

University of Baghdad

College of Science

Department of Chemistry



جامعة بغداد

كلية العلوم

علوم الكيمياء

# الكيمياء اللاعضوية

## العملي

المرحلة الثالثة

اعداد

م.م. اسيل حكمت

م.م. ندى احمد

م.م. رشا خضر حسين

## Chemistry of Vanadium

### Introduction

The aim of this experiment is to focus the light on the different oxidation states of vanadium.

Vanadium is one of the first transition metal series and the first element in group Va, its electronic configuration is  $4s^2 3d^3$ . It can exist in several oxidation states +2, +3, +4 and +5. The most stable oxidation states are +5 and +4 and the less stable is +2.

**The oxidation state (+5):** The molecular state of soluble vanadate in solution provides very interesting examples of anionic condensation steadily and spontaneously increasing as the pH is lowered.

In acid solution, the oxide  $(V_2O_5)_n$  reveals a feeble basic character, by yielding the oxyanions  $VO_3^-$  (vanadate) and  $VO^{2+}$  (vanadyl).

Table: Molecular states of vanadium oxy-anions

pH	> 13	~ 10	9	7	7-2,2	< 2
	$VO_4^{3-}$	$V_2O_7^{4-}$	$V_4O_{11}^{6-}$	$V_2O_6^{4-}$	$(V_2O_5)_n$ with O as red coll. dispersion or red ppt.	$VO_3^-$ , $VO^{2+}$
	Ortho salt readily soluble	pyrosalt	So-called meta-vanadate as such sparingly soluble			
	←	colorless	→	yellow	brown	pale yellow

The common "meta-vanadate" usually written, for example, as  $NH_4VO_3$ , appears actually to be condensed structures. To obtain a stable acid solution of quinquevalent vanadium, the sparingly soluble  $NH_4VO_3$  is dissolved first in aqueous sodium hydroxide, giving the soluble and colorless ortho-vanadate  $Na_2VO_4$  and then the solution is strongly acidified, when there results the pale yellow solution of the salts of the vanadate and vanadyl cations, stable indefinitely in acid solution.

### The oxidation state (+4):

The ions  $VO_3^-$  and  $VO^{2+}$  are easily reduced (e.g. by oxalic acid or sulphurous acid) to the blue vanadyl IV cation  $VO^{2+}$  according to the following equation:



$VO^{2+}$  is blue in color, its common name "vanadyl ion". In the basic medium the hypovanadate  $V_4O_6^{4-}$  ion is predominant.

Introduce about 5ml of dilute sulphuric acid into the conical flask, stopper it, and shake vigorously with the amalgam, before again decantation into the vanadate solution. A second washing of the flask in the same way with a further portion of dilute acid should suffice to transfer the fully reduced product quantitatively to the vanadate solution. Heat the now blue solution, and titrate it with solution of (0.1N)  $\text{KMnO}_4$ .

The deep blue color of the reduction product in (2), and the final stage of (3), is due to the cation  $(\text{VO})^{2+}$ , the sulphate being  $\text{VO}\cdot\text{SO}_4$ . The final lilac tint in experiment (3) is probably due to the simple (hydrated) cation  $\text{V}^{2+}$ . The development of the blue color at the end of experiment (3) arises from the reaction:-



The cation  $\text{VO}^{2+}$  is stable in air, but  $\text{V}^{2+}$  is rapidly oxidized on exposure.

#### 4- Preparation of Ammonium bis-oxalatovanadyl(IV) hydrate:



To a solution of 5g oxalic acid crystals (4mmol) in the least volume of boiling water add 1.4g (1mmol) of ammonium oxalate.

When the latter has dissolved, add to the hot solution in portion 2.3 g (2mmol) of ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ .

After all the vanadate has been added and the vigorous effervescence of carbon dioxide has almost ceased, boil the blue solution for a few minutes to complete the reduction. Cool the liquid to room temperature, add 50ml of ethanol, and allow the mixture to stand overnight. Then decant from the dark blue "oil" that will have separated. When the "oil" is now shaken with about 25ml of fresh alcohol, it is converted into a dark blue-gray granular solid, which is filtered off.



#### The determination of the ratio vanadium / oxalate in the complex oxalate

Dissolve about 0.2g of the complex salt in 5ml dilute sulphuric acid, heat the solution to about 60°C, then titrate with (0.1N)  $\text{KMnO}_4$  solution until a permanganate pink color is developed. In this procedure the oxalate groups are destroyed, and the vanadium oxidized to the quinquevalent stage as vanadate.

A few crystals of sodium sulphite are added to the oxidized solution, which is then gently heated while the reduction to a blue solution of vanadyl sulphate proceeds. Finally expel all excess of sulphur dioxide by boiling, and titrate the cooled solution again with (0.1N)  $\text{KMnO}_4$  solution.

### Calculations:

Since the two titrations are nearly in a ratio of 5:1 the vanadium / oxalate ratio must be  $(\text{C}_2\text{O}_4)_2 / \text{V}$ .

The volume of the  $\text{KMnO}_4$  solution in the first titration ( $V_1$ ) is equivalent to the oxidation of oxalate ion and vanadium (IV) ion as in the following equations:



By the addition of sodium sulphite the V (+5) which was obtained in the previous step will reduce again to V (+4) according to the following equations:



The volume of  $\text{KMnO}_4$  used (in the second step) ( $V_2$ ) will be equivalent to the amount of V (+4) present in the prepared oxalate complex salt:



$$\therefore \text{The ratio of } \frac{(\text{C}_2\text{O}_4)_2}{\text{V}} = \frac{V_1 \cdot V_2}{V_2}$$

## Chemistry of Chromium

### Oxidation States:

Chromium shows oxidation states from -2 to +6 inclusive in its compounds. The highest has marked oxidizing properties and the +3 state is more important in the range and stability of its compounds.

Formal oxidation states of -2 and -1 are found respectively in the complex anions  $[\text{Cr}(\text{CO})_5]^{2-}$  and  $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ . The 0 state is found in  $\text{Cr}(\text{CO})_6$  and the +1 in  $[\text{Cr}(\text{bipy})_2]^+$ . The 2, 2'-bipyridyl complex is obtained from  $[\text{Cr}(\text{bipy})_2]^{3+}$  by reducing this in aqueous solution.

Chromium (II) can be made by the reduction of chromium (III) with zinc in acidic solution but an inert atmosphere is necessary to prevent oxidation back to the +3 state.  $\text{Cr}^{2+}$  is strongly reducing:



$E^\circ$  is sufficiently negative for  $\text{Cr}^{2+}$  to be able to reduce acidic aqueous solutions to hydrogen. If, however, chromium (II) is obtained in the form of one of its water-insoluble complexes, then this oxidation state is quite stable towards aerial oxidation, for example in  $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CrSO}_4(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ . Other compounds of chromium (II) include the oxide and the four binary halides.

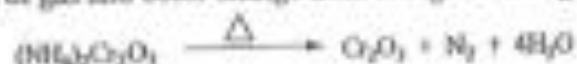
Many compounds of chromium (III) are known and have been well characterized because they are kinetically inert; in other words they are extremely slow to react and can be isolated and studied at leisure. From a structural point of view chromium (III) compounds are often isomorphous with the corresponding iron (III) and aluminium (III) compounds.

Chromium (IV) and (V) are generally found in combination with oxygen or fluorine but not many compounds of either oxidation state are known.

In the +6 state, chromium is always combined with oxygen (a possible exception is  $\text{CrF}_6$  which may exist at low temperatures). The best-known compounds are the oxide and salts of chromic,  $\text{H}_2\text{CrO}_4$ , and dichromic,  $\text{H}_2\text{Cr}_2\text{O}_7$ , acids. Other chromium (VI) compounds include  $\text{CrO}_2\text{Cl}_2$  and  $\text{CrO}_2\text{F}_2$ .

### Preparation of Chromium(III) Oxide:

Put a clean and dry crucible on a gentle flame then gradually place 1.5g of ammonium dichromate in the crucible while it is on the flame. In each single addition a flash of light will be observed as a result of "self oxidation-reduction" of the dichromate. The product ( $\text{Cr}_2\text{O}_3$ ) will splash and attach with evolution of gas and color change from orange to dark green.



Describe the ability of chromium (III) oxide to be soluble in water, in acidic and in basic medium.



### Preparation of Chromium (III) Sulphate:

Fuse 1g of potassium hydrogen sulphate on a flame. To the fused sample add gradually chromium oxide (in amount equivalent to the hydrogen sulphate). What is the color of the product?



### Preparation of Potassium Chromate:

- Fuse a mixture of 3g of potassium nitrate and 2.5g of potassium carbonate in a crucible directly on the flame.
- Add gradually 0.25g of chromium oxide to the melt with continuous heating until the color of the mixture changes from green to yellow.
- (Important) leave the crucible to cool, then add hot dist. water until all the precipitate will dissolve, filter off if the solution is not clear. Concentrate the solution to 2/3 of its original volume, separate solid chromate at 80°C.



### The relation between Chromate and Dichromate:

Dissolve few amount of potassium chromate in dist. water (about 1 ml), add few drops of dilute sulphuric acid, and observe the change in color. Add dropwise a solution of sodium hydroxide (1%); the yellow color will be return.



The concentration of chromate and dichromate is depending on concentration of hydrogen ion.



### Reduction of Chromium (VI) to Chromium (III)

#### 1- Reduction by potassium iodide in acidic medium:

Add dropwise a solution of potassium iodide to the dichromate solution which has been acidified with dilute sulphuric acid. The red color will appear as a result of intermediate oxidation state between Cr (VI) and Cr (III), and then a black precipitate will be formed. Extract the precipitated iodine by carbon tetrachloride, what is the color of the extracted solution?



#### 2- Reduction by potassium iodide in basic medium:

Prepare chromium solution then add few drops of potassium hydroxide followed by potassium iodide. A red color will appear and then disappear, and a yellow solution will formed. What conclusions can you made from these results?

#### 3- Reduction by Hydrogen Peroxide:

Dissolve 0.5g of potassium dichromate in 70 ml of perchloric acid (10%), add the hydrogen peroxide gradually, the color will change indicating the occurrence of the reduction. Add excess of hydrogen peroxide to complete the reduction. Boil the solution to remove the excess peroxide.

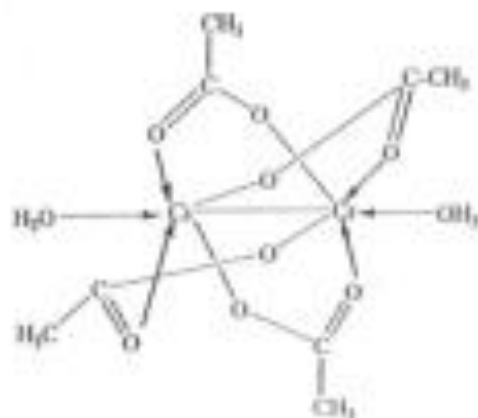


### Preparation of Chromous Acetate, $\text{Cr}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$

Chromium (II) salts are extremely sensitive to oxidation and must be prepared under an inert atmosphere. Before starting the preparation, check that your 'dry-box' (or bag) is in good condition and well flushed with nitrogen. Water for use in the box should be boiled and cooled under nitrogen. Solvents should be distilled under nitrogen.

$\text{Cr}(\text{II})$  is readily oxidized to  $\text{Cr}(\text{III})$  in oxygen atmosphere and it can't be stabilized for long period in aqueous solution because it reduces water releasing hydrogen. The instability may be depending on the acidity of the solution and on the anions presents.

$\text{Cr}(\text{II})$  has an ability to form dimeric complexes with a covalent metal-metal bond and the most stable complex is the diamagnetic red  $\text{Cr}(\text{II})$ -acetic complex  $[\text{Cr}_2(\text{CH}_3\text{-COO})_4(\text{OH})_2]$ .



### Procedure:

Place 17g zinc in beaker and add a solution of 10g hydrated chromic chloride,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , in 11.6ml water. Pour in 21ml concentrated hydrochloric acid and cover a beaker with a watch glass. After about 15 min. the solution will have turned blue. Rinse the watch glass, filter the solution in a Buchner funnel and rinse with water. Immediately add slurry of 27.5g sodium acetate in 35.5ml water. Stir with a glass rod until the red chromium (II) acetate is precipitated. Filter and wash several times with small portions of water until the washings are free of chloride. Wash finally with a little ethanol, followed by a little ether. Record the yield and ampoule a portion of the product.



## Chemistry of Nickel

This element has the outer electronic configuration  $3d^8 4s^2$  and its higher important oxidation state is +4. With nickel trend towards the decrease stability of the higher oxidation states continues and the main common oxidation state is nickel +2. This is the only important oxidation state in aqueous solution, where it forms the green hexa-aquanickel (II) ion. This ion occurs in some hydrated nickel (II) salts, for example  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $NiSO_4 \cdot 6H_2O$ ,  $NiSO_4 \cdot 7H_2O$  and  $Ni(ClO_4)_2 \cdot 6H_2O$ . Note that  $NiCl_2 \cdot 6H_2O$  contains *trans*-  $NiCl_2 \cdot 4H_2O$  units.

Nickel (II) readily forms complexes, the main structural types be octahedral, tetrahedral and square planar. Amines form blue octahedral complexes, for example  $[Ni(NH_3)_6]^{2+}$  and  $[Ni(ethylenediamine)_3]^{2+}$ .

The tetrahedral complexes of nickel (II) are usually intensely blue. Typical tetrahedral complexes are  $(NiCl_4)^{2-}$  and  $NiCl_2(PPh_3)_2$ .

Square planar nickel (II) complexes are diamagnetic and often brown, red or yellow in color. Typical nickel (II) square planar complexes are  $[Ni(CN)_4]^{2-}$ ,  $NiEt_2(PPh_3)_2$  and bis(dimethylglyoximate) nickel(II).

### Reactions of Nickel (II):

These tests illustrate the reactions of nickel (II) and should be carried out on a solution of nickel (II) nitrate or nickel (II) chloride.

For the tests 1-4 record all observations, interpret the results and give the equations where possible.

Materials required: 0.2 mol dm<sup>-3</sup> Nickel chloride or nickel nitrate  
0.5 mol dm<sup>-3</sup> Nickel chloride  
2 mol dm<sup>-3</sup> Sodium hydroxide  
Ammonia (s.g. 0.880) and 2 mol dm<sup>-3</sup> ammonia  
2 mol dm<sup>-3</sup> Potassium thiocyanate  
Pyridine  
Hydrogen sulphide  
2 mol dm<sup>-3</sup> Hydrochloric acid  
1 Per cent solution of dimethylglyoxime in absolute ethanol

- 1- To the nickel (II) solution (3ml) add excess 2 mol dm<sup>-3</sup> sodium hydroxide (4ml) and then concentrated aqueous ammonia (5ml).
- 2- Add 2 mol dm<sup>-3</sup> potassium thiocyanate solution (3ml) to the nickel (II) solution (3ml) followed by a few drops of pyridine.

- 3- Bubble hydrogen sulphide through the nickel (II) solution (3ml), which has been acidified with  $2 \text{ mol dm}^{-3}$  hydrochloric acid (2 drops), and then add aqueous  $2 \text{ mol dm}^{-3}$  ammonia (20 drops).
- 4- Add an alcoholic solution of dimethylglyoxime to the nickel (II) solution, which has been acidified with  $2 \text{ mol dm}^{-3}$  hydrochloric acid (2 drops), followed by a small excess of  $2 \text{ mol dm}^{-3}$  ammonium hydroxide.

### Hexa-amminenickel(II) Chloride $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$

This is an example of an octahedral nickel (II) complex.

Materials required: Nickel chloride hexahydrate  
0.880 Ammonia

Dissolve nickel chloride hexahydrate (12g) in concentrated aqueous ammonia (about 24ml) slowly to the rapidly stirred solution until the green precipitate of nickel hydroxide has dissolved. Allow the mixture to stand at room temperature for 30 min and then remove the crystals of hexa-amminenickel(II) chloride by filtration on a Buchner funnel. Wash the precipitate with ammonia of s.g. 0.880 (about 50ml); and allow the product to dry at room temperature in air. Calculate the percentage of product.

#### 1- Analysis for Ammonia:

Materials required: Standard  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide  
Standard  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid  
Methyl orange indicator

Dissolve the complex (0.2g, accurately weighed) in  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid (70 ml) and titrate the excess acid with the  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide, using methyl orange as indicator.

#### 2- Analysis for Nickel:

Accurately weight the complex (0.3g) into a 500 ml beaker provided with a watch-glass and stirring rod. Add  $6 \text{ mol dm}^{-3}$  hydrochloric acid (3ml) and dilute the solution to 100 ml. Heat the solution to  $75^\circ\text{C}$  and add the alcoholic dimethylglyoxime (35 ml). Immediately add  $2 \text{ mol dm}^{-3}$  ammonia solution dropwise with stirring until precipitation occurs and then add excess ammonia (20 drops). Heat the mixture on a water bath for 25 min. Test the solution for complete precipitation, when the red

precipitate has settled, by adding a few drops of dimethylglyoxime solution. Allow the precipitate to stand at room temperature for 1 h and collect the precipitate by filtration through a weighed sintered-glass crucible. Wash the precipitate with cold water until the washings are free from chloride ion. Dry the precipitate at 100-120°C for 60 min, allow cooling in a desiccator and weighing. Repeat the drying until the sintered-glass crucible and precipitate are a constant weight.

3- Determine the percentage of ammonia in the complex and assuming that the molecular formula of the red precipitate is  $\text{Ni}(\text{C}_2\text{H}_5\text{O}_2\text{N}_2)_2$  calculate the percentage of nickel in the nickel-ammonia complex. Compare these results with the theoretical figures.

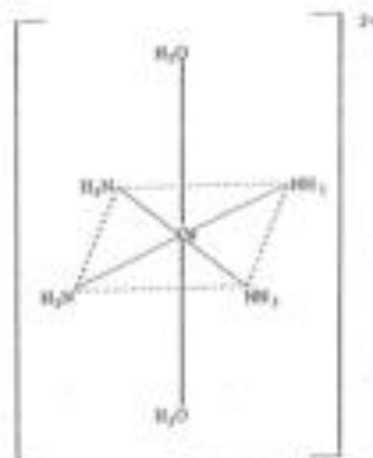
## Chemistry of Copper

This element has the outer electronic configuration  $3d^{10}4s^1$  and the single  $s$  electron can be removed to give copper (I). This oxidation state is sometimes compared with the alkali metal ions but there is little similarity and copper (I) is best considered as a typical transition metal ion. Cuprous compounds are diamagnetic and colorless except when color results from the anion or from charge transfer bands. The stability of copper (I) in aqueous solution is low, as shown by its oxidation potentials, and it disproportionates to give copper (II) and copper metal, however many cuprous salts are insoluble in water.



If potassium iodide is added to a copper (II) solution, cupric iodide is formed but this rapidly decomposes to give a precipitate of cuprous iodide and iodine.

Most cupric salts dissolve in water to give the blue hexa-aqua ion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (Fig. below). If ammonia is added, up to four water molecules can be replaced stepwise to give the complex  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ . However, it is difficult to replace the last two water molecules because of the Jahn-Teller effect.



Structure of complex  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  showing the four short Cu-N bonds (0.205 nm) and the two longer Cu-O bonds (0.259 nm and 0.237 nm).

There are many amine complexes of copper (II) and they are all intensely colored than the hexa-aqua ion. The stronger ligand field of the amine causes the single absorption band in the visible spectrum of the hexa-aqua ion to move to shorter wavelengths as the water molecules are replaced by the ligand. Copper (II) forms halide ion complexes of the type  $[\text{CuX}_4]^{2-}$  ( $X = \text{Cl}, \text{Br}$ ) which have distorted tetrahedral structures. For example, when lithium bromide hydrobromic acid is added to cupric bromide the anion  $[\text{CuBr}_4]^{2-}$  is formed.

Copper (III) occurs in a number of compounds, for example  $\text{KCuO}_2$  and  $\text{K}_3\text{CuF}_6$ . Diamagnetic complexes of the type  $\text{K}_2\text{Cu}(\text{IO}_6) \cdot 7\text{H}_2\text{O}$  are formed when an oxidizing agent is added to an alkaline copper (II) solution containing iodate or tellurate.

### Reactions of Copper:

These tests illustrate the reactions of copper (II). They should be carried out on a solution of copper (II) sulphate.

For the tests (1-5) record all observations and interpret the results and give the equations where possible.

Materials required:  $0.5 \text{ mol dm}^{-3}$  Copper sulphate pentahydrate

$2 \text{ mol dm}^{-3}$  Sodium hydroxide

Concentrated hydrochloric acid

Granulated zinc and granulated copper

Ammonium thiocyanate

Pyridine

Potassium iodate or sodium tellurate

Sodium hypochlorite

$2 \text{ mol dm}^{-3}$  Hydrochloric acid

$2 \text{ mol dm}^{-3}$  Cupric chloride

- 1- To the cupric sulphate solution (3ml) add  $2 \text{ mol dm}^{-3}$  sodium hydroxide (6ml), whereupon a precipitate is formed. Divide this suspension into three portions:
  - a- Boil the solution.
  - b- Add concentrated hydrochloric acid (4 ml) carefully while shaking the solution to produce mixing.
  - c- Add 60 per cent sodium hydroxide (6 ml) to the solution and warm the mixture gently.
- 2- To the copper solution add a small piece of zinc.
- 3- To the copper (II) solution (5 ml) add ammonium thiocyanate (0.5g) followed by pyridine (1 ml).
- 4- To the copper (II) solution (4 ml) add potassium iodate (or sodium tellurate) (0.5g) followed by sodium hypochlorite (0.5 g). Acidify the mixture with  $2 \text{ mol dm}^{-3}$  hydrochloric acid and identify the gas that is liberated.

5- To the  $2 \text{ mol dm}^{-3}$  cupric chloride (5 ml) add granulated or powdered copper metal (1g) and  $2 \text{ mol dm}^{-3}$  hydrochloric acid (2 ml). Boil the mixture for about 5 min. cool and add water slowly.

### Tetra-ammine di-aquacopper (II) Sulphate Hydrate



This is an example of the preparation of an octahedral copper (II) complex in aqueous medium where only four of the water molecules of the hexa-aqua ion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  are replaced by the ligand.

**Materials required:** Copper sulphate pentahydrate

Ammonia

Ethyl alcohol

Dissolve cupric sulphate pentahydrate (6.2 g) in concentrated aqueous ammonia (10 ml). Stir the solution for 5 min. add ethyl alcohol (10 ml) slowly to the blue solution and allow the mixture to remain at room temperature for 30 min. Cool it in an ice-water bath and collect the crystals that are deposited by filtration on a Buchner funnel. Wash the product with an equal volume mixture (50 ml) of 0.880 s.g. ammonia and ethanol, followed by pure ethanol and then ether to remove alcohol. Calculate the percentage of the product.

### Analysis for Sulphate:

Dissolve the complex (0.4 g, accurately weighed) in water (150 ml) acidified with concentrated hydrochloric acid (2 ml). Add to this solution with stirring a solution of 5 per cent barium chloride (10 ml), cover with a watch-glass and leave the solution on a boiling-water bath for 1 h. Remove the solution from the water bath, allow the precipitate to settle and test the clear supernatant liquid with a few drops of barium chloride solution for complete precipitation. If no precipitate is obtained, collect the barium sulphate by filtration on a weighed sintered-glass crucible, using gentle suction. Wash the precipitate with warm water until the filtrate gives no precipitate with silver nitrate solution. Dry the crucible and the precipitate at  $110^\circ\text{C}$  for 1 h, allow cooling in a desiccator and weighing. Repeat the drying until the sintered-glass crucible and contents are a constant weight. Calculate the theoretical and practical percentage of sulphate in the complex.

### Analysis of Copper:

Dissolve the complex (0.1g) in 25ml acetic acid (0.2M), and then add 0.25g potassium iodide (KI), titrate with (0.1N) sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), using starch as indicator (5 drops).

## Coordination Compounds

This part includes preparation of some coordination compounds and studied their properties. Three coordination compounds have been selected below to represent the main categories.

1- Positive charge coordination compounds:

Chloro pentaammine cobalt (III) chloride. This salt has formula  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ .

2- Uncharged coordination compounds:

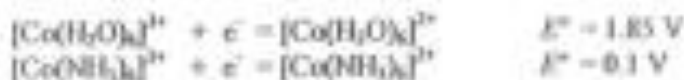
The nonionic compound trinitrotriammine cobalt(III) has formula  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ .

3- Negative charge coordination compounds:

The salt potassium hexa isothiocyanato cobaltate (III) include negative ion complex and has the formula  $\text{K}_4[\text{Co}(\text{NCS})_6] \cdot 4\text{H}_2\text{O}$ .

## Chemistry of Cobalt

This element has the outer electronic configuration  $3d^7 4s^2$  and its highest significant oxidation state is +4. The two most important oxidation states are cobalt (II)  $[\text{Ar}] 3d^7$  and cobalt (III)  $[\text{Ar}] 3d^6$ , and in an aqueous solution containing no complexing agents, cobalt (III) is easily reduced to cobalt (II). However cobalt (III) is more stable in the presence of a complexing agent such as ammonia as shown by the electrode potentials.



Cobalt (II) forms both octahedral and tetrahedral complexes but they are labile and they have a strong tendency to be oxidized by molecular oxygen. The complexes are usually prepared in an inert atmosphere. In aqueous solution the cobalt (II) ion is pale pink.

Tetrahedral cobalt (II) complexes are often highly colored owing to their lower order of symmetry relative to the octahedral complexes.

Cobalt (III) salts are difficult to prepare because the ion is a strong oxidizing agent and the chemistry of this oxidation state is largely that coordination compounds. Cobalt (III) usually forms octahedral complexes and it has a strong affinity for nitrogen donors such as ammonia, amines (e.g., ethylenediamine), nitro groups and nitrogen bonded  $-\text{SCN}$  groups as well as water molecules and halide ions.

### Preparation of Chloropenta-amminecobalt(III) Chloride:

Add a mixture of 10g of ammonium chloride dissolved in (15ml) of concentrated ammonia (density  $0.88\text{g}/\text{dm}^3$ ) to a cold saturated water solution of 5g of cobalt (II) chloride. Add 2ml of hydrogen peroxide solution (30%) in one dosage then add 3ml of hydrogen peroxide drop by drop while the solution is stirred rapidly after each addition.

Neutralize the solution by concentrated hydrochloric acid and then add excess hydrochloric acid (about 5ml). Boil the solution mixture until the pink color disappears then cool in ice bath, the purple precipitate filtered off. Dissolve the precipitate in hot ammonia solution (2%). Neutralize by hydrochloric acid then heat the solution to boiling and leave it to cool, when crystals of penta-amminecobalt (III) chloride are deposited. Collect the purple crystalline product by filtration, wash it with acetone then dry it in vacuum desiccator.

### Properties of the Prepared Compounds:

To confirm the ionic properties of the prepared compound and to make sure that the anion is chloride ion we can follow this procedure:

Dissolve a small amount of prepared compound in dist. water (the solution should be clear), add two drops of silver nitrate, the white precipitate (silver chloride) will appear immediately.

We can replace the negative ion ( $\text{Cl}^-$ ) in the compound by another negative ion as follows:

1- Displacement by bromide ion to form the complex  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}_2$

Dissolve 1g of chloride salt in distilled water acidify with dilute sulphuric acid then cool in ice bath. Add hydrogen bromide solution (33%). Filter off the red crystals then wash with alcohol.

2- Displacement by sulphate ion  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

Dissolve 1g of chloride salt in 3ml of concentrated sulphuric acid (the addition will be carried out in hood), cool the solution then add 5ml of ethanol. Collect the produced crystals by filtration, wash with alcohol then identify the presence of sulphate ion by dissolving a small amount of precipitate in hot water (clear solution), add few drops of concentrated barium chloride solution. The white precipitate of barium sulphate will be formed immediately.

3- Displacement by nitrate ion  $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$

Dissolve a small amount of chloride salt in hot distilled water (minimum amount of water). Cool the solution and add concentrated nitric acid in amount enough to precipitate red-violet crystals (nitrate salt). The detection of nitrate ion carries out by brown ring method.



### Trinitro-triamminecobalt (III), $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

This compound is a nonionic (non electrolyte) coordination compound. It can be prepared from pure cobaltous acetate.

#### (1) Purification of commercial cobaltous carbonate:

Mix 7 g of (technical) cobalt carbonate with about 50 ml of hot water, and then dissolve the carbonate by adding 15-20 ml of concentrated hydrochloric acid in portions. Filter the hot solution into a solution of 15 g of potassium bicarbonate in warm water. Then boil the liquid with the reprecipitated cobalt carbonate, and maintain the boiling temperature for about 10 min. Filter off the carbonate, using a rather large filter-funnel. And wash the solid with hot water. Finally dissolve the carbonate into the (emptied) filter-flask with a hot mixture of 40 ml of water and 10 ml of glacial acetic acid.

#### (2) Preparation of cobaltous acetate:

Dissolve 3.5g of the pure cobaltous carbonate into a hot mixture of 20 ml water and 5 ml of glacial acetic acid.

#### (3) Preparation of Coordination Compound Trinitro-triamminecobalt (III), $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$

Add the cooled solution of cobaltous acetate to a solution of 15 g of sodium nitrite in 70 ml of concentrated ammonia (d=0.880). cool the whole in an ice-bath, and at 10°C or below add slowly, while mixing by vigorous shaking, 20 ml of "20 volume" hydrogen peroxide, and then allow the mixture to remain in the ice-bath for 20 min. Then transform the deep brown liquid to a beaker (600 ml capacity) on which the level of the liquid is marked (by adhesive label, or other means). Add 0.5 g of decolorizing charcoal, and heat over a flame (in the draught Cupboard, in such ammonia escapes). The color of the liquid soon becomes yellow, and after 30-45 min. yellow solids begins to separate over from the hot liquid. The color of the mixture is obscured by the charcoal, but may be observed by swirling a thin layer round the beaker. During the heating the volume of the contents of the beaker should be maintained undiminished, by the addition of water as necessary.

When the separation of yellow solid indicates that the reaction is ended, cool the beaker and contents in ice, and then filter. Wash the crude solid with ice-cold water, and then with ethanol. To separate from the charcoal and recrystallize proceed as follows: Take a volume of water equal in ml to thirty times the weight of the air-dried crude product in grams, acidify with a few drops of acetic acid, and then boil. Add and dissolve the crude complex: filter while hot from residual

charcoal, and set the filtrate aside for crystallization. Wash the solid thoroughly with cold water after collecting on a filter, and dry it at normal temperature.

### The Analysis of Trinitro-Triamminecobalt (III)

#### (a) Percentage of nitro group:

Dissolve 0.1-0.15g weighed into a beaker, in about 20ml of hot water. Add 5 ml of a 10 per cent aqueous solution of sodium hydroxide, and boil the whole until the precipitation of cobaltic oxide is complete (5min.). Filter through a folded paper into a tap-funnel; wash the residual oxide well with hot water, uniting washings with the main filtrate. Set aside the filter with cobaltic oxide and also the beaker with some adherent oxide (see below).

Place in a flask 75 ml of an approximately 0.05-normal solution of ceric delivering it below the level of the ceric solution, and wash out the funnel into the oxidizing agent. After cooling the solution to normal temperature add potassium iodide, and titrate the liberated iodine with standardized deci-normal sodium thiosulphate. Treat 25 ml of the ceric solution with potassium iodide, and titrate the iodine as before. Ceric sulphate oxidizes nitrite quantitatively to nitrate.

#### (b) Percentage of cobalt:

Carefully extract the filter-paper with the cobaltic oxide from the funnel, fold it and then insert it into a glass-stoppered bottle. Wash out the beaker used for the original decomposition with acidified aqueous potassium iodide, and then add the wash solution to the glass-stoppered bottle. Titrate the liberated iodine with standardized sodium thiosulphate solution (deci-normal), until the disintegrated paper is perfectly white. During the titration the bottle should be frequently stoppered and well shaken.

## Study of Geometric, Linkage Atom and Hydrated Isomerism

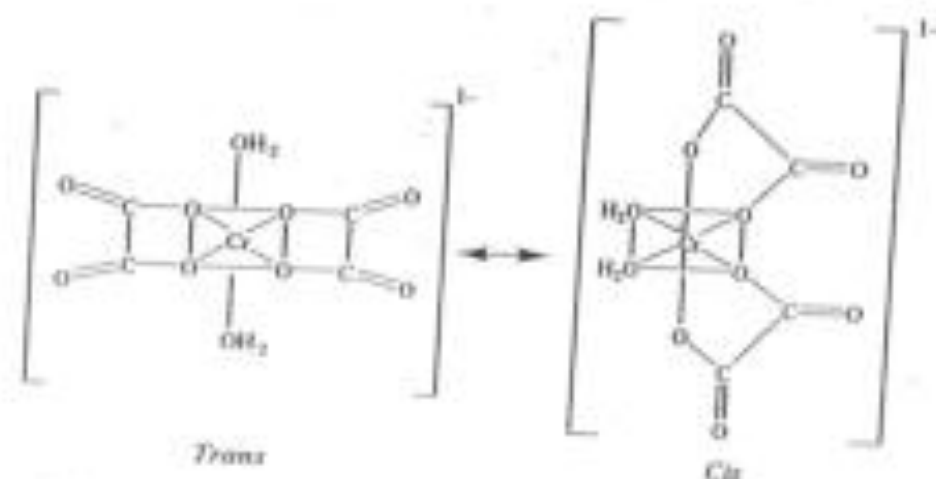
### I. Geometric isomerism

#### Potassium dioxalato-diaquo-chromate (III) dihydrate

##### (1) Cr form: $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$

Powder in a dry mortar 12 g (7 mol) of oxalic acid crystal,  $H_2C_2O_4 \cdot 2H_2O$ , 4 g (1 mol) of potassium dichromate. Mix the powders as intimately as possible by gentle regrinding in the mortar. Moisten an evaporating basin (10 cm. diameter) with water, and then allow nearly all the water to drain away. Introduce the mixture at the centre of the basin in

a compact heap, which will become moistened for a few millimeters upwards from its base. Cover the basin with a glass, and set it on a very gentle hot-plate. After a short interval a vigorous spontaneous reaction sets in (accompanied with some frothing due to the escape of steam and carbon dioxide), and, rapidly spreading through the mixture causes it to liquefy to a deep-colored syrup, in this reaction the potassium dichromate will be reduced to chrome (III) by oxalic acid and then chrome (III) react with excess of oxalate to produce the coordination compound.



Without waiting for the thick liquid to cool, pour over it about 20ml of ethanol, and while warming the basin on the hotplate triturate the product of the reaction until it solidifies, using a metal spatula at first and a small pestle later. If complete solidification cannot be effected with one portion of alcohol, decant the liquid, replace it with another 20 ml of alcohol, warm and resume the trituration, until the product is finally entirely crystalline and granular.

The salt, unlike the *trans* isomer, is intensely dichromic, appearing in the solid state almost black in diffused daylight, but deep purple in artificial lighting.

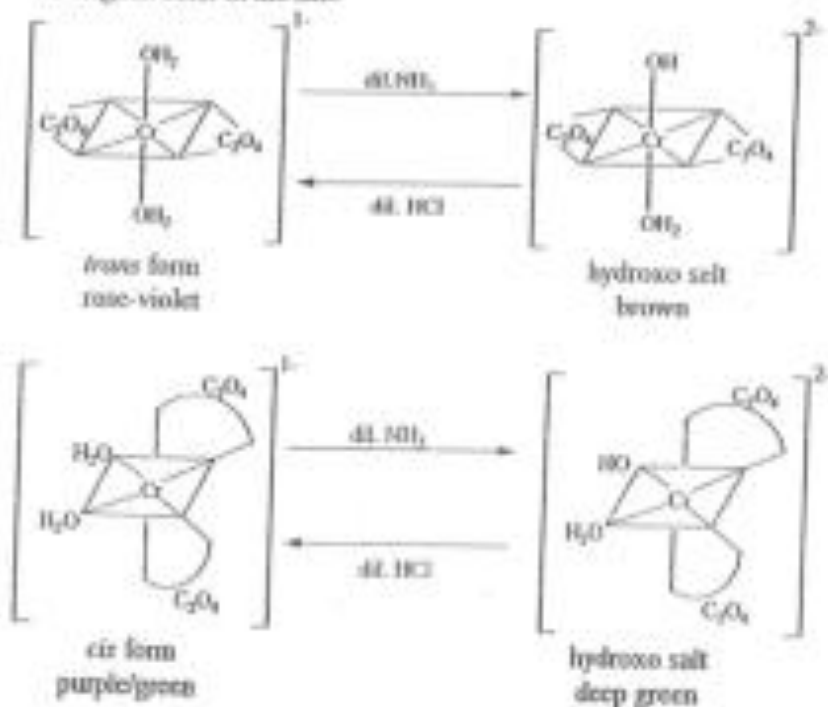
**(2) *Trans* form:  $K[Cr(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$**

In a beaker of not less than 300ml capacity, provided with a cover-glass, dissolve 12g (7mol) of oxalic acid crystals,  $H_2C_2O_4 \cdot 2H_2O$ , in the minimum of boiling water. Introduce in small portions a solution of 4g (1mol) of potassium dichromate also dissolved in the minimum of hot water, covering the beaker while the violet interaction proceeds. When

mixing is complete cool the beaker and its contents, and then transferred the dark-colored solution to a glass crystallizing dish (or evaporating basin), and allow spontaneous evaporation at normal temperature, to about one-third of the original bulk (36-48hr). Collect the deposited crystals on a suction filter wash with alcohol.

(In the solution an equilibrium, *trans*  $\rightleftharpoons$  *cis*, is established, probably favouring the freely soluble *cis* form, but the low solubility of the *trans* isomer causes its deposition in pure condition as the solution is concentrated. If the evaporation is allowed to proceed too far, the deposited solid ultimately becomes a mixture with increasing proportion of the *cis* form as the bulk is diminished.)

The following reactions can be employed as a delicate test for the purity of the two isomers. Irrigate a 'pinch' of the salt, placed on a small filter-paper resting on a watch-glass, with a few drops of dilute aqueous ammonia. With the *cis* salt a deep-green solution rapidly forms, and spreads over the filter-paper, no solid remaining. With the *trans* isomer, if pure, there is no green color, but a light-brown solid forms and remains undissolved. In each case irrigation with dilute hydrochloric acid restores the original color of the salt.



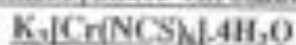
**(a) Percentage of oxalate:**

Weigh 0.3g of the salt into a beaker; add 10ml of water, and 10ml of a 10 per cent solution of potassium hydroxide. Boil the mixture until no more green precipitate forms (10min), filter off the chromic hydroxide, and wash it well on the filter with hot water. After acidification with sulphuric acid, titrate the united filtrate and washings at about 60°C with decinormal permanganate. (It is advisable to preserve the last wash-water separate, and confirm the efficiency of the washing, by observing whether one drop of the solution of permanganate permanently colors it, after acidification and heating.)

**(b) Percentage of chromium:**

Weigh 0.2g into a flask, and oxidize it to dichromate by means of potassium bromate, by warming with 50ml of water acidified with 3ml of concentrated sulphuric acid. When complete solution is reached, add 1.5g of (solid) potassium bromate, and then boil for 10min. Dissolve 5g of ammonium sulphate in a small volume of hot water, filter if necessary, and then add to the hot solution, in which chromium is now present entirely as chromic acid. Boil the whole until nearly all the excess of bromine has been volatilized (30-45min), and then add 10ml of normal hydrochloric acid, and again boil until starch-iodide paper is not stained when held in the steam. Cool the liquid, add 10ml of concentrated hydrochloric acid, and 1g of potassium iodide. Titrate the liberated iodine with (decinormal) thiosulphate, standardized by means of potassium dichromate.

**(3) Potassium hexathiocyanato-chromate (III) tetrahydrate**



In a porcelain dish, set over a small flame, heat 3g (6mmol) of potassium thiocyanate just to fusion (m.p. 172°C). While continuing heating gently, sift on to the fused salt, in small portions from a spatula, 4g (1mmol) of potassium chrome alum; after each addition the contents of the dish should be well mixed by stirring. As the alum is added the red-violet mixture becomes less and less pasty, and finally is almost solidified. To avoid its deliquescence the product is allowed to cool in a desiccator. The solid is then quickly scraped from the dish into 20ml of ethanol contained in a mortar, and well crushed and triturated with the solvent. After filtering from insoluble potassium sulphate the deep violet-colored solution is quickly concentrated on the boiling water-bath, until purple crystalline crusts are formed, which are finally dried *in vacuo* over sulphuric acid.

the material may be recrystallized by dissolving it in a small volume of ethanol, and allowing the solution to evaporate spontaneously at normal pressure over sulphuric acid (for this purpose methanol is preferred to ethanol on account of its greater volatility).



## 2. Hydrated isomerism of chloro-aquachrom (III) compounds

This kind of isomerism is uncommon. It is present in coordination compounds consist of transition metal ions with an electric configuration  $d^3$  and  $d^6$  as  $(Cr^{3+})$  and  $(Co^{3+})$  respectively.

In this kind of isomerization, one of the coordinated ligands with metal ion will replace by  $H_2O$  molecule as in the following examples:



Another example:

a- $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	Deep green
b- $[Cr(H_2O)_3Cl]Cl_2 \cdot H_2O$	Green
c- $[Cr(H_2O)_6]Cl_3$	Grey blue

## 3. Preparation of Linkage isomers

The complex  $[Co(NO_2)(NH_3)_5]Cl_2$  exists in two forms, Co-NO<sub>2</sub> and Co-ONO. The difference is clearly demonstrated by the infrared spectra of the compounds. Both isomers are prepared from  $[Co(NH_3)_5Cl]Cl_2$ , the product depending on the pH.

### Procedure:

Dissolve 1g chloropentaamminecobalt (III) chloride in (10ml) dist. water in which 2.5ml 10% ammonia has been added. Filter to remove the precipitated cobaltous oxide, cool and dried the solution into two parts:

### (1) Preparation of Nitropentaamminecobalt (III) Chloride



Acidify one part of the above solution by the addition of (2N) hydrochloric acid. Now add 1.25g sodium nitrite and heat until the red precipitate first formed has completely dissolved. Add 12.5ml concentrated hydrochloric acid. Cool in ice for about one hour, collect the brownish-yellow crystals which separate on a filter paper wash with alcohol and dry in air.