[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

CONTRIBUTIONS TO THE STUDY OF RUTHENIUM. X. THE "ISOMERIC" CHLORIDES

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When in 1844 Claus[1] discovered ruthenium, he prepared two double chlorides with potassium, to which he assigned the formulas K_2RuCl_5 and K_2RuCl_6. The first was formed when the precipitated oxide of ruthenium, or the volatile tetroxide, was dissolved in hydrochloric acid and treated with potassium chloride; the second when aqua regia was used. This was quite in harmony with salts of the other platinum metals. Claus also assigned the probable formula of $RuCl_2$ to the compound giving a conspicuous blue color when ruthenium solutions are treated with zinc, hydrogen sulfide or other strong reducing agents.

Later[2] it was shown that the supposed K_2RuCl_6 was a nitroso salt, K_2RuCl_5NO, which contains nearly the same percentage of ruthenium. The error of Claus was occasioned by his having determined the chlorine only by loss, and by having considered the atomic weight of ruthenium as 104.57.

The first salt has since the days of Claus passed for K_2RuCl_5, a pentachloro-ruthe*nite*, though the corresponding cesium and rubidium salts have appeared to be monohydrates, and a monohydrate of the potassium salt has also been described.[3] No efforts to oxidize this salt to K_2RuCl_6 have been effective.

Later, Howe[4] described a new monohydrate of K_2RuCl_5, which differed very markedly from the former salt in properties, especially in stability toward hydrolysis and in being converted into K_2RuCl_6 by the action of chlorine. This was formed from the earlier K_2RuCl_5 by boiling with dilute alcohol in acid solution, and was called an "aquo" salt. The corresponding rubidium and cesium salts were also prepared, as well as similar salts with bromine[5] in the place of chlorine. Attention was called to the apparent isomerism between these two series of pentachlororuthenites.

The composition of the blue compound, supposed by Claus to be $RuCl_2$, was considered by Joly[6] to be $RuCl_2OH$, but in our work in this Laboratory[7]

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[1] Claus, *Bull. acad. sci., St. Petersburgh*, **3**, 38, 311, 354 (1845).

[2] (a) Joly, *Compt. rend.*, **107**, 998 (1888); (b) **108**, 854 (1889). (c) Howe, THIS JOURNAL, **16**, 388 (1894).

[3] Miolati and Tagiuri, *Gazz. chim. ital.*, **30** (II), 511 (1900).

[4] Howe, THIS JOURNAL, **26**, 543 (1904).

[5] Howe, *ibid.*, **26**, 942 (1904).

[6] Joly, *Compt. rend.*, **114**, 291 (1892).

[7] Howe, Howe, Jr., and Ogburn, THIS JOURNAL, **46**, 335 (1924).

we satisfied ourselves that the compound contains bivalent ruthenium, and is $RuCl_2$ as Claus inferred, or at least $(RuCl_2)_x$. Remy[8] has more recently considered it to contain univalent ruthenium, basing his opinion on its being formed by the reduction of K_2RuCl_5, two units, as measured by the action of sodium amalgam. Zintl and Zaimis[9] also assume univalent ruthenium in the blue solution, basing their view on the potentiometric titration of "$RuCl_3$" with $CrSO_4$ or $Ti_2(SO_4)_3$, where with one equivalent they obtain a pale yellow solution, while with the next drop the blue begins to appear.

There are thus two problems insufficiently cleared up in connection with the chlorides of ruthenium, (1) the apparent isomerism in the K_2RuCl_5 series and (2) the valence of ruthenium in the blue compound.

Aoyama[10] proposed calling the original K_2RuCl_5 the *alpha* salt, the dehydrated "aquo" salt *beta*, and added a third isomer, formed by the dechlorination of the hexachloro salt, K_2RuCl_6, in hydrogen chloride gas, which he called a *gamma* salt. Gutbier,[11] however, showed that the *beta* and *gamma* salts are identical, and that both, when dissolved in dilute HCl, crystallize out as the "aquo" salt. The *alpha* and *beta* salts he considered to be isomers.

Briggs[12] accounts for the seeming isomerism by assigning the formula $2K_2RuCl_5.3H_2O$ to the "aquo" salt. He states that the water should be weighed directly and not determined by loss, and that the salt must be heated in oxygen, since heating in air gives low results for the water. It is quite true that heating in air gives lower results than heating in oxygen, but the results in air check, especially in the case of the cesium salt, for the formula originally proposed for the "aquo" salt, $Cs_2RuCl_5.H_2O$. When heated in oxygen, ruthenium is slightly oxidized to the volatile tetroxide, which may account for the higher results of Briggs.

The reaction between hydrochloric acid and ruthenium tetroxide has been studied by a number of workers in the effort to throw light upon the chlorides. When the volatile tetroxide is collected in hydrochloric acid and potassium chloride added, the ordinary pentachloro salt is obtained, with the ratio K_2RuCl_5, and this has generally been accepted as containing trivalent ruthenium, though there has been but a single attempt[13] to verify this. Howe[14] found that by the action of a solution of cesium chloride in concentrated hydrochloric acid a salt was obtained with the formula $Cs_2RuO_2Cl_4$, which is quite unstable; a similar osmium salt was obtained

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[8] Remy and Wagner, *Ber.*, **60**, 493 (1927).

[9] Zintl and Zaimis, *Ber.*, **60**, 842 (1927).

[10] Aoyama, *Z. anorg. Chem.*, **138**, 249 (1924).

[11] Gutbier and Niemann, *ibid.*, **141**, 312 (1925).

[12] Briggs, *J. Chem. Soc.*, **127**, 1042 (1925).

[13] Charonnat, *Compt. rend.*, **180**, 1271 (1925).

[14] Howe, This Journal, **23**, 779 (1901).

by Wintrebert.[15] The free acid of the ruthenium salt, $H_2RuO_2Cl_4.3H_2O$, was prepared by Aoyama[10] by the action of hydrogen chloride gas on the tetroxide. Krauss[16] let RuO_4 act on hydrochloric acid and potassium iodide and estimated the liberated iodine, finding that the ruthenium was reduced five units, that is, apparently, to K_2RuCl_5. On the other hand, he[16a] and others[17] have obtained hexachloro-ruthenates, M_2RuCl_6, either directly from RuO_4 or from the K_2RuO_4 in the peroxide melt; but the conditions of formation of the hexachloro-ruthenates have not been reproducible, and treatment of the "aquo" salts with chlorine has been relied on to prepare these salts. The hexabromo salts have been prepared in an analogous way.

Some two years ago, Charonnat[13] suggested that the true formula for the ordinary pentachloro salt is K_2RuCl_5OH, basing his view upon the action of this salt on potassium iodide, and on the formation of the "aquo" salt by the action of hydrochloric acid on the oxalato-ruthenite, $K_3Ru(C_2O_4)_3$, in which the ruthenium is undoubtedly trivalent. Owing to lack of any details or analyses, and to the fact that most other ruthenium salts give pentachloro salts on treatment with hydrochloric acid, his view, though correct, has not obtained recognition; to Charonnat belongs the credit for the final solution of this perplexing problem. The fact that the pentachloro salt liberates iodine from potassium iodide has long been known, and Gall and Lehmann[18] have studied this reaction with a view to its analytical possibilities. They have concluded that there is an equilibrium, $RuCl_3 + HI \rightleftharpoons RuCl_2 + HCl + I$, which seems to be the case.

This reaction between the pentachloro salt and potassium iodide has recently been worked on in this Laboratory in the effort to complete the third step[19] in the determination of ruthenium, namely, to determine the ruthenium in the RuO_4 distillate. Failing to obtain satisfactory results with potassium iodide, evidently because of the above equilibrium, stannous chloride was tried, and in this work the surprising result was obtained that both K_2RuCl_5 and K_2RuCl_6 were each reduced one unit, and each gave the "aquo" salt on its reduction. In other words, *the valence of ruthenium is four, not only in K_2RuCl_6, but also in what has always passed for K_2RuCl_5.* The formula of the latter salt proves to be K_2RuCl_5OH, as suggested by Charonnat, and it is a one-fourth hydrolyzed hexachloro-ruthe*nate*. This was established both by analysis and also by recrystallization. K_2RuCl_5OH was recrystallized from very concentrated hydrochloric acid and K_2RuCl_6 obtained, while when K_2RuCl_6 was re-

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[15] Wintrebert, *Thesis*, Bordeaux, **1902**.

[16] (a) Krauss, *Z. anorg. Chem.*, **117**, 111 (1921); (b) **136**, 62 (1924).

[17] Howe, THIS JOURNAL, **23**, 784 (1901), Analysis 11.

[18] Gall and Lehmann, *Ber.*, **59**, 2856 (1926).

[19] Howe and Mercer, THIS JOURNAL, **47**, 2931 (1925).

crystallized from a less concentrated hydrochloric acid (under 6–8 *N*), the product was K_2RuCl_5OH. Since this is the ordinarily obtained compound of ruthenium, it would seem probable that the hydrated oxide of ruthenium, usually considered to be $Ru_2O_3.xH_2O$, is really $RuO_2.xH_2O$, since its solution always leads to H_2RuCl_5OH.

This also clears up the formation of the "aquo" salt, which is now to be recognized as the ordinary salt of trivalent ruthenium. Of the many different substances used in its formation,[20] such as alcohol, glucose, stannous chloride, etc., all are reducing agents, and the reaction is merely the reduction of quadrivalent to trivalent ruthenium. In some cases, as with alcohol, the reduction is slow, and has often failed to go to completion, resulting in impure salts and aberrant analyses. This also explains the ready oxidizability of the "aquo" salt to the hexachloro salt by chlorine, and why the hexachloro salt could not be formed from the pentachloro salt by oxidation.

It further follows from this work that the ruthenium in the blue solution is bivalent, since it is formed by reducing $Ru^{iv}Cl_3OH$ (H_2RuCl_5OH) two units. The yellow solution obtained by Zintl and Zaimis[9] by its reduction one unit was the solution of the trivalent "aquo" salt.

The following chloro salts of ruthenium would thus seem to be well established; in most of the cases the corresponding bromo salts have also been prepared and are wholly analogous.

A. $M_2Ru^{vi}O_2Cl_4$ (M = H, Rb, Cs); the hydrogen salt formed by the action of gaseous hydrogen chloride on RuO_4; the rubidium and cesium salts by the action of rubidium or cesium chloride solution in very concentrated hydrochloric acid on RuO_4.

B. $M_2Ru^{iv}Cl_6$ (M = NH_4, K, Rb, Cs); formed by the action of chlorine on $M_2Ru^{iii}Cl_5.H_2O$; by action of very dilute cold hydrochloric acid on the K_2RuO_4 melt;[21] by recrystallization of $M_2Ru^{iv}Cl_5OH$ from concentrated hydrochloric acid.

B(*a*). $Cs_2Ru^{iv}Cl_6.H_2O$; formed by the action of a solution of cesium chloride on a solution of RuO_4 in hydrochloric acid;[22] efforts to obtain the rubidium and potassium hydrated salts in pure form were not successful.

C. $M_2Ru^{iv}Cl_5OH$ (M = NH_4, K, Rb, Cs); formed whenever a solution of RuO_4 in hydrochloric acid (except in very concentrated acid) is treated with an alkali chloride; when a solution of a ruthenate, M_2RuO_4, is treated with hydrochloric acid; when the solution of any oxide of ruthenium, except one precipitated from the "aquo" salt, in hydrochloric acid is treated with an alkali chloride; when a hexachloro-ruthenate,

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[20] Howe and Haynes, THIS JOURNAL, **47**, 2924 (1925).

[21] Antony and Lucchesi, *Gazz. chim. ital.*, **29** (II), 82 (1899); see also private communication from Antony, THIS JOURNAL, **26**, 546 (1904).

[22] Ref. 16 (a), p. 117.

$M_2Ru^{iv}Cl_6$ is recrystallized from hydrochloric acid, unless the latter is very concentrated.

D. $M_2Ru^{iii}Cl_5.H_2O$ (M = NH_4, K, Rb, Cs); formed by the reduction of any of the salts of quadrivalent ruthenium in hydrochloric acid solution by alcohol, oxalic acid or other organic substance, stannous chloride or potassium iodide; also by the spontaneous oxidation in the air of the blue solution of bivalent ruthenium.[17] These are the only crystalline salts of trivalent ruthenium, and are properly called pentachloro-ruthe*nites* (ruthen*i*at of Gutbier). It might be wise, however, to continue the use of the term "aquo"-ruthenites to distinguish them from the old pentachloro-ruthenites, which now become pentachloro-(hydroxy-)ruthen*a*tes.

E. $M_2Ru^{iii}Cl_5$; formed only by the dehydration of the "aquo" salt, or dechlorination of the hexachloro-ruthenates (Aoyama's *gamma* and *beta* salts). These have not been obtained in a crystallized form and cannot, of course, be regarded as definite salts with a coördination number of five, but are of the same nature as the K_2SO_4 and $Al_2(SO_4)_3$ in dehydrated alum.

In all of these salts ruthenium has a coördination number of six and thus one of the few remaining compounds with an apparent coördination number of five is deleted from the list.

Experimental Work

The starting point of all the work described in this paper was ruthenium tetroxide, distilled by a current of chlorine from an alkaline sodium hypochlorite solution of various ruthenium compounds and residues. As the material was free from osmium, the purity of the ruthenium obtained was assured. The hypochlorite solutions were placed in a tubulated retort, chlorine (from a chlorine cylinder) led in until the deep red color of the ruthenate changed into the golden yellow of the tetroxide, when the chlorine stream was cut off and the retort rapidly heated to boiling. The RuO_4 passed over with the steam and was collected in a small amount of concentrated hydrochloric acid in an Erlenmeyer flask immersed in ice-water. With care no loss of the tetroxide occurred. On standing, the RuO_4 was completely converted into either H_2RuCl_6 or H_2RuCl_5OH, according to the concentration of the hydrochloric acid. If the amount of the RuO_4 is small, it dissolves in the hydrochloric acid and the conversion into the chloride is rapid; if the amount is larger, it collects in drops of liquid RuO_4, which dissolve only slowly. The solutions of the chloride were concentrated to any desired degree and the salts formed by the addition of alkali chloride. If the solutions were quite concentrated, the salts precipitated on addition of the chloride; if more dilute the crystalline salts were obtained on evaporation. A similar procedure was used for recrystallization of the salts, these being dissolved in hot water sufficiently acidified with hydrochloric acid to prevent further hydrolysis. For the preparation of the "aquo" salts, solutions of quadrivalent ruthenium, either of the acid or of the salts, were boiled in rather dilute condition with about one-fourth their volume of alcohol until the lightening of the color indicated reduction to trivalent ruthenium. Often the reduction was not complete, as was later revealed both by color and by analysis of the salts.

It has been supposed by some that the "aquo" salt is converted into the M_2RuCl_5OH by the action of concentrated hydrochloric acid, and in some of the earlier work in this Laboratory there seemed to be indication of this. To test this point, a particularly pure sample of $K_2Ru^{iii}Cl_5.H_2O$ was dissolved in dilute hydrochloric acid and twice evaporated on a hot-plate with concentrated hydrochloric acid to crystallization. The only crystals obtained were those of the original "aquo" salt, and the solution retained the color of the pure "aquo" salt. Later it was found that in cases where the quadrivalent salt had apparently been obtained from the trivalent salt by the action of hydrochloric acid, the latter salt had been originally contaminated by the quadrivalent salt owing to incomplete conversion by alcohol.

The difficulty of *complete* conversion of the salts of the three series, M_2RuCl_6, $M_2Ru^{iv}Cl_5OH$ and $M_2Ru^{iii}Cl_5.H_2O$, into one another should be emphasized; it results in great difficulty in preparing pure salts for analysis, and is undoubtedly responsible for many irregularities in analytical figures.

The analyses were carried out, as usual, in this Laboratory, by heating the salt in a stream of purified and dried hydrogen and collecting the evolved hydrogen chloride in a solution of silver nitrate, The combustion tube was of Jena glass, one end drawn out somewhat, and so bent as to dip directly into the silver nitrate solution. It was heated in an electric combustion furnace with the top so hinged that the tube could be inspected, if desired, during heating. The salt was contained in a small boat of fused quartz. The precipitated silver chloride was collected and weighed in a Gooch filter and dried in an electric oven at 110°. Thus far the analysis gives, from the loss in weight in the boat, the $Ru + 2MCl$, and, from the weight of the silver chloride, the chlorine "connected with the ruthenium."[23] Any water or hydroxyl present will appear as loss. As already noted, Briggs has called attention to the fact that such a water determination is unreliable, since all the errors fall on the loss. This is brought out by an inspection of a large series of analyses, where the loss

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[23] In most cases, the residue in the boat was treated with hot water, the ruthenium filtered, burned and reheated in hydrogen; the alkali chloride evaporated in a fused quartz crucible and weighed. Frequently, as Briggs has pointed out, a little of the alkali chloride is not dissolved out by a single extraction, and hence the ruthenium results are often a little high and those for the alkali chloride correspondingly low. A number of experiments showed that this error was generally less than 0.1%.

shows considerable variation. Further, of course, it does not discriminate between water and hydroxyl. For this reason, in a number of cases, the water from the hydroxyl group was determined directly by absorption in phosphorus pentoxide. As it was necessary to heat the salt to a fairly high temperature to insure the decomposition of the hydroxyl, the chlorine connected with the ruthenium was also evolved. In earlier work this chlorine was retained by passing over heated silver foil; more recently anhydrous sodium carbonate was used. The front of the combustion tube was filled for a distance of ten centimeters with recently heated, anhydrous sodium carbonate, and a layer of the same was placed over the salt in the combustion boat. Air was drawn through the tube by a suction pump, being dried by a calcium chloride tube and a phosphorus pentoxide tube before entering the combustion tube. The absorption phosphorus pentoxide tube was guarded by a calcium chloride tube and two sulfuric acid drying bottles, these serving also as a gage for the velocity of the air current. Several blanks were run before each series of analyses. The temperature used varied, in some cases being sufficiently high to fuse the sodium carbonate. This method was tested on $Rb_2MnCl_4.2H_2O$ and found to be accurate.

In considering the experimental work on each of the three series of chloro salts, the establishment of the formula has been first given, followed by the results of *all* the analyses made, as well as the origin of the salts, except in those cases in which there were evident analytical errors. It has been thought best to give all the analyses, in order that the material may be available to others who are working in this field and who may find some different interpretation.

Work on Series B; the Hexachloro-ruthenates, M_2RuCl_6

As these salts have already been well established as being formed by the action of chlorine on the "aquo" salts, it was further desirable only to determine whether they could also be formed by the action of concentrated hydrochloric acid on the pentachloro-hydroxy-ruthenates, thus confirming the constitution of the latter, and also to determine the amount of reduction in valence by the action of stannous chloride. The ordinary pentachloro-ruthenate (actually K_2RuCl_5OH) was recrystallized from concentrated hydrochloric acid. The crystals obtained resembled in every way those of the hexachloro-ruthenate, K_2RuCl_6.

Anal. Calcd. chlorine removable by hydrogen: for K_2RuCl_6, 36.13; for K_2RuCl_5OH, 28.43; for K_2RuCl_5, 29.78. Found: 34.89.

It is probable that the conversion into the hexachloro salt was not complete; the analysis of a second crop of crystals, the hydrochloric acid having become less concentrated by evaporation, gave only 27.85% of chlorine, corresponding to the pentachloro-hydroxy salt.

Titration of the recrystallized salt with stannous chloride to the "aquo" salt: Theoretical for reduction of one valence, 25.89; for reduction to bivalent ruthenium, 12.94. Found: ruthenium (six titrations), 24.10 to 25.31%.

This established the fact that the hexachloro salt is formed from the pentachloro salt by recrystallization from concentrated hydrochloric acid; hence, since oxidation under these conditions is out of the question, the valence of ruthenium in the pentachloro salt is the same as in the hexachloro salt, that is, *four*. From this standpoint the pentachloro salt is to be looked on as a one-fourth hydrolyzed hexachloro salt.

TABLE I

ANALYSES

	Calcd.	(23)[a]	(24)[b]	Antony[c]
Taken, g.		0.2336	0.2549	
Ru + 2KCl, %	63.87	64.82	64.69	....
Ru, %	25.89	...	...	25.912
2KCl, %	37.98	...	...	37.936
Cl_4, %	36.13	34.89	35.26	36.074
Cl_6, %	54.163	...	...	54.146

TITRATION WITH $SnCl_2$ TO PINK "AQUO" SOLUTION

	Calcd.	(23)	(23)	(23)	(23)	(24)	(24)
Taken, g.	...	0.0837	0.0853	0.1041	0.1033	0.0347	0.0835
Ru, %	25.89	25.31	24.47	23.42	24.27	23.91	24.64

	Calcd.	(24)	(24)	(24)	(24)	(25)[a]	(25)
Taken, g.	...	0.1066	0.1124	0.1083	0.1319	0.1379	0.1301
Ru, %	25.89	24.69	24.07	23.03	24.39	24.10	24.64

[a] (23), (25): K_2RuCl_5OH recrystallized from concentrated hydrochloric acid.

[b] (24). Precipitated from concentrated solution of the "aquo" salt by chlorine.

[c] Antony's salt (Ref. 21) was prepared by the action of very dilute hydrochloric acid on a potassium ruthenate, K_2RuO_4, melt containing potassium chlorate, and concentrated in a vacuum in the cold. Under these conditions neither further reduction nor hydrolysis took place.

Work on Series C; the Pentachloro-hydroxy-ruthenates, $M_2Ru^{iv}Cl_5OH$

In establishing the constitution of these salts, the crucial point, aside from the ordinary analysis, is the determination of the water and of the change of valence by the action of stannous chloride or potassium iodide.

The Potassium Salt.—In the two most reliable preparations (8) and (10), second and third crop recrystallizations, we have, as regards water directly determined by absorption in phosphorus pentoxide, the following results.

Anal. Calcd. for K_2RuCl_5OH: H_2O, 2.40; for $K_2RuCl_5.H_2O$: H_2O, 4.54. Found: 2.79, 2.23.

Results obtained as regards valence, by reduction with stannous chloride to the "aquo" salt:

Theoretical for reduction of one valence, 27.18. Ruthenium (seven[24] titrations), 24.05 to 26.64 per cent. The "aquo" salt (trivalent ruthenium) gives no reduction.

In the reduction by potassium iodide, no satisfactory end-point could be obtained, but the results (given below) point also to a reduction of one valence.

The Rubidium and Cesium Salts, Rb_2RuCl_5OH and Cs_2RuCl_5OH.—No new direct determinations of water were made with these salts, and little reliance can be placed on the water analyses of the earlier work, though the existence of a monohydrate of the cesium salt and possibly of the rubidium salt is distinctly pointed out. These salts are too slightly soluble for titration work.

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[24] Two titrations giving 20.12 and 19.89 are omitted here as the salt was evidently contaminated by "aquo" salt.

These results, and numerous other titration experiments with the free acid (given in the following paper) seem to leave no doubt but that the salts formed when RuO_4 is dissolved in hydrochloric acid and an alkali chloride added, contain quadrivalent ruthenium, and that, unless the acid is very concentrated, the formula of such salts is M_2RuCl_5OH. The same is probably true regarding the bromo salts, as they seem to resemble the chloro salts in every particular.

TABLE II

ANALYSES OF POTASSIUM PENTACHLORO-HYDROXY-RUTHENATE, K_2RuCl_5OH

	Calcd.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Taken, g.	...	0.3369	0.3194	0.3719	0.3074	0.2818	0.2606	0.2964	0.2819	0.2780
Ru + 2KCl, %	67.03	68.82	68.99	68.73	68.44	68.18	69.07	68.35	68.11	67.70
Ru, %	27.18	27.68	27.90	27.75	27.88	28.03	28.36	27.80	...	27.12
2KCl, %	39.85	40.49	40.56	40.56	40.35	40.28	40.08	39.91	...	39.60
Cl_3 + OH, %	32.97	31.18	31.01	31.27	31.56	31.58	30.93	31.64	31.89	32.30
Cl_3, %	28.43	28.35	28.38	28.82	28.97	27.82	27.14	28.82	27.85	30.35
OH (loss), %	4.54	2.85	2.62	2.48	2.74	3.76	3.79	2.82	4.04	1.95

Water determinations by phosphorus pentoxide absorption

	Calcd.	(5)	(6)	(6)	(6)	(6)	(7)	(8)	(10)	(6)	(1)	(3)
Taken, g.	..	0.2496	0.3610	0.3058	0.4802	0.3718	0.4190	0.3434	0.4839	0.3104	0.3124	0.1914
H_2O, %	2.40	1.62	.89	2.00	1.24	1.05	1.53	2.79	2.23	2.12	2.11	.99

Valence determination by reduction to rose ("aquo") $K_2Ru^{iii}Cl_5.H_2O$ solution[a]

	Calcd.	(5)	(5)	(6)	(6)	(7)	(7)	(8)	(8)	(9)
Taken, g.	...	0.1023	0.1035	0.1038	0.1046	0.1034	0.1075	0.1092	0.1053	0.1068
Ru, %	27.18	24.68	24.05	20.12	19.89	25.68	25.68	25.54	24.84	26.64

Valence reduction[b]

	(6)	(6)	(6)	(5)
Taken, g.	0.1053	0.1343	0.1512	0.0693
Valence reduction	.960	.854	.904	1.020

[a] Reduction by stannous chloride, iodine-starch indicator; the figures found represent the percentage of ruthenium in the salt, assuming the ruthenium to be reduced one valence.

[b] Reduction by KI and titration with $Na_2S_2O_3$ solution and starch indicator. No satisfactory end-point was obtained, and hence these figures can be looked on as only approximate. The results, however, point very clearly to a reduction of one valence, that is, from quadrivalent to trivalent ruthenium.

Origin of salts

(1), (2): Recrystallized salt; dissolved in hot, dilute hydrochloric acid and concentrated acid added to about 6 *N*; brilliant black crystals.

(3), (4): Crystallized out from mother liquor of (1) while evaporating on hot plate; similar to (1).

(5): Recrystallized from dilute hydrochloric acid; brown.

(6): Recrystallized from 6 *N* hydrochloric acid on hot plate; black crystals but probably contaminated by a little "aquo" salt.

(7): Solution of RuO_4 in rather strong hydrochloric acid precipitated hot by KCl solution; fine black powder with bluish tint.

(8): Recrystallized salt, second crop; about 5 *N* acid.

(9): Evaporated filtrate from K_2RuCl_6 formed by leading chlorine into solution of the "aquo" salt; strong hydrochloric acid; evidently contained some unhydrolyzed K_2RuCl_6.

(10): Third crop from (8).

With the above may be compared the original analyses of the same salt by Claus,[25] and the analyses by Miolati and Tagiuri.[3]

TABLE III

EARLIER ANALYSES

Component, %	Theory	Claus			Miolati and Tagiuri	
Ru	27.18	28.48	28.96	28.91	27.11	...
2KCl	39.85	41.30	40.80	41.08	39.21	...
Cl_3 + OH (loss)	32.97	30.22	30.24	30.04	30.01[a]	32.73
Cl_5	47.38	...	48.30	48.95	...	...

[a] Miolati and Tagiuri determined the chlorine only by loss, which would include also the hydroxyl group.

TABLE IV

ANALYSES[26] OF RUBIDIUM PENTACHLORO-HYDROXY-RUTHENATE, Rb_2RuCl_5OH

	Calcd.	(12)[c]	(13)[a]	(14)[b]	(15)[a]	(16)[c]	(17)[c]
Taken, g.	...	0.3235	0.2925	0.2598	0.2480	0.2027	0.1809
Ru + 2RbCl, %	73.79	...	...	...	...	...	72.17
Ru, %	21.78	22.13	22.46	22.25	23.15	22.39	20.95
2RbCl, %	51.81	53.59	51.93	51.90	50.64	52.58	51.16
Cl_3 + OH, %	26.41	...	...	...	...	...	27.83
Cl_3, %	22.78	22.90	22.42	23.37	23.01	23.09	21.75
OH (loss), %	3.63	2.26	3.18	2.08	...	...	6.08 (0.27 at 145°)
$H_2O(P_2O_5)$, %	1.93	...	...	...	2.66	...	...

[a] Recrystallized salt.

[b] From warm hydrochloric acid.

[c] From hot dilute hydrochloric acid.

TABLE V

ANALYSES OF CESIUM PENTACHLORO-HYDROXY-RUTHENATE, Cs_2RuCl_5OH

	Calcd.	(18)[a]	(18)[a]	(18)[a]	(19)[a]	(18)[a]	(20)[b]	(21)[c]	(22)[b]
Taken, g.	...	0.2779	0.2676	0.5029	0.1927	0.2802	0.4019	0.7412	0.4019
Ru + 2CsCl, %	78.02	...	76.46	76.75	76.85	76.73	...	...	...
Ru, %	18.11	...	18.87	18.32	17.80	...	18.61	...	...
2CsCl, %	59.91	...	58.56	58.43	58.85	...	...	...	...
Cl_3 + OH, %	21.98	...	23.50	23.24	23.14	23.27	...	...	...
Cl_3, %	18.94	19.22	19.13	19.16	20.03	19.13	19.11	...	...
OH (loss), %	3.04	...	4.37	4.08	3.11	4.14	...	...	...
H_2O (P_2O_5), %	1.60	...	...	...	...	...	...	6.00	3.28

[a] Crystallized from evaporated solutions of H_2RuCl_5OH and cesium chloride; about 5 *N* hydrochloric acid.

[b] Recrystallized from dilute hydrochloric acid; earlier analyses.[26]

[c] Crystallized from hot solution of H_2RuCl_5OH and cesium chloride in dilute hydrochloric acid on cooling. The water of this analysis corresponds to a monohydrate, $Cs_2RuCl_5OH.H_2O$ (theory, H_2O = 6.04). (Analysis (17) of the rubidium salts points in the same direction, though this salt lost only 0.27 at 145°.) As the solution was only weakly acid, it is not unlikely that such a salt may have crystallized out, but the amount of the salt was too small to make a complete analysis, and this evidence is too slender to establish the existence of a monohydrate.

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[25] Ref. 1, p. 353.

[26] Only a single new analysis of this salt was made, but for the sake of completeness

Work on Series D; the Pentachloro-ruthenites, $M_2Ru^{iii}Cl_5H_2O$ (the "Aquo" Series of Howe and *Beta* Series of Aoyama)

The Potassium Salt.—Briggs[12] considers this salt to have the formula $2K_2RuCl_5.3H_2O$, basing his view on his determination of water by loss in two analyses and one determination of water by combustion in oxygen. The recorded analyses of this salt are given below.

TABLE VI

ANALYSES RECORDED

	Calcd. for $K_2RuCl_5.H_2O$	Calcd. for $2K_2RuCl_5.3H_2O$	(a)[4] 0.3927 g.	(a)[4] 0.4792 g.	(a)[4] 0.4335 g.	(b)[12]	(b)[12]	(b)[12]
Ru, %	27.09	26.48	26.84	26.84	..	26.7	26.7	26.6
2KCl, %	39.75	38.82	39.30	40.27	..	..	..	..
Cl_3, %	28.35	27.68	27.78	...	..	...	..	..
H_2O, %	4.80	7.03	...	6.07[a]	4.82[b]	7.05[c]	7.0[d]	7.1[d]
2K, %	20.85	20.36	...	...	..	20.3	20.4	20.2
5Cl, %	47.25	46.13	...	...	..	46.0	45.9	46.1

[a] Loss between 140 and 180° (possible incipient decomposition).

[b] Absorbed in phosphorus pentoxide (heated to decomposition in current of air).

[c] By combustion and absorption in calcium chloride.

[d] Loss.

Stannous chloride, even in excess, was found to have no action on this salt; 0.1785 g. of salt was titrated with 0.1 *N* stannous chloride; 0.14 cc. was used, equivalent to 0.81% of quadrivalent ruthenium, thus indicating the presence of a very small quantity of unreduced salt, as generally happens in the reduction by alcohol.

The Cesium Salt, $Cs_2RuCl_5.H_2O$.—Since the "aquo" salts are not easy to prepare in a state of assured purity, it was hoped to get better results with the cesium salt, which is less soluble. RuO_4 was dissolved in hydrochloric acid, and the diluted solution boiled with alcohol. This solution was then either treated with cesium chloride and evaporated to crystallization, or was first evaporated and precipitated by a solution of cesium chloride. At times the salt was recrystallized from hydrochloric acid of varying strengths, and again solutions of the salt were precipitated by alcohol. The salt was sometimes obtained as fine, rose prisms similar to the potassium salt; sometimes "whetstone" crystals were obtained, similar to uric acid, or these may have been possibly a variety of the rose prisms; the rose prisms were generally accompanied by minute spherules, often adhering to the prisms and of a paler color, or sometimes as a dark powder; in one case (38) a sample consisting almost entirely of rose prisms recrystallized as apparently pure spherules. When precipitated by alcohol the salt was generally obtained as a buff, felt-like mass which under high powers of the microscope seemed to be made up of very minute rose prisms. Efforts to separate different forms of crystals by fractional crystallization were unsuccessful. As will be seen from inspection of the analyses, there are frequently considerable variations, but none of these are large enough to indicate the presence of an impurity differing materially in composition. In particular, no evidence was found of any sesquihydrate, as postulated by Briggs. The water present in the salt could not have been greater than the loss after accounting for the Cl_3, Ru and 2CsCl directly weighed. This loss in no instance exceeded 3.76%, and averaged 3.02 (16 analyses); theory requires 3.20 for the monohydrate, and 4.73 for Briggs'

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it is worth while to put the earlier analyses on record in this connection; the composition of the salt was at that time supposed to be $Rb_2Ru^{iii}Cl_5.H_2O$. [Howe, THIS JOURNAL, **23**, 786 (1901).]

formula for a sesquihydrate. The average of three water determinations by absorption in P_2O_5 is 3.35.

It would thus appear that the formula $Cs_2RuCl_5.H_2O$ is established, and it is probable that the general formula for the chloro-ruthenites is $M_2RuCl_5.H_2O$, in which the ruthenium has a valence of *three* and a coördination number of *six*.

TABLE VII

ANALYSES OF CESIUM PENTACHLORO-RUTHENITE, $Cs_2RuCl_5.H_2O$

	Calcd.	(*a*)	(*b*)	(26)	(27)	(28)	(29)	(30)	(31)	(32)
Taken, g.	...	0.1493	0.2636	0.2658	0.2728	0.2627	0.3215	0.2433	0.2498	0.2740
Ru + 2CsCl, %	77.90	...	...	77.20	75.95	77.46	79.35	77.60	77.74	77.81
Ru, %	18.07	17.88	18.25	17.95	17.85	18.16	17.29	19.19	18.09	18.31
2CsCl, %	59.82	60.15	59.45	59.39	58.05	59.44	62.05	58.36	59.53	59.88
Cl_3 + H_2O, %	22.11	...	...	22.80	24.05	22.54	20.65	22.40	22.26	22.19
Cl_3, %	18.90	18.93	18.76	20.02	20.39	19.89	18.24	20.49	19.91	18.48
H_2O (loss), %	3.20	2.97	3.74	2.78	3.75	2.64	2.41	1.91	2.35	3.71

	(33)	(34)	(29)	(35)	(36)	(37)	(38)	(36)	(35)	(35)
Taken, g.	0.2676	0.2672	0.2557	0.2559	0.3466	0.2665	0.2327	0.2574	0.1623	0.2842
Ru + 2CsCl, %	77.77	77.62	78.38	77.80	77.32	77.71	77.74	...	...	...
Ru, %	18.57	18.23	17.34	18.29	18.32	18.07	19.90	...	...	...
2CsCl, %	59.68	59.99	61.11	59.44	59.06	59.51	57.80	...	...	...
Cl_3 + H_2O, %	22.23	22.38	21.62	22.20	22.68	22.29	22.26	...	...	...
Cl_3, %	19.19	18.93	18.63	18.69	18.90	18.79	20.19	...	...	...
H_2O (loss), %	3.06	3.65	2.99	3.50	3.76	3.50	2.07	...	...	...
H_2O (P_2O_5), %	...	...	...	...	...	...	...	3.21	3.33	3.52

Origin of salts

(*a*): Precipitated by alcohol from blue solution (electrolytically reduced) of $RuCl_2$ which had spontaneously oxidized in presence of hydrochloric acid and cesium chloride; buff powder.[26]

(*b*): From evaporation of a solution of Cs_2RuCl_6 containing alcohol; rose prisms.[26]

(26): From cold conc. hydrochloric acid; fine brown powder; largely "whetstones."

(27): From cold conc. hydrochloric acid; largely minute rose prisms.

(28): From warm conc. hydrochloric acid; dark brown powder; mainly rose prisms.

(29): From hot conc. hydrochloric acid; dark buff; largely spherules with prisms.

(30): From hot conc. hydrochloric acid; buff; chiefly rose prisms.

(31): Precipitated by alcohol; fine buff powder; chiefly rose prisms.

(32), (34): Precipitated by alcohol; fine buff felt; minute rose prisms.

(33): Precipitated by alcohol; darker buff felt than (32) and 34); minute rose prisms.

(35): Solution of RuO_4 in hydrochloric acid diluted and boiled with alcohol until color lightened, cesium chloride added, evaporated and cooled; fourth crop of crystals; almost pure rose prisms.

(36): Same, third crop; rose prisms with very small amount of dark powder.

(37): Same, first crop; rose prisms (?) in whetstone form.

(38): From solution of rose prisms containing some spherules; alcohol added and evaporated on warm plate in vacuum; apparently pure spherules. It may be noted that salts (29) and (38), both consisting largely of spherules, vary rather widely in analysis from theory, but in opposite directions.

Summary

The work described in this paper indicates that there is no isomerism among the known complex chlorides of ruthenium; that what has been

considered the series $M_2Ru^{iii}Cl_5$ containing trivalent ruthenium, in reality contains quadrivalent ruthenium, of formula $M_2Ru^{iv}Cl_5OH$; that what has been considered an "aquo" series is actually the ordinary series of trivalent ruthenium, but always crystallizing as a monohydrate of formula $M_2Ru^{iii}Cl_5.H_2O$. In all of these salts the coördination number of ruthenium is *six*. Also Claus' view that the blue solution of reduced ruthenium contains the metal in bivalent form is again confirmed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WASHINGTON AND LEE UNIVERSITY]

CONTRIBUTIONS TO THE STUDY OF RUTHENIUM. XI
A VOLUMETRIC ESTIMATION OF RUTHENIUM

BY JAS. LEWIS HOWE

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The estimation of ruthenium, except in crystallized compounds, has always been difficult. Neither hydrogen sulfide nor metals, as zinc or magnesium, precipitate ruthenium completely from any of its solutions, and while it can be precipitated by caustic alkalies, it is impossible to wash the gelatinous precipitate free from salts. Somewhat more than a year ago it was found in this Laboratory[1] that ruthenium in a finely divided form could be completely dissolved in alkaline sodium hypochlorite solution and the ruthenium distilled quantitatively from this solution as ruthenium tetroxide after treatment with a stream of chlorine; but no simple method was found by which the ruthenium in the distillate could be estimated.

The reduction of quadrivalent ruthenium by stannous chloride, as described in the preceding paper, affords a solution of the problem. The volatile ruthenium tetroxide is condensed in concentrated hydrochloric acid, preferably in a small Erlenmeyer flask surrounded by ice. A two-necked Wolff bottle with ground-glass joints may be used if the amount of ruthenium is considerable, but with small quantities (as is usual in the analysis of alloys) we have found no difficulty in condensing all the RuO_4 in an Erlenmeyer flask. After all the ruthenium tetroxide has been reduced by the hydrochloric acid, which is apparent by the disappearance of any drops of liquid ruthenium tetroxide, the solution is boiled until all absorbed chlorine has been eliminated. It is then titrated with a solution of stannous chloride of about 0.05 N strength. The stannous chloride solution is standardized immediately before using against 0.1 N iodine solution with starch indicator.

In titrating the ruthenium solution, the stannous chloride can be added until the dark, brownish-red solution of quadrivalent ruthenium changes to the light red or rose of trivalent ruthenium. As this end-point is often

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[1] Howe and Mercer, THIS JOURNAL, 47, 2926 (1925).