

LABORATORY MANUAL

SIC2017 - Practical of Inorganic Chemistry II

Department of Chemistry | Faculty of Science

Safety in the Second Year Laboratory

Further information in the details of the safety and health practice in Universiti Malaya can be found at:



Occupational Safety &
Health and Environment
(OSHE), Universiti
Malaya



Universiti Malaya
Safety Handbook

The University has a statutory obligation to comply with the safety requirements and you, as a student, have a duty to abide by the regulations. The following notes are to guide you in good laboratory practice and to familiarize yourself with the safety aspects of your laboratory work.

Emergency Telephone Numbers:

- National Emergency Number 999
(Mobile phone, dial 112)
- Universiti Malaya Security Office +603 7967 7070
- Universiti Malaya Medical Centre (UMMC)
Emergency Department +603 7949 2892
- Universiti Malaya Students' Health Clinic +603 7967 6445
- Occupational Safety & Health and Environment
(OSHE) +603 7967 6597
- Department of Chemistry Office +603 7967 4204
- Pantai Fire Station (Jalan Pantai Baru) +603 2282 4444
- Pantai Police Station (Jalan Pantai Baru) +603 2282 2222

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 action of fellow workers in the laboratory. Therefore, it is in everyone's best interest to follow safety 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. Basically this includes laboratory coats, safety glasses, 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 your need to determine the odor 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 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 neighbor.
- 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 personal 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: _____

Detailed Rubrics for Level II and III Laboratory Classes

Section A: Attendance and Responsibility (Total 20%)

1. Attendance (5%)

Score	Criteria
0	Student did not attend without any valid reasons.
5	Student is present.

2. Pre-entering lab (5%)

Score	Criteria
0	No preparation of experimental procedure.
3	Summary of procedures too brief, lack of details and confusing.
5	Presents easy to follow steps in lab experimental, logical and adequately detailed.

3. Proper attire (5%)

Score	Criteria
0	No proper attire – covered shoes, safety goggles and lab coat.
3	Covered shoes and lab coat available but no safety goggles.
5	Safety attire checked.

4. Promptness (5%)

Score	Criteria
0	Student is late for more than 15 minutes without any valid reasons.
3	Student is late for not more than 15 minutes without any valid reasons.
5	Student is always prompt.

Notes:

1. The student **MUST** attend the laboratory session to be eligible for obtaining marks. **NO** marks will be given at all if the student did not attend any laboratory sessions without valid reasons.

2. If the student did not attend any of the laboratory session, there **MUST** be an official explanation (i.e., if Covid-19: MySejahtera Screenshot; Sick: MC from doctor; representing UM in activities: Official Letter from the Department/Faculty/University, etc.; Family reasons: Death of family member, etc.).

Section B: Lab Performance – Skills and Technique (Total 20%)

Score	Criteria
0-5	No skill is demonstrated.
6-10	Wrong glassware used, wrong technique, spillage and wasting of chemicals.
11-15	Right glassware used, incorrect or lack of lab technique.
16-20	Presents correct lab skill, clean and tidy.

Section C: Lab Jotter (Total 10%)

Score	Criteria
0	No jotter or student did not show raw data to the lecturer-in-charge; student exhibit evidence of data forging and/or plagiarism.
1-3	Raw data are out-of-place; major data or observations missing; no proper labelling.
4-6	Some key data or observations missing. Presentation need major improvement.
7-8	Almost all raw data and key observations written. Presentation can still be improved.
9-10	Raw data and observations tabulated/written in a clear and tidy manner, with correct units and no evidence of data forging and/or plagiarism.

Section D: Lab Report (Total 40%)**(I) Short Report**

Section	Score	Criteria
Title (5 marks)	0	No title.
	1	Too brief (e.g. "Lab Report", "Mercury in Fish", "Synthesis of Cinnamic Acid" or "Boiling Point of Water").
	2-3	Too long or does not identify the complete subject of study (e.g. "Determination of iron", "Determination of lead", etc.).
	4-5	Identify the complete subject of study and encapsulates the purpose of the report/study (e.g. "Kinetics of the hydrolysis of <i>t</i> -butyl chloride at 30 °C", "Synthesis of triphenylcarbinol via Grignard reaction" or "Determination of iron in red meat via spectrophotometry").
Results (Data, figures, graphs, tables, observations, % yield, etc.) (35 marks)	0	Section missing completely.
	1-10	No flow of results. Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing or incorrect, numerical data did not have correct significant figures, etc.
	11-20	Most figures, graphs, tables OK, some still missing some important or required features.
	21-30	All figures, graphs, tables are correctly drawn, but some have minor problems (e.g. incorrect significant figures, incomplete observation) or could still be improved.

	31-35	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions. Observations clearly stated. Numerical data contains correct significant figures and units.
Discussion (35 marks)	0	Section missing completely.
	1-10	Lack of attempt to relate experimental findings and data with contemporary theories. Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	11-20	Some attempt to relate experimental findings and data but using inaccurate theories. Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	21-30	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.
	31-35	All of the important trends and data comparisons have been interpreted correctly and discussed; good understanding of results is conveyed.
Safety Precautions (5 marks)	0	Section missing completely.
	1	Sentences are incomplete, focusing on minor points or lack important steps.
	2-3	State only 1-2 major and most important safety precautions.
	4-5	State at least 3 major and most important safety precautions.
Conclusions (10 marks)	0	Section missing completely.
	1-3	Conclusion missing the important points or is not supported by the experimental results.
	4-6	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	7-8	All important conclusions have been drawn, could be better stated.
	9-10	All important conclusions have been clearly made, student shows good understanding.
References (5 marks)	0	Section missing completely.
	1-3	Incomplete references to the books or any other sources used in report.

	4-5	Correct in-text citations and the references in the reference list conform to all respects of 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).
Appearance and Formatting (5 marks)	1	Sections out of order, too much handwritten copy, sloppy formatting.
	2	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.
	3	All sections in order, formatting generally good but could still be improved.
	4-5	All sections in order, well-formatted, very readable.

Total section D marks = $(x/100) \times 40\%$

(II) Full Report

Section	Score	Criteria
Title (5 marks)	0	No title.
	1	Too brief (e.g. "Lab Report", "Mercury in Fish", "Synthesis of Cinnamic Acid" or "Boiling Point of Water").
	2-3	Too long or does not identify the complete subject of study (e.g. "Determination of iron", "Determination of lead", etc.).
	4-5	Identify the complete subject of study and encapsulates the purpose of the report/study (e.g. "Kinetics of the hydrolysis of <i>t</i> -butyl chloride at 30 °C", "Synthesis of triphenylcarbinol via Grignard reaction" or "Determination of iron in red meat via spectrophotometry").
Introduction (Including objectives) (10 marks)	0	Section missing completely.
	1-3	Very little background information provided, or information is incorrect.
	4-6	Some introductory information, but still missing some major points.
	7-8	Introduction is nearly complete, missing some minor points.

	9-10	Introduction complete and well-written; provides all necessary background principles for the experiment with evidence of extra reading.
Experimental Procedure (10 marks)	0	Section missing completely.
	1-3	No sub-sections, missing several important experimental details or not written in paragraph format. Parts have been included under the wrong sub-section.
	4-6	Written in paragraph format, still missing some important experimental details.
	7-8	Written in paragraph format, important experimental details are covered, some minor details missing.
	9-10	Well-written in paragraph format, all experimental details are covered.
Results (Data, figures, graphs, tables, observations, % yield, etc.) (25 marks)	0	Section missing completely.
	1-7	No flow of results. Figures, graphs, tables contain errors or are poorly constructed, have missing titles, captions or numbers, units missing or incorrect, numerical data did not have correct significant figures, etc.
	8-15	Most figures, graphs, tables OK, some still missing some important or required features.
	16-20	All figures, graphs, tables are correctly drawn, but some have minor problems (e.g. incorrect significant figures, incomplete observation) or could still be improved.
	21-25	All figures, graphs, tables are correctly drawn, are numbered and contain titles/captions. Observations clearly stated. Numerical data contains correct significant figures and units.
Discussion (25 marks)	0	Section missing completely.
	1-7	Lack of attempt to relate experimental findings and data with contemporary theories. Very incomplete or incorrect interpretation of trends and comparison of data indicating a lack of understanding of results.
	8-15	Some attempt to relate experimental findings and data but using inaccurate theories. Some of the results have been correctly interpreted and discussed; partial but incomplete understanding of results is still evident.
	16-20	Almost all of the results have been correctly interpreted and discussed, only minor improvements are needed.

	21-25	All of the important trends and data comparisons have been interpreted correctly and discussed; good understanding of results is conveyed.
Safety Precautions (5 marks)	0	Section missing completely.
	1	Sentences are incomplete, focusing on minor points or lack important steps.
	2-3	State only 1-2 major and most important safety precautions.
	4-5	State at least 3 major and most important safety precautions.
Conclusions (10 marks)	0	Section missing completely.
	1-3	Conclusion missing the important points or is not supported by the experimental results.
	4-6	Conclusions regarding major points are drawn, but many are misstated, indicating a lack of understanding.
	7-8	All important conclusions have been drawn, could be better stated.
	9-10	All important conclusions have been clearly made, student shows good understanding.
References (5 marks)	0	Section missing completely.
	1-3	Incomplete references to the books or any other sources used in report.
	4-5	Correct in-text citations and the references in the reference list conform to all respects of 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).
Appearance and Formatting (5 marks)	1	Sections out of order, too much handwritten copy, sloppy formatting.
	2	Sections in order, contains the minimum allowable amount of handwritten copy, formatting is rough but readable.
	3	All sections in order, formatting generally good but could still be improved.
	4-5	All sections in order, well-formatted, very readable.

Total section D marks = $(x/100) \times 40\%$

Section E: Assessment of Understanding/Revision on Conducted Experiments (10%)

Score	Criteria
x	Test/Quiz/Lab Presentation, etc.

* For Section E: Assessment - it is up to the lecturer in-charge to decide whether he/she wants to carry out the method of assessment (simple test, presentation, etc). If he/she chooses not to, the 10% marks will be allocated back to Section D: Lab report (i.e. total marks/100 × 50%)

** Late Report Submission: -1 mark / day

Guide for Lecturers to Evaluate Skills and Techniques (Section B)

This is a simple guide for lecturers to evaluate candidates' laboratory skills and techniques. Some simple examples are shown below:

Example 1: Filtering solids using a Buchner funnel

1-5 m: The candidate does not even know what a Buchner funnel and filtering flask are, even after demonstration.

6-10 m: The candidate used a filter paper, funnel, and conical flask to filter the crystals.

11-15 m: The candidate used a Buchner funnel and filtering flask to filter. However, he/she did not cut the filter paper properly, did not wet the filter paper prior to pouring the solution, did not clamp the Flask with a retort stand.

16-20 m: The candidate used a Buchner funnel and filtering flask to filter. The candidate proceeds with clamp the filtering flask with a retort stand, cutting the filter paper to the appropriate size according to the Buchner funnel, wet it with the appropriate solvent, and pour the solution carefully until in such most of the crystals are inside the Buchner funnel.

Example 2: Acid-base titration

1-5 m: The candidate does not even know what a burette and pipette are, even after demonstration.

6-10 m: The candidate handled the pipette wrongly; filled the burette and read the volume meniscus wrongly (i.e. meniscus not parallel with the eye); did not clamp the burette securely with a retort stand; did not use the correct acid-base indicator or did not use any indicator at all.

11-15 m: The candidate used a pipette and burette correctly and clamped the burette with a retort stand and used the correct acid-base indicator. However, he/she used a beaker for the titration instead of a conical flask or did not remove the trapped air bubbles in the burette prior to titration.

16-20 m: The candidate used a pipette and burette correctly and clamped the burette with a retort stand and used the correct acid-base indicator. During titration, he/she used proper glassware and removed the trapped air bubbles in the burette prior to titration.

Example 3: Operating a UV-visible spectrophotometer

1-5 m: The candidate does not even know how to operate a UV-visible spectrophotometer, even after demonstration.

6-10 m: The candidate did not calibrate the spectrophotometer with the appropriate blank solutions before the experiment or the candidate used the wrong blank solution as reference.

11-15 m: The candidate used a calibrated spectrophotometer to do experiment but did not wipe the cuvette clean with a tissue paper prior to doing the experiment or the candidate did not rinse the cuvette properly after use.

16-20 m: The candidate used a calibrated spectrophotometer to do experiment and used the cuvette properly.

Guide for Lecturers to Evaluate Students' Understanding of Experiments (Section E)

The evaluation for Section E should encompass what have the students learned throughout the laboratory session. Examples of methods to conduct the evaluation:

- (a) Written test:
e.g. How do you determine which layer is organic or aqueous in a separating funnel?

OR

- (b) Student conduct one of the experiments without any input from the lecturer and assessment is carried out during the experiment:
e.g. Students carry out a recrystallisation of benzoic acid themselves.

OR

- (c) Presentation of experimental results (oral or any method deemed suitable):
e.g. Students presenting their experiment results.

OR

- (d) Any other methods deemed suitable.

LIST OF EXPERIMENT

No.	EXPERIMENT	PAGE	WEEK
1	SYNTHESIS AND NITRATION OF TRIS(ACETYLACETONATO)COBALT(III) COMPLEX	15	
2	ISOMERISM OF DICHLOOROBIS(ETHYLENEDIAMINE)COBALT(III) CHLORIDE	17	
3	KINETICS OF DICHLOOROBIS(ETHYLENEDIAMINE)COBALT(III) CHLORIDE	19	
4	PREPARATION AND ANALYSIS OF POTASSIUM CIS-DIAQUADIOXALATOCHROMATE(III) DIHYDRATE	21	
5	SYNTHESIS AND STUDIES OF THE ABSORPTION SPECTRUM OF COPPER(II) COMPLEXES	23	

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 can form a stable delocalized ring as shown in Figure 2.

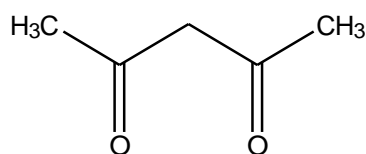


Figure 1

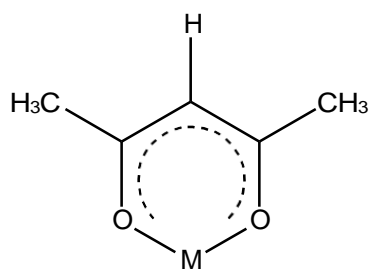


Figure 2

The first part of this experiment involves the synthesis of tris(acetylacetonato)cobalt(III) complex, $\text{Co}(\text{acac})$. 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

A. 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) 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.

B. Nitration of Co(acac).

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

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

ISOMERISM OF DICHLOROBIS(ETHYLENEDIAMINE)COBALT(III) CHLORIDE

1. INTRODUCTION

The purpose of this experiment is to prepare and study the kinetics of the interconversion of some of the isomers of a typical coordination compound. Historically, isomerism has played a central role in establishing the basic concepts of coordination chemistry upon which so much of modern inorganic chemistry is based. On the other hand, the reaction kinetics of coordination compounds is an area of continuing intense research activity. Much of the present interest in the mechanisms of the reactions of coordination compounds stems from their relevance to enzyme reactions where the active site frequently involves coordination to a metal ion.

The first part of this experiment involves the preparation of the *cis* and *trans* isomers of dichlorobis(ethylenediamine)cobalt(III) chloride while in the second part (in Experiment 3), the rate of conversion for the racemic *cis* isomer to the *trans* isomer is followed spectrophotometrically.

2. LEARNING OUTCOME

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

- 1) Differentiate the isomers of coordination compounds with spectroscopic methods.

3. METHODOLOGY

A. Preparation of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride.

To a solution of 16 g of cobalt(II) chloride hexahydrate in 50 cm³ of water contained in a 500 cm³ Erlenmeyer (or conical) flask, add with stirring 60 g of a 10% solution of ethylenediamine. A vigorous stream of air is drawn through the solution for 1-2 hours. Add 35 cm³ of concentrated hydrochloric acid and evaporate the solution on a steam bath until a crust forms over the surface (ca. 75 mL).

Cool the solution and stand overnight before filter the bright green plates of the hydrochloride, *trans*-[Coen₂Cl₂]Cl·HCl. Wash the sample with alcohol, follows by ether and left to dry. Grind the dried crystals finely using a pestle and mortar, then transfer to a porcelain dish and dry in oven at 110°C. At this temperature the hydrogen chloride is eliminated, and the crystals have

converted into a dull green powder. Yield expected is ca. 8 g. (50 % based on ethylenediamine used).

B. Preparation of the *cis* isomer.

A solution of the *trans* form yields the less soluble *cis* form upon evaporation to dryness over a steam bath. Dissolve about 2 g of the *trans* complex in 10 mL of water in an evaporating dish. Allow the solution to concentrate on the steam bath. The solution will change from green to purple. When the purple crust is formed (do not wait until the crust fully dried up), immediately place the evaporating dish in an ice bath. Allow the crust to harden in the ice bath.

If the purple crust changes to green, the evaporation will be repeated by adding 10 mL of water. This process should not be repeated more than three times as further repetition of evaporation may cause substantial decomposition that affects the formation of *cis* complex. Collect the purple complex by filtration. Finally, unchanged *trans* form may be washed out with a little cold water.

4. REFERENCES

- 1) Brice, L. K. (1962) *J. Chem. Educ.*, 39 (12), 634.
- 2) Brasted, R. C. & Hirayama, C. (1958). *J. Am. Chem. Soc.*, 80, 4, 788–794.
- 3) Busch, D. H. (1964). *J. Chem. Educ.*, 41 (2), p 77.

ISOMERIZATION KINETICS OF DICHLOROBIS(ETHYLENEDIAMINE)COBALT(III) CHLORIDE

1. INTRODUCTION

Geometrical isomers are different compounds having distinct physical properties and often displays different colours. They also frequently containing bidentate ligands which occupy two coordination sites such as ethylenediamine. Complexes of cobalt(III) are known to have octahedral structures. In solution, these ions undergo racemisation and ligand substitution reactions relatively slower as compared to the complexes of other transition metals. Two general important questions when considering all chemical reactions, how far and how fast? How far- concerns the feasibility of carrying out a reaction, that is determining the equilibrium position of a reaction and the latter concerns how fast the equilibrium position is established which is known as chemical kinetics. Numerous rules and concepts can aid the prediction of whether a particular reaction will occur at which most of thermodynamic considerations. The prediction of how fast a chemical reaction will occur is comparably more difficult. The definitive factor controlling the rate of reaction with the mechanism of reaction involves a detailed time picture of exactly how the molecules and atoms are interacting during the reaction. The rate expression for a chemical reaction is based on data obtained from a kinetic study conducted in the laboratory. From the experimental rate expression, a detailed mechanism for the reaction can be developed.

2. LEARNING OUTCOME

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

- 1) Determine the rate of conversion of *cis* isomer to *trans* isomer.

3. METHODOLOGY

In methanol solution the purple *cis* form is isomerized to the (thermodynamically) more stable green *trans* form. In order to follow the reaction by spectrophotometry, it is necessary to record the spectra of both the *cis* and the *trans* isomer separately. To save time the following procedure is adopted.

Prepare a solution (0.02 M; 28 mg in 50 cm³) of the *trans* isomer in methanol and record its UV- visible spectrum. Repeat this procedure for the *cis* isomer by recording the UV spectrum immediately after the solution has been prepared; then quickly place the solution, tightly

stoppered, into a constant temperature bath at 35°C. Meanwhile from an examination of the spectra (discuss with your Demonstrator) select the most appropriate wavelength to follow the reaction. Measure the optical density D at this wavelength at 15 minutes intervals for about 90 min. by withdrawing samples from the thermostated solution. D_{∞} May be measured by allowing the mixture to stand overnight.

The isomerization reaction is first order. Then $\ln\{cis\} = -kt + c$. It is easily shown that $\ln(D - D_{\infty}) = -kt + C'$ so that a plot of $\log(D - D_{\infty})$ against time should give a straight line of slope $-k/2.303$. (Note that since the reaction is first order neither the extinction coefficient for the two isomers nor the initial concentration of the *cis* isomer need be known). From your results, determine k and the half-life for the reaction.

4. REFERENCES

- 1) Brice, L. K. (1962) *J. Chem. Educ.*, 39 (12), 634.
- 2) Brasted, R. C. & Hirayama, C. (1958). *J. Am. Chem. Soc.*, 80, 4, 788–794.

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

Potassium cis-diaquadioxalatochromate(III) dihydrate, $K[Cr(H_2O)_2(C_2O_4)_2] \cdot 2H_2O$ 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) Develop synthetic skills in preparing coordination complex using mechanochemical method.
- 2) Understand the concept of coordination complexes – combination of metal ion and ligands.

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

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.

B. Analyses

(i) Analysis of the oxalate content in $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$

The analysis should be done in duplicate.

Weigh 0.3 g of the dried $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ in a beaker, and add 10 mL water followed by 20 mL potassium hydroxide (10%). Heat the mixture until chromium(III) hydroxide (green precipitate) is completely precipitated (about 60 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.**

(ii) Analysis of the chromium content in $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$

The analysis should be done in duplicate.

Dissolve all the residue from the filtration in Part B(i), in ~5 mL concentrated hydrochloric acid. Transfer the solution into a 100 mL volumetric flask and add distilled water until calibration mark. Measure the absorbance of the solution by using spectrophotometer at wavelength of 611 nm. Determine the concentration of chromium ion by comparing the absorbance obtained with the calibration curve provided.

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.

5. REFERENCES

- 1) Werner, A. (1914). *Ann. Phys.*, 406, 261.
- 2) Palmer, W. G. (1962). *Experimental inorganic chemistry*. Cambridge University Press, New York.

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 $t_{2g}^6 e_g^3$ 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

A. Preparation of copper(II) complexes

(i) *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

(ii) Bis(acetylacetonato)copper(II), $\text{Cu}(\text{acac})_2$

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.

(iii) Potassium bis(oxalato)cuprate(II) dihydrate, $K[Cu(C_2O_4)_2] \cdot 2H_2O$

Dissolve 12.3 g potassium oxalate monohydrate ($K_2C_2O_4 \cdot H_2O$) in 35 mL distilled water and heat the solution to 90°C. Dissolve 4.1 g copper(II) sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) 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.

B. The visible spectrum of copper(II) complexes

You are provided with the following solutions:

For the preparation of $Cu^{2+}-NH_3$:

- a) 0.01 M $Cu(NO_3)_2$ and 2 M NH_4NO_3
- b) 0.10 M NH_3

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

- a) 0.01M $Cu(NO_3)_2$ 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	$Cu^{2+}-NH_3$	1:1
2	$Cu^{2+}-NH_3$	1:2
3	$Cu^{2+}-NH_3$	1:3
4	$Cu^{2+}-NH_3$	1:4
5	$Cu^{2+}-en$	1:1
6	$Cu^{2+}-en$	1:2
7	<i>cis</i> -bis(glycinato)copper(II) monohydrate	Solvent: distilled water
8	Bis(acetylacetonato)copper(II), $Cu(acac)_2$	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.

5. REFERENCES

- 1) Baker, A. T. (1998). The Ligand Field Spectra of Copper(II) Complexes. *Journal of Chemical Education*, 75(1), 98-99.
- 2) Cotton, F. A. & Wilkinson, G (1999). *Advanced Inorganic Chemistry*, 6th ed. Wiley: New York, pp 769–770.