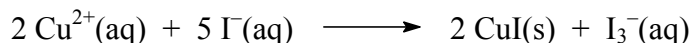


## Synthesis and Analysis of a Coordination Compound

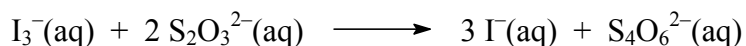
In addition to forming salts with anions, transition metal cations can also associate with neutral molecules (and ions) through a process called **ligation**. These are generally referred to as **coordination compounds** or **complex ions**. The ligands are covalently bonded to the metal ion thus producing a new compound. In this lab, you will synthesize and isolate such a coordination compound using copper(II) ion as the cation and ammonia as the ligand. The reaction carried out can be described by the following reaction:



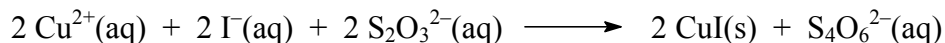
Since copper(II) ion can be smoothly reduced to copper(I) with iodide ion, a redox titration can be used to determine the copper content of the unknown. The precipitate formed (CuI) in this experiment can absorb significant amounts of iodine and cause erroneous titration results. To prevent this, potassium thiocyanate (KSCN) is added, which preferentially adsorbs onto the surface of the solid and keeps the iodine available for titration. A titration in which iodine is titrated to find another component indirectly is called an iodimetric titration. The substance of interest ( $\text{Cu}^{2+}$  in this case) is reduced with an excess of  $\text{I}^-$  to form iodine as **triiodide ion**,  $\text{I}_3^-$ :



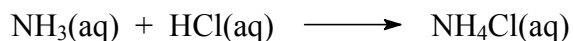
The triiodide produced is titrated with standard thiosulfate ion,  $\text{S}_2\text{O}_3^{2-}$ :



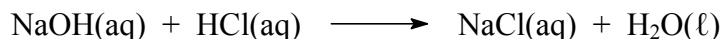
The triiodide ion acts as its own indicator, going from a red-brown to colorless. Starch is added near the end for blue to colorless transition that is easier to see. The overall titration stoichiometry is:



The ammonia content of the complex can be determined through a backtitration technique. A known number of moles of HCl (excess) is added to convert the  $\text{NH}_3$  from the complex into  $\text{NH}_4^+$ :



The number of moles of HCl that remain is determined by titration with standard NaOH:



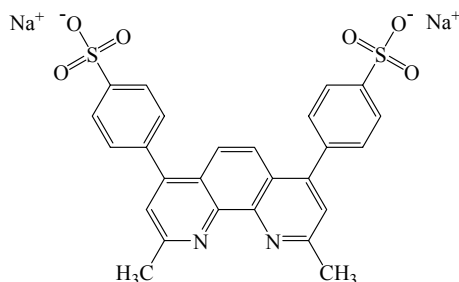
The moles of  $\text{NH}_3$  is obtained from the difference between the known amount of HCl added and the moles determined by titration.

Finally, there is an alternative way to determine the Cu in the complex that relies on the intensity of color of a compound made from the copper ion in the complex. **Spectroscopic** methods of

analysis are usually preferred when the analysis of many similar samples is required. For many metal ions, a specific complex is formed which is often quite selective for a particular element. The absorbance (A) at a particular wavelength of visible light, is proportional to the concentration of the complex in the solution:

$$A = \epsilon bc$$

where  $\epsilon$  is the **molar absorptivity** (a proportionality constant), **b** is the pathlength of the sample holder (usually 1 cm) and **c** is the concentration in M. Knowing the absorbance of an unknown solution allows for the calculation of concentration, provided  $\epsilon$  is known.  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^+$  with hydroxylamine hydrochloride and allowed to form a yellow complex with the disodium salt of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disulfonic acid (below)



The molar absorptivity of the complex at 480 nm is 13,500 L/mole·cm.

## Procedure

### Synthesis of Copper Complex

1. Construct a hot-water bath by heating water in a 250-mL beaker on a hotplate. Add 6.0 g of powdered copper(II) sulfate pentahydrate (record the exact mass to 0.0001 g) to about 7 mL of distilled water in a 100-mL beaker. Heat the mixture in the hot-water bath, with occasional shaking, until it is all dissolved.
2. **In the hood**, slowly add 15 M ammonia while stirring. The initially formed precipitate will dissolve to form a clear dark-blue solution when enough ammonia has been added (approximately 25 mL).
3. Slowly, with mixing, add 50 mL of methanol. Cool the beaker in an ice-water bath for several minutes.
4. Setup a suction flask and Büchner funnel with the appropriate filter paper. Isolate the precipitate on the filter paper under vacuum. Wash with about 10 mL portions of methanol (2 times), keeping the filtercake moist at all times. Dry by applying vacuum for 15 minutes.

5. Weigh a labeled, clean, dry 250-mL beaker. Record the mass on the label. Place the mostly dry filtercake in the beaker and remove the filter paper. Break up the solid into a powder and allow it to dry (covered with a watchglass) until next week.

### Preparation of 0.1 M NaOH Solution

1. Rinse a 250-mL beaker with distilled water and dry it. Using a top-loading balance, carefully pour about 2.0 g of NaOH **into** the 250-mL beaker. Do this relatively quickly as the NaOH will absorb water from the air. Do not worry about getting the mass exact. NaOH can cause severe burns, so **never** touch the pellets. Clean any spills.
2. Add **about** 50 mL of distilled water to the beaker to dissolve the pellets. Swirl the beaker carefully to dissolve most of the pellets. Carefully pour this solution into a clean 500-mL polyethylene bottle. Rinse the beaker with more distilled water and add to the polyethylene bottle. Add distilled water to **near** the top of the bottle. Mix thoroughly.

### Standardizing NaOH Solution

1. Clean three 125-mL Erlenmeyer flasks and rinse them with distilled water. Fill a weighing vial (about  $\frac{1}{4}$  full) with potassium hydrogen phthalate ( $\text{HKC}_8\text{H}_4\text{O}_4$ ), a **monoprotic** acid, abbreviated as KHP. Bring the flasks, the weighing vial, a calculator and your notebook into the balance room. Weigh, by difference (using a paper collar), between 0.2500 and 0.3000 g samples into the Erlenmeyer flasks (make sure you can tell the flasks apart).
2. Add distilled water to the 50 mL mark on the flasks and swirl to dissolve the sample completely. The exact amount of water is not important. Add 2 – 3 drops of phenolphthalein indicator.
3. Rinse the buret with two or three samples (~10 mL) of your NaOH solution and fill with fresh titrant to the top. Open the stopcock **fully** and allow it to drain until the meniscus goes below the 0.00 mL mark. This should eliminate any air bubbles from the tip, but check this **carefully**. Record the initial volume to **0.01 mL**.
4. Place the flask containing the KHP solution on a white background and position it under the buret, with the tip of the buret just below the top of the Erlenmeyer. Titrate to a persistent, but very faint, pink color which will disappear when you swirl. Record the final volume. Perform three total titrations.

### Preparation of 0.2 M HCl Solution

1. Measure (graduated cylinder) about 8 mL of 6.0 M HCl solution into a 250-mL polyethylene bottle. Add distilled water to **near** the top of the bottle. Mix thoroughly.

### Standardizing HCl Solution

1. Pipet 10.00 mL samples of the HCl solution into 3 125-mL Erlenmeyer Flasks. Add water to the 50 mL mark on the flasks. Add 2 – 3 drops of phenolphthalein indicator, and titrate with your standardized NaOH solution to the same endpoint as before.

### Determination of Copper in Unknown

1. Into each of three dry 125-mL Erlenmeyer flasks weigh **by difference** approximately 0.12 g of your unknown to the nearest 0.1 mg.
2. Prepare a buret with standard sodium thiosulfate solution and record the initial volume to 0.01 mL.
3. Add 15.0 mL of 6 M acetic acid to each sample and swirl until the solid has dissolved. Then add about 20 mL of distilled water. Titrate each sample one at a time in the following way. Weigh, in separate 50-mL beakers, 0.2 g of KSCN and 0.6 g of KI. Add the solid KI, swirl to mix, cork the flask and store in the dark for 3 minutes.
4. After the 3 minutes, quickly titrate the sample until the solution just turns a pale gold color (do not over shoot!). Add the solid KSCN and 3 – 4 drops of starch indicator (dark blue color develops). Swirl to mix thoroughly, then continue to titrate dropwise until the blue color disappears, revealing a gray or white precipitate. Record the volume of thiosulfate required for each sample in a table similar to the one above.

### Determination of Ammonia in Unknown

1. Into each of three dry 125-mL Erlenmeyer flasks weigh **by difference** approximately 0.2 g of your unknown to the nearest 0.1 mg.
2. Clean, condition, and fill two burets as follows: fill one buret with your standardized 0.2 M HCl solution and the other with standardized 0.1 M NaOH solution. Record the initial volume of each buret (to 0.01 mL)
3. Pipet 25.00 mL of HCl into one of the sample flasks. Add 2 mL of deionized water and 5 – 6 drops of methyl red indicator. Swirl the solution gently to dissolve all the solid.
4. If the acid is present in excess (as it should be), the solution should have a pink color characteristic of the acid form of methyl red. If not, more HCl must be added (if so, remember to record the exact volume of additional HCl added). Titrate the pink solution with the standardized NaOH until the color changes sharply from pink to nearly colorless. Overtitration produces a green, turbid solution due to the precipitation of  $\text{Cu}(\text{OH})_2$ . [If you overtitrate slightly you can add more HCl dropwise until the solution turns pink again (record the additional HCl!), then approach the endpoint again by titrating with NaOH.] Record the total amount of NaOH used. Repeat the whole process with two more samples of compound.

## Spectroscopic Determination of Cu

1. Weigh a 0.1 g sample of the complex (known to 0.1 mg) in a 250-mL volumetric flask. Add 30 mL of 6 M HNO<sub>3</sub>, mix thoroughly by swirling, and dilute to the mark with distilled water. Stopper and mix by inverting the flask (letting it drain **completely** in both directions) **at least** 10 times.
2. **Pipet** 1.00 mL of the resulting solution into a 100-mL volumetric flask.
3. Pipet 5.00 mL of 10% hydroxylammonium chloride solution, 5.00 mL of 0.1% 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate solution, and 20.00 mL of 10% ammonium acetate solution. Mix thoroughly by swirling and dilute to the mark. Stopper and mix by inverting the flask as in step 1
4. Measure the absorbance of the solution at 480 nm, using the blank provided (the solution above without any complex added).

## Questions

1. What information is needed to determine the theoretical yield of the complex?
2. In the determination of NH<sub>3</sub>, why is it not really important how much HCl is added as long as you know **exactly** how much?

## Data Treatment

1. Calculate the molarity of NaOH.
2. Calculate the molarity of HCl.
3. Determine the mass percent of Cu<sup>2+</sup> in the complex.
4. Determine the mass percent of NH<sub>3</sub> in the complex.
5. Assuming 100 g of sample, determine the smallest, whole number ratio of **moles** NH<sub>3</sub> to moles Cu<sup>2+</sup> in the complex.
6. Give the formula of the complex, assuming one Cu<sup>2+</sup> ion.
7. Calculate the mass percent of Cu<sup>2+</sup> based on the absorbance data.