

PURIFICATION AND PROPERTIES OF DICHLOROTETRAQUACHROMIUM (III) CHLORIDE 2-HYDRATE¹

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In preparing to study reactions of chlorochromium (III) ions, problems were encountered in making the starting material in high purity. This note describes the solution of these problems and also gives properties and methods of analysis which may be of value to workers in the field.

The green chromic chloride, labeled $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, available in two brands as analyzed reagent grade material, was found to be deficient in chloride. It seems to lose HCl on standing to form oligated polymers (Rollinson, 1956). By analysis as described below, various samples gave ratios of Cl/Cr of 2.76/1 to 2.84/1, below the 3/1 mole ratio of the formula. Recrystallization followed by acetone and ether washing, as recommended by Elving and Zemel, 1957, and by King, 1936, raised this ratio only to 2.83/1 to 2.93/1. (One better result was obtained by this method; see procedure below). The method to be described here regularly produced the compound with ratio $3.000 \pm 0.005/1$ and with one third its chloride initially ionized in water.

PROCEDURE

The starting material may be the fresh, granular, reagent grade chromic chloride, or that prepared by recrystallization from HCl solution, or that made by the reaction of CrO_3 with HCl (King, 1936). The chromic chloride was ground to a fine powder and dried over CaSO_4 , Drierite. The powder was placed in a mortar, covered with dry, reagent grade acetone and ground well. This was found to be the important step in removing the "polymer" which gave a green-brown acetone solution. Washing with acetone on the filter was not found to be efficient unless large quantities of acetone were used. The acetone-ground powder was then transferred to a sintered-glass filter and the acetone washing continued until the filtrate was colorless. After rinsing with dry ether, the residue was stored in a desiccator. A crust of dark, sticky matter sometimes formed on top of the residue if the acetone was not removed with ether. Repetition of the acetone grinding and washings gave a product of high purity. After removal of the main part of organic vapor, storage in the 2-hydrate form was achieved at water vapor pressure about 1

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mm of Hg, over $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ — $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ or over solid NaOH in contact with its saturated solution. (See properties, below.)

ANALYSES

The solid can be weighed in a covered vessel on a rapid balance without significant error from moisture. Aliquots containing 0.3 to 0.4 g. were pipetted into 50.00 ml of standardized 0.1 M AgClO_4 , heated to boiling, and allowed to stand several hours. One ml. of concentrated HClO_4 was added and the excess silver ion titrated with a standard chloride solution, using a pH meter with a glass-silver electrode pair to detect the end point (Elving and Zemel, 1957). This gave the total chloride. The same solution can next be analyzed for chromium as follows: add 100 ml. water, 0.5 g. AgNO_3 , 5 g. $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 10 ml. each of concentrated H_2SO_4 and H_3PO_4 , boil for 15 minutes, cool, and titrate with standardized Fe (II) solution using diphenylaminesulfonic acid as indicator.

For the uncoordinated chloride, the solid can be weighed into ice-cold 6M HClO_4 and immediately titrated with the AgClO_4 solution as described above (Elving and Zemel, 1957). The total chloride can then be found on the same sample by adding excess AgClO_4 solution, heating and standing as described above, and titrating the remaining silver ion. This gave results in the range 2.91/1 to 3.00/1 for the ratio of total chloride to initially ionized chloride.

From the formula, $\text{CrCl}_2(\text{H}_2\text{O})_4\text{Cl} \cdot 2\text{H}_2\text{O}$, one calculates Cr as 19.52% and Cl as 39.92%. Two batches of the compound prepared by this method gave 19.50 and 39.88; and 19.50 and 39.95.

PROPERTIES

The material prepared by this method is an apple-green powder, contrasting with the dark green crystals (wet or impure?) described in Mellor, 1931.

The material is rapidly dissolved by water, slightly soluble in acetone, nearly insoluble in ether, and turns to the violet color of hexaquachromium (III) ion within a few hours in 0.1 M water solution. The material retains its green color for days in acid solutions, whether or not there is excess chloride present.

An approximate experiment was performed to find out how fast the coordinated chloride is released in solutions of several acid concentrations: ionized chloride was titrated in solutions each initially 0.06 M in $\text{CrCl}_2(\text{H}_2\text{O})_4^+$ ion but of different HClO_4 concentrations. The periods of time taken for half the first bound chloride to ionize at room temperature were: 25 hours in 6 M HClO_4 , 11 hours in 2 M, and 8 hours in 0.2M. The second chloride, from $\text{CrCl}(\text{H}_2\text{O})_5^{++}$, came off much more slowly; virtually none having ionized in nine days, starting from $\text{CrCl}_2(\text{H}_2\text{O})_4^+$, in the 6 M and 2M HClO_4 solutions. In 1M,

0.5M and 0.2 HClO₄ solutions, about 2, 4, and 8% of the second chloride ionized in nine days. Little is known about the hydrolytic reactions under conditions of high acidity (Stranks, 1960). Further work is planned on these reactions and equilibria.

The compound coalesces and melts gradually over the range 88-90°C. (Mellor, 1931, reported over 90°).

A hygrostatic study, using five humidities in the range 10⁻⁵ to 6 mm. of Hg water vapor pressure, showed that the 2-hydrate was stable at 1 mm H₂O pressure (NaOH and its saturated solution). The 6 mm. hygrostat (CaCl₂ and its saturated solution) also gave little change in weight. Common "anhydrous" CaCl₂ removed much of the 2-hydrate water in three weeks, while P₂O₅ removed all of it, 13.5% of the sample weight. It should be noted that P₂O₅ dehydration may not stop at this point, (Mellor, 1931.) One preparation of the 2-hydrate retained its water during three months storage over CaCl₂•H₂O-CaCl₂•2H₂O, about 1-2 mm. H₂O pressure at room temperature. The hygrostat mixture was prepared from CaCl₂ plus about 20% of its weight of water. In this way, primary standard CrCl₂•(H₂O)₄Cl•2H₂O can be kept for reaction studies, etc., which was the object of this work.

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NEWS OF TENNESSEE SCIENCE

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Biology Division—Oak Ridge National Laboratory

Alexander Hollaender attended the Third International Congress on Photobiology in Copenhagen, Denmark, July 31-August 5. Dr. Hollaender is President of the International Committee on Photobiology, and he gave the opening plenary session lecture which was entitled "Finsen and Basic Research."

Takashi Makinodan left Oak Ridge August 30 for Tokyo, Japan, to attend the eighth International Congress of Hematology, September 4-10, and present an invited paper on "An immunological approach to study radiation-induced blood chimeras." While in Japan, Dr. Makinodan will consult with scientists on problems related to radiation effects on hematopoietic tissues, genetic aspects of mechanism of antibody formation, and other problems at Hiroshima University; National Institute of Genetics, Mishima; Shinshu University, Matsumoto-shi; National Institute of Health, Tokyo; and the

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