

Synthesis of $\text{Cr}(\text{acac})_3$ and $\text{Co}(\text{acac})_3$

Inorg Chem Exp #1

2018 Fall

TA: 최재혁

Process of Inorganic Chemistry Experiment

Synthesis

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graph TD; A[Synthesis] --> B[Purification]; B --> C[Characterization];
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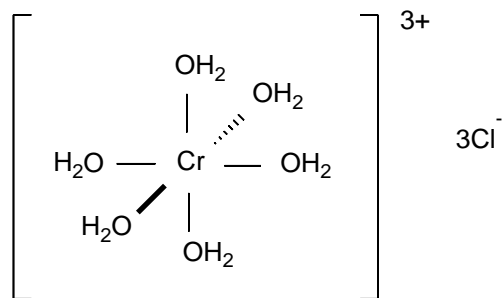
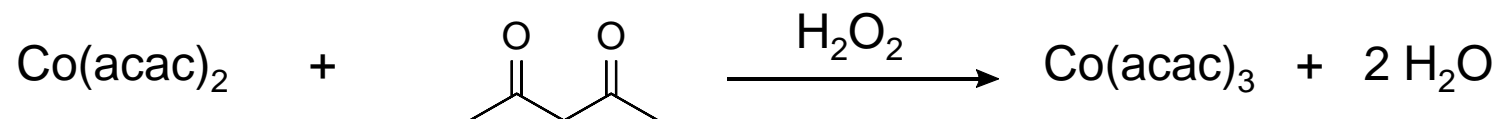
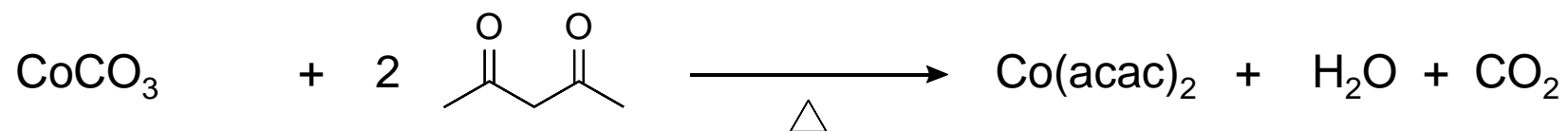
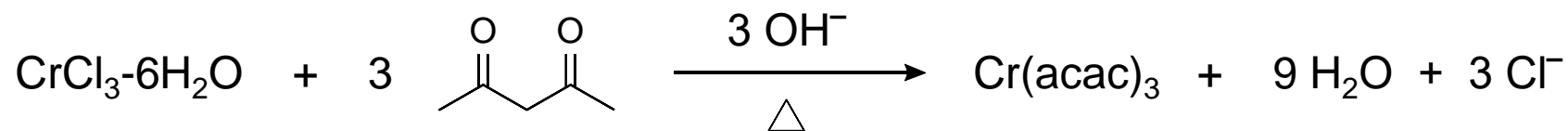
Purification

- **Recrystallization**
- Column chromatography

Characterization

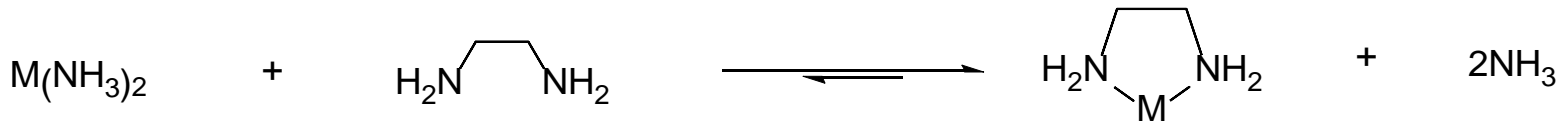
- **NMR**, IR, UV, Single Crystal X-ray diffraction
- Elemental Analysis, Mass Spectrometry

Synthesis of $M(\text{acac})_3$ ($M = \text{Cr}$ and Co)

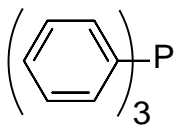


Chelate Effect

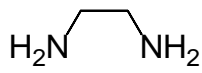
→ Chelating ligands have a higher affinity to binding to the metal compared to the monodentate ligands.



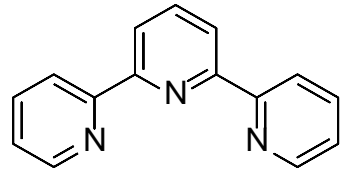
$$\Delta G = -RT \ln K = \Delta H - T \Delta S$$



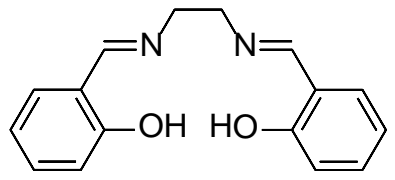
Monodentate



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 °C.
- Transfer the flask from the water bath, and add 2.5 mL of 30 % **H₂O₂ DROPWISE. (Caution: Vigorous reaction)**
- Reheat, then add more 2.5 mL of 30 % **H₂O₂ DROPWISE.**
- Heat the mixture to 100 °C 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.



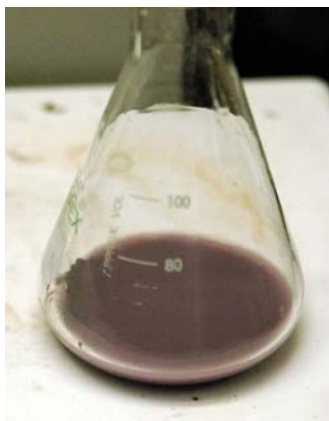
Procedure 2. Purification-Recrystallization

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-Recrystallization

- 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

$$\mathbf{A} = \log(\mathbf{I}_0/\mathbf{I}), \text{ where } \mathbf{I}_0 = \text{incident intensity} \\ \text{and } \mathbf{I} = \text{measured intensity}$$

- Beer-Lambert Law

$$\mathbf{A} = \boldsymbol{\varepsilon} \mathbf{b} \mathbf{c}, \text{ where } \boldsymbol{\varepsilon} = \text{extinction coefficient (L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}), \\ \mathbf{b} = \text{optical path length (cm),} \\ \text{and } \mathbf{c} = \text{molar concentration (mol}\cdot\text{L}^{-1})$$

$\boldsymbol{\varepsilon} = 10^3 \sim 10^5 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for fully allowed transition.

$\boldsymbol{\varepsilon} = 10^0 \sim 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ for orbitally forbidden transition.

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

Procedure 3. Characterization-UV

Selection Rule

1. Laporte Selection rule

→ For centrosymmetric molecules, electronic transitions that conserve parity are **forbidden**.

(g → g or u → u)

2. Spin Selection rule

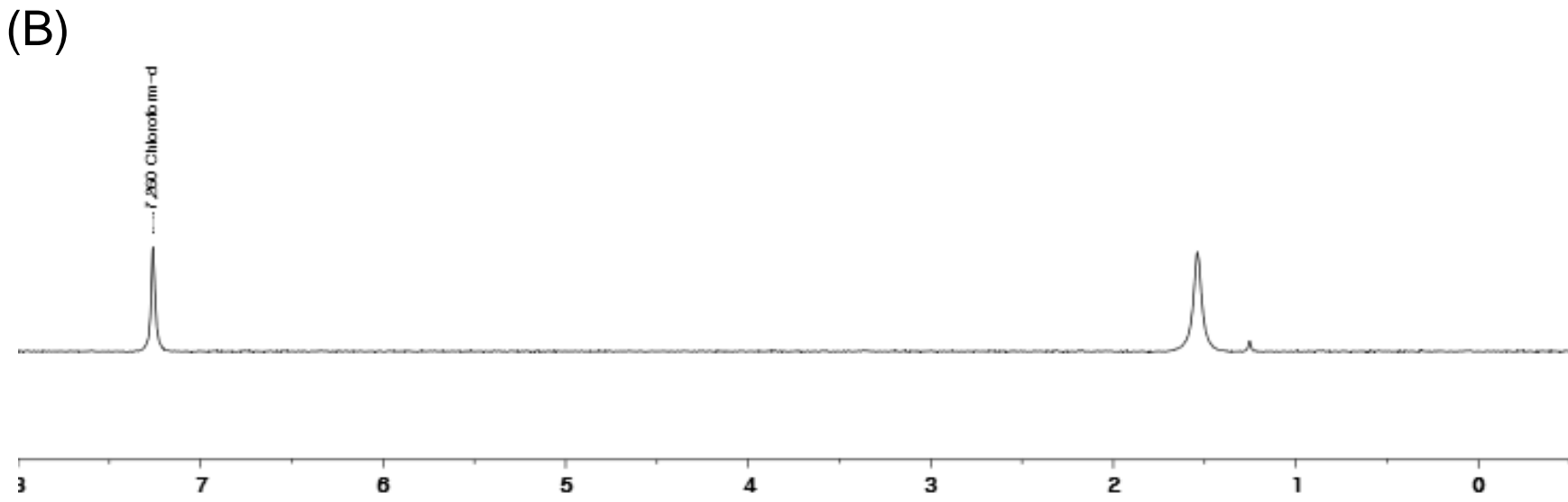
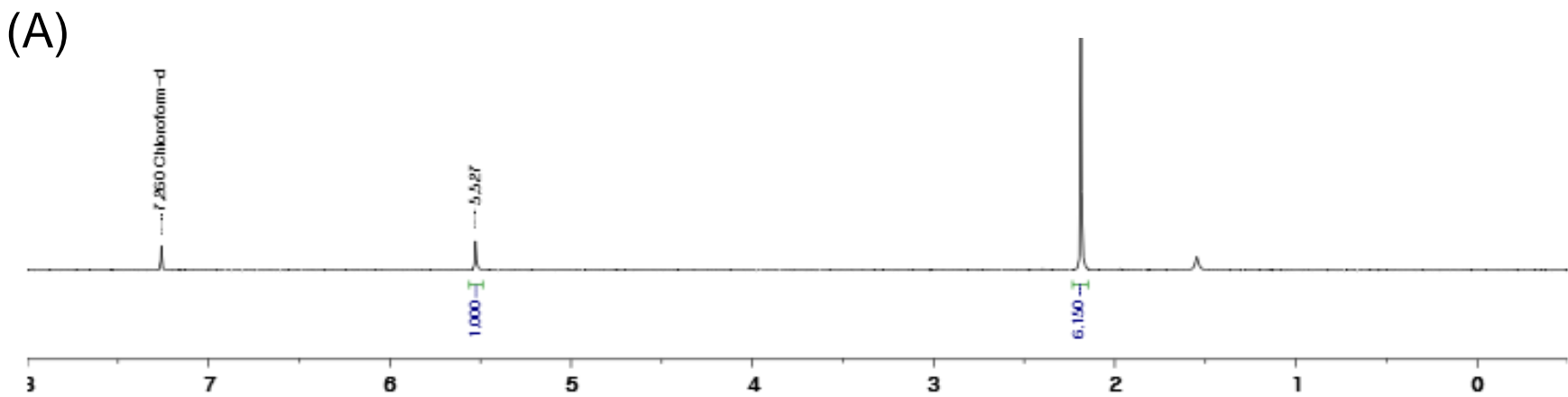
→ Transitions with same spin state is **allowed**.

ex) Metal d-d transition

→ Spin allowed, Laporte forbidden

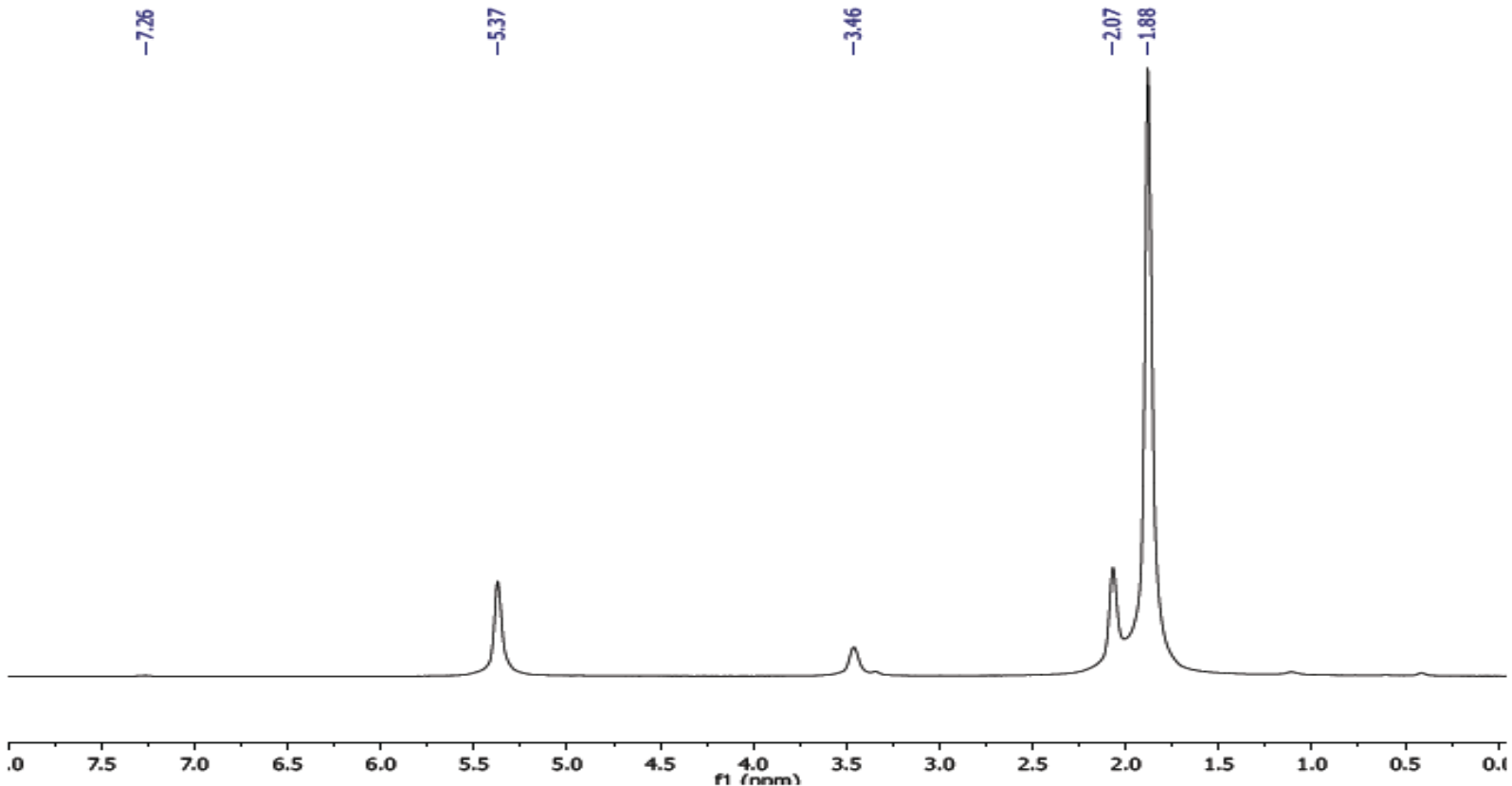
Procedure 3. Characterization-NMR Spectroscopy

One is $\text{Co}(\text{acac})_3$ and another is $\text{Cr}(\text{acac})_3$. Which is which?



Procedure 3. Characterization-NMR Spectroscopy

This is acetylacetone NMR data. Explain this peak splitting.



Procedure 3. Characterization-NMR Spectroscopy

d-orbital splitting of the octahedral complex

