**Hebron University**

**Faculty of Science and Technology**

**Chemistry Department**

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| ***Inorganic Chemistry Lab Manual*** |

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***Prepared***

***by***

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**Laboratory Safety**

These regulations regarding safe laboratory practice are intended to help you work safely with chemicals. Safe laboratory practice is based on understanding and respecting chemicals, not fearing them. These guidelines cover ordinary hazards and apply to any laboratoryexperiments you will encounter. During laboratory lecture, the instructor will discuss specific safety precautions relevant to any one experiment. The laboratory textbook or handout will point out specific hazards and precautions. Before beginning an experiment, have this information on hand and understand it thoroughly. Do not hesitate to consult the instructor if you have questions about an experiment or these regulations. Remember that Material Safety Data Sheets are available online.

It is your responsibility to read and follow the safety regulations in this document and to follow them in the laboratory. Any other safety handouts or special precautions mentioned during laboratory lecture must also be observed.

Failure to follow laboratory safety rules and procedures may cause injury to you or your colleagues. For the first violation, you may be asked to leave the laboratory for the day; however, for repeated violations, you may be dropped from the laboratory portion of the course with a grade of E. Call unsafe practices by colleagues to his or her attention and (if necessary) to the attention of the instructor.

**I. Safety Regulations and Precautions**

Accidents in the laboratory are often the result of carelessness or ignorance. Stay alert and pay constant attention to your own and to your neighbors' actions. The safetyprecautions outlined below will be useless unless you plan every experiment, understand every operation, and think through the consequences of every procedure before you perform it. The following common accidents often occur simultaneously: fire, explosion, chemical & thermal burns, cuts from broken tubing & thermometers, absorption of toxic (but non-corrosive) chemicals through the skin, and inhalation of toxic fumes. Less common (but nonetheless dangerous) is the ingestion of toxic chemicals. Each of these accident types is discussed in a general way below; more specific reference to certain hazards will be found in the experiment information handouts.

**1.Laboratory Use**. You may work in instructional laboratories only during regularlyscheduled times on authorized experiments with supervision by an authorized teaching assistant or member of the faculty. Working alone in the laboratory is strictly forbidden.

**2.Safety Equipment**. It is your responsibility to know the location and operation of fireextinguishers, shower & eye wash stations, fire blankets, and any other safety equipment provided in the laboratory.

**3.Eye Protection**. **SAFETY GOGGLES MUST BE WORN AT ALL TIMES** when inthe laboratory. Students with prescription glasses are also required to wear safety goggles. Students who do not follow the eye-protection requirement will be asked to leave the laboratory. It is more the rule than the exception for flying glass and spattered chemicals to hit the face. Even if students are not conducting a reaction or other operation, their neighbors are working and may have an accident which spatters themselves or other students.

Note that most prescription glasses (even with hardened lenses) do not meet OSHA standards for protection against flying debris. Glasses (compared to goggles) offer only modest splash protection even when fitted with side shields. Plastic prescription lenses may be attacked by certain laboratory solvents.

**4.Clothing**. Long hair and billowy clothing must be confined when in the laboratory.Shoes are mandatory; aprons are recommended. Sandals (or open-toed shoes) and shorts or short skirts are inappropriate. Lab coats are encouraged, particularly on days when strong acids or bases will be used.

**5.Fire**. Open flames are to be used only with permission in specified locations. Make it aworking rule that water is the only nonflammable liquid you are likely to encounter. Treat all others in the vicinity of a flame as you would gasoline. Specifically—never heat **any** organic solvent with a flame in an open vessel (such as a test tube, Erlenmeyer flask,or beaker). Such solvents should be heated with a steam bath (not a hotplate) and the flammable vapors drawn off with an aspirator tube by working in a hood. Never keep a volatile solvent (such as ether, acetone, or benzene) in a beaker or an open Erlenmeyer flask. The vapors will creep along the bench, ignite, and flash back if they reach a flame.

It is your responsibility to know where the nearest shower and fire extinguisher are located and how to operate them. Always point an extinguisher at the outer reaches of a flame and work inward. Call for additional extinguishers.

**5.Explosion**.Neverheat a closed system or conduct a reaction in a closed system (unlessspecifically directed to perform the latter process and then only with frequent venting). Before starting a distillation or chemical reaction, make certain that the system is vented. The result of an explosion is flying glass and spattered chemicals, both usually hot and corrosive.

**6.Chemical and Thermal Burns**. Many inorganic chemicals (such as the mineral

acids and alkalis) are corrosive to the skin and eyes. Likewise, many organic chemicals (such as acid halides, phenols, and so on) are corrosive and often toxic. If they are spilled on the benchtop, in the hood, or on a shelf, clean them up before you leave the spill area.

**7.Cuts**. The most common laboratory accident is the cut received while attempting toforce glass tubing into a rubber stopper or rubber tubing onto a stirring rod, a thermometer, or the sidearm of a filtration flask. Lubricate the stopper and use a gentle rotating pressure on the glass part. Severed nerves and tendons are common injuries caused by improper manipulation of glass tubes and thermometers. Always pull rather than push on the glass. In addition to these safety precautions, remember to use caution when inserting syringe needles into plastic tubing.

**8.Absorption of Chemicals**. Keep chemicals off the skin. Many organic substances arenot corrosive, do not burn the skin, or do not seem to have any serious effects;

nevertheless, they are absorbed through the skin and may have serious consequences. Other chemicals will give a serious allergic reaction upon repeated exposure, as evidenced by severe dermatitis. For the organic laboratory, it may be advisable to wear gloves when handling some reagents. The best type of glove to wear depends upon the reagent used and specific information will be given in lab lecture for individual chemicals. Gloves provide only a temporary layer of protection against chemicals on your skin. If gloves become discolored, develop holes, or begin to deteriorate, remove them immediately, wash your hands thoroughly and get a new pair.

**9.Inhalation of Chemicals**. Keep your nose away from organic chemicals. Many of thecommon solvents are toxic if inhaled in any quantity or for any length of time. Do not evaporate excess solvents in the laboratory; on the contrary, use the hood or a suitable distillation apparatus with a condenser. Some compounds (such as acetyl chloride) will severely irritate membranes in the eyes, nose, throat, and lungs, while others (such as benzyl chloride) induce eye irritation and tears. When in doubt, use the hood, or better yet, consult the laboratory instructor about the chemicals required for a particular experiment.

**10.Ingestion of Chemicals**. The following are common ways of accidentally ingestingharmful chemicals:

* 1. By pipette
	2. From dirty hands
	3. From contaminated food or drink
	4. By using chemicals taken from the laboratory.

i) Pipettes must be fitted with suction bulbs to transfer chemicals. Never use mouth suction.

ii)Do not eat or drink in the laboratory. Use water taps outside the laboratory

 when thirsty—not laboratory taps.

iii)Neveruse chemicals (such as salt and sugar) from the laboratory or stockroomas

 food additives. The source containers may be contaminated or mislabeled.

iv)Neveruse laboratory glassware as food or drink containers.

v)Neverstore food or drink in a laboratory refrigerator or ice machine;

vi)Never consume ice from an ice machine that is located in the lab.

**11**.**Accident Reports.** Allaccidents (including contact with chemicals, any cuts, burns, or

inhalation of fumes) must be reported to an instructor immediately. Any treatment beyond

 emergency first aid will be referred to the student infirmary. Severe emergencies will be

 referred to the hospital Emergency Department.

**Experiment 1**

**Synthesis and purification of Cr(acac)3**

**Introduction**

Coordination compounds (or complexes) consist of a central atom surrounded by various other atoms, ions, or small molecules (called ligands). There is only a tenuous distinction at best between coordination complexes and molecular compounds. The most common dividing line is that complexes have more ligands than the central atom oxidation number. Silicon tetrafluoride, SiF4, would not be a coordination compound, as there are four ligands on the Si(IV). But [SiF6]2- would be considered a coordination compound as there are six ligands on the Si(IV). In this experiment, the coordination compound tris(2,4-pentanedionato)chromium(III) or tris(acetylacetonato)chromium(III) is synthesized and characterized.

 In the presence of base, 2,4-pentanedione, acacH, readily loses a proton to form the acetylacetonate anion, acac-, as shown.



Hydrogen atoms on -carbon atoms that are adjacent to carbonyl, C==O, groups are relatively acidic. The three different representations of the acetyl acetonate anion are called resonance forms (they differ only in the location of the electrons).

 In this experiment, the basic solution needed to remove the proton from the acac is provided by generating ammonia, NH3, via the hydrolysis of urea:

(NH2)2C=O + H2O  2NH3 + CO2

In water, ammonia acts as a base to provide the hydroxide ion

NH3 + H2O **↔** NH4+(aq) + OH-(aq)

This allows formation of the more reactive (H2O)5CrOH2+ species, which may react with acac to give (H2O)4Cr(acac)2+. Continued hydrolysis of urea, though, keeps the solution slightly basic and effects conversion of (H2O)4Cr(acac)2+ to give (H2O)2Cr(acac)2+ and finally to Cr(acac)3. The product is nonpolar and electrically neutral and has very limited solubility in water. It thus precipitates from the aqueous solution shortly after its formation.

Acetyl acetonate is an example of a bidentate (bi-two, dent-teeth) ligand, since it can bond to a metal via both oxygen atoms. Ligands of this type are also often called chelating (chelos-claw) ligands. Three acac ligands are therefore needed to complete the octahedral coordination about the central metal ion, giving formula [M(acac)3]n+. The structure of the chromium(III) complex is shown in the Figure. Since the outer part of the complex consists of organic groups, most metal acetylacetonates are hydrophobic, and insoluble in water. The equation for synthesis of the complex and structure of the compound is shown below

CrCl3•6H2O(aq) + 3 acac-(aq)  Cr(acac)3(s) + 3 Cl-(aq) + 6 H2O



**(I)Synthesis of Tris(acetylaceonato)chromium(III)**

**Experimental Procedure**

Place 100 ml of distilled water in a 200-ml Erlenmeyer flask and add to it 5.32 grams (0.2 mole) of chromium(III) chloride hexahydrate,CrCl3.6H2O. After this has dissolved, add 20 grams of urea and 11.8 ml(0.12 mole) of acetylacetone. Cover with a watch glass and heat the mixture by placing the reaction flask in a large beaker of boiling water for 1.5 to 2 hours. After a while, deep maroon crystals will begin to form as the urea releases ammonia and the solution becomes basic. Cool the reaction flask to room temperature and collect the product by suction filtration. With several small quantities of distilled water wash the crystals while they are still on the filter and air dry. Transfer the crystals to a screw cap bottle for storage. Calculate the percent yield based on the amounts of product.

 The Cr(acac)3 is not in a pure state and may have precipitated with impurities trapped in the crystal lattice. It is , however, readily purified by recrystallization from a two solvent system.

**Questions:**

1) What is the percent yield? Is it possible to get better than 100 percent yield of a crude

 product? Explain.

2) Why is NaOH not used ( instead of urea) to make the solution basic?

3) Why was a steam bath used to heat the reaction flask instead of a direct flame?

4) How does urea make the solution basic?

**(II). Recrystallization and melting point determination of Cr(acac)3**

The Cr(acac)3 complex is soluble in many solvents less polar than water ("organic solvents") and may be purified using a technique called *recrystallization.* One method of recrystallization uses two solvents- one in which the material is quite soluble, and one in which it is not very soluble. The original batch of impure crystals is dissolved in the "good" solvent and then recrystallized by adding "poor" solvent. The melting point of the product is taken for comparison with that of Cr(acac)3 as reported in the literature.

**Procedure**:

Test the solubility of the product in several solvents as follows:

Place about 0.1 g of the crude crystals in a test tube and add 1 mL of solvent and shake briskly. Record your observations. If the product does not dissolve in cold solvent heat the tube gently in hot water bath, then shake it and notice if the complex dissolves. Try these solvents: toluene, hexane, ethanol, chloroform, ...etc.

Make a table of your results by writing + for soluble and - for insoluble then decide which solvent or solvent combination is suitable for recrystallization.

A good combination for recrystallization is toluene-hexane or benzene- petroleum ether. Dissolve the product in the minimum amount of warm benzene. Add petroleum ether dropwise with swirling until crystals begin to appear. Stopper the flask and allow to stand. Cool the flask in an ice bath. Collect the crystals by filtration and air dry. Calculate the percent yield on the amount of your product. Determine the melting point.

**Questions:**

1) Define: a good solvent, supersaturation.

2) What conditions must two solvents meet to be a good two-solvent recrystallization

 system?

3) Write formulas for all solvents used in your solubility study of Cr(acac)3, and arrange

 them in order of increasing polarity.

4) Many inorganic salts are very soluble in water but insoluble in alcohol. Suggest

 a solvent pair to recrystallize such salts.

**(III). Molecular Weight determination of Cr(acac)3**

 The molecular weight determination of Cr(acac)3 can be achieved by the method of depression of freezing point of the solvent after dissolving a certain amount of the compound and using the following relationship:

∆T =km

 Where ∆T is the depression of freezing point of the solvent after dissolving a certain mass of the compound.

 k is the cryoscopic constant of the solvent

 and m is the molal concentration in units of moles per 1000gm of the solvent

 then M =(g1)( k) 1000/(g2) (∆T)

where g1 is the weight of sample used

 g2 is the weight of solvent used

**Procedure**:

 Obtain from the stock room the molecular weight apparatus consisting of three test tubers, a one- hole stopper, and a thermometer graduated in 0.1 °C. Place approximately 2 grams of biphenyl in one of the small test tubes and set up your apparatus.

 Heat the apparatus in a water bath until the biphenyl melts. It is best not to have the thermometer in the system at this time. Rather, stopper the test tube containing biphenyl to keep out any moisture from the water bath. After the biphenyl melts, insert the thermometer and continue heating until the temperature of the melt reaches 80 °C. Remove the flame and carefully lower the water bath from the test tube and set the bath away from the apparatus. Begin to record the temperature at 15-second intervals, with mild stirring of the melt with the thermometer between readings. Stirring is done to prevent the melt from supercooling, which may result in a lower freezing point than expected. Continue reading until the temperature drops to around 60 °C. After the melt has solidified, do not attempt to stir the mixture. Repeat the melting procedure and record a second set of temperatures. Weigh into the second small test tube approximately 0.35 grams of Cr(acac)3 and approximately 1.65 grams of biphenyl . Add the Cr(acac)3 to the test tube before the biphenyl. When the biphenyl melts, it runs down over the Cr(acac)3 and dissolves it more readily. Determine the freezing point for biphenyl and Cr(acac)3-biphenyl solution. The cryoscopic constant(Kf) of biphenyl is 8.0. Calculate the molecular weight of Cr(acac)3

**Questions**

1-If your Cr(acac)3 were impure, how would that affect your molecular weight results? Why?

2- Calculate the percentage error of your determination of molecular weight of Cr(acac)3?

3- What is the molality of Cr(acac)3-biphenyl solution suggested for this experiment?

4- Show that the relationship

 M = (g1)(k)(1000)/(g2)(∆T)

5- Describe briefly the following:

1. Supercooling.
2. Colligative property
3. Biphenyl.

**(IV) Structure of Cr(acac)3: Infrared spectra of AcAc and Cr(acac)3**

 Acetylacetone and its chromium(III) complex make a particularly interesting system for an infrared study. The free ligand is an unusual molecule in that it is capable of existing in an equilibrium mixture between two “tautomeric” forms, the diketo and the enol forms.

Clues to the presence of each form should be available in the infrared spectrum of acetylacetone. When Chromium(III) is added to acetylacetone , the acidic proton is displaced by a metal ion carrying a much larger, +3, charge. The effect of this metal ion on the acetylacetone group should be reflected in the frequencies of the absorption bands in the infrared spectrum of Cr(acac)3.The metal-oxygen bonds should also give rise to one or more absorptions not observed in the spectrum of acetylacetone itself.

**Procedure**

Study the operation of spectrophotometer before use . Prepare a solution of approximately 5 percent by mass of Cr(acac)3 in CCl4. Fill one cell with this solution and the other cell with CCl4, place them in the spectrophotometer and record the spectrum. It may be necessary to record the spectrum at more than one concentration in order to observe all the absorption bands. Repeat with acetylacetone. Try to identify and label the various absorptions using IR charts.

**Questions**

1. What infrared absorption bands do Cr(acac)3 have that acetylacetone does not? To what vibrations can you assign any new bands?
2. Would it be possible to detect urea in your Cr(acac)3 sample by infrared spectroscopy? Where in the infrared region might you expect urea to absorb strongly? Why?
3. One of the vibrational modes of the CH2 group is assigned to a band at 2925cm-1. What is the wavelength in angestroms and nanometers of this radiation? What is the frequency of this radiation?
4. What is the purpose of using a double-beam method to measure the IR spectrum?

**Experiment 2**

**Colorimetric determination of the percentage of Chromium in Cr(acac)3**

**Objective**

To measure the purity of Cr(acac)3 sample prepared in the previous experiment quantitatively by measuring the percentage of Cr by mass in the sample using Spectrophotometric technique.

**Introduction**

The preparation of a chemical substance necessarily goes well beyond the mixing of reagents under the conditions required to yield the desired product. The substance obtained from a reaction mixture is almost contaminated with solvents, starting materials and often products of side reactions. It is often desirable to know quantitatively how pure the compound is. This can be done by measuring the weight percent of some elements in the product. In this experiment you will determine the percentage of chromium in Cr(acac)3 by a method that involves measuring the light at some certain wavelengths of a solution of CrO42- ions. The technique is known as Colorimetry or Spectrophotometry.

When there is a very readily accessible colored ion into which the transition metal can be removed, in this case Cr+3 → CrO42- yellow, it is convenient to use Spectrophotometric method to measure the weight percent of the metal present. This technique depends on the simple fact that the color intensity of a solution containing colored ions is proportional to the concentration of those ions and the length of the path that light must travel through the solution. This can be estimated using Beer-Lambert law : **A=** **ɛ** **b c , or A = -log T, where T= I/Iº**

Where A= Absorbance

 **ɛ** = Molar absorptivity coeffecient ( or molar extinction coefficient ) in L/mol. cm

**b** = Cell width (cm)

**c** = Concentration (mol/L)

**T** = Transmittance

**I, Iº** = intensity of Transmitted and Incident radiation, respectively

Prior to making the colorimetric measurements, the Cr(acac)3 must be converted into the colored ion CrO42-. This is done by treating a basic aqueous solution of Cr(acac)3 with H2O2. It is essential that the solution be basic since H2O2 is capable of being either an oxidizing or reducing agent.

**Basic solution-oxidation**:

2Cr3+ + 3HO2- + 7OH- → 2CrO42- + 5H2O

**Acidic solution-reduction:**

Cr2O72-

The CrO4

Cr2O72-

+ 3H2O2 + 8H+ → 2Cr3+ + 7H2O + 3O2

-2 does not exist in an acidic solution; it is converted into the dichromate species according to the reaction

**2CrO42- + 2H+ ↔ Cr2O72-** **+ H2O**

For this reason, Cr2O72- is shown in the acidic reduction reaction.

The chromate ion has a yellow color, which means that it absorbs light in the visible region of the spectrum. The wavelength of maximum absorption (λmax ) is around 370 nm.

**Experimental Procedure**

**Part I: Preparation of standard chromate solutions**

**1-** Weigh between 0.26 and 0.28 g of K2Cr2O7 and dry it at 110 ºC for an hour and transfer the sample into a 500 ml volumetric flask.

**2-** Add 5 ml of 6 M NaOH and dilute to the volume with distilled water. The addition of NaOH to the Cr2O72- solution will bring about a color change as the following reaction occurs :

**Cr2O72- + 2OH- → 2CrO42-** **+ 2H2O**

**3-** Transfer by burette 32 ml of this solution into a 250 ml volumetric flask.

**4-** Add 10 ml of 6M NaOH and dilute to volume with distilled water.

**5-** Prepare four solutions from this stock solution by transferring 35, 25, 15 and 5 ml of this solution into 50 ml volumetric flask and dilute with distilled water.

**Part II: Preparation of Cr(acac)3 sample**

**1-** Weigh accurately 0.210 ± 20 mg sample in 500 ml Erlenmeyer flask.

**2-** Add 25 ml of concentrated H2SO4 and stir until all dissolved.

**3-** Carefully add 25 ml of water down the flask then heat the solution gently to ensure the dissolution of all the Cr(acac)3.

**4-** Cool the solution to room temperature and carefully add 4 ml of 30 % H2O2 and 30 ml of distilled water.

**5-** Cool again and carefully add 140 ml of 6M NaOH solution in small amounts. When the solution become alkaline, it will turn yellow as the peroxide oxidizes the Cr3+ to CrO42-. Keep the solution cool during the addition of the NaOH.

**6-** Add 10 ml more of 6M NaOH solution and 16 ml of H2O2 solution and boil the mixture until it turns bright yellow.

**7-** Cool and transfer into 500 ml volumetric flask, wash with distilled water and dilute to the volume.

**8-** Transfer 25 ml of the mixture with burette into another 500 ml volumetric flask and add 25 ml of 6M NaOH solution and dilute to the volume.

**9-** Allow the solution to cool to room temperature before making the absorbance measurements.

**Data Analysis**

**Colorimetric Measurements**

To obtain the measurement of the absorbance for a given sample, proceed as follows:

**1-** Zero the colorimeter by filling the cell with distilled water, inserting it in the instrument and adjusting the meter to zero absorbance.

**2-** Rinse the cell several times with the CrO42- solution, fill it with the solution, dry it and place it in the colorimeter and then read the absorbance.

**3-** Several readings should be taken for each sample and an average value is recorded.

**4-** Plot a graph of absorbance vs. concentration and show that the CrO42- ion obeys Beer's law.

**5-** Measure the absorbance of the CrO42- solution prepared from Cr(acac)3 and determine the CrO42- concentration from the graph.

**6-** Calculate the percentage of chromium in the original sample of Cr(acac)3

**Experiment 3**

**Synthesis of Cobalt Coordination Compounds: [Co(NH3)5Cl]Cl2, [Co(NH3)5ONO]Cl2, and [Co(NH3)5NO2]Cl2**

 **Object:**

To prepare the following compounds:

 [Co(NH3)5Cl]Cl2 is chloropentaamminecobalt(III) chloride.

 [Co(NH3)5ONO]Cl2  is niritopentaamine cobalt(III) chloride.

 [Co(NH3)5NO2]Cl2 is nitropentaammine cobalt(III) chloride

 **Theory:**

**Co+2 + NH4+ + 4NH3 +1/2 H2O2 → [Co(NH3)5H2O]3+**

**[Co(NH3)5H2O]3+ + 3Cl- → [Co(NH3)5Cl]Cl2 + H2O**

**[Co(NH3)5Cl]+2 + H2O → [Co(NH3)5H2O]+3 + Cl-**

**[Co(NH3)5H2O]+3 +NO2- → [Co(NH3)5ONO]+2 +H2O**

**[Co(NH3)5ONO]+2 in cold → [Co(NH3)5NO2]+2**

 At room temperature, [Co(NH3)5ONO]Cl2 is formed in which oxygen is coordinated to the metal. At low temperature,[Co(NH3)5NO2]Cl2 is formed in which nitrogen is coordinated to the metal. Thus, these two compounds are isomers and have linkage isomerism.

Another ligands that can show linkage isomerism is NCS- and NCO-.

 Here only H2O2 is used as oxidizing agent for the oxidation of the metal because it forms water

complex and H2O becomes a ligand, then Cl- replaces H2O. Because there is no direct coordination between Cl- and the metal, until water is present in the complex, other oxidizing agents are not used in the synthesis of complexes because H2O is not formed, and they coordinate the metal and form anion

**I.Preparation of [Co(NH3)5Cl]Cl2**

In the fume hood, completely dissolve 10 g of NH4Cl in ~60 mls of concentrated aqueous ammonia in a 400 ml beaker. With continuous stirring, add 20 g of powder cobalt(II) chloride-hexahydrate in small portions. With continued stirring of the resulting brown slurry, **SLOWLY** add 16 mls of 30% H2O2 which will cause effevervenscence. After the effervescence has stopped, **SLOWLY** add ~60 mls of concentrated HCl. With continued stirring, heat on a hot plate and maintain 85 oC for 20 minutes.

Cool mixture to room temperature in an ice bath and filter (using a Buchner funnel) the crystals of [Co(NH3)5Cl]Cl2 and wash it with 40 ml of ice cold water.Dry the product in an oven below 100 oC.

Weigh the product. Calculate the theoretical yield and calculate the percent yield of the product.

**II.Preparation of [Co(NH3)5ONO]Cl2**

In the fume hood, completely dissolve 10 g of [Co(NH3)5Cl]Cl2

in 15 mls of concentrated ammonia in 160 mls of distilled water. Stir and heat if necessary to dissolve Cool the solution to ~10 o

C. Add 2 M HCl dropwise (about 35 ml) with stirring until the solution is neutral to litmus. Dissolve 10 g of sodium nitrite in the solution followed by 10 mls of 6 M HCl.

Cool mixture to room temperature 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 5-6, 5 ml portions of ice water (distilled water cooled in ice) and then 5-6, 5 ml portions of alcohol. Note the color of your product.

Allow the product to air dry for several hours.

Weigh the product. Calculate the theoretical yield and calculate percentage yield of the product.

**III.Preparation of [Co(NH3)5NO2]Cl2**

 Dissolve 4 grams of [Co(NH3)5ONO]Cl2 in 40 ml of hot water containing few drops of aqueous ammonia. Add while cooling in ice bath drop by drop 40 ml of concentrated HCl. Cool the solution thoroughly giving crystals of this product. Filter it and wash it with alcohol. Dry it at room temperature. By adding ether, thin compound is dried fast

**Physical Properties**

1. All the three complexes are soluble in water but insoluble in non- polar solvents such as ether, alcohol, chloroform, benzene, CCl4, nitrobenzene.
2. The colour and melting points are

[Co(NH3)5Cl]Cl2 is purple-red , m.p = 219 °C

[Co(NH3)5ONO]Cl2 is pale yellow, m.p = 145° C

[Co(NH3)5NO2]Cl2 is yellow –brown, m.p=210 °C

 **Data Sheet**

**I.Preparation of Transition Metal Coordination Compounds**

 1-Color of:

[Co(H2O)6]Cl2

[Co(NH3)5Cl]Cl2

 2-Mass of starting material

 3-Coordination compound prepared:

 4-Chemical reactions:

 Preparation I:

Preparation II:

Preparation III:

 5-Theoretical yield of compound prepared (show calculations):

 6-Experimental yield of compound prepared:

1. Percent yield of compound prepared (show calculations):

**Questions:**

 1-Did your synthesis produce the desired product? Cite the evidence to support

 your answer.

2-Draw the structure for each of the following compounds (be sure to correctly indicate the difference in metal-ligand bonding between the last two compounds):

[Co(H2O)6]Cl2

[Co(NH3)5Cl]Cl2

[Co(NH3)5ONO]Cl2

[Co(NH3)5NO2]Cl2

 3-Name the following compounds

1. K4[Ni(CN)4]
2. [Ni(NH3)6]Br2

 4-Write the formula of the following compounds:

1. potassium diaquatetrabromovanadate(III)
2. pentaaquabromomanganese(III) sulfate

**Experiment 4**

**Ion exchange separation of Chromium(III) complexes**

"Green chromium chloride" is actually trans-dichlorotetraaquachromium(III) chloride dihydrate. It separates as green crystals from solutions of chromium(III) in hydrochloric acid. The salt is fairly soluble (almost 600 g in 1 litre of water) and the solution owes its green colour to the cation. The absorption spectrum of a solution of the salt in pure water is, however, not constant over time; the solution is therefore not in equilibrium, and the maxima in the spectrum gradually shifts to shorter wavelengths. This means that chloride is substituted by a ligand higher in the spectrochemical series, in case of water. The green cation can be said to hydrolyse. The hydrolysis is slow, just as substitution reactions on chromium(III) are in general. The hydrolysis takes place in two steps according to

Cr(H2O)4Cl2+ + 2H2O  Cr(H2O)5Cl 2+ + Cl- + H2O  Cr(H2O)63+ + 2 Cl-

The two consecutive dissociation constants are 130 M and 16 M respectively.

The three chromium(III) complexes have different charges which make them very different with respect to electrostatic interactions with negatively charged particles. This is the fundamental principle behind the successful separation of different cations on a column of an ion exchange resin.

**Ion exchange chromatography**

An ion exchange resin is, in short, a solid polymer containing groups with negative charges on the surface. These negatively charged groups may be sulfonates, phosphonates or carboxylates attached to the polymer. Just as in clay minerals the negative charge of the ion exchange resin is neutralised by cations, which are more or less loosely attached to the negative surface, balancing the net charge to zero in the material. The force by which cations are bound to the polymer depends on the cation properties, mainly its size and the magnitude of its charge. In the ready-to-use resin the cation may be the proton (on sulphonate resins) or e.g. the sodium ion. These ions are only loosely attached to the negative groups and may therefore be substituted by other cations, which bind better. The first step is therefore to pour a solution containing a mixture of cations on the top of a column filled with the resin, which will take up the best binding cations first staying in the top layer of the material. Further down the column the less strongly binding cations bind in layers in order of decreasing binding strength.

In the present case the cation with three positive charges will bind first and the cations with a smaller charge will bind in lower layers. If all three of the above chromium complexes are present, the order of binding will be

Cr(H2O)63+> Cr(H2O)5Cl2+> Cr(H2O)4Cl2+

The second step is to take the ions off the resin. This is affected by the addition of acid of some concentration. The protons will compete with the three cations for the anionic sites on the resin and since the Cr(H2O)4Cl2+ with only one charge is the weakest bonded cation, it is substituted by protons first. This competition can be expressed by the following scheme

cationresin + H+aq  cationaq+ H+resin

It is obvious, that the larger the acidity of the solution the more is the equilibrium shifted to the right.

In the present case, when an acid of a certain concentration is passed through a column of the

resin with the three different cations attached to the negative sites of the resin, the

Cr(H2O)4Cl2+ can be liberated to the solution, while the two other cations stick to it. This

leaves a solution with only Cr(H2O)4Cl2+ ions (plus acid) and the two other cations remaining

on the column in two layers. Now, if the acid concentration is raised it is Cr(H2O)5Cl2+,

which is the next cation to loose the competition to the protons for the negative sites on the

resin. Cr(H2O)5Cl2+ will accordingly be liberated to the acid solution. The hexaaqua-

chromium(III) ion with its three charges will only be caught by protons if the acid concentration

is raised further.

The principle of ion exchange between sites on a stationary phase an a bypassing solution is called ion exchange chromatography. The principle finds wide spread use to separate mixtures and isolate pure compounds, and is also operating in soil where clay minerals and humus bind cations in equilibrium with the soil solution, taken up by plants.

In this experiment the commercial salt "green chromium chloride" is used as a starting material for the preparation of the two products of hydrolysis and the purity of the three complex cations brought about by the use of cation exchange chromatography. This serves as a way to record absorption spectra of the pure compounds.

**Experimental procedure**

Safety note: perchloric acid is an oxidising agent, which - when pure - can react vigorously with organic matter and other reducing agents. The reactions normally need some activation to proceed and may then react in a self speeding reaction, an explosion. The concentrations of perchloric acid used here are safe to handle when precaution is taken to keep them away from organic compounds and reducing agents.

Solutions of perchloric acid and chromium(III) are collected in a labelled container for further waste management.

**Preparation of Ion Exchange Column**

Prepare around 15 ml of slurry of the resin Dowex 50W-X8 (50-100 mesh, H+-form) and pour it slowly but steady into a buret (Ø ~1 cm), which is filled with deionised water and equipped with a plug of glass wool near the open stopcock. The drips of liquid are continuously collected in a beaker below the column. When all the slurry has been added, a 5

1. layer of see sand is added (in a water slurry) onto the top of the resin. The see sand is denser than the resin and helps avoiding the upper layer of the resin to be whirled up when aqueous solutions are added to the top of the column. After having allowed enough water to pass through the column to leave the effluent colourless, the column is ready for use. Be sure, that the see sand is always covered by 1 cm of liquid to avoid it being partly drained out leaving channels and irregularity - the column should be as homogenous as possible to give the best separation.

***trans*-Dichlorotetraaquachromium(III)**

Weigh out 2.35 g (8.8 mmol) of "green chromium chloride" to make a 0.35 M stock solution of chromium(III) in 2 ml of 0.1 M perchloric acid and water in a 25 ml measuring flask. Record the time of dissolution and keep the solution at room temperature.

Add 5 ml of the stock solution to the cation exchange column and open the buret stopcock to allow the liquid sink through the column. When the surface just above the top of the see sand layer, pour on 0.1 M perchloric acid, which acts as an eluent. The green colour is seen to

move down the column, and the most intensely coloured green portion is colleted, when it drips out of the buret. Collect at least 5 ml for the recording of an absorption spectrum (800 - 350 nm), using a cuvettes of OS or QS quality, and 0.1 M perchloric acid as the reference.

**Chloropentaaquachromium(III)**

The dichlortetraaquachromium(III) when heated shortly is hydrolysed to chloropentaaqua-chromium(III) . Heat 5 ml of the stock solution in a conical flask in a water bath (~ 100 oC) for 3 minutes. Now add 5 ml of deionised water and pour the now cooled solution into the buret as in the first experiment. First flush with 0.1 m perchloric acid to remove the unreacted dichlorotetraaquachromium(III). Next elute with 1.0 M perchloric acid to get out and collect 5 ml of the most intensely coloured fraction of chloropentaaquachromium(III) in the same way as before. Record a spectrum as specified above.

**Hexaaquachromium(III)**

Boil a mixture of 5 ml of the stock solution and 5 ml of deionised water for 5 minutes, and add the solution to the buret as above. Use sufficient 1.0 M perchloric to get the unreacted complexes out and then elute with 4.0 M perchloric acid. Again collect 5 ml of the most intensely coloured fraction of hexaaquachromium(III) and record the spectrum as specified above.

**Atomic Absorption Spectrometry( AAS)**

The concentration of chromium in each of the fractions is determined using atomic absorption spectrometry (AAS). The absorbance is measured relative to a standard curve available (0.2 – 2.0 mM). The fractions should be diluted in order to get the reading within the concentration range of the standard curve.

**Report**

1. Report the recorded visible absorption spectra of the three fractions supposed to contain each of the three chromium complexes in question.
2. Record and report the concentration of chromium in each of the three solutions.
3. Characterise each spectrum by values of (λ,ε)max and (λ,ε)min , ε being the molar absorptivities calculated from the observed absorbances at the extrema.
4. Comment on the validity of the average environment rule used in this case using both sets of maxima.
5. What would have been the overall result if hydrochloric, instead of perchloric acid, had been used throughout the experiments.

**Experiment 5**

**Synthesis of Copper(II) Acetate Monohydrate**

**Introduction**

The first compound with metal-metal bonds was found to have the formula Ta6Cl14.7H2O. Its structure was shown to consist of an octahedron of mutually bonded tantalum atoms, with each edge of the octahedron being bridged by a chlorine. The formula would be represented by [Ta6Cl12]Cl2. Hundreds of compounds with metal-metal bonds are now known. Compounds are currently known containing not only M-M single bonds, but also double, triple, and even quadruple bonds.

**Structure of rhodium(II) acetate alcoholate**



Copper(II) acetate dihydrate exhibit a structure similar to that of rhodium(II) acetate alcoholate which has a short metal-metal bond that is quite short (2.386 Ang.) which indicates the presence of a rhodium-rhodium bond in this compound. Copper(II) acetate dihydrate may contain a copper-copper bond where there is only a weak coupling of the unpaired electrons on the Cu(II) ions (d9). Thus, while the ground state is diamagnetic, there is a low energy excited state that is paramagnetic. This excited state is appreciably populated at room temperatue and the complex therefore appears to be paramagnetic. As the temperature increases, the magnetic moment increases as well. An alternative explanation to this behavior is described as an antiferromagnetic coupling of the unpaired spins. Structural determination shows that the two copper atoms are separated by a distance of 2.64 Å. This compares with a 2.56 Å. interatomic distance in metallic copper, making the assumption of a Cu-Cu bond more controversial.

Copper(II) acetate dihydrate is prepared by a route involving the intermediate formation of a tetraamine complex, conversion of the tetraamine complex to a precipitated hydroxide, and subsequent reaction with acetic acid.

CuSO4.5H2O(aq) + 4NH3(aq)  [Cu(NH3)4]2+(aq) + SO42-(aq)

[Cu(NH3)4]2+(aq) + 2NaOH  Cu(OH)2(s) + 4NH3(aq) + 2Na+(aq)

2Cu(OH)2(s) + 4CH3COOH  [Cu(CH3COO)2.H2O]2(aq)

The solvent ligands can be easily removed by heating in vacuum to yield the non-adducted complexes.

**Procedure:**

1) In a 10-mL beaker equipped with a magnetic stirring bar, dissolve 160 mg (1.0 mmol) of copper(II) sulfate or 250 mg (1.0 mmol) of copper(II) sulfate pentahydrate in 5.0 mL of water. Stir the mixture, and warm it to 40-50o C on a sand bath (or a hot plate) to aid the dissolution.

2) Using a Pasteur pipet, add 50% NH3 (aq) to the warm, stirred, light blue solution, until the intense blue color of the copper ammonium complex is evident. During this addition, a precipitate of copper hydroxide may form initially, but will dissolve on further addition of the NH3 (aq) solution.

3) Add 80 mg (2.0 mmol) of sodium hydroxide flakes to the deep blue solution, and stir the mixture for 15-20 min at 55-65oC. A light blue solid of copper(II) hydroxide precipitates during this time.

4) Allow the mixture to cool to room temperature and collect the precipitate by vacuum filtration using a Hirsch funnel. Wash the blue solid with three 2-mL portions of warm water.

5) Transfer the amount of Cu(OH)2 to a 10-mL beaker, and dissolve it in the minimum amount of 10% acetic acid. Warming on the sand bath with stirring aids the dissolution process. Concentrate the solution nearly to dryness (HOOD) by warming it on a sand bath under a slow stream of nitrogen.

6) Collect the beautiful deep blue crystals that form by filtration using a Hirsch funnel. Dry the product on a clay plate or on filter paper.

**Characterization of Product:**

Acquire the IR spectrum of the product as a KBr pellet. Determine the magnetic moment of the product. Does it correspond to that of a diamagnetic or paramagnetic complex at room temperature? If paramagnetic, how many unpaired electrons seem to be present?

**Questions:**

1) What physical indications, other than magnetic moment, might lead one to conclude

 that a metal-metal bond is present?

2) Even when the magnetic susceptibility seems to indicate that a metal-metal bond is

 present, the low magnetic susceptibility might be due to other reasons. Discuss this

 point.

3) One of the largest classes of metal-metal bonded compounds are the metal carbonyl

 clusters. Discuss the bonding in two such members of this class.

4) Metal clusters are under active investigation as "mimics" to bulk metals in catalysis.

 Perform a literature search and discuss several examples of metal clusters that were

 studied in this manner.