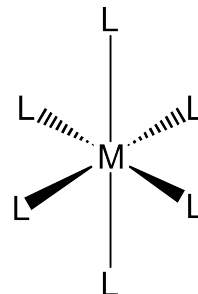


Experiment 10

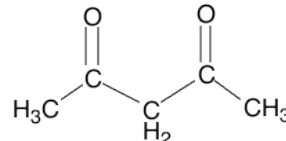
Synthesis and Recrystallization of Metal–Ligand Complexes Containing the Ligand Acetylacetonone

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.

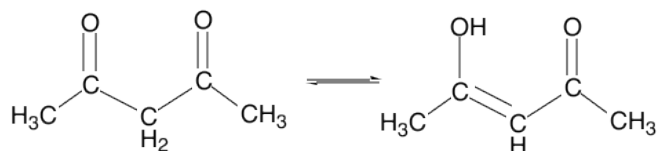


The bond between the metal and the ligand—in which both electrons come from the ligand—is called a dative, or coordinate covalent bond. A metal that accepts a lone pair of electrons is a Lewis acid, while the electron-pair donor is a Lewis base. The study of coordination complexes provides inorganic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

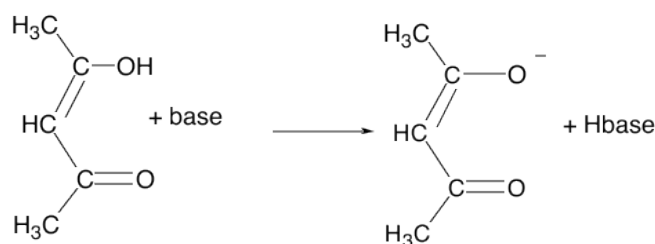
Ligands such as ammonia, NH_3 , and the chloride ion, Cl^- , can donate only a single pair of electrons and are called monodentate ligands. A coordination complex including monodentate ligands typically has 4–6 ligands arranged around the metal in an octahedral (see figure above), square planar, or tetrahedral 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.



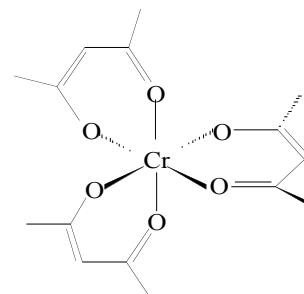
In this experiment we will synthesize a series of metal–ligand complexes using the ligand acetylacetonone, whose structure is shown in the figure to the right, and four different metal ions. The two oxygens in acetylacetonone, which are double-bonded to carbons, are called ketone groups. There is another 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 acetylacetonone that binds with metals.



Before acetylacetonone 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 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 abbreviated $\text{Cr}(\text{acac})_3$.

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

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 three, complete the syntheses described below.

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

Preparation of $\text{Co}(\text{acac})_3$

Weigh 1.0 g of powdered CoCO_3 into a 50-mL Erlenmeyer flask and add 8 mL of acetylacetonate. 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% H_2O_2 will damage skin! Wear gloves or be extra careful!

Using a disposable pipet, slowly add 6 mL of 10% hydrogen peroxide, H_2O_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 H_2O_2 , reheat the mixture to 80°C and then slowly add an additional 6 mL of H_2O_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 $\text{Cr}(\text{acac})_3$

Heat a water bath on a stirring hotplate. Weigh 1.30 g of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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). 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.; Pawlikowski, M. A. *J. Phys. Chem.* 1958, 62, 440.

Preparation of $\text{Mn}(\text{acac})_3$

Weigh 1.0 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 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 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 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 $\text{Fe}(\text{acac})_3$

Weigh 1.3 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 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'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.

Recrystallization of $\text{M}(\text{acac})_3$ complexes

Each of you will need to try to recrystallize one or more of your compounds. Collectively you will likely use at least half of your samples for crystallization attempts—sometimes it takes multiple tries to get something that works! You should at least try one form of layering, and you can use either or both of the other methods as well. The more things you try, the better luck you will have a growing large crystals. You should definitely try more than one type of solvent combination.

Crystallization of an inorganic (or organic!) product is often a critical step in a synthesis procedure. It frequently allows you to purify the product, or to grow larger crystals that are suitable for X-ray structural analysis. Since X-ray crystallographic analysis is frequently necessary to identify inorganic substances definitively, this is an important skill in inorganic chemistry. Unfortunately, in synthetic procedures, you will sometimes be given little detailed information about how to carry out such a procedure, so you

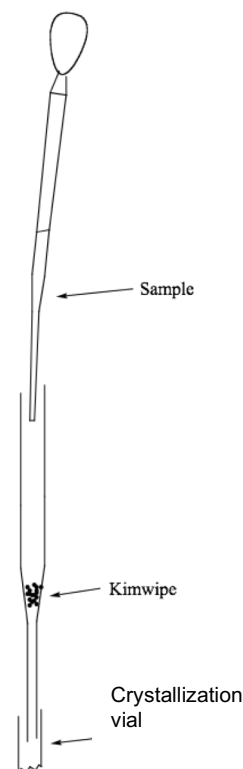
need to learn to “fly by the seat of your pants”, so to speak, when it comes to purifying your product through recrystallization. Although it can take multiple trials to get it right, the procedures themselves are typically not very difficult.

Note: Make sure that you have recorded the yield of your dry product before starting your recrystallization attempts!

Your lab instructor will inspect each person’s recrystallization attempts and initial your lab notebook.

Solubility Testing

The first step in any crystallization procedure is to determine the solvents in which a product is soluble and insoluble. Typically the solubilities of the product in a range of solvents having different degrees of polarity are tried (see polarity index on the following page). A group such as water, methanol, acetone, acetonitrile, methylene chloride, ethyl ether, toluene, and pentane, for example provide such a range. As a class we will divide up the work to save time!



Solubility tests can be done with just a small amount (the very tip of a spatula, enough so you can just see it) of product in about a 1/2 mL of solvent. Indicate the solubility of the compound as soluble, slightly soluble, or insoluble. When you are testing solubilities, be on the lookout for significant color changes to the product—sometimes this can mean that the product is decomposing in the solvent (which we want to avoid), or that the solvent is coordinating (binding) to the product. Be sure to note these. Test your compound for solubility in the range of solvents provided so that the class as a whole has results for all 4 compounds in the solvents provided.

As a class you should also use the miscibility table (at the end of this handout), and a reference (online or handbook) to determine both the density and the boiling point of each of the solvents. This data will help you decide which solvents might be appropriate for the methods below. Each person must try at least two different methods described below.

Layering

One of the best methods for crystallization is layering. This consists of creating two layers of solvents, one more dense than the other. The layers are carefully made so that they mix as little as possible but they can then mix slowly over time through diffusion of the layers. When you have a list of the solvents that appear to dissolve the product without decomposing it, look up these solvents on the solvent miscibility table that is attached. The trick is to find a solvent that the compound is soluble in that is miscible with another solvent in which the product is insoluble. Two solvents are immiscible if they form two unmixable layers like oil and water, and miscible if they can

be mixed (for crystallization, you want the layers to eventually mix!). If you add enough of the solvent that the product is insoluble in to a solution of the product dissolved in a soluble solvent, product will precipitate from the solution. The more carefully the solvents are added together, the better the chance for large crystals!

Dissolve your compound in one of the solvents that dissolves the product. Try to use a minimal amount of solvent (your solution should be very darkly colored). If the compound does not dissolve completely in your initial solvent, you can remove small particles by making a filter from a disposable pipette and a small wad of a Kimwipe. Push the wad of paper into the pipette down into the narrow part of the pipette with another long pipette. The Kimwipe will serve as your filter. Then run your solution through the top of the pipette to filter it! After you have a solution of your product you will have to add this together with the solvent that the product is insoluble in. You can either add the insoluble solvent very carefully on top of your solution of product, slowly dribbling it down the sides of the vial using a pipette, the “top-down” method. Alternatively, you can add the solution of product underneath the insoluble solvent, by taking the pipette directly to the bottom of the vial and then dispensing the solution: the “bottom up” method. If you use this method, stop before you have dispensed all of the liquid so you don’t send up a big bubble that will disturb the layers.

Either way, you should do this recrystallization in a container that can be closed up very tightly, such as a small vial with a screw-cap lid, Erlenmeyer with a stopper, etc. Parafilm alone will definitely not work because some of the solvents will actually eat through the parafilm. **Note: When designing your layering, try to get the more dense solvent to be the one that ends up on the bottom, otherwise the layers will mix immediately upon adding the second one.**

If you are careful enough, you should be able to layer one solvent on top of the other so that you have two distinct layers. When these layers diffuse together slowly, crystals will (hopefully!) form at the interface! **Carefully** put your solutions somewhere it will not be bumped (like in the bottom cabinet of your lab drawers) and check on them periodically to see if the crystals are growing. If you don’t see crystals, make sure your solution hasn’t evaporated through a leaky lid, that the initial solution of your compound is concentrated enough, and that you’ve added enough of the insoluble solvent (adding more of the latter is a quick thing to try if you don’t get crystals the first time).

Vapor diffusion

Vapor diffusion is similar to layering in that you use two solvents that are miscible, one that the compound is soluble in, and one that the compound is insoluble in. Make a solution of the compound in the soluble solvent. Filter with a pipette as described earlier to remove any small pieces of undissolved solid. Place that solution in a small open vial. Then place that whole vial inside a bigger vial or screw-cap container of some sort (the stockroom has a variety you can check out) that contains a bit of the insoluble solvent. Being careful not to tip the open vial, place a tight lid on the bigger vial. As long as the solvents are reasonably volatile, they will change places over time

and increase the concentration of the insoluble solvent in the smaller vial until crystals form and precipitate out of solution.

Slow Evaporation

Slow evaporation is perhaps the easiest method of crystallization, however the timing is very important to make sure that you do not let the solution go completely to dryness. Make a concentrated solution of your compound in the soluble solvent and filter (as explained above) to remove any undissolved particles. Place that solution in a small glass vial. Then either put a cap on the vial very loosely (probably the better method) or stretch some parafilm over the top of the cap and poke a couple of holes in it. The latter method can be problematic if the solvent used dissolves parafilm (for instance methylene chloride!). **Keep checking on your solution to make sure to stop it before the solution has evaporated completely (you can do this by putting the lid on tightly once the crystals have formed).**

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 your lab pages and a brief report addressing the following:

A. Each synthesis requires that the metal ion be in a +3 oxidation state and requires that acetylacetonate 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, acetylacetonate 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.

B. Explain your recrystallization procedures and the results each of them gave you.

SOLVENT MISCIBILITY TABLE

Solvent	Polarity Index	Refractive Index @20 C	UV(gm) Cutoff @1AU	Boiling Point(°C)	Viscosity (cP)	Solubility in water (%w/w)
Acetic Acid	6.2	1.372	230	118	1.26	100
Acetone	5.1	1.359	330	56	0.32	100
Acetonitrile	5.8	1.344	190	82	0.37	100
Benzene	2.7	1.501	280	80	0.65	0.18
n-Butanol	4.0	1.394	254	125	0.73	0.43
Butyl Acetate	3.9	1.399	215	118	2.98	7.81
Carbon Tetrachloride	1.6	1.466	263	77	0.97	0.08
Chloroform	4.1	1.446	245	61	0.57	0.815
Cyclohexane	0.2	1.426	200	81	1.00	0.01
1,2-Dichloroethane ¹	3.5	1.444	225	84	0.79	0.81
Dichloromethane ²	3.1	1.424	235	41	0.44	1.6
Dimethylformamide	6.4	1.431	268	155	0.92	100
Dimethyl Sulfoxide ³	7.2	1.478	268	189	2.00	100
Dioxane	4.8	1.422	215	101	1.54	100
Ethanol	5.2	1.360	210	78	1.20	100
Ethyl Acetate	4.4	1.372	260	77	0.45	8.7
Di-Ethyl Ether	2.8	1.353	220	35	0.32	6.89
Heptane	0.0	1.387	200	98	0.39	0.0003
Hexane	0.0	1.375	200	69	0.33	0.001
Methanol	5.1	1.329	205	65	0.60	100
Methyl-t-Butyl Ether ⁴	2.5	1.369	210	55	0.27	4.8
Methyl Ethyl Ketone ⁵	4.7	1.379	329	80	0.45	24
Pentane	0.0	1.358	200	36	0.23	0.004
n-Propanol	4.0	1.384	210	97	2.27	100
iso-Propanol ⁶	3.9	1.377	210	82	2.30	100
Di-Iso-Propyl Ether	2.2	1.368	220	68	0.37	100
Tetrahydrofuran	4.0	1.407	215	65	0.55	100
Toluene	2.4	1.496	285	111	0.59	0.051
Trichloroethylene	1.0	1.477	273	87	0.57	0.11
Water	9.0	1.333	200	100	1.00	100
Xylene	2.5	1.500	290	139	0.61	0.018

Miscible
 Immiscible

Immiscible means that in some proportions two phases will be produced

Synonym Table

- ¹ Ethylene Chloride
- ² Methylene Chloride
- ³ Methyl Sulfoxide
- ⁴ Tert-Butyl Methyl Ether
- ⁵ 2-Butanone
- ⁶ 2-Propanol