Experiment 11

Synthesis of Metal–Ligand Complexes Containing the Ligand Acetylacetone

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

The bond between the metal and the ligand—in which both electrons come from the ligand—is called a dative, or coordinate covalent bond. A metal that accepts a lone pair of electrons is a Lewis acid, while the electron-pair donor is a Lewis base. The study of coordination complexes provides inorganic chemists with a broader understanding of chemical reactivity, from the functioning of enzymes that contain metal ions to the working of industrial catalysts.

Ligands such as ammonia, NH₃, and the chloride ion, Cl⁻, can donate only a single pair of electrons and are called monodentate ligands. A coordination complex including monodentate ligands typically has 4–6 ligands arranged around the metal in an octahedral (see figure above), square planar, or tetrahedral geometry. Other ligands have two or more lone pairs of electrons, each of which binds to the metal. A single ligand binding to a metal through two lone pairs is a bidentate chelating ligand. If two bidentate ligands form a complex, we call the complex a bis-chelate; if three ligands bind, we call it a tris-chelate.

In this experiment we will synthesize a series of metal–ligand complexes using the ligand acetylacetone, whose structure is shown in the figure to the right, and four different metal ions. The two oxygens in acetylacetone, 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 below; although not present in significant amounts, it is this second form of acetylacetone that binds with metals.

Before acetylacetone will bind with a metal, we must first remove the hydrogen bound to the oxygen in its enol form. This is accomplished using a base, which leaves the structure shown below.
Depending on the metal ion, two or three acetylacetone ligands are required to form a metal–ligand complex, giving the metal a coordination number of 4 or 6. In the case of \(\text{Cr}^{3+}\), 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 acetylacetone is abbreviated “acac–” when deprotonated, and “Hacac” when it is protonated. The metal–ligand complex shown to the right, therefore, is abbreviated Cr(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**

As your group must juggle four different syntheses, carefully read each procedure and develop a plan for completing your work in a timely manner. Prepare an outline in your lab notebook of who will do what so that you can work efficiently when in lab.

**Experimental Procedure**

Working in groups of two or three, complete the syntheses described below.

*Caution: Reactions that require heating acetylacetone must be performed in the hood!*

**Preparation of Co(acac)\(_3\)**

Weigh 1.0 g of powdered \(\text{CoCO}_3\) into a 50-mL Erlenmeyer flask and add 8 mL of acetylacetone. 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% \(\text{H}_2\text{O}_2\) will damage skin! Wear gloves or be extra careful!*

Using a disposable pipet, slowly add 6 mL of 10% hydrogen peroxide, \(\text{H}_2\text{O}_2\), 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 \(\text{H}_2\text{O}_2\), reheat the mixture to 80°C and then slowly add an additional 6 mL of \(\text{H}_2\text{O}_2\). 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’s lab. Weigh the compound to obtain the mass of your product.

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 CrCl$_3$•6H$_2$O 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 acetylacetone.

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).


Preparation of Mn(acac)$_3$

Weigh 1.0 g of MnCl$_2$•4H$_2$O 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 0.2 g of KMnO$_4$ in 10 mL of deionized water. As KMnO$_4$ is difficult to dissolve, you will need to stir this solution for some time. When the KMnO$_4$ is dissolved, add the solution dropwise to the your mixture of MnCl$_2$•4H$_2$O 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 KMnO$_4$ 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’s lab. Weigh the compound to obtain the mass of your product.

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(NO$_3$)$_3$•9H$_2$O 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 crys-
talline 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’s lab. Weigh the compound to obtain the mass of your product.

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
Place each compound in a separate vial and label each vial with the compound’s name and formula, the mass obtained, and the names of your group members. Turn these in along with a report addressing the following:

Each synthesis requires that the metal ion be in a +3 oxidation state and requires that acetylacetone 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 with a +3 oxidation state, explain how its oxidation state was adjusted. Identify the oxidizing agent and the reducing agent, and write the appropriate chemical reaction.

(2) In each synthesis, acetylacetone is added as Hacac. As a result, each synthesis includes a base that converts Hacac to acac⁻. Identify the base in each synthesis and write the appropriate chemical reaction.