

# Some Experiments for M. Sc in Inorganic Chemistry

COMPILED BY:

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## Course Name: Inorganic Chemistry Laboratory

- Expt. No. 1:** Study of a redox reaction: Standardization of potassium permanganate by oxalic acid
- Expt. No. 2:** Metal ion estimation: Quantitative estimation of copper (II), calcium (II) and chloride in a mixture
- Expt. No.3:** Colorimetry: Simultaneous determination of chromium and manganese in a solution by visible spectroscopy.
- Expt. No.4:** Co-ordination complex: Synthesis and characterization of potassium tris-oxalato chromate (III) trihydrate
- Expt. No.5:** Solid phase synthesis of *trans*-bis glycinato copper(II).
- Expt. No.6:** Synthesis and characterization of *tris*-triphenylphosphine copper(I) nitrate
- Expt. No.7:** Ligand synthesis for multimetal complex: Preparation of *bis*-(N,N-disalicylidene ethylenediamine)  $\mu$ -aquo-dicobalt
- Expt. No.8:** Non-metal complex: Synthesis and characterization of bis-pyridine iodide nitrate
- Expt. No.9:** Synthesis of penta amminechlorocobalt(III)chloride
- Expt. No.10:** Preparation of tetrabutylammoniumoctamolybdate(VI) .
- Expt. No.11:** Preparation of tris-acetylacetonato iron (III).
- Expt. No.12:** Nano-chemistry: Preparation of manganese dioxide nanoparticles
- Expt. No.13:** Synthesis of copper (II) complex of 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclo tetra deca-4, 1, 1-dinene with perchloric acid
- Expt. No.14:** Preparation of *cis* and *trans*-dichloro bis (ethylenediamine) cobalt (III) chloride
- Expt. No.15:** Preparation of *bis*-(diisopropylamine) chloro phosphate
- Expt. No.16:** Preparation of bis-dichlorotriphenyl phosphine nickel (II)
- Expt. No.17:** Synthesis of hexaammine cobalt(III) chloride
- Expt. No.18:** Preparation of potassium *bis*(peroxo)-oxo- (1, 10-phenanthroline) vanadium (V) trihydrate
- Expt. No.19:** Preparation of tetra-butylammoniumhexa molybdate (VI)

## Experiment No.1

### Standardization of potassium permanganate by oxalic acid:

Commercially available potassium permanganate generally contains impurity. Thus it cannot be used as a primary standard. In order to make standard potassium permanganate solution it requires standardized by a primary standard.

Equivalent weight of  $\text{KMnO}_4 = [ 2 \text{KMnO}_4 / 10 ] = 31.61$ , which is derived from the equation



### Preparation of potassium permanganate:

Weigh potassium permanganate (3-3.2 g) with an ordinary balance. Take the weighed potassium permanganate in a beaker (250 ml). Add distilled water (100 ml); cover the beaker with a watch glass, heat the solution to boiling, and allow it to cool to the room temperature. Filter the solution through a funnel containing glass wool. The filtered solution should be stored in a stopper clean; glass bottle. The solution should be stored in the dark except when in use.

### Standardization:

1. Rinse a clean burette (50 ml) thrice with 5 ml portions of the potassium permanganate solution. Fill up the burette with potassium permanganate solution up to the zero mark, note the upper meniscus. Examine that the jet of the burette is completely filled with the solution and no air bubble is left behind.
2. Prepare a solution of sulphuric acid (1:2): Add conc. sulphuric acid (10 ml) to water (10 ml) with stirring and cooling if necessary.

**Precautions:** Heat is evolved during mixing so care is to be taken. (Discuss with laboratory staff or supervisor)

3. Pipette out standard oxalic acid (0.1M, 10 ml) into a beaker (250 ml). Add sulphuric acid (1: 2 in water, 10-15 ml) and then add boiling water to dilute it to about 100 ml. Now titrate the solution with potassium permanganate solution. At first add potassium permanganate solution small quantities at a time with stirring; the pink color of potassium permanganate will take some time to discharge its colour at the beginning. So initial addition should be very slow. When some potassium permanganate solution has been added, the pink color will be discharged quickly. Now add potassium permanganate solution more quickly with stirring. Near the end point when the rate of disappearance of the pink color slows down, add potassium permanganate solution drop wise with stirring until with one drop makes the whole solution pink. (The pink color persists for 30 seconds, after which the color may be discharged again).
4. Note the volume of potassium permanganate solution added. Repeat the operation thrice.

### Calculations:

Let volume of  $\text{KMnO}_4$  solution =  $V_1$  ml, Strength of oxalic acid =  $S_1$  (N)

Therefore, strength of  $\text{KMnO}_4$  solution =  $(10 \times S_1) / V_1$  (N)

## Experiment No.2

### Quantitative estimation of copper (II), calcium (II) and chloride from a mixture:

In this experiment the chloride ion is separated by precipitation with silver nitrate and estimated. Whereas copper(II) is estimated by iodometric titration and Calcium by complexometric titration

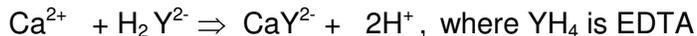
#### Iodometric estimation of copper (II):

Copper solution oxidizes potassium iodide and liberates iodine; liberated iodine is estimated by sodium thiosulphate. The reactions involved are:



#### Complexometric estimation of calcium (II):

During the complexometric titration of calcium (II), copper (II) ion can interfere if eriochrome black-T indicator is used. So copper (II) is reduced to copper (I) by using hydrazine hydrate and precipitated as copper thiocyanate by using ammonium thiocyanate. A calcium (II) ion is then titrated with ethylene diamine tetraacetic acid (EDTA).



No sharp end point can be obtained for calcium (II) with eriochrome black-T indicator, so small amount of Mg-YH<sub>2</sub> should be added to get a sharp end point.

#### Gravimetric estimation of chloride:

Chloride can be estimated gravimetrically by precipitating it as silver chloride. An aqueous solution of chloride is generally acidified with dilute nitric acid to prevent precipitation of other silver salts.



#### Requirements:

1. Stock solution of Cu<sup>2+</sup>, Ca<sup>2+</sup> and Cl<sup>-</sup> ions.
2. Sodium thiosulphate
3. Starch solution
4. Potassium iodide
5. Eriochrome Black-T
6. Nitric acid
7. Ammonium thiocyanate
8. Ethylene diamine tetra acetic acid
9. Hydrazine hydrate
10. Ammonia buffer
11. Silver nitrate

#### Procedure:

##### Estimation of copper (II):

Take stock solution (25 ml) in a conical flask (250 ml) and add potassium iodide (1 g) to it. Iodine is liberated in the solution. Titrate the liberated iodine with standard sodium thiosulphate solution (0.1 M).

### Estimation of calcium (II):

Take stock solution (25 ml) in a conical flask (250 ml). Add hydrazine hydrate (1 drop), a colourless solution will be observed. To this, add a solution of ammonium thiocyanate or potassium thiocyanate (10%, 5 ml) and filter the white precipitate. Take the filtrate in a conical flask and add ammonia-ammonium chloride buffer solution (2 ml, pH=10) and add Mg-EDTA (1 ml) to the filtrate. Titrate the solution with standard EDTA (0.01 M solution) using eriochrome black-T indicator. Calculate the amount of calcium in wt / lit and also express it as ppm.

### Estimation of chloride:

Take stock solution (25 ml) in a conical flask. Acidify the solution with dilute nitric acid (1M, 10 ml), and then add silver nitrate solution (0.2 g / ml water). This will give a white precipitate of silver chloride. Filter the precipitate in a preweighed crucible. Place the crucible along with the precipitate in an oven (~ 50°C) for 1hr after that cool the crucible to room temperature and weigh. Repeat the process of heating and weighing till constant weigh is obtained. Find out the weigh of silver chloride formed and find out the amount of silver.

## Experiment No.3

### Simultaneous determination of chromium and manganese in a solution by visible spectroscopy:

This experiment is concerned with the simultaneous spectro-photometric determination of two solutes in a solution. The absorbance's are additive, provided there is no reaction between the two solutes. Hence we may write

$$A_{\lambda_1} = \lambda_1 A_1 + \lambda_1 A_2 \quad (1) \quad \text{and} \quad A_{\lambda_2} = \lambda_2 A_1 + \lambda_2 A_2 \quad (2)$$

Where  $A_1$  and  $A_2$  are the measured absorbances at the two wavelengths  $\lambda_1$  and  $\lambda_2$ ; the subscripts 1 and 2 refer to the two different substances, and the subscripts  $\lambda_1$  and  $\lambda_2$  refer to the different wavelengths. The wavelengths are selected to coincide with the absorption maxima of the two solutes; the absorption spectra of the two solutes should not overlap appreciably, so that substance 1 absorbs strongly at wavelength  $\lambda_1$  and weakly at wavelength  $\lambda_2$ , and substance 2 absorbs strongly at  $\lambda_2$  and weakly at  $\lambda_1$ . Now  $A = \epsilon c l$ , where  $\epsilon$  is the molar absorption coefficient at any particular wavelength,  $c$  is the concentration ( mol L<sup>-1</sup> ) and  $l$  is the thickness, or length, of the absorbing solution (cm). If we set  $l = 1$  cm then

$$A_{\lambda_1} = \lambda_1 \epsilon_1 c_1 + \lambda_1 \epsilon_2 c_2 \quad (3) \quad \text{and} \quad A_{\lambda_2} = \lambda_2 \epsilon_1 c_1 + \lambda_2 \epsilon_2 c_2 \quad (4)$$

Solutions of the these simultaneous equations gives

$$c_1 = (\lambda_2 \epsilon_2 A_{\lambda_1} - \lambda_1 \epsilon_2 A_{\lambda_2}) / (\lambda_1 \epsilon_1 \lambda_2 \epsilon_2 - \lambda_1 \epsilon_2 \lambda_2 \epsilon_1) \quad (5)$$

$$c_2 = (\lambda_1 \epsilon_1 A_{\lambda_2} - \lambda_2 \epsilon_1 A_{\lambda_1}) / (\lambda_1 \epsilon_1 \lambda_2 \epsilon_2 - \lambda_1 \epsilon_2 \lambda_2 \epsilon_1) \quad (6)$$

The values of molar absorption coefficients  $\epsilon_1$  and  $\epsilon_2$  can be deduced from measurements of the absorbances of pure solutions of substances 1 and 2. By measuring absorbance of the mixture at wavelengths  $\lambda_1$  &  $\lambda_2$ , the concentrations of the two components can be calculated.

**Requirements:**

1. 0.001 M, 0.0005 M and 0.00025 M solutions of potassium dichromate (in 1 M sulphuric acid and 0.7 M phosphoric acid)
2. 0.001 M, 0.0005 M and 0.00025 M solutions of potassium permanganate (in 1 M sulphuric acid and 0.7 M phosphoric acid)

**Procedure:**

1. Prepare a series of solutions: Potassium dichromate 0.001 M, 0.0005 M and 0.00025 M in mixed solvent of sulphuric acid (1 M) and phosphoric acid (0.7 M).
2. Prepare a series of solutions: Potassium permanganate 0.001M, 0.0005 M and 0.00025 M in sulphuric acid (1 M) and phosphoric acid (0.7 M).
3. Measure the absorbance A for each of the three solutions of potassium dichromate and also each of the three solutions of potassium permanganate at both 440 nm and 545 nm by taking 1ml solution each. Calculate  $\epsilon$  in each case by  $A = \epsilon cl$  and record the mean values for dichromate (2) and permanganate (1) at the two wavelengths.
4. Mix potassium dichromate (0.001 M) and potassium permanganate (0.0005 M) in the following amounts shown in table 1 in 100 ml beakers. In each case total volume of solution should be 50 ml. To each of these solutions add 1.0 ml of concentrated sulphuric acid, (a set of typical results included in table I for guidance). Measure the absorbance of each of the mixtures at 440 nm. Calculate the absorbance of the mixtures from

$$A_{440} = 440 \epsilon_{Cr} C_{Cr} + 440 \epsilon_{Mn} C_{Mn}$$

$$A_{545} = 545 \epsilon_{Cr} C_{Cr} + 545 \epsilon_{Mn} C_{Mn}$$

Preparation of mixture of solutions:

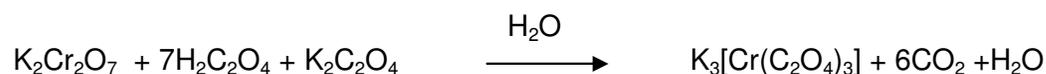
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> solution (mL)	KMnO <sub>4</sub> solution (mL)	Absorbance (observed)	Absorbance (calculated)
50	0		
45	5		
40	10		
35	15		
25	25		
15	35		
5	45		
0	50		

5. Record the absorbance of the unknown solution (supplied) at 545nm and 440 nm. Calculate the concentrations of permanganate and dichromate in this solution.

### Experiment No.4

#### Synthesis and characterization of potassium tris oxalato chromate (III) trihydrate:

The experiment is based on the following equation:



#### Requirements:

- |                                  |                           |                          |
|----------------------------------|---------------------------|--------------------------|
| 1. Potassium dichromate          | 6. Sodium hydroxide       | 11. Sulphuric acid       |
| 2. Potassium oxalate monohydrate | 7. Potassium permanganate | 12. Silver nitrate       |
| 4. Oxalic acid dihydrate         | 8. Oxalic acid            | 13. Ammonium persulphate |
| 5. Potassium iodide              | 10. Starch solution       | 14. Sodium thiosulphate  |

#### Procedure:

Make a solution of potassium oxalate monohydrate (2.3 g, 12.5 mmol) and oxalic acid dihydrate (5.5 g, 43.6 mmol) in water (110-120 ml). To this solution add solid potassium dichromate (1.9 g, 6.45 mmol) in small portions with constant stirring. Concentrate the solution nearly to dryness. On cooling deep green shiny crystals of potassium tris-oxalato chromium (III) trihydrate will be formed. Filter the solid and dry by pressing between filter paper.

#### Tasks:

- |                            |   |
|----------------------------|---|
| 1. Calculate percent yield | 4. Find out the molar conductance in water  |
| 2. Estimate chromium       | 5. Record the visible spectra and interpret |
| 3. Estimate oxalate        | 6. Record IR spectra and interpret          |

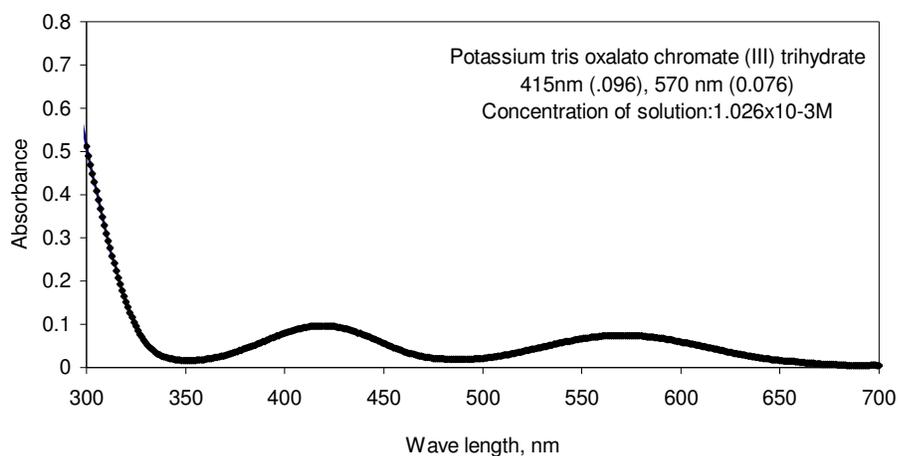
#### Estimation of chromium:

Dissolve an accurately weighed sample (in the range 0.10 – 0.15 g) of the complex in distilled water (100 ml). To this add sulphuric acid (5N, 5 ml), ammonium persulfate (~1 g) and silver nitrate solution (0.1M, 0.1 ml). Heat the solution under boiling condition for half an hour and the color of the solution is orange yellow at this stage. Cool the solution to room temperature and estimate the chromium iodometrically.

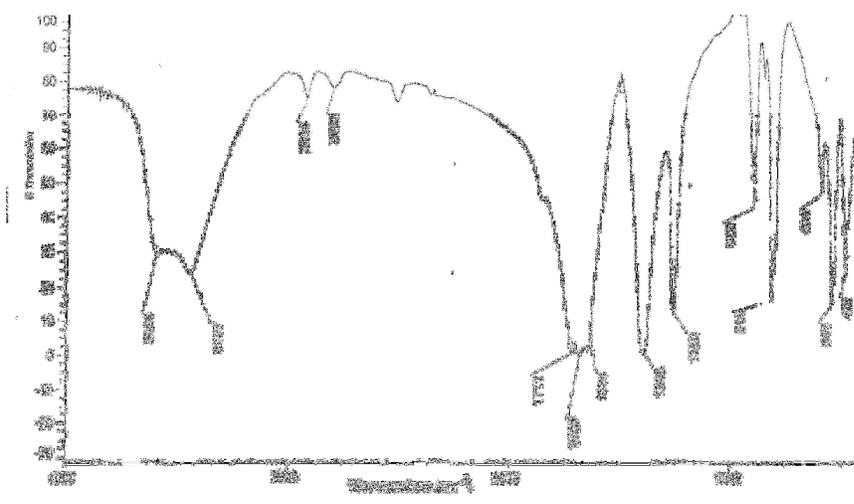
### Estimation of oxalate:

Dissolve an accurately weighed sample (in the range 0.10 – 0.15 g) of the complex in of distilled water. Warm the solution after adding sulphuric acid (5N, 3 ml) and then carefully add dilute sodium hydroxide solution (50-70 ml) (in the initial stage use a concentrated solution and at the near neutral point use a dilute solution) until no more precipitation of the hydrated chromium oxide is observed (excess use of alkali should be avoided). Digest the solution hot, filter, and wash thoroughly with enough water. Combine the filtrate and washings, acidify with sulphuric acid (5N, 15 ml), warm to 70°C and then titrate with standard potassium permanganate solution. (**Two sets of experiments should be conducted simultaneously**).

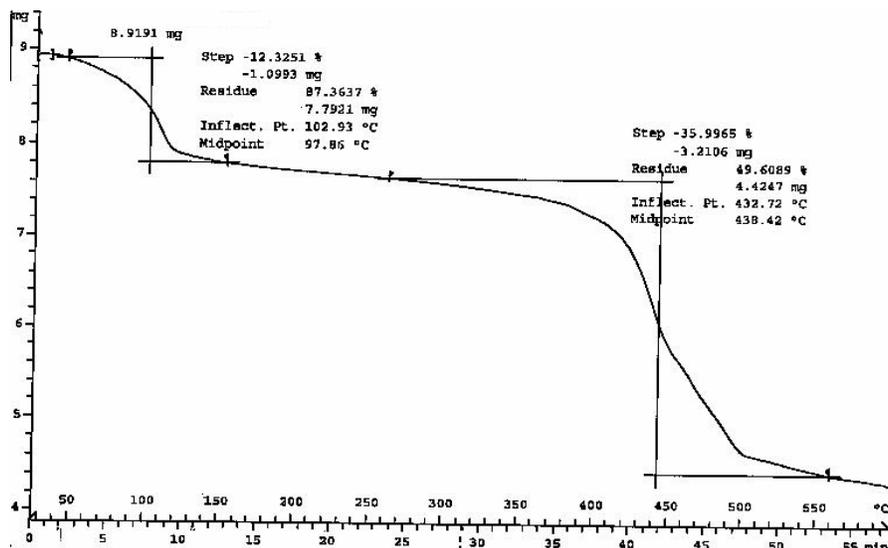
### UV-Visible spectra (MeOH) of potassium tris oxalato chromate (III) trihydrate



### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of potassium tris oxalato chromate (III) trihydrate



## Thermogram (10<sup>0</sup>C / min) of potassium tris oxalato chromate (III) trihydrate



### Experiment No.5

#### Solid phase synthesis of *trans*- bis glycinato copper (II):

##### Requirements:

1. Copper(II)acetate monohydrate
2. Glycine
3. Methanol / Ethanol
4. Diethyl ether
5. Sodium thiosulphate
5. Potassium iodide

##### Procedure:

Mix accurately weighed amount of copper (II) acetate monohydrate (2 g, 10 mmol) and glycine (2 g, 26.64 mmol) in an agate mortar at room temperature. Grind the mixture thoroughly in the mortar. Transfer the paste to a watch glass and leave it for 2 hrs. The colour of the mixture will change from green to pale blue. In 2 hrs, all the reactants will be exhausted. Wash the product with alcohol followed by ether and dry it in vacuum.

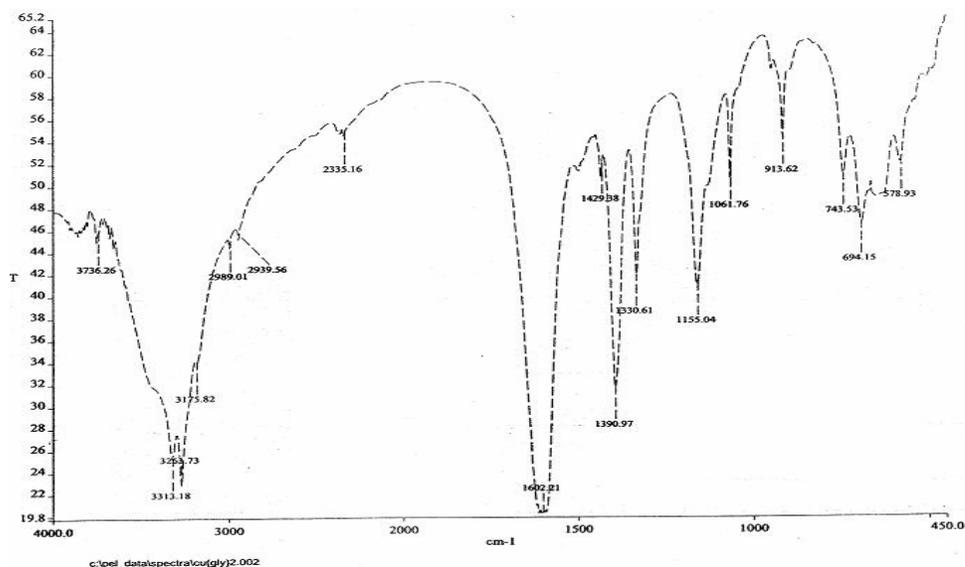
##### Tasks:

1. Calculate percentage yield
1. Estimate copper
2. Find out the molar conductance in water
1. Record the IR spectra of glycine and the complex and interpret.

##### Estimation of copper:

Decompose an accurately weighed ( 0.10 - 0.15 g ) copper complex in sulphuric acid (1M). The resulting solution contains aqueous-copper sulphate, estimate copper iodometrically.

## FT-IR Spectra (KBr, $\text{cm}^{-1}$ ) of *trans*- bis glycinato copper (II)



### Experiment No.6

#### Synthesis and characterization of *tris*-triphenylphosphine copper (I) nitrate:

##### Requirements:

1. Copper (II)nitrate pentahydrate
2. Ethanol
3. Triphenyl phosphine
4. Nitric acid
5. Sodium hydroxide
6. Sulphuric acid
7. Sodium thiosulphate
8. Potassium iodide
9. Starch

##### Procedure:

Dissolve a solution of copper (II) nitrate trihydrate ( 0.365 g, 1.5 mmol) in minimum amount of ethanol and in another beaker dissolve triphenylphosphine ( 1.965 g, 7.5 mmol) in 30 ml ethanol (warm the solution to dissolve). Mix the two solutions, reflux for half an hour and cool. Filter the white crystalline solid and wash with ethanol. (If necessary recrystallize from methanol)

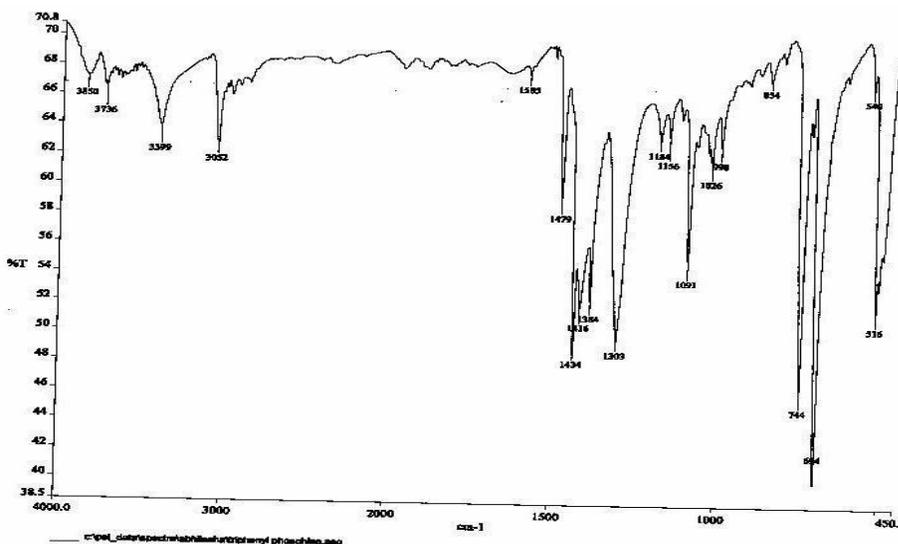
##### Tasks:

1. Calculate percent yield
2. Estimate copper
3. Record the IR spectra of the complex and interpret.

## Estimation of copper:

Decompose an accurately weighed (0.10 - 0.15 g) copper complex, by heating with minimum volume of concentrated nitric acid. To the resulting oily mass, add water and filter. Treat the filtrate with dilute alkali to precipitate copper hydroxide. Filter solution and reject the mother liquor. Wash copper hydroxide with water and dissolve it with dilute sulphuric acid (10 ml, 1M). The resulting solution contains aqueous-Copper sulphate, estimate copper iodometrically.

## FT-IR Spectra (KBr, $\text{cm}^{-1}$ ) of *tris*-triphenylphosphine copper (I) nitrate



## Experiment No.7

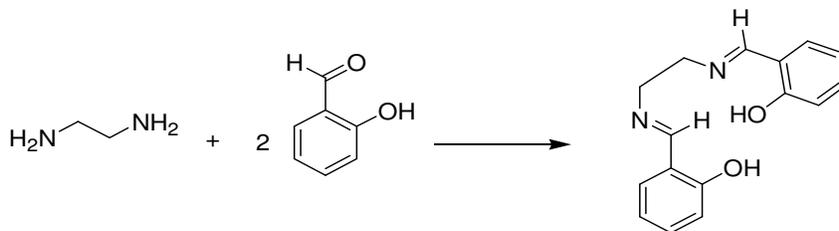
### Preparation of bis(N, N' disalicylaldehyde)- $\mu$ - aquadacobalt (II):

#### Requirements:

1. Salicylaldehyde
2. Cobalt (II) chloride hexahydrate
3. Ethanol
4. 1-nitroso-2 naphthol
5. Ethylene diamine
6. Acetic acid
7. Methanol
8. Hydrochloric acid
9. Hydrogen peroxide
10. Sodium acetate trihydrate
11. Sodium hydroxide
12. Bis-(N, N' disalicylidene ethylene diamine)

### Preparation of bis-(N,N-disalicylidene ethylenediamine):

The preparation of bis-(N,N-disalicylidene ethylenediamine) is based on the following equation:



**Procedure:**

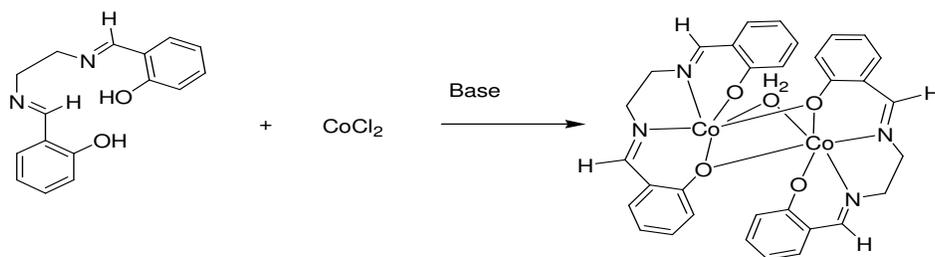
Dissolve salicylaldehyde (3.05 g, 0.025 mol) in ethanol (25 ml) in a round bottom flask. Heat the solution to  $\sim 70^{\circ}\text{C}$  and add a solution of ethylenediamine (0.75 g, 0.0125 mol) dissolved in ethanol (3 ml). Heat the resulting yellow solution under reflux for 30 mins. Reduce the volume of the solution to half by evaporating the solvent and after cooling, filter the yellow crystalline precipitate under suction and wash with ice-cold ethanol. Recrystallize the product from methanol and dry at room temperature under vacuum. Determine the melting point and calculate the percent yield.

**Tasks:**

1. Calculate the percent yield
2. Determine the melting point
3. Record and interpret the IR spectra
4. Record and interpret the nmr spectra

**Preparation of bis(N, N' disalicylaethylene-diamine)- $\mu$ - aquadnicobalt(II):**

The preparation of bis (N, N' disalicylaethylene-diamine)- $\mu$ - aquadnicobalt (II) is based on the following equation:

**Procedure:**

Dissolve finely ground N,N'-disalicylidene ethylenediamine (1.34 g) in water (150 ml) and to this solution add sodium hydroxide (3.9 g) and sodium acetate trihydrate (5 g). Continue stirring for 10-15 minutes. While stirring is continued add a solution of cobalt (II) chloride hexahydrate (1.23 g) dissolved in hot water (25 ml). Stir the reaction mixture until it turns to a reddish-brown paste. Allow the reaction mixture to stand for at least 15 minutes. Centrifuge the reaction mixture until most of the mother liquor has been removed and a hard cake remains. Wash the precipitate three times with water (each time with about 10 ml of water). Remove the cake from the centrifuge tube and mix thoroughly with water (75 ml) so that no large particles remain and uniform slurry is obtained. The cake is further centrifuged as dry as possible. It is then broken into small pieces and dried at  $100^{\circ}\text{C}$  under reduced pressure.

## Tasks:

1. Calculate the percent yield.
2. Record the IR spectra.
3. Measure the molar conductivity

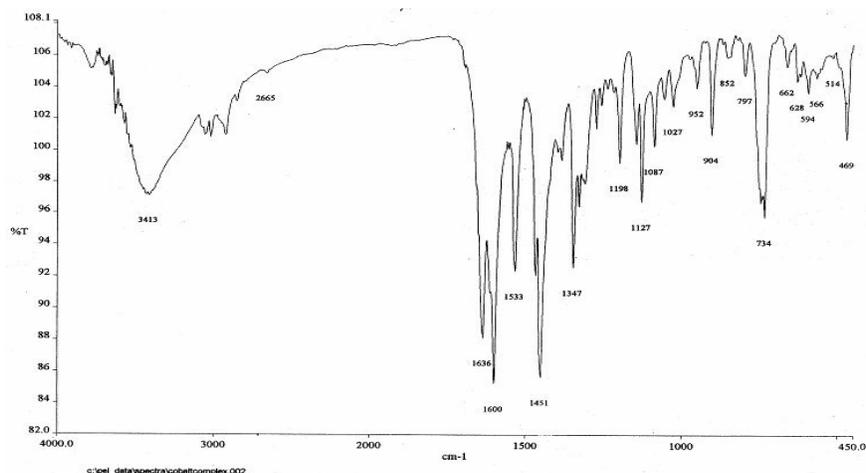
## Estimation of cobalt:

Take an accurately weighed amount (range 0.1 to 0.2 g) of the cobalt (II) complex in minimum amount of hot dilute hydrochloric acid (1:1). Treat the solution with sodium hydroxide (5%) in order to get cobalt (II) hydroxide. Use of excess alkali is to be avoided. Centrifuge the precipitate and wash carefully with distilled water. Filter the precipitate and oxidize it to cobalt (III) by treating with a small amount of hydrogen peroxide (1 ml, 30% v/v) solution. Remove the excess peroxide by boiling for nearly 30 min. Dissolve the precipitate in warm acetic acid and dilute it to 200 ml with water. Add 1-nitroso-2-naphthol reagent drop wise to the warm solution with stirring. A red-brown precipitate of  $\text{Co}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3$  will appear. Filter the precipitate through a pre-weighed sintered glass crucible and dry in an oven at  $\sim 110^\circ\text{C}$  and weigh. (Repeat the weighing, until the value is constant). Find out the percentage of cobalt.

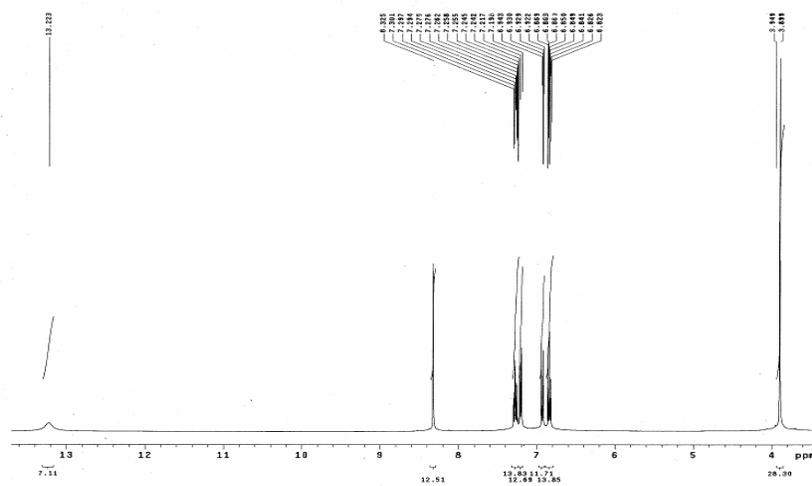
## Preparation of the reagent

Dissolve 1-nitroso-2-naphthol in glacial acetic acid (4g / 100 ml) and then add hot distilled water (100 ml). The cold filtered solution should be used immediately.

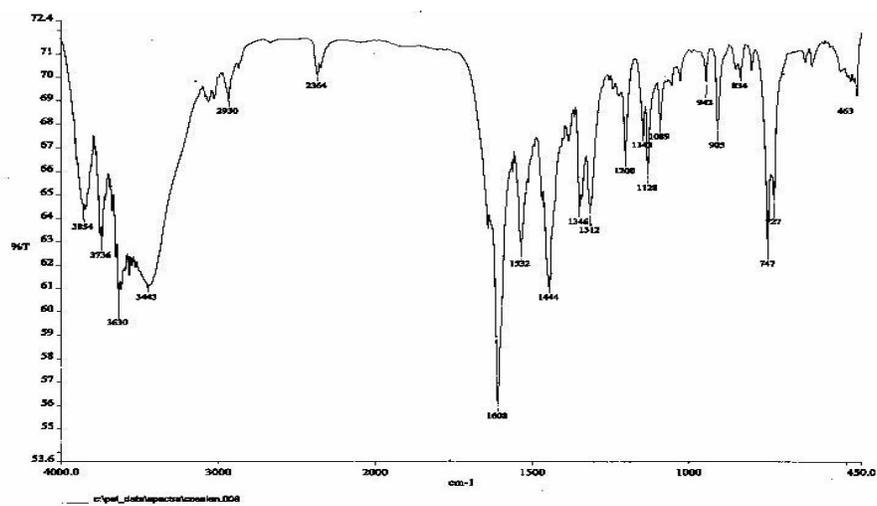
## FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of bis-(N,N-disalicylidene ethylenediamine)



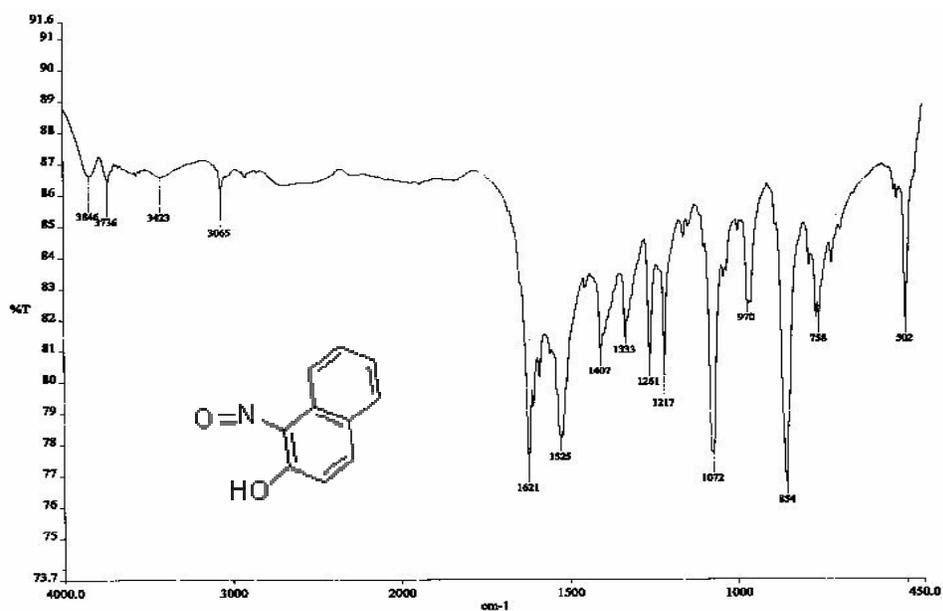
**<sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, ppm) of bis-(N,N-disalicylidene ethylenediamine)**



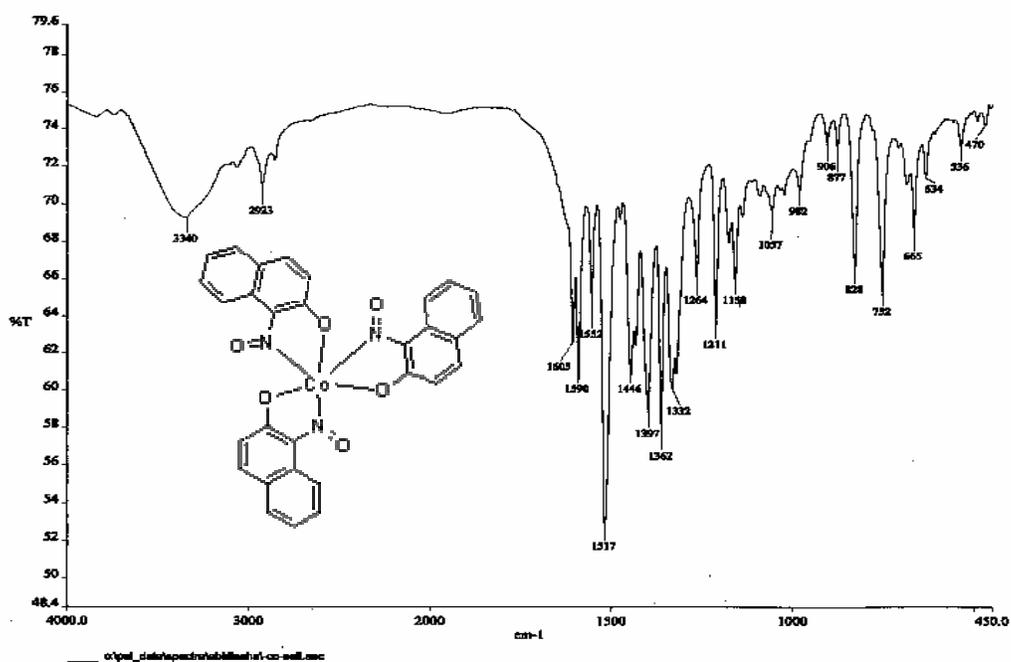
**FT-IR spectra (KBr, cm<sup>-1</sup>) of bis (N, N' disalicylaethylene-diamine)-μ- aquadibalt(II)**



### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of 1-nitroso-2-naphthol



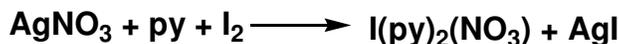
### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of tris- 1- nitroso- 2- naphthalato cobalt (III)



## Experiment No.8

### Synthesis and characterization of *bis*-pyridine iodo nitrate:

The experiment is based on the following reaction:



where py = pyridine

#### Requirements:

1. Silver nitrate
2. Pyridine
3. Iodine
2. Chloroform
5. Diethylether

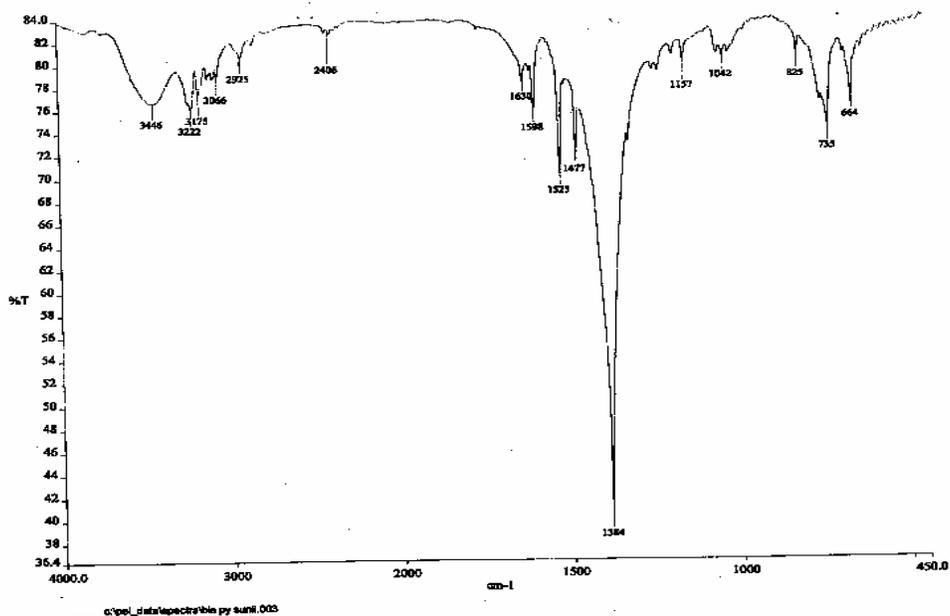
#### Procedure:

Dissolve silver nitrate (1.7 g) in pyridine (5 ml) and add iodine (2.5 g) in chloroform (50 ml). The solution is allowed to stand for half an hour to get a yellow precipitate. Filtered off the precipitate and wash it with diethylether (25 ml). Collect the filtrate and evaporate on water bath to obtain the product. Calculate the yield and estimate iodine in the complex iodometrically. Record the IR and interpret the spectra.

#### Tasks:

1. Estimate iodine
2. Record IR and interpret the spectra.
3. Calculate the percent yield

FT-IR Spectra (KBr,  $\text{cm}^{-1}$ ) of bis-pyridine iodo nitrate



## Experiment No.9

### Synthesis of penta amminechlorocobalt (III) chloride:

The experiment is based on the following reaction:



#### Requirements:

- |                                     |                      |                      |
|-------------------------------------|----------------------|----------------------|
| 1. Cobalt (II) chloride hexahydrate | 2. Hydrogen peroxide | 3. Ammonium chloride |
| 4. Hydrochloric acid                | 5. Ammonia           | 6. Acetone           |
| 7. Silver nitrate                   | 8. Nitric acid       |                      |

#### Procedure:

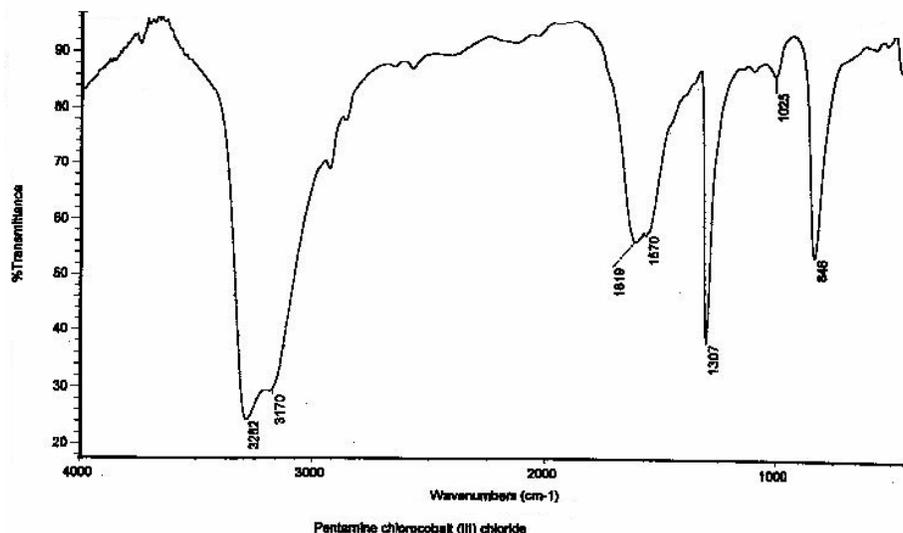
Dissolve Cobalt (II) chloride (1.8 g) in water (2.5 ml). In a separate flask make slurry of ammonium chloride (5.6 g) in conc. aqueous ammonia (5.6 ml). Add the cobalt solution to the slurry, and stir well. Add hydrogen peroxide (1.1 ml, 30%) with a dropper very slowly (two drops at a time with caution) while stirring vigorously. Heat the resulting mixture on the steam bath until thick slurry is obtained. If the slurry shows a blue tint, either the evaporation is proceeding too fast or the hydrogen peroxide was added too rapidly. Add hydrochloric acid (3 M, 22.5 ml) and heat at 60°C for 10 min. Cool the solution to room temperature and filter in a Buchner funnel with suction. (Use a highly retentive paper to prevent the fine crystals from passing through.) Wash the product with three 2 ml portions of ice water and then with three 2 ml portions acetone and dry under suction.

Transfer the product plus filter paper to a solution of ammonia (2 M, 68 ml). Warm the resulting solution on a steam bath (60°C maximum). After the entire solid has dissolved, filter the hot solution with suction. Reheat the filtrate on the steam bath with stirring. At five minutes intervals slowly add hydrochloric acid (12 M) three times portions (17 ml each). Cool the solution to room temperature and filter. Wash the product with water (2 ml) three times followed by three times washing with acetone (2 ml).

#### Tasks

1. Calculate the percent yield.
2. Estimate ionic chloride.
3. Find out the molar conductance.

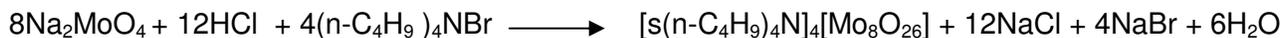
## FT-IR spectra (KBr, cm<sup>-1</sup>) of penta amminechlorocobalt (III) chloride



### Experiment No.10

#### Preparation of tetra butylammonium octamolybdate (VI):

The experiment is based on the following reaction:



#### Requirements:

1. Sodium molybdate dihydrate
2. Hydrochloric acid
3. Ethanol
4. Tetrabutyl ammonium bromide
5. Acetone
6. Diethyl ether
7. Acetonitrile
8. Methyl red
9. Sulphuric acid
10. Ammonium acetate
11. Oxine
12. Acetic acid

#### Procedure:

Acidify a solution of sodium molybdate dihydrate (2.50 g, 10.4 mmol) in water (6 ml) with hydrochloric acid (6N, 2.6 ml, 15 mmol) in an Erlenmeyer flask. Add a solution of tetrabutylammonium bromide (1.7 g, 5.2 mmol) in water (10 ml) with vigorous stirring to cause immediate formation of a white precipitate. After stirring for 10 minutes, collect the precipitate by filtration with suction, and wash successively with water (10 ml), ethanol (10 ml), acetone (10 ml) and diethyl ether (10 ml). Dissolve this crude product in minimum amount of acetonitrile and keep at 0°C overnight to get colorless block-shaped crystals. Collect the crystals by suction filtration and dry for 12h *in vacuo*. The transparency of the crystals is lost upon drying.

### Tasks:

4. Estimate molybdenum.
5. Record IR and interpret the spectra.
6. Calculate the percent yield

### Estimation of molybdenum:

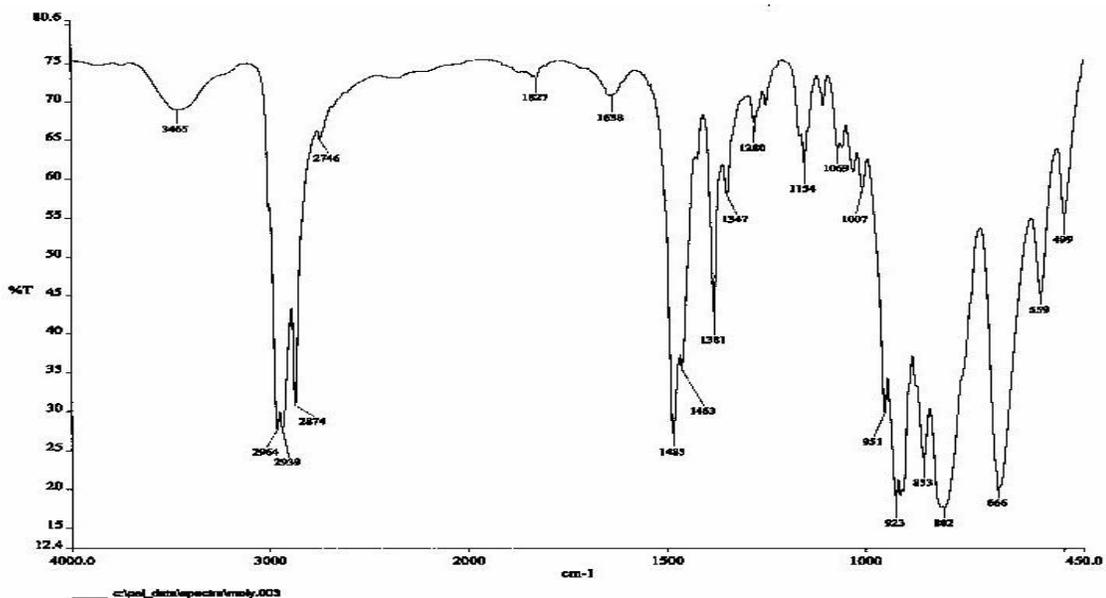
Neutralize an accurately weighed sample (in the range 0.10 – 0.15 g, in about 30 ml of water, check with methyl red) and then acidify with a few drops of sulphuric acid (1M). Add ammonium acetate (2M, 5 ml), dilute to 50-100 ml, and heat to boiling. Precipitate the molybdenum by the addition of 3% solution of *oxine* in dilute acetic acid, until the supernatant liquid becomes perceptibly yellow. Boil the solution gently and stir for 3 minutes, filter through a sintered glass crucible (of known initial weight), wash with hot water until free from the oxine, and dry to constant weight at 130-140°C. Weight as  $\text{MoO}_2(\text{C}_9\text{H}_6\text{ON})_2$ .



8-Hydroxyquinoline (Oxine)

**Oxine reagent:** May be prepared by dissolving oxine (4 g) in warm glacial acetic acid (8.5 ml) followed by, pouring it in water (80 ml), and diluting the solution to 100 ml.

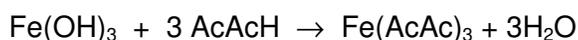
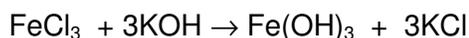
### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of tetrabutylammonium octamolybdate (VI)



## Experiment No.11

### Preparation of tris -acetylacetonato iron(III) :

The experiment is based on the following reactions:



AcAc H = acetylacetone

#### Requirements:

1. Iron (III) chloride
2. Diphenyl amine
3. Potassium hydroxide
4. Acetylacetone
5. Mercurous chloride
6. Tin chloride

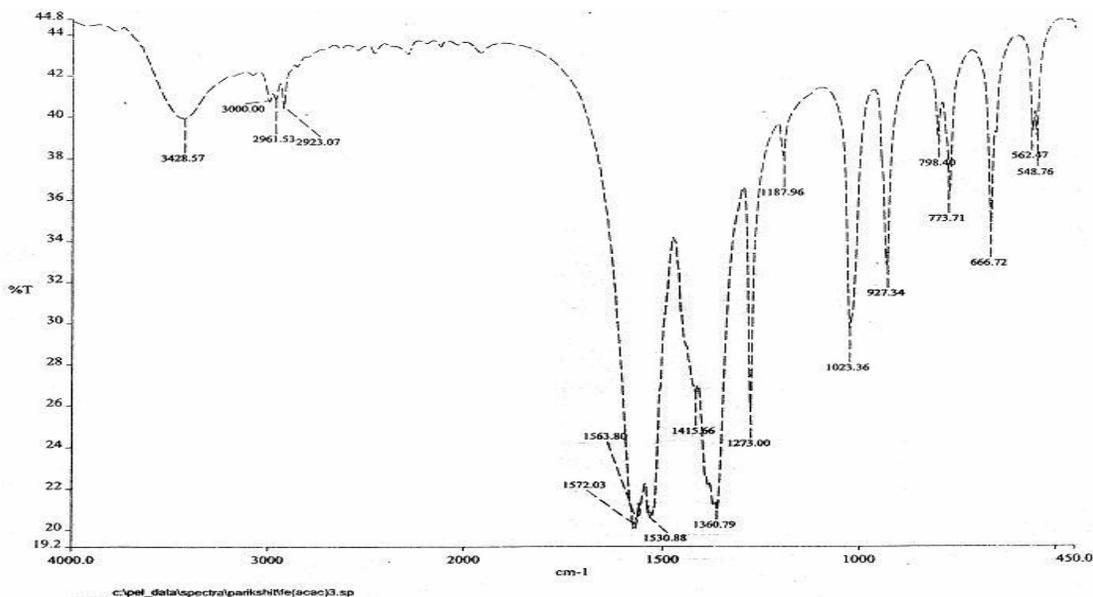
#### Procedure:

Dissolve anhydrous iron (III) chloride (1.5 g, 9.24 mmol) in water (10 ml) in a 50 ml beaker followed by the addition of aqueous solution of potassium hydroxide (20%) in parts with constant stirring to precipitate the metal as its hydroxide. Continue the addition of alkali till the pH of the solution is raised to.8 (ca). Allow the suspended precipitate to settle and by doing this the supernatant liquid will become colorless. Wash the flocculants several times with water by decantation, finally by filtration through Whatman No. 42 filter paper and again washing twice with cold water. Quantitatively transfer the precipitate into a 50 ml beaker containing water (5 ml). Add distilled acetylacetone (3.5 ml, 29.5 mmol) to the slurry and mix thoroughly with a glass rod. Allow the mixture to attain room temperature with occasional stirring. An exothermic reaction is set leading to the formation of deep red shiny crystals of Fe (acac)<sub>3</sub>. Place the reaction container in an ice-water bath for 15 min. Filter the compound through Whatman No.42 filter paper and dry in vacuum over fused Calcium chloride.

#### Tasks:

1. Calculate the percent yield
2. Record IR and assign the peaks.
3. Estimate Iron

## FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of tris -acetylacetonato iron(III)



### Experiment No.12

#### Preparation of manganese dioxide nano-particles:

##### Requirements:

1. Manganese sulphate monohydrate
2. Potassium permanganate
3. Sodium hydroxide

##### Procedure:

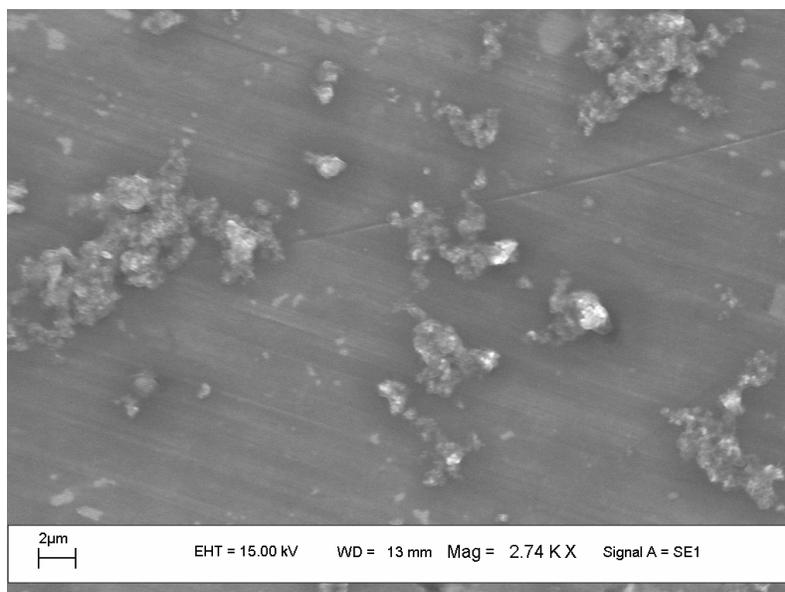
Prepare the following solutions

1. Manganese sulfate monohydrate, (1.69 g, 10 mmol) in water (3 ml).
2. Sodium hydroxide (2.5 mol, 2.4 ml).

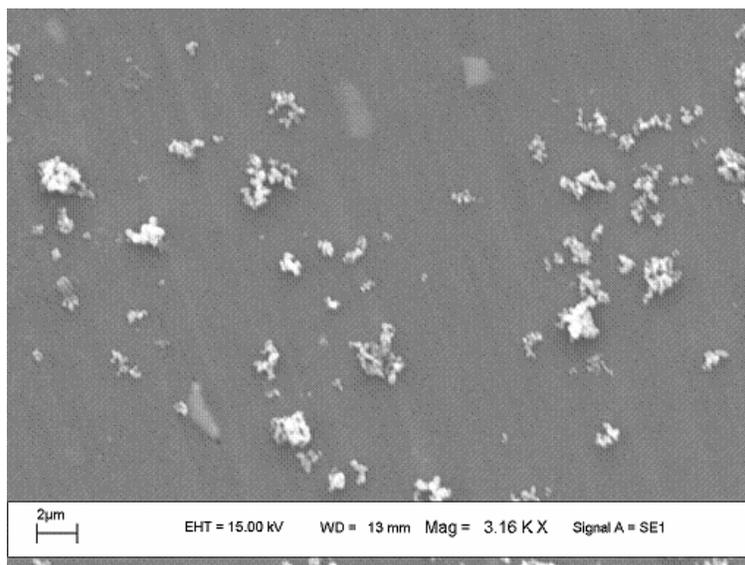
Add simultaneously these two solutions to a hot solution of potassium permanganate (1.9 g, 1.0 mmol) in water (15 ml). Stir the solution for 1hr and isolate the brown precipitate of manganese dioxide by filtration. Dry the product in a dessicator under vacuum and grind finely. Record the powder X-ray diffraction and SEM.

Repeat the experiment by adding cetyltrimethyl ammonium bromide (CTAB, 0.5 g) to manganese solution (Step 1).

**Scanning electron microscopic view of manganese dioxide nano-particles**



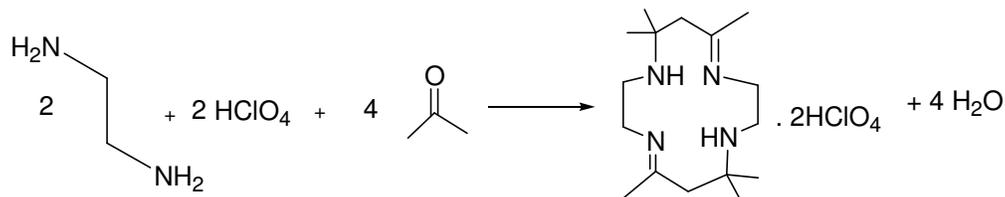
**Scanning electron microscopic view of manganese dioxide nano-particles (prepared by adding CTAB)**



## Experiment No.13

### Synthesis and characterization of co-crystals of 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclo tetra deca-4, 1, 1-dinene with perchloric acid

The experiment is based on the following equation



#### Requirements:

1. Acetone
2. Perchloric acid
3. Ethylenediamine

#### Procedure:

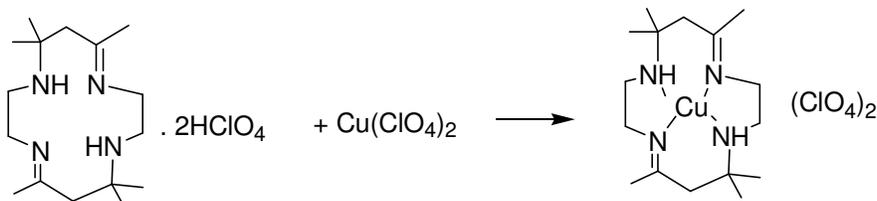
Take a solution of ethylenediamine (1 g, 0.33 mol) in dry acetone (25 ml) in a beaker (250 ml). Add a solution of perchloric acid (2.79 g, 60 %) dropwise to the solution with constant stirring. (Caution: The experiment should be carried out in hood. Use of organic substrate/ protic organic solvent with perchlorate may cause explosion). The solution will become orange red. Once the addition of perchloric acid is completed, cool the reaction mixture to room temperature. A fine white crystalline product will be formed, filter the product. Wash the residue with acetone (5 ml) and dry in a desiccator over  $\text{P}_2\text{O}_5$  as desiccant.

#### Tasks:

1. Report the yield.
2. Record the  $^1\text{H}$  NMR and interpret
3. Record the IR spectra and interpret.

## Synthesis of copper (II) complex of 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclo tetra deca-4, 1, 1-dinene with perchloric acid

The complexation is based on the following equation:



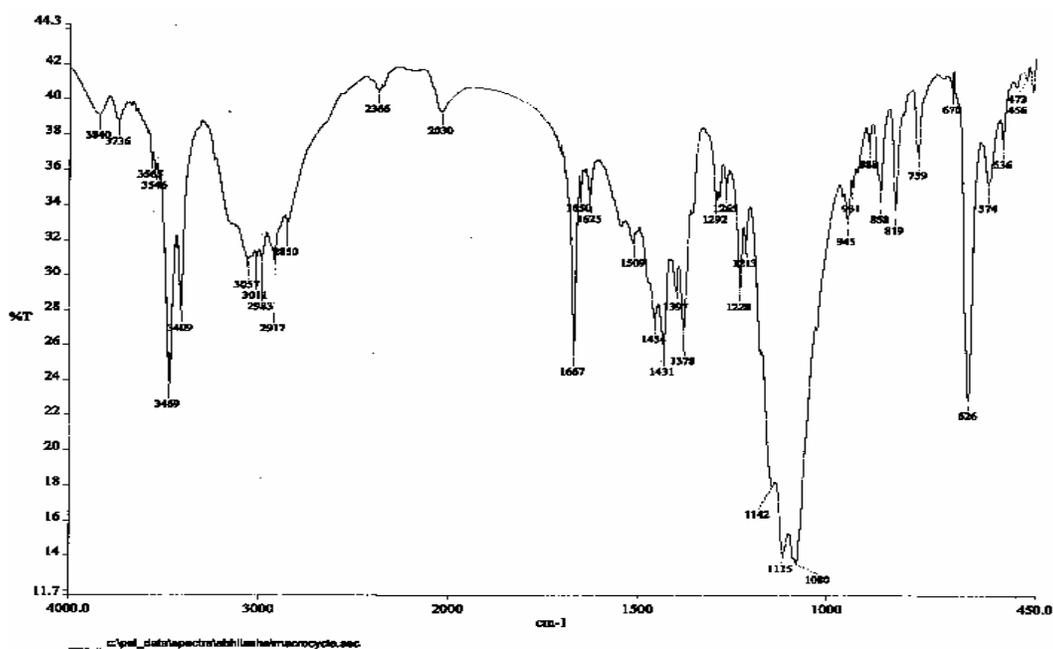
### Procedure:

Take the co-crystals of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo tetra deca-4, 1,1-dinene with perchloric acid (10.1 mmol) in methanol (25 ml) in a beaker (100 ml) and to this solution add a solution of copper(II) perchlorate hexahydrate (10 mmol) in methanol (10 ml) and stir at room temperature for 15 min. Neutralize the reaction mixture by adding dilute sodium hydroxide. Concentrate the methanol solution by putting the solution over water bath. On cooling violet crystalline complex is obtained. Filter the solid and report the yield.

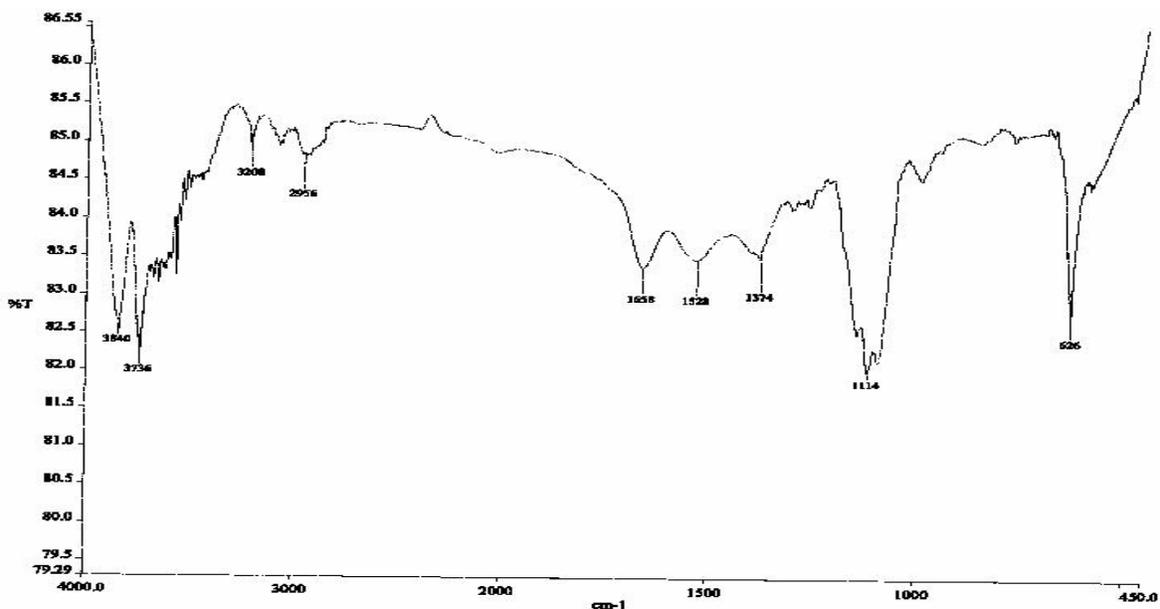
### Tasks:

1. Record the IR spectra and interpret
2. Record the ESR spectra and interpret

### FT-IR spectra (KBr, cm<sup>-1</sup>) of 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclo tetra deca-4, 1, 1-dinene with perchloric acid



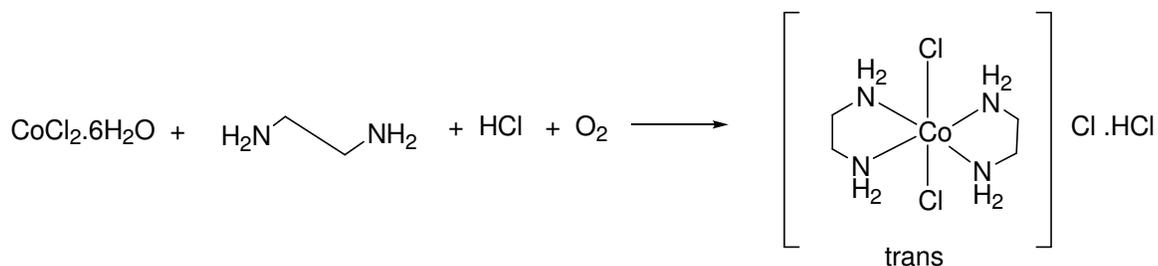
FT-IR spectra (KBr,  $\text{cm}^{-1}$ ) of copper (II) complex of 5, 7, 7, 12, 14, 14-hexamethyl-1, 4, 8, 11-tetraazacyclo tetra deca-4, 1, 1-dinene with perchloric acid



Experiment No.14

Preparation of *cis* and *trans*-dichloro bis (ethylenediamine) cobalt (III) chloride

The experiment is based on the following equation



Requirements:

1. Cobalt(II) chloride hexahydrate
2. Ethylenediamine
3. Hydrochloric acid
4. Ethylalcohol
5. Diethylether

Procedure:

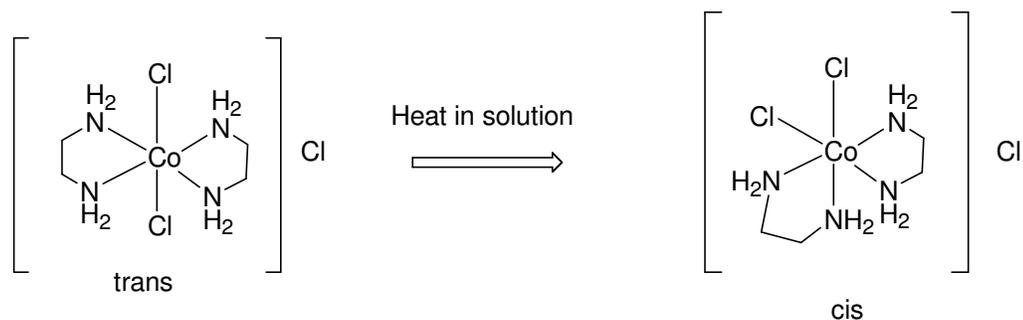
To a solution of cobalt(II) chloride hexahydrate (1.60 g, 6.7 mmol) in water (5 ml) add a solution of ethylenediamine (6 g, 1.5 mmol) with stirring. Pass a vigorous stream of air through the solution for

10–12 hrs. To the reaction mixture add concentrated hydrochloric acid (3.5 ml) and evaporate the solution on a steam bath until the volume reduces to approximately 10 ml. Cool the solution and allow it to stand overnight. Bright green square plates of the hydrochloride of the *trans*-dichloro bis (ethylenediamine) cobalt (III) chloride will be formed. Filter the precipitate; wash it with ethylalcohol and diethylether. Dry the solid at 110<sup>0</sup>C. At this temperature the hydrogen chloride will be lost, and the crystals will transform to dull-green powder.

**Tasks:**

1. Calculate yield.
2. Estimate ionic chloride in the complex.
3. Estimate cobalt on the complex
4. Find out the molar conductance
5. Interpret the visible spectra of the complex

**Conversion of *trans* to the *cis*-form**

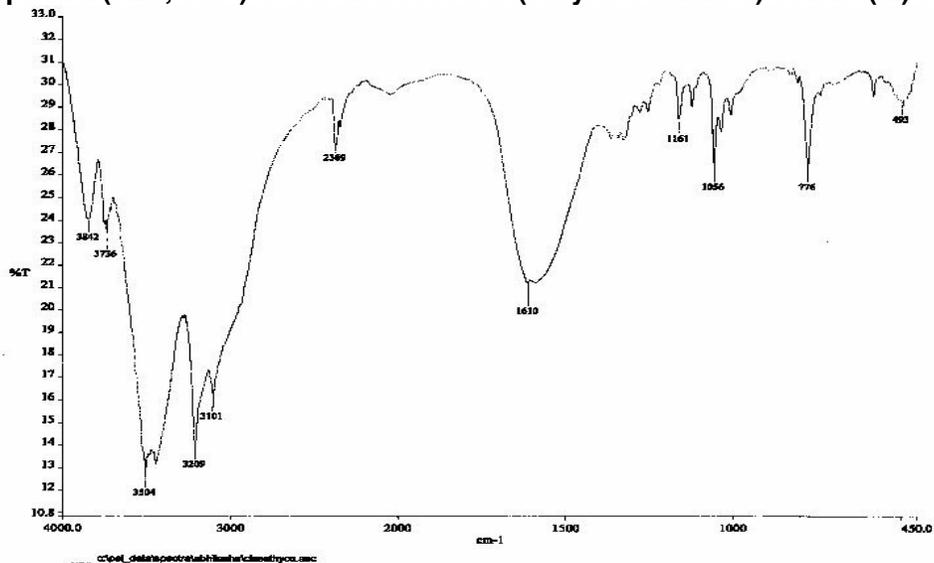


Conversion of *trans*-dichloro bis (ethylenediamine) cobalt (III) chloride to the *cis* form is brought about by evaporating a solution of the *trans*-dichloro bis (ethylenediamine) cobalt (III) chloride to dryness on a steam bath. The unchanged *trans*-form may be removed by washing with cold water. The transformation is completed by repeating the evaporation step. It should be repeated not more than two or three times, as some decomposition may take place.

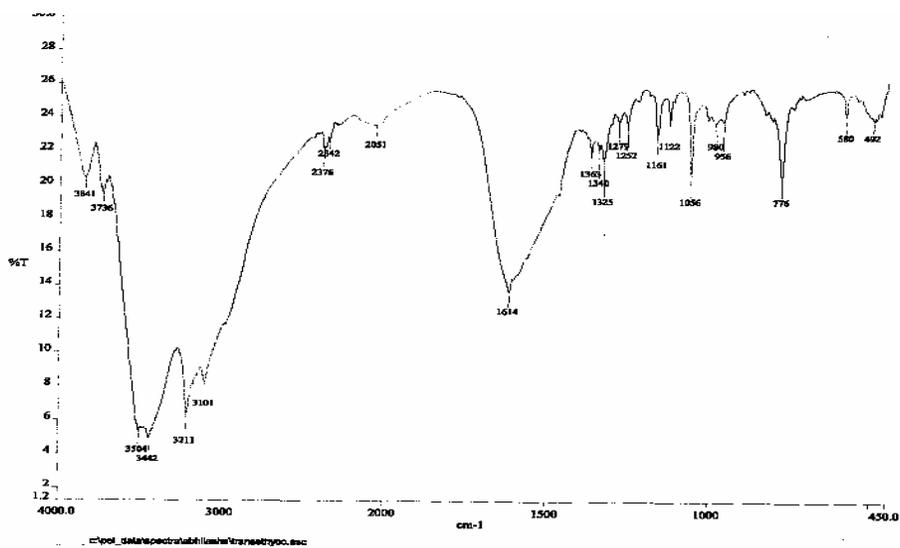
## Tasks:

1. Calculate yield
2. Record the visible spectra and compare it with *cis*-form

### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of *cis*-dichloro bis (ethylenediamine) cobalt (III) chloride



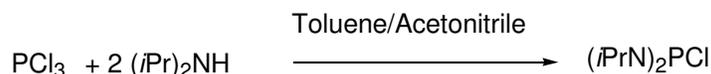
### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of *trans*-dichloro bis (ethylenediamine) cobalt (III) chloride



## Experiment No.15

### Preparation of *bis*-(diisopropylamine) chloro phosphate

The experiment is based on the following equation



Where *iPr* = isopropyl group

#### Requirements:

1. Phosphorus trichloride
2. Acetonitrile
3. Toluene
4. Di-isopropylamine

#### Procedure:

Take a solution of toluene (dry, 20 ml) and phosphorus trichloride (1.92 g, 1.4 mmol) in a two necked round bottom flask (100 ml) equipped with a reflux condensed and pressure equalizing dropping funnel (100 ml). The reflux condenser is to be attached to an out-let for continuous flow of nitrogen. Place a magnetic bar in the solution and flash a stream of nitrogen gas via side arm equipped with an inlet. Place diisopropylamine (6.09 g, 60 mmol) in toluene (10 ml) in the dropping funnel and add this solution within 10 minutes to the phosphorus trichloride solution. Maintain the temperature of the reaction mixture at 20°C by placing it over an ice bath during the addition. A white precipitate will appear. Stir the solution and reflux it for 2 hrs. Filter the reaction mixture under nitrogen and remove the solvent under vacuum. Place the white residue using a sintered glass crucible under nitrogen and quickly wash it with acetonitrile (dry, 30 ml). The washing is to be done very rapidly under vacuum, since the product partially is soluble in acetonitrile. Store the white crystals of *bis*-(diisopropylamine)chloro phosphate in a desiccator.

#### Tasks:

1. Calculate yield
2. Record the proton and phosphorus NMR of the compound

## Experiment No.16

### Preparation of bis-chloro bis-triphenyl phosphine nickel (II)

The reaction is based on the following equation



#### Requitements:

1. Nickel(II) chloride hexahydrate
2. Acetic acid
3. Triphenylphosphine

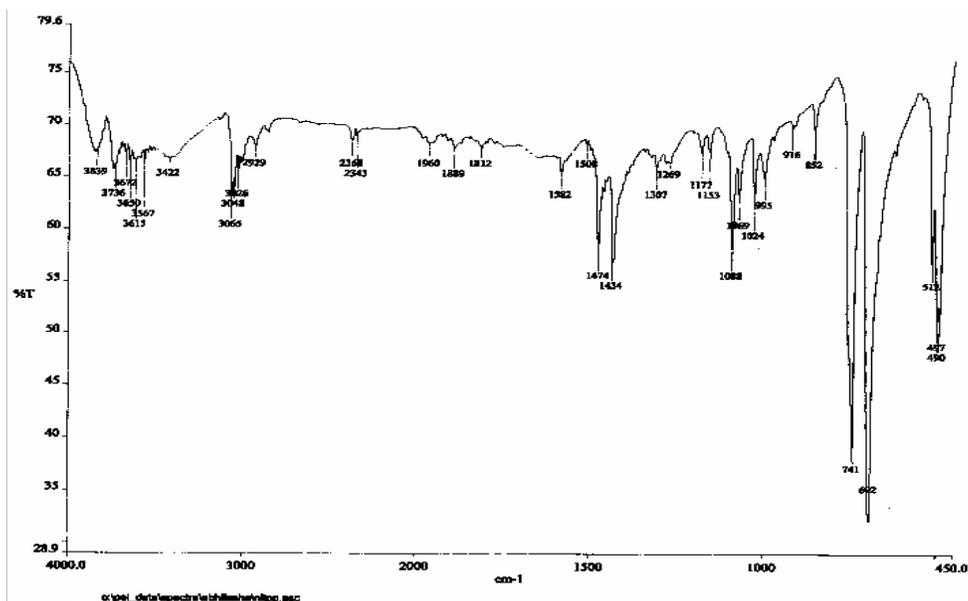
#### Procedure:

To a solution of nickel(II) chloride hexahydrate (1.19 g, 5 mmol) in water (2 ml), add glacial acetic acid (50 ml). To this add a solution of triphenyl phosphine (2.62 g, 10 mmol) dissolved in acetic acid (15 ml). Olive green microcrystalline precipitate will be formed. Keep the solution and the precipitate in contact with the mother liquor for 24 hrs. Dark blue crystals will appear. Separate the solid by filtration and collect the solid, dry them by pressing between filter papers.

#### Tasks:

1. Calculate yield
2. Estimate nickel in the complex
3. Estimate chloride in the complex
4. Record the visible spectra of the complex and interpret

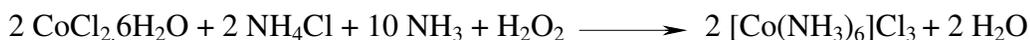
## FT-IR spectra (KBr, cm<sup>-1</sup>) of bis-chloro bis-triphenyl phosphine nickel (II)



### Experiment No.17

#### Synthesis of hexaammine cobalt(III) chloride

The experiment is based on the following equation



#### Requirements:

1. Cobalt (II) chloride hexahydrate
2. Ammonium chloride
3. Hydrochloric acid
4. Activated charcoal
5. Hydrogen peroxide
6. Ammonia
7. Sulphuric acid

#### Procedure:

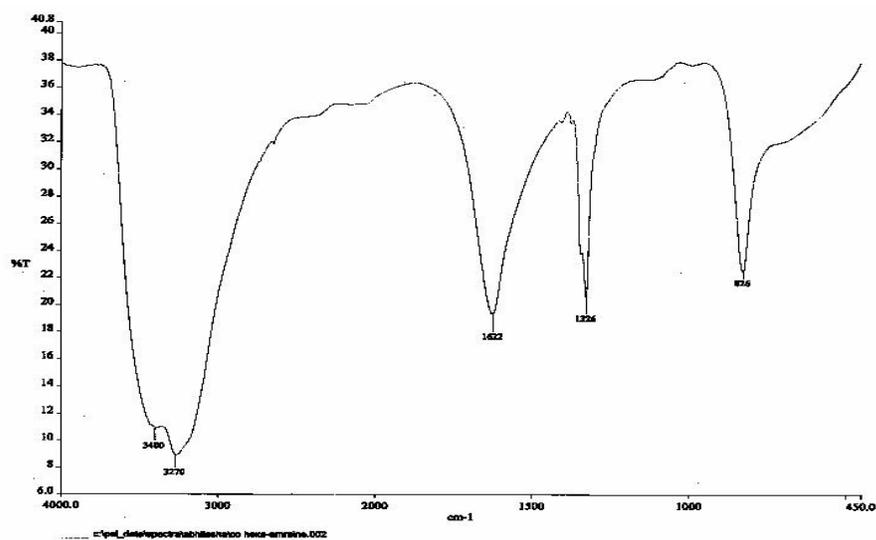
Dissolve ammonium chloride (1.2 g, 2.2 mmol) in water (3 ml). Heat the paste till it starts boiling. Add cobalt(II) chloride hexahydrate (1.8 g, 7.5 mmol) to the paste. Take activated charcoal (0.2 g) in a separate flask and add the paste to this. Cool the flask and its contents under running water. Add concentrated ammonia (4.5 ml, 20% v/v) to the solution and cool the mixture to 10<sup>0</sup> C (approximately). Add slowly hydrogen peroxide (2.4 ml, 30% v/v) to the solution with a dropper. Swirl the flask gently

during the addition. Heat the solution on steam bath at 50-60<sup>0</sup> C until the pinkish tint disappears from the solution (~20 min). Cool the solution in an ice bath and filter through a buchner funnel. Transfer the residue to a boiling solution of hydrochloric acid (15 ml, 0.5 M). Heat the solution with stirring until the solution boils and filter the hot solution using a buchner funnel under suction. Filter the precipitate and dry the product at 110<sup>0</sup>C for an hour.

**Tasks:**

1. Calculate yield
2. Estimate chloride in the complex
3. Find out the molar conductance

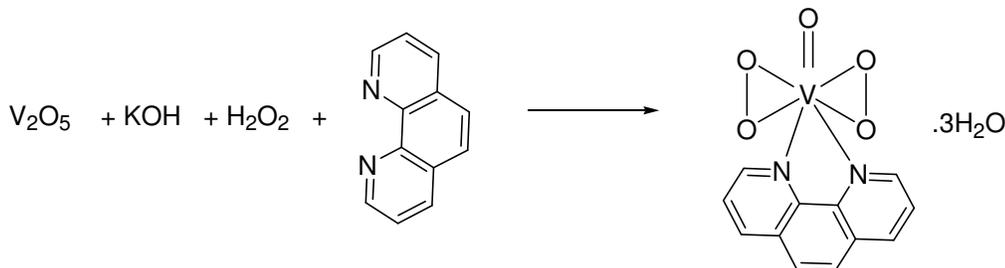
**FT-IR spectra (KBr, cm<sup>-1</sup>) of hexaammine cobalt(III) chloride**



## Experiment No.18

### Preparation of potassium *bis(peroxo)-oxo-(1, 10-phenanthroline) vanadium (V) trihydrate*

The experiment is based on the following equation:



#### Requirements:

1. Vanadium pentoxide
2. Ammonium persulphate
3. Potassium hydroxide
4. Silver nitrate
5. Hydrogen peroxide
6. Potassium iodide
7. Sodium thiosulphate
8. Starch solution
9. Potassium permanganate
10. Boric acid
11. Ethanol
12. Sulphuric acid
13. Phenanthroline

#### Procedure:

Dissolve a mixture of vanadium pentoxide (0.91g) and potassium hydroxide (0.65 g) in water (10 ml) [a few drops of hydrogen peroxide solution]. Cool the resultant clear solution over an ice-bath. Add hydrogen peroxide (30% v / v, 10 ml) drop wise to the ice-cold solution followed by of ethanolic solution of phenanthroline (1.6 g in 8 ml). Immediately crystals of the compound will appear. Wash the compound with ethanol. Dry it under vacuum.

**CAUTION:** Hydrogen peroxide in basic medium with organic substrates can cause explosion so handle under fume-cup board with shield.

#### Tasks:

1. Calculate yield

2. Estimate vanadium
3. Estimate peroxide
4. Record IR spectra and interpret the spectra
5. Record TG.

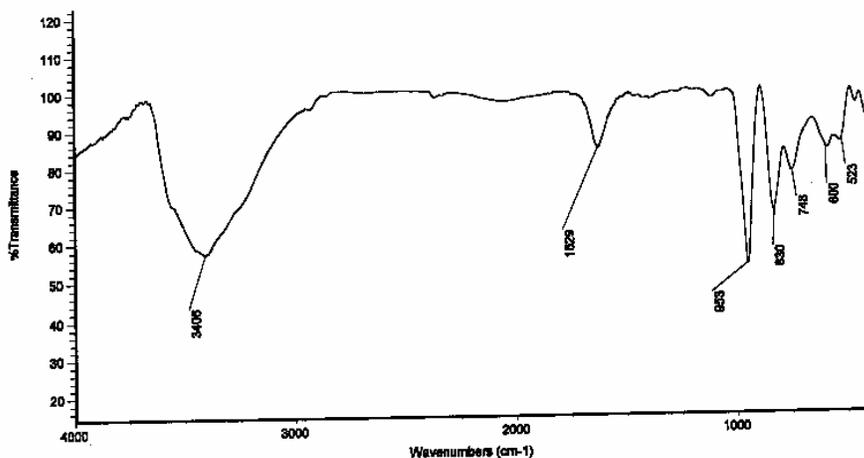
#### Estimation of vanadium:

Dissolve an accurately weighed sample (in the range 0.10 – 0.15 g) of the complex in distilled water (~100 ml) and boil the solution for 20 min. Cool the solution. Add ammonium persulfate (~1 g) and also add one or two drops of silver nitrate solution (1 M). After addition of silver nitrate solution boil the solution for half hr. Cool the solution to room temperature. Estimate the vanadium iodometrically by adding potassium iodide followed by titration of liberated iodine with sodiumthiosulphate.

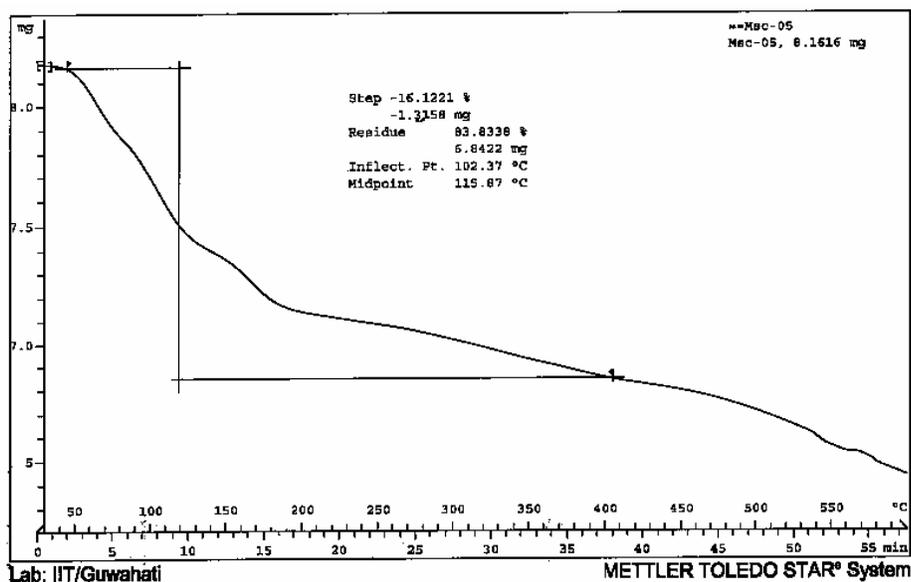
#### Estimation of peroxide:

Dissolve boric acid (2g, 32.3 mmol) in water (~100ml). To this solution, add an accurately weighed sample (in the range 0.10 – 0.15 g) of the complex and sulphuric acid (25 ml, 5 N). Titrate the solution with standard potassium permanganate (0.1 N) solution.

#### FT-IR spectra (KBr, $\text{cm}^{-1}$ ) of potassium *bis*(peroxo)-oxo-(1,10-phenanthroline) vanadium (V) trihydrate



**Thermogram (10<sup>0</sup> C / min) of potassium *bis*(peroxo)-oxo-(1,10-phenanthroline) vanadium (V) trihydrate**



**Experiment No.19**

**Preparation of tetra-butylammoniumhexa molybdate (VI)**

The experiment is based on the following equation:



**Procedure:**

Take a solution of sodium molybdate dihydrate (2.5 g, 10.3 mmol) in water (10 ml). Acidify with hydrochloric acid (2.9 ml, 17.4 mmol) in a conical flask (50 ml) with vigorous stirring over a period of one minute at room temperature. Add a solution of tetrabutyl ammonium bromide (1.2 g, 3.75 mmol) in water (2 ml) with vigorous stirring to form a white precipitate. Heat the resulting slurry to 80<sup>0</sup> C with stirring for 45 mins. During this period the white solid changes to yellow. Collect the crude product with suction filtration and wash it with water (20 ml). Crystallize the product from acetone. After 24 hrs

collect the yellow crystalline product with suction filtration. Wash the product with diethyl ether and dry in vacuum.

**Tasks:**

1. Calculate yield
2. Estimate molybdenum in the complex
3. Record IR and interpret the spectra

**FT-IR spectra (KBr,  $\text{cm}^{-1}$ ) of tetra-butylammoniumhexa molybdate (VI)**

