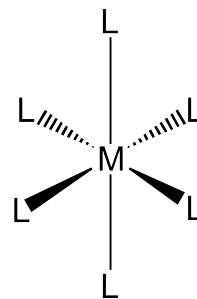


Experiment 10

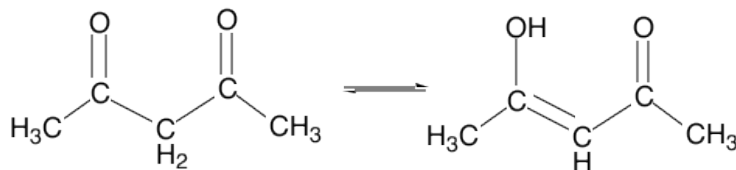
Synthesis of Metal–Ligand Complexes Containing the Ligand Acetylacetonate

Many of the compounds inorganic chemists study include transition metals. One important aspect of a transition metal's chemistry is that it can form a coordination complex with molecules and ions—we call these ligands when they bind to metals—that have one or more lone pairs of electrons that they can donate to form a chemical bond. The figure to the right, for example, is an octahedral coordination complex that consists of a central metal atom, M, bound to six ligands, L. This compound is also called a metal–ligand complex.

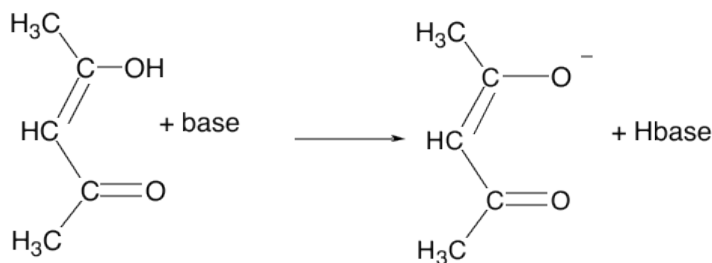


Ligands such as ammonia, NH_3 , and the chloride ion, Cl^- , donate a single pair of electrons and are called monodentate ligands. Other ligands have two or more lone pairs of electrons, each of which binds to the metal. A single ligand that binds to a metal through two lone pairs, for example, is a bidentate ligand.

In this experiment you will synthesize a metal–ligand complex using the bidentate ligand acetylacetonate, whose structure is shown on the left side of figure below, with one of four metal ions. The oxygens in acetylacetonate, which are double-bonded to carbons, are called ketone groups. There is another important form of this ligand, called an enol, in which a proton on the central carbon atom moves to one of the double-bonded oxygens, as shown on the right side of the figure below; although not present in significant amounts, it is the enol form of acetylacetonate that binds with metals.

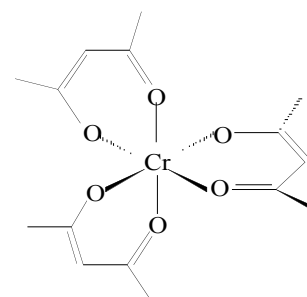


Before acetylacetonate can bind with a metal, we must first remove the hydrogen bound to the oxygen in its enol form. This is accomplished using a base, as shown below.



Depending on the metal ion, two or three acetylacetonate ligands are required to form a metal–ligand complex, giving the metal a coordination number of 4 or 6. In the case of Cr^{3+} , for example, the metal–ligand complex, which is shown to the right, has three ligands. Because each ligand has a charge of -1 , the metal–ligand complex is neutral.

Chemists often adopt shorthand names for metal complexes and their ligands. The ligand acetylacetonate is abbreviated “acac $^-$ ” when deprotonated, and “Hacac” when it is protonated. The metal–ligand complex shown to the right, therefore, is $\text{Cr}(\text{acac})_3$.



Because the products of these reactions are neutral and have non-polar organic “shrubbery” on the outside, they are insoluble in water and precipitate from the reaction mixture in which they form. This is a tremendous benefit because it enables us to recover easily the metal–ligand complex from its reaction mixture.

Pre-lab Assignment

Carefully read through all four syntheses so that you are familiar with the general procedure; the specific metal-ligand complex that you will synthesize will be provided to you when you arrive in lab.

Experimental Procedure

Caution: Any reaction that requires heating acetylacetonone must be performed in the hood!

Preparation of Co(acac)₃

Weigh 1.0 g of powdered CoCO₃ into a 50-mL Erlenmeyer flask and add 8 mL of acetylacetonone. Add a small magnetic stir bar and cover with a small watch glass. Using a ring-stand and clamp, place the reaction vessel in a water bath on a stirring hot plate, ensuring that the flask does not touch the bottom of the water bath and that the liquid level in your flask remains below the level of water in your water bath. Refill the water bath as necessary. Stir the reaction using the magnetic stir bar and heat the reaction to about 80°C. Once you reach 80°C, maintain this temperature for approximately 5 minutes and then turn off the heat.

Caution: 10% H₂O₂ will damage skin! Wear gloves or be extra careful!

Using a disposable pipet, slowly add 6 mL of 10% hydrogen peroxide, H₂O₂, dropwise at a rate of 1-2 mL/min while continuing to stir the solution. It is important that you add the peroxide slowly as the reaction will bubble vigorously and you do not want it to boil over!

After adding the H₂O₂, reheat the mixture to 80°C and then slowly add an additional 6 mL of H₂O₂. After the second addition of peroxide is complete, remove the water bath and place the flask directly on the hotplate and briefly bring the solution to a boil. Cool the mixture to room temperature, then place in an ice bath for about 15 minutes or until crystallization appears complete. Filter the product using a Büchner funnel, washing remnants out of the reaction flask with deionized water (2 rinses of 5 mL each). Wash with several small (2-3 mL) volumes of cold ethanol (make sure you chill your ethanol first or it will dissolve your compound). Place your product in your lab drawer and allow it to dry until next week.

This procedure is modified from Bryant, B. E.; Fernelius, W. C. *Inorg. Synth.* 1957, 5, 188.

Preparation of Cr(acac)₃

Heat a water bath on a stirring hotplate. Weigh 1.30 g of CrCl₃•6H₂O into a 50-mL Erlenmeyer flask. Include a small magnetic stirring bar, add 20.0 mL of distilled water, and stir briefly. When the chromium compound has dissolved, add 5.0 g of urea and 4.0 mL of acetylacetonone.

Using a ring-stand and clamp, place the reaction vessel in a water bath on a stirring hot plate, ensuring that the flask does not touch the bottom of the water bath and that the liquid level in your flask remains below the level of water in your water bath. Refill the water bath as necessary. Stir the reaction using the magnetic stir bar and heat the reaction to a temperature greater than 90°C. Heat the mixture, uncovered and with vigorous stirring, for approximately one hour. As the urea releases ammonia and the solution becomes basic, deep maroon crystals will begin to form.

After one hour, allow the reaction to cool to room temperature, and then place it in an ice bath to complete crystallization (*Note: if you do not see solid after 1 h, continue to heat and stir until you do; sometimes it takes a bit longer!*). Collect the product by vacuum filtration using a Büchner funnel. Wash out the flask and the crystals on the filter with plenty of deionized water (about 3 rinses of 10 mL each). Place your product in your lab drawer and allow it to dry until next week..

This procedure is modified from Charles, R. G.; Pawlikowski, M. A. *J. Phys. Chem.* 1958, 62, 440.

Preparation of Mn(acac)₃

Weigh 1.0 g of MnCl₂•4H₂O and 2.6 g of sodium acetate trihydrate into a 100-mL Erlenmeyer flask, add a stirring bar, and dissolve the solids in a minimal amount of distilled water (add a very small amount at a time until the solids dissolve completely). When the solids are dissolved, add 4.0 mL of acetylacetone with continued stirring.

Prepare a second solution containing 200 mg of KMnO₄ in 10 mL of deionized water. As KMnO₄ is difficult to dissolve, you will need to stir this solution for some time. When the KMnO₄ is dissolved, add the solution dropwise to the your mixture of MnCl₂•4H₂O and sodium acetate trihydrate. When finished, use a disposable pipet to add 1-2 mL of water to the flask or beaker originally containing the KMnO₄ solution and then use this water to rinse down the walls of the reaction flask to ensure all of the permanganate is added to the reaction mixture. After stirring the mixture for about five minutes, add dropwise a second portion of sodium acetate trihydrate (2.6 g dissolved in a minimal amount of water) to the reaction mixture. Heat the resulting mixture directly on a hotplate for 10 minutes at about 70°C (put a thermometer directly in the reaction flask) and then set aside to cool to room temperature. Collect the dark brown precipitate using a Büchner funnel. Use small portions of deionized water (2 rinses of 5 mL each) to wash any remaining crystals out of the reaction flask. Place your product in your lab drawer and allow it to dry until next week.

This procedure is modified from Fernelius, W. C., Blanch, J. E. *Inorg. Synth.* 1957, 5, 130.

Preparation of Fe(acac)₃

Weigh 1.3 g of Fe(NO₃)₃•9H₂O into a 50-mL Erlenmeyer flask and dissolve in 7.0 mL of distilled water. Add a magnetic stir bar, stir the solution, and then add a mixture of 1.0 mL of acetylacetone in 7.0 mL of methanol. Add a solution containing 1.3 g of sodium acetate trihydrate in 7.0 mL of distilled water, and briefly heat the mixture on a hotplate until some of the methanol has boiled away (you should see a decrease in the volume of the reaction mixture). Cool the reaction mixture to room temperature, and then place it in an ice bath for approximately 15 minutes. Filter the red crystalline solid using a Büchner funnel, and wash the flask and crystals using distilled water (2 rinses of 5 mL each). Place your product in your lab drawer and allow it to dry until next week.

This procedure is modified from Charles, R. G. *Inorg. Synth.* 1963, 7, 183.

Compounds and Waste Disposal

All waste must be disposed of properly in the appropriate waste container.

Write Up

Determine the mass of your dried product, place it in a vial, and label the vial with your compound's name, its formula, and the mass obtained. Turn these in along with a brief report that addresses the following for all four of the metal-ligand complexes (that is, for both the one you synthesized and for the three you did not synthesize).

Each synthesis requires that the metal ion be in a +3 oxidation state and requires that acetylacetonone be present in its weak base form, acac^- , instead of its weak acid form, Hacac .

- (1) For those syntheses in which the metal ion is not initially present in a +3 oxidation state, report the metal ion's initial oxidation state, indicate whether it needed to be oxidized or reduced, identify the reagent in the synthesis that served as the oxidizing agent or the reducing agent, and write the balanced reaction. You should expect to use your textbook or internet resources to help you with these tasks.
- (2) In each synthesis, acetylacetonone is added to the reaction mixture as Hacac . As a result, each synthesis includes a base that converts Hacac to acac^- . Identify the reagent in each synthesis that served as the base for this deprotonation and write the balanced reaction. You should expect to use your textbook or internet resources to help you with these tasks.