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CONTRIBUTIONS TO THE STUDY OF RUTHENIUM, IV.¹

THE CHLORIDES.

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IN his early work upon ruthenium, Claus described two classes of chlorides, $\text{Ru}^{\text{III}}\text{Cl}_3, 2\text{XCl}$, and $\text{Ru}^{\text{IV}}\text{Cl}_4, 2\text{XCl}$, corresponding to two of the general types among the metals of the platinum group; the former made by the action of hydrochloric acid upon any of the soluble oxides or hydrated oxides, the latter, generally at least, by oxidation with nitric acid. The trichloride is formed also when chlorine acts directly upon the metal, especially in the presence of alkaline chlorides.

In addition to these chlorides, Claus called attention to the fact that by the action of hydrogen sulphide, the deep red-brown solution of ruthenium trichloride becomes dark azure-blue, probably owing to reduction to a bichloride, $\text{Ru}^{\text{II}}\text{Cl}_2$. No further advance was made on the chlorides till A. Joly² showed that the chloride obtained by oxidation with nitric acid is not as Claus had supposed the tetrachloride, but a nitrosochloride, RuCl_3NO . More recently U. Antony³ has shown that by adding potassium

¹ Read in abstract at Denver meeting of the American Chemical Society.

² *Compt. rend.*, **107**, 994 (1888); **108**, 854 (1889).

³ *Gazz. chim. Ital.*, **20**, 1 (1889).

ruthenate, K_2RuO_4 , to hydrochloric acid, the true tetrachloride, $Ru^{IV}Cl_4 \cdot 2KCl$, is really formed, and it appears quite possible that Claus may have had this salt in hand, and in one case have analyzed it. He did not at all events distinguish it from the nitrosochloride. Joly¹ also studied the azure-blue solution of the reduced chloride and concluded that it contains an oxychloride, $RuCl_2OH$.

The nitrosochloride series of salts has been quite fully worked out by Joly,² Brizard,³ and the author.⁴ The present paper extends the trichloride series of Claus and the tetrachloride series of Antony, to some of the cesium and rubidium members, and presents two members of a new series, $RuO_3Cl_2 \cdot 2XCl$, an oxychloride intermediate between the tetroxide and tetrachloride. A few notes are appended on the blue solution.

Ruthenium Tetrachloride.—When hydrochloric acid, or free or nascent chlorine, acts upon ruthenium compounds, in almost every case, the trichloride is the resultant product. Joly, as well as the author, tried in vain, by various methods of chlorination, to form the tetrachloride. Apparently $RuCl_3$ will not take up another atom of chlorine. Antony first wittingly prepared the chloride, using potassium chlorate to oxidize the ruthenium to ruthenate, thus insuring the absence of a nitrate and hence of nitrosochloride formation. The solution of the ruthenate was then added to dilute hydrochloric acid. On the other hand, when the acid is added to the ruthenate, even at a temperature below zero, and the solution concentrated in the cold, the trichloride is the only product I have been able to obtain. The study of the conditions of formation of the tetrachloride are much enhanced in difficulty by the close resemblance of its solutions to those of the trichloride. I have as yet noted but a single analytical reaction in which the two compounds differ sufficiently to be readily distinguished, and this reaction demands the dry salt free from acid and in a fairly pure state; nor is it easy, even by the microscope, to distinguish the presence of the tetrachloride in a mixture.

The starting point of the work of the present paper was generally ruthenium tetroxide, RuO_4 , distilled from the alkaline ruthenate solution by a current of chlorine. In the earlier part of

¹ *Compt. rend.*, 114, 291 (1892).

² *Loc. cit.*

³ *Bul. Soc. Chim.* [3] 13, 1092 (1895); *Compt. rend.*, 122, 730 (1896).

⁴ *This Journal*, 16, 388 (1894).

my work, the ruthenate was formed by fusing metallic ruthenium, or ruthenium residues of any kind (which must be free from osmium) with caustic potash and saltpeter, in a silver dish. The introduction of sodium peroxide into the laboratory has occasioned much economy of time and trouble in this operation. The ruthenium, in any finely divided form, is slightly mixed in a nickel dish with three or four times its volume of sodium peroxide and warmed with occasional stirring till it becomes nearly but not quite completely fused. The conversion into sodium ruthenate is rapid and generally complete, and the melt is readily soluble in a small quantity of water. To avoid undue heating, it is well to rest the nickel dish in a beaker full of cold water, or on a piece of ice, while dissolving the melt. The strong solution of the ruthenate is poured into a small tubulated retort, and through it is passed a fairly rapid current of chlorine. As the solution becomes saturated, the ruthenium tetroxide begins to pass off as a golden yellow vapor, and may be completely removed from the solution by gently warming and finally bringing to a boil. When it is desired merely to obtain a pure ruthenium, the tetroxide may be led directly into dilute alcoholic potash, but when the pure tetroxide is desired, an adapter is arranged leading into a large, stoppered test-tube, and from this any uncondensed tetroxide together with the chlorine is led into an aqueous solution of potash. Beyond the potash bottle may be placed a bottle of alcoholic potash, which will effectually retain every trace of ruthenium. Before the introduction of the aqueous potash bottle, it was found that the vapors of alcohol diffused slightly into the tetroxide tube, causing decomposition. In one instance owing to the stopping of the chlorine current a little of the alcoholic potash was drawn over into the tube, which then contained perhaps 3 or 4 grams of the tetroxide. A very violent explosion occurred which shattered the apparatus, and filled the room with dense black smoke. This ruthenium soot, evidently an oxide, differs from any described anhydrous oxide, in being very soluble in dilute hydrochloric acid. The trichloride is formed.

If the absence of osmium be assured, this method of preparing the tetroxide or of purifying ruthenium is very satisfactory, being fairly expeditious and without danger. The fumes of ruthenium tetroxide, though somewhat suffocating, appear to have the

irritating and poisonous qualities of the osmium tetroxide to a very slight degree if at all.

When ruthenium tetroxide is treated with hydrochloric acid in the cold, it is slightly soluble to a light reddish yellow solution. On standing, or on warming, the solution becomes dark red and chlorine is evolved. The rapidity of this change is proportional to the strength of the acid, and to the temperature. In five times normal acid, at ordinary temperature, some unchanged RuO_4 is present in the solution after standing several days. The primary product obtained on treating the dark red solution with an alkaline chloride is the trichloride, of formula $\text{Ru}^{\text{III}}\text{Cl}_3\text{XCl}$ generally at least with one molecule of water, and until recently no other compounds have been recognized.

If, however, ruthenium tetroxide is covered with water, in which it is but slightly soluble, a strong solution of cesium (or rubidium) chloride added, and the whole acidified with a small amount of hydrochloric acid, the tetroxide is gradually converted into the double salt of the oxychlorrythenate to be described in the next paragraph. This salt on boiling with concentrated hydrochloric acid is converted into the double salt of ruthenium tetrachloride, but some of the trichloride seems to be formed at the same time. Many efforts were made to obtain the tetrachloride directly from the tetroxide, but the exact conditions of the reaction were not found: the tetrachloride, however, not seldom appeared in the products. The best specimen obtained (analysis 3) was the second crop of crystals from evaporating the filtrate from the precipitation by alcohol of the reaction products of the tetroxide, cesium chloride, and concentrated acid. The previous crop had consisted of a mixture of the tetrachloride, and a rose salt to be mentioned later. Cesium and rubidium chlorrythenates, $\text{Cs}_2\text{Ru}^{\text{IV}}\text{Cl}_6$ and $\text{Rb}_2\text{Ru}^{\text{IV}}\text{Cl}_6$, when well crystallized, consist of black, almost opaque, regular octahedra, resembling the corresponding salt of the other platinum metals; when precipitated from solutions by alcohol, they are buff powders, hardly distinguishable as crystalline. They are almost insoluble in cold water, barely tinting the water brown; on heating, the solution becomes darker and slightly purplish, the salt being decomposed. If now a drop of concentrated hydrochloric acid is added, a deep purple color is noticeable in the brown solution, but it soon disappears, leaving the solution brownish. This reaction, which is very sat-

isfactory if the salt is quite pure, is the only one yet found which differentiates clearly the tetrachloride from the trichloride. The tetrachloride is less soluble in concentrated hydrochloric acid than the trichloride; is fairly soluble in hot dilute hydrochloric acid. The solution in hydrochloric acid resembles that of the trichloride, save for a slight cast of pink to the deep red concentrated solutions, and a pure yellow in dilute solutions, as against the reddish cast to the yellow of the trichloride.

The alkalis give a dull greenish blue precipitate (or color only with ammonia); with all other reagents tested, the reactions in no wise differed from those of the salts of ruthenium trichloride. When acidified with hydrochloric acid and boiled in dilute solution, especially with alcohol, the solution becomes rose, and on slow evaporation the rose prisms described later are found together with the octahedra of the unchanged tetrachloride.

Cesium and Rubidium Oxychlorruthenate, $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ and $\text{Rb}_2\text{RuO}_2\text{Cl}_4$ ($2\text{CsCl}, \text{RuO}_2\text{Cl}_2$, and $2\text{RbCl}, \text{RuO}_2\text{Cl}_2$).—These salts are slowly formed by the action of a solution containing little hydrochloric acid and much alkaline chloride, on excess of ruthenium tetroxide, in the cold. Owing to the volatility of the tetroxide and its instability, especially in the presence of any organic vapors, the best method of preparing the salt was found to be as follows: Two or three grams of ruthenium tetroxide (more or less water is in the distillate used) were poured into a glass weighing-tube of 3 cm. diameter. A few cubic centimeters of a quite concentrated solution of cesium (or rubidium) chloride were added and a few drops of concentrated hydrochloric acid. The tube is then stoppered and shaken from time to time. The stopper must be occasionally removed to permit the escape of the chlorine generated. In the course of twenty-four hours, a considerable crop of the crystals of the salt may be removed, dried on a tile, and after the volatilization of the ruthenium tetroxide which will be present, the salt may be washed by a trace of hydrochloric acid. Successive crops may be obtained. These salts consist of dark purple isometric crystals, showing the octahedron, cube, and rhombic dodecahedron. They are quite soluble in cold hydrochloric acid to rose solution, yellow on dilution; from *cold* solution, the salt crystallizes out unchanged, even in the presence of alcohol.

On heating with hydrochloric acid, chlorine is evolved and the

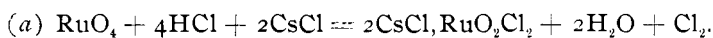
corresponding salt of ruthenium tetrachloride crystallizes out.

The characteristic reaction of the oxychlorrythenate is its instant decomposition by water. When even a very small crystal is let fall into a drop of water on a watch-glass, it at once dissolves and decomposes, rendering the whole drop a black liquid. At the same time there is noticeable a marked odor of ruthenium tetroxide. The salt is also decomposed by sulphuric and nitric acids with the evolution of the same odor.

These two salts belong to a type with very few representatives. Péligot by the action of hydrochloric acid on potassium uranate obtained $2\text{KCl}, \text{UO}_2\text{Cl}_2, 2\text{H}_2\text{O}$, and Sendtner prepared the corresponding bromide.

By the action of hydrofluoric acid on potassium tungstate, Berzelius obtained $2\text{KF}, \text{WO}_2\text{F}_2, \text{H}_2\text{O}$ and two or three other analogous tungstates. The chlorotungstate WO_2Cl_2 , like the corresponding MoO_2Cl_2 and CrO_2Cl_2 , exhibits no tendency to form salts. Piccini's ammonium fluotitanate, $3\text{NH}_4\text{F}, \text{TiO}_2\text{F}_2$, seems rather of the nature of a peroxide.

The uniform nature of the oxychlorrythenate was evident under the microscope, before and after recrystallization. The absence of water or of hydroxyl groups in the salt was shown by heating in oxygen stream in a tube guarded at either end with a phosphorus pentoxide tube (see Analysis 9). This shuts out the possibility of the salt being $\text{Ru}(\text{OH})_2\text{Cl}_2$. The formation of the salt and its decomposition with hydrochloric acid are shown by the formulas :



The odor of ruthenium tetroxide, when the salt is decomposed by water or other acids than hydrochloric, may be the odor of ozone, the formation of which would be readily explicable. When ruthenium tetroxide comes in contact with any organic substance it is instantly decomposed, and it may well be that the oxide is decomposed before stimulating the olfactory nerves, and the odor recognized is that of ozone, formed by the decomposition of the oxide. At least the two odors resemble each other very closely.

Ruthenium Trichloride Salts.—The salts of the lighter alkali metals have been fully described by Clans and Joly. Cesium and rubidium chlorides show the familiar tendency to form complex

salts with ruthenium trichloride, according to the conditions of experiment. The normal salts are $\text{Cs}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ and $\text{Rb}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$, the presence of the water of crystallization being confirmed by Analyses 13 and 17. The water is slowly driven off by heat and at 250° one atom of chlorine is very slowly lost.

Indications of more complex salts were obtained and several analyses of these are appended. In most of these cases there is no assurance that the salt, always difficult to dry, was pure or uniform (except 21), but the fact that salts of approximately the same composition were obtained from different sources, points to the probability that they are definite compounds.

One salt, however, of this class is characterized by forming uniform, transparent, rose prisms, with extinction parallel to the prism. These are deposited from the rose solution obtained when a slightly acid solution of the tetrachloride is heated with considerable excess of water and alcohol. It is also deposited from the filtrate after the electrolytic reduction of the trichloride. It is also probably formed in dilute solutions of the trichloride, but it has not been analyzed, nor positively identified from this source. It is not very soluble in hydrochloric acid, and is very slightly soluble in water. It can be crystallized apparently unchanged from hydrochloric acid, but on evaporating to dryness in hydrochloric acid solution, some tetrachloride is formed. The composition of these rose prisms is $\text{Cs}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$, the same as that of the normal cesium salt of the trichloride, but they are very distinct from that salt, and should probably be looked upon as an *aquo* salt, $2\text{CsCl} \cdot \text{Ru}(\text{OH}_2)\text{Cl}_3$, corresponding to the tetrachloride, $2\text{CsCl} \cdot \text{RuCl}_4$.

Ruthenium Dichloride (?).—Forty years before the discovery of ruthenium by Claus, Vanquelin had noticed the azure-blue color produced by the action of zinc upon certain solutions, a reaction which he attributed to osmium. One of the most characteristic reactions of trivalent ruthenium is this blue color formed by the action of hydrogen sulphide. Since it is produced by the action of reducing agents upon the solution of ruthenium trichloride, Claus attributed it to the formation of a bichloride, but he did not separate the salt. When a mixture of chlorine and carbon monoxide is passed over finely divided ruthenium at a comparatively low temperature, a very voluminous powder is obtained which contains anhydrous trichloride, as shown by Joly. This

is insoluble in water, acids, and strong alcohol, but is freely soluble in dilute alcohol, to the same dark azure-blue solution. On distilling the solution in vacuum, Joly obtained what he considered to be an oxychloride, and he looked upon the blue solution as $\text{Ru}(\text{OH})\text{Cl}_2$. Inasmuch as in the solution of this variety of the trichloride, aldehyde is formed, and since the blue color is produced in every case by a reducing action, it seems to me probable, that a true bichloride is present. In spite of much effort, I have not succeeded in preparing a pure salt from the blue solution, but several that have been prepared point to a compound of the formula $3\text{CsCl}, 2\text{RuCl}_2, 2\text{H}_2\text{O}$. These were formed by reducing a solution of ruthenium trichloride in an electrolytic cell, and immediately adding a solution of cesium or rubidium chloride. The fine precipitate varies from dark greenish blue to olive-green, oxidizes with great rapidity, and is very difficult to filter and wash, even under suction. Analyses of a number of the precipitates are given, two of which, 24 and 25, point to the above formula. In the others the amount of chlorine is too large in proportion to the ruthenium for RuCl_2 , though in every case less than is required for RuCl_3 . The addition of cesium chloride to the blue alcoholic solution of the anhydrous trichloride causes a precipitate much resembling that from the solution obtained by electrolytic reduction, but it has not yet been found possible to filter it off and wash it. The investigations upon the blue solution are still being carried on.

Another investigation now in progress may also be mentioned in this connection. An attempt was made to reduce the trichloride of ruthenium by stannous chloride. If the salt is not completely in solution a fugitive greenish blue solution is produced, but in general the dark yellowish red solution of the trichloride becomes much lighter, and if dilute, is almost completely decolorized. On adding water to this solution a yellow flocculent precipitate is formed, which contains all the ruthenium which was in the solution. This precipitate is insoluble in hot water, but easily soluble in hydrochloric acid, from which it is again precipitated on dilution. From the hydrochloric acid solutions are obtained two crystalline salts: one consists of white to pale yellow octahedra of cesium (or rubidium) chlorostannate, thus showing an oxidation of the tin; the other crystals are brilliant red (apparently) octahedra. These seem to be perfectly uniform

and analysis shows them to contain both tin and ruthenium.

For the material used in my work, I am indebted to Johnson, Matthey and Co., of London, for crude ruthenium; to Baker & Co., of Newark, N. J., for the use of several ounces of iridosmium; and to the Imperial Academy of Sciences, through its president and Professor N. N. Beketoff, director of its laboratory, for a considerable quantity of ruthenium.

ANALYTICAL WORK.

The analysis of most of the salts described in this paper was carried out by heating 0.2 to 0.35 gram of the salt contained in a platinum or at times in a porcelain boat, in a combustion tube in a current of hydrogen. The hydrochloric acid evolved was collected in a solution of silver nitrate, guarded by a second silver nitrate solution, to prove complete absorption of the gas. This gave the chlorine freed from the ruthenium by heat. The residue, consisting of ruthenium and alkali chloride, was extracted with hot water, followed by dilute acid. The alkali chloride was then determined, either by evaporation or by precipitation of the chlorine. The ruthenium was heated in a hydrogen stream before weighing; occasionally the ruthenium, on being brought to the air, glowed, and was slightly oxidized, giving results a little too high.

For the direct determination of water, or hydroxyl groups, the salt was heated in oxygen in a porcelain boat, and several coils of silver foil kept in front of the boat. The rear end of the combustion tube was guarded by a phosphorus pentoxide tube, and the gas from the tube passed through a weighed phosphorus pentoxide tube. The chlorine given off in the oxygen stream was almost completely held by the first silver coil. After heating in oxygen, the phosphorus pentoxide tube was removed, silver nitrate solution substituted, and the analysis continued in a hydrogen stream in the usual way. The only defect of this method is that, even at the low heat used, a small quantity of ruthenium is volatilized in the oxygen; hence, where this method was used the ruthenium is a little low.

Cesium Chlorruthenate, Cs_2RuCl_6 .—Dark brown to black powder; under the microscope black octahedra; larger crystals are dark purplish red by transmitted light. It is almost insoluble in water, very slightly soluble in hydrochloric acid. It is best dissolved in

hot dilute hydrochloric acid, giving a reddish yellow solution, a decided yellow on dilution. The aqueous solution somewhat decomposed on boiling. The usual ruthenium reactions were given with potassium thiocyanate, and with ammonia and thiosulphate. The purple of this latter reaction comes more quickly than with the trichloride salts.

1. Filtrates from $\text{Cs}_2\text{RuO}_2\text{Cl}_4$ (formed from RuO_4 , CsCl , and HCl), boiled with hydrochloric acid, precipitated by alcohol as buff powder and recrystallized from hydrochloric acid, 0.2171 gram.

2. The alcoholic filtrate (similar to 1) evaporated somewhat giving on cooling black and red ($\text{Cs}_2\text{Ru}(\text{OH})_2\text{Cl}_3$) crystals, extracted with warm hydrochloric acid in which red crystals are more soluble, 0.4220 gram.

3. From 2 by further evaporation. Resembles black sand, 0.6118 gram.

4. From $\text{Cs}_2\text{Ru}(\text{OH})_2\text{Cl}_3$ (rose prisms) by boiling with concentrated hydrochloric acid. Contains small amount of trichloride, 0.2038 gram.

	1.	2.	3.	4.	Theory.
Ruthenium	17.69	17.94	17.64	17.51
Chlorine (with ruthenium) ..	23.76	22.54	24.05	22.11	24.44
Cesium	46.63	46.00	45.59	45.82
Chlorine (with cesium)	12.42	12.27	12.16	12.22

Rubidium Chlorruthenate, Rb_2RuCl_6 .—Octahedra, similar to the cesium salt.

5. Crystallized out of evaporated alcoholic filtrate from precipitation of salt formed by warming RuO_4 with RbCl and strong hydrochloric acid, 0.2914 gram.

	5.	Theory.
Ruthenium.....	21.20	20.93
Chlorine (with ruthenium).....	28.78	29.22
Rubidium.....	35.12	35.24
Chlorine (with rubidium).....	14.99	14.61

Cesium Oxylchlorruthenate, $\text{Cs}_2\text{RuO}_2\text{Cl}_4$, or $2\text{CsCl}, \text{RuO}_2\text{Cl}_2$.—Dark reddish purple powder; under microscope regular octahedra. Decomposed instantly by water, giving black precipitate. Soluble in cold hydrochloric acid to rose solution; evolves chlorine with hot hydrochloric acid; decomposed by sulphuric acid and nitric acid, giving odor of RuO_4 (O_3 ?); deflagrates slightly on heating. Formed by the action of cesium chloride and dilute hydrochloric acid on RuO_4 with little water.

6. First crop of crystals, 0.2955 gram.
7. Second crop, 0.3635 gram.
8. 6 and 7 mixed, 0.4538 gram.

	6.	7.	8.	Theory.
Ruthenium	20.51	21.76	18.86	18.76
Chlorine (with ruthenium) ..	12.91	13.72	13.11
Cesium	48.29	48.76	49.18	49.11
Chlorine (with cesium)	12.25	12.45	13.12	13.11
Oxygen	5.9I

Rubidium Oxychlorruthenate, $\text{Rb}_2\text{RuO}_2\text{Cl}_4$.—Similar to cesium salt. Formed in a similar manner, except in closed vessel. Second crop of crystals, washed with hydrochloric acid.

9. Heated in oxygen with silver coils and phosphorus pentoxide tubes, 0.2843 gram.

10. Heated in hydrogen, 0.2995 gram.

	9.	10.	Theory.
Ruthenium	22.09	22.70	22.76
Chlorine (with ruthenium) ..	15.78	16.07	15.88
Rubidium	38.80	38.43	38.31
Chlorine (with rubidium)	16.09	15.93	15.88
Oxygen	6.53	7.17

In 9 the increase in weight in the phosphorus pentoxide tube was 0.0021 gram. The formula $\text{Rb}_2\text{Ru}(\text{OH})_2\text{Cl}_4$ would have required 0.0114 gram.

In 10 the oxygen was determined by loss of weight in hydrogen less chlorine given off.

Cesium Aquochlorruthenate, $\text{Cs}_2\text{Ru}(\text{OH})_2\text{Cl}_3$ or $2\text{CsCl}, \text{Ru}(\text{OH})_2\text{Cl}_3$.—Rose prisms several millimeters long, no end faces, extinction parallel to edges of prism, when fine, as when precipitated by alcohol, a buff powder. Very slightly soluble in water, more soluble in hydrochloric acid to rose solution, pink on dilution. Crystallizes unchanged from solution in hydrochloric acid, but evaporated with hydrochloric acid on water-bath is partly converted into Cs_2RuCl_6 .

11. Precipitated by alcohol from blue filtrate from electrolytically reduced RuCl_3 and CsCl ; buff powder, 0.1493 gram.

12. From evaporated filtrate after partial precipitation of Cs_2RuCl_6 (Analysis 1) by alcohol. Rose prisms, 0.2636 gram.

	11.	12.	Theory.
Ruthenium	17.88	18.25	18.07
Chlorine (with ruthenium) ...	18.93	18.76	18.90
Cesium	47.48	46.93	47.23
Chlorine (with cesium)	12.67	12.52	12.60
Water (by loss)	2.97	3.74	3.20

Cesium Ruthenium Trichloride, $\text{Cs}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ or $2\text{CsCl} \cdot \text{RuCl}_3 \cdot \text{H}_2\text{O}$.—Dark brown powder; under the microscope, tables, probably orthorhombic; when thin, brown; when thicker, dark brownish red. Some crystals one or two millimeters long exhibit base, pinacoids and dome. The chemical properties are those of ordinary salts of ruthenium trichloride. Fairly soluble in water and hydrochloric acid.

13. Formed by action of RuO_4 on hydrochloric acid and addition of cesium chloride. Recrystallized from dilute hydrochloric acid. Analysis in oxygen with phosphorus pentoxide tubes, 0.4019 gram.

	13.	Theory.
Ruthenium	18.61	18.07
Chlorine (with ruthenium).....	19.11	18.90
Cesium	47.23
Chlorine (with cesium)	12.60
Water (by phosphorus pentoxide) .	3.28	3.20

Rubidium Ruthenium Trichloride, $\text{Rb}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$, or $2\text{RbCl} \cdot \text{RuCl}_3 \cdot \text{H}_2\text{O}$.—Properties and formation similar to cesium salt.

14. RuO_4 treated with concentrated hydrochloric acid and RbCl cold; recrystallized from hydrochloric acid, 0.3235 gram.

15. Same method but warm hydrochloric acid; recrystallized, 0.2925 gram.

16. Same method, warm hydrochloric acid; minute brown transparent tables, not recrystallized, 0.2598 gram.

17. Same, recrystallized, analysis in oxygen with phosphorus pentoxide tubes, 0.2480 gram.

18. RuO_4 precipitated as hydrated oxide by alcoholic potash. Precipitate dissolved in hydrochloric acid and RbCl added to hot solution. Crystallized out on cooling. Heated to 260° two hours. A subsequent experiment showed that this salt continued to lose weight very slowly at 260° during upwards of a week and only becomes constant when one atom of chlorine has been given off, 0.2027 gram.

	14.	15.	16.	17.	18.	Theory.
Ruthenium	22.13	22.46	22.25	23.15	22.39	21.73
Chlorine (with ruthenium) .	22.90	22.42	23.37	23.01	23.09	22.74
Rubidium	37.88	36.27	37.45	35.78	37.17	36.48
Chlorine (with rubidium) ..	15.71	15.66	14.45	14.83	15.41	15.19
Water	2.26 ¹	3.18 ¹	2.08 ¹	2.66 ²	4.58 ³	3.85

¹ By difference.

² By phosphorus pentoxide.

³ 3.11 at 260° + 1.47 by difference.

Complex Cesium Salts of Ruthenium Trichloride.—Analyses give evidence of the existence of a number of these salts, though the formulas cannot be considered as established, as there is no certainty that the substance analyzed was completely uniform. Analyses of three of these salts are appended.

19. Fine brown powder, precipitated by cesium chloride from a solution of RuO_4 in concentrated hydrochloric acid, 0.5496 gram.

20. Minute brown crystals precipitated by alcohol from the filtrate from 19, 0.0744 gram.

They both correspond most closely to the formula $3\text{CsCl}, 2\text{RuCl}_3, 3\text{H}_2\text{O}$.

	19.	20.	Theory.
Ruthenium.....	19.81	20.97	20.84
Chlorine (with ruthenium)...	22.04	20.37	21.81
Cesium.....	41.63	42.74	40.91
Chlorine (with cesium).....	11.10	11.43	10.90
Water (by loss).....	5.37	4.09	5.54

21. Black crystals, seemingly uniform octahedra, crystallized on cooling from a strongly acid solution of hydrated oxide of ruthenium and cesium chloride in hydrochloric acid, 0.1217 gram.

Corresponds best to $3\text{CsCl}, 2\text{RuCl}_3, \text{H}_2\text{O}$.

	21.	Theory.
Ruthenium.....	20.53	21.64
Chlorine (with ruthenium).....	22.72	22.65
Cesium.....	42.28	42.46
Chlorine (with cesium).....	11.27	11.33
Water (by loss).....	1.20	1.91

22. Brown powder, on evaporation of filtrate from 12, 0.1774 gram.

23. Dark chocolate brown powder. Buff alcoholic precipitate from warmed RuO_4 , CsCl , and dilute hydrochloric acid, dissolved in dilute hydrochloric acid and evaporated nearly to dryness. Deposited from hot solution during evaporation, 0.1209 gram.

22 and 23 correspond best to the formula $5\text{CsCl}, 3\text{RuCl}_3, \text{H}_2\text{O}$.

	22.	23.	Theory.
Ruthenium.....	20.41	20.02	20.54
Chlorine (with ruthenium)...	21.00	21.45	21.50
Cesium.....	45.46	45.45	44.79
Chlorine (with cesium).....	12.12	12.12	11.94
Water (by loss).....	1.01	1.38	1.21

Lower Chloride of Ruthenium, RuCl_2 (?).—The following

analyses are given to indicate the composition of the blue solution formed on the electrolytic reduction of ruthenium trichloride. The concentrated solution was either added to a strong solution of cesium chloride, or vice versa, with or without the addition of alcohol. The precipitate was immediately filtered on a Hirsch funnel and washed with dilute hydrochloric acid and alcohol, and dried on a tile.

	24.	25.	26.	27.	28.
Ruthenium	24.16	22.40	17.30	18.56	18.02
Chlorine (with ruthenium)	16.15	16.39	17.11	17.46	15.80
Cesium	43.96	43.89	50.01	49.75	50.51
Chlorine (with cesium)	11.73	11.78	13.35	13.27	13.46
Water (by loss)	4.18	4.22	3.37	3.16	4.91
Ratio Ru : Cl (with Ru)	1:1.9	1:2.1	1:2.84	1:2.7	1:2.5
Ratio Cl (with Cs) : Cl (with Ru)	1:1.4	1:1.4	1:1.27	1:1.3	1:1.17
Weight of analysis	0.1672	0.2188	0.1289	0.1794	0.2714
		29.		30.	
Ruthenium		23.43		22.23	
Chlorine (with ruthenium)		21.65		21.54	
Rubidium		34.02		...	
Chlorine (with rubidium)		14.13		...	
Water (by loss)		2.89		2.72	
Ratio Ru : Cl (with Ru)		1:2.64		1:2.77	
Ratio Cl (with Rb) : Cl (with Ru)		1:1.53		...	
Weight of analysis		0.1626		0.2168	

Except in the case of 24 and 25 there is evidently no approximation to a definite compound, the substances being varying mixtures of $2\text{CsCl}, \text{RuCl}_3 \cdot \text{H}_2\text{O}$ with a reduced chloride. 24 and 25 would indicate that the composition of this chloride is $3\text{CsCl}_2, 2\text{RuCl}_2 \cdot \text{H}_2\text{O}$, or if Joly's supposition is correct, $3\text{CsCl}, 2\text{Ru}(\text{OH})\text{Cl}_2$. The theoretical composition of the former salt is

Ruthenium	22.93
Chlorine (with ruthenium)	16.00
Cesium	45.00
Chlorine (with cesium)	12.00
Water	4.06

but in spite of the tolerable agreement of Analyses 24 and 25, the formula cannot be considered as established, and it is hoped that by varying the conditions of its preparation, a salt of assured purity may be obtained.