$\frac{1}{2}00$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$; $u\ \frac{1}{2}+u\ 0$, $\frac{1}{2}-u\ u\ 0$, $\bar{u}\ \frac{1}{2}-u\ 0$, $\frac{1}{2}+u\ \bar{u}\ 0$, $\frac{1}{2}+u\ u\ \frac{1}{2}$, $u\ \frac{1}{2}-u\ \frac{1}{2}$, $\frac{1}{2}-u\ \bar{u}\ \frac{1}{2}$, $\bar{u}\ \frac{1}{2}+u\ \frac{1}{2}$, with u equal to 0.135. The structure of potassium cyanate is shown to be closely similar to that of the trinitride; the unit of structure has a = 6.070 Å., and c = 7.030 Å.

Neither sodium nor potassium trinitride shows molecular segregation; the trinitride ion is, however, easily distinguished. This ion is shown to possess not a ring structure, but a linear arrangement of the three nitrogen atoms. Possible electronic configurations are discussed in light of these results.

A consideration of the previously studied structures of sodium and potassium acid fluoride is shown to indicate that the acid fluoride ion is similar in structure to the trinitride ion and the cyanate ion.

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

CONTRIBUTIONS TO THE KNOWLEDGE OF RUTHENIUM
VIII. THE ISOMERIC CHLORIDES[1]

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In 1844 the metal ruthenium was discovered by Claus, and its double chloride, K_2RuCl_5 (Claus' formula, $2KCl_2.Ru_2Cl_6$), described and analyzed,[2] attention being called by Claus to the similarity of this to the corresponding rhodium salt, K_2RhCl_5. Later Claus prepared another chloride by the action of aqua regia on ruthenium compounds and naturally ascribed to this the formula K_2RuCl_6 (modern formulation). In 1888 Joly[3] showed that this second chloride was in reality the nitrosochloride, $K_2Ru(NO)Cl_5$. The error of Claus was not unnatural, since the other platinum metals furnished analogous salts under this procedure. He determined the ruthenium and the potassium chloride directly, and the remainder of the chlorine by loss; the difference between the value for $NOCl_3$ and that for Cl_4 is within the limits of his experimental error. He had also noted that potassium pentachlororuthenite, K_2RuCl_5, cannot be directly chlorinated to the hexachlororuthenate, K_2RuCl_6. In 1899 Antony and Lucchesi[4] described the true hexachlororuthenate, K_2RuCl_6, which they formed by the action of concd. hydrochloric acid on potassium ruthenate, K_2RuO_4, though ordinarily the pentachloro-

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[1] This paper is partly based upon the thesis presented by Lawrence P. Haynes in partial fulfilment of the requirements for the degree of Master of Science at Washington and Lee University, June, 1925.

[2] Claus, *Bull. acad. sci. St. Petersburg*, **3**, 367 (1845).

[3] Joly, *Compt. rend.*, **107**, 994 (1888); **108**, 854 (1889).

[4] Antony and Lucchesi, *Gazz. chim. ital.*, **29**, i, 312; ii, 82 (1899).

ruthenite is the result of this reaction. The following year Miolati and Tagiuri[5] obtained a monohydrate of the pentachlororuthenite, $K_2RuCl_5.H_2O$, by precipitation from the acidified trichloride solution with potassium chloride *in the cold.* From the evaporated mother liquor the anhydrous salt crystallizes. The rubidium and cesium pentachlororuthenites described by Howe[6] crystallize as monohydrates. The results reached by Gutbier[7] indicate that all of the alkali pentachlororuthenites crystallize as monohydrates, but he also obtained the anhydrous potassium and cesium salts.

In going over this work again, we find that when the potassium salt crystallizes from a hot acidified solution, it consists largely of the anhydrous form, dark, brown-red, tetragonal octahedra or plates, depending on the development of the basal plane; when formed from a cold solution there is present a larger or smaller quantity of red-buff, feather-like crystals, much more soluble and apparently the hydrated form. Three different lots of these red-buff air-dried crystals (0.1886, 0.2528 and 0.2624 g.) lost at 120°, respectively, 3.55, 1.46 and 1.67%; calcd. for $K_2RuCl_5.H_2O$: 4.80%. The dark, brown-red crystals from hot solution gave from 0.2329, 0.2467, 0.2455, 0.2316 and 0.3636 g., respectively, 28.12, 28.21, 28.31, 27.94 and 27.91% of ruthenium; calcd. for K_2RuCl_5, 28.47%; for $K_2RuCl_5.H_2O$, 27.09%. It appears that even when crystallized from a hot solution, some of the monohydrate may be present.

The original analyses of Claus[2] give 28.96, 28.48 and 28.91% of ruthenium, using 1.096, 0.990 and 1.003 g., respectively, of the salt, indicating that the material he had prepared was anhydrous.

In 1901 it was noted by Howe[8] that when an acidified solution of the pentachlororuthenite was heated with alcohol, the dark, brown-red color slowly changed to rose, and from the solution there crystallized rose prisms of the formula $K_2RuCl_5.H_2O$, called by Howe "aquo"-chlororuthenate. The corresponding ammonium, rubidium and cesium salts were prepared, as well as the potassium and rubidium aquo-bromoruthenates. When the concentrated solutions of these aquo salts were treated with chlorine and bromine, respectively, the hexahalogen salts, M_2RuCl_6 and M_2RuBr_6, were precipitated. Attention was called to the apparent existence here of a remarkable isomerism, both between the ordinary monohydrate, $K_2RuCl_5.H_2O$, and the aquo salt, which for distinction was written $K_2Ru(H_2O)Cl_5$, and between the ordinary anhydrous pentachlororuthenite and the dehydrated aquo salt, both of the formula

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[5] Miolati and Tagiuri, *Gazz. chim.*, **30**, i, 511 (1900).

[6] Howe, This Journal, **23**, 786 (1901).

[7] Gutbier, Falco and Vogt, *Z. anorg. Chem.*, **115**, 225 (1921).

[8] Howe, This Journal, **26**, 544 (1904); Ref. 6, p. 775.

K_2RuCl_5. The dehydrated aquo salt when dissolved crystallizes again as the aquo salt. (As will be noted later in this paper, Aoyama has designated the ordinary pentachlororuthenites as the alpha series, and the aquo series as beta, while Briggs has called the former the Miolati series and the latter the Howe series. The terms alpha and beta or aquo will be used in this paper.)

The monohydrate of the alpha series was found by Lind and Bliss[9] to be two-thirds hydrolyzed—to $Ru(OH)_2Cl$—in dilute solution, while the corresponding salt of the beta series is only one-third hydrolyzed—to $Ru(OH)Cl_2$—under similar conditions.[10] Howe also stated that the potassium aquo salt, after dehydration at 225°, showed on solution the original properties of the aquo salt. This observation is correct when the solution has been allowed to stand for several hours.

More recently Aoyama[11] has described what he considers to be a third isomer of K_2RuCl_5, which he calls the gamma, formed by heating the hexachlororuthenate, K_2RuCl_6, in a current of dry hydrogen chloride at 540–560°. On repeating Aoyama's work, Gutbier and Niemann[12] conclude that Aoyama's gamma salt is identical with the dehydrated salt of the beta series.

To throw light on this point the following experiment was undertaken. 1.5154 g. of the aquo salt, $K_2Ru(H_2O)Cl_5$, was heated in an air-bath for 24 days, with gradually increasing temperature. Up to 180° the loss was slight, amounting in 16 days to less than 1%. Constant weight was reached at 225°, with a loss of 4.77%; calcd.: H_2O, 4.80%.

The hexachlororuthenate, K_2RuCl_6, was prepared by leading a stream of chlorine into a cold, saturated solution of the aquo salt, $K_2Ru(H_2O)Cl_5$. The black precipitate (0.7968 g.) was dried and heated in a porcelain boat in a combustion tube in a stream of dry hydrogen chloride. Up to 500° there was very little loss, but at a temperature somewhat above 520° the loss was 9.53%; calcd. for loss of one chlorine atom, 9.45%.

The dechlorinated salt showed all the properties given by Aoyama for his gamma salt, and similar properties were shown by the dehydrated beta salt. A comparison of the properties of the different chlorides is given in Table I. In addition to these comparisons, portions of the gamma salt and of the dehydrated beta salt were dissolved in acidulated water and allowed to crystallize. The crystals obtained in each case were examined under the microscope, and found to be identical with crystals of the aquo (beta) salt.

The solutions of the dehydrated aquo salt and of the dechlorinated hexachloro salt are not at first identical with the solutions of the aquo salt. The beta K_2RuCl_5 dissolves to form a pure yellow solution, which only after several hours' standing acquires the red color of the aquo salt.

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[9] Lind and Bliss, THIS JOURNAL, **31**, 868 (1909).

[10] Lind, *Thesis*, Massachusetts Institute of Technology, **1903.**

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

[12] Gutbier and Neimann, *ibid.*, **141**, 312 (1925).

TABLE I

COMPARATIVE PROPERTIES OF THE POTASSIUM RUTHENIUM CHLORIDES

	K_2RuCl_5 Alpha salt	$K_2Ru(H_2O)Cl_5$ Beta (aquo) salt
Solution in water.	Slowly dissolves to pale reddish yellow solution.	Pale pink solution, easily soluble.
Addition of Cl.	No change.	Darkens; in concd. solution gives black-green ppte., leaving pale yellow solution.
Addition of NaOH solution.	Green solution, giving dark ppte. on standing.	Loses color, giving black ppte. on boiling.
Addition of H_2S.	Becomes colorless, and then gives dark brown ppte., leaving supernatant liquid azure-blue.	Becomes colorless, then darkens; gives black ppte. with no blue solution.

	K_2RuCl_5 Dehydrated beta salt	K_2RuCl_5 Dechlorinated hexa salt	K_2RuCl_6 Hexa salt
Solution in water.	Dissolves readily to pure yellow solution. Slightly fluorescent.	Dissolves readily to pure yellow solution. Slightly fluorescent.	Rapidly dissolves to reddish-yellow solution. Quickly hydrolyzes.
Addition of Cl.	Darkens slightly on standing.	Darkens slightly on standing.	No change.
Addition of NaOH solution.	Blue solution, becoming pale green; dirty green ppte. on boiling.	Blue solution, becoming pale green; dirty green ppte. on boiling.	Loses color; then dirty green.
Addition of H_2S.	Beautiful green solution, which upon standing changes to a deep blue. This blue may persist several days, and then becomes opaque, giving black ppte.		Becomes colorless, and then a purplish-brown ppte.

The pure yellow solution is characterized by turning blue on the addition of sodium hydroxide, a reaction which it does not give after standing for some hours. The yellow solution when first formed is not darkened by chlorine, though it darkens with bromine and gives a black precipitate.

Two very recent efforts have been made to solve the problems connected with the isomerism of the ruthenium chlorides. Briggs[13] considers that the normal alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which the ruthenium has a coördination number of 6. Briggs refers to this water as being very firmly held, and according to Gutbier[14] not completely given off at 200°; but in several of the analyses given by Gutbier, Falco and Vogt, the salt was dehydrated at 120° and 125°, and the corresponding cesium salt also lost its water at 120°. Briggs gives to the aquo salt the formula $2K_2RuCl_5.3H_2O$. As far as analyses go this is possible, and is in accord with one published analysis of Howe, but not with the others (both chloro- and bromo-series), nor with numerous other unpublished analyses. It is difficult to see how so slight a difference in hydration could occasion so profound a difference in properties; the distinction between these two series must be much more deeply seated. Briggs

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

[14] Ref. 7, p. 230.

did not prepare the hexachloro salt by the chlorination of the aquo salt, but on leading chlorine through a solution of the aquo salt he obtained crystals to which he assigns the formula $K_2(RuCl_5OH.H_2O)$, and by bubbling air through a similar solution he obtains a salt with the formula $K_2RuCl_5.K_2RuCl_5OH$. This would seem rather to be the ordinary alpha salt, partially in the anhydrous form and partly the monohydrate.

In the preparation of the hexachlororuthenates from the aquo salts, it was found necessary to have the solutions so concentrated and strongly acid that the hexa salt precipitates on leading in chlorine or bromine. The concentration of the mother liquor from the hexa salt seems to yield, chiefly at least, the alpha pentachlororuthenate. Efforts to prepare a mixed salt by chlorination of the aquobromide, or bromination of the aquochloride, have thus far failed, the results being quite similar to those reported by Briggs on the addition of chlorine or air to the aquo-chloride. These reactions are being further investigated, as well as the stability of solutions of the hexa salts. These appear on evaporation of their solution to be more or less converted into the penta (alpha) salt, analogous to the hexachloro-iridates.

The other recent contribution to the subject is that of Charonnat,[15] who accepts the monohydrate formula of both the alpha and the beta series, but considers that in the alpha salts the ruthenium is quadrivalent, and that the salts are in fact hydroxychlororuthenates, of formula $X_2Ru^{IV}Cl_5(OH)$; in the beta salts the ruthenium is tervalent and these are true aquo salts, of formula $X_2Ru^{III}(H_2O)Cl_5$, and converted into the hexa salts by addition of chlorine. He bases his views on three facts: (1) the alpha and not the beta salts liberate iodine from potassium iodide, an argument which is by no means conclusive; (2) the aquo salt is formed when the oxalato-ruthenite, $K_3Ru(C_2O4)_3$, is treated with hydrochloric acid, but it is also true that the beta series is formed from the alpha series by treatment with oxalic acid and many other organic compounds; (3) the beta series is formed from the alpha series by the prolonged action of reducing agents, but that their formation is due to reduction remains to be established.

The conditions of the conversion of the alpha salt into the beta have been studied by us and the following results obtained.

Three portions of a fairly concentrated solution of K_2RuCl_5 (alpha) acidulated with hydrochloric acid were diluted to 200 cc. each, and 20 cc., 50 cc. and 100 cc., respectively, of alcohol added. They were allowed to boil slowly. The sample containing 50 cc. of alcohol was the first to lose its deep red color and become rose and transparent. The one with 100 cc. was the next to change, while the one with 20 cc. was much slower in being converted.

Two solutions of the same concentration and with the same amount of alcohol, to one of which a few crystals of the beta salt had been added, were boiled under similar

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

conditions. The solution to which the crystals had been added was the first to be converted, indicating the catalytic action of the beta salt on the reaction.

Other "aquating" agents were tested. The conversion was rapidly effected with saccharose, dextrose and phenol; less rapidly with *n*-butyl and *iso*propyl alcohols. Amyl alcohol gave a deep purple color, which gradually changed into the rose of the beta salt. Methanol acted very slowly and no conversion was effected with acetic acid. With pyrocatechol the darkening of the solution precluded following the color change, but here, as in all the other cases except with saccharose and dextrose, microscopic examination of the evaporated residue showed crystals of the beta salt. In the case of methanol, alpha crystals were also present, indicating incomplete conversion.

The conversion was also produced by stannous chloride. In this case the addition of sufficient water to hydrolyze the stannic chloride present gives a flocculent yellow precipitate, the solution of which in hydrochloric acid gives on evaporation octahedral crystals varying in color from buff to a quite deep rose. These crystals appear to be solid solutions of the beta salt in potassium chlorostannate. In all cases the amount of ruthenium present was small, never more than a few per cent. Similar crystals were prepared by crystallizing mixed solutions of the chlorostannate with the beta salt, but the solubility in the solid phase seems to be confined within narrow limits.

In this connection it may be noted that Gutbier and Zwicker[16] prepared a series of hexachlororuthenates of organic bases by adding the chloride of the organic base to a solution of (alpha) ruthenium trichloride (H_2RuCl_5), dissolving any precipitate formed in hydrochloric acid, and leading chlorine (or bromine vapor in the case of the hexabromides) into the cold clear solution. Here, in the presence of the organic base, the alpha salt, which does not take up chlorine, had evidently been converted into the beta salt, which then formed the hexahaloruthenate.

While there are still many points in connection with the halogen salts of ruthenium which are obscure, and a number of formulas which are not clearly established, the following may be considered reasonably certain.

1. The alpha series exists as M_2RuCl_5 and as $M_2RuCl_5.H_2O$; it gives a deep, brownish-red solution; it yields two chlorine atoms to hydrolysis; it does not take up chlorine.
2. The alpha series is converted into the beta series by the action of certain organic and reducing agents.
3. The beta salts give a rose-red solution; they yield one chlorine atom to hydrolysis; they are converted into the hexachloride by chlorine.
4. The beta salts are "aquo" salts, and hold their water much more firmly than the alpha salts; they are probably isomers of the monohydrates of the alpha series.
5. The dehydrated beta salts are identical with those produced from the hexa salts by the loss of one atom of chlorine; the formula of these salts is M_2RuCl_5, and while isomers of the anhydrous alpha salt, they are not identical with it; on solution they give, after standing for a little time, the beta salt.

As far as examined, the behavior of the bromo salts is similar to that of the chloro salts.

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[16] Gutbier and Zwicker, *Ber.*, **40**, 690 (1907).