Synthesis of $Cr(acac)_3$ and $Co(acac)_3$

Process of Inorganic Chemistry Experiment

Synthesis

Purification

- Recrystallization

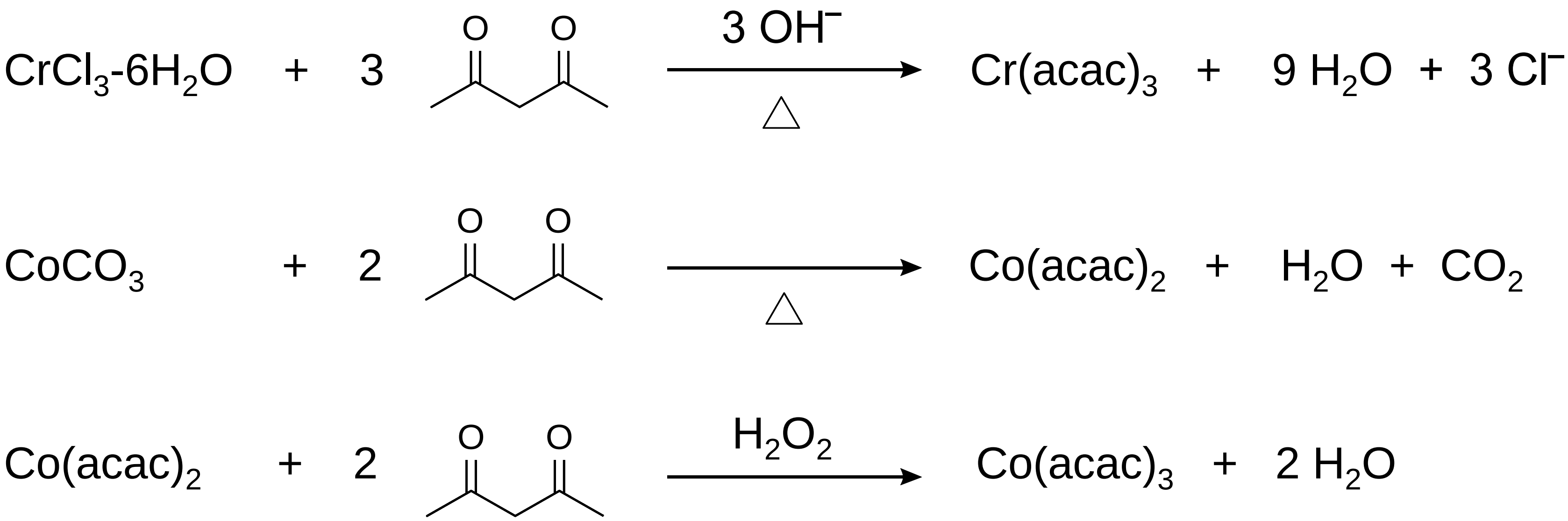
- Column chromatography

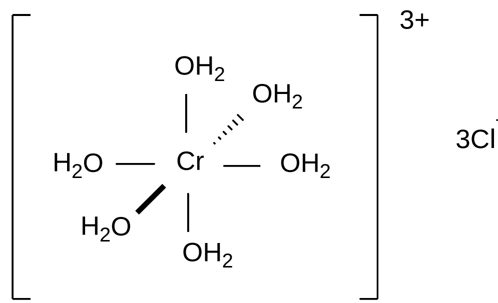
Characterization

- **NMR**, IR, UV, Single Crystal X-ray diffraction

- Elemental Analysis, Mass Spectrometry

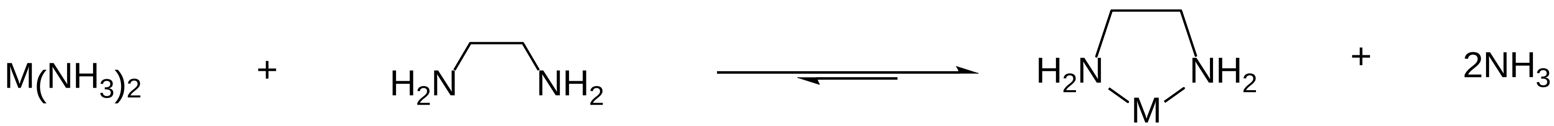
Synthesis of $M(acac)_3$ (M = Cr and Co)



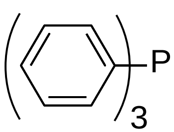


Chelate Effect

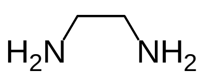
➔ Chelating ligands have a higher affinity to binding to the metal compared to the monodentate ligands.



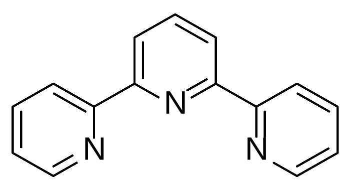
$$\Delta \mathbf{G} = -RTlnK = \Delta \mathbf{H} - \mathbf{T}\Delta\mathbf{S}$$



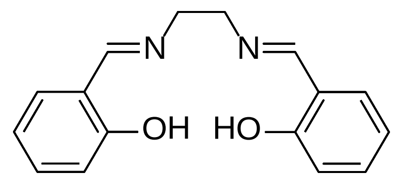
Monodentate



Bidentate



Tridentate



Tetradentate

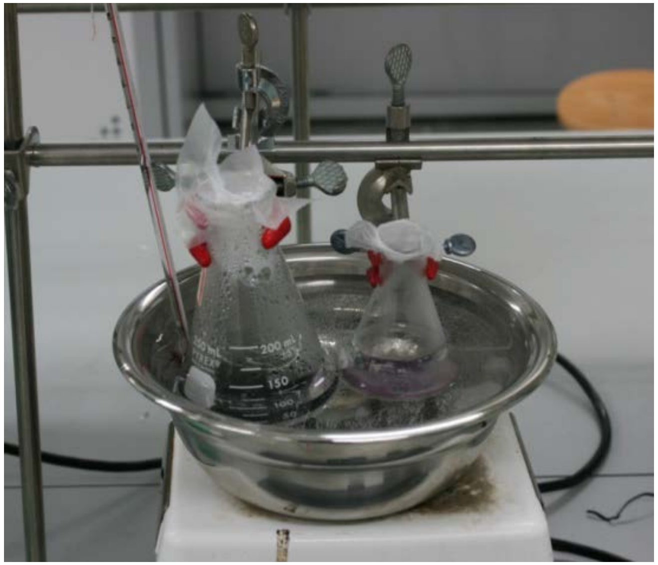
Procedure 1. Synthesis

<$Cr(acac)_3$>

- 50 mL of distilled water & 2.66 g of chromium(III) chloride hexahydrate in a 100 mL Erlenmeyer flask.
- Add 10 g of urea & 5.9 mL of acetylacetone.
- Heat the mixture for 1.5 hr.

<$Co(acac)_3$>

- 1.25 g of cobalt(II) carbonate and 10 mL of acetylacetone in a 50 mL Erlenmeyer flask.
- Heat the mixture to 100 ºC.
- Transfer the flask from the water bath, and add 2.5 mL of 30 % H_2O_2 **DROPWISE. (Caution: Vigorous reaction)**
- Reheat, then add more 2.5 mL of 30 % H_2O_2 DROPWISE.
- Heat the mixture to 100 ºC for 1 hr.



•Tips!!

- **First heat the water bath and then weigh the compounds**
- **Put two flasks in the same boiling water bath.**
- **Prepare a cold ethanol for the purification**

Procedure 1. Purification

<$Cr(acac)_3$>

- Cool down the reaction mixture to room temperature.
- Filter the mixture and wash the violet solid with distilled water.
- Dry and measure the mass.

<$Co(acac)_3$>

- Cool down the reaction mixture in an ice-salt bath for 30 minutes.
- Filter the mixture and wash the green solid with distilled water and small amount of cold ethanol.
- Dry and measure the mass.

Procedure 2. Purification-Recrystalization

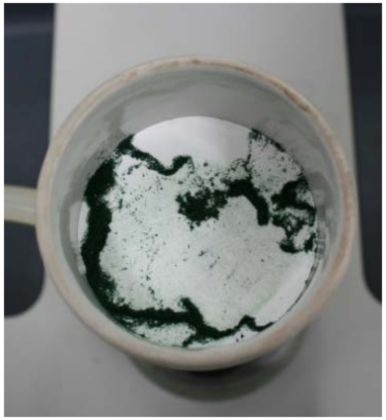
Solvent	Boiling point	Dielectric constant	Density
Non-Polar Solvents			
Hexane	69 °C	2.0	0.655 g/ml
Benzene	80 °C	2.3	0.879 g/ml
Toluene	111 °C	2.4	0.867 g/ml
Diethyl ether	35 °C	4.3	0.713 g/ml
Chloroform	61 °C	4.8	**1.498 g/ml**
Ethyl acetate	77 °C	6.0	0.894 g/ml
Polar Aprotic Solvents			
1,4-Dioxane	101 °C	2.3	**1.033 g/ml**
Tetrahydrofuran (THF)	66 °C	7.5	0.886 g/ml
Dichloromethane (DCM)	40 °C	9.1	**1.326 g/ml**
Acetone	56 °C	21	0.786 g/ml
Acetonitrile (MeCN)	82 °C	37	0.786 g/ml
Dimethylformamide (DMF)	153 °C	38	0.944 g/ml
Dimethyl sulfoxide (DMSO)	189 °C	47	**1.092 g/ml**
Polar Protic Solvents			
Acetic acid	118 °C	6.2	**1.049 g/ml**
n-Butanol	118 °C	18	0.810 g/ml
Isopropanol (IPA)	82 °C	18	0.785 g/ml
n-Propanol	97 °C	20	0.803 g/ml
Ethanol	79 °C	24	0.789 g/ml
Methanol	65 °C	33	0.791 g/ml
Formic acid	100 °C	58	**1.21 g/ml**
Water	100 °C	80	1.000 g/ml

Procedure 2. Purification-Recrystalization

- Take ~ 0.2 g of each sample.
- Dissolve in warm toluene. (small amount) to form saturated solution.
- Add few drops of petroleum ether slowly. → crystals will form.
- Add more petroleum ether.
- Filter and wash with petroleum ether.
- Dry and measure mass .

<$Cr(acac)_3$>

<$Co(acac)_3$>



Procedure 3. Characterization-UV

- The energy in the UV and visible light region is used to excite species to higher electronic energy levels.
- The absorbance, ***A***, is defined as

$$\boldsymbol{A} = \mathbf{log(I_0/I)}\text{, where } \mathbf{I_0} = \text{incident intensity}$$

$$\text{and } \mathbf{I} = \text{measured intensity}$$

- Beer-Lambert Law

$$\boldsymbol{A} = \boldsymbol{\varepsilon}\mathbf{bc}\text{, where } \boldsymbol{\varepsilon} = \text{extinction coefficient } (\mathrm{L \cdot mol^{-1} \cdot cm^{-1}}),$$

$$\mathbf{b} = \text{optical path length (cm)},$$

$$\text{and } \mathbf{c} = \text{molar concentration } (\mathrm{mol \cdot L^{-1}})$$

$\boldsymbol{\varepsilon} = 10^3 \sim 10^5\ \mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$ for fully allowed transition.
$\boldsymbol{\varepsilon} = 10^0 \sim 10^3\ \mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$ for orbitally forbidden transition.
$\boldsymbol{\varepsilon} = 10^{-5} \sim 10^0\ \mathrm{dm^3 \cdot mol^{-1} \cdot cm^{-1}}$ for spin forbidden transition.

Procedure 3. Characterization-UV

Selection Rule

1. Laporte Selection rule
   ➔ For centrosymmetric molecules, electronic transitions that conserve pairity are forbidden.
   ($g \rightarrow g$ or $u \rightarrow u$)

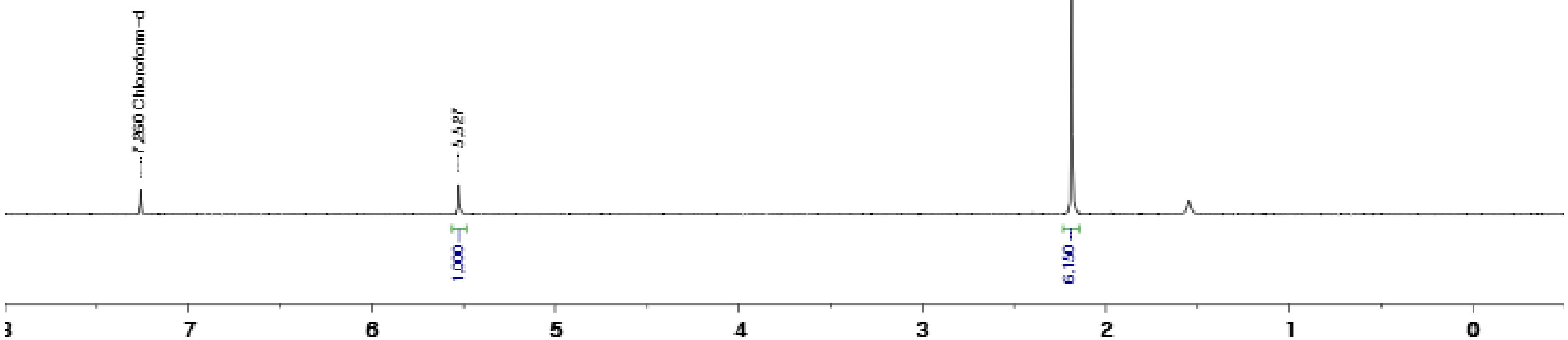
2. Spin Selection rule
   ➔ Transitions with same spin state is allowed.

ex) Metal d-d transition
   ➔ Spin allowed, Laporte forbidden

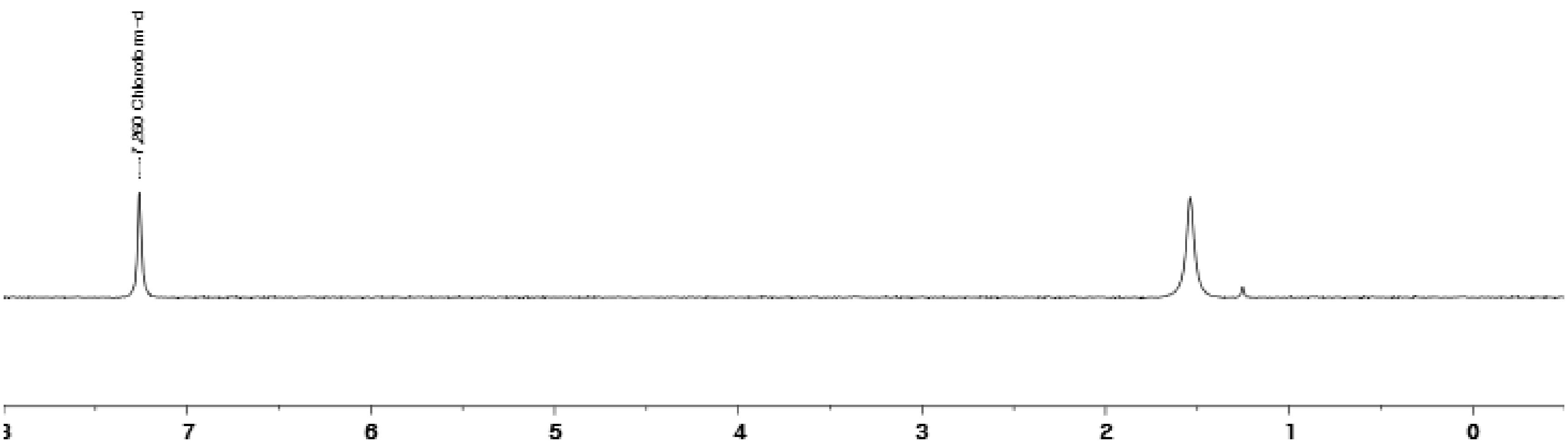
Procedure 3. Characterization-NMR

One is $Co(acac)_3$ and another is $Cr(acac)_3$. Which is which?

(A)

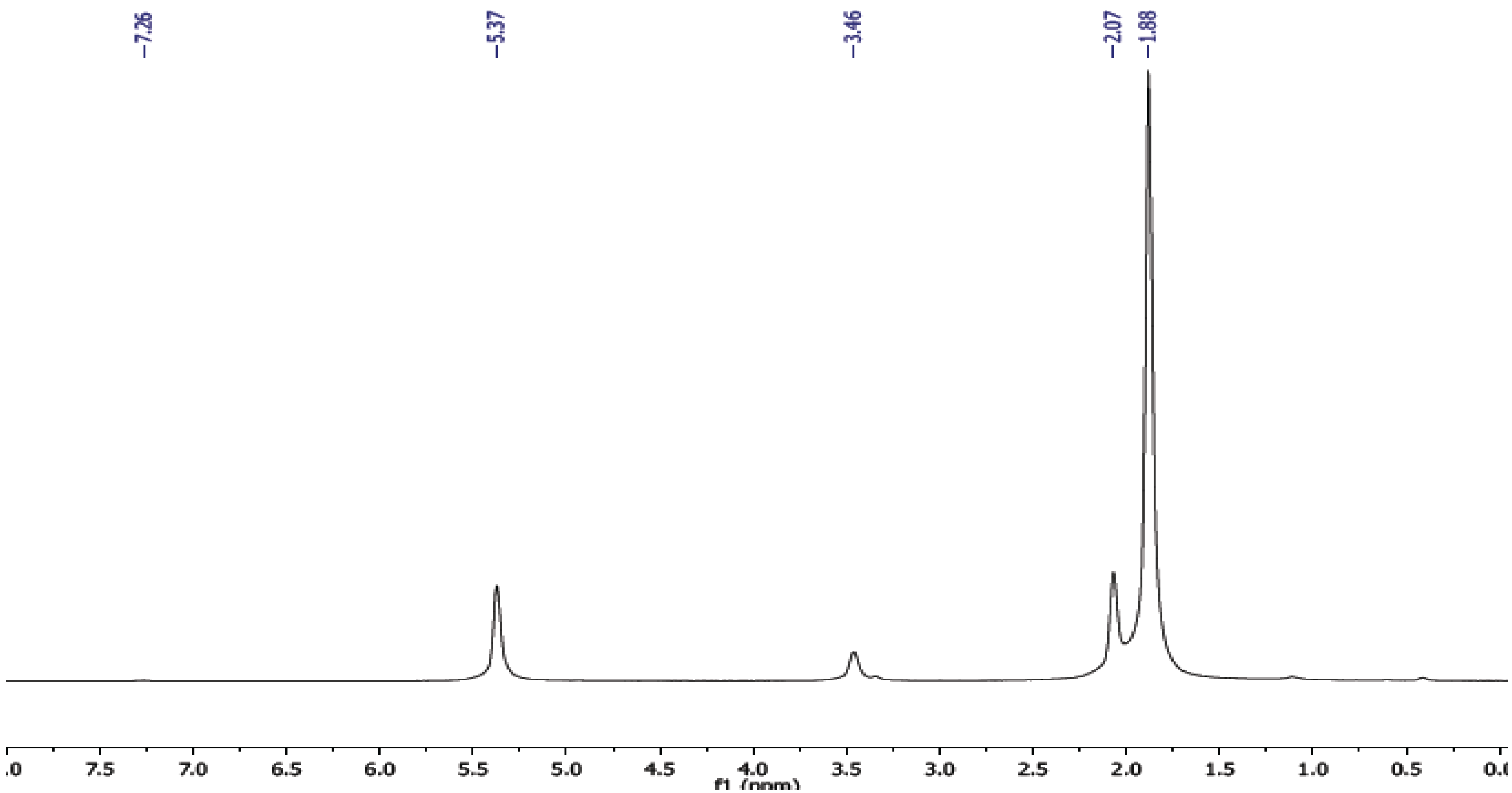


(B)



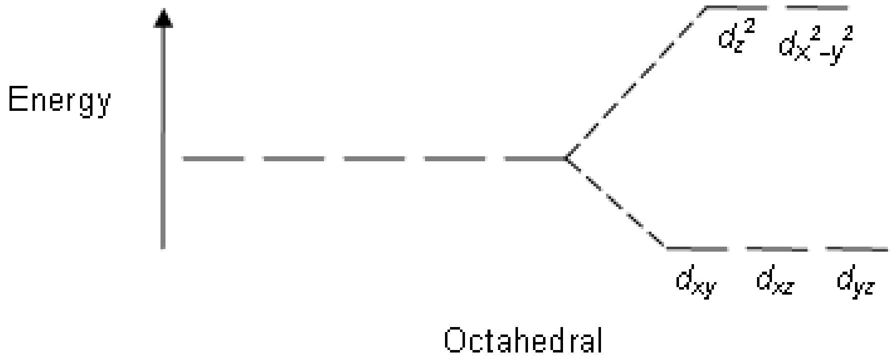
Procedure 3. Characterization-NMR

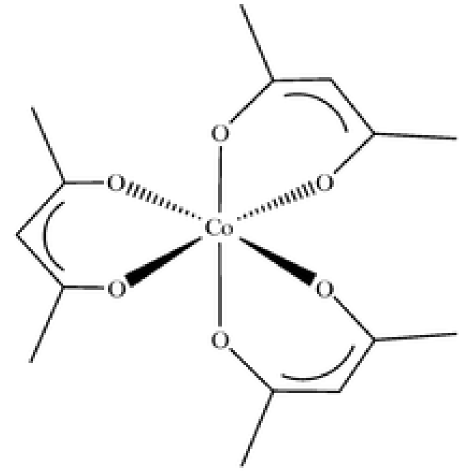
This is acetylacetone NMR data. Explain this peak splitting.

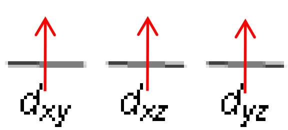


Procedure 3. Characterization-NMR

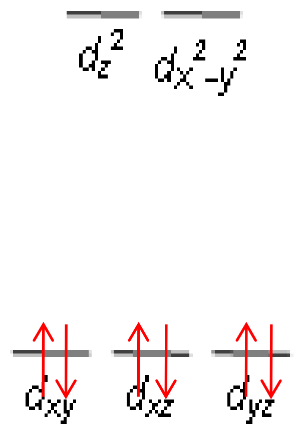
d-orbital splitting of the octahedral complex



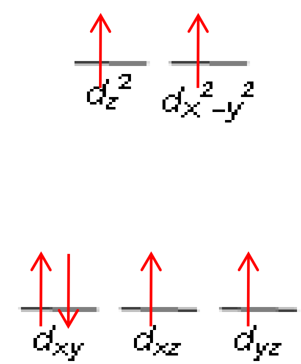




$Cr(acac)_3$



$Co(acac)_3$
If low spin



$Co(acac)_3$
If high spin