Chem 163: synthesis and analysis of a copper(ii) coordination compound

CHEM 163: SYNTHESIS AND ANALYSIS OF A COPPER(II) COORDINATION COMPOUND INTRODUCTION In this multi-week experiment, you will synthesize a compound and then analyze it to determine its empirical formula. The substance you will prepare is a vividly colored coordination compound of copper. Based on the reagents used in the synthesis procedure, you can assume that the final compound contains copper(II), ammonia, sulfate, and water. In your analysis, you goal is to figure out the mole ratio of each component in the final compound. In other words, you will solve for x, y, z and a in the formula $Cu_x(NH_3)_y(SO_4)_z - aH_2O$. Based on the way the formula is written you can assume that ammonia and sulfate are acting as ligands and counter-ions, respectively. The water, in contrast, is water of hydration. That is, it is incorporated into the crystal lattice of the solid compound in a noncovalent manner, usually by hydrogen bonds, and with a specific stoichiometry. Synthesis To prepare your own sample of the coordination compound, you'll start with solid copper(II) sulfate pentahydrate, $CuSO_4 - 5H_2O$. Once dissolved in water, the copper ions take on water molecules as neutral ligands: copper(II) ions exist as the hexaquacopper(II) complex ion in aqueous solution. After adding concentrated ammonia, NH_3 ligands displace the water molecules covalently bound in the original copper complex, and a dramatic color change occurs. In your lab report, you will be able to explain this color change using crystal field theory and the relative energies of copper's d orbitals in the two complexes. The copper(II) ammonia complex is a water-soluble ion; in order to precipitate and isolate the final product, an ionic compound, you need to decrease the solubility of the compound. A convenient way of doing this is to

add a large amount of ethanol, CH3CH2OH, to the aqueous solution. Ethanol is miscible with water but is much less polar, 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, and the synthesis procedure ends with filtration, rinsing, and drying of the visually stunning product. The next several parts of the lab involve analysis of your copper(II) coordination compound to determine its empirical formula. Gravimetric Analysis of Sulfate The amount of sulfate in your product will be determined with a simple gravimetric analysis, a method that depends on the accurate weighing of a certain sample. You will selectively react the sulfate in the copper(II) compound using an aqueous solution of lead(II) acetate. The entire sulfate in the copper(II) complex sample should precipitate as PbSO4 during this metathesis reaction. After careful filtering and drying of the precipitate, you can use the mass of PbSO4 to calculate the amount of sulfate in the sample of the copper(II) compound. Volumetric Analysis of Ammonia You will measure the ammonia content of the product with a simple but colorful titration. A standard HCl solution will be provided to titrate all the ammonia contained in a sample of your copper(II) compound. Since this is a strong acid-weak base titration, the equivalence point occurs at pH < 7, and methyl orange is a good indicator to use. Methyl orange changes from orange-yellow to red at the endpoint of the titration; however, due to the brightly colored copper(II) compounds produced during the titration you should observe several interesting color changes. The solution starts out deep blue becomes a blue-green suspension, and then a pea-green suspension when 70% of the HCl has been

added. By the time 85% of the acid has been added, the suspension is golden yellow. The endpoint occurs when the suspension becomes a pumpkin-orange solution. A red-orange solution is passed the endpoint. Spectrophotometric Analysis of Copper(II) The last analysis to conduct is by spectrophotometry, that is, the measurement of light and its interaction with matter. In this situation, you can take advantage of the fact that aqueous copper(II) ions absorb light in the visible region of the electromagnetic spectrum, as shown in the spectrum below. Notice that maximum absorbance occurs around 645 nm, which corresponds to orange light (Figure 1). To your eye, the solution appears blue because blue light is not absorbed. That is, blue light is transmitted through the sample, while orange light is absorbed. No other species in the copper(II) compound (not NH_3, SO_4^{2-}, or H_2O) absorbs visible light, so the light absorbed by the entire sample at 645 nm can be used as a measure of the amount of copper(II) present.* According to Beer's Law, there exists a linear relationship between the molar concentration of a species and the amount of light it absorbs for a specified range of concentration. You can see evidence of this with your own eyes, without any instrumentation: A copper(II) solution with a molarity of 0. 02 M appears twice as dark as one with a concentration of 0. 01 M. By using a spectrophotometer, the relationship is quantitative. Given the absorbance of a sample you can calculate the concentration of copper(II). Beer's Law is applied most accurately when a calibration graph is used. To do so, several solutions of known concentration (the standards) are prepared, and the absorbance of each is measured. As shown below on a sample calibration graph, a plot of absorbance (A) vs. concentration (molarity) will result in a

straight line, and the equation of this line can be determined by linear regression. Given a copper solution of unknown concentration, you can measure the absorbance of the unknown, and then use the calibration graph to determine the molarity. For example, using the calibration graph in Figure 2, if an unknown solution has an absorbance of 0. 451, the concentration of the copper can be calculated using the equation of the line. *Î» max also occurs at 665 nm and > 750 nm. Figure 2 Finally, once the mass percentages of ammonia, copper and sulfate have been determined, the mass percentage of the remaining component, water, is calculated by subtraction of the known percentages from 100%. PROCEDURE General Notes - This lab will take about three lab periods to complete. You and your instructor will work together to plan a schedule for conducting all the parts of the experiment. - Keep your data well organized: There are several parts of this lab, and you may be collecting data for more than one part at a time. Also, note that you will write descriptive observations for several parts, in addition to collecting quantitative data in data tables. - Respect significant digits in the recording of data and the calculations with that data. Part I: Synthesis of the Copper(II) Coordination Compound Safety Concerns: Concentrated ammonia releases caustic and toxic fumes. Work in the fume hood, as much as possible, on all parts involving ammonia. Waste Concerns: Dispose of all solutions containing copper in the designated waste jar for this lab. 1. Weigh out 10 grams of copper(II) sulfate pentahydrate ($CuSO_4$ - $5H_2O$) to the nearest centigram, and record the actual mass used. Record your observations of the original compound's appearance. Place the crystals in a 250 mL beaker. 2. Add about 10-15 mL of water to the solid and then, in

a hood, add 20 mL of 15 M NH3 (concentrated ammonia.) Stir to dissolve the crystals, carefully holding the beaker up to the light to see whether crystals still remain. 3. Over a period of 1 minute, slowly add 20 mL of 95% ethanol to the solution. Stir and cool to room temperature. Record your observations of any change that occurs. 4. In a beaker prepare a 30 mL solution from 15 mL of concentrated ammonia and 15 mL of 95% ethanol. Mix well and set aside. 5. Set up a vacuum filtration apparatus using a vacuum flask, three pronged clamp, tubing, Buchner funnel, and ring stand. Lay flat a circle of filter paper in the Buchner funnel, and moisten it with water so that it lies flat and covers all the holes in the funnel. Connect the apparatus to the vacuum nozzle (yellow handles) and turn on the suction. Carefully pour your reaction mixture into the funnel, swirling the slurry of liquid and solid as you go so that you transfer as many of the crystals as possible into the funnel. If a significant amount of crystals stay behind you can retrieve them by scraping or by using some of the filtrate (mother liquor), in the filter flask, to rinse the crystals free. It is okay to carefully disconnect the filtration apparatus to remove some filtrate, and then reassemble it all to continue filtering. 6. Once all the mother liquor has been sucked out of the crystals, use the solution you prepared in step 4 to wash the crystals. Turn the aspirator off, make sure the vacuum is broken, and pour about 10 mL of the ammonia-ethanol mixture into the funnel. Use the smooth end of a fire-polished glass rod to break up all clumps of solid, dispersing the crystals evenly in the solution. Be careful not to tear the filter paper. Turn on the aspirator to remove the liquid. Repeat this two more times with the remaining amounts of ammonia-ethanol mixture. In the same manner, wash the solid twice with 10 mL portions of

95% ethanol. Finally, wash the solid twice with 10 mL portions of acetone. 7. At this point your crystals should be nearly dry. You may continue rinsing with acetone if you feel that the product is still wet with solvent. Finally, leave the aspirator on and pull air through the crystals for about 5 minutes. Break up the crystals and lightly press them against the funnel so that the entire sample becomes well dried. Record the appearance of your product at this point. Does it appear homogeneous? 8. Weigh a large watch glass and empty the crystals on to it, now weigh the watch glass and compound. Cover with a tissue and leave the sample in your drawer to continue drying until the next lab period. 9. When you return to lab make sure the final product is dry of all solvent. Record its mass to the nearest centigram. Also record the crystals' appearance and note any heterogeneity to the sample. PART II: Analysis of Product A. Gravimetric Analysis of Sulfate 1. To the nearest 0. 1 milligram, weigh about 1 gram of your dry coordination compound in a 100 mL beaker. Record the actual mass of the sample. Obtain a piece of filter paper for use in Step 4, and record its mass to the nearest 0. 1 milligram. 2. Dissolve the crystals in about 10 mL of 6 M nitric acid. 3. Obtain about 5-6 mL of 1 M lead(II) acetate. Add it dropwise to the solution of your compound and record observations of any changes that occur. Continue to add lead(II) acetate until the precipitation is complete-6 mL of lead(II) acetate may be sufficient. Check for completeness: (1) allow the precipitate to settle to the bottom of the beaker leaving a clear solution above the solid, (2) add one drop of lead(II) acetate on the beaker wall, allowing the drop to run down the glass and into the solution, and (3) watch carefully for more precipitation as the lead(II) acetate hits the clear solution. The lack of precipitation after the

addition of drops of lead(II) acetate signals the completion of the reaction. 4. Collect all the precipitate and measure the mass accurately in the following manner. First, filter the precipitate by gravity filtration. Use a conical funnel and the filter paper you weighed in Step 1, folded in half once, then again. Open up the filter paper and gently push it into the funnel, using some water to get the paper to adhere to the funnel and stay in place. The entire filtration process may take some time: fill the funnel half full with the slurry, wait for it to drain, and repeat until all the reaction mixture has been transferred to the filter. While waiting for gravity to do its part, you can set up the second trial of this part or work on any other part of this lab. 5. For your results to be accurate, you must be absolutely sure that the entire sulfate has been precipitated. Check the filtrate for unreacted sulfate by adding a few more drops of lead(II) acetate. If more precipitate forms in the filtrate, you should add 1 mL of the lead(II) acetate and refilter. 6. For accurate results, you must also be sure that you have collected all the precipitate on the filter paper, and that it is not contaminated with other substances. Use small volumes of water to rinse out any solid remaining in the original reaction beaker. Finally, rinse the solid and the filter paper with additional amounts of water. Record your observations of the solid and the filter paper, during the rinsing, and realize that appearance indicates when all copper-containing compounds have been rinsed free. Last, rinse the precipitate with about 10 mL of acetone. 7. Gently remove the filter paper with the wet precipitate and place on a watch glass, where the solid can continue to dry until the next lab period. Keep in mind that wet filter paper tears very easily, and you do not want to lose any of your precipitate. 8.

Repeat steps 1-7, for a second trial. 9. When the two samples are completely dry, record the mass of the solid and filter paper together, to the nearest 0. 1 milligram. 10. You may choose to do a third trial of this analysis. B. Volumetric Analysis of NH3 1. To the nearest 0. 1 milligram, weigh out about 1 gram of your compound, and record the actual mass. Dissolve it in about 30 mL of deionized water in an Erlenmeyer flask. 2. Add 10 drops of methyl orange indicator, and titrate with the standard HCl solution provided for the class. (Don't forget to record the actual molarity of the standard HCl solution for your data!) Review the description of the titration in the introduction of this experiment, so you know what progression of colors to expect. Remember that the disappearance of the precipitate is the clearest indicator of the equivalence point, though the colors will help you know when the end point is approaching. 3. Record the results of your titration, and conduct a second trial. Check to see if your two trials agree within 1%. You can't simply compare the final volumes of HCl used; instead, divide the volume of HCl by the mass of compound titrated for each trial. If these values agree within 1% for the two trials, you don't need to conduct a third trial. Otherwise, titrate a third sample. C. Spectrophotometric Analysis of Copper(II) Ion 1. Review the instructions for using the Spec-20 spectrophotometers. Adjust the wavelength to 645 nm and allow the lamp to warm up. 2. Prepare 2 sets (#, #') of five standard solutions using the volumes in Table 1 as a guide. Prepare these solutions in 2 x 5 clean, dry, and labeled test tubes. Be sure to mix the solutions well using a pipet but do not remove the pipet. The copper(II) stock solution and the nitric acid solution will be available in self-zeroing burets. Be sure to record the actual volumes used, in your data

tables, to the proper number of significant figures. Table 1: Standard Solutions for Spectrophotometric Analysis Sample Number Volume of Stock Cu2+ Solution (mL) Volume of 1 M HNO3 (mL) 0, 0' 0. 00 10. 00 1, 1' 2. 00 8. 00 2, 2' 4. 00 6. 00 3, 3' 6. 00 4. 00 4, 4' 8. 00 2. 00 Quantitatively prepare only two solutions of your own compound using the amounts shown in Table 2 as a guide. Table 2: Solutions of the Coordination Compound for Spectrophotometric Analysis Sample Number Mass of Compound (g) Volume of 1 M HNO3 (mL) 5 About 0. 12 10. 00 6 About 0. 24 10. 00 Note: Depending on time-constraints, your instructor may have you work with another student, sharing data for the absorbance values of the standards. If so, it is important that you use the same Spec-20 as the other student; the absorbance readings in your calibration curve and for your samples of compound should all come from the same instrument. 3. Talk to the instructor about properly using the Spec 20. Obtain two matched cuvettes. With nothing in the cuvette holder adjust the left knob such that the spectrophotometer reads 0% transmittance. Use one cuvette filled with deionized water to adjust right knob such that the spectrophotometer reads 100% transmittance. Use the other cuvette to record the absorbance values at 645 nm of samples 0-4 and repeat these measurements with a freshly prepared set of standards, 0'-4'. Measure the absorbance of samples 5 and 6 after each standard set has been measured. CALCULATIONS To calculate the formula of the coordination compound you synthesized, you will first use simple stoichiometric calculations to determine the mass % of every component (sulfate, ammonia, copper, and water). Then you will use the percent composition of the whole compound to calculate mole ratios of the

empirical formula; that is, the subscripts in the formula. Here are some formulas and other things to remember: [pic] - You will have two or three trials from the gravimetric analysis of sulfate. Calculate mass % SO_4^{2-} for each of the trials, and then a final average with standard deviation. If you have more than two trials and one is an obvious outlier, you may choose to drop the problematic value, but you should note this in your lab report or talk with your instructor about it. - The mass of the precipitate collected in the gravimetric analysis is not pure sulfate, of course. Use the formula of the precipitate to convert grams of precipitate to grams of sulfate. - Use the stoichiometric ratio between ammonia and HCl in a simple neutralization reaction to calculate the amount of NH_3 in your compound. You don't have to write a balanced reaction in which HCl is reacting with the whole copper compound. - For the spectrophotometric data, calculate an average absorbance value for each standard and unknown (A = -logT = -log(%T/100). Construct a calibration graph as described in the introduction and on page 40 and use it to calculate the molarity of copper in each of the two solutions of your unknown, separately. For each solution, use molarity and volume to calculate moles, and then grams of copper in the sample. - The mass % of water is determined by subtraction when the other three percentages are known. - Once you have the mass % of every component, you can derive the empirical formula. If needed, review your CHEM 161 notes and text for a refresher. Remember to round each coefficient to integer values in your final formula. CHEM 163 Lab Report Format Synthesis and Analysis of a Cu(II) Coordination Compound The partially word-processed report will consist of the following 9 sections (exact order is worth points). Word-processed

sections are in bold. 1. Title: Top of page: Provide the experiment title in YOUR own words (do not use the manual's title), the date the experiment was performed, and your name first followed by your partner's name. 2. Introduction and Purpose: Using YOUR own words, interest the reader in the investigation and explain what is being determined, generally how the investigation is conducted, and why this determination is important in the greater sense. Avoid plagiarism by citing information that is not yours. 3. Procedure: Use the following reference: Loftus, C.; Cabasco-Cebrian, T.; Wick, D. " Laboratory Manual for CHEM 163" spring 2012 Edition, Department of Chemistry, Seattle Central Community College, pp ??? Include the relevant page numbers for the investigation. If you change a given procedure, you must outline, briefly, exactly what was done differently.   Websites may be referenced simply, such as www. google. com. You must also put in when the website was last updated. 4. Results: Embed a properly labeled table with units showing, for each trial, (a) the mass of compound, the mass of $PbSO_4$ + filter paper and the mass of the filter paper, (b) the mass of compound and the volume of ? M HCl, and (c) the mass of compound and the calculated concentration of Cu^{2+}. Embed and complete a table similar to that below into your document.

Species	SO_4^{2-}	NH_3	Cu^{2+}	H_2O
Trial 1 (%)	36. 06			
Trial 2 (%)	39. 72			
Mean(%)	37. 89			
Stdev(%)	2. 59			
Mean(stdev)(%)	38(3)			

Embed an absorbance/concentration table for each sample in each trial clearly showing original absorbances and corrected absorbances Embed an excellent and properly formatted plot of absorbance vs. concentration (standard curve). Make sure that a LINEST table is embedded and print the line equation with errors on your plot. 5.

Calculations: Show ONE detailed representative calculation (significant digits important) each for %SO42-, %NH3, and %Cu2+. Show the calculations of the remaining water percentage and empirical formula. 6. Conclusion (follow basic grammar and spelling rules): State the empirical formula of your coordination compound. 7. Discussion: If there are any uncertainties in your conclusion state these and explain alternative possibilities. Be sure to calculate the % relative error only (not the % relative uncertainty). You will need to consult other resources (cite them) to determine the actual formula. Observations are crucial for supporting any alternative formula due to an impurity or unexpected compound formation. 8. Post-Lab Questions: To be announced. 9. Raw Data: Attach at the back of your report a Xeroxed copy of Lab Staff signed raw data from your notebook. How to Make a Proper Standard Curve 1) Average the two 1 M HNO3 blank absorbance readings. 2) Subtract the average 1 M HNO3 blank absorbance from each of the standard absorbance readings 1-4 AND each 1 M HNO3 blank. 3) You should have 10 data points to construct the standard curve (2 x 4, Cu2+ solutions plus 2, 1 M HNO3 solutions) 4) Add a trendline and calculate slope and intercept with errors using a linest analysis. Recall that Beer's Law (A = Îµbc) has the y-intercept equal to zero. Your line might be close to zero but close to zero is still non-zero. [pic] Uncertainty in [pic] [pic] You will calculate the uncertainty in x for each unknown If you had run four trials of 0. 2000 g of compound use the value of ¼ in place of 1 for the first term of the square root.

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87x + 0. 002 max 0. 451 = 2. 99x + 0. 018 min max x = max [Cu2+] = 0.

156 M min x = min [Cu2+] = 0. 145 M y = 2. 93(6)x + 0. 010(8) [pic]