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ZIRCONIUM FERROCYANIDE AND FERRICYANIDE

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There are only casual references in the literature to the possible existence of zirconium ferrocyanide and ferricyanide and these concern mainly their use as qualitative tests.

Some of the older texts state that potassium ferrocyanide gives a yellow precipitate in neutral solutions of zirconium salts. De Boisbaudran² stated that this precipitate was given also in acid solutions even when very dilute. Of course, on account of hydrolysis a neutral solution would remain such only for a very brief time. Before this Hornberger³ had gone into the matter more in detail and reported the precipitate as yellow-white and insoluble in excess of the precipitant. When precipitated hot the yellow color became yellow-blue and the odor of hydrogen cyanide was detected. When dried it was blue with a touch of green. It was insoluble in water but soluble in acids with evolution of hydrogen cyanide. For analysis he dissolved the precipitate in sulfuric acid diluted with 25% of water. From his results he calculated the formula, $3Zr(CN)_2 \cdot 2Fe(CN)_6$, which he compared with Turnbull's Blue, $3Fe(CN)_2 \cdot 2Fe(CN)_6$. This, as he remarked, involved the assumption of bivalent zirconium.

Zirconium Ferrocyanide.—In the following experiments 0.1 *M* solutions of zirconium oxychloride, $ZrOCl_2 \cdot 8H_2O$, and potassium ferrocyanide were prepared. The first was used freshly prepared. The precipitate formed on addition of potassium ferrocyanide was white and flocculent or curdy. It was insoluble in excess of either reagent and unchanged in color. On prolonged exposure or drying in the air the color changed from yellow to blue and bluish-green. The precipitate remains white for some time when covered with cold, boiled water. It cannot be filtered to approximate dryness without changing color. The zirconyl chloride used was very nearly free from iron. The changes in color are doubtless due to decomposition and freeing of iron from partial decomposition of the ferrocyanide.

The fresh precipitate is soluble in conc. sulfuric acid. Decomposition, however, is indicated by changes of color. This is avoided by making a smooth paste of the ferrocyanide with water, then dissolving in acid and diluting to about $\frac{1}{4}$ strength. Acid of this strength directly applied fails to effect solution. When ammonium hydroxide is added to complete precipitation, but in as slight excess as possible, a precipitate of zirconium hydroxide $Zr(OH)_4$ is obtained and the ammonium ferrocyanide and sulfate are removed in the filtrate. The precipitate was dried and ignited to the dioxide. The filtrate and washings were combined and titrated by standard potassium permanganate.

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² De Boisbaudran, *Compt. rend.*, **94**, 1625 (1882).

³ Hornberger, *Ann.*, **181**, 232 (1876).

Two sets of analyses were performed in duplicate with products from solutions at room temperature, the zirconyl chloride solution being used immediately after preparation. The first contained 0.8 g. of $ZrOCl_2 \cdot 8H_2O$ and the second 2.0 g.

- Expt. 1 a. $ZrO = 0.0730$; $Fe(CN)_6 = 0.0463$; ratio 1.57
 b. $ZrO = 0.0719$; $Fe(CN)_6 = 0.0466$; ratio 1.54
 Expt. 2 a. $ZrO = 0.2767$; $Fe(CN)_6 = 0.1987$; ratio 1.39
 b. $ZrO = 0.2779$; $Fe(CN)_6 = 0.1958$; ratio 1.41

In a third experiment the zirconyl chloride solution was first boiled so as to become thoroughly hydrolyzed, and then was cooled.

- Expt. 3 a. $ZrO = 0.1450$; $Fe(CN)_6 = 0.0424$; ratio 3.42
 b. $ZrO = 0.1436$; $Fe(CN)_6 = 0.0431$; ratio 3.33

When water is present no normal zirconium salt can be formed; zirconyl salts are found instead, or basic zirconyl salts more or less hydrolyzed under the influence of dilution, time and temperature. Taking certain hypothetical salts for purpose of comparison it is seen that $(ZrO)_2 \cdot Fe(CN)_6$ has the ratio 1.01; $ZrO(OH)_2 \cdot (ZrO)_2 Fe(CN)_6$, 1.51; $3ZrO(OH)_2 \cdot 4(ZrO)_2 Fe(CN)_6$, 1.39; $9ZrO(OH)_2 \cdot 2(ZrO)_2 Fe(CN)_6$, 3.27. The analytical results show that the hydrolysis proceeded too rapidly under the conditions of the experiments to yield zirconyl ferrocyanide, $(ZrO)_2 \cdot Fe(CN)_6$. Only basic ferrocyanides were obtained corresponding to different stages in the hydrolysis.

Zirconium Ferricyanide.—The older texts report that no precipitate is formed when a solution of potassium ferricyanide is added to solutions of zirconium salts. Rose,⁴ however, reported such a precipitation.

It was found that no precipitate was formed when 0.2 *M* solutions of zirconyl chloride and potassium ferricyanide were mixed, nor were precipitates obtained when more concentrated solutions were used, nor when either salt was added in excess. When such mixtures were slowly evaporated in a desiccator the only crystals formed were those of potassium ferricyanide. The rest of the mass was amorphous and varicolored from green to blue and darkening almost to black. This we interpret as indicating that zirconyl ferricyanide, if formed, is too soluble to appear as a precipitate and is easily decomposed. Similar results were obtained when solutions of zirconyl sulfate were used.

The formation of a basic zirconyl ferricyanide is much easier, however, and this accounts for the observation of Rose. When dilute solutions of zirconyl chloride are strongly hydrolyzed by boiling and potassium ferricyanide then added, a bright yellow, flocculent precipitate was obtained which, like the ferrocyanide, changed to green, blue and almost black on drying.

Two g. of zirconyl chloride octahydrate was dissolved in 100 cc. of water, the solution boiled for 30 minutes, cooled and precipitated with

⁴ Rose, *Ann. Phys. Pogg.*, **48**, 575 (1840).

as little excess of potassium ferricyanide as possible. The precipitate was washed by decantation with about 3 liters of water. This was found more easily soluble and in somewhat more dil. sulfuric acid than the ferrocyanide previously described and the solution remained unchanged for some days, in which also it differed from the ferrocyanide. The solution was diluted about 10-fold, sodium hydroxide added in very slight excess, the zirconium hydroxide filtered off, ignited and weighed as the dioxide. The ferricyanide radical was determined volumetrically by reduction to ferrocyanide and titration with standard potassium permanganate. In a second set of experiments, 4 g. of zirconyl chloride octahydrate was used. In both sets the results were checked by using aliquot parts for the analyses

	ZrO G.	Fe(CN) ₆ G.	Ratio
I a.	0.1724	0.0255	6.762
b.	0.1726	0.0185	9.326
II a.	0.5276	0.0774	6.815
b.	0.2788	0.0409	6.812
c.	0.2619	0.0383	6.847

The result for ferricyanide in Set Ib was rejected as faulty from some error in analysis. Omitting this, therefore, the average ratio is 6.809. Calculating this ratio from a hypothetical hydrolyzed zirconium ferricyanide $m\text{ZrO}(\text{OH})_2 \cdot n(\text{ZrO})_3\text{Fe}(\text{CN})_6$ the ratio at which m and n are both unity equals 2.012; when $m = 10$ and $n = 1$ the ratio is 6.540; when $m = 11$ and $n = 1$ the ratio is 7.043; when $m = 21$ and $n = 2$ the ratio is 6.791. The results indicate a constancy of proportion too great for an indefinite adsorption compound and so the formation of a definite very basic compound in which the acid radical is retained even after repeated washings with water. The most probable formula would be $21\text{ZrO}(\text{OH})_2 \cdot 2(\text{ZrO})_3\text{Fe}(\text{CN})_6$. In this less than $1/10$ as much acid is left as is present in the compound representing the first stage of hydrolysis from the normal zirconium ferricyanide.

Summary

1. Precipitates are formed when potassium ferrocyanide is added to solutions of zirconium salts. These are basic zirconyl ferrocyanides, unstable in the air, and their composition depends upon the extent of hydrolysis. Thus, a freshly prepared solution of zirconyl chloride gives a substance of the formula, $\text{ZrO}(\text{OH})_2 \cdot (\text{ZrO})_2\text{Fe}(\text{CN})_6$, and one that has been hydrolyzed by boiling gives a substance of the formula, $9\text{ZrO}(\text{OH})_2 \cdot 2(\text{ZrO})_2\text{Fe}(\text{CN})_6$.

2. Potassium ferricyanide gives no precipitate in freshly prepared solutions of zirconyl chloride. After boiling, the very basic compound $21\text{ZrO}(\text{OH})_2 \cdot 2(\text{ZrO})_3\text{Fe}(\text{CN})_6$ is precipitated.