The Isomeric Chlororutheniates.—In a recent number of This JOUR-
NAL Howe and Haynes[1] have referred to my paper on the potassium chloro-
rutheniates[2] and it is necessary for me to correct certain inaccuracies in
their communication.

According to Howe and Haynes "Briggs considers that the normal
alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which ruthenium has a co-
ordination number of 6," also "Briggs gives to the aquo salt the formula
$2K_2RuCl_5.3H_2O$ . . . . . . It is difficult to see how so slight a difference in hy-
dration could occasion so profound a difference in properties."

As a matter of fact the third paragraph of my paper reads as follows:
"It has been found that in Miolati's series (alpha series) there are at least
two compounds having the formulae $K_2RuCl_5.H_2O$ and $2K_2RuCl_5.3H_2O$,
respectively. In Howe's series (aquo series) the only salt prepared in the
pure state had the formula $2K_2RuCl_5.3H_2O$, although some slight evidence
was obtained for the existence of other compounds having the formulae
$K_2RuCl_5.H_2O$ and $K_2RuCl_5.2H_2O$." In the seventh paragraph of my paper
I expressed the view that ruthenium probably functions with the co-
ordination number 8 in all these compounds. Reference was also made to
the possibility that the coördination number may be different in the two
series, namely, seven in the one and eight in the other, but *nowhere* have I
suggested a coördination number six as stated by Howe and Haynes.

Again, in referring to the compound $K_2RuCl_5.K_2RuCl_5OH$ which I
obtained from the aquo salt by bubbling air through the heated, strongly
acid solution, Howe and Haynes suggest "This would seem to be the or-
dinary alpha salt, partially in the anhydrous form and partly the mono-
hydrate." The oxidation product, however, is quite different in properties
(crystalline form, solubility and color) from the alpha salt.

The existence[2] of such substances as $2K_2RuCl_5.3H_2O$ (with constitutional
water), $K_2RuCl_5.K_2RuCl_5OH$ and $K_5Ru_3Cl_{14}.3H_2O$ shows that in the chloro-
rutheniates there is a polynuclear complex in which chloride ions or water
molecules are shared by the ruthenium ions. Various cases of isomerism
are then possible according to the particular components which are shared.

Assuming a binuclear complex and coördination number of eight, then if
the coördinated ions or molecules are arranged around the ruthenium ion,
not at the corners of a cube but at the corners of the polyhedron obtained
by rotating one face of a cube in its own plane[3] through $45°$, either two, three
or four components may be shared, the two polyhedra in the complex
having a common edge, a common triangular face or a common square face
respectively. With a common edge the formula would be $2K_2RuCl_5.4H_2O$.

[1] Howe and Haynes, This JOURNAL, **47**, 2920 (1925).

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

[3] This figure gives the stable arrangement of eight electrons around a positive core
according to Föppl [see J. J. Thomson, *Phil. Mag.*, **41**, 515 (1921)].

A common triangular face would give $2K_2RuCl_5.3H_2O$, and a common square face $2K_2RuCl_5.2H_2O$. Owing to the comparatively slight solubility of the alpha salts, and the ease with which both series undergo hydrolysis in neutral solution, molecular-weight determinations would have little value, and I therefore suggested in my paper the desirability of an X-ray investigation of these substances which I personally, however, am not in a position to undertake.

Charonnat's Views.—The suggestion made by Charonnat[4] that the alpha series contain quadrivalent ruthenium appears improbable for the following reasons in addition to those mentioned by Howe and Haynes: (1) the alpha series is formed directly from $RuCl_3$ and KCl as observed by Miolati and Tagiuri[5] and by Gutbier, Falco and Vogt;[6] (2) a reducing agent is not necessary to convert the alpha salt into the aquo salt; this change can be brought about by hydrochloric acid alone;[2] (3) by oxidizing the aquo salt with oxygen the alpha salt is not obtained, but instead a totally different substance having the formula $K_2RuCl_5.K_2RuCl_5OH$.

Finally, I would stress the following conclusions at which I arrived after a careful and protracted investigation of the potassium chlororutheniates.

1. No deductions with regard to the formula of any individual preparation can be drawn with safety unless *every* constituent is directly estimated during the analysis. It is quite useless to determine one or two constituents only.

2. Water cannot be determined by merely heating the compounds. The only satisfactory method is to determine hydrogen by combustion over lead chromate in an atmosphere of oxygen. If air is used the results obtained are liable to be too low.

Addendum

Owing to the kindness of the Editor, I have had an opportunity of reading the Note by Professor Howe, which follows.

If the compound formulated as K_2RuCl_5 had a binuclear complex as in the formula $K_4(Cl_4RuCl_2RuCl_4)$, the coördination number of the ruthenium would be six. A formula can also be devised with coördination number eight, the complex being quadrinuclear with four ruthenium ions in a ring, each pair of ruthenium ions sharing three chloride ions. At present we have no knowledge of the actual molecular weight of the compound.

It would appear from Professor Howe's references to the water content of his preparations that there are at least two "aquo"-salts in accordance with the suggestions made in my paper. If his preparations have consisted chiefly or entirely of the compound $K_2RuCl_5.H_2O$, whereas mine were

4 Charonnat, *Compt. rend.*, **180**, 1271 (1925).

5 Miolati and Tagiuri, *Gazz. chim. ital.*, **30**, II, 511 (1900).

6 Gutbier, Falco and Vogt, *Z. anorg. Chem.*, **115**, 225 (1921).

certainly $2K_2RuCl_5.3H_2O$, the difference in behavior on chlorination might possibly be explained.

BIRSTALL, NR. LEEDS, ENGLAND   S. H. C. BRIGGS
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The Isomeric Ruthenium Chlorides.—The statement in the recent paper of Howe and Haynes[1] that "Briggs considers that the normal alpha salt is a monohydrate, $K_2RuCl_5.H_2O$, in which the ruthenium has a co-ordination number of 6," was based on a misunderstanding of his paper. He there states:[2] "It is evident that the coördination number of ruthenium is greater than 6 in the compound $2K_2RuCl_5.3H_2O$." It was wrongly assumed that in $K_2RuCl_5.H_2O$ he considered the number to be 6, as would naturally be expected. There is no reason for assuming a higher co-ordination number for ruthenium in this compound. On the other hand, the anhydrous form, K_2RuCl_5, which seems undoubtedly to exist, would call for a coördination number of 5.

With Briggs' conclusion that "no deductions with regard to the formula of any individual preparation can be drawn with safety unless *every* constituent is directly estimated during analysis," I should heartily agree, if the sentence were qualified by writing it "no *complete* deduction." In practically all of our recent analyses of the halo-ruthenium salts, we have heated the salt in hydrogen, recovering the evolved halogen in silver nitrate solution. Thus, for example, in the analysis of $K_2RuCl_5.H_2O$ ("aquo" salt), $2KCl + Ru$ is left in the boat, and Cl_3 collected as silver chloride. There can be no more water than is indicated by loss, and as this has in no case amounted to $1^1/_2 H_2O$, we have been unable to accept Briggs' formula, $2K_2RuCl_5.3H_2O$, for the "aquo" salt.

CONTRIBUTION FROM   JAS. LEWIS HOWE
WASHINGTON AND LEE UNIVERSITY
LEXINGTON, VIRGINIA
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The Reaction between Selenium Tetrachloride and Copper.—The reactions between the chlorides of selenium and copper are comparatively much simpler than those between the oxychloride and the same metal.[1] We have determined the course of the reactions both with the monochloride and with the tetrachloride, by analysis. Our results with the former compound agree with those obtained about the same time by Lenher and Kao.[2] On account of qualitative observations we consider that the reaction probably proceeds according to Equations 3 and 4 below.

[1] Howe and Haynes, THIS JOURNAL, **47**, 2920 (1925).

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

[1] Ray, THIS JOURNAL, **45**, 2090 (1923).

[2] Lenher and Kao, *ibid.*, **48**, 1550 (1926).