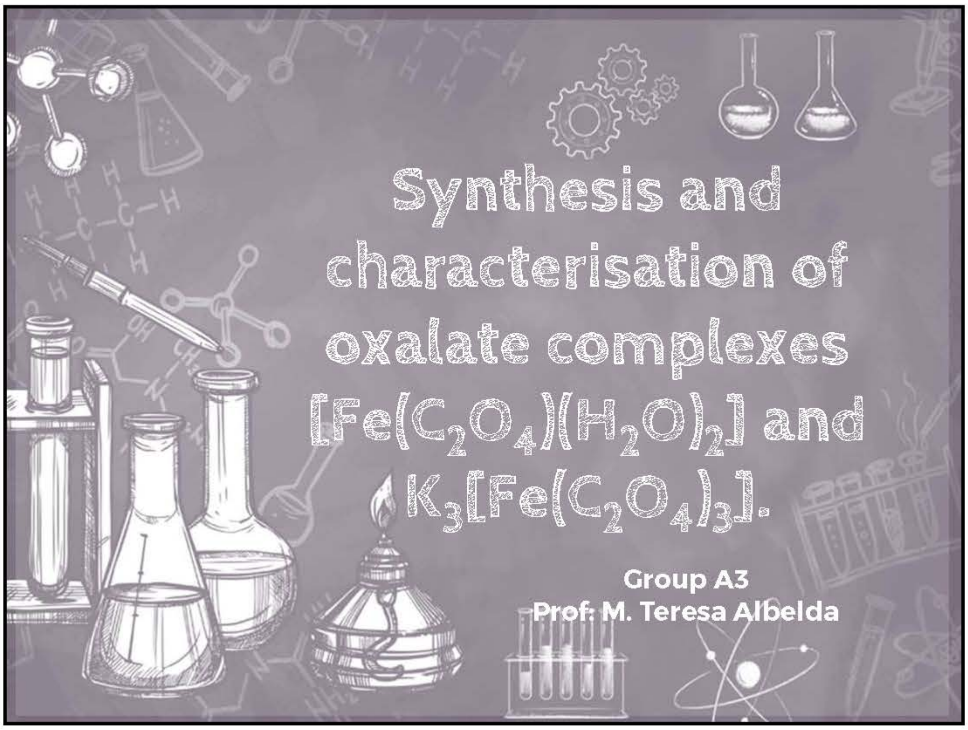


Synthesis and characterisation of oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ and $K_3[Fe(C_2O_4)_3]$.

Group A3
Prof. M. Teresa Albelda

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

The aim of this practice is to synthesise two oxalate complexes, one with Fe(II) ($[Fe(C_2O_4)(H_2O)_2]$) and another with Fe(III) ($K_3Fe(C_2O_4)_3]$) showing different modes of coordination of the oxalate ligand.

A brief introduction to metal complexes, synthesis of metal oxalates, and experimental procedures, can be seen in the following video:

https://www.youtube.com/watch?v=eNENz-KlOcw

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

Objectives:

1. Synthesis of two oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ and $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$.
2. Determination of the formula for potassium salt through thermal drying and conductivity measurements in aqueous solution.
3. Reactivity assays of Fe(III) complex.
4. Thermal decomposition assay of Fe(II) oxalate.
5. Characterisation of the coordination modes of oxalate ligand (bidentate and bis-bidentate) in the complexes using IR spectroscopy.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

Previous questions:

1. Draw a flow diagram for the synthesis made during this practice. Calculate the moles of reagents used in each step.

A) Synthesis of $[Fe(C_2O_4)(H_2O)_2]$

7.5g of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$
+ 25 mL H_2O (warm)
+ 1mL H_2SO_4 3M

↓ Heat to dissolve while stirring

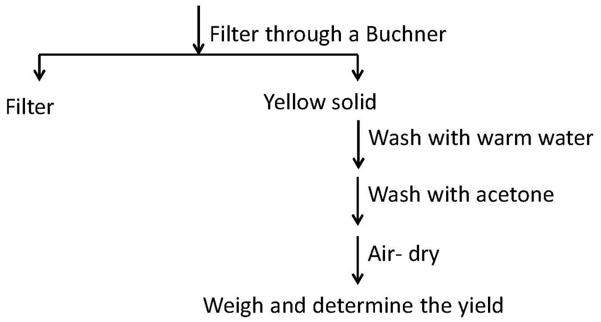
↓ Add 3.75 g oxalic acid in 40 mL water

↓ Heat to boiling while stirring

↓ Decant the supernatant and add 15 mL of warm H_2O while stirring.

↓ Filter through a Buchner

Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$



Filter through a Buchner

Filter

Yellow solid

Wash with warm water

Wash with acetone

Air- dry

Weigh and determine the yield

- **Mohr's salt $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$**

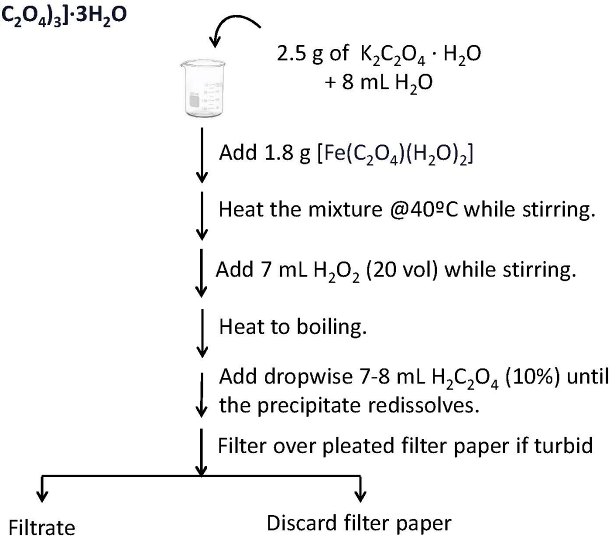
$$7.5\ \text{g} \times \frac{1\ mol\ (\mathrm{NH_4})_2\mathrm{SO_4}\cdot\mathrm{FeSO_4}\cdot 6\mathrm{H_2O}}{392.13 g} = 0.0191\ moles\ (\mathrm{NH_4})_2\mathrm{SO_4}\cdot\mathrm{FeSO_4}\cdot 6\mathrm{H_2O}$$

- **Oxalic acid $H_2C_2O_4 \cdot 2H_2O$**

$$3.75\ \text{g} \times \frac{1\ mol\ \mathrm{H_2C_2O_4}\cdot 2\mathrm{H_2O}}{126.07\ g} = 0.0297\ moles\ \mathrm{H_2C_2O_4}\cdot 2\mathrm{H_2O}$$

Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

B) Synthesis of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$



2.5 g of $K_2C_2O_4 \cdot H_2O$
+ 8 mL H_2O

Add 1.8 g [$Fe(C_2O_4)(H_2O)_2$]

Heat the mixture @40ºC while stirring.

Add 7 mL H_2O_2 (20 vol) while stirring.

Heat to boiling.

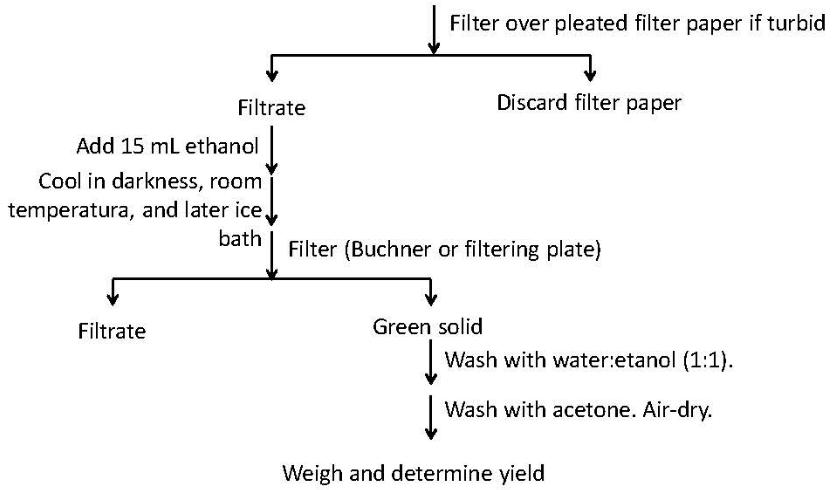
Add dropwise 7-8 mL $H_2C_2O_4$ (10%) until the precipitate redissolves.

Filter over pleated filter paper if turbid

Filtrate

Discard filter paper

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$



Filter over pleated filter paper if turbid

Filtrate

Discard filter paper

Add 15 mL ethanol

Cool in darkness, room temperatura, and later ice bath

Filter (Buchner or filtering plate)

Filtrate

Green solid

Wash with water:etanol (1:1).

Wash with acetone. Air-dry.

Weigh and determine yield

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

- $K_2C_2O_4 \cdot H_2O$

$$2.5\text{ g} \times \frac{1\,mol\ K_2C_2O_4 \cdot H_2O}{184.2\ g} = 0.0136\ moles\ K_2C_2O_4 \cdot H_2O$$

- $[Fe(C_2O_4)(H_2O)_2]$

$$1.8\text{ g} \times \frac{1\,mol\ [Fe(C_2O_4)(H_2O)2]}{179.895\ g} = 0.01\ moles\ [Fe(C_2O_4)(H_2O)2]$$

C) Determination of potassium salt formula

- $K_3[Fe(C_2O_4)_3]{\cdot}3H_2O$

$$1.0\text{ g} \times \frac{1\,mol\ K_3[Fe(C_2O_4)_3]{\cdot}3H_2O}{491.15\ g} = 0.00204\ moles\ K_3[Fe(C_2O_4)_3]{\cdot}3H_2O$$

Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

D) Reactivity assays

- **$K_3[Fe(C_2O_4)_3]{\cdot}3H_2O$**

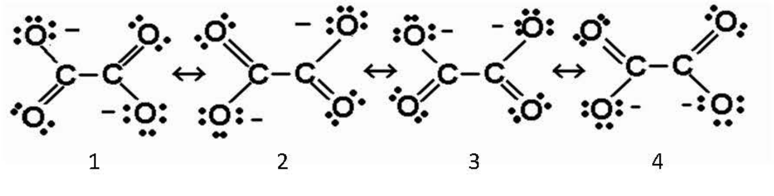
$$0.25\ \mathrm{g} \times \frac{1\,mol\ \mathrm{K_3[Fe(C_2O_4)_3]{\cdot}3H_2O}}{491.15\ g} = 0.00051\ moles\ \mathrm{K_3[Fe(C_2O_4)_3]{\cdot}3H_2O}$$

- **[$Fe(C_2O_4)(H_2O)_2$]**

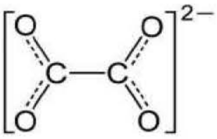
$$0.25\ \mathrm{g} \times \frac{1\,mol\ \mathrm{[Fe(C_2O_4)(H_2O)2]}}{179.895\ g} = 0.0028\ moles\ \mathrm{[Fe(C_2O_4)(H_2O)2]}$$

Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

2. Write the Lewis structure of oxalate ion. What are the coordination modes?

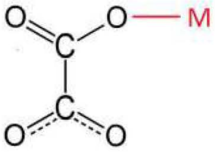


Structures 1 and 2 contribute equally to the whole system, as well as structures 3 and 4. This is supported by a simple symmetry analysis where structures 2 and 4 can be obtained by a 180 deg. rotation along the C-C axis of structures 1 and 3, respectively. Oxalate anion structure possesses two delocalised negative charges.

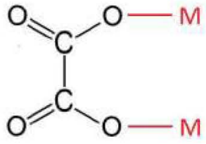


Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

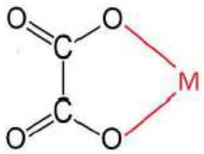
Coordination modes of oxalate anion:



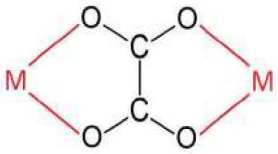
Monodentate ligand



Bridge ligand



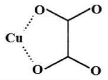
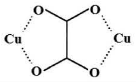
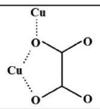
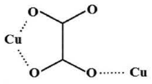
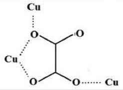
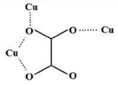
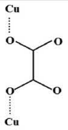
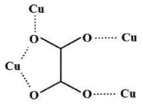
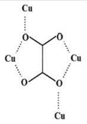
Bidentate ligand



Bis-bidentate ligand

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

Coordination modes observed for the oxalate groups in copper(II) complexes:

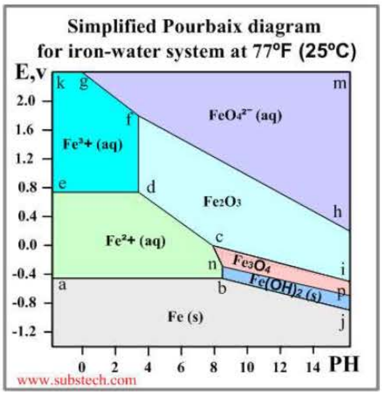
		
μ–oxalato–κ^2O^1,O^2	μ–oxalato– $1\kappa^2O^1,O^2{:}2\kappa^2O^{1a},O^{2a}$	μ–oxalato– $1\kappa^2O^1,O^2{:}2\kappa O^{1a}$
		
μ–oxalato– $1\kappa^2O^1,O^2{:}2\kappa O^{1a}$	μ_3–oxalato– $1\kappa^2O^1,O^2{:}2\kappa O^1{:}3\ \kappa O^{2a}$	μ_3–oxalato– $1\kappa^2O^1,O^2{:}2\kappa O^1{:}3$ κO^{1a}
		
μ–oxalato– $1\kappa O^1{:}2\kappa O^2$	μ_4–oxalato– $1\kappa^2O^1,O^2{:}2\kappa O^1{:}3\kappa O^{1a}{:}$ $4\kappa O^{2a}$	μ_4–oxalato– $1\kappa^2O^1,O^2{:}2\kappa O^1{:}3\kappa O$ $^{1a},O^{2a}{:}4\kappa O^{2a}$

A. Świtlicka-Olszewska *et al.* ***New J. Chem.***, 2014, **38**, 1611-1626

Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

3. Why is the synthesis of Fe(II) oxalate is carried out in an acidic medium?

Fe(II) and ferrous oxalate are oxidised quickly in air during the dissolution, generally within an induction period of a few hours, unless an acidic environment or an inert atmosphere is maintained.



Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

Moreover, synthesis should be done due to the extreme insolubility of iron (III) hydroxide, $Fe(OH)_3$.

We can write the oxidation reaction, somewhat simplified, as:

$$Fe^{2+}(aq) + 6H_2O(l) \longrightarrow Fe(OH)_3(s) + 3H_3O^+(aq) + e^-$$

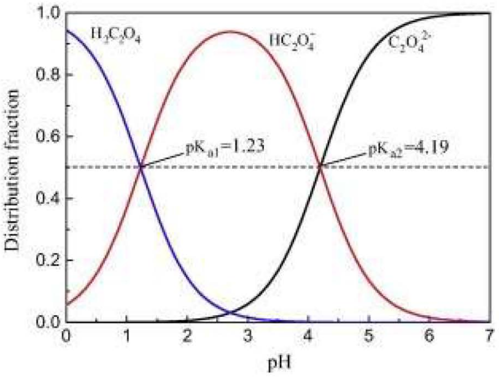
The *Ksp* (solubility product) value for $Fe(OH)_3$ is very small: 2.79×10^{-39}. From the equilibrium reaction it is easy to understand that acidic conditions (high [H_3O^+]) push the equilibrium to the left, thus preventing oxidation.

This also explains why Mohr's Salt resists oxidation much better than simple ferrous sulphate, as the ammonium ion provides some acidity.

In alkaline conditions, the oxidation of ferrous ions to ferric ions is very fast.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

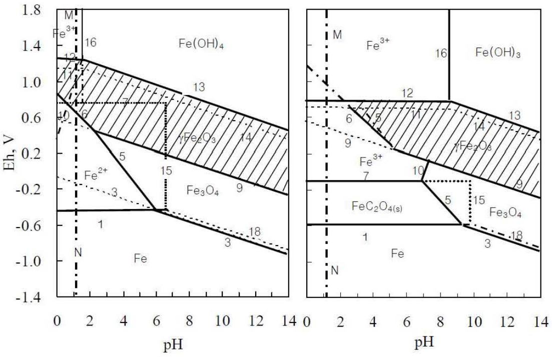
At pH of less than 2, the $C_2O_4^{2-}$ concentration is negligible. In such solutions, the active species is $HC_2O_4^-$ rather than $C_2O_4^{2-}$. At a pH higher than 3, almost complete ionisation of oxalic acid is observed. In this region, the active species are both $HC_2O_4^-$ and $C_2O_4^{2-}$. Above pH 4, the concentration of $HC_2O_4^-$ is less than that of $C_2O_4^{2-}$, and at above pH 6 the concentration of $HC_2O_4^-$ becomes negligible.



Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

In Eh-pH diagrams, the predominance of $FeC_2O_4(s)$ is clearly shown for the system containing 0.21M oxalate (right-sided graph). Without oxalate, Fe_2O_3 and Fe_3O_4 will be dissolved forming Fe^{2+}, whereas in the presence of oxalate solid, $FeC_2O_4(s)$ is the predominant species existing over a wide range of pH from acidic zone to > pH7 in the potential range where of iron oxide dissolution occurs. This implies that solid $FeC_2O_4(s)$ will be finally formed when the oxalate concentration is 0.21M (as shown in this graph) or higher.

Equilibrium diagrams show that in low acid solutions (higher than pH 3), the only thermodynamically stable complex ions of bivalent and trivalent iron are $[Fe(C_2O_4)_2]^{2-}$ and $[Fe(C_2O_4)_3]^{3-}$.



Eh-pH system diagrams for: (a) $Fe-H_2O$ and (b) $Fe-H_2O-0.21$ M $H_2C_2O_4$ (from Sukhotin and Khentov, 1980).

Oxalate complexes [Fe(C_2O_4)(H_2O)$_2$] i K_3[Fe(C_2O_4)$_3$]

4. What is the concentration of a hydrogen peroxide solution of 20 volumes?

$$2\,H_2O_2\,(aq) \rightarrow 2\,H_2O\,(l) + O_2$$

Hydrogen peroxide of 20 volumes means that 1 mol of H_2O_2 produces 20L of O_2 under normal pressure and temperature (T = 273.15 K and P = 1 atm). Thus, considering O_2 as an ideal gas:

$$nO_2 = \frac{P \cdot V}{R \cdot T} = \frac{1\,atm \cdot 20L}{0.082\frac{atm \cdot L}{K \cdot mol} \cdot 273.15K} = 0.8923\,moles$$

Let's look at the reaction stoichiometry:

$$0.8923\,moles\,O_2 \times \frac{2\,moles\,H_2O_2}{1\,mol\,O_2} \times \frac{1}{1L} = 1.7846\,M$$

Oxalate complexes [Fe(C_2O_4)(H_2O)$_2$] i K_3[Fe(C_2O_4)$_3$]

5. Why ethanol is added in step B.4 in the synthesis of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$?

Since the salt produced, $K_3[Fe(C_2O_4)_3]$, is soluble in water, it will not precipitate from an aqueous solution. However, when ethanol (a miscible liquid) is added to the solution the resulting solvent system of water-ethanol is less polar than water. This reduction in the polarity of the solvent system, coupled with cooling of the mixture causes the salt to precipitate.

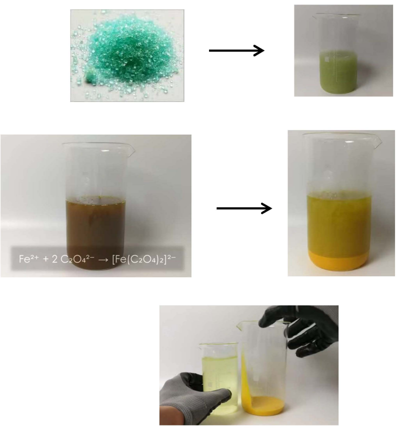
$$3K^+(aq) + [Fe(C_2O_2)_3]^{3-} \rightarrow K_3[Fe(C_2O_2)_3](s)$$

Alcohol is added to the solution to cause the complex iron salt to precipitate since it is less soluble in alcohol than in water.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

Experimental procedure:

A) Synthesis of $[Fe(C_2O_4)(H_2O)_2]$



7.5g of $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$
+ 25 mL H_2O (warm)
+ 1mL H_2SO_4 3M

↓ Heat to dissolve while stirring

↓ Add 3.75 g oxalic acid in 40 mL water

↓ Heat to boiling while stirring

↓ Decant the supernatant and add 15 mL of warm H_2O while stirring.

↓ Filter through a Buchner

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

↓ Filter through a Buchner

Filter

Yellow solid

↓ Wash with warm water

↓ Wash with acetone

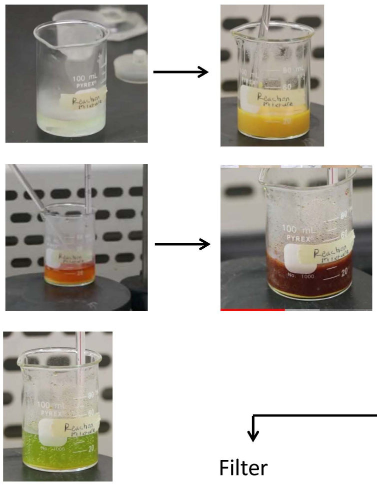
↓ Air- dry

Weigh and determine the yield

www.youtube.com/watch?v=Zmod4ROIzIQ

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

B) Synthesis of $K_3Fe(C_2O_4)_3]\cdot 3H_2O$



2.5 g of $K_2C_2O_4 \cdot H_2O$
+ 8 mL H_2O

Add 1.8 g $[Fe(C_2O_4)(H_2O)_2]$

Heat the mixture @40ºC while stirring.

Add 7 mL H_2O_2 (20 vol) while stirring.

Heat to boiling.

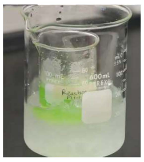
Add dropwise 7-8 mL $H_2C_2O_4$ (10%) until the precipitate redissolves.

Filter over pleated filter paper if turbid

Filter

Discard filter paper

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$



Filter over pleated filter paper if turbid

Filter

Discard filter paper

Add 15 mL ethanol

Cool down in darkness, room temperature and later ice bath

Filter (Buchner or filtering plate)

Filter

Green solid

Wash with water:etanol (1:1).

Wash with acetone. Air-dry.

Weigh and determine the yield

www.youtube.com/watch?v=bOvnCpgFRzg

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

C) Determination of potassium salt formula

- Number of hydration molecules

Grind 1.5 g of dry $K_3Fe(C_2O_4)_3]$

↓ Weigh 1.000 g in a tared watch glass

↓ Heat in stove @110ºC until weight remains constant

Determine the water hydration number

- Determination of electrolyte type

Prepare 50mL of 10^{-3} M $K_3Fe(C_2O_4)_3]$

↓ Measure specific conductivity

↓ Calculate molar conductivity

↓ Compare results with the data in Annex 1

Determine the type of electrolyte in the complex

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

D) Reactivity assays

1. Exposure to UV light

Weigh 0.25 g of dry $K_3[Fe(C_2O_4)_3]$

↓ Dissolve in 5mL water + 10 drops glacial acetic acid

↓ Stir the solution and transfer to a watch glass

Leave the watch glass exposed to UV light during 30 min

2. Exposure to light

Dissolve some $K_3[Fe(C_2O_4)_3]$ and divide in two test tubes

Tube A	Tube B
↓	↓
Cover with aluminum foil and keep in darkness	Expose to light
↓	↓
Add 1 drop phenanthroline	Add 1 drop phenanthroline

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

3. Thermal decomposition

0.5 g of $[Fe(C_2O_4)(H_2O)_2]$ in test tube

↓ Heat with the flame of a burner

↓ Leave the solid to cool

↓ Flip the tube and leave the solid exposed to air

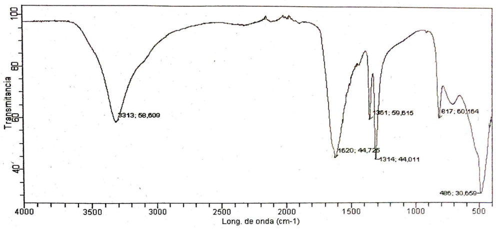
Approach a magnetic bar to the solid

https://www.youtube.com/watch?v=vPnqLSyoEy8

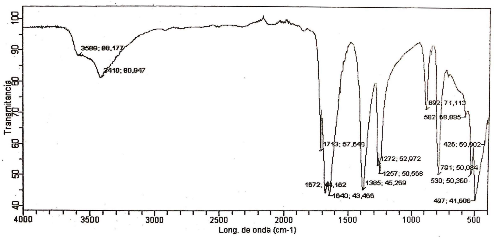
Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

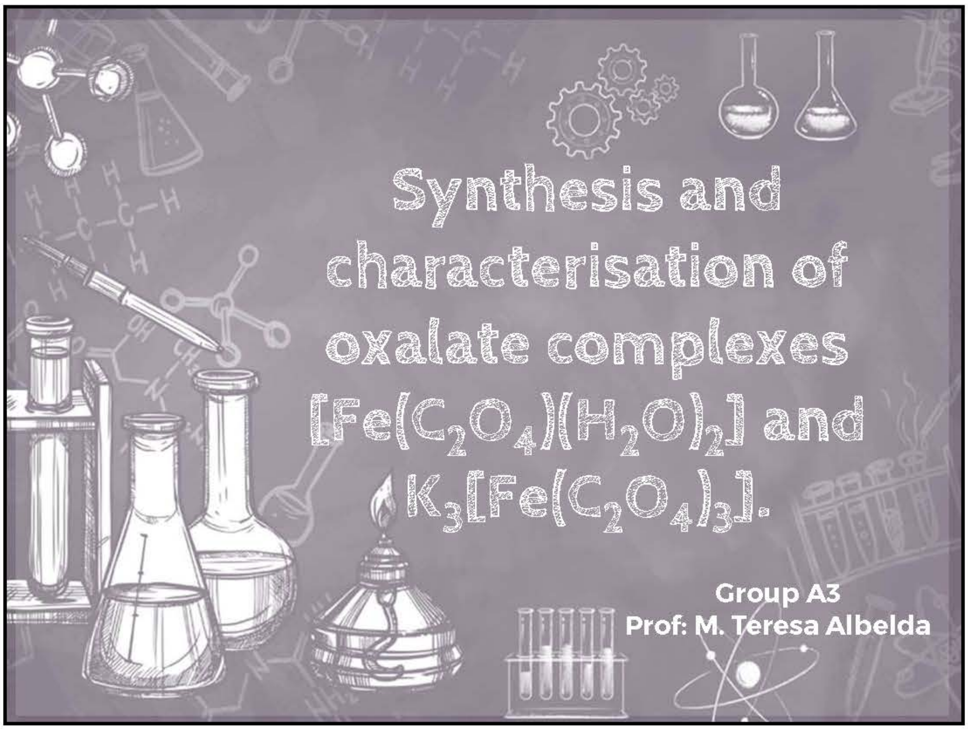
E) IR Spectra of synthetised oxalate complexes

IR spectrum $[Fe(C_2O_4)(H_2O)_2]$



IR spectrum $K_3Fe(C_2O_4)_3]$





Synthesis and characterisation of oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ and $K_3[Fe(C_2O_4)_3]$.

Group A3
Prof: M. Teresa Albelda

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

Additional questions

1. Write and adjust the chemical reactions that take place in steps A and B. What could be the insoluble intermediate product that is formed in the synthesis of the Fe(III) complex.

Synthesis A: $[Fe(C_2O_4)(H_2O)_2]$

$$(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O \xrightarrow{H_2O,\ H^+} Fe^{2+} + 2NH_4^+ + 2SO_4^{2-}$$

$$H_2C_2O_4{\cdot}2H_2O \longrightarrow 2H^+ + C_2O_4^{2-} + 2\,H_2O$$

$$Fe^{2+} + C_2O_4^{2-} + 2\,H_2O \longrightarrow [Fe(C_2O_4)(H_2O)_2]$$

Global reaction:

$$(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O\ (aq) + H_2C_2O_4{\cdot}2H_2O\ (aq) \rightleftharpoons [Fe(C_2O_4)(H_2O)_2] + (NH_4)_2SO_4 + 4\,H_2O + H_2SO_4$$

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

Synthesis B: $K_3[Fe(C_2O_4)_3]$

$$2[Fe(C_2O_4)(H_2O)_2] + 3K_2C_2O_4 \cdot H_2O + H_2C_2O_4 \cdot 2H_2O + H_2O_2 \rightleftarrows 2\ K_3[Fe(C_2O_4)_3] \cdot 3H_2O + 5\ H_2O$$

- Ferrous oxalate, FeC_2O_4, is a finely divided precipitate and tends to be colloidal. However, heating the solution causes it to coagulate and facilitates separating the precipitate from the solution. Potassium oxalate is added to the ferrous oxalate precipitate and this produces a **slightly basic** solution for the oxidation of the ferrous ion to ferric ion by hydrogen peroxide.
- Hydrogen peroxide was then added to oxidise the iron to the +3 state.

$$2[Fe(C_2O_4)(H_2O)_2]\ (s) + C_2O_4{}^{2-}\ (aq) + H_2O_2\ (aq) + 2H^+(aq) \rightleftarrows Fe_2(C_2O_4)_3\ (s) + 6H_2O\ (l)$$

- The temperature is maintained at 40ºC to increase the rate of oxidation of the Fe^{2+} to Fe^{3+}. This, however, was done slowly since the heat liberated from the addition of the peroxide could be sufficient to decompose the peroxide itself. Thus, the complete oxidation would not be possible, and the resulting solution would be a mixture of two complexes.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

- After complete oxidation, the excess hydrogen peroxide was removed by additional heat. Oxalic acid was then introduced to convert the iron(III) oxalate to trioxalatoferrate (III) ion.

$$Fe_2(C_2O_4)_3\ (s) + 3\ H_2C_2O_4\ (aq) + 6\ H_2O(l) \rightarrow 2\ [Fe(C_2O_4)_3]^{3-}\ (aq) + 6\ H_3O^+\ (aq)$$

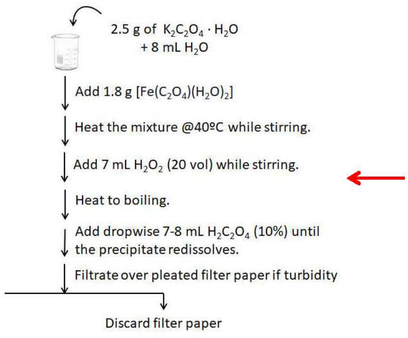
- After being formed, the Fe^{3+} complex reacted with potassium ion to form the salt $K_3[Fe(C_2O_4)_3]$.

$$3\ K^+(aq) + [Fe(C_2O_4)_3]^{3-}(aq) \rightarrow K_3[Fe(C_2O_4)_3)(s)$$

- Note that oxalate ligand in the complex comes from three different sources: iron (II) oxalate complex $[Fe(C_2O_4)(H_2O)_2]$; potassium oxalate salt; and oxalic acid.
- The presence of the pair oxalate/oxalic acid forms a buffer to maintain the optimal pH range during the reaction. This buffer also prevents precipitation of $Fe(OH)_3$.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

- Potassium oxalate was added producing a **slightly basic** solution for the oxidation of the ferrous ion to the ferric ion by hydrogen peroxide.
- The hydroxide ion concentration of the solution is high enough (pH = 4) that some of the Fe^{3+} reacts with hydroxide to form ferric hydroxide (brown precipitate).
- With the addition of more oxalic acid, the ferric hydroxide dissolves and the soluble complex is formed.



2.5 g of $K_2C_2O_4 \cdot H_2O$ + 8 mL H_2O

Add 1.8 g $[Fe(C_2O_4)(H_2O)_2]$

Heat the mixture @40ºC while stirring.

Add 7 mL H_2O_2 (20 vol) while stirring.

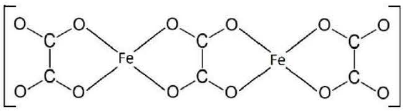
Heat to boiling.

Add dropwise 7-8 mL $H_2C_2O_4$ (10%) until the precipitate redissolves.

Filtrate over pleated filter paper if turbidity

Discard filter paper

$Fe(OH)_3$ Brown precipitate



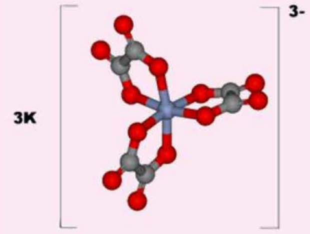
Brown precipitate $Fe(C_2O_4)_3$

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

2. Justify the different solubility in water of the two synthetised complexes.

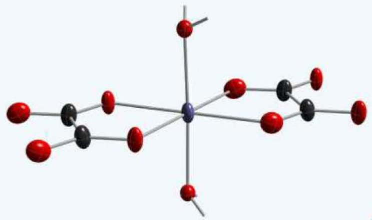
$K_3[Fe(C_2O_4)_3]$

Soluble in water.
It is a salt with a cation and an anion complex.



$[Fe(C_2O_4)(H_2O)_2]$

Insoluble in water.
It is a neutral compound.



Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

3. Interpret the measurements in step C.

$K_3Fe(C_2O_4)_3$]

- To experimentally determine the formula of a hydrate salt, the salt was heated on a stove to very high temperature. High levels of heat drive off the water molecules. The mass of the hydrate differs from the mass of the anhydrous salt because of the mass of water that was removed during heating.
- We weighed 1.002 g of potassium salt in a watch glass. Total weigh after vigorous heating was 35.569 g.
- Take the mass of the hydrate and subtract the mass of the anhydrate to obtain the mass of water. Calculate the moles of water:

$$m(\text{salt+watch glass})_{\text{initialal}} - m(\text{salt+watch glass})_{final} = 35.712 - 35.569 = 0.143\ g$$

$$0.143\ g \times \frac{1\ mol}{18.01528\ g} = 0.0079377\ moles\ \ H_2O$$

- Divide the mass of anhydrate by the molar mass of anhydrate to obtain moles of anhydrate.

$$m\ (\text{anhydrate}) = 35.712 - 34.71 = 0.859\ g \Rightarrow 0.859\ g \times \frac{1\ mol}{373.145\ g} = 0.002302\ moles$$

Oxalate complexes [$Fe(C_2O_4)(H_2O)_2$] i $K_3[Fe(C_2O_4)_3]$

- Find the water-to-anhydrate mole ratio dividing the moles of water by the moles of anhydrate:

$$\frac{0.0079377}{0.002302} = 3.4 \cong 3 \text{ water molecules}$$

Thus, the molecular formula of the complex is: $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$

- To make conductivity measurements, we need to prepare 50 mL of a 10^{-3}M solution of the $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$:

$$10^{-3}M \times 0{,}05L \times 491{,}24271 \frac{g}{mol} = 0.025\ g$$

We weighed the amount and after measuring the conductivity, the value that we obtained was:

Λ = 429 μS/cm a T = 25 °C.

We can then calculate molar conductivity:

$$\Lambda_M = 10^3 \times \frac{\Lambda}{M} = \frac{S/cm}{mol/L} = \frac{S/cm}{mol/1000cm^3} = \frac{S \cdot 1000\ cm^3}{cm \cdot mol} = \frac{S \cdot cm^2}{mol}$$

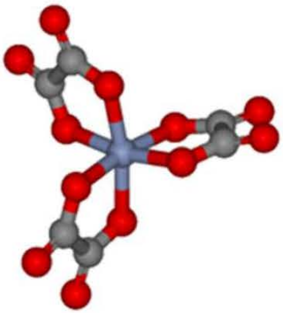
$$1L = 1\ dm^3 = 1000\ cm^3$$

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

$$\Lambda_M = 10^3 \times \frac{\Lambda}{M} = \frac{S/cm}{mol/L} = \frac{S/cm}{mol/1000cm^3} = \frac{S\cdot 1000\ cm^3}{cm\cdot mol} = \frac{S\cdot cm^2}{mol}$$

$$\Lambda_M = 10^3 \times \frac{429\cdot 10^{-6}\ S/cm}{10^{-3}\ mol/L} = 429\ \frac{S\cdot cm^2}{mol} = 429\ \Omega^{-1}\cdot cm^2\cdot mol^{-1}$$

A comparison between the measured value and theoretical values from the table, shows a 3:1 electrolyte type, which corresponds to the proposed structure for the complex with one metal and three ligands.



Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

4. What is the result of the exposure to light of tris(oxalate)ferrate(III) anion? Write a chemical reaction that explains it.

- After exposure to UV light, a precipitate was obtained. In addition, bubbles appeared in the solution.
- When exposed to light, the complex reacts according to the following equation. It is an intramolecular photochemical redox reaction. Fe(III) is reduced to Fe(II), and oxalate ligand is oxidised to carbon dioxide.

$$\begin{array}{c} (1e^- + Fe^{3+} \rightleftarrows Fe^{2+})x2 \\ C_2O_4{}^{2-} \rightleftarrows 2CO_2 + 2e^- \\ \hline 2Fe^{3+} + C_2O_4{}^{2-} \rightleftarrows 2Fe^{2+} + 2CO_2 \end{array}$$

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

- Complex $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$, which is ionic, is soluble in water and undergoes this reaction:

$$K_3[Fe(C_2O_4)_3]{\cdot}3H_2O \rightleftarrows 3K^+(aq) + [Fe(C_2O_4)_3]^{3-}(aq) + 3H_2O$$

$$2[Fe(C_2O_4)_3]^{3-}(aq) \xrightarrow{h\nu} 2Fe^{2+}(aq) + 5C_2O_4{}^{2-}(aq) + \uparrow 2CO_2(g)$$

- Thus, Fe^{2+} reacts with oxalate anion and water to produce an Fe(II) complex (reaction in synthesis A). This complex is a neutral compound, so it is not soluble in water and precipitates:

$$Fe^{2+}+C_2O_4{}^{2-}+2H_2O \rightleftarrows \downarrow[Fe(C_2O_4)(H_2O)_2](s)$$

https://aca.scitation.org/doi/10.1063/1.4918803

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

- The second assay also shows the intramolecular photochemical redox reaction that takes place when $K_3[Fe(C_2O_4)_3]$ is exposed to light.
- Dissolve a small amount in two test tubes. Cover one of them with aluminum foil and keep in darkness, while the other remains uncovered and exposed to light.

- Add a drop of a phenanthroline solution to both tubes. The solution in the tube that was exposed to light becomes red. The solution in the tube kept in darkness intensifies its yellow colour. In the first tube, Fe(III) was reduced to Fe (II) and reacts specifically with phenanthroline to produce a red complex. This assay is selective for Fe in oxidation state +2 (positive assay gives red colour).

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

5. Write and adjust the chemical reaction corresponding to the thermal decomposition of the Fe(II) oxalate. Which are the decomposition products? What happens to the residue of the decomposition when in contact with air? Explain this.

When we start to heat, the yellow solid becomes brown, and it becomes darker with further heating. When we flip the tube, the solid reacts with O_2 from the air and we observe sparks. The final solid is attracted to magnets.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

When heating starts, the process of dehydration takes place, and so the solid becomes brown as a result of a complete loss of two water molecules (170–230 ºC). The process of thermal decomposition follows with a redox reaction; Fe(II) is reduced to Fe(0) and oxalate anion is oxidized to CO_2 which maintains an O_2-free environment. When Fe(0) reacts with O_2, Fe(II) oxide and Fe(III) are formed. Both oxides yield Fe_3O_4 through an exothermic reaction, so we can observe sparks.

$$[Fe(C_2O_4)(H_2O)_2] \xrightarrow{\Delta} Fe(C_2O_4)_2 + 2\,H_2O\ (g) \uparrow$$

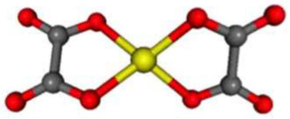
$$Fe(C_2O_4)_2 \xrightarrow{\Delta} Fe + 4\,CO_2(g) \uparrow$$

$$3Fe + 2O_2 \longrightarrow Fe_2O_3 + FeO \longrightarrow Fe_3O_4 + Q$$

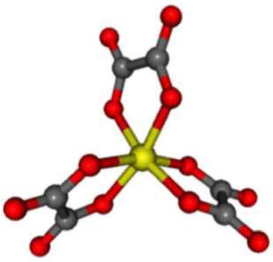
It is generally agreed that the thermal decomposition process occurs in two steps: dehydration followed immediately by a redox reaction.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

6. According to the recorded IR spectra, what conclusion can be drawn about the modes of coordination of the oxalate ligand in the two iron complexes isolated? Propose possible structures for both compounds according to the results obtained during the practice.



$[Fe(II)(C_2O_4)_2]^{2-}$



$[Fe(III)(C_2O_4)_3]^{3-}$

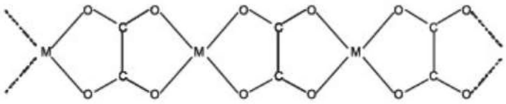
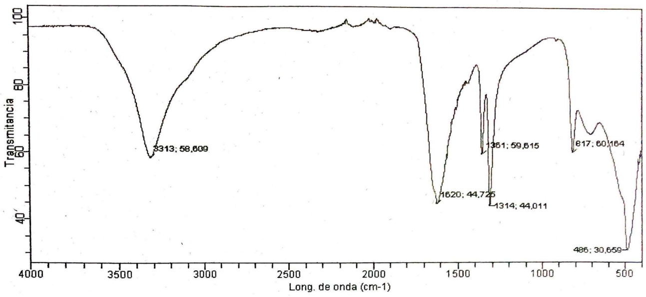


Figure 1. Schematic drawing of the infinite chain arrangement present in M^{II} oxalates of composition $M^{II}(C_2O_4)\cdot 2H_2O$.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

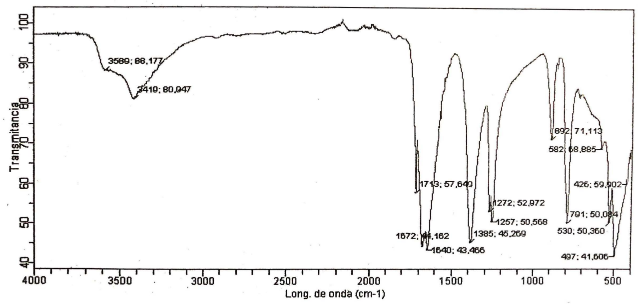
IR Spectrum$[Fe(C_2O_4)(H_2O)_2]$



3311 cm^{-1}: Stretching vibration O-H (H_2O) .
1620, 1361 i 1314 cm^{-1}: Stretching vibration C-O.
817 cm^{-1}: Bending vibration O-C-O and stretching vibration C-C.
486 cm^{-1}: Stretching vibration Fe-O.

Oxalate complexes $[Fe(C_2O_4)(H_2O)_2]$ i $K_3[Fe(C_2O_4)_3]$

IR Spectrum $K_3Fe(C_2O_4)_3]$



1713, 1672 i 1640 cm^{-1}: Stretching vibration carbonyl C=O.

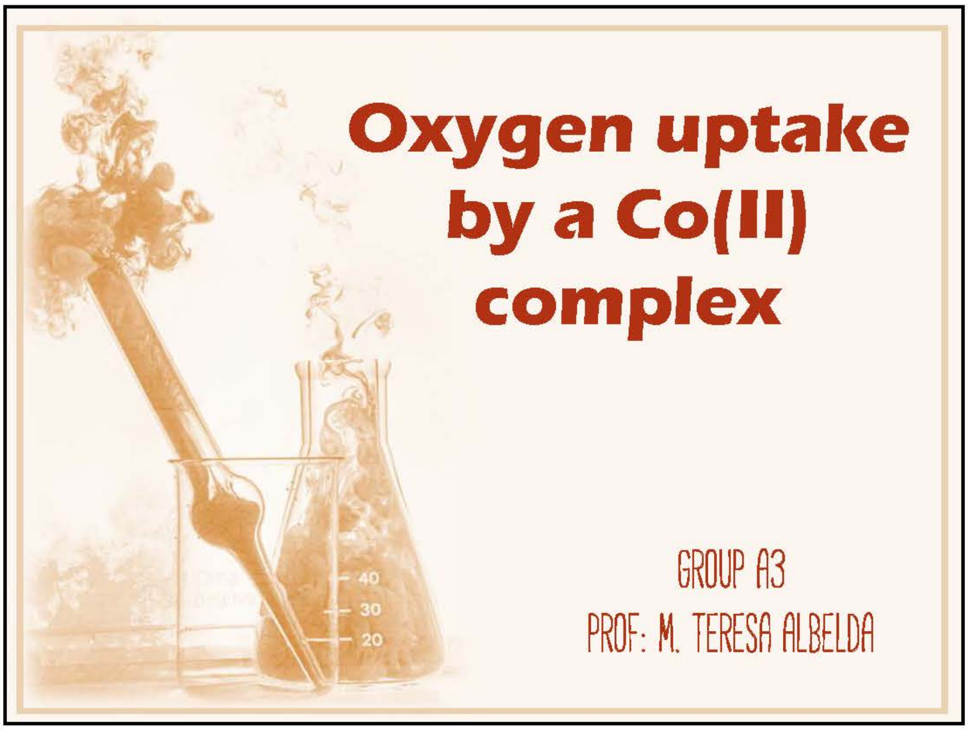
1385 cm^{-1}: Stretching vibration C-O and stretching vibration C-C.

1272, 1257 i 892 cm^{-1}: Stretching vibration C-O and bending vibration O-C=O.

791 cm^{-1}: Bending O-C=O and stretching vibration Fe-O.

530 cm^{-1}: Stretching vibration Fe-O.

497 cm^{-1}: Bending deformation (ring) O-C=O .



Oxygen uptake by a Co(II) complex

GROUP A3

PROF: M. TERESA ALBELDA

OXYGEN UPTAKE BY A CO(II) COMPLEX

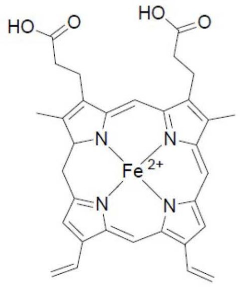
The aim of this practice is to synthesise the inactive form of Co(salen) using a modification of the Bailes and Calvin method. The complex will be activated forming an adduct with DMSO. The activated form will be used to determine the number of moles of O_2 absorbed per mol of [Co(salen)]

https://www.youtube.com/watch?v=WcaeG75MhQM

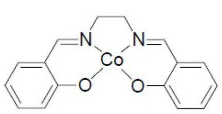
OXYGEN UPTAKE BY A CO(II) COMPLEX

Introduction

- Cobalt (II) forms square planar complexes. Among them the most studied are those that form Co(II) with Schiff bases, which are tetradentate ligands with N and O as donor atoms.
- The complex Co(salen) [where salen = N,N-bis(salicylaldehyde)ethylenediimine] reversibly binds O_2, thereby acting as a carrier and mimicking the role of hemoglobin as an oxygen transporter.



Ferrous Heme



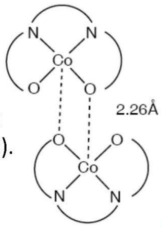
Co(salen)

OXYGEN UPTAKE BY A CO(II) COMPLEX

- When Co(salen) was first prepared, it was observed that the red-brown crystals darkened on exposure to air. However, it was not until five years later that it was established that the colour change was due to reversible uptake of O_2.
- [Co(salen) complex exists in two different solid forms, depending on the synthetic process followed for its preparation.

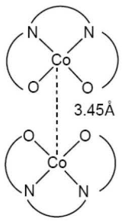
'Inactive' form

- Red-dark colour
- Dimeric [Co(salen) units one unit located one above other, but displaced.
- Shorter distance Co-O (2.26Å between the two dimeric units).



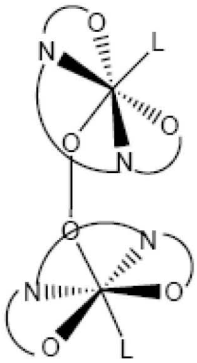
'Active' form

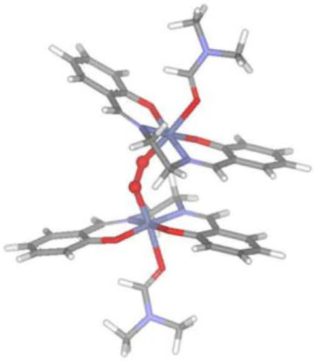
- Brown color
- Dimeric [Co(salen) units one unit located directly above other.
- Longer distance Co-Co (3.45Å between the two dimeric units.



OXYGEN UPTAKE BY A CO(II) COMPLEX

- With donor solvents in the presence of oxygen, [Co(salen)] is able to form adducts rapidly. The compound is diamagnetic and contains two atoms of Co(III) with a peroxo bridge between the two metal centres.

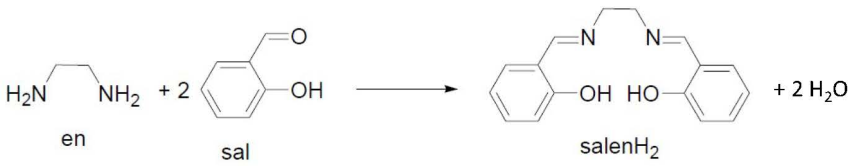




OXYGEN UPTAKE BY A CO(II) COMPLEX

Previous questions

1. Write and adjust the reaction between salicyaldehyde and ethylenediamine to obtain H_2salen.



H_2salen is a Schiff-base ligand formed by the condensation of two molecules of salicylaldehyde (sal) with ethylenediamine (en).

OXYGEN UPTAKE BY A CO(II) COMPLEX

2. Read carefully the experimental procedure and draw the flowchart diagram for the synthesis of [Co(salen)].

https://www.jove.com/science-education/10430/synthesis-of-an-oxygen-carrying-cobalt-ii-complex

1) Synthesis of H_2salen

1.6 mL salicylaldehyde
+ 25 mL hot 96% ethanol

↓ Heat and dissolve while stirring

↓ Add 0.5 mL ethylenediamine (dropwise)

↓ Heat and stir during 3 minutes

↓ Cool in an ice bath. Yellow crystals will appear.

↓ Filter through a Buchner

OXYGEN UPTAKE BY A CO(II) COMPLEX

↓ Filter through a Buchner

Filtrate

Yellow crystals

↓ Wash with cold ethanol

↓ Air- dry

Weigh and determine the yield

OXYGEN UPTAKE BY A CO(II) COMPLEX

2) Synthesis of [Co(salen)]

1.17 g H_2salen
+ 60 mL 96% ethanol

↓ Flush with N_2 while stirring 5-10 min.

↓ Connect the condenser and immerse the flask in a 70-80ºC water bath

↓ Add solution of cobalt acetate (side neck)
(1.09 g of $Co(CH_3CO_2)_2 \cdot 4H_2O$ in 7.5 mL hot H_2O)

↓ Reflux for 1 hour. Precipitate becomes dark red.

↓ Cool the solution under N_2

↓ Filter through Buchner or filter plate

Filtrate | Dark red precipitate

OXYGEN UPTAKE BY A CO(II) COMPLEX

↓ Filter (Buchner or filtering plate)

Filtrate | Dark red solid

↓ Wash with water (3 times)

↓ Wash with ethanol.

↓ Air- dry

Weigh and determine yield

OXYGEN UPTAKE BY A CO(II) COMPLEX

3. Write and adjust the reaction for the synthesis of [Co(salen)]. Why is it necessary to bubble N_2 (gas) during the procedure?

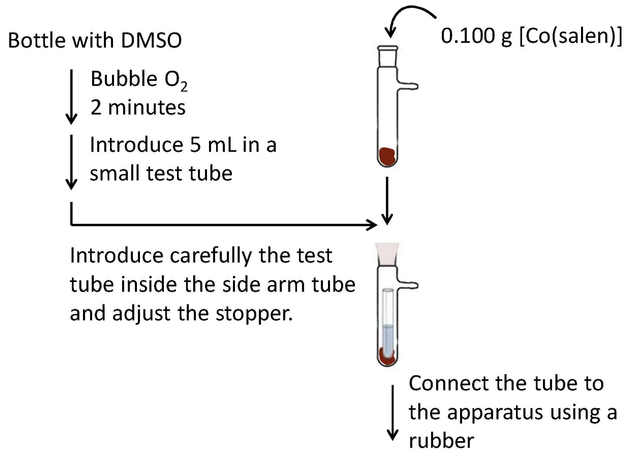
$$\mathrm{Co(OAC)_2 + H_2salen \longrightarrow [Co(salen)] + 2\ HOAc}$$

It is necessary to bubble N_2 (gas) during the procedure to create an anaerobic atmosphere, so Co(II) is not oxidised to Co(III) and the complex that is obtained is the inactive form.

OXYGEN UPTAKE BY A CO(II) COMPLEX

4. Draw the flowchart diagram for the experimental section #3.

3) Determination of the number of moles of oxygen absorbed per mol of complex.



Bottle with DMSO

Bubble O_2
2 minutes

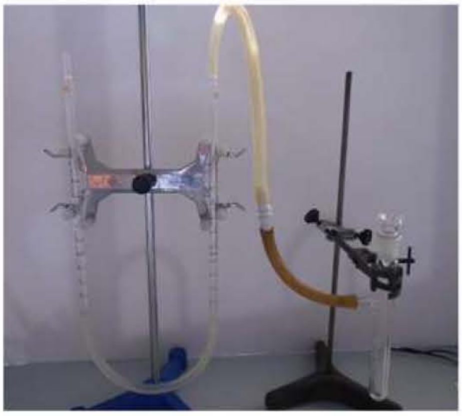
Introduce 5 mL in a small test tube

0.100 g [Co(salen)]

Introduce carefully the test tube inside the side arm tube and adjust the stopper.

Connect the tube to the apparatus using a rubber

OXYGEN UPTAKE BY A CO(II) COMPLEX



Connect the tube to the apparatus system using a rubber

Adjust the movable arm to make the water levels equal on both sides.

Adjust the movable arm to make the water levels equal on both sides.

Record the level of water (V_1)

Invert the side-arm tube, so DMSO will form an adduct with [Co(salen)] able to absorb O_2

Shake until no changes occur (10-20 minutes)

Adjust the movable arm to make the water levels equal on both sides.

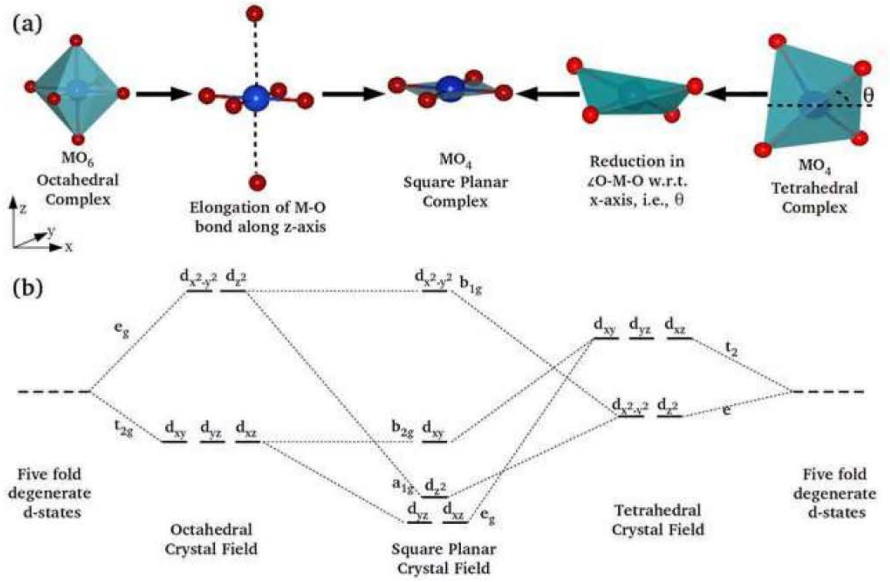
Record the level of water (V_2)

OXYGEN UPTAKE BY A CO(II) COMPLEX

5. The most frequent stereochemistry for Co(II) complexes are octahedral (high spin) and tetrahedral. A remarkable aspect of cobalt (II) complexes is that square planar complexes are sometimes formed. Using crystal field theory, draw the energy level diagram for the geometries mentioned above and determine the magnetic moment value for each.

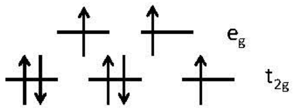
The element cobalt is in group 9 of the periodic table. The oxidation state +2 gives a d^7 electron configuration, Co(II) is a d^7 ion. To determine the occupancy of individual d orbitals, we would need to know something about the geometry of the complex in which the ion is found.

OXYGEN UPTAKE BY A CO(II) COMPLEX



OXYGEN UPTAKE BY A CO(II) COMPLEX

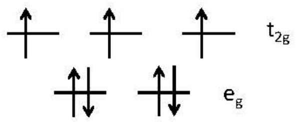
Co(II) d^7



Octahedral
High spin complex

$e_g^2t_{2g}^5$

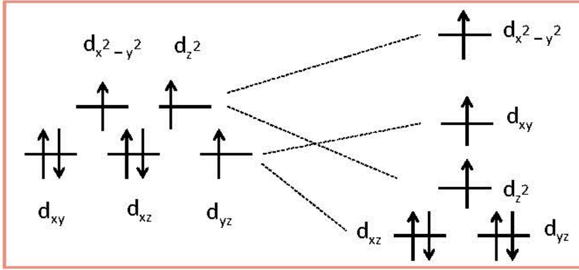
$\mu = \sqrt{n \cdot (n+2)} = \sqrt{15} = 3.87\ MB$



Tetrahedral
High spin complex

$e_g^4t_{2g}^3$

$\mu = \sqrt{n \cdot (n+2)} = \sqrt{15} = 3.87\ MB$

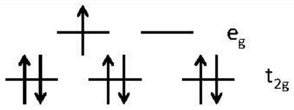


Square planar
High spin complex

$\mu = \sqrt{n \cdot (n+2)} = \sqrt{15}$
$= 3.87\ MB$

OXYGEN UPTAKE BY A CO(II) COMPLEX

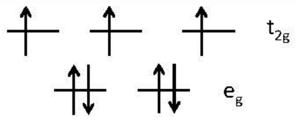
Co(II) d^7



Octahedral
Low spin complex

$e_g^6 t_{2g}^1$

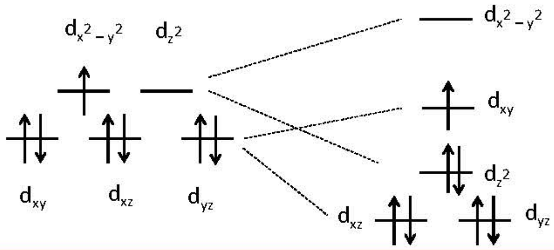
$\mu = \sqrt{n \cdot (n+2)} = \sqrt{3} = 1.73\ MB$



Tetrahedral
Low spin complex

$e_g^4 t_{2g}^3$

$\mu = \sqrt{n \cdot (n+2)} = \sqrt{15} = 3.87\ MB$



Square planar
Low spin complex

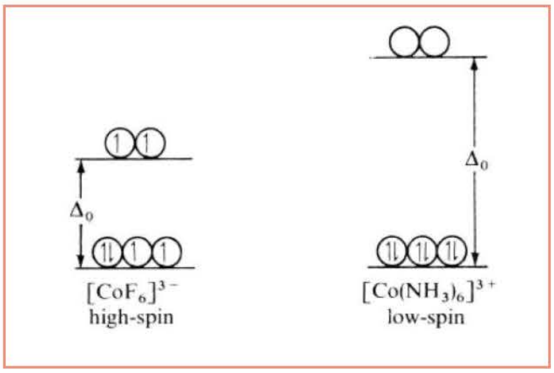
$\mu = \sqrt{n \cdot (n+2)} = \sqrt{3}$
$= 1.73\ MB$

OXYGEN UPTAKE BY A CO(II) COMPLEX

6. Give a reasoned explanation for the fact that almost all Co(III) complexes are octahedral (low spin). What magnetic moment do they exhibit?

- When observing cobalt(III), we know that cobalt must lose three electrons. The first two to go are from the 4s orbital and cobalt becomes:[Ar]$4s^0 3d^7$. Then, the next electron leaves the 3d orbital and the configuration becomes: [Ar]$4s^0 3d^6$. Thus, we can see that there are **six electrons that need to be included in crystal field diagrams**.
- The normal tendency is for electrons to remain unpaired. Energy sufficient to overcome the repulsive interaction of two electrons occupying the same orbital is required to cause pairing. Secondly, in the presence of a crystal field, ***d* orbital electrons will tend to occupy low-energy orbitals and thus avoid, as much as possible, repulsive interaction with ligands**. If the stability thus gained (Δ) is large enough to overcome the loss in stability due to electron pairing, then electrons couple and the result is a **low-spin complex**. Whenever the crystal field splitting (Δ) is insufficient, electrons remain unpaired and **the complex is a high-spin type**.
- The pairing of these electrons **depends on the ligand**.

OXYGEN UPTAKE BY A CO(II) COMPLEX



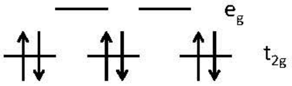
Relative crystal field splittings (Δ_o) of the *d* orbitals in high-spin and low-spin octahedral cobalt(III) complexes. The magnitude of the crystal field splitting determines whether *d* electrons in a metal ion will pair up.

- With strong field ligands (like ammonia), electrons will adopt a low spin configuration.
- With weak field ligands (like fluorine), the result will be a high spin complex.

OXYGEN UPTAKE BY A CO(II) COMPLEX

- The crystal field splitting is also strongly influenced by the oxidation state of the metal ion and the type of *d* electrons present. In general, the higher the oxidation state of the metal ion, the larger will be the crystal field splitting. The complex $[Co(NH_3)_6]^{3+}$ is a diamagnetic low-spin complex, whereas $[Co(NH_3)_6]^{2+}$ is a paramagnetic high-spin complex.
- The crystal field splitting in the cobalt(III) complex is about twice as great as in the cobalt(II) complex; this results in the pairing of electrons. One can attribute the larger Δ_o for cobalt(III) to the fact that ligands can approach more closely the slightly smaller and higher-charged metal ion and hence interact more strongly with its *d* orbitals.

Co(III) d^6



Octahedral
Low spin complexes

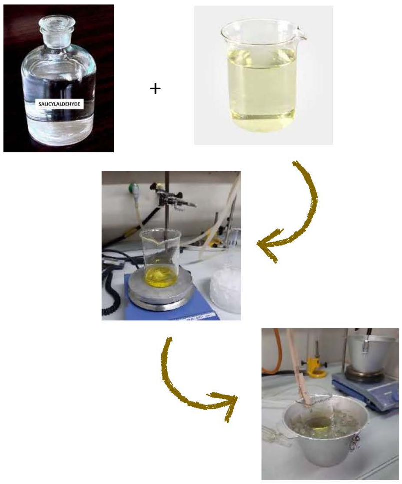
$e_g^6 t_{2g}^0$

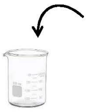
$\mu = 0\ MB$

OXYGEN UPTAKE BY A CO(II) COMPLEX

Experimental procedure

1) Synthesis of H_2salen





1.6 mL salicylaldehyde
+ 25 mL hot 96% ethanol

↓ Heat to dissolve while stirring

↓ Add 0.5 mL ethylenediamine (dropwise)

↓ Heat and stir during 3 minutes

↓ Cool in an ice bath. Yellow crystals will appear.

↓ Filter through a Buchner

OXYGEN UPTAKE BY A CO(II) COMPLEX

↓ Filter off through a Buchner

Filtrate

Yellow crystals

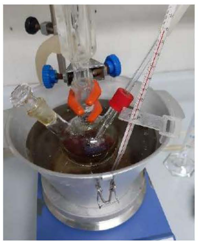
↓ Wash with cold ethanol

↓ Air- dry

Weigh and determine the yield

OXYGEN UPTAKE BY A CO(II) COMPLEX

2) Synthesis of [Co(salen)]



1.17 g H_2salen
+ 60 mL 96% ethanol

↓ Flush with N_2 while stirring 5-10 min.

↓ Connect the condenser and immerse the flask in a 70-80ºC water bath

↓ Add solution of cobalt acetate (side neck) (1.09 g of $Co(CH_3CO_2)_2{\cdot}4H_2O$ in 7.5 mL hot H_2O)

↓ Reflux for 1 hour. Precipitate becomes dark red.

↓ Cool the solution under N_2

↓ Filter through Buchner or filter plate

- Filtrate
- Dark red precipitate

OXYGEN UPTAKE BY A CO(II) COMPLEX

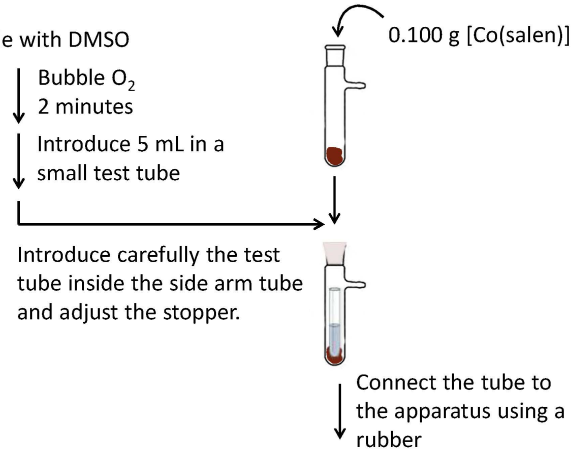
↓ Filter (Buchner or filtering plate)

- Filtrate
- Dark red solid
  - ↓ Wash with water (3 times)
  - ↓ Wash with ethanol.
  - ↓ Air- dry

Weigh and determine the yield

OXYGEN UPTAKE BY A CO(II) COMPLEX

3) Determination of the number of moles of oxygen absorbed per mol of complex.



Bottle with DMSO

Bubble O_2
2 minutes

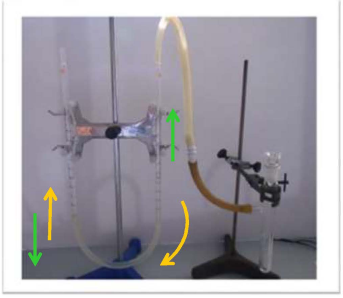
Introduce 5 mL in a
small test tube

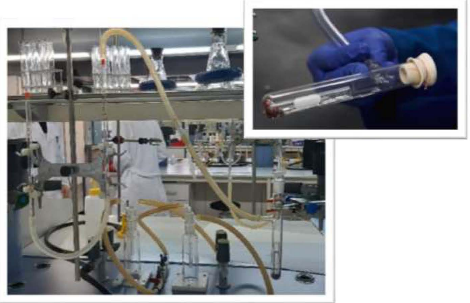
0.100 g [Co(salen)]

Introduce carefully the test
tube inside the side arm tube
and adjust the stopper.

Connect the tube to
the apparatus using a
rubber

OXYGEN UPTAKE BY A CO(II) COMPLEX





Connect the tube to the apparatus system using a rubber

Adjust the movable arm to make the water levels equal on both sides.

Adjust the movable arm to make the water levels equal on both sides.

Record the level of water (V_1)

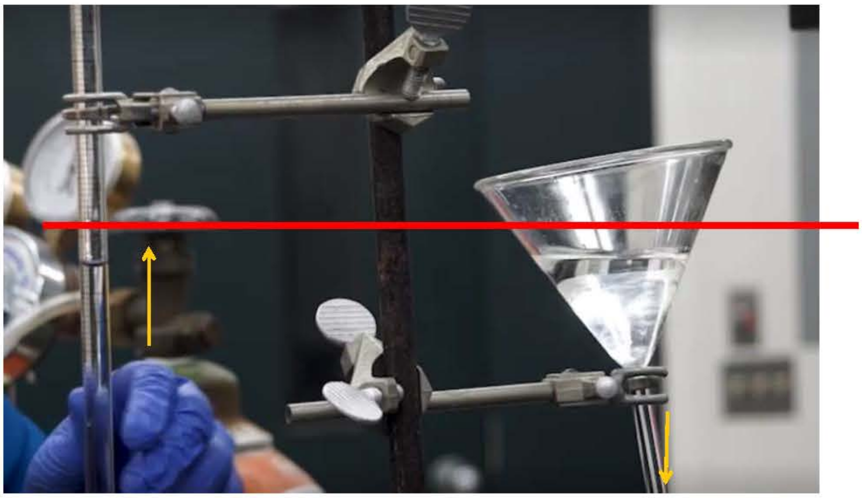
Invert the side-arm tube, so DMSO will form an adduct with [Co(salen)] able to absorb O_2

Shake until no changes occur (10-20 minutes)

Adjust the movable arm to make the water levels equal on both sides.

Record the level of water (V_2)

OXYGEN UPTAKE BY A CO(II) COMPLEX



https://www.jove.com/science-education/10430/synthesis-of-an-oxygen-carrying-cobalt-ii-complex

Oxygen uptake by a Co(II) complex

GROUP A3

PROF: M. TERESA ALBELDA

Additional questions

1. Calculate the percent yield obtained in the process of synthesis of H_2salen. Data: density of salicylaldehyde = 1.164 g/mL; density of ethylendiamine = 0.895 g/mL.

Salicylaldehyde → $\rho = \frac{m}{V} = 1.164$ m = 1.164 × 1.6 = 1.8624 g

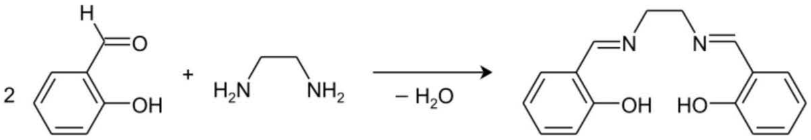
1.8624 g × $\frac{1\ mol}{122.12g}$ = 0.01525 moles salicylaldehyde

Ethylenediamine → $\rho = \frac{m}{V} = 0.895$ m = 0.895 × 0.5 = 0.4475 g

0.4475 g × $\frac{1\ mol}{60g}$ = 0.007458 moles ethylenediamine

- Looking at the stoichiometry, 1 mol of ethylenediamine reacts with 2 moles of salicylaldehyde. 0.0075 moles ethylenediamine require 0.015 moles of salicylaldehyde, which after calculation, is a small excess. Thus, ethylenediamine is the limitant reagent.

OXYGEN UPTAKE BY A CO(II) COMPLEX



$$0.007458 \text{ moles ethylenediamine} \times \frac{1\ mol\ H_2salen}{1\ mol\ ethylenediamine} \times \frac{268.31\ g}{1\ mol\ H_2salen} = 2.0011g\ H_2salen$$

(%) Yield $= \frac{mass\ exp.}{mass\ theor.} \times 100 = \frac{1.53g}{2.011g} \times 100 = 76\%$

OXYGEN UPTAKE BY A CO(II) COMPLEX

2. Calculate the percent yield obtained in the synthesis of [Co(salen)].

$$Co(OAC)_2 + H_2salen \longrightarrow [Co(salen)] + 2\ HOAc$$

Calculating the limitant reagent:

H_2salen → $1.17\ g\ H_2salen \times \frac{1\ mol\ H_2salen}{268.31\ g} = 0.0044\ moles\ H_2salen$

Cobalt (II) Acetate → $1.09\ g\ Co(OAc)_2 \cdot 4H_2O \times \frac{1\ mol\ Co(OAc)_2}{248.93\ g} = 0.0044\ moles\ Co(OAc)_2$

So, we can say both reagents are in a stoichiometric ratio

OXYGEN UPTAKE BY A CO(II) COMPLEX

$$0.0044\ \text{mol Co(OAc)}_2\cdot 4\text{H}_2\text{O}\times\frac{1\ mol\ [Co(salen)]}{1\ mol\text{Co(OAc)}_2\cdot 4\text{H}_2\text{O}}\times\frac{325.24\ g}{1\ mol\ [Co(salen)]}=1.431\ g\ [Co(salen)]$$

$$\textbf{(\%) Yield}=\frac{mass\ exp.}{mass\ theor.}\times 100=\frac{1.27\ g}{1.431\ g}\times 100=88.8\ \%=89\%$$

OXYGEN UPTAKE BY A CO(II) COMPLEX

3. Determine the number moles of oxygen absorbed by [Co(salen)] in the presence of DMSO. What is the ratio Co:O_2?

$$\textbf{2[Co(salen)] + 2 DMSO + O}_2 \longrightarrow \textbf{[Co(salen)(DMSO)]}_2\textbf{O}_2$$

V_1 = 7.0 mL

V_2 = 3.2 mL

$V_{O_2} = V_1 - V_2$ = 7.0 – 3.2 = 3.8 mL

https://www.jove.com/science-education/10430/synthesis-of-an-oxygen-carrying-cobalt-ii-complex

OXYGEN UPTAKE BY A CO(II) COMPLEX

- Firstly, we calculate the number of O_2 moles that are absorbed:

P·V = n·R·T →

$$n = \frac{1\,atm \times 3.8 \cdot 10^{-3} L}{0.082\,\frac{atm \cdot L}{K \cdot mol} \times 294K} = \frac{3.8 \cdot 10^{-3}\ mol}{24.108} = 0.000158\,mol\,O_2$$

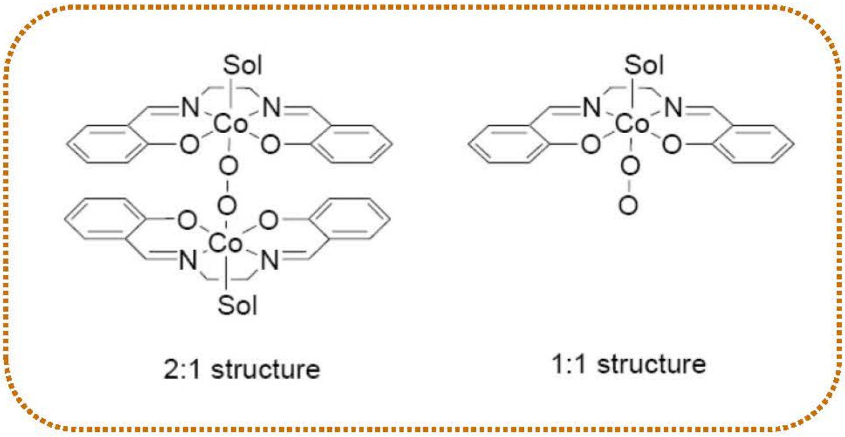
- We can then calculate the moles of [Co(salen)]:

$$0.1\text{ g}\,[Co(salen)] \times \frac{1\,mol\,[Co(salen)]}{325.24\,g} = 0.000308\,mol\,[Co(salen)]$$

- Finally, we calculate the ratio Co:O_2:

$$\frac{n_{Co}}{n_{O_2}} = \frac{0.000308}{0.000158} = 1.95{\sim}2$$

OXYGEN UPTAKE BY A CO(II) COMPLEX



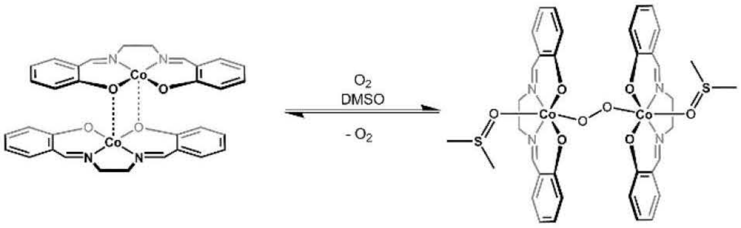
2:1 structure

1:1 structure

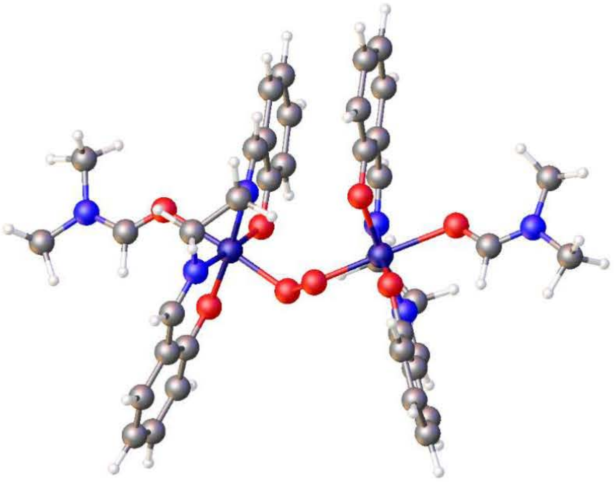
OXYGEN UPTAKE BY A CO(II) COMPLEX

4. According to the results in the previous question, write down the chemical reaction for obtaining the adduct between [Co(salen)], DMSO, and oxygen. Draw a structure for the oxygenated product and describe it. What is the oxidation state of cobalt and oxygen in this adduct?

$2[Co(salen)] + 2\,DMSO + O_2 \longrightarrow [Co(salen)(DMSO)]_2O_2$



OXYGEN UPTAKE BY A CO(II) COMPLEX



Structure of $[Co(salen)(dmf)]_2O_2$

OXYGEN UPTAKE BY A CO(II) COMPLEX

- [Co(salen)], salcomine, is both a Lewis acid and a reductant.
- Coordination of O_2 may be considered as oxidative-addition processes. Oxidative addition is a process that increases both the oxidation state and the coordination number of a metal centre.
- We consider that the following reaction takes place:

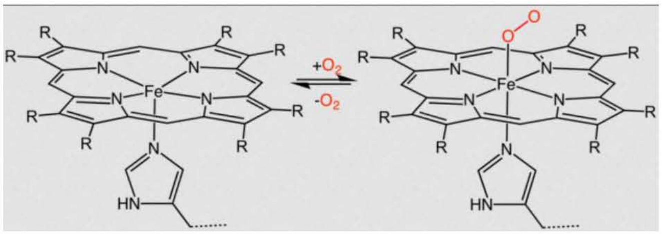
$$(\mathrm{Co}^{2+} \rightleftarrows \mathrm{Co}^{3}+ 1e^{-}+) \text{ x } 2$$

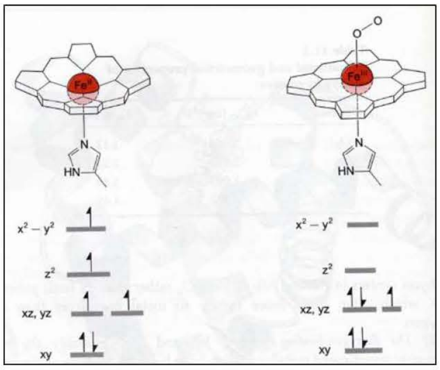
$$O_2+2e^{-} \rightleftarrows O_2{}^{2-}$$

$$2\mathrm{Co}^{2+}+O_2 \rightleftarrows 2\mathrm{Co}^{3+}+O_2{}^{2-}$$

The adduct formed between [Co(salen)], DMSO and oxygen exhibits two cobalt atoms in an oxidation state +3 and each one of the oxygen atoms in the bridge molecule is a peroxide oxygen with oxidation state -1.

OXYGEN UPTAKE BY A CO(II) COMPLEX





SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION.

Group A3
Prof: M. Teresa Albelda

The aim of this practice is to synthesise the acetylferrocene using a catalyst. Since this reaction is not complete, the crude of the reaction has to be purified by means of column chromatography. The oxidation of ferrocene yields the ferrocenium cation.

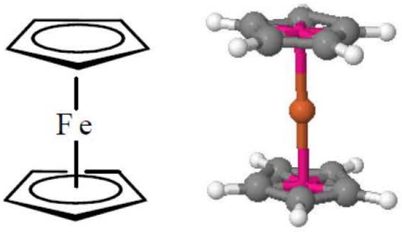
Objectives:

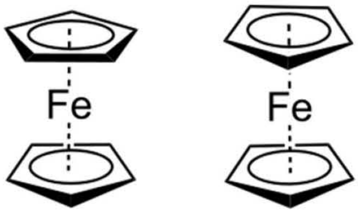
1. Acetylation reaction between ferrocene and acetic anhydride.
2. Follow the progress of a reaction using TLC.
3. Purification of acetylferrocene by means of column chromatography.
4. Oxidation reaction of ferrocene.

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION

Introduction

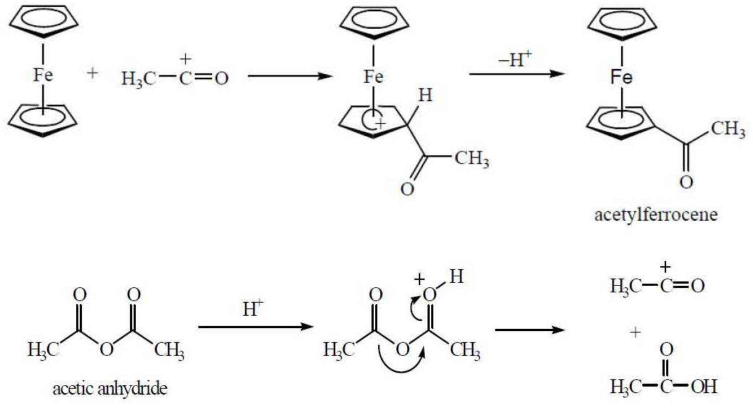
The structure of the organometallic compound ferrocene is composed of two planar five-membered ring sandwichs with an iron atom between them. Each ring in ferrocene has six delocalised pi electrons and a formal –1 charge; the iron atom has a formal +2 charge. With a planar structure and six delocalised pi electrons in each ring, ferrocene is aromatic and has many properties similar to benzene and its derivatives.





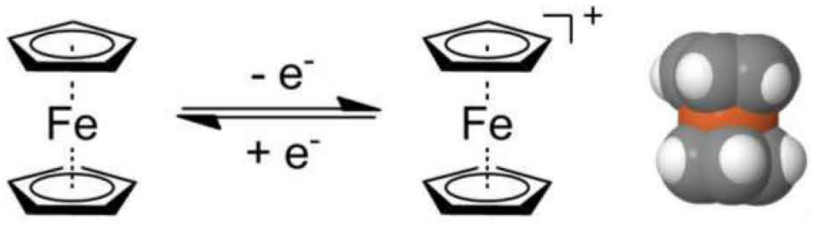
Staggered conformation (most stable) and eclipsed conformer.

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION



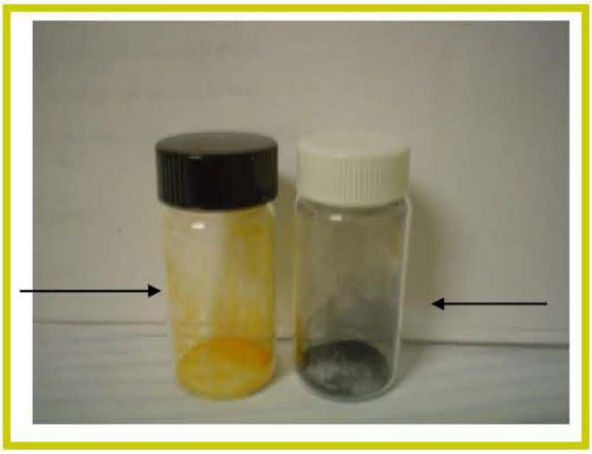
Ferrocene does not undergo addition reactions typical of cyclopentadiene, but undergoes electrophilic aromatic substitution. The Friedel-Crafts acylation reaction of ferrocene involves the addition of the acylium cation to one of the carbon atoms on the ring, followed by loss of a proton (to solvent). The acylium cation is produced from acetic anhydride, which also serves as a solvent for this reaction.

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION



Ferrocene	Ferrocenium
Yellow orange colour	Blue-purple colour
d^6, Fe^{2+}, $18e^-$	d^5, Fe^{3+}, $17e^-$
Could be functionalised with non-oxidant electrophiles.	Could be isolated as a salt BF_4^-, PF_6^- Could react with nucleophiles.
Diamagnetic	Paramagnetic

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION



Ferrocene

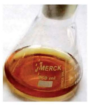
Ferrocenium

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION

Experimental Procedure

Synthesis of acetylferrocene
$Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_3)]$
(In hood)

0.45g of ferrocene
+ 9mL acetic anhydride



+ 6 drops of phosphoric acid

Follow the progression of the reaction by TLC (hexanes:ethyl acetate 10:1) at 0, 25, and 45 minutes →

Heat 45 min in water bath at 60-70ºC (use temp-probe)

Pour the mixture onto 20 g of ice

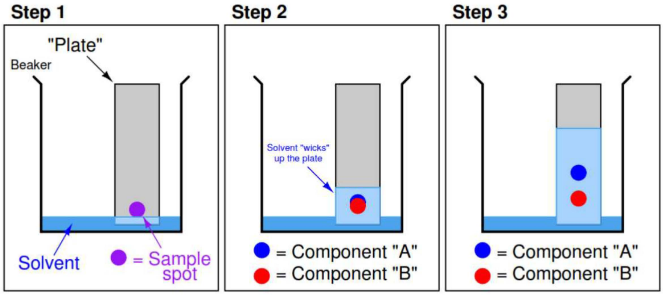
Neutralise with 6M NaOH (aprox 15 mL) and $NaHCO_3$

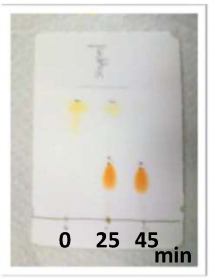
Extract 3 times with 5 mL cloroform (each)
https://www.youtube.com/watch?v=EFiFPoOzqtk

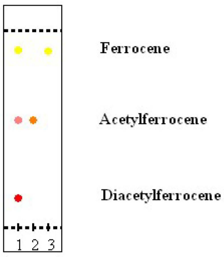
Evaporate to dryness

https://www.youtube.com/watch?v=jks_IxQSqog

SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION





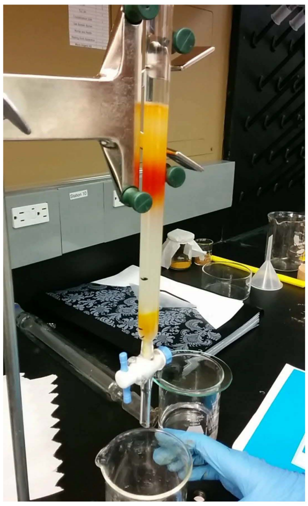


SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION

Purification of acetylferrocene

(In hood)

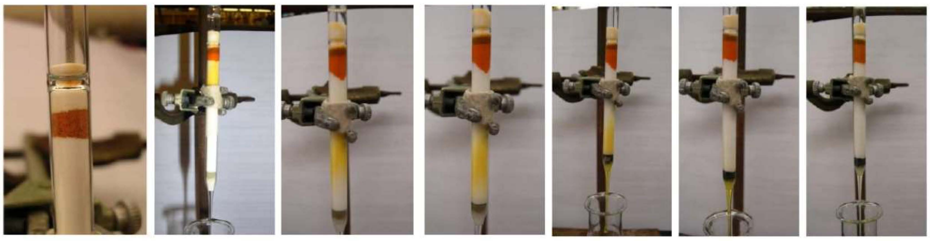
- Purification of the crude product obtained previously will be carried out by means of column chromatography using silicagel and hexanes: ethyl acetate 10:1 as eluent.
- A column is prepared by packing a solid absorbent into a cylindrical glass tube. There are two different ways to pack process chromatography columns: dry packing and slurry packing https://www.youtube.com/watch?v=IXn0Mfp_gII
- We will use a Pasteur pipette to load the sample on the chromatography column: https://www.youtube.com/watch?v=LVOkvLPp1gA
- Ferrocene (fraction 1) is eluted first with hexanes and is visible as a yellow band. Acetylferrocene is eluted next (fraction 2) and is visible as an orange band.
- Evaporate the solvents from the fractions, determine the weights and calculate yield.



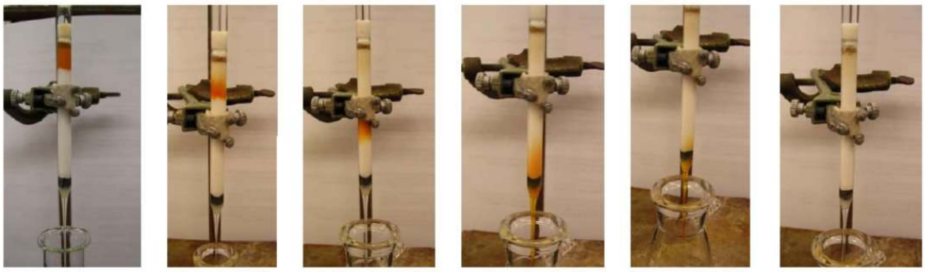
SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION

Elution of ferrocene

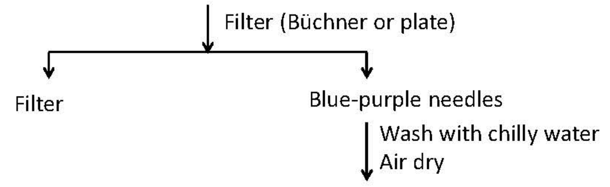
https://www.youtube.com/watch?v=IENVkIlBIW4



Elution of acetylferrocene



SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION



Filter (Büchner or plate)

Filter

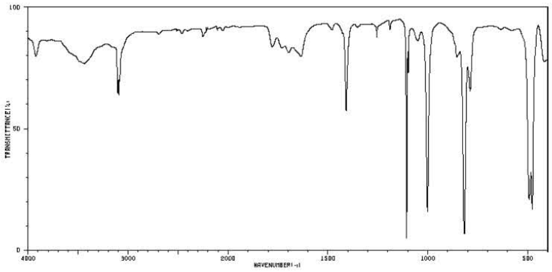
Blue-purple needles

Wash with chilly water
Air dry

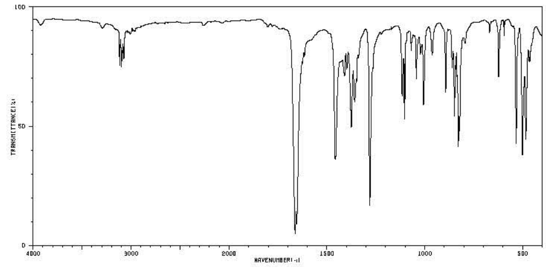
SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION

IR Spectra

IR spectrum of ferrocene

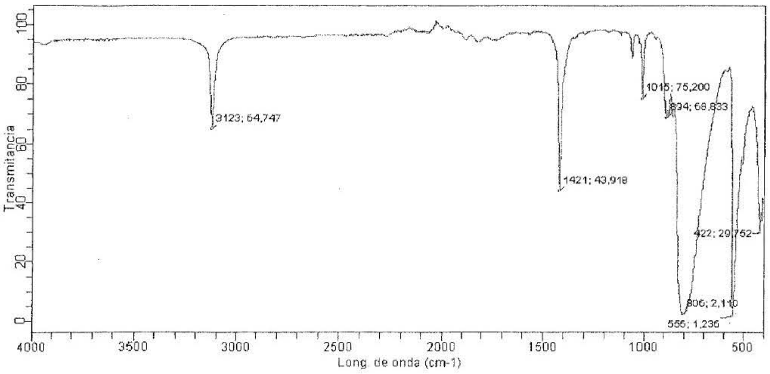


IR spectrum of acetylferrocene



SYNTHESIS AND PURIFICATION OF ACETYLFERROCENE. SYNTHESIS OF FERROCENIUM ION

IR spectrum of hexafluorphosphate of ferrocenium



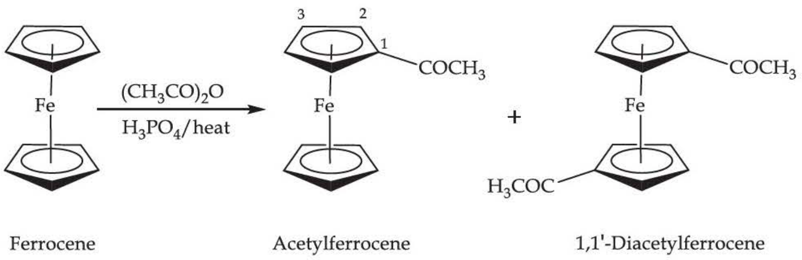
PREPARACIÓ I PURIFICACIÓ D’ACETILFERROCÈ.
SÍNTESI DEL FERRICINI

Grup D1
Prof: M. Teresa Albelda

PREPARACIÓ I PURIFICACIÓ D’ACETILFERROCÈ.
SÍNTESI DEL FERRICINI

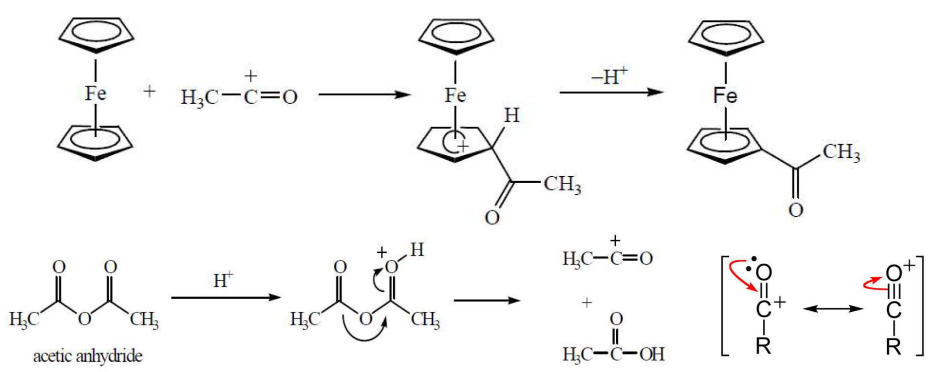
Qüestions addicionals

1. Escriviu l’equació de la reacció de l’acetilferrocè



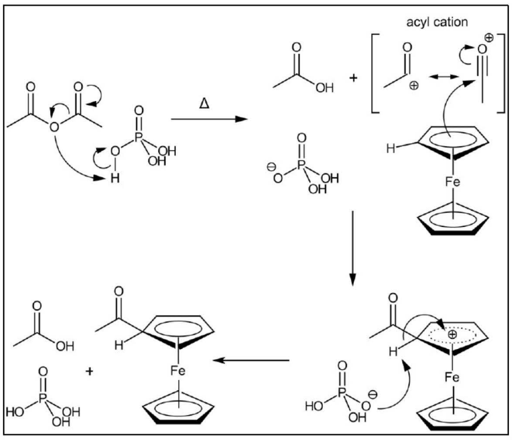
En aquesta reacció, el ferrocè reacciona amb l’anhídrid acètic i usa àcid fosfòric com a catalitzador. El producte obtingut funcionalitza un dels anells del ferrocè amb un grup acetil, però també pot obtenir-se el producte diacetilat, és a dir, el producte que conté dos grups acetil, un en cadascun dels anells.

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI



Aquesta reacció és una **reacció de Friedel i Crafts**. Es tracta de **reaccions** de substitució electrofílica aromàtica en les quals en un compost aromàtic un dels àtoms d'hidrògen és substituït per un grup alquil o acil. L'ió acil es forma mitjançant la reacció de l'anhídrid acètic amb l'àcid fosfòric.

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

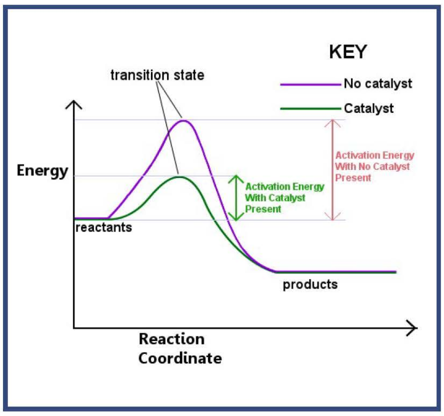


1. El primer pas de la reacció és la formació de l'electròfil. L'àcid fosfòric protona l'oxigen de l'anhídrid acètic i dona lloc a una espècie molt més reactiva (l'ió acil) i àcid acètic.
2. D'altra banda, el ferrocè conté dos anells aromàtics molt estables. No obstant això, quan l'escalfem, l'anell superior pot desplaçar-se i fer que els electrons estiguen més localitzats i la molècula de ferrocè actue com a nucleòfil. El ferrocè reacciona amb l'ió acil i forma un intermediari.
3. L'últim pas de la reacció consisteix en el restabliment de l'aromaticitat i la recuperació del catalitzador. La reacció es troba desplaçada cap a la formació de producte a causa de l'alta estabilitat que aporta l'aromaticitat.
4. Hi afegim NaOH al final de la reacció per tal de convertir l'excés d'anhídrid acetic i l'àcid acetic produït estequiomètricament durant el procés en acetat de sodi. També per a neutralitzar l'àcid fosfòric que hem fet servir de catalitzador.

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ.
SÍNTESI DEL FERRICINI

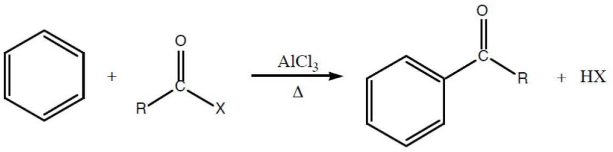
2. Quin és el paper que té el catalitzador? Proposeu una equació que ho mostre.

El paper del catalitzador sempre consisteix a augmentar la velocitat de reacció perquè disminueix l'energia d'activació.

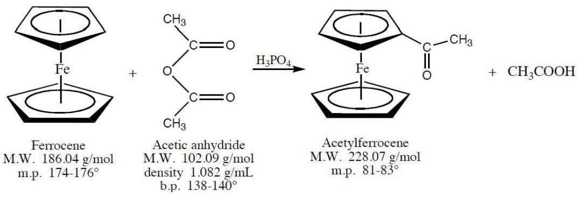


1. En aquest cas, el paper del catalitzador consisteix a protonar l'anhídrid acètic per a generar l'ió acil, l'electròfil de la reacció.
2. L'ió acil és un electròfil feble, ja que l'estructura ressonant amb la càrrega positiva sobre l'àtom de carboni és la minoritària. Per la qual cosa, sols reaccionarà amb sistemes aromàtics que presenten una elevada densitat electrònica. Rarament s'observa diacilació en el mateix anell.
3. D'altra banda, l'àcid fosfòric restableix l'aromaticitat del producte final desprotonant l'anell de ferrocè.

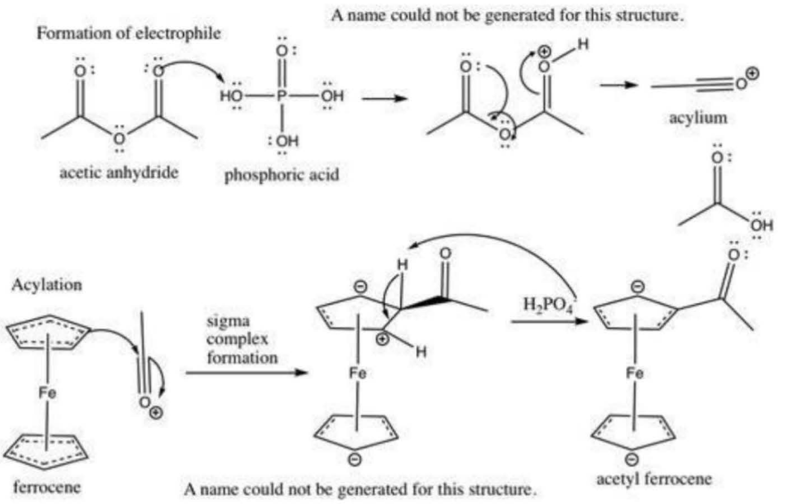
PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ.
SÍNTESI DEL FERRICINI



Aquesta seria l'equació general per a una acilació de Friedel i Crafts en què s'empra com a catalitzador un àcid de Lewis ($AlCl_3$). Perquè la reacció tinga lloc, cal que l'anell aromàtic siga molt ric en electrons i no posseïsca grups electroatraients. En el cas del ferrocè, com que els dos anells de tipus ciclopentadienil presenten una gran densitat electrònica, aquest metal·locè és molt reactiu amb agents electrofílics, molt més encara que el mateix benzè, i això indica que té els electrons molt més disponibles. Per tant, mentre que l'acilació de Friedel i Crafts del benzè ocorre mitjançant l'ús de $AlCl_3$ com a catalitzador, el ferrocè pot ser acilat amb anhídrid acètic usant àcid fosfòric com a catalitzador en condicions més suaus.



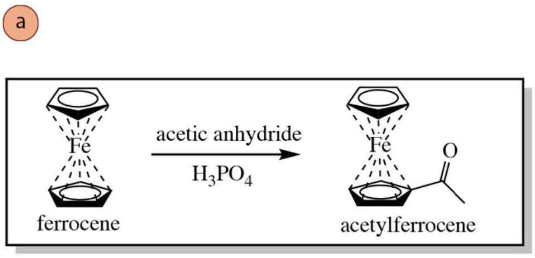
PREPARACIÓ I PURIFICACIÓ D’ACETILFERROCÈ. SÍNTESI DEL FERRICINI

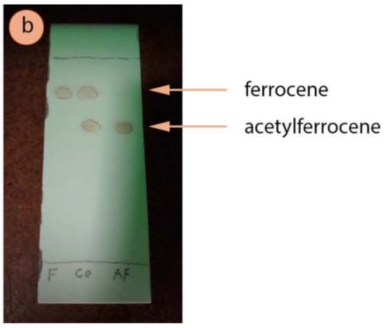


PREPARACIÓ I PURIFICACIÓ D’ACETILFERROCÈ. SÍNTESI DEL FERRICINI

3. Quin compost s’elueix primer, $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_3)]$ o $[Fe(\eta^5\text{-}C_5H_5)_2]$? Per què?

El compost que s’elueix en primer lloc és el menys polar de tots dos, és a dir, el ferrocè, **$[Fe(\eta^5\text{-}C_5H_5)_2]$**. La funcionalització d’un dels anells amb un grup acetil serveix per a augmentar la polaritat de l’acetilferrocè, ja que aquest posseeix un grup carbonil que quedarà més retingut amb la fase estacionària que també és polar.





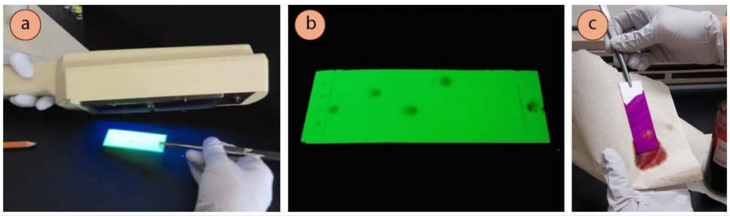
PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

4. Com es pot establir la situació dels compostos eluïts en una placa cromatogràfica si són incolors? Quins mètodes es poden aplicar per a detectar l'elució de compostos incolors d'una columna cromatogràfica?

En el cas de la separació del ferrocè i acetilferrocè, la situació dels compostos, tant en la placa cromatogràfica com en la columna, es pot diferenciar gràcies a la distinta coloració que té cadascun. El ferrocè té color groc i l'acetilferrocè color taronja.

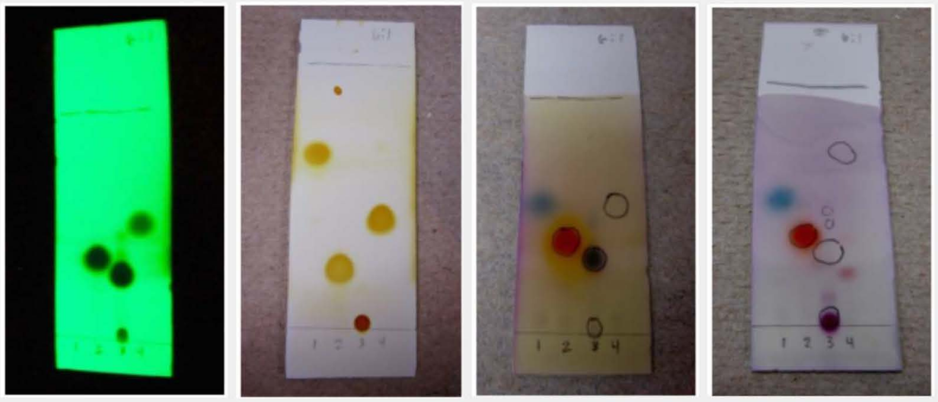
No obstant això, podem diferenciar la situació dels compostos en les plaques cromatogràfiques o columnes encara que no presenten coloració.

Alguns d'ells poden visualitzar-se amb la llum ultraviolada (la majoria de compostos aromàtics) o bé es poden emprar agents reveladors.



PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

Llum ultraviolada	**Iodur**	***p*-anisaldehid**	**Vainil·lina**
Aromàtics i sistemes conjugats	Reacciona amb aromàtics	Aldehids, cetones i alcohols	Aldehids, cetones i alcohols



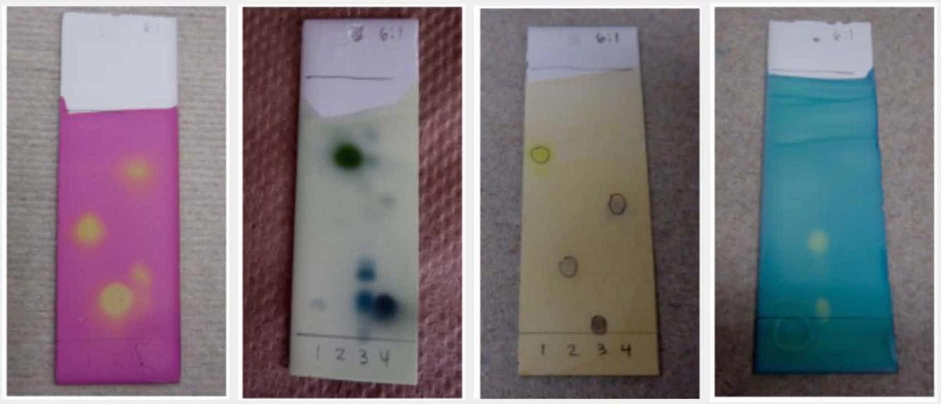
PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ.
SÍNTESI DEL FERRICINI

Permanganat
Alquens, alquins i grups que poden oxidar-se (aldehids i alcohols)

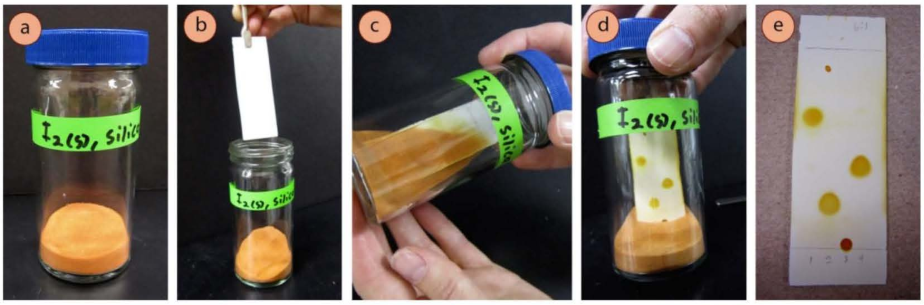
Àcid fosfomolíbdic
Alcohols, fenols, alquens i compostos carbonílics

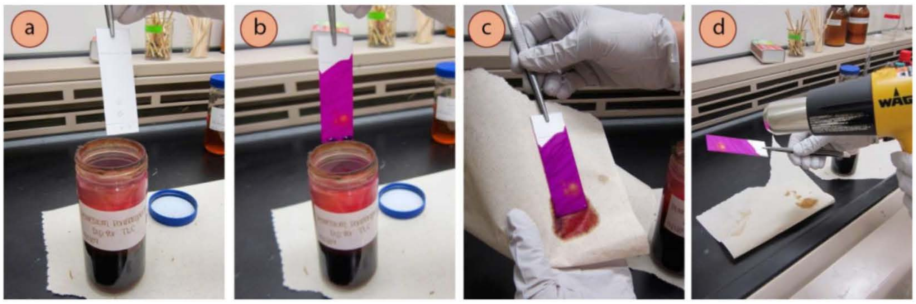
Clorur de ferro(III)
Fenols

Verd de bromocresol
Compostos àcids



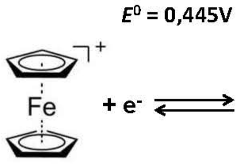
PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ.
SÍNTESI DEL FERRICINI





PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ.
SÍNTESI DEL FERRICINI

5. Escriviu l'equació de la reacció d'obtenció del ferricini.



E^0 = 0,77V

$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

$$[Fe(\eta^5\text{-}C_5H_5)_2] \rightleftharpoons [Fe(\eta^5\text{-}C_5H_5)_2]^+ + e^-$$

$$Fe^{3+} + [Fe(\eta^5\text{-}C_5H_5)_2] \rightleftharpoons Fe^{2+} + [Fe(\eta^5\text{-}C_5H_5)_2]^+$$

$E^{0\prime} = E_{ox} - E_{red}$ = 0,77 – 0,445 = 0,325 V

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ.
SÍNTESI DEL FERRICINI

6. Calculeu-ne la constant d'equilibri. Es produirà quantitativament?

$$a\ Ox_a + b\ Red_b \rightleftharpoons a'\ Red_a + b'\ Ox_b$$

$\Delta G = \Delta G^{0\prime} + RT \ln Q$ $\qquad$ $\Delta G < 0$ procés espontani

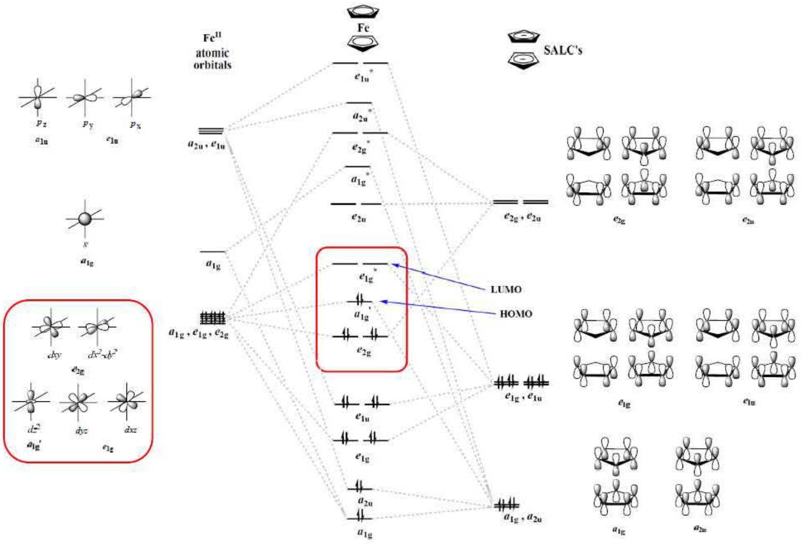
$$Q = \frac{[Red_a]^{a'}\,[Ox_b]^{b'}}{[Ox_a]^{a}\,[Red_b]^{b}} \qquad \boxed{E = E^{0\prime} - \frac{RT}{\nu F} \ln Q}$$ Equació de Nernst

En l'equilibri, $E = 0$ i $Q = K_{eq}$ → $\ln K_{eq} = \dfrac{\nu F E^{0\prime}}{RT}$ → $\log K = \dfrac{n E^{0\prime}}{0{,}059}$

$K = 10^{5,5}$ < 10^7 → No és quantitativa

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

7. Com és la configuració electrònica dels dos complexos?

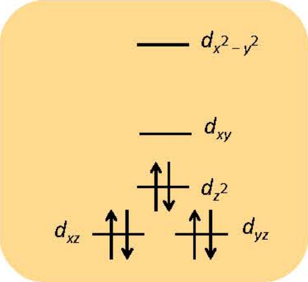


PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

Ferrocè → geometria planoquadrada de baix espín

Fe^{2+}, d^6

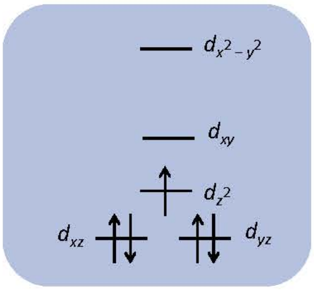
Diamagnètic



Ferricini → Geometria planoquadrada de baix espín

Fe^{3+}, d^5

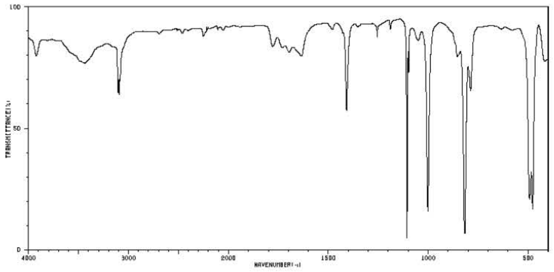
Paramagnètic, 1e$^-$ desaparellat



PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

Informació addicional

Espectre IR del ferrocè



3.000 cm^{-1}: vibració de tensió (*stretching*) C-H

1.500 cm^{-1}: vibració de tensió C=C

1.120 cm^{-1}: Moviment d'asimetria dels anells

1.005 cm^{-1} : vibració de flexió (*bending*) C-H (en el pla)

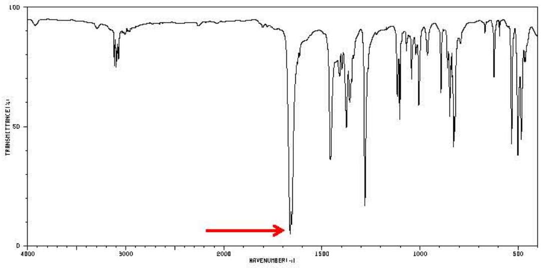
1.061 cm^{-1}: vibració simètrica de tensió N-O

475 cm^{-1}: vibració de tensió Fe-C

811 cm^{-1}: vibració de flexió C-H (fora del pla)

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

Espectre IR de l'acetilferrocè



3.100 cm^{-1}: vibració de tensió C-H

1.660 cm^{-1}: vibració de tensió C=O

1.457 i 1.378 cm^{-1}: moviment de rotació -CH_3

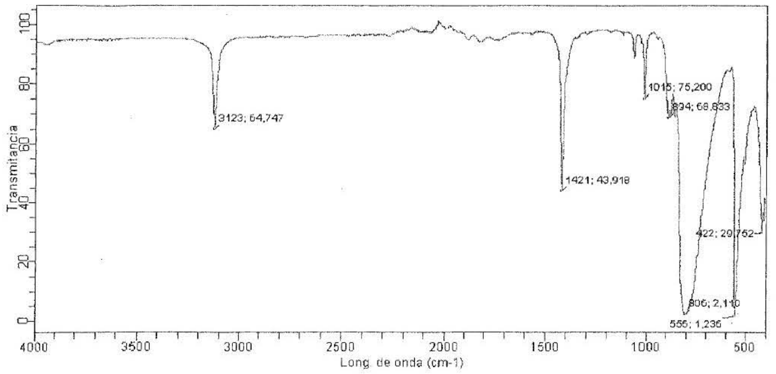
1.102 cm^{-1}: moviment d'asimetria dels anells

822 cm^{-1}: vibració de flexió C-H (fora del pla)

500 cm^{-1}: vibració de tensió Fe-C

PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

Espectre IR de l'hexafluorofosfat de ferricini



PREPARACIÓ I PURIFICACIÓ D'ACETILFERROCÈ. SÍNTESI DEL FERRICINI

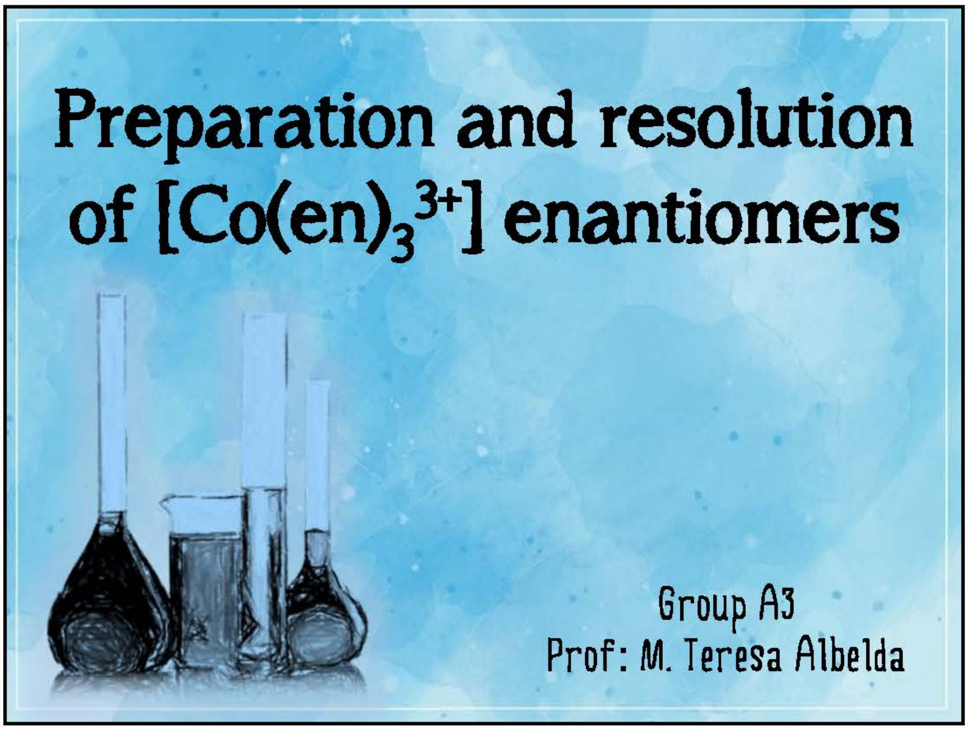
3.123 cm^{-1}: vibració de tensió C-H

1.421 cm^{-1}: vibració de tensió C=C

806 cm^{-1}: vibració de flexió C-H (fora del pla)

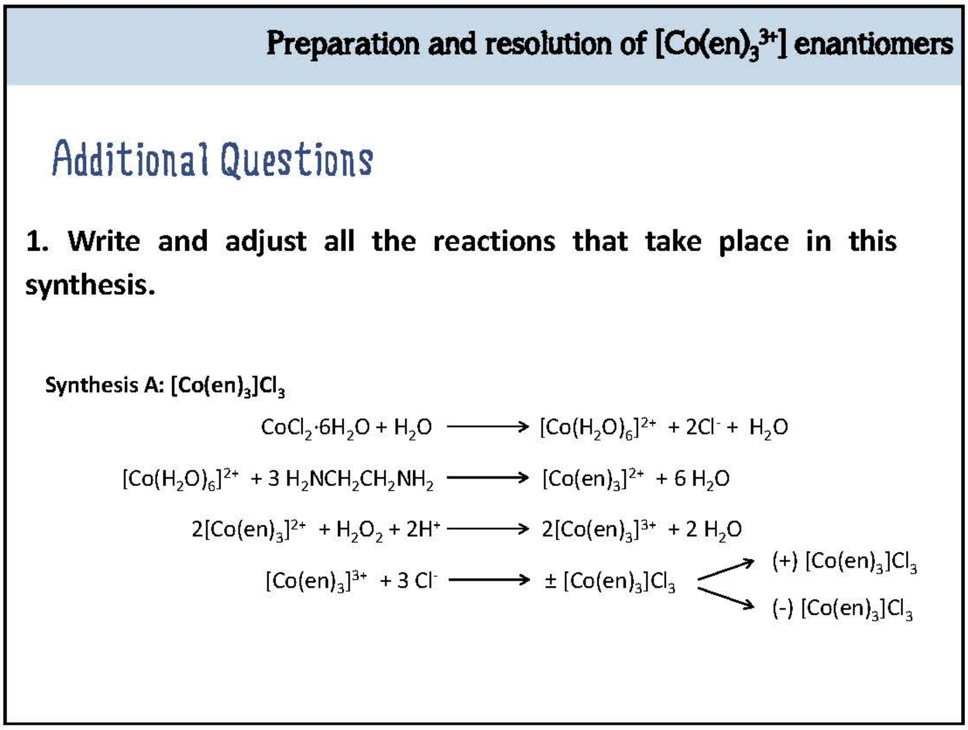
556 cm^{-1}: vibració de tensió Fe-C

422 cm^{-1}: vibració de tensió P-F



Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Group A3
Prof: M. Teresa Albelda



Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Additional Questions

1. Write and adjust all the reactions that take place in this synthesis.

Synthesis A: $[Co(en)_3]Cl_3$

$$CoCl_2{\cdot}6H_2O + H_2O \longrightarrow [Co(H_2O)_6]^{2+} + 2Cl^- + H_2O$$

$$[Co(H_2O)_6]^{2+} + 3\,H_2NCH_2CH_2NH_2 \longrightarrow [Co(en)_3]^{2+} + 6\,H_2O$$

$$2[Co(en)_3]^{2+} + H_2O_2 + 2H^+ \longrightarrow 2[Co(en)_3]^{3+} + 2\,H_2O$$

$$[Co(en)_3]^{3+} + 3\,Cl^- \longrightarrow \pm\,[Co(en)_3]Cl_3 \begin{array}{l} \nearrow (+)\,[Co(en)_3]Cl_3 \\ \searrow (-)\,[Co(en)_3]Cl_3 \end{array}$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Synthesis B.2: $[(+)Co(en)_3][(+)tart]Cl{\cdot}5H_2O$

$$\pm\ [Co(en)_3]Cl_3 + [(+)tart]^{2-} \longrightarrow \tfrac{1}{2}\ [(+)\ Co(en)_3][(+)tart]^{+} + \tfrac{1}{2}\ [(-)\ Co(en)_3][(+)tart]^{+} + 3Cl^{-}$$

$$[(+)\ Co(en)_3][(+)tart]^{+} + Cl^{-} + 5H_2O \xrightarrow{NaOH} [(+)\ Co(en)_3][(+)tart]Cl{\cdot}5H_2O\ (s)$$

Synthesis B.4: $[(+)Co(en)_3]I_3{\cdot}H_2O$

$$[(+)\ Co(en)_3][(+)tart]Cl{\cdot}5H_2O\ (s) \xrightarrow[NaOH]{H_2O} [(+)\ Co(en)_3]^{3+} + [(+)tart]^{2-} + Cl^{-} + 5H_2O$$

$$[(+)\ Co(en)_3]^{3+} + 3\ I^{-} + H_2O \longrightarrow [(+)\ Co(en)_3]I_3{\cdot}H_2O\ (s)$$

Synthesis B.4: $[(-)Co(en)_3]I_3{\cdot}H_2O$

$$[(-)\ Co(en)_3][(+)tart]^{+}\ (aq) + 3\ I^{-} + H_2O \xrightarrow{NaOH} [(-)\ Co(en)_3]I_3{\cdot}H_2O\ (s)$$

Synthesis B.5: Racemization of $[(+)Co(en)_3]I_3{\cdot}H_2O$ or $[(-)Co(en)_3]I_3{\cdot}H_2O$

$$[(-)\ Co(en)_3]I_3{\cdot}H_2O\ (s) + H_2O + C_{activated} + I^{-} \longrightarrow [(\pm)\ Co(en)_3]I_3{\cdot}H_2O\ (s) + H_2O + C_{activated} + I^{-}$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

2. Determine the yield of all isolated products. Comment on the results obtained.

Synthesis A: $[Co(en)_3]Cl_3$

$$9.05\ g\ CoCl_2{\cdot}6H_2O \ \ x\ \ \frac{1\ mol\ CoCl_2{\cdot}6H_2O}{238\ g} \ \ x\ \ \frac{1\ mol\ [Co(en)_3]Cl_3}{1\ mol\ CoCl_2{\cdot}6H_2O} \ \ x\ \ \frac{345.5\ g}{1\ mol\ [Co(en)_3]Cl_3} =$$

= 13.13g is the mass of $[Co(en)_3]Cl_3$ that can be obtained with a 100% yield.

If you obtained, for example 11.49 g, the yield of that reaction is:

$$\text{Yield} = \frac{11.49\ g}{13.13\ g}\ x\ 100 = 87.5\%$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Synthesis B.2: $[(+)Co(en)_3][(+)tart]Cl \cdot 5H_2O$

$$7.2\ \text{g}\ [Co(en)_3]Cl_3 \times \frac{1\ \text{mol}\ [Co(en)_3]Cl_3}{345.5\ \text{g}} \times \frac{1\ \text{mol}\ [(+)Co(en)_3][(+)tart]}{2\ \text{mol}\ [Co(en)_3]Cl_3} \times \frac{514.5\ \text{g}}{1\ \text{mol}\ [(+)Co(en)_3][(+)tart]} =$$

= 5.36 g is the mass of $[(+)Co(en)_3][(+)tart]Cl \cdot 5H_2O$ that can be obtained with a 100% yield.

If you obtained, for example 3.0 g, the yield of that reaction is:

$$\text{Yield} = \frac{3.0\ \text{g}}{5.36\ \text{g}} \times 100 = 56\ \%$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Synthesis B.4: $[(+)Co(en)_3]I_3 \cdot H_2O$

$$2.0\ \text{g}\ [(+)Co(en)_3][(+)tart]Cl \cdot 5H_2O \times \frac{1\ \text{mol}\ [(+)Co(en)_3][(+)tart]}{514.5\ \text{g}} \times \frac{1\ \text{mol}\ [(+)Co(en)_3]I_3 \cdot H_2O}{1\ \text{mol}\ [(+)Co(en)_3][(+)tart]} \times$$

$$\times \frac{638\ \text{g}}{1\ \text{mol}\ [(+)Co(en)_3]I_3 \cdot H_2O} = $$ 2.48 g is the mass of $[(+)Co(en)_3]I_3 \cdot H_2O$ that can be obtained with a 100% yield.

If you obtained, for example 2.3 g, the yield of that reaction is:

$$\text{Yield} = \frac{2.3\ \text{g}}{2.48\ \text{g}} \times 100 = 92.7\ \%$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Synthesis B.4: $[(-)Co(en)_3]I_3{\cdot}H_2O$

$$7.2\text{ g }[Co(en)_3]Cl_3 \times \frac{1\text{ mol }[Co(en)_3]Cl_3}{345.5\text{ g}} \times \frac{1\text{ mol }[(-)Co(en)_3][(+)tart]}{2\text{ mol }[Co(en)_3]Cl_3} \times \frac{1\text{ mol }[(-)Co(en)_3]I_3}{1\text{ mol }[(-)Co(en)_3][(+)tart]}$$

$$\times \frac{638\text{ g}}{1\text{ mol }[(-)Co(en)_3]I_3}$$

= 6.64 g is the mass of $[(-)Co(en)_3][(+)tart]Cl{\cdot}5H_2O$ that can be obtained with a 100% yield.

If you obtained, for example 3.5 g, the yield of that reaction is:

$$\text{Yield} = \frac{3.5\text{ g}}{6.64\text{ g}} \times 100 = 52.7\ \%$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

3. In the purification of both (+) and (-) $[Co(en)_3]I_3{\cdot}H_2O$, the compounds were washed with water containing NaI. What is the purpose of the NaI?

- Addition of NaI **prevents the dissolution** of the solid.

- Precipitation is favoured due to the **common ion effect**.

Adding a common ion decreases solubility, as the reaction shifts toward the left to relieve the stress of the excess product. Adding a common ion to a dissociation reaction causes the equilibrium to shift left, toward the reactants, causing precipitation.

https://study.com/academy/lesson/the-common-ion-effect-and-selective-precipitation.html

$$[(+)\ Co(en)_3]I_3{\cdot}H_2O\ (s) \underset{NaI}{\rightleftarrows} [(+)\ Co(en)_3]^{3+} + I^-$$

- Removes tartrate anion forming the salt, sodium tartrate, which is soluble in water.

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

4. If $[\alpha]_D$ of pure $[(+)Co(en)_3]I_3 \cdot H_2O$ is +89º, what percentage of this enantiomer is present in the sample? Assume that the only impurity is $[(-)Co(en)_3]I_3 \cdot H_2O$. Do the same for the other enantiomer. Use that data to recalculate the yields obtained for each synthesised enantiomer.

$[(+)Co(en)_3]I_3 \cdot H_2O$

a) The first step is to calculate the magnitude of the rotation, specific rotation, from the data obtained with the polarimeter:

Path length:	1 dm	**Volume:**	25 mL
m (g):	0.34 g	**Temperature:**	21.8ºC
α measurements	1.126	1.140	1.130
α (average)		1.132	

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

$$[\alpha]_\lambda^T = \frac{\alpha}{lc} = \frac{1.132}{1\frac{0.34}{25}} = \frac{1.132}{0.0136} = 83.23\text{º}$$

Correction of temperature using the following equation:

$$[\alpha]_\lambda^{20} = [\alpha]_\lambda^T \cdot [1 + 0.0001\,(T - 20) =$$
$$83.23 \cdot [1 + 0.0001\,(21.8 - 20)] =$$
$$83.23 \cdot 1.00018 = 83.24\text{º}$$

b) The second step is to calculate the percent optical purity (X) of the complex:

$$X = \frac{[\alpha]_\lambda\ measured}{[\alpha]_\lambda\ standard} \times 100 = \frac{83.24\text{º}}{89\text{º}} = 93.5\%$$

Preparation and resolution of $[Co(en)_3^{3+}]$ enantiomers

c) Third step is to calculate the percentage of enantiomer:

$$\%\ enantiomer = x + \frac{(100 - x)}{2} = 93.5 + \frac{(100 - 93.5)}{2} = 93.5 + 3.25 = 96.8\ \%$$

d) The last step is to recalculate the yield of the reaction:

The calculated yield for the synthesis of $[(+)Co(en)_3]I_3 \cdot H_2O$ was 92.7% assuming 100% of enantiomer purity. With a 96.8% of enantiomer purity, the yield of the reaction is:

$$Yield = 92.7 \cdot \frac{96.8}{100} = 89.7\%$$

Preparation and resolution of $[Co(en)_3^{3+}]$ enantiomers

$[(-)Co(en)_3]I_3 \cdot H_2O$

Path length:	1 dm	**Volume:**	25 mL
m (g):	0.31 g	**Temperature:**	22ºC
α (average)	-0.518		

a)

$$[\alpha]_{\lambda}^{T} = \frac{\alpha}{lc} = \frac{-0.518}{1 \cdot \frac{0.31}{25}} = -41.77^{\text{º}}$$

$$[\alpha]_{\lambda}^{20} = [\alpha]_{\lambda}^{T} \cdot [1 + 0.0001\ (T - 20) =$$

$$-\ 41.77 \cdot [1 + 0.0001\ (22 - 20)] = -41.8^{\text{º}}$$

b)

$$X = \frac{[\alpha]_{\lambda}\ measured}{[\alpha]_{\lambda}\ standard} \times 100 = \frac{-41.8^{\text{º}}}{-89^{\text{º}}} = 47\%$$

c)

$$\%\ enantiomer = 47 + \frac{(100 - 47)}{2} = 47 + 26.5 = 73.5\ \%$$

d)

$$Yield = 52.7 \cdot \frac{73.5}{100} = 38.7\%$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

$[(+)Co(en)_3][(+)tart]Cl\cdot 5H_2O$

Path length:	1 dm	**Volume:**	25 mL
m (g):	0.17 g	**Temperature:**	21.8ºC
α (average)	0.601		

a) $$[\alpha]_\lambda^T = \frac{\alpha}{lc} = \frac{0.601}{1\cdot\frac{0.17}{25}} = 88.4º$$

$$[\alpha]_\lambda^{20} = [\alpha]_\lambda^T \cdot [1 + 0.0001\ (T-20) =$$

$$88.4 \cdot [1 + 0.0001\ (21.8 - 20)] = 88.42º$$

b) $$X = \frac{[\alpha]_\lambda\ measured}{[\alpha]_\lambda\ standard} \times 100 = \frac{88.42º}{102º} = 86.7\%$$

c) $$\%\ enantiomer = 86.7 + \frac{(100 - 86.7)}{2} = 86.7 + 6.65 = 93.35\ \%$$

d) $$Yield = 56 \cdot \frac{93.35}{100} = 52.3\ \%$$

Preparation and resolution of $[Co(en)_3{}^{3+}]$ enantiomers

Racemic mixture

Path length:	1 dm	**Volume:**	25 mL
m (g):	0.22 g	**Temperature:**	23ºC
α (average)	0.078		

a) $$[\alpha]_\lambda^T = \frac{\alpha}{lc} = \frac{0.078}{1\cdot\frac{0.22}{25}} = 8.86º$$

$$[\alpha]_\lambda^{20} = [\alpha]_\lambda^T \cdot [1 + 0.0001\ (T-20) =$$

$$8.86 \cdot [1 + 0.0001\ (23 - 20)] = 8.86º$$

b) $$X = \frac{[\alpha]_\lambda\ measured}{[\alpha]_\lambda\ standard} \times 100 = \frac{8.86º}{89º} = 9.96\ \%$$

c) $$\%\ enantiomer = 9.96 + \frac{(100 - 9.96)}{2} = 9.96 + 45.02 = 54.98\ \%$$

d) We have obtained more percentage (55%) of the positive enantiomer in the racemic mixture. This is the reason we did not obtain $[\alpha]_D = 0$.

Preparation and resolution of [Co(en)$_3$$^{3+}$] enantiomers

Additional Calculations

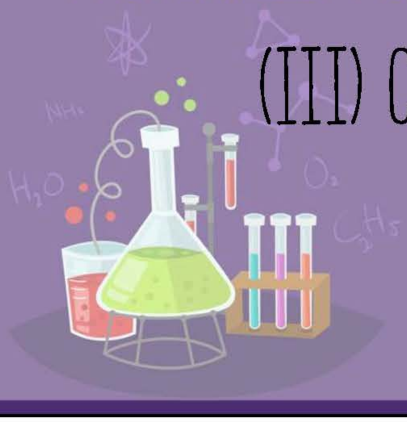
(+) tartaric acid

Path length:	1 dm	**Volume:**	25 mL
m (g):	5.035 g	**Temperature:**	20.6ºC
α measurements	2.561	2.560	2.564
α (average)	2.562	**$[\alpha]^{20}_{D}$**	+12.4

$$[\alpha]^{T}_{\lambda} = \frac{\alpha}{lc} = \frac{2.562}{1 \cdot \frac{5.035}{25}} = 12.73º$$

$$[\alpha]^{20}_{\lambda} = [\alpha]^{T}_{\lambda} \cdot [1 + 0.0001\,(T - 20) =$$
$$12.73 \cdot [1 + 0.0001\,(20.6 - 20)] = 12.73º$$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES



Group A3
Prof: M. Teresa Albelda

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

The aim of this practice is to synthesise and study (using IR) the following mononuclear complexes of cobalt (III) $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_6]Cl_3$, $[Co(ONO)(NH_3)_5]Cl_2$ and $[Co(NO_2)(NH_3)_5]Cl_2$.

Objectives:

1. To explore the reactivity of Co(III) complexes vs Co(II) complexes.
2. To investigate nitro- and nitrito- linkage isomerism in pentaamminecobalt(III)

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Preliminary questions:

1. Why does the general method for the synthesis of a Co(III) complex generally begin from Co(II) salts?

Because coordination compounds of Co(III) undergo ligand exchange very slowly compared with complexes of many other transition metal ions. This is why Co(III) complexes are considered inert, and therefore kinetically stable compounds. For example,

$$[Co(NH_3)_6]^{3+}_{(aq)} + 6H_3O^+_{(aq)} \rightarrow [Co(H_2O)_6]^{3+}_{(aq)} + 6NH^+_{4(aq)}$$

has an equilibrium constant of 10^{64}. The large equilibrium constant suggests that the complex ion $[Co(NH_3)_6]^{3+}$ is thermodynamically unstable. This reaction is highly thermodynamically favoured, yet the inert $[Co(NH_3)_6]^3$ complex ion lasts for weeks in acidic solutions because the rate of reaction is very slow.

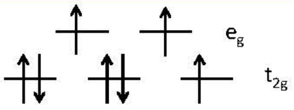
SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

On the contrary,

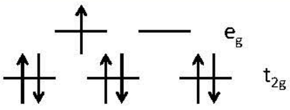
$$[Co(NH_3)_6]^{2+}_{(aq)} + 6H_3O^+_{(aq)} \rightarrow [Co(H_2O)_6]^{2+}_{(aq)} + 6NH^+_{4(aq)}$$

This reaction is virtually complete in a few seconds. The $[Co(NH_3)_6]^{2+}$ complex is thermodynamically unstable and labile. The inert complex has Co(III) while the labile one has Co(II). Both ammine complexes are octahedral, and in the case of Co(III), a d^6 species, the t_{2g} levels are filled. Co(II), on the other hand, has partially filled e_g orbitals.

Co(II) d^7

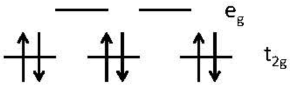


High spin complexes



Low spin complexes

Co(III) d^6



Low spin complexes

Crystal field stabilisation energy is highest for low-spin d^6 complexes, which accounts in part for the extraordinarily large number of Co(III) complexes known. These highly stabilised low spin Co(III) complexes are considered inert.

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

2. Is it possible to oxidise Co^{2+} (aq) with hydrogen peroxide?

If we take into consideration the standard potential of both couples:
E^0 (Co^{3+}/Co^{2+}) = 1.82V
E^0 (H_2O_2/H_2O) = 1.77V
Hydrogen peroxide cannot oxidise Co^{2+} to Co^{3+}. But, in our case we are considering the oxidation of Co(II) amminocomplexes. When hydrogen peroxide is added to an alkaline cobalt(II) solution, oxidation occurs to give cobalt(III) complexes. The air oxidation in an alkaline ammonia solution can also be effected via hydrogen peroxide giving the hexaamminecobalt(III) ion.

$$4[Co(NH_3)_6]^{2+}{}_{(aq)} + O_{2(g/aq)} + 4H^+{}_{(aq)} \Longrightarrow 4[Co(NH_3)_6]^{3+}{}_{(aq)} + 2H_2O_{(l)}$$

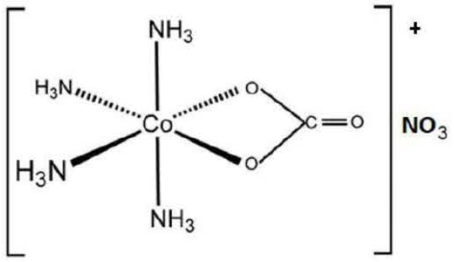
$$2[Co(NH_3)_6]^{2+}{}_{(aq)} + H_2O_{2(g/aq)} + 2H^+{}_{(aq)} \Longrightarrow 2[Co(NH_3)_6]^{3+}{}_{(aq)} + 2H_2O_{(l)}$$

$$+1.82V \text{ for } [Co(H_2O)_6]^{3+}{}_{(aq)} + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}{}_{(aq)}$$

$$+0.10V \text{ for } [Co(NH_3)_6]^{3+}{}_{(aq)} + e^- \rightleftharpoons [\ Co(NH_3)_6]^{2+}{}_{(aq)}$$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

3. How is the carbonate anion is coordinated with the metal ion?

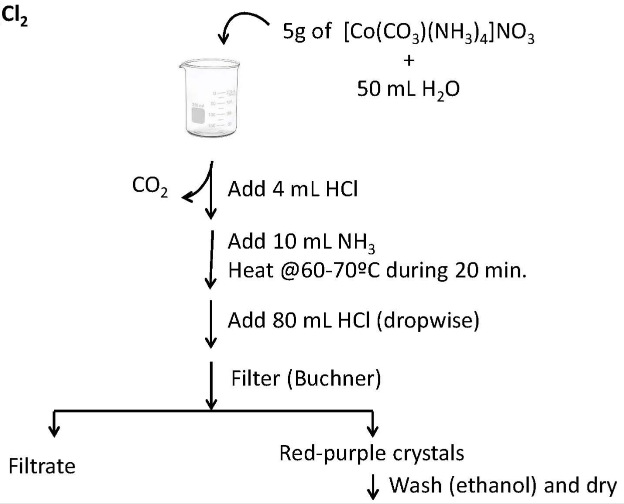


SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Experimental procedure

Synthesis of $[Co(NH_3)_5Cl]Cl_2$

(In fume hood)



5g of $[Co(CO_3)(NH_3)_4]NO_3$
+
50 mL H_2O

CO_2

Add 4 mL HCl

Add 10 mL NH_3
Heat @60-70ºC during 20 min.

Add 80 mL HCl (dropwise)

Filter (Buchner)

Filtrate

Red-purple crystals

Wash (ethanol) and dry

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

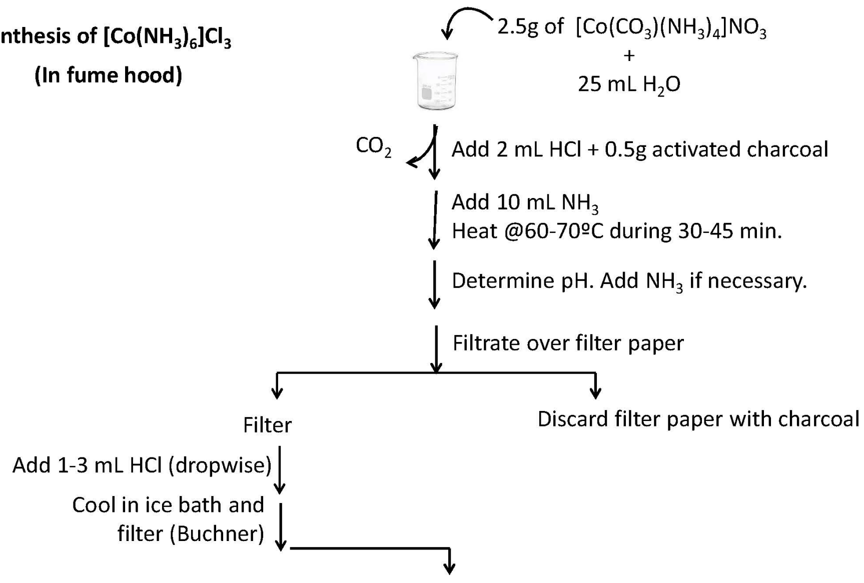
Starting material of $[Co(CO_3)(NH_3)_4]NO_3$

Different steps in the synthesis procedure

Final product $[Co(NH_3)_5Cl]Cl_2$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Synthesis of $[Co(NH_3)_6]Cl_3$
(In fume hood)



2.5g of $[Co(CO_3)(NH_3)_4]NO_3$
+
25 mL H_2O

CO_2

Add 2 mL HCl + 0.5g activated charcoal

Add 10 mL NH_3
Heat @60-70ºC during 30-45 min.

Determine pH. Add NH_3 if necessary.

Filtrate over filter paper

Filter

Discard filter paper with charcoal

Add 1-3 mL HCl (dropwise)

Cool in ice bath and
filter (Buchner)

Wash with 4M HCl and ethanol. Then dry.

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Starting material of
$[Co(CO_3)(NH_3)_4]NO_3$

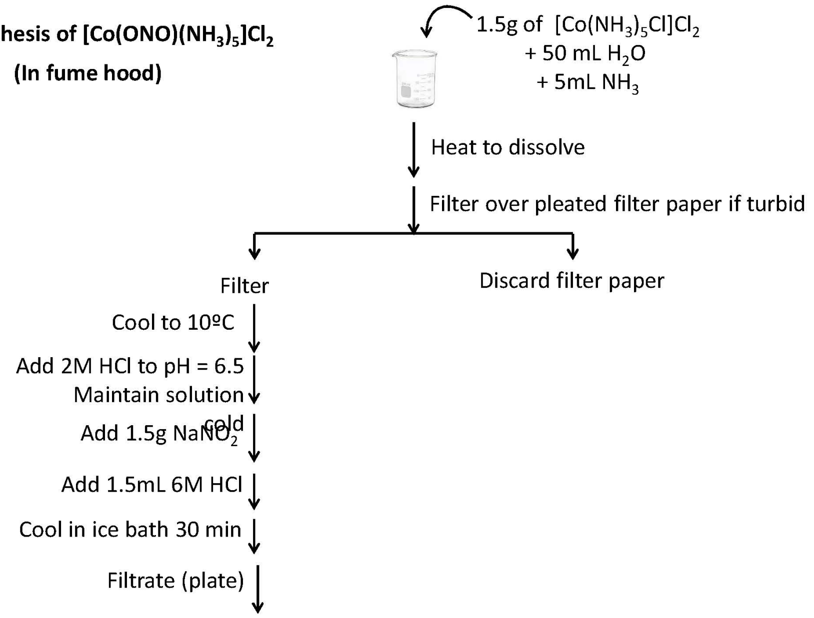
Colour of the solution during
synthesis procedure

Final product
$[Co(NH_3)_6]Cl_3$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Synthesis of $[Co(ONO)(NH_3)_5]Cl_2$

(In fume hood)



1.5g of $[Co(NH_3)_5Cl]Cl_2$
+ 50 mL H_2O
+ 5mL NH_3

Heat to dissolve

Filter over pleated filter paper if turbid

Filter

Discard filter paper

Cool to 10ºC

Add 2M HCl to pH = 6.5
Maintain solution cold

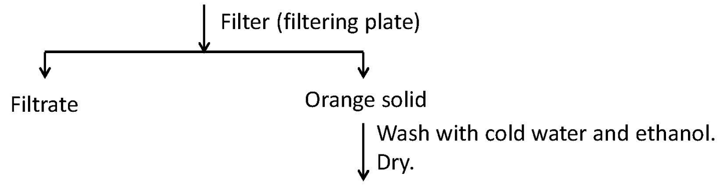
Add 1.5g $NaNO_2$

Add 1.5mL 6M HCl

Cool in ice bath 30 min

Filtrate (plate)

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES



Filter (filtering plate)

Filtrate

Orange solid

Wash with cold water and ethanol.
Dry.

Colour of the solution during synthesis procedure

Final product $[Co(ONO)(NH_3)_5]Cl_2$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Synthesis of $[Co(NO_2)(NH_3)_5]Cl_2$

(In fume hood)

1.5g of $[Co(ONO)(NH_3)_5]Cl_2$
+ 20 mL H_2O (warm)
+ 6-7 drops NH_3

↓ Cover with a watch glass

↓ Gently heat until colour change

↓ Cool in ice bath

↓ Add 10mL conc. HCl

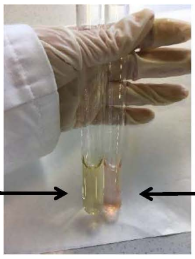
↓ Let solution crystalise and then filter (Buchner)

- Yellow solid
  - ↓ Wash with ethanol. Dry.
- Filtrate

Crystals $[Co(NO_2)(NH_3)_5]Cl_2$

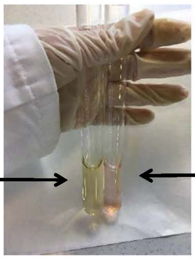
SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Isomers interconversion



Nitrite complex solution →

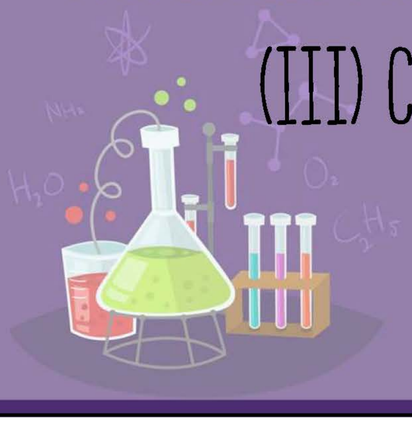
← Nitrite complex solution + heat in water bath



Nitrite complex solution →

← Nitrite complex solution + 4M HCl + irradiate UV light

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

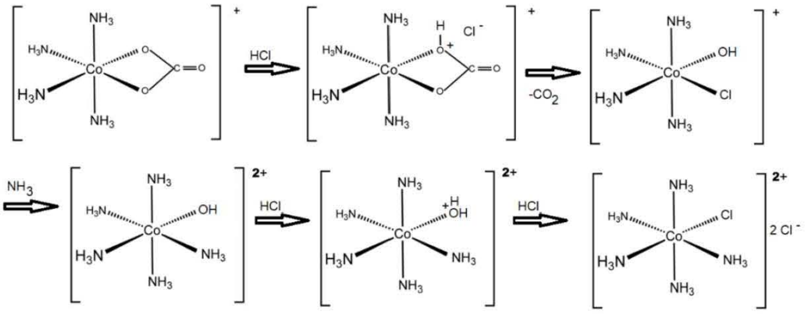


Group A3
Prof: M. Teresa Albelda

Additional questions

STEP A: SYNTHESIS OF $[Co(NH_3)_5Cl]Cl_2$

A-4 Write and adjust all the reactions that take place in this synthesis.



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Addition of HCl leads to the rupture of carbonate ligand, releasing CO_2 to the medium of reaction. Please, notice that the bonds that are broken are those from the carbonate molecule, not all metal-ligand bonds. The formation of a gas that is released favours the reaction to the right side. The coordination sphere of cobalt is composed of four ammonia ligands, one chloride and one hydroxyl group. This OH^- group is not a 'good leaving group'. That is the reason why we can only substitute chloride for ammonia when we add concentrated NH_3 to the solution. When we add HCl in the last step to obtain the precipitated complex, acidification transforms –OH into $–OH_2$ which is a 'good leaving group' enabling the entrance of one chloride ligand in the coordination sphere of cobalt.

Order of leaving groups:

Excellent Worst

$HCO_3^- >> NO_3^- > I^- \approx H_2O \approx Br^- > Cl^- \approx SO_4^- > SCN^- > F^- > CH3COO^- > NCS^- > NO_2 > NH_3 > OH^- > CN^-$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

$[Co(CO_3)(NH_3)_4]^+ + H^+ \rightarrow [Co(NH_3)_4(OH)(Cl)]^+$

$[Co(NH_3)_4(OH)(Cl)]^+ + NH_3 \rightarrow [Co(NH_3)_5(OH)]^{2+}$

$[Co(NH_3)_5(OH)]^{2+} + H^+ \rightarrow [Co(NH_3)_5(OH_2)]^{3+}$

$[Co(NH_3)_5(OH_2)]^{3+} + HCl \rightarrow [Co(NH_3)_5Cl]^{2+} + H_2O$

$[Co(NH_3)_5Cl]^{2+} + 2\,Cl^- \rightarrow [Co(NH_3)_5Cl]Cl_2$ (solid)

$[Co(CO_3)(NH_3)_4]^+ + HCl \rightarrow [Co(NH_3)_4(OH)Cl]^+ + CO_2\,(g)$

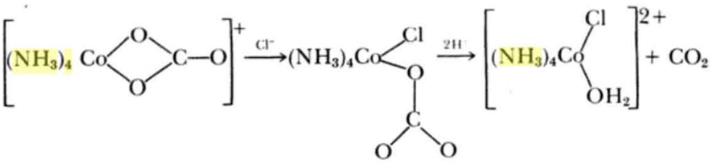
$[Co(NH_3)_4(OH)Cl]^+ + NH_3\,(aq) \rightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$

$[Co(NH_3)_5(OH)]^{2+} + 3HCl \rightarrow [Co(NH_3)_5Cl]Cl_2\,(s) + H_2O + 2H^+$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

A-5 If Co(III) complexes are inert for the ligand substitution, why is an instant release of CO_2 observed when the complex carbonate solution is acidified?

As was remarked previously, the bonds that are broken are those from the carbonate molecule, not metal-ligand bonds, that explains the rapid gas formation. The most probable mechanism which is proposed for this step is the following:



The fact that the rupture of the O-C bond occurs in the intermediate has been established using ^{18}O isotopic exchange reactions in different carbonate complexes.

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

A-6 Why is there only one additional ligand of NH_3 in the coordination sphere of the metal?

As it was remarked previously, after the acidification of the carbonate complex, the complex that is present in solution is $[Co(NH_3)_4(OH)Cl]^+$.
This OH^- group is not a 'good leaving group'. That is why we only can substitute chloride for ammonia when we add concentrated NH_3 to the solution.

$$[Co(NH_3)_4(OH)Cl]^+ + NH_3\ (aq) \rightarrow [Co(NH_3)_5(OH)]^{2+} + Cl^-$$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

STEP B: SYNTHESIS OF $[Co(NH_3)_6]Cl_3$

B-1 What is the role of activated charcoal in this synthesis?

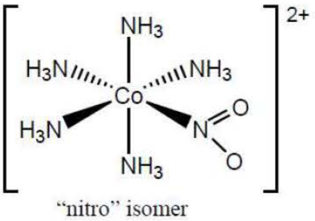
The activated charcoal increases the speed of the reaction by helping in the formation of the bonds between Co and NH_3. Thus it is used to increase the reaction of the ligand exchange. The charcoal is made from finely divided carbon sheets that provide a large surface area. The holes on the surface of the charcoal are used to enable the reaction of the ligand exchange to take place.
Moreover, activated charcoal helps to remove excess of NO_3^- to avoid precipitation of $[Co(NH_3)_6]NO_3$.

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

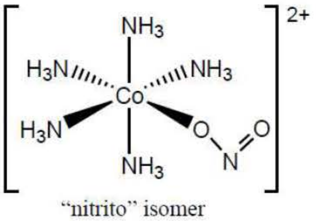
STEP C: SYNTHESIS OF $[Co(ONO)(NH_3)_5]Cl_2$

C-1 Which of the two isomers is more stable?

Linkage isomerism involves ligands that are capable of bonding through one type of atom in one situation and another type of atom in a different situation. The nitrite ligand can link to metals through the N atom (‘nitro’ complexes) or the O atom (‘nitrito’ complexes). The ‘nitro’ complex is more stable. Thus, the nitrito isomer is less stable, and can be converted to the nitro isomer slowly by standing at room temperature, or quickly by heating or adding HCl to a solution containing the nitrito compound or using UV light.



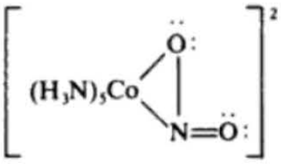
“nitro” isomer



“nitrito” isomer

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

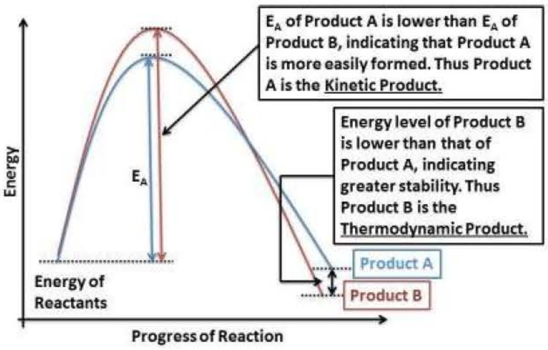
Transformation of nitrito isomer into nitro isomer probably takes place *via* this heptacoordinated intermediate.



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

C-2 Why the nitrite complex is obtained first?

Because the complex that is obtained first is the kinetic product; the reaction takes place with low activation energy. Nitrite complex is easily formed following probability and statistics. Since the molecule O-N-O has two atoms of oxygen and only one atom of nitrogen, it is more likely to bind the metal centre using an oxygen atom than using nitrogen.



E_A of Product A is lower than E_A of Product B, indicating that Product A is more easily formed. Thus Product A is the <u>Kinetic Product.</u>

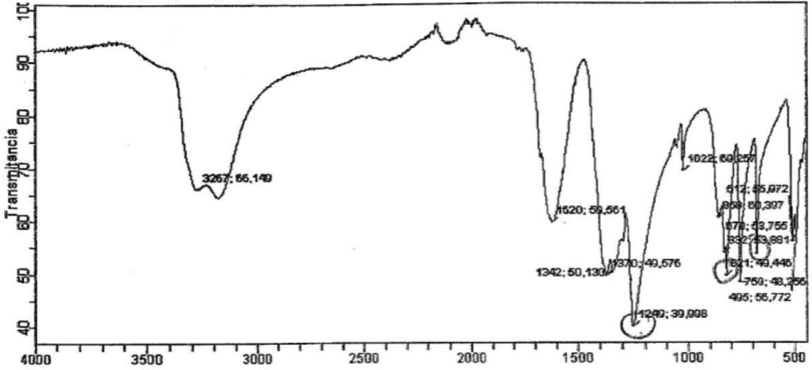
Energy level of Product B is lower than that of Product A, indicating greater stability. Thus Product B is the <u>Thermodynamic Product.</u>

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

STEP D: IR CHARACTERISATION

D-1 Assign the peaks corresponding to the ligands in the different complexes

IR spectrum of $[Co(CO_3)(NH_3)_4]^+$



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

3267 cm^{-1} : Stretching vibration N-H

1620 cm^{-1} : Antisymmetric stretching C=O

1370 cm^{-1} : Stretching N-O

1342 cm^{-1} : Rocking vibration N-H

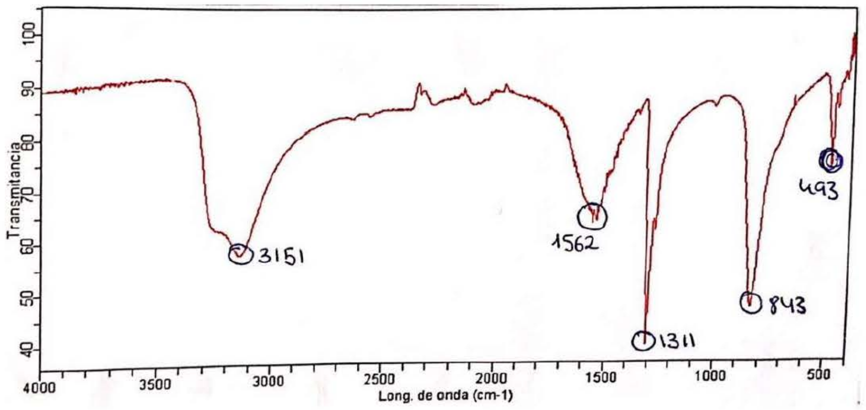
1249 cm^{-1} : Symmetric stretching C=O

821 cm^{-1} : Stretching CO_3 out of plane

679 cm^{-1} : Rocking vibration CO_3 in the plane

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

IR spectrum of $[Co(NH_3)_5Cl]Cl_2$



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

3151 cm^{-1} : Antisymmetric stretching N-H

1562 cm^{-1} : Degenerated deformation vibration NH_3

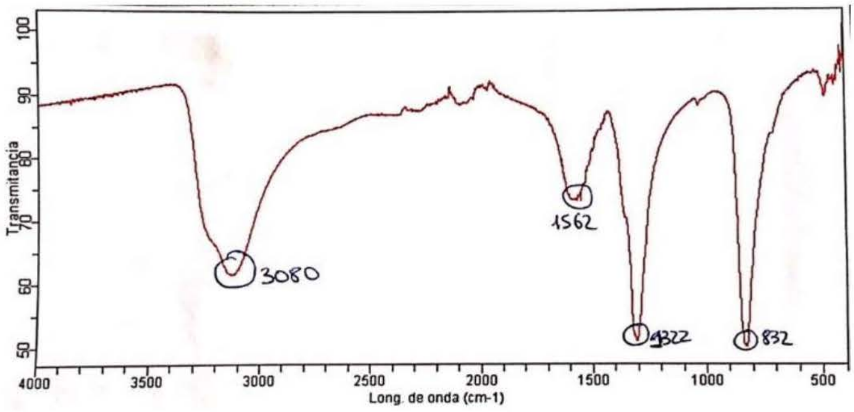
1311 cm^{-1} : Rocking vibration N-H

832 cm^{-1} : Symmetric deformation vibration N-H and vibration Co-Cl

493 cm^{-1} : Stretching vibration Co-NH_3

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

IR spectrum of $[Co(NH_3)_6]Cl_3$



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

3080 cm^{-1} : Antisymmetric stretching N-H

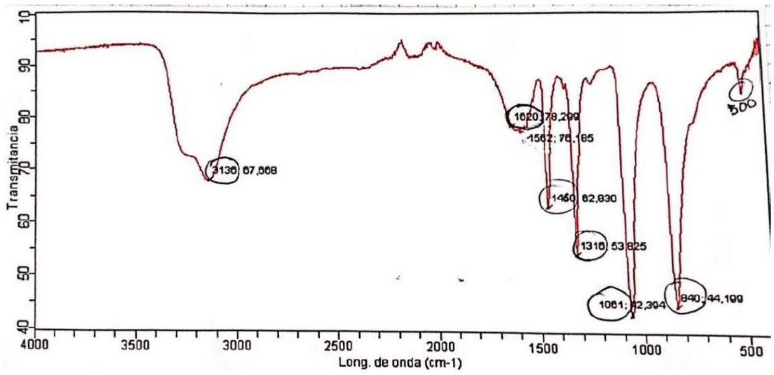
1562 cm^{-1} : Degenerated deformation vibration NH_3

1322 cm^{-1} : Rocking vibration N-H

832 cm^{-1} : Symmetric deformation vibration N-H and vibration Co-Cl

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

IR spectrum of $[Co(ONO)(NH_3)_5]Cl_3$



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

3136 cm^{-1} : Antisymmetric stretching vibration N-H

1620 cm^{-1} : Degenerated deformation vibration NH_3

1460 cm^{-1} : Antisymmetric vibration N=O

1316 cm^{-1} : Rocking vibration N-H

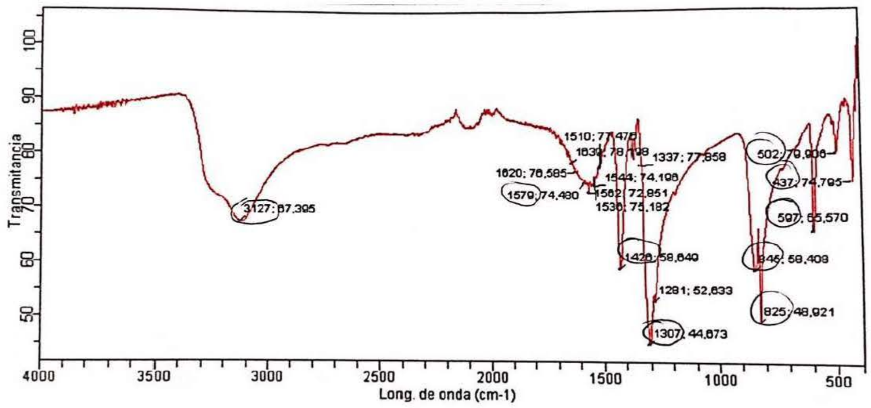
1061 cm^{-1} : Symmetric stretching vibration N-O

840 cm^{-1} : Bending NH_3

500 cm^{-1} : Stretching vibration $Co-NH_3$

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

IR spectrum of $[Co(NO_2)(NH_3)_5]Cl_3$



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

3127 cm^{-1} : Antisymmetric stretching vibration N-H

1579 cm^{-1} : Degenerated deformation vibration NH_3

1426 cm^{-1} : Antisymmetric vibration N=O

1307 cm^{-1} : Rocking vibration N-H

845 cm^{-1} : Bending NH_3

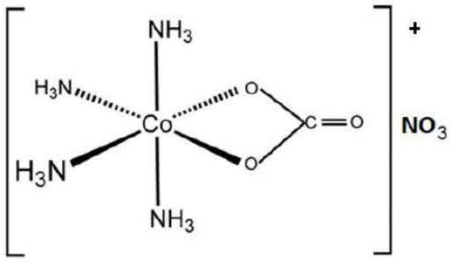
825 cm^{-1} : Wagging NO_2

502 cm^{-1} : Stretching vibration Co-NH_3

473 cm^{-1} : Deformation vibration Co-NO_2

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

D-2 In the case of the carbonate complex, indicate which is the preferred mode of coordination.



SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

D-3 Compare the spectra of the complexes containing nitro and nitrite ligands and indicate the differences between them.

Complex	Antisymmetric stretching NO	Symmetric stretching NO	Bending NO_2	Wagging NO_2	Stretching Co-N
$[Co(NO_2)(NH_3)_5]Cl_3$	1428 cm^{-1}	1310 cm^{-1}	824 cm^{-1}	594 cm^{-1}	499 cm^{-1}
$[Co(ONO)(NH_3)_5]Cl_3$	1468 cm^{-1}	1065 cm^{-1}	825 cm^{-1}	-	-

SYNTHESIS AND STUDY OF SOME PROPERTIES FOR SEVERAL COBALT (III) COMPLEXES

Additional Information

I- < Br- < SCN- < Cl- < F- ≤ OH- , ONO- < OH_2 < NCS- < $NCCH_3$ < NH_3 , py < NO2- < CN- , NO , CO.

Ligands that produce a small Δ are called weak-field ligands and are on the left end of the series. Ligands that produce a large Δ are called strong-field ligands and are on the right end of the series.

Assuming the above series to be correct (since the spectrochemical series in not an absolute ordering of ligands) the observed order in the series varies somewhat from one complex to another.

I have found in most of the articles that the strong field ligands start from CO and generally go up to NH_3 or (up to NCS-. But from NH_3 to NCS- they are not as strong as the above mentioned).

The weak field ligands start from H_20 and go to I-.

Strong: NCS- < $NCCH_3$ < NH_3 , py < NO2- < CN- , NO , CO.

Weak: I- < Br- < SCN- < Cl- < F- ≤ OH- , ONO- < OH_2