

Synthesis of Chromium(II) Acetate Hydrate

Introduction

Chromium may adopt many formal oxidation states ranging from -4 to $+6$. Most familiar of the compounds with the highest oxidation number ($+6$) are those containing CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ ions. The most stable compounds of chromium contain the $+3$ oxidation state, but many compounds containing the $+2$ oxidation state are known that are stable in the absence of oxygen (air). The name chromium (Gk. *chroma* means color) was given to the element because it forms a large number of colored compounds. The Cr(II) ion is readily oxidized:



thus to successfully complete a synthesis its compounds must be protected from air. The Cr(II) ion is also a strong reducing agent which is capable of reducing water producing hydrogen gas. Cr(II) has been used extensively in studying the mechanisms of electron-transfer reactions.

In this experiment the red, diamagnetic chromium(II) acetate hydrate solid will be prepared. The starting material for the synthesis is potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ which is reduced by zinc metal in the presence of strong acid (HCl). During this reduction reaction there are many informative color changes as chromium cycles through a number of its oxidation states. First the orange colored Cr(VI) is reduced to green Cr(III), and finally to blue Cr(II). Chromium(II) acetate hydrate is brick red dimeric complex with molecular formula $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$ and was first synthesized in 1844. Interestingly, Huheey (*Inorganic Chemistry*, 3rd ed., Harper and Row, New York, 1983), points out that this compound is prepared in inorganic synthesis courses as a *“test of skill and patience - unless it is absolutely dry it is readily oxidized in air.”* Thus, you will be challenged as many generations of inorganic students before you have been. *Will your product remain brick red in a sealed vial for more than 1 week?*

Chromium acetate hydrate, because of its relative stability, is often used as the starting material for other less stable Cr(II) compounds such as $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$. There has been considerable interest in the dimeric structure of $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$ because it has a relatively short Cr–Cr distance, so much so that it suggests the possibility of a quadruple bond. As you answer the questions at the end of the experiment you will learn more about its structure and other properties.

Procedure

Obtain a side-arm test tube, rubber stopper, Tygon and glass tubing needed to assemble the apparatus shown in the Fig. 1. (Some of these will already be preassembled.) Clamp the test tube securely on a ring stand and place inside the fumehood. Weigh out 1.0 g of potassium dichromate, being careful not to drop any of the compound on or around the balance (see MSDS). Weigh out 5.0 g of mossy zinc and transfer both the potassium dichromate and zinc to the side-arm test tube. Do not place the stopper and glass tubing on the test tube at this time. In a 30-mL beaker dissolve 4.5 g of sodium acetate trihydrate in 4 mL of deionized water. This solution may have to be gently heated on a hot plate in order to obtain complete solution. Make certain that this solution is at room temperature before proceeding.

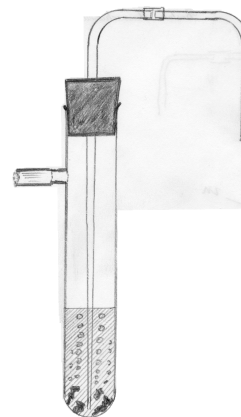


Figure 1.

The next part of the experiment must be done in the hood. All

students working in the area are to wear safety glasses, and those working directly on the experiment should wear protective gloves. Your instructor will give you specific directions about the following procedure.

Pour 10 mL of concentrated hydrochloric acid (12 M) into a 30-mL beaker. (*Depending upon the size of the mossy zinc particles it is possible that some dilution of the acid will be made - see instructor.*) With the side-arm test tube set at a slight angle add the hydrochloric acid *dropwise* to the side-arm test tube. Immediately the zinc begins to react with the acid evolving considerable amounts of hydrogen gas. Because the evolution of hydrogen gas will carry hydrogen chloride out of the tube make certain to keep your hands away from the mouth of the test tube. Continue the addition of the acid, making certain that the resulting foam from the reaction does not rise to the height of the side-arm. This procedure should be continued for 15 to 20 minutes until the solution has gone through all the color changes described above. Sometimes it is difficult to determine a blue-green solution from a blue one. Your instructor will assist you at this point if necessary.

While the reaction is proceeding take approximately 10 mL of water in a test tube and shake vigorously with one drop of ether. This will remove air from the water. Stopper tightly and place this test tube in a small ice bath for use as a wash solution later in the experiment. Also set aside in two small test tubes of 5-mL ethanol and 5-mL ether.

Finally, when the solution is blue, indicating the presence of Cr(II), add fairly rapidly 10 to 15 more drops of the acid and immediately insert the stopper and glass tubing into the side-arm test tube. ***Be extremely careful not to jam the thin glass tubing into a piece of Zn at the bottom of the test tube. If you break the glass tip at this stage the experiment will likely be ruined.*** Adjust the clamp so that the test tube is vertical as shown in the Figure 1 and place the beaker containing the sodium acetate solution under the glass tubing with the 90° bend. Pinch off the Tygon tubing at the side-arm and allow the positive pressure of the hydrogen gas to carry the Cr(II) solution through the glass tubing into the beaker containing the sodium acetate solution. Transfer as much of the solution as possible without allowing the glass transfer tube to touch the sodium acetate solution. The deep red chromium acetate should immediately form. Immerse this beaker in an ice bath for a few minutes and prepare a filtration assembly using a 30-mL medium frit glass filter. Filter the cold deep red solution making certain not to suck too much air through the sample to avoid oxidation. As soon as the liquid is no longer visible break the vacuum and add 3 mL of the ice cold water. Suck the water through the filter and break the vacuum. Repeat the process with two more 3-mL water washes, one 5-mL ethanol wash, and one 5-mL of ether wash. Pass air through the sample for approximately 30 seconds then break the vacuum. Collect the sample, and spread it out on a filter paper or porcelain plate to allow the remaining ether to evaporate. Place the sample in a tared sample bottle and weigh to determine the yield of product.

Dispose the filtrate in the waste container marked chromium(II) acetate waste. Fill the side-arm test tube half-full with water and add this to the same waste container, being careful not to dispose of the zinc in the same container (decant the liquid). Repeat the process twice more. You may now rinse the test tube under the tap and dispose of the zinc in a laboratory trash can.

Reaction of Chromium(II) Acetate Hydrate

Take a small test tube and add 5 to 10 drops of dilute iodine in CCl_4 . This pink colored solution will be available in the laboratory. Add an equal amount of water to the test tube. Add a spatula tip full of chromium(II) acetate hydrate to the solution and shake vigorously. Observe any color changes that occur in either the organic or aqueous layer.

Laboratory Report

1. Submit your sample, clearly labeled with your name on it.
2. the percent yield on the quantity of potassium dichromate starting material. Also include in your report any unexpected observations or difficulties encountered.
3. Your written report should contain balanced equations for the syntheses. Use standard reduction potentials of *all redox species* present to determine the various redox reactions which may occur during the procedure. Based upon the various cell potentials discuss which redox reactions are likely to be prevalent.
4. Write balanced equations for the reaction with iodine?
5. Sketch the structure of $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$?
6. Determine the point group symmetry of $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$.
7. From the literature determine the Cr–Cr bond distance in $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$ and one analogous complex? Do the metal-metal bond lengths differ? Why so? Summarize the arguments for and against the presence of a metal-metal quadruple bond.
8. Suggest an alternative method, with reference citations, for the preparation of chromium(II) compounds?

References

Greenwood, N. N. and Earnshaw, A., "Chemistry of the Elements," Pergamon Press, Oxford, 1984.

Housecroft, C. and Sharpe, A. G., "Inorganic Chemistry," Prentice Hall, Harlow, England, 2001.

Cotton, F. A. and Wilkinson, G., "Advanced Inorganic Chemistry, 5th Ed." John Wiley, New York, 1988. Other editions of this classic reference work including the 6th Ed. present good overview of the chemistry of Cr(II).