

As was to be expected, this confirms in a general way, the statement relative the difficulty with which caffen is shaken out of solutions containing a large proportion of sulphuric acid ; in no way, however, does it agree with the data given by Gomberg, who by ten successive treatments with chloroform removed only 34.85 per cent., while my figures show that when a ten per cent. sulphuric acid was used, with but three extractions, fully ninety per cent. was recovered, and even with a still stronger acid (1 + 9 by volume), three portions of chloroform removed about sixty-five per cent.

UNIVERSITY OF ILLINOIS. SCHOOL OF PHARMACY.

### CONTRIBUTION TO THE KNOWLEDGE OF THE RUTHENOCYANIDES.

BY JAS. LEWIS HOWE.

Received August 27, 1896.

POTASSIUM ruthenocyanide was described by Claus, in 1854, in his "Beiträge zur Chemie der Platinmetalle." The salt was formed by fusing ammonium rutheninitroschloride<sup>1</sup> (tetrachloride of Claus) with potassium cyanide. The attempt was also made to form it by fusing potassium ferrocyanide with ruthenium, but it was found impossible to separate the ferrocyanide and ruthenocyanide. It is probable that some of Claus' experiments were carried out with a ruthenocyanide contaminated with ferrocyanide, from the fact that he describes copper ruthenocyanide as brown, whereas, when free from the ferrocyanide, it is pale green. Potassium ruthenocyanide in reactions and crystallization resembles very closely the ferrocyanide, except that when pure it is white. Its crystallography as well as that of the isomorphous ferrocyanide and osmocyanaide are described by A. Dufet.<sup>2</sup>

Preparation of potassium ruthenocyanide for the purpose of carrying out experiments upon it not yet completed, gave occasion to the work recorded in this paper.

In the Claus method of preparation, a large proportion of the ammonium rutheninitroschloride is decomposed with separation of metallic ruthenium, and while a part of the ruthenocya-

<sup>1</sup> Joly : *Compt. rend.*, 108, 854, 1889 ; Howe : *J. Am. Chem. Soc.*, 16, 358, 1894.

<sup>2</sup> *Compt. rend.*, (1895), 120, 377.

nide formed crystallizes out from a solution of the melt, in large square pseudorhombic plates, much is left in the solution and cannot be directly separated from the potassium cyanide and other salts present. Attempts were therefore made to use other methods of formation with the following results :

1. Potassium rutheninitrosochloride,  $K_2RuCl_5NO$ , fused with potassium cyanide, gave rather better results in ruthenocyanide, there being rather less decomposition than was the case with the ammonium salt.

2. Ruthenium trichloride,  $RuCl_3$ , fused with potassium cyanide gave a fair product of ruthenocyanide.

3. Metallic ruthenium, fused with potassium cyanide, was slightly acted upon, giving a trace of ruthenocyanide.

4. Metallic ruthenium, fused with potassium cyanide and a little potassium hydroxide, gave rather stronger reaction than case 3, but the amount of ruthenocyanide formed was very small.

5. The melt formed by fusion of ruthenium in potassium hydroxide and nitrate, containing potassium ruthenate,  $K_2RuO_4$ , was dissolved in water and boiled with potassium cyanide. The deep orange-red solution was quickly decolorized and the ruthenium was converted into ruthenocyanide with little loss. A considerable proportion could be obtained in the usual square crystals. This process could, by modification, probably be made the most satisfactory method of forming the ruthenocyanide, presenting one decided advantage that metallic ruthenium, or oxides, can be used, thus avoiding the necessity of preparing the nitrosochloride or chloride.

6. Ruthenium trichloride was boiled with a strong solution of potassium cyanide. The ruthenocyanide, crystallizing in the usual square form, was obtained, but very much contaminated with a greenish by-product not yet investigated, probably analogous to Prussian blue.

7. Potassium rutheninitrosochloride was boiled with a strong solution of potassium cyanide. The solution was slowly decolorized, considerable of the greenish by-product being formed. From this solution there crystallized thick straw-colored hexago-

nal plates, which will be considered further on. The quantity of the product is not satisfactory.

8. The Weselsky method<sup>1</sup> of forming double cyanides was tried. Hydrocyanic acid was led into a solution of the nitrosochloride, in which barium carbonate was suspended, until effervescence ceased. The solution gave no reaction for ruthenocyanide. Its color had changed to the brown-yellow of the trichloride, but gave no reaction for this with potassium thiocyanate, or with ammonia and sodium thiosulphate. On warming, the solution gelatinized to a firm hydrogel, insoluble in hot aqua regia, but soluble in boiling potassium hydroxide. This last solution was unchanged on acidification with hydrochloric acid, and gave the potassium ferrocyanide reaction for nitrosochloride, but no reaction for trichloride. The dried jelly was easily explosive on heating. It presents an interesting analogy to Jackson's<sup>2</sup> hydrogel of cobaltocyanide and is being further studied.

9. The Weselsky method was also applied to ruthenium trichloride. The merest trace of ruthenocyanide was formed, and the solution, little changed in color, no longer gave reactions for the trichloride.

10. The nitrosohydroxide of Joly, formed by the precipitation of the chloride by potassium carbonate, is easily soluble in potassium cyanide and converted into ruthenocyanide by prolonged boiling.

The following reactions of ruthenocyanide may be noted :

No precipitates are formed with the caustic alkaline earths, their ruthenocyanides being soluble in water.

Lead acetate gives a fine white precipitate, soluble in nitric acid.

Silver nitrate gives a white curdy precipitate, insoluble in both ammonia and in nitric acid.

Ferric chloride gives a rich purple precipitate, closely resembling Prussian blue in its chemical properties. In pure water it is soluble, but is precipitated from this solution by salts or alcohol. It forms a very beautiful and intense dye, adhering with

<sup>1</sup> Weselsky, *Sitzber. Akad. Wien.*, 60, ii. (1870), 261; *Ber. d. chem. Ges.*, 2, 588, 1869.

<sup>2</sup> Jackson: *Ber. d. chem. Ges.*, 29, 1020, 1896.

great persistence to cotton fiber, on which it has been precipitated. It is decomposed very readily by alkalis with precipitation of ferric hydroxide, re-forming, however, on the addition of acids, unaffected by dilute acids, but permanently decomposed by strong acids. It is a most delicate reaction for the detection of ruthenocyanide.

Ferrous sulphate gives a pale blue precipitate, which gradually changes to the purple above mentioned, and instantly if bromine water is added.

Copper sulphate gives a very pale green flocculent precipitate (not brown as given by Claus).

With salts of the following metals precipitates are formed insoluble in hydrochloric acid: Cadmium, white (soluble in hot acid); zinc, white; tin (both stannous and stannic), white; mercury, white; bismuth, white (insoluble in nitric acid); nickel, dirty green (changing to blue with hydrochloric acid); cobalt, pale red; platinum, yellow-green; manganese gives a white precipitate soluble in hydrochloric acid. With gold there is no immediate precipitate, but a gradual darkening and separation of a dark precipitate, the solution becoming green.

Bromine water changes the solution to a dark red, which does not give the trivalent ruthenium reaction. Iodine also seems to alter the solution.

No reaction with hydrogen sulphide, ammonium sulphide, or thioacetic acid.

Nitric acid has no effect in the cold, but when heated slightly reddens the solutions. It then shows no signs of a reaction analogous to that of the nitroprussides.

It is acted on by potassium nitrite with sulphuric acid, and when neutralized gives a fugitive rose red with ammonium sulphide.

It gives no apparent reaction with ruthenium trichloride or nitrosochloride.

Two methods of purification, applicable to such portions of the ruthenocyanides as cannot be separated by crystallization, may be used. The most satisfactory is the precipitation in dilute solution by lead acetate and thorough washing with hot water to remove any lead chloride present. Suspension of the lead

ruthenocyanide (carbonate, cyanide, etc.) in much water and decomposition with dilute sulphuric acid. Filtration and addition of baryta water till nearly neutral and then of barium carbonate in excess; warming, filtration, and evaporation to crystallization of the barium ruthenocyanide from which other ruthenocyanides may be formed by double decomposition.

The other method of purification which is applicable especially to all residues, is precipitation with ferric chloride in slightly acid solution, washing with acidified water, as far as possible (the purple begins to dissolve as the salts are washed out) and decomposing with baryta water. This method, while very useful for recovery of residue, does not give so pure a product as the first method.

The hexagonal crystals described above, in process 7, presented points of interest, in that it seemed not impossible that they contained the nitroso group of the nitrosochloride from which they were formed. When dissolved in water they showed every reaction of the ordinary square crystals of the ruthenocyanide, but they could not be converted into the square form by recrystallization nor could their yellowish tint be removed. The crystals are anhydrous while the white crystals contain three molecules of water of crystallization. On heating they explode with considerable violence while the square crystals decompose very gently. On recrystallization they show prismatic forms, with many twins resembling staurolite crosses, and others resembling aragonite twins. Though perfectly hexagonal in form, they do not seem to belong to the hexagonal system. After conversion into the lead, hydrogen, barium, and back into the potassium salt by the first method of purification described, and further precipitation of this potassium salt by alcohol and recrystallization from water, crystals were obtained which were square, white, and in every respect, crystallographically as well as chemically, resembled the ordinary potassium ruthenocyanide. This was verified by analysis of the barium salt and partial analysis of the potassium salt.

It is evident that the hexagonal crystals are not a nitrosocyanide, and it seems possible that the form may be conditioned by

some trace of impurity. They are being further studied at present.

ANALYSIS OF POTASSIUM AND BARIUM RUTHENOCYANIDES.

*Potassium ruthenocyanide*,  $K_4Ru(CN)_6 \cdot 3H_2O$ , formed by boiling a solution of potassium rutheninitroschloride with potassium cyanide; purified by conversion through lead, hydrogen, and barium salts.

	Per cent.
I. Loss of water in four days standing over sulphuric acid.	10.84
II. " " " at 120° .....	10.90
III. " " " in 30 hours standing over sulphuric acid.	11.25
Theory for $K_4Ru(CN)_6 \cdot 3H_2O$ .	3H <sub>2</sub> O = 11.53

The crystals, especially when small, are so efflorescent that it is difficult to obtain uneffloresced salt for analysis, and the following are calculated for the dehydrated salt.

	Theory for $K_4Ru(CN)_6$ .	I.	Found. II.	III.
Potassium.....	37.76	37.22	38.32	37.28
Ruthenium.....	24.53	23.90	24.22	24.44

This corresponds to the potassium ruthenocyanide described by Claus.

*Barium ruthenocyanide*,  $Ba_2Ru(CN)_6 \cdot 6H_2O$ , (new) formed from the ordinary form of the potassium salt.

Pale straw-colored, diamond-shaped (up to one-half cm. long) monoclinic crystals, or larger crystal rosettes, slightly soluble in cold, more easily in hot water, slowly lose water of crystallization over sulphuric acid, lose five and a half molecules of water at 100° but retain one-half molecule to nearly 200°, thus resembling barium ferrocyanide. The barium ruthenocyanide from the hexagonal form of the potassium salt was similar, but was not obtained in well enough defined crystals to identify positively with the preceding, but analysis shows the constitution to be the same.

The method of analysis was the following: The salt was heated in a platinum boat (in two cases porcelain was used and attacked, so that the ruthenium was contaminated by silica—Analyses I and V) in an oxygen current, and the carbon

dioxide evolved collected in an absorption apparatus. The proportion given off was variable, but usually a little more than five atoms. The boat was then heated in a hydrogen current, to reduce the oxide of ruthenium formed. The boat was then placed in a carbon dioxide apparatus and treated with hydrochloric acid and the remainder of the carbon dioxide collected. The barium chloride was then filtered off from the ruthenium and determined as sulphate; the ruthenium, after burning the filter paper and heating in a hydrogen current in a porcelain boat, was estimated as the metal. It was not found possible to arrive at any agreement in different analyses as to the loss on heating the barium salt in air, or oxygen, or subsequently in hydrogen. While most of the carbon of the cyanogen is burned to carbon dioxide, a part remains as barium carbonate. The remainder of the barium seems to fluctuate between oxide and peroxide, while a variable portion of the ruthenium is oxidized. The analyses show conclusively that six atoms of carbon are present in the salt derived from the nitrosochloride, hence one cyanogen group cannot be replaced by the nitroso group.

The results of several analyses are as follows :

	Theory for Ba <sub>2</sub> Ru (CN) <sub>6</sub> . 6H <sub>2</sub> O.	From RuCl <sub>3</sub> and KCN sol.	Found.						
			I.	From RuCl <sub>3</sub> NO by fusion.			From RuCl <sub>3</sub> NO by solution.		
				II.	III.	IV.	V.	VI.	VII.
Barium.....	42.90	....	....	....	42.46	43.32	42.27	42.54	
Ruthenium.....	15.86	16.41 (with SiO <sub>2</sub> )	15.67	....	15.72	17.92 (with SiO <sub>2</sub> )	15.80	15.60	
5½H <sub>2</sub> O (100°).....	15.67	15.67	15.63	....	15.68	....	....	15.53	
6H <sub>2</sub> O (200°).....	16.83	16.68	16.85	...	16.69	16.71	16.56	16.68	
5 C .....	9.37	....	....	....	....	....	....	....	
6 C .....	11.23	....	....	....	....	....	....	....	
C from combustion .....	....	....	....	9.91	9.16	9.96	....	9.98	
C in residue .....	....	....	....	2.65	2.03	....	....	2.30	
Total carbon.....	....	....	....	12.56	11.19	....	....	12.28	

WASHINGTON AND LEE UNIVERSITY,  
LEXINGTON, VA., June, 1896.