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Studies on Chromium (III)-hexacyanoferrate (II)-complexes and the Related Compounds

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Though the color reaction between chromium (II) ions and potassium hexacyanoferrate (II) had been left unfamiliar, it has recently attracted attention of the investigators for the characteristic natures of its products different from those produced by the reaction of most of other heavy-metal ions with potassium hexacyanoferrate (II).

The reaction products, however, have not been isolated because of their great solubility in water, so their chemical compositions remained undetermined after a variety of electrochemical and spectrophotometric investigations were carried out applying a continuous variation method.

Separation of the reaction products

In the present work, by means of gel chromatography (using Sephadex column) taking advantage of its function of molecular sieve, the reaction products were isolated: at least three complex compounds differing with each other in color, chemical composition and molecular size—a reddish-brown complex, a green complex were separated from the reaction mixture.

The success in separation made it possible to study the chemical composition, structure and properties of the reaction products putting them under direct inspections and measurements. The three products separated all consisted of K, Cr, Fe and CN.

Chemical composition, molecular size and molecular weight of the Cr(III)*-hexacyanoferrate* (II)*-complexes*

The reddish-brown substance was the main product in which more than 90% of the reacted Cr(III) ions were contained, and was the smallest of the three substances in molecular size. The solid obtained from the aqueous solution of the reddish-brown substance by evaporation in vacuo at 30°C was determined by chemical analysis to have the empirical formula $K_5CrFe_2(CN)_{12}\cdot 7H_2O$.

The blue substance, empirical formula $KCrFe_6(CN)_{17}$, proved to be of exceedingly high molecular size and estimated to have a molecular weight higher than 4 millions.

The green substance, of medium molecular size between the foregoing two substances, is less stable in color and other properties than the two.

In determination of molecular weight of the reddish-brown complex, a new trial—molecular weight determination of the inorganic complicate-structured electrolyte of molecular weight in the range of 300 to 5000 by means of ultra-centrifuge —was made and proved to be very useful for this purpose. In this measurement,

molecular weight of the reddish-brown complex was identical to its empirical formula weight.

Structure study of the Cr(III)-*hexacyanoferrate* (II)-*complexes*

From the structure study of the reddish-brown complex and the blue complex by means of visible and ultraviolet spectra and infrared spectra, the following was known:

The raddish-brown complex (in aqueous solution, log $\varepsilon=4$ at the frequency 80×10^{13} sec^{-1}) comprises binuclear complex-ion of interesting structure having the linkage as described below.

$$\begin{array}{c}(OH_2)_c\\ |\\ (NC)_b\text{-}Fe(II)\text{-}(CN)_a\text{-}Cr(III)\text{-}(NC)_a\text{-}Fe(II)\text{-}(CN)_b\end{array}$$

$$(a+b=6,\ 2a+c=6,\ a=1 \text{ or } 2)$$

The blue complex, an inorganic macromolecular complex, comprises Fe-CN, Fe-CN-Fe, N-Cr and H_2O-Cr bonds, where Fe includes Fe(II) and Fe(III). The structure can be understood to be similar to that of soluble Prussian blue, some Fe(III) ions in which are replaced by Cr(III) ions as shown below.

$$\text{-Fe(II)-CN-Fe(III)-NC-Fe(II)-CN-Cr(III)-NC-Fe(II)-CN-Fe(III)-NC-}$$

Applications

The intensely blue-colored inorganic macromolecular complexes such as Cr(III)-hexacyanoferrate (II)-blue complex and so-called "soluble Prussian blue", macromoleculologically purified by molecular sieve, were found excellently useful as an index reagent in the experimental measurement of the void volume (external volume), Vo, of the gel column in gel chromatography.

On the other hand in the course of studying about the reaction products, necessity for determining chemical compositions of the complexes under consideration and the related compounds lead us to a number of new or improved methods or technics of elementary analysis for Cr, Fe, K, and CN.

One of them is a new method of determining cyano and cyanide type nitrogen of inorganic cyano complexes and cyanide salts by Kjeldahl's process, valid for a sample in aqueous solution as well as in solid state. This method, enabling accurate determination even when the sample is in aqueous solution by ordinary Kjeldahl's process without adding any cumbersome device or procedure, is recommended for the use in inorganic and coordination chemistry, chemistry in the environmental problems and other field.