet chloride having three chlorine ions and of the ordinary green chloride with one chlorine ion. It is evident that a mixture of these two salts in approximately equal weights would have given the results obtained. In order to settle this point, some of the suspected mixture was treated with an excess of dry acetone, which is a solvent for the green salt, but not for the violet one. Some violet salt remained, showing that a mixture had actually been present. The acetone solution of the green salt was evaporated over sulphuric acid and an analysis made of the resulting green crystals for chlorine precipitable at 0° . This gave 14.5 per cent. of chlorine. Calculated for ordinary green chloride, 13.3 per cent.

The violet chloride was heated at from 65° - 67° for fifteen hours; loss in weight, 0.0677 gram. The salt was now moistened with 1 cc. of absolute alcohol containing 3 or 4 drops of water to restore the water lost during heating; the salt was then spread on porous plates and placed in a desiccator without drying agent for some hours, after which it was pressed between filter-paper and analyzed. There was found, in the cold. 16.6, 15.56,

and 15.29, and, on warming, a total of 39.29 per cent. of chlorine. There had been, then, a complete transformation of the violet into the ordinary green salt.

A number of attempts were now made to prepare Peligot's salt, having two-thirds of the chlorine precipitable, in the cold by a soluble silver salt.

(1) The mixture of violet and green chlorides, obtained as stated above, by heating the violet salt, was dissolved in alcohol and then evaporated to crystallization over sulphuric acid. As there was present in the solution both the salt with one chlorine ion and that with three such ions, the intermediate salt, if capable of existence in solution, would be likely to be present. If now this intermediate salt were less soluble in alcohol than either of the others, then, on evaporating the alcohol, this salt might be obtained.

The analysis of crystals gave the following results: 14.57 per cent. of chlorine at 0°.

Thus the ordinary green chloride was obtained and not the one described by Peligot, showing that the former is less soluble in alcohol than the latter.

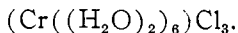
(2) Violet chloride was dissolved in water (1 gram salt in 2 grams water) and evaporated over sulphuric acid.

Analysis of the green crystals obtained gave 15.02 per cent. of chlorine at 0° and 24.49 per cent. on warming; in all 39.51 per cent.

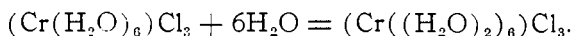
Here again the ordinary green salt was obtained.

(3) Five grams of green chloride were dissolved in 5 cc. of water and heated to boiling to convert it in part into the violet modification; the intermediate form, if capable of existence, should be present here. The solution was now cooled quickly, 25 cc. of alcohol added, then an excess of ether, the lower layer drawn off, reprecipitated with ether and evaporated over sulphuric acid.

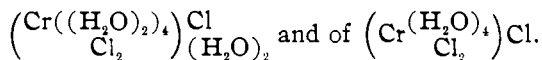
Analysis for chlorine, immediately precipitable at 0°, gave 16.88 per cent., and 23.24 per cent. additional was obtained on standing, or 40.12 per cent. in all. It will thus be seen that the ordinary green chloride is less soluble in water, alcohol, acetone and ether than is the salt with two chlorine ions and probably always separates instead of the latter. Hence, Peligot could scarcely have obtained the salt, two-thirds of whose chlorine is immediately precipitated in the cold.

Violet Chromium Chlorine with 12 Molecules of Water,

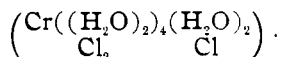
—According to Werner's theory, water has a marked tendency to enter into the hydrates in the form of double molecules. Thus, in the alums, the trivalent metal atom is considered the central atom of a complex which contains in addition six doubled water molecules; salts of the type of chromium and aluminum sulphates also contain such molecules. Again, the constitution of the green chromic chloride with 10 molecules of water is best explained on the theory that the green salt with 6 molecules of water takes up, in neutral solution, below $+6^\circ$, four additional water molecules, forming a complex containing four doubled water molecules in addition to two chlorine atoms. It seemed probable that the corresponding violet salt is capable of existence in the crystalline form and that it could be prepared by properly cooling a saturated solution of the ordinary violet salt,



Accordingly, a solution was made in the proportion of 2 grams of violet salt in 1 gram of water and this was gradually cooled with frequent stirring to -18° . Neither salt nor ice crystals separated; the tube was now surrounded with solid carbon dioxide and ether and cooled; no salt crystals were obtained.

Heat of Solution of

—The heat of solution of the ordinary violet and green chlorides had already been determined by Recoura as $+12.02$ K and -0.04 K respectively. It seemed of interest, therefore, to determine, also, that of the two modified green salts, *i. e.*, to determine the heat of hydration in the second case, and the effect on the heat of solution of doubling the water molecules of the complex in the first compound.

Preparation of the Green Chloride

—The green chloride with 6 molecules of water was dissolved in water (1 part water to 2 parts of salt), filtered, and the filtrate

placed in a freezing-mixture. The large prismatic crystals which separated were filtered out, dried between filter-paper and analyzed, giving 15.30 per cent. of chromic oxide. Calculated, 15.38 per cent.

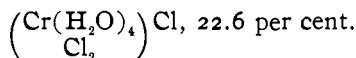
Two determinations were made with the following result:

Substance.		Water.	
Grams.			
7.39		100	No temperature change could be detected.
2.95		50	

We have here, evidently, a salt with approximately zero heat of solution; comparing this result with that obtained by Recoura for the ordinary green salt (-0.02 K per gram-molecule), it is evident that the doubling of the water molecules of the complex has only a slight effect on the heat of solution.

Heat of Solution of the Chloride with 4 Molecules of Water.—This salt was prepared in the usual manner from the green salt with 6 molecules of water, by keeping it in a vacuum over sulphuric acid for thirty days.

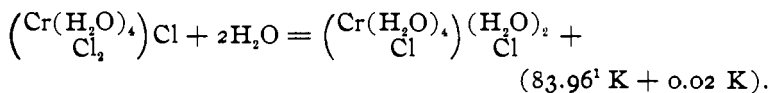
Analysis of the resulting salt gave 22.4 per cent. of chromium. Calculated for



DETERMINATION OF HEAT OF SOLUTION.

Weight of salt. Grams.	Weight of water. Grams.	Water equivalent of calorimeter. Grams.	Rise.	Heat of solution. K.
1.58	100	7.72	0.53	83.37 K
6.05	100	7.72	2.06	84.56 K

Since the salt formed here is undoubtedly the green chloride with 6 molecules of water and goes into solution above $+6^\circ$ as such, the value found here is practically the heat of hydration of the green chloride with 4 molecules of water, or the heat evolved in the addition of 2 gram-molecules of water to 1 gram-molecule of the green salt having 4 molecules of water.



Preparation of Violet Chromic Bromide $(\text{Cr}(\text{H}_2\text{O})_6)\text{Br}_3$.—The preparation of this compound, according to the method of

¹ Average value obtained.

Recoura, is even more tedious than that of the violet chloride; it, therefore, seemed desirable to ascertain whether it is practicable to prepare it by direct precipitation from chrom-alum. However, while enough was done to show that this method could be employed, it was finally decided to begin with the violet chromium sulphate.¹ Accordingly, 6 grams of this substance were dissolved in 15 cc. of water and saturated with hydrobromic acid gas at $+10^{\circ}$ C. Even at this dilution the sulphate salts out somewhat, but for the most part goes into solution again on stirring. The precipitate was filtered out and treated as directed by Recoura; the weight of the crystals was 3.4 grams, nearly sulphate-free.

Five grams of sulphate were dissolved in 20 cc. of water and treated as in the preceding experiment. The weight of the crystals was 3 grams of practically pure violet bromide. While no further work was done to perfect this method, it is believed that it could be made to yield even better results.

Violet Chromic Iodide.—The literature of this substance is very slight. Moissan,² in a brief discussion of the preparation and properties of chromous iodide (CrI_2), alludes to chromic iodide (sesquiodüre) as yielding chromous iodide on reduction by hydrogen. Up to the present time it has been known only in solution.

The most feasible method for the preparation of this substance seemed to be that by double decomposition between violet chromium sulphate and barium iodide.

Gubser has shown that the violet sulphate may be precipitated from the solution of the violet chloride or bromide by the addition of excess of concentrated sulphuric acid in the cold. This suggested the possibility of directly precipitating the violet sulphate from chrom-alum.

Preparation of Violet Chromic Sulphate from Chrom-alum by Direct Precipitation by Means of Concentrated Sulphuric Acid.—Preliminary experiments showed that sulphuric acid precipitates the sulphate from a saturated solution of chrom-alum (1 part alum to 6 parts water); however, much better results were obtained if the alum was dissolved in 30 per cent. sulphuric acid.

¹ Prepared according to the method which is described later. *Compt. rend.*, **102**, 548 (Gubser: *Loc. cit.*, 40).

² *Ann. Chim.*, [5], **25**, 409 (1852).

Accordingly, 100 grams of alum were dissolved in a cooled mixture of 100 cc. of sulphuric acid and 330 cc. of water, the solution filtered and 250 cc. of concentrated acid slowly added at +15 to +20 with thorough stirring. The crystals were filtered out, washed well with alcohol and dried; weight, 66 grams.

(1) Thirty-three grams of these crystals were dissolved in 125 cc. of water and 125 cc. of concentrated sulphuric acid added; weight of the dried crystals, 17.5 grams. The analyses gave 14.38 per cent. chromium. Calculated for $\text{Cr}_2(\text{SO}_4)_3, 18\text{H}_2\text{O} = 14.54$ per cent.

(2) The remaining portion (33 grams) was dissolved in 33 cc. of water and precipitated with 75 cc. of alcohol; weight of the crystals obtained, 18 grams. The analysis gave 14.61 per cent. of chromium.

The method was now varied somewhat in that diluted hydrochloric acid, instead of sulphuric acid, was employed as a solvent for the alum. 100 grams of alum were dissolved in a cooled mixture of 300 cc. of water and 100 cc. of concentrated hydrochloric acid, and 225 cc. of sulphuric acid were added at +10° to +15°. The yield was 55 grams, or 77 per cent. of the theoretical. The analysis gave 14.35 per cent. chromium.

Preparation of Violet Chromic Iodide from Violet Chromic Sulphate and Barium Iodide.—12.3 grams of barium carbonate were suspended in 30 cc. of water, and hydriodic acid gas was passed in until solution was effected; 14.5 grams of violet chromic sulphate (thrice precipitated) were added, thoroughly stirred, a trace of sulphate was titrated out, and filtered. The concentrated solution was violet, the dilute solution greenish. A little of the solution, heated to 40° on the water-bath, became brownish, due, no doubt, to the formation of a basic salt, since the solution gave no test for free iodine. A portion of the iodide solution, placed over sulphuric acid in a desiccator, formed a gummy mass. The remainder of the solution was saturated with hydriodic acid at about 10°. Considerable difficulty was experienced at first in inducing crystallization and this led to attempts to precipitate the iodide directly from the sulphate and the chloride. In each case, however, the precipitate was the sulphate mixed with a trace of iodide.

Renewed attempts were therefore made by the original method, and these were finally successful. The crystals were filtered as

dry as possible, and washed well in dry chloroform in which they were practically insoluble, then spread on porous plates and placed over sulphuric acid.

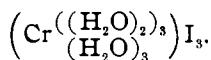
The crystals are a very deep violet, almost black; the pulverized substance, however, is olive-green. They are quite hygroscopic and are soluble in alcohol. They are also, like those of the bromide, quite soluble in acetone (distinction from violet chloride).

The analysis gave 8.57, 8.8, 8.7 and 9.05 per cent. of chromium, and 63.93 and 64.1 per cent. of iodine. Calculated for $(\text{CrH}_2\text{O})_6\text{I}_3$: Cr, 9.6; I, 70.4; for $(\text{Cr}(\text{H}_2\text{O})_9)\text{I}_3$: Cr, 8.76; I, 63.99.

The salt, on standing, shows a tendency to decompose, separating hydriodic acid.

A second sample was made, as previously stated, except that the saturation with hydriodic acid was much less rapid toward the close, and the crystals much larger, some of them being nearly a centimeter in length. These were dried over solid caustic potash. The analysis gave 8, 5, 8.89 and 8.76 per cent. chromium, and 63.63 and 63.94 per cent. iodine.

This substance then apparently contains three doubled water molecules in the complex and its formula is



It is interesting to note that Varenne¹ has produced, by the action of hydrobromic acid on ammonium or potassium trichromate and cooling the solution to 0°, crystals of a violet bromide having the composition $\text{CrBr}_3 \cdot 8\text{H}_2\text{O}$. This substance, like the iodide, is greenish in dilute water solution.

The iodide is evidently not isomorphous with the violet chloride and bromide. A crystallographic study of the iodide is desirable, but the crystals obtained were not sufficiently perfect to render such a study practicable.

Determination of the molecular weight by the Beckmann method:

¹ *Compt. rend.*, **93**, 727.

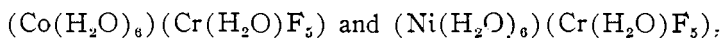
	Weight of water. Grams.	Weight of substance. Grams.	Depression.	Molecular weight.
(1)	14.46	0.8475	0.665°	165.5
(2)	14.46	1.4275	1.1205°	163.0
(3)	14.46	1.4275	1.1265°	162.1

In order to test the stability of this substance in solution, the lowering of the freezing-point was redetermined after the solution had stood at ordinary temperature for forty-eight hours. The result is given in No. 3, above.

The calculated molecular weight is $\frac{594.6}{4} = 148.6$.

The Double Fluorides of Chromium with Zinc and with Copper.—The interesting double fluorides of vanadium and chromium respectively with cobalt, nickel and manganese, have been studied by Christensen and by Peterson.¹ The double fluoride of vanadium and cobalt was prepared as follows: Vanadium trifluoride was added to a solution of cobalt carbonate in hydrofluoric acid. The crystals which separated were purified by recrystallization from water, but were too small for accurate crystallographic study; however, on crystallizing slowly from dilute hydrofluoric acid solution, beautiful, large crystals were obtained and measured. Analysis showed that the proper formula is $\text{CoF}_2\text{VF}_{3.7}\text{H}_2\text{O}$ or $(\text{Co}(\text{H}_2\text{O})_6)(\text{VF}_5(\text{H}_2\text{O}))$.

This salt was found to be very stable toward heat, no water being given off below 200°. The double fluorides of chromium, with cobalt and nickel, respectively, were now prepared by a method analogous to that employed in the preparation of the cobalt vanadium salt, and were found to have an analogous composition, *viz.*,



and to be isomorphous with that substance. The corresponding manganese salt had already been made by Christensen. It was thus shown that cobalt, nickel and manganese form, with vanadium and chromium, compounds which are analogous in respect to preparation, composition, crystalline form, and behavior on heating. The double fluorides of vanadium with zinc and copper were also prepared by Peterson, but were not closely investigated.

¹ *J. prakt. Chem.*, 40, 44.

Experimental Portion.—It was decided to prepare and examine the double fluorides of chromium with zinc and with copper.

The zinc salt was prepared according to the method of Peterson by bringing together, in hydrofluoric acid solution, molecular quantities of chromic fluoride and zinc fluoride and evaporating to saturation on the water-bath. The resulting crystals were twice recrystallized from hydrofluoric acid solution.

The analysis was made as follows: A weighed quantity of the double salt was decomposed in a platinum dish with concentrated sulphuric acid. The chromium was then oxidized by means of nitric acid and potassium chlorate, the zinc precipitated as carbonate and weighed as the oxide. The chromate was now reduced and the chromium determined in the usual manner as oxide.

A sample was heated at 200° to determine loss of water.

The result of analysis was: Zinc, 20.08 and 19.5 per cent. in the first sample and 19.46 per cent. in the second; 15.8 per cent. of chromium in the first and 15.5 per cent. in the second; and 35.6 per cent. of water at 200° . Calculated for $(\text{Zn}(\text{H}_2\text{O})_6)(\text{CrF}_5\text{H}_2\text{O})$: Zn, 19.29; Cr, 15.4; H_2O , 37.2 per cent.

The salt is analogous in composition to the salts of Peterson and Christensen; however, the water is expelled, to some extent, below 200° .

Copper Chromium Fluoride.—This salt was prepared, like the preceding, by concentrating, on a water-bath, a solution of molecular proportions of chromic and copper fluorides in hydrofluoric acid. It was twice crystallized from hydrofluoric acid.

The analysis gave 21.3 per cent. copper, 17.5 and 17.2 per cent. chromium, and 28.8 per cent. of water at 200° . Calculated for $(\text{Cr}(\text{H}_2\text{O})\text{F}_5)(\text{Cu}(\text{H}_2\text{O})_4)$: Cu, 21.18; Cr, 17.2; H_2O , 29.5; for $(\text{Cr}(\text{H}_2\text{O})\text{F}_5)(\text{Cu}(\text{H}_2\text{O})_6)$: Cu, 18.7; Cr, 15.4; H_2O , 37.2.

The composition of this salt, then, is not analogous to that of the chromium zinc salt, since this contains only 5 and not 7 molecules of water of crystallization. This is in harmony with what is known in regard to the capacity of the other copper salts to take up water of crystallization. In hydrated salts of copper, in general, the coördination number of the copper in the complex is 4.

Chromic Acetates.—Our knowledge of these interesting compounds is mainly due to Recoura.¹ This investigator prepared

¹ *Compt. rend.*, 129, 209.

a solution of the normal salt by double decomposition between the violet chromium sulphate and barium acetate. He considered the salt thus obtained normal, since (1) all the chromium was immediately precipitated by fixed alkali in the cold, and (2) the heat of neutralization of the salt by sulphuric acid was exactly equal to that of sodium acetate by the same acid, *viz.*, 12.17 calories.

The freshly prepared solution of this salt was green, but changed, on standing, successively into three salts in which 1, 2, and 3 molecules of acetic acid are present in the complex, or in direct combination with the chromium. In each of these abnormal forms he found the chromium non-precipitable by sodium hydroxide in the cold. Recoura finally prepared the normal acetate in the solid state by dissolving freshly precipitated chromic hydroxide in the calculated amount of glacial acetic acid, drying well with the pump, and completing the drying on porous plates. The substance was a lilac-gray powder forming a yellowish green solution. As a result of a gravimetric determination of the chromium and a volumetric determination of the acetic acid, Recoura assigned to this substance the formula $\text{Cr}(\text{H}_2\text{O})_5(\text{C}_2\text{H}_3\text{O}_2)_3$. Now there is some reason for believing that while this salt was normal in solution, the solid was not really normal; in the first place, the solid substance obtained was not crystalline, but amorphous; and in the second place the salt should probably have had 6 and not 5 molecules of water. It seemed of interest, therefore, to prepare, if possible, the normal acetate in the crystalline form with a view of settling its composition and properties. Accordingly, 11.2 grams of lead acetate were dissolved in 10 cc. of water, 7 grams of the violet sulphate added, stirred thoroughly, and filtered as quickly as possible. The solution was greenish blue by reflected light and violet by transmitted light.

An attempt was made to precipitate the normal salt from this solution by means of glacial acetic acid, but the salt came down as a slimy mass; this method was therefore abandoned.

A portion of the solution was cooled to 0°C ., and after many unsuccessful attempts to induce crystallization, a few beautiful blue-violet crystals were obtained. These were filtered out, spread on a porous plate and placed in a desiccator over glacial acetic acid to minimize loss of acid. After some hours they were pressed between filter-paper and analyzed. There was found

by titration 51.9, 51.82 and 50.8 per cent. of acetic acid; and by precipitation 15.99 per cent. of chromium. Calculated for $(\text{Cr}(\text{H}_2\text{O})_5)(\text{C}_2\text{H}_3\text{O}_2)_3$: Cr, 16.33; $\text{C}_2\text{H}_3\text{O}_2$, 55.4; for $(\text{Cr}(\text{H}_2\text{O})_6)(\text{C}_2\text{H}_3\text{O}_2)_3$: Cr, 15.4; $\text{C}_2\text{H}_3\text{O}_2$, 52.5.

These results are not conclusive. The salt had evidently lost acetic acid. The chromium was thus brought too high. The results, however, indicate that this acetate has 6 instead of 5 molecules of water.

Numerous attempts were subsequently made to prepare this substance, in part using lead acetate and violet sulphate, and later silver acetate and violet chloride; in only one instance did sufficient crystals separate for an analysis, and these were lost in the following manner: Acetate crystals, to the weight of about 1 gram, separated from the solution at $+2^\circ\text{C}$. To increase the yield, the flask was surrounded with crushed ice and allowed to stand in the ice-chest for some hours; when it was again examined it was found that most of the crystals had disappeared. The explanation of their disappearance is probably this: The original solution was, of course, at first, supersaturated with the normal salt at the temperature of the experiment; however, the concentration of this salt was continually diminishing, owing to the somewhat rapid formation of the abnormal salts described by Recoura; the solution finally reached the state of unsaturation with respect to the normal salt and the crystals began to dissolve.

All succeeding attempts to prepare this salt in quantity have been unsuccessful; it is hoped, however, that the substance may again be obtained and further investigated.

The writer desires to acknowledge his indebtedness to Prof. A. Werner for his active interest in this work.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
February 24, 1904.

ON THE NON-EXISTENCE OF ARSENIC PENTACHLORIDE.

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Received April 6, 1904.

BY PASSING an excess of chlorine into arsenic trichloride cooled at -34° , and then allowing the temperature to rise to -30° , Baskerville and Bennett¹ obtained a substance which contained

¹ This Journal, 24, 1070.