

## Experiment 12

# Synthesis and Analysis of Coordination Compounds

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## Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise. The questions should be answered on a separate (new) page of your lab notebook. Be sure to show all work, round answers, and include units on all answers. Background information can be found in Chapter 23 in your textbook (Brown and LeMay).
- Follow the guidelines in the "Lab Notebook Policy and Format for Lab Reports" section of the lab manual to complete in your lab notebook the following sections of the report for this lab exercise: Title, Lab Purpose, Procedure and Data Tables.

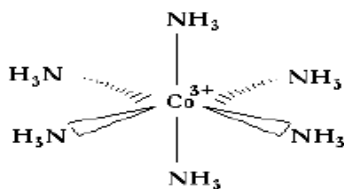
## Purpose

In this experiment you will synthesize the coordination compound tetramminecopper(II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ . You will then determine its absorbance curve and compare it to other copper complexes. Finally, you will use spectroscopy to determine the formula of a copper containing coordination compound.

## Background

Coordination complex compounds play a vital role in our everyday lives. For example, the molecule heme in the oxygen-bearing protein hemoglobin contains coordinated iron atoms. Chlorophyll, the molecule that enables plants to carry on photosynthesis, is a coordination compound of magnesium.

Coordination complex ions involve a transition metal surrounded by anions and/or neutral molecules called ligands. For example, a  $\text{Co}^{+3}$  ion can interact with 6 ammonia molecules forming the complex hexaamminecobalt(II):



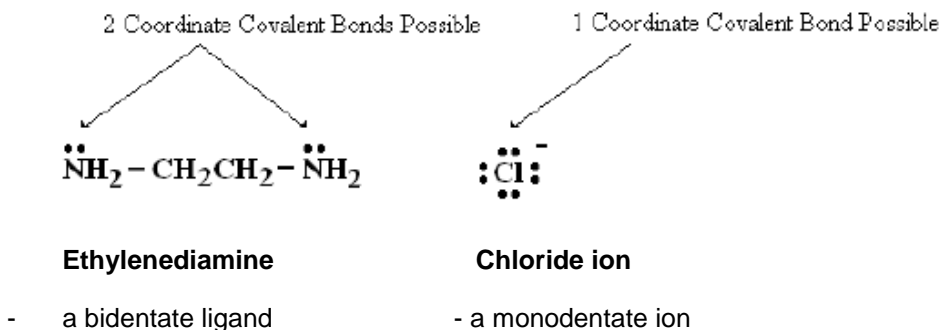
Cobalt has a coordination number of six in  $\text{Co}(\text{NH}_3)_6^{3+}$

The central transition element tends to form 2, 4, or 6 bonds with ligands. The number of bonds formed is called the coordination number. For example, iron in hemoglobin, cobalt in Vitamin B12, and magnesium in chlorophyll all have coordination number 6. Copper often has coordination number 4 while silver and gold can have coordination number 2.

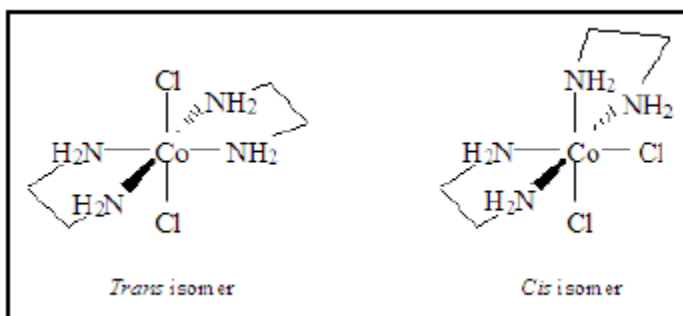
The ligands involved in coordination compounds also have their own terminology. Some ligands (e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , amines, halides, nitrite) form only one bond with a metal. We call these monodentate (one-

tooth) ligands. The formula of a monodentate ligand with a metal having coordination number 6 would be:  $MX_6$  (for example,  $Co(H_2O)_6^{+2}$  or  $[Fe(H_2O)_5Cl]^{+2}$ ). Each ligand can bind to one of the 6 possible positions on the metal ion.

Other ligands are bidentate (two-toothed) which means they can form two bonds to the central metal ion. Ethylenediamine, commonly abbreviated “en”, is such a molecule. It contains two nitrogen atoms each of which have lone pairs of electrons which will be attracted to (bond with) the positively charged central metal ion. When ethylenediamine bonds with a metal atom having coordination number six, the resulting formula will be  $M(en)_3$  (for example,  $Co(en)_3^{+3}$ ). This formula indicates that three ethylenediamines bonded to one cobalt ion.



Another example of complex ion using a bidentate ligand would be,  $Co(en)_2Cl_2^+$ . Here again, the coordination number is six. One bond is formed between  $Co^{3+}$  ion and each chloride ion,  $Cl^-$ , ligand. The remaining four bonds are formed by the two ethylenediamine ligand. Because each “en” ligand in our Complex is bidentate, two different isomers of the complex are possible; a cis form and a trans form. These are pictured below:



Note that “corners” in this diagram between the  $NH_2$  represent the carbons in the ethylenediamine chain.

In nature, we also find ligands which can form three bonds to the metal ion in the complex (tridentate ligands), for example, diethylenetriamine and or even more than three bonds (polydentate ligands) for example, EDTA.

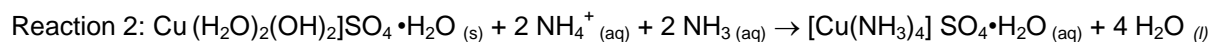
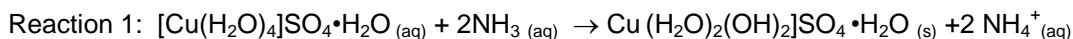
## Synthesis of tetraamminecopper(II) sulfate monohydrate $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

### What is tetraamminecopper (II) sulfate monohydrate $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ ?

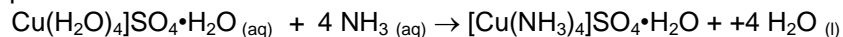
The name "tetraamminecopper(II)" indicates that four ammonia molecules (called ammine in coordination compound lingo) molecules are covalently bonded to the copper(II) ion. The formula is written  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . The square brackets signify that the four ammonia molecules and the  $\text{Cu}^{2+}$  ion act as a group, with a +2 charge. This ion will combine with sulfate ( $\text{SO}_4^{2-}$ ) to make a neutral ionic compound  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ . This group will form part of the solid crystal  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ , in which there is one molecule of water forming a hydrated species.

In part A of the lab, we will synthesis the coordination compound tetraamminecopper(II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ . This will be accomplished by adding concentrated ammonia ( $\text{NH}_3$ ) to copper (II) sulfate pentahydrate which will displace the water molecules bound in the original copper complex, and a dramatic color change occurs.

The reaction of ammonia with the copper(II) sulfate pentahydrate is a two-step process. In the first step, solid copper (II) hydroxide is formed which is light blue in color. The  $\text{Cu}(\text{OH})_2(\text{s})$  dissolves as additional quantities of ammonia are added in the second step to form the dark blue  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  complex. The equations for the process are below



The overall net equation for the reaction is:



The copper(II) ammonia complex is water-soluble. In order to precipitate and isolate the final product, you need to decrease the solubility of the ionic compound. A convenient way of doing this is to add a large amount of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ , to the aqueous solution. Ethanol is much less polar than water, and as the amount of ethanol in the mixture increases, the solubility of ionic compounds decreases. After the addition of ethanol, your coordination compound will appear as a crystalline solid. The synthesis procedure ends with filtration, rinsing, and drying of the product.

The next parts of the lab involve analysis of your copper(II) coordination compound and comparing it to other copper (II) coordination compounds. Your goal will be to make 3.00 grams of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  which should be enough to use in next part of the lab.

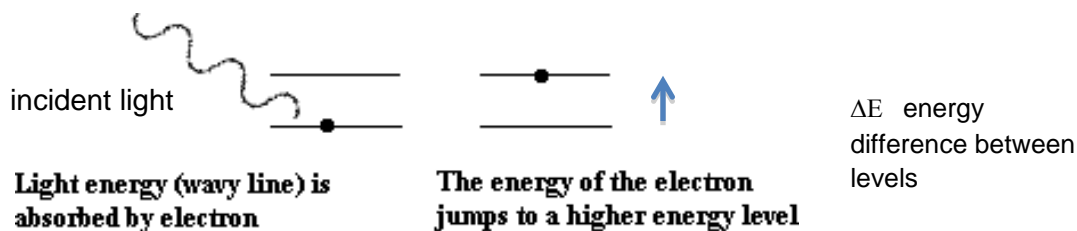
### Color of complex ions

In part B of the lab you will measure the absorbance spectrum of your product tetraamminecopper (II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  and compare it to other copper complexes. Depending on the ligand used to form the complex, the color of a complex ion will vary. The color of a complex is due to an electron in the metal ion absorbs the energy of visible light causing it to "jump" from one energy level to a higher one. This subtracts that color from the visible spectrum as the light is absorbed. For coordination complexes, the wavelength of light that is absorbed is related to the crystal field splitting energy. Our goal

in Part B of the lab is to determine the wavelength at which a coordination complex absorbs light so that we can then calculate the crystal field splitting energy for that complex.

## Absorption of light

When an atom absorbs a single photon of light, it causes the electron to "jump" to a higher energy level. The difference between energy levels ( $\Delta E$ ) equals the energy of the photon absorbed.



**The wavelength of light absorbed is inversely proportional to the energy level difference**

Furthermore, recall from Chem1A that this energy is related to the wavelength of light absorbed by

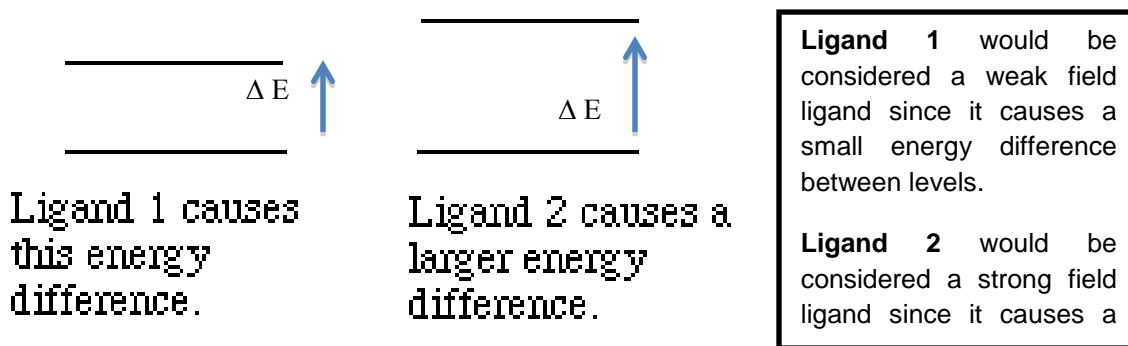
$$\Delta E = hc/\lambda$$

Equation 1

## Crystal Field Theory

Crystal field theory states that electrostatic interactions between the electron pairs of the ligands and the d-sublevel electrons of the transition metal ion (recall that electrons repel each other) lead to a splitting of the d-sublevel orbitals into groups with different energies. Electrons from a ligand will approach the d orbitals of the transition metal when bonding. The closer these ligands approach a particular orbital, the higher the energy of the electrons placed in that orbital.

When comparing complexes containing different ligands, the presence of different ligands will cause the spacing between the energy levels of the transition metals d orbitals to increase or decrease. This will change the wavelength of light needed to cause the electron to jump (and therefore the color of that light).



Ligand 1 causes a smaller gap in energy between the transition metal's d-orbitals compared to ligand 2. This leads to Ligand 2 requiring a higher energy light to cause the electron to jump. Considering Equation 1, if  $\Delta E$  is larger, the wavelength of light  $\lambda_{\max}$  that the complex absorbs will be lower. In theory, there is only one specific wavelength that is absorbed. In practice, however, there is a range of wavelengths that are absorbed with one of the wavelengths being

the wavelength of maximum absorption  $\lambda_{\max}$ . Once we measure the wavelength absorbed by the sample, we can calculate the energy difference between these levels using Equation 1. An example is below.

### Example

If the value of the maximum wavelength is 500 nm, then the energy of one photon of that light is given by:

$$\begin{aligned}\Delta E &= \frac{hc}{\lambda} \\ &= \frac{(6.62 \times 10^{-34} \text{ J}\cdot\text{s})(3 \times 10^8 \text{ m/s})}{(500 \times 10^{-9} \text{ m})} \\ &= 3.972 \times 10^{-19} \text{ Joules of energy/photon}\end{aligned}$$

### Determining the formula of coordination complex by color measurement

In Part C of the lab, you will be assigned one ligand to combine with copper. The goal will be to determine the formula of the resulting complex (i.e. the subscript on the ligand in formula)

Goal: In the formula  $\text{CuL}_x$ , what's the value  $x$  for your ligand?

Another way of saying this is what is the ratio of copper to ligand in your complex.

We will determine the ratio of your assigned ligand to copper by combining the ligand and copper together while varying the amounts of each (i.e. the ratio). In each case, the ligand and copper will form a colored solution, but the darkness (absorbance) will not always be the same. If we add too much of the copper solution for the amount of ligand, there will be left over copper and the solution will be light in color. On the other hand, if we add too much of the ligand for the amount of copper, there will be left over ligand and the solution will be light in color. When the amount of copper and ligand have been added in the correct ratio, the maximum amount of the complex will form and the solution will appear darker. We will measure our samples' absorbances to find the correct ratio of copper to ligand. The general equation for the reaction you will be doing is below



## Procedure

**Safety:** Wear your goggles at all times. In Part A, concentrated (15.0 M) ammonia is toxic if inhaled or ingested. Ethanol is highly flammable. Keep all open flames away from it. The addition of denaturants makes the 95% ethanol highly poisonous. Copper (II) sulfate is moderately toxic by ingestion and is a skin and respiratory irritant. Many of the ligands you will be working with in Parts B and C are harmful if ingested.

**Waste:** All waste must be disposed of in the labeled waste containers.

### Part A: Synthesis of tetraamminecopper (II) sulfate monohydrate $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

1. Based on the calculation you performed in the pre-lab, weigh out the calculated amount of copper(II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) needed to prepare 3.00 grams of tetraamminecopper (II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ . Place the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  into a 150 mL beaker and record the exact weight of the solid in your lab notebook.
2. Add 10-15 mL of distilled water to the weighted  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and stir to dissolve the solid.

**Note:** If the solid does not dissolve completely, gently heat the beaker by placing it on a wire gauze above a Bunsen burner in a hood. Do not heat the solution to boiling. Be sure not to burn the solid onto the bottom of the beaker. Stir often to prevent this. If you have heated the sample, allow it to cool to room temperature by placing it in an ice bath (using ice and tap water) before going on to the next step.

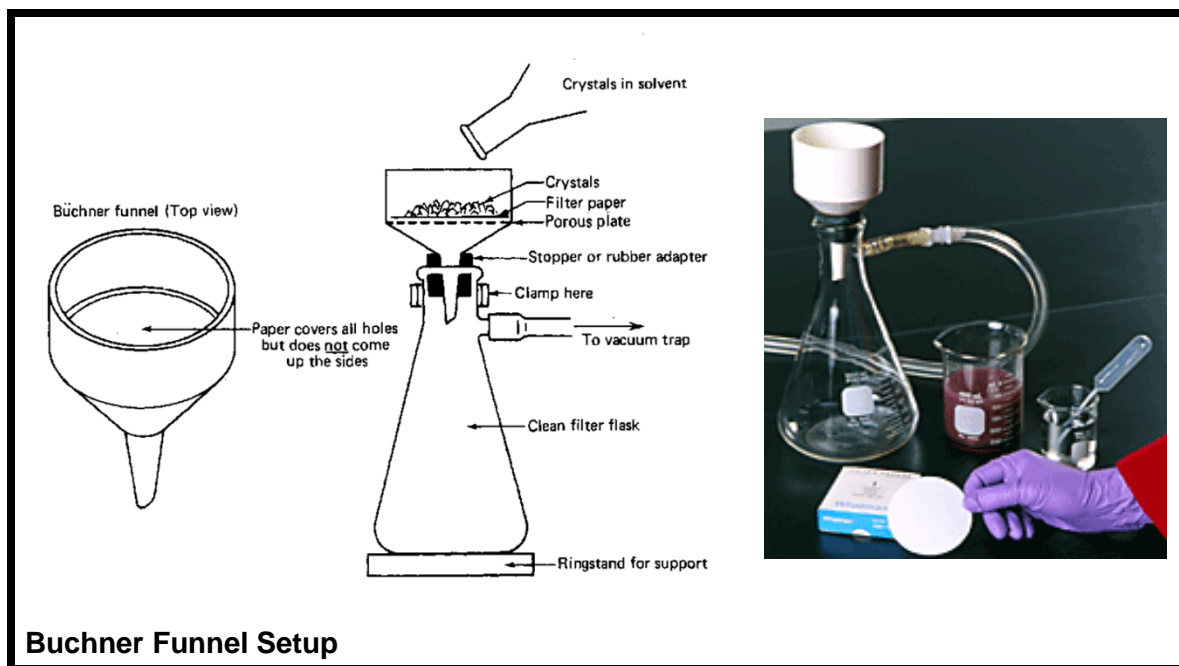
3. In the fume hood, slowly, with stirring, add **two and a half times (2.5x)** the calculated mL of 15.0 M ammonia ( $\text{NH}_3$ ) needed to convert all of your  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  to  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ . You may measure the  $\text{NH}_3$  with a graduated cylinder. The large excess of  $\text{NH}_3$  is needed to ensure that the complete reaction occurs (remember Le Chatelier's Principle?).

Initially as the  $\text{NH}_3$  is added, you will see the light blue precipitate of  $\text{Cu}(\text{OH})_2$  form (see reaction 1 in the Background section). It should dissolve when you have added all of the  $\text{NH}_3$ .

4. To decrease the solubility of the tetraamminecopper(II) complex, add approximately 25 mL of ethanol with stirring. The deep blue precipitate of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  should form.
5. Place the reaction beaker in a 400 mL beaker of ice water and allow it to stand for 10 minutes so that crystals settle out.

*The next three steps can be done while waiting for your crystals to settle:*

6. In a small beaker, prepare 20 mL of a solution by combining 10 mL each of concentrated (15.0 M) ammonia and 95% ethanol. Cool this solution in a larger beaker of ice water.
7. Obtain a piece of filter paper and a dry and clean weigh boat and record their combined mass (be sure they are both dry when you mass them together).
8. Set up the Buchner vacuum funnel shown below. Be sure to moisten the filter paper so adheres to the funnel.



9. When you are ready to filter your sample, turn on the water at the sink to create a vacuum, and then pour your sample into the Buchner funnel. This will go more quickly if you first decant the supernatant liquid through the funnel before transferring the crystals from the beaker. A rubber policeman or spatula may be used to help move the crystals.

10. Use small portions of your cooled ammonia/ethanol mixture to transfer any remaining crystals from the beaker to the funnel.

11. Use any of remaining cooled ammonia/ethanol mixture in small portions to wash your crystals in the top of the funnel. Keep the vacuum on as you wash your crystals until you observe no more liquid draining from the funnel.

12. When your product appears to be dry, transfer your product **along with** the filter paper into the weight boat you used earlier.

13. Allow the precipitate to air dry until the next lab period by carefully placing it into your lab drawer.

14. At the start of the next lab period, weigh the dried precipitate in your lab notebook.

15. Calculate your percent yield. Recall that

$$\% \text{ yield} = \text{actual yield} / \text{theoretical yield} \times 100$$

### Part B: Analysis of your tetraamminecopper (II) sulfate monohydrate $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and comparison to other copper complexes using spectroscopy

In order to do a spectroscopic comparison of your tetraamminecopper (II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  to other copper complexes, we will first need to prepare an aqueous solution of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ .

1. Prepare an solution of  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  by weighing and then dissolving 0.10 grams of your product from Part A into 25 mL of distilled water. The distilled water may be obtained using a graduated cylinder.

Then, in the hood, add 25 mL of 6 M  $\text{NH}_3$ . Record the color of this sample in your notebook. Keep this sample covered until you are ready to use it to keep down odors in the lab.

2. Prepare samples of copper with other ligands as indicated below by combining 5 drops of 0.1M copper(II) sulfate with 5 mL of 0.1 M solutions of each ligand in a small test tube. Be sure to mix each sample. Record the color each appears in your notebook.

Test Tube	0.1661 M Copper (II) Sulfate	0.1661 M ligand
1	5 drops $\text{CuSO}_4$	5mL diethylenetriamine
2	5 drops $\text{CuSO}_4$	5 mL ethylenediamine
3	5 drops $\text{CuSO}_4$	5 mL EDTA
4	5 drops $\text{CuSO}_4$	5 mL sodium salicylate

3. For each of your five samples (including the  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  solution you prepared), determine the value of  $\lambda_{\text{max}}$  using a Vernier Spectrometer. Record the values of  $\lambda_{\text{max}}$  in your notebook. Only consider the visible region of the spectrum (400 – 700 nm) region. If you do not recall how to do this, consult the Vernier Spectrometer directions earlier in this lab manual.

4. Calculate the energy difference between the d orbitals in each complex using Equation 1 in J/photon and kJ/mole

5. Organize your data into a table with columns for the name of the ligand, color of the solution,  $\lambda_{\text{max}}$  and the energy difference between the d orbitals in each complex in J/photon and kJ/mole.

6. Rank the ligands from strongest field ligand to weakest field ligand.

### Part C: Determining the formula of coordination complex by color measurement

1. Each group will be determining the formula of only one complex. Ask your instructor which ligand you will be using in this part of the lab.

2. Prepare ten samples of your complex using the chart below to vary the ratio of copper to ligand.

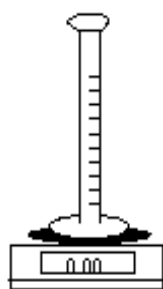
Sample	mass of 0.1661 M Cu solution ( $\text{CuSO}_4$ )	mass of assigned 0.1661 M ligand solution
1	0.10 g	0.90 g
2	0.15 g	0.85 g
3	0.20 g	0.80 g
4	0.30 g	0.70 g
5	0.35 g	0.65 g
6	0.40 g	0.60 g
7	0.45 g	0.55 g
8	0.50 g	0.50 g
9	0.55 g	0.45 g
10	0.60 g	0.40 g

3. You will use the balance to prepare solutions as described below.

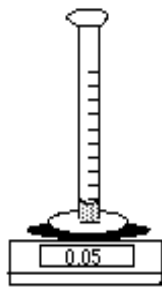
- Place the graduated cylinder on the balance and press the tare bar. Add  $\text{Cu}^{2+}$  solution and reweigh.
- Add ligand until the total mass is 1.00 gram
- Add deionized water to the 5 mL mark on the graduated cylinder



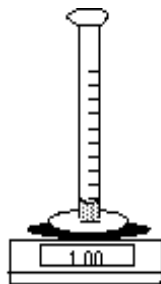
- d. Pour into a small test tube, pour back into the cylinder, and back into the small test tube. This mixes the solution.



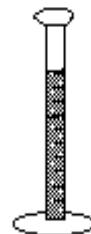
Place the graduated cylinder on the balance and press the tare bar so the reading is 0.00g



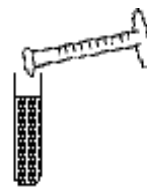
Add between 1 drop and 0.8g of copper solution and reweigh. Record the value in your notebook.



Add ligand until the total mass is 1.00g



Add water to a fixed volume whose value depends on the intensity of the color. For some complexes, 5 mL works well but others need to be diluted further to get an absorbance reading less than 1.

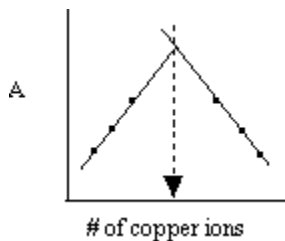


Transfer to a vial pouring back and forth a few times to mix.

4. After you have prepared all ten solutions, measure the absorbance for each solution you prepared. Record the absorbance at the value of  $\lambda_{\text{max}}$  you determine in Part B.

5. Graph absorbance versus the mass of copper solution used and determine ratio of copper to ligand that gave the maximum absorbance.

This is what the ideal graph looks like:



mass of copper solution

Your graph of absorbance versus mass of copper solution should look like this. You are to find the ratio of copper to ligand that gives the maximum absorbance.

If you don't get a nice triangle, make additional solutions to add to your data.

6. Use the graph to determine the formula of your complex. Record the formula and explain how you arrived at it in your notebook.

**What does the value of the mass of copper at the maximum absorbance tell you?**

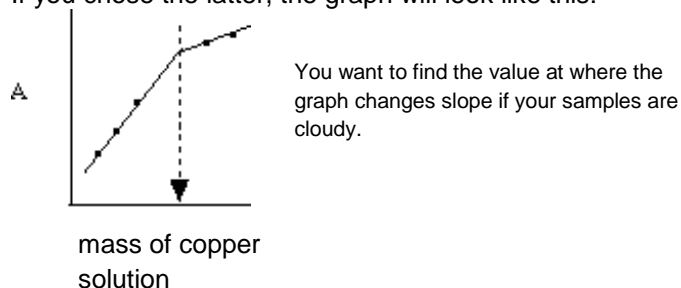
It gives you a good clue on the number of ligands attached to the metal ion. For example, suppose the maximum absorbance is at 0.50 g of copper solution to 0.50 g of ligand solution. Since the concentrations of each solution are the same, the moles of copper equal the moles of ligand in this sample. The ratio of Cu to L would be 1:1. Therefore, the formula of the sample is CuL.

What if the maximum is at 0.20 grams of copper solution and 0.80 grams of ligand solution? The ratio would be 1 mole of copper to 4 moles of ligands. The formula would be CuL<sub>4</sub>

One complicating factor is that with some ligands an precipitate forms at low concentrations of ligand. You can do three things if this happens:

- filter the solution
- let the solution settle and draw off the top clear layer
- graph the cloudy solution

If you chose the latter, the graph will look like this:



## Data Tables and Calculations For Part A and C of the lab

You will need to prepare and organize your own data tables for this part of the lab. The tables need to be done **before** you come to lab as part of your pre-lab assignment.

For reminders and hints:

- Data should be organized into tables with either a line or a box for each number you will need to record.
- Tables should be clearly labeled with the quantity to be recorded along with the unit it will be recorded in.
- Besides measured quantities you should leave room and label areas for quantities that will be calculated. Sample calculations should be shown as well.

**Sample data table for Parts B only is below**

Ligand used	Color of Complex	$\lambda$ max	$\Delta E$ in J/photon	$\Delta E$ in KJ/mole
$\text{NH}_3$				
diethylenetriamine				
ethylenediamine				
EDTA				
sodium salicylate				

Be sure to rank the ligands from strongest field ligand to weakest field ligand.

## Post- Lab Questions

1. Give three errors in technique that would lower the percent yield in the synthesis of tetramminecopper (II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  (Part A of the lab).

2. The reaction of ammonia with copper (II) ions is an example of a Lewis Acid- Lewis Base reaction. Which is the acid and which is the base?

3. Name the following complex compounds or ions.

- $[\text{Al}(\text{H}_2\text{O})_6]\text{Br}_3$
- $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$
- $\text{K}_3[\text{FeF}_6]$
- $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$
- $\text{K}_2[\text{SnCl}_6]$

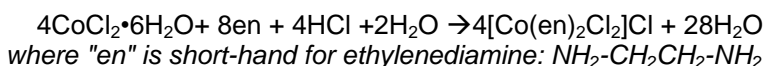
4. Write the formula for each of the following complex compounds or ions.

- Hexaamminecobalt (III) chloride
- Diamminetetrabromoplatinum (VI) bromide
- Tetraaquacadmium (II) nitrate
- Sodium tetracyanocuprate (I)
- Silver hexacyanoferrate (II)

5. Determine the oxidation number for each of the transition metal atoms or ions

- $[\text{V}(\text{OH}_2)_6](\text{NO}_3)_3$
- $(\text{NH}_4)_2[\text{CoCl}_4]$
- $\text{K}_4[\text{Mn}(\text{CN})_6]$
- $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$

6. Consider the synthesis of the coordination compound, transdichlorobis(ethylenediamine)cobalt(III) chloride. The reaction is shown below:



If the reaction is done with 8.25 grams of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 7.35 g of en, how many grams of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  will be produced? Assume HCl and  $\text{H}_2\text{O}$  are in excess.

7. Coordination compounds involve transition metals. Write the ground state electron configuration for each of the following

Cu

$\text{Cu}^{2+}$

Co

$\text{Co}^{2+}$

$\text{Co}^{3+}$

## Pre-Lab Questions

1. Calculate the mass of copper(II) sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) needed to prepare 3.00 grams of tetramminecopper (II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  according to the overall reaction on the first page of the lab.
2. Calculate the volume of 15.0 M ammonia ( $\text{NH}_3$ ) needed to prepare 3.00 grams of tetramminecopper (II) sulfate monohydrate  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$  according to the overall reaction on the first page of the lab.
3. If a the complex  $\text{Ni}(\text{NH}_3)_4^{2+}$  has a maximum absorbance at 740 nm, calculate the energy of one photon that is absorbed by the complex.
- 4a. If  $\text{Fe}^{2+}$  forms a complex with ethylenediamine (en), what will the formula be? Assume  $\text{Fe}^{2+}$  has a coordination number of 6.
- 4b. If  $\text{Ag}^+$  forms a complex with chloride, what will the formula be? Assume  $\text{Ag}^+$  has a coordination number of 2.
5. Define the following terms
  - a. complex ion
  - b. ligand