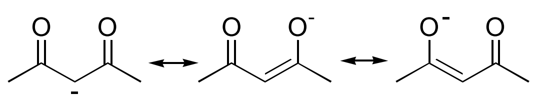
Preparation and Analysis of Tris(2,4-pentanedionato)[1] and Tris(1,1,1-trifluoro-2,4-pentanedionato[2] Complexes of Cobalt(III)

Inorganic Chemistry I (CHE-258), Gustavus Adolphus College, Spring 2004

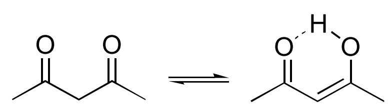
Introduction

The ligands that will be used in these preparations are the anions of 2,4-pentanedione (known more informally as acetylacetone) and of a partly fluorinated analog, 1,1,1-trifluoro-2,4-pentanedione. The structures of 2,4-pentanedione and its anion are illustrated below. The parent ketone exists as an equilibrium mixture of keto and enol tautomers in which the enol form constitutes 16% of the mixture (measurement made in water), much higher than the percent of enol to be found in an ordinary ketone. Intramolecular hydrogen bonding and the formation of an extended π system lend extra stability to the enol form in this case.

Note that the anion is an enolate of the parent ketone; the negative charge is thus highly delocalized by resonance. The two oxygen atoms, the carbonyl carbon, and the central carbon atom form part of a continuous π system, and are thus coplanar. Two geometries, E and Z, are possible for the free anion. The Z conformation is normally encountered when the anion acts as a ligand, since this conformation, which can form a chelate complex, coordinates best to the metal.

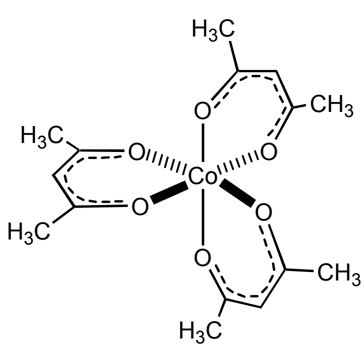


resonance forms of the enolate ion formed by deprotonation of 2,4-pentanedione



keto and enol forms of 2,4-pentanedione

2,4-Pentanedione is the most common representative of a large group of ligands that form especially stable and useful chelate complexes with a large variety of metals. The Z isomer of the enolate has a highly favorable geometry for complexation: the π system of the enolate holds the ligating oxygens in a favorable position for coordination, and the resulting metal-enolate complex is a six-membered ring that has little strain energy. The structure of tris(2,4-pentanedionato)cobalt(III) is shown below.



tris(2,4-pentanedionato)cobalt(III)

The special stability of these systems can be also be inferred from certain types of chemistry that can be performed on the system, such as electrophilic substitution of the methine hydrogen without disturbance of the chelate structure.

Synthesis of acac (2,4-pentanedionato) complexes and their analogs is often straightforward due to the stability of the products and to the ease with which the precursor enolates are generated under mild conditions. Most ketones have a high pK_a, and thus require strong bases for deprotonation. 1,3-Diketones (and other dicarbonyl compounds whose two carbonyl groups are related in a 1,3 manner), in contrast, have such low pK_a's that they can be extensively deprotonated by bases such as carbonate or ammonia. Acetylacetone, for example, has a pK_a of ca. 9; in contrast, the pK_a of acetone is ca. 20. 1,1,1-Trifluoro-2,4-pentanedione is even more acidic than 2,4-pentanedione, due to the electron-withdrawing effect of the three fluorine atoms.

The preparation of $Co(acac)_3$ begins with technical grade cobalt(II) carbonate and a large excess of 2,4-pentanedione, which serves as the reaction solvent as well as for generation of the enolate. It is, in addition, necessary to oxidize Co(II) to Co(III); this is done with 10% hydrogen peroxide. Approximate percent yields of $Co(acac)_3$ and $Co(tfa)_3$ will be included in your report. The cobalt carbonate starting material has a poorly-defined composition: in addition to carbonate, it contains hydroxide, oxide, and water, thus making an exact calculation of the percent yield difficult. For this calculation, we will assume that the composition of the cobalt carbonate is approximately $CoCO_3 \bullet 1.2H_2O$.

A similar procedure, using a smaller excess of the more expensive 1,1,1-trifluro-2,4-pentanedione, will be used for synthesis of $Co(tfa)_3$ (tfa = enolate of 1,1,1-trifluoro-2,4-pentanedione). In the $Co(tfa)_3$ procedure, wet *t*-butyl alcohol is used as the solvent, rather than excess ketone.

When a tris(acac), tris(tfa) or similar complex of a metal cation with a 3+ charge is formed, the resulting electrically neutral complex possesses some properties that one normally associates with organic compounds rather than classical coordination complexes. The ‘shells’ of methyl groups that surround the metal atoms are hydrophobic, thus leading to relatively high solubility of the complexes in organic solvents; this contrasts with the behavior observed for other complexes that you have prepared in other experiments. In addition, the complexes have significant volatility, since the intermolecular forces within the crystals are relatively low. This is particularly true for the fluorinated complexes, since the low polarizability of fluorine makes the van der Waals forces between the molecules exceptionally weak. Thus, tris(acac), tris(tfa), and similar complexes can often be purified by sublimation or distillation.

Experimental Procedures for Preparation and Analysis of $Co(acac)_3$ and $Co(tfa)_3$

1. Tris(2,4-pentanedionato)cobalt(III)[1]

Hazards:

1. Be sure to wear gloves and goggles when you are handling 10% hydrogen peroxide; it is highly corrosive to both eyes and skin.
2. Do not tighten the cap on the 10% hydrogen peroxide stock bottle. Pressure due to gaseous oxygen from the decomposition of hydrogen peroxide can cause the bottle to burst if the cap is tightened.

Dispense 15 mL of 10% hydrogen peroxide into a clean 25 mL graduated cylinder.

Place 1.25 g of technical grade hydrated cobalt carbonate, 10 mL of 2,4-pentanedione, and a thermometer in a 125 mL Erlenmeyer flask, and heat to 85°C on a hot plate in the hood.

Hold the flask with Erlenmeyer flask tongs, then add, <u>in a cautious, portionwise manner</u>, with swirling, 15 mL of 10% hydrogen peroxide, taking care to avoid excessive foaming of the reaction mixture. After all of the hydrogen peroxide has been added, keep the flask warm until oxygen evolution is no longer seen.

After cooling the flask to room temperature, chill it in an ice bath. Suction filter the mixture on a Büchner funnel, then rinse the solid on the funnel with cold 95% ethanol.

After the solid has air-dried, recrystallize it as follows. Place the solid and 25 mL of toluene in a 125 mL Erlenmeyer flask. *In the hood, on a hot plate (DO NOT USE A BURNER)*, bring mixture to a boil. Remove any undissolved solid by decantation or by gravity filtration through a fluted filter paper. Add ca. 35 mL of heptane to the hot solution, allow the solution to cool to room temperature, then cool in an ice bath. Separate the product by suction filtration, then spread it out on a watch glass to air-dry.

2. Tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III)[2]

Hazards:

1. Be sure to wear gloves and goggles when you are handling 10% hydrogen peroxide; it is highly corrosive to both eyes and skin.
2. Do not tighten the cap on the 10% hydrogen peroxide stock bottle. Pressure due to gaseous oxygen from the decomposition of hydrogen peroxide can cause the bottle to burst if the cap is tightened.

Dispense 15 mL of 10% hydrogen peroxide into a clean 25 mL graduated cylinder.

Place 0.5 g of technical grade cobalt carbonate, ca. 0.5 mL of deionized water, 5 mL of *t*-butyl alcohol, and 1.7 mL of 1,1,1-trifluoro-2,4-pentanedione (measured with a syringe) in a 125 mL Erlenmeyer flask.

In the hood, heat the mixture to a low boil on a hot plate until most or all of the solid dissolves to give a dull grape-colored solution (the *t*-butyl alcohol will reflux from the sides of the Erlenmeyer flask).

While keeping the solution hot, hold the flask with Erlenmeyer flask tongs, then add hydrogen peroxide solution, *in a cautious, portionwise manner, with swirling*, to the grape-colored solution. The reaction mixture should begin to darken and take on a brown tinge. *Do not add the hydrogen peroxide too fast, or the reaction mixture will froth out of the flask due to O_2 production from decomposition of excess H_2O_2; however, the H_2O_2 should be added as rapidly as is practicable.* Heat until a mixture of green and pink-purple phases is seen. This is the point at which most of the *t*-butyl alcohol has evaporated, and solid $Co(tfa)_3$ has precipitated. Continue heating for about 0.5-1 minute more, then set the reaction flask aside to cool to room temperature.

After the flask cools to room temperature, suction filter the mixture on a Büchner funnel. Rinse the solid on the funnel with deionized water until the filtrate is colorless. While rinsing, break up any lumps with a spatula. Remove the $Co(tfa)_3$ and filter paper from the funnel. Dry the $Co(tfa)_3$ by pressing it between filter papers, followed by air-drying at ambient temperature.

Preliminary TLC analysis of $Co(acac)_3$ and $Co(tfa)_3$

Make separate solutions of small amounts (ca. 10 mg) of the $Co(acac)_3$ and $Co(tfa)_3$ in a small amount (ca. 0.5-1 mL each) of acetone in small test tubes. Spot the two solutions side by side on a plastic-backed silica gel strip, and elute the chromatogram with toluene. Record the data that you need for calculation of the R_f value of each spot.

Preparative TLC of $Co(tfa)_3$

Once you have established the nature of the chromatographic behavior of the compounds, you will be ready to do your part of a class-wide preparative TLC project. Make a more concentrated solution of $Co(tfa)_3$ (dissolve ca. 50 mg of $Co(tfa)_3$ in ca. 0.5-1 mL of acetone), then place a streak of the solution across the origin of a new, larger, glass-backed TLC plate. Develop the chromatogram in a 400 mL beaker covered with a watch glass and containing a shallow layer of toluene and a filter paper liner saturated with toluene.

Allow the chromatogram to develop until the solvent front has migrated approximately halfway up the TLC plate (this will take approximately four minutes). If, at this point, separation of the components is good, remove the TLC plate from the developing chamber, let it air-dry, then repeat the chromatography starting at the opposite end of the plate (if separation in the first run is inadequate, allow the solvent front to continue to migrate until an acceptable separation of the components is achieved).

During this second elution, allow the solvent front to migrate until it encounters the fastest-migrating band of the first chromatogram. At this point, let the front migrate a short distance further until the aforementioned band has been significantly narrowed. Remove the TLC plate from the chamber and allow it to air-dry.

Only the green bands are to be used in the next step. If you have a purple/pink band at the origin, do not scrape it off of the TLC plate.

Scrape off the silica gel bands that contain the individual components, and

************ *keep the samples separate and clearly identified.* ***********

Identify the components as 'fastest-moving band' (higher R_f) and 'slowest-moving band' (lower R_f). Your instructor will collect the samples from everyone in the class for extraction of the separated components. The collective sample will be used for NMR analysis of the products.

Spectroscopy

Record or obtain from your instructor ^1H NMR, ^{13}C NMR, ^{19}F NMR, and infrared spectra, as appropriate, for the compounds that you prepared.

References Cited

1. Shalhoub, G. M. *J. Chem. Ed.* **1980**, *57*, 525-526.
2. Jensen, Ashley J.; O'Brien, Brian A. *J. Chem. Ed.* **2001**, *78*, 954.

Laboratory Report Instructions

2,4-Pentanedionato and 1,1,1-Trifluoro-2,4-pentanedionato Complexes of Co(III)

Percent Yield

Calculate the approximate percent yields of $Co(acac)_3$ and of the mixture of $Co(tfa)_3$ isomers, assuming that the hydrated cobalt carbonate has the composition $CoCO_3 \cdot 1.2H_2O$ and is the limiting reagent.

TLC Analysis

Calculate the R_f values for each component that was seen for TLC analysis of $Co(acac)_3$ and $Co(tfa)_3$. Provide a brief, qualitative rationale for the differences in the R_f values.

Infrared Analysis

Identify the C-H stretching and carbonyl stretching bands in the infrared spectra of $Co(acac)_3$ and one of the $Co(tfa)_3$ isomers. In addition, identify the C-F stretching absorptions in the $Co(tfa)_3$ spectrum.

The frequencies of the carbonyl absorptions are shifted to lower wavenumbers than one finds for the carbonyl stretch of an ordinary dialkyl ketone. Provide a brief, reasonable explanation for the direction of the shift.

NMR Analysis

$Co(acac)_3$

Assign the signals in both the ^{13}C and ^{1}H NMR spectra. (Note: the integration in the ^{1}H spectrum may not correspond exactly to the expected values, probably due to different relaxation times of the different types of protons.)

$Co(tfa)_3$

Decide, on the basis of the of the ^{1}H and ^{19}F NMR spectra, which TLC component is *mer*-$Co(tfa)_3$ and which is *fac*-$Co(tfa)_3$. Models or careful drawings of the compounds will be highly useful references for this analysis. Provide a rationale for your decision.

Assign the signals (to the extent possible) for the ^{1}H and ^{19}F NMR spectra. In cases where an assignment cannot be made with complete assurance, explain why a decision cannot be made based on the available data. (Note: the integration in the ^{1}H spectrum may not correspond exactly to the expected values, probably due to different relaxation times of the different types of protons.)

Assign, to the extent possible, the ^{13}C NMR signals of the mixture of *mer*-$Co(tfa)_3$ and *fac*-$Co(tfa)_3$. In cases where an assignment cannot be made with complete assurance, explain why a decision cannot be made based on the available data.

In addition, measure and report the ^{13}C-^{19}F coupling constant (in Hz) for the trifluoromethyl carbons (the value of the coupling constant will be nearly the same for each of the different trifluoromethyl groups) and for the carbonyl groups that are adjacent to the trifluoromethyl groups (again, the coupling constants will be nearly the same within this group of carbonyl carbons).

Preparation and Analysis of Tris(2,5-pentanedionato) and Tris(1,1,1-trifluoro-2,4-pentanedionato) Complexes of Cobalt(III)

Pre-lab Questions

1. Write a balanced equation for the oxidation of Co^{2+} to Co^{3+} by hydrogen peroxide in acidic solution.

2. Why is gas evolved during the oxidation described in question (1)?

3. How many stereoisomers of $Co(tfa)_3$ are possible? Are any of them enantiomers?

4. Would you expect tris(1,1,1,5,5,5-hexafluoroacac)chromium(III) to be more, or less volatile than tris(acac)chromium(III)? Offer an explanation for your conclusion.

5. Why is 2,4-pentanedione more acidic than an ordinary ketone?