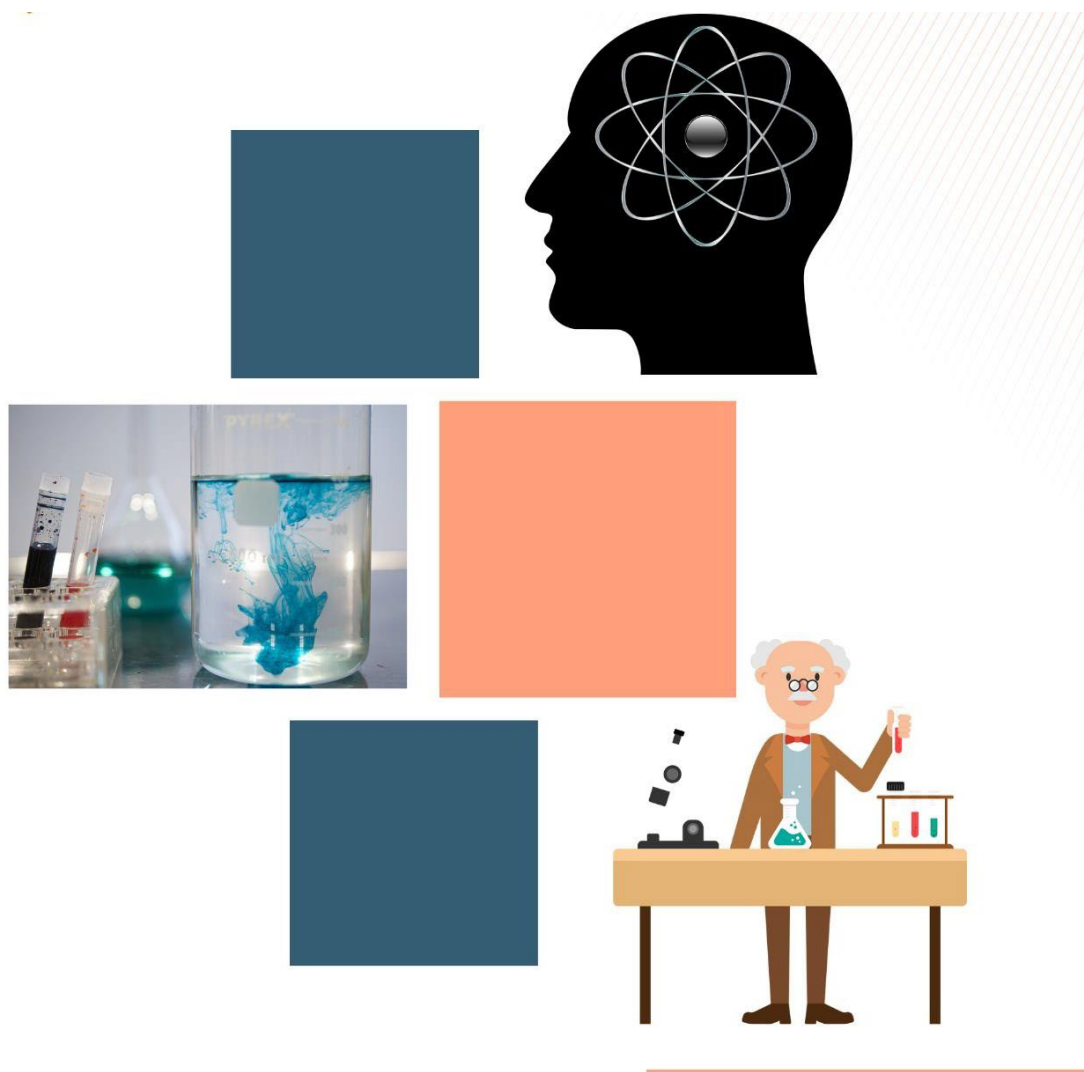




UNIVERSITI
MALAYA



Laboratory Manual
SIC2001- Practical of Inorganic Chemistry II

Jabatan Kimia, Fakulti Sains

Laboratory Safety Rules

Safety is the primary concern in any chemical laboratory. Chemicals, particularly organic chemicals, are almost all potentially hazardous. Fortunately, with sensible and correct precautions, the risks can be minimized if certain basic safety practices are followed. The responsibility for laboratory safety lies with everyone working in the particular laboratory. Sensible laboratory conduct does not mean memorizing a list of rules! The true test is the actual conduct in the laboratory and safety rules apply to all laboratory activities. Each person's safety is affected by the actions of fellow workers in the laboratory. Therefore, it is in everyone's best interest to follow safe work practices. The guidelines below are recommended for working safely in the laboratory.

- Know the location of all exits for the laboratory and the building.
- Know the location of the alarm and fire extinguishers and how to operate them.
- Know the location and use of safety showers, eye-washes and safety aid boxes.
- Know the location of the nearest telephone that can be used during an emergency.
- Never work alone in the laboratory. If you must work alone, make someone is aware of your location and let him or her call or check on you periodically.
- **Safety glasses or goggles must be worn at all times.**
- You might find them a nuisance to wear, but your eyes are very precious.
- If you wear contact lenses, try to avoid wearing them in the laboratory. If you must wear contact lenses, your goggles must seal particularly well to your face.
- Do not eat, drink or smoke in the laboratory.
- Wear protective clothing in the laboratory. This includes laboratory coats, safetyglasses, proper shoes and gloves (if necessary).
- Long hair should be tied back. Other articles of clothing that may become entangled should also be secured.
- Do NOT smell or taste chemicals. If you need to determine the odour of any chemical, waft it gently towards your nose with your hand – do not stick your nose in the container and inhale.
- Know the potential hazards of the materials and equipment with which you will work.
- Follow good housekeeping practices, that is, clean up as you go. Work areas must be kept clean. Do not clutter the work areas, aisles and exits.
- Store away apparatus that are not in immediate use, either in a cupboard or storeroom. Wash your hands carefully before leaving the laboratory.
- **Do not wear laboratory coats, gloves or other personal protective clothing out of the laboratory and into non-laboratory areas.** This clothing may have become contaminated.
- **Report all accidents and injuries**, however small, immediately to the Lecturer-in-charge or demonstrator or the laboratory assistants.
- In the interest of safety and security, work is permitted only during scheduled laboratory periods.
- Dispose of organic chemicals only in designated waste bottles. Chemical wastes are segregated into three groups and stored separately, viz, halogenated wastes (examples are chloroform, dichloromethane, carbon tetrachloride), non-halogenated wastes (examples are acetone, alcohol, toluene, xylene) and other wastes such as mercury and organometallics.

Additional Guidelines for Students

Remember that in a laboratory you have fellow students opposite you and by the side of you. They do not know what you are doing, but they hope and expect that what you are doing is sensible and safe. Always think carefully about what you are about to do.

- Know the Lecturer-in-charge and the laboratory workers of the laboratory.

- Undergraduates are not allowed to work or even be in any of the teaching laboratories at any time outside of the specified laboratory hours unless they have explicit permission from the Lecturer-in-charge. This includes before and after class and during lunch hour.
- Come to laboratory periods on time and be prepared by studying the experiment and planning your activities before you come to the laboratory.
- Write everything you do and see in your notebook so that you can trace your actions and make corrections if necessary.
- Do not use cracked or broken glassware.
- Check glassware before using it.
- Never use open flames, unless instructed by the Lecturer-in-charge. If flames are permitted, plan your experiments so that you never leave your flame unattended. There are other sources of heat such as steam baths and hot plates.
- **Handle all chemicals with care and read labels before attempting to get them.**
- Use a spatula to get solid chemicals. Never use your fingers.
- **Be careful not to contaminate reagents with your spatulas or droppers. If you take too much of a chemical or reagent, give it to a fellow student - do not return it to the bottle.**
- Do not wander off with the only bottle of a reagent that everyone needs; keep it in its assigned location. Do not pipette by mouth. Use only mechanical pipetting devices.
- Never look directly into the mouth of a flask containing a reaction mixture.
- Never point a test tube or reaction flask towards yourself or your neighbour.
- When using a separating funnel, vent frequently and remove the stopper immediately upon setting it upright for separation.
- **Never use a thermometer as a stirrer!** If a mercury thermometer breaks, immediately contact the Lecturer-in-charge or the demonstrator.
- Turn off water, burners or electrical equipment when not in use.
- Wash your glassware at the end of the laboratory day. You will have clean and dry glassware ready to go for the next laboratory class.
- Make sure glassware or equipment is kept in the correct locker - your locker or the common locker.
- Clean your work area and equipment used before leaving the laboratory.

Hereby, I, _____, with matric no. _____ have read, understood and will obey the safety rules in the laboratory.

Signed by,

Witnessed by,

.....

.....

Name: _____

Lecturer in-charge: _____

Date: _____

(official stamp)

Date: _____

(Note to student: Print TWO copies of Pages 1 & 2, sign and return ONE copy to the Lecturer in charge; and keep the other copy to yourself)

Lab Report Guidelines & Marking Scheme for Practical

Section 1 Lab Performance (Total 20%)

1. Pre-entering lab (5%)

Score	Criteria
0	No preparation for experimental procedure, no proper attire-shoes; goggles; lab coat.
1-2	The summary of procedures is too brief, lacks details and is confusing; incomplete safety attire.
3-5	Presents easy-to-follow steps in lab experimental, logical and adequately detailed; safety attire checked.

2. Skill & Techniques (15%)

Score	Criteria
0	No skill is demonstrated.
1-5	Wrong glassware used, wrong technique, spillage and wasting of chemicals.
6-10	Right glassware used, incorrect or lack of lab technique.
10-15	Presents correct lab skill, clean and tidy.

Section 2: Lab report (Total 60%)

Section	Total Mark	Rubric	
Title	5	0-1	<ul style="list-style-type: none"> No title, or Too brief (e.g. "Lab report"; "Mercury in fish"; Ascorbic acid in fruits", etc).
		2-3	<ul style="list-style-type: none"> Too long, or Does not identify the complete subject of study (E.g "Determination of mercury"; "Determination of lead", etc).
		4-5	Identify the complete subject of study and encapsulates the purpose of the report/study.
Objective	15	0	Section missing completely.
		1 - 7	<ul style="list-style-type: none"> Be too vague, ambitious or broad in scope. Just repeat each other in different terms. Just be a list of things related to the topic. Contradict with methods. Does not identify subject of study.
		8 - 15	<ul style="list-style-type: none"> Concise and brief. Be interrelated and describes how to achieve that objective. Clearly identify the subject of study. Related to the experiment that has been done.
Introduction	10	0	Section missing completely.
		1 - 5	Background info only from lab manual
		6 - 10	<ul style="list-style-type: none"> Clearly written, well structured, with

			<p>evidence of extra reading.</p> <ul style="list-style-type: none"> • Clear outline of study's hypotheses. • Does show something novel in it as compared to the supplied handout/laboratory manual. • Does include the rationale for performing the experiment.
Experimental	10	0	Section missing completely.
		1 - 5	<ul style="list-style-type: none"> • One or more subsections (e.g. chemicals or instrumentation) are missing. • Confusing statement. • Parts have been included under the wrong subsection.
		6-10	Contains all of the relevant information about the method used; clearly and systematically described in such a way that a reader could replicate the study from the description.
Results	20	0	No Discussion section.
		1-6	Very lack attempt to relate experiment findings and collected data.
		6-12	Showing attempt to discuss the findings and collected data, but using inaccurate theories and justifications.
		13-20	Able to demonstrate analysis skill in discussing the and appropriate statements to justify the experiment outcome.
Discussion	20	0	No Discussion section.
		1-6	Very lack attempt to relate experiment findings and collected data.
		6-12	Showing attempt to discuss the findings and collected data, but using inaccurate theories and justifications.
		13-20	Able to demonstrate analysis skill in discussing the and appropriate statements to justify the experiment outcome.
Safety caution	5	0	Section is not present.
		1-3	Sentences are not in complete, focusing on minor or lack important steps.
		4-5	Tabulate at least 3 major and most important safety caution.
Conclusions	10	0	Section missing completely
		1 – 5	<ul style="list-style-type: none"> • Conclusion is drawn but not supported by experimental evidence. • No sensible conclusion is drawn. • No clear evidence of a thorough understanding of the experiment and/or theory behind the experiment.

		6 – 10	<ul style="list-style-type: none"> • Conclusion is drawn and supported by experimental evidence. • Sensible conclusion is drawn. • Shows clear evidence of a thorough understanding of the experiment and/or theory behind the experiment.
References	5	0	Reference not included in the report
		1 - 3	Incomplete references to the books or any other sources used in report.
		4 - 5	<ul style="list-style-type: none"> • References in the text and in the reference list conform in all respects to the formatting convention (e.g. APA format) • Complete references to the books or any other sources used in report. • References in text are matched with references in reference list (e.g. no missing references)
Total Mark	100		

Section 3 Assessment of Understanding/Revision on conducted experiments (20%)

Score	Criteria
0	Unable to answer any questions.
1-5	Very little attempt to answer question correctly.
6-10	Most answers are incorrect, and some are irrelevant to the question type.
11-15	Some answers maybe very short or incomplete.
16-20	Questions are answered to the best of abilities and answers match the question types.

Late Report -1 marks / day

*For Section 3 Assessment-it is up to the lecturer in-charge to decide whether want to carry out a simple test or not. If choose not to, the 20% marks will be allocated back to Section 2- Lab report.

SYNTHESIS AND NITRATION OF TRIS(ACETYLACETONATO) COBALT(III) COMPLEX

1. INTRODUCTION

Acetylacetonone (Figure 1) is a ligand which can form complexes with most metal ions. This ligand is able to form a stable delocalized ring as shown in Figure 2.

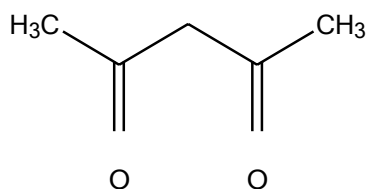


Figure 1

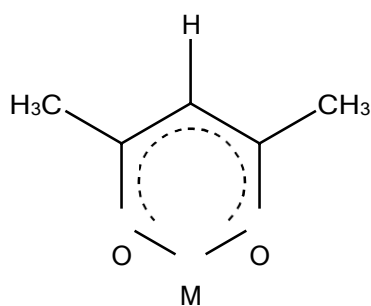


Figure 2

The first part of this experiment involves the synthesis of tris(acetylacetonato)cobalt(III), $\text{Co}(\text{acac})$. The second part involves modification of the chemical properties of ligands when coordinated to metallic ions.

2. LEARNING OUTCOMES

On successful completion of the course, students will be able to:

- 1) Develop synthetic skills and elaborate on the structure determination using infrared (IR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy

3. METHODOLOGY

Preparation of $\text{Co}(\text{acac})$.

Heat a mixture of 1.25 g cobalt(II) carbonate and 10 mL acetylacetonone in a 125 mL conical flask to 90°C . While stirring vigorously using a magnetic stirrer, carefully add 15 mL of 10% hydrogen peroxide drop wise (about 15 minutes drop wise (about 15 minutes) to avoid strong effervescent. When all the hydrogen peroxide has been added, cool the mixture in an ice-salt

bath, filter green crystal formed and dry it in the oven at 110°C. Purify the crystal by adding toluene and heat the mixture until it boils (in a fume cupboard). Filter the hot solution and while it is hot, add about 75 mL heptane or petroleum ether into the hot solution. Cool the solution in an ice-salt bath, filter the solid by suction and leave it to dry at room temperature. Record your yield.

Nitration of Co(acac).

This part of the experiment is to be done in pairs.

- 1) Weigh 1.08 g copper(II) nitrate trihydrate and 0.5 g Co(acac) and place them in a dry beaker. Add 20 mL acetic anhydride to the mixture in the beaker, cover with a watch glass and stir vigorously at room temperature. After stirring for 30 minutes, carefully pour the mixture into an iced sodium acetate solution prepared by mixing 7.5 g sodium acetate, 60 mL water and 60 g ice. Greenish oil will be separated from the solution. The green oil is solidified by adding ethanol until the solution becomes cloudy. Filter the precipitate under suction and wash it with water (5 mL) and finally with ethanol. Recrystallize the crude product from chloroform-ethanol mixture. Record your yield and the IR spectrum for Co(acac) and the nitrated product and describe their differences.

4. QUESTIONS

- 1) What is the role of 10% H₂O₂ in the reaction and suggest what can be used to substitute this chemical?
- 2) Record the ¹H-NMR spectrum for Co(acac) and the nitrated product using chloroform, purified specially for NMR (obtain the solvent from the laboratory assistant). Discuss the spectrum of Co(acac) and compare it with the spectrum of acetylacetone (given).
- 3) Which part of the acetylacetone ligand in Co(acac) is nitrated? Explain your answer.

5. REFERENCES

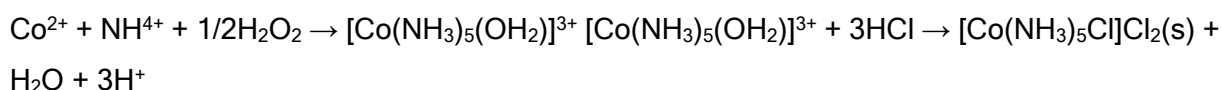
- 1) Glidewell, C. Metal Acetylacetonate Complexes: Preparation and Characterisation. In Inorganic Experiments, Third Edition; Woolins, D., Ed.; Wiley-VCH: Weinheim, Germany, 2010; pp 109-119.
- 2) Evans, D. F. The Determination of the Paramagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance. Proc. Chem. Soc. 1959, 2003-2005

**SYNTHESIS OF COBALT COORDINATION COMPOUNDS: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$,
 $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ AND $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$**

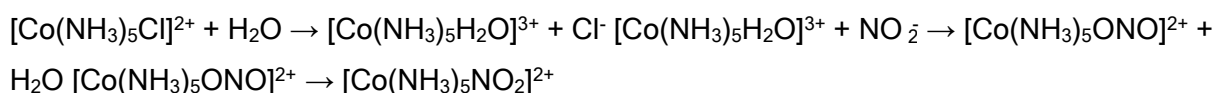
1. INTRODUCTION

Divalent cobalt is more stable than trivalent cobalt for simple salts of cobalt, with only a few salts of Co(III) known (e.g. CoF_3). Formation of a coordination complex stabilizes a higher oxidation state as evidenced by a number of octahedrally coordinated complexes. In this experiment, you will prepare 3 cobalt complexes; 1 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, 2a and 2b (two classical linkage isomer compounds, $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$, respectively).

1) Synthesis scheme of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ involves the following unbalanced equations:



2) Synthesis of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ involves the following:



Safety Precautions: Be especially careful in handling ammonia, concentrated hydrochloric acid and 30% hydrogen peroxide!

2. LEARNING OUTCOMES

On successful completion of the course students will be able to:

- 1) Develop synthetic skills in preparing coordination complexes.
- 2) Understand the concept of stereoisomerism that is possible in coordination complexes.
- 3) Characterize the complexes using infrared (IR) and ultraviolet (UV) spectroscopic techniques.

3. METHODOLOGY

Preparation of [Co(NH₃)₅Cl]Cl₂ (1)

In the fume hood, completely dissolve 6 g of NH₄Cl in ~40 mL of concentrated ammonia solution in a 400 mL beaker. With continuous stirring, add 12 g of cobalt(II) chloride-hexahydrate **in small portions** which will give to brown-coloured slurry. Slowly, add 10 mL of 30% H₂O₂ followed by 30 mL of concentrated HCl **dropwise**. Heat the mixture on a hot plate and maintain at 85° C for 20 minutes. Cool mixture to room temperature and later in an ice bath. Filter (using a Buchner funnel) the crystals of [Co(NH₃)₅Cl]Cl₂. Wash with 5 mL of ice water (distilled water cooled in ice). Note the colour of your product. Dry the product in an oven at 100° C for 2 hours and then weigh the product to determine the percent yield before collecting an IR and UV-Vis spectra.

Preparation of [Co(NH₃)₅ONO]Cl₂ (2a)

In the fume hood, completely dissolve 2.5 g of [Co(NH₃)₅Cl]Cl₂ in a solution of 5 mL of concentrated ammonia solution in 40 mL of distilled water. Stir and heat if necessary to dissolve. A black precipitate of cobalt oxide may form. Cool the solution to ~10°C and separate the mixture by filtration. Dissolve 2.5 g of sodium nitrite in the filtrate followed by addition of 2.5 mL of 6 M HCl.

Cool the mixture in an ice bath for at least 45-50 minutes and filter (using a Buchner funnel) the precipitated crystals of [Co(NH₃)₅ONO]Cl₂. Wash with 5 mL of ice water (distilled water cooled in ice) and then 5 mL of alcohol. Note the colour of your product. Allow it to dry on the lab bench for approximately one hour before collecting an IR and UV-Vis spectrum. Do not dry in a drying oven. Discard the waste in the appropriate waste container in the fume hood. Weigh the product. Calculate the theoretical and experimental percent yield.

The product [Co(NH₃)₅ONO]Cl₂ is not stable and will isomerize to [Co(NH₃)₅NO₂]Cl₂. Ensure you have sufficient time in the laboratory session to collect the IR spectrum of the product on the same day as the synthesis.

Preparation of [Co(NH₃)₅NO₂]Cl₂ (2b)

In the fume hood, completely dissolve 2.5 g of [Co(NH₃)₅Cl]Cl₂ in a solution of 5 mL of concentrated ammonia solution in 40 mL of distilled water. Stir and heat if necessary to dissolve. A black precipitate of cobalt oxide may form. Cool the solution to ~10°C and separate the mixture by filtration. Dissolve 2.5 g of sodium nitrite in the filtrate followed by

addition of 2.5 mL of 6 M HCl. Gently warm the solution to $\sim 60^{\circ}\text{C}$ for 15 minutes and add 3 mL of 6 M NH_4OH .

Cool the mixture and add 20 mL of concentrated HCl. Filter (using a Buchner funnel) the precipitated crystals of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$. Wash with ethanol and allow the product to air dry for several hours. Note the colour of your product. Weigh the product. Calculate the theoretical and experimental percent yield. Collect the IR spectrum and the UV-Vis spectrum.

4. QUESTION

- 1) What kind of isomerism can be observed in complexes prepared in this experiment? Identify the types of isomerism and draw the structures.

5. REFERENCES

- 1) The Synthesis and Characterization of Inorganic Compounds, Jolly, Prentice-Hall, 1991.
- 2) Consult Chemistry, The Central Science, 9th Edition, Brown, LeMay, Bursten, Chapter 24 for additional information about coordination compounds.

SPECTROPHOTOMETRIC ANALYSIS OF A TWO-COMPONENT SYSTEM

1. INTRODUCTION

For a solution containing two or more coloured components which do not interact with each other, their absorbance are additive. This means that the absorbance of the mixture at a specific wavelength is the sum of the absorbance of the individual component in the mixture at that particular wavelength. For a substance which obeys the Beer- Lambert's law, the absorbance (A) is given by:

$$A = \epsilon/lc$$

where ϵ is the molar absorptivity ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), l is the path length (cm), and c is the concentration in mol dm^{-3} .

If the path length is fixed, that is by using a 1 cm cell throughout the analysis, then ϵ and l can assume a proportional constant, k . The above equation becomes:

$$A = kc \dots\dots\dots (1)$$

For a two-component mixture, where the absorbance possesses the additivity property, the absorbance at a wavelength λ is given by:

$$A(\lambda) = A_1(\lambda) + A_2(\lambda) \dots\dots\dots (2)$$

Where $A_1(\lambda)$ and $A_2(\lambda)$ are the absorbance of component 1 and component 2 at wavelength λ , respectively. By assuming equation 1 into equation 2, the absorbance at λ is:

$$A(\lambda) = k_1(\lambda)c_1 + k_2(\lambda)c_2 \dots\dots\dots (3)$$

Similarly, the absorbance at λ' is:

$$A(\lambda') = k_1(\lambda')c_1 + k_2(\lambda')c_2 \dots\dots\dots (4)$$

The proportional constants, $k_1(\lambda)$, $k_1(\lambda')$, $k_2(\lambda)$ and $k_2(\lambda')$ are determined by measuring absorbance of pure solutions of component 1 and component 2 at λ and λ' .

The concentrations of component 1 and 2 (c_1 and c_2 respectively) can be calculated by solving equation 3 and equation 4 simultaneously.

2. LEARNING OUTCOMES

On successful completion of the course students will be able to:

- 1) Prove the additivity of absorbance for a two-component mixture. This is important as a large number of coloured substances interact with each other in a mixture and hence cannot be studied by this technique.
- 2) Determine the suitable wavelength (λ and λ') for the analysis. For a two-component system, the most suitable wavelength is where the absorbance for the first component is the strongest while the absorbance of the second component is the weakest.

3. METHODOLOGY

- 1) Switch on the spectrophotometer and leave it to warm up for at least 15 minutes.
- 2) Obtain about 100 mL of 0.1880 M cobalt(II) stock solution and about 100 mL of 0.0500 M chromium(III) stock solution. Prepare the following solutions in 50 mL volumetric flasks from the stock solutions:
 - a. 0.0376 M, 0.0752 and 0.150 M cobalt(II) solutions.
 - b. 0.0100 M, 0.0200 M, 0.0300 M and 0.0400 M and chromium(III) solutions.
 - c. A solution containing a mixture of 0.0752 M cobalt(II) and 0.0200 M chromium(III) ions.
- 3) Measure the absorbance, from 375 nm to 625 nm in increment of 10 nm, for the following solutions:
 - a. 0.0752 M cobalt(II) solution (from 2(a))
 - b. 0.0200 M chromium(III) solution (from 2(b))
 - c. mixture of 0.0752 M of cobalt(II) and 0.0200 M chromium(III) ions (from 2(c)).
- 4) Plot the graph of absorbance versus wavelength for the three solutions on the same graph paper. Determine the wavelengths at which chromium(III) ion and cobalt(II) ion have maximum absorbance. (The theoretical λ_{\max} for cobalt(II) ion and chromium(III) ion is 510 nm and 575 nm respectively.)
- 5) Measure the absorbance of all the solutions prepared in 2(a) and 2(b) at λ_{\max} 510 nm and 575 nm. Plot graphs of absorbance versus concentration for chromium(III) ion

and cobalt(II) ion, and determine the proportional constants, k_{Cr} and k_{Co} at each λ_{max} from the slope of the graphs.

- 6) Obtain a solution containing a mixture of cobalt(II) and chromium(III) ions of unknown concentrations. Pipette 25 mL of the solution into a 50 mL volumetric flask.
- 7) Add distilled water to the calibration mark, shake the flask thoroughly and measure its absorbance at 510 nm and 575 nm. Calculate the concentrations of cobalt(II) and chromium(III) ions in the solution.

4. QUESTIONS

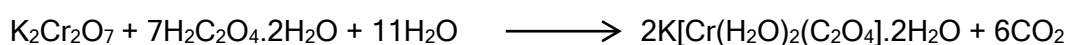
- 1) Discuss why the Co and Cr complexes display different colours?
- 2) What do you understand about the absorption spectroscopy?
- 3) Suggest another pair of wavelength which can be used to determine the concentration of cobalt (II) and chromium (III) ions in a mixture.

5. REFERENCE

- 1) D.A. Skoog, D.M. West, F.J. Holler, and S.R. Crouch, Analytical Chemistry. An Introduction, 3rd Edition, Saunders College Publishing, 2000.
- 2) Christian, G.D., Analytical Chemistry, 6th edition. New Jersey. John Wiley, 2004.

PREPARATION AND ANALYSIS OF POTASSIUM CIS-DIAQUADIOXALATOCHROMATE(III) DIHYDRATE**1. INTRODUCTION**

Potassium cis-diaquadioxalatochromate(III) dihydrate, $K[Cr(H_2O)_2(C_2O_4)] \cdot 2H_2O$ is prepared from oxalic acid dihydrate, potassium dichromate and water. The reaction equation is:



This salt is dichroic, and in the solid state has a black colour in diffuse sunlight but has a deep purple colour under artificial light. In solution, the salt is purple to red depending on the light that is transmitted, and does not give a precipitate with barium chloride.

2. LEARNING OUTCOMES

On successful completion of the course students will be able to:

- 1) Understand the concept of coordination complexes – combination of metal ion and ligands.

3. METHODOLOGY**Synthesis of $K[Cr(H_2O)_2(C_2O_4)] \cdot 2H_2O$**

Grind in two separate dry mortars, oxalic acid dihydrate (12 g, 0.095 mol) and potassium dichromate (4 g, 0.013 mol). Then, mix the two powders thoroughly. Meanwhile, wash a 10 cm radius evaporating dish with distilled water, remove as much water as possible so that the dish is slightly wet and place the mixed powder in the centre of the wet dish. The evaporating dish should be placed on the bench top, away from other items. Continue to grind the mixed powder using the pestle. After a while, the reaction should start spontaneously (the reaction is accompanied with frothing as carbon dioxide is released) and results in the formation of a thick syrup.

While the syrup is still warm, pour about 20 mL ethanol onto it. Heat the evaporating dish on a hot plate, and stir the syrup until it solidifies to a dry powder. Initially, use a metal spatula to triturate the mixture, and then use the pestle to break the hardened dough into a powder. If the dough does not solidify with the use of one portion of ethanol, decant the ethanol, add another 20 mL ethanol and repeat the above steps.

Analysis of the oxalate content in $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 2H_2O$

The analysis should be done in duplicate.

Weigh 0.3 g of the dried $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 2H_2O$ in a beaker, and add 10 mL water followed by 10 mL potassium hydroxide (10%). Heat the mixture until chromium(III) hydroxide (green precipitate) is completely precipitated (about 40 minutes). Filter off the precipitate and wash it with hot distilled water. Combine the filtrate and the washings. Wash the precipitate once more, but keep the final washing separately. Acidify the filtrate with sulfuric acid, and heat it to about 70°C. Titrate against standard potassium permanganate (0.02 M).

Check the completeness of the titration by adding a drop of potassium permanganate to the last washing that you have kept separately; the washing should be acidified and heated as before.

Analysis of the chromium content in $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 2H_2O$

(Oxidation to dichromate using potassium persulfate)

The analysis should be done in duplicate.

Weigh accurately about 0.2 g of the dried $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 2H_2O$ and dissolve it in 50 mL water in a 250 mL conical flask. Add 2 mL silver nitrate solution (0.1 M) followed by 10 mL potassium persulfate solution (10%). Heat the mixture for 20 min, allow to cool and add 10 mL sulphuric (10%) and 2 mL phosphoric acid (10%). Cool the solution. Add 10 mL concentrated hydrochloric acid and 1 g potassium iodide. Titrate the liberated iodine with thiosulfate solution (0.05 M) that has been standardized against potassium chromate.

4. QUESTIONS

- 1) Calculate the percentage of oxalate and chromium ions in the salt.
- 2) Discuss the geometry of the complex prepared.
- 3) Give the type of isomerism that occur in the Cr(III) complexes and draw the structures.

SYNTHESIS AND STUDIES OF THE ABSORPTION SPECTRUM OF COPPER(II) COMPLEXES

1. INTRODUCTION

The valence electronic configuration of “free” copper(II) ion is $3d^9$. At room temperature, the valence electronic configuration of copper(II) ion is $t_{2g}^6e_g^3$ due to the presence of ligands in solution. The ion shows an unsymmetrical broad band in the visible spectrum because of the electronic transition $(t_{2g})^6(e_g)^3 \rightarrow (t_{2g})^5(e_g)^4$.

In this experiment, you will prepare three Cu(II) complexes, namely *cis*-bis(glycinato)copper(II) monohydrate, bis(acetylacetonato)copper(II), and potassium bis(oxalato)cuprate(II) dihydrate. You will then record the visible spectrum of these complexes, calculate their Δ_o (or $10Dq$) values and then prepare a spectrochemical series for several copper(II) complexes based on Δ_o values.

2. LEARNING OUTCOMES

On successful completion of the course students will be able to:

- 1) Develop synthetic skills in preparing the copper(II) complexes.
- 2) Understand the correlation between the choice of ligands, the splitting of electrons in the d orbitals and the results observed from the electronic spectra.

3. METHODOLOGY

Preparation of copper(II) complexes

(a) *cis*-bis(glycinato)copper(II) monohydrate, $[\text{Cu}(\text{NH}_2\text{CH}_2\text{CO}_2)_2]\cdot\text{H}_2\text{O}$

Dissolve 1.5 g (6.0 mmol) copper(II) sulphate in 12 mL HCl (1 M). Add 0.75 g (10.0 mmol) glycine to the mixture and heat for 15 minutes. Add sodium hydrogen carbonate (NaHCO_3) to the hot mixture until precipitation is complete (avoid adding too much NaHCO_3). Filter the precipitate by suction and purify by recrystallization using hot distilled water. Collect the purified crystals and dry in an oven. Record your yield

(b) Preparation of bis(acetylacetonato)copper(II), Cu(acac)2

Dissolve 1.25 g (12.5 mmol) acetylacetone in 50 mL aqueous solution of NaOH (0.25 M, 12.5 mmol). Dissolve 1.55 g copper(II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; 6.25 mmol) in 50 mL distilled water. Then, mix the two solutions. Filter the precipitate formed by suction and recrystallize using dioxan. Collect the purified crystals and dry in air. Record your yield.

(c) Preparation of potassium bis(oxalato)cuprate(II) dihydrate, $\text{K}[\text{Cu}(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$

Dissolve 12.3 g potassium oxalate monohydrate ($\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) in 35 mL distilled water and heat the solution to 90°C . Dissolve 4.1 g copper(II) sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in 8 mL distilled water, and heat the solution to 90°C . Filter the solution while still hot, and slowly with stirring, add the hot filtrate to the hot solution of potassium oxalate. Cool the mixture in an ice bath, filter the crystals formed and wash with cold water, followed by ethanol and finally acetone. Dry the crystals in air. Record your yield.

The Visible Spectrum of Copper(II) Complexes

You are provided with the following solutions:

For the preparation of $\text{Cu}^{2+}\text{-NH}_3$:

- a) 0.01 M $\text{Cu}(\text{NO}_3)_2$ and 2 M NH_4NO_3
- b) 0.10 M NH_3

For the preparation of $\text{Cu}^{2+}\text{-en}$:

- a) 0.01M $\text{Cu}(\text{NO}_3)_2$ and 1 M KNO_3
- b) 0.10 M ethylenediamine (en)

Prepare the solutions as shown in the table below and determine the visible spectrum for each of the solution prepared.

	Solution	mol/ solvent ratio
1	$\text{Cu}^{2+}\text{-NH}_3$	1:1
2	$\text{Cu}^{2+}\text{-NH}_3$	1:2
3	$\text{Cu}^{2+}\text{-NH}_3$	1:3
4	$\text{Cu}^{2+}\text{-NH}_3$	1:4
5	$\text{Cu}^{2+}\text{-en}$	1:1
6	$\text{Cu}^{2+}\text{-en}$	1:2
7	<i>cis</i> -bis(glycinato)copper(II) monohydrate	Solvent: distilled water
8	bis(oxalato)cuprate(II) dihydrate	Solvent: chloroform
9	potassium bis(oxalato)cuprate(II) dihydrate	Solvent: distilled water

Obtain the visible spectrum of an aqueous solution of copper(II) from the laboratory assistant.

4. QUESTIONS

- 1) Calculate for the Δ_o copper(II) complexes that you have prepared, assuming that their geometry is octahedral, and the spectrum analysed using the crystal field theory.
- 2) Comments on the shape of the bands observed.
- 3) Prepare the spectrochemical series for the following copper(II) complexes: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, $[\text{Cu}(\text{C}_2\text{O}_4)_2]^{2+}$, $\text{Cu}(\text{acac})_2$, and $\text{Cu}(\text{gly})_2$.
- 4) $\text{Cu}(\text{II})$ ion is not suitable for the accurate determination of Δ_o although it is easily prepared and stable. Explain why.