The Synthesis and Analysis of Copper(II) Carboxylates

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Synthesis is unique to chemistry. Chemists make compounds, separate them from their reaction mixtures, and then determine their purity. These synthetic procedures had their origins in alchemy and, in their incarnation in modern industry, they have resulted in drugs and materials that have increased our lifetimes and have made our lives more enjoyable. Appropriate synthetic projects for the introductory laboratory should demonstrate some of the characteristics of the synthetic process:

1. the same compound can be made by a number of different synthetic methods,
2. that the separation of the compound depends upon the method of preparation, and
3. that some methods of analysis are more appropriate than others for some compounds.

Students enjoy making compounds, and their enjoyment is proportional to the extent that they have some ownership of the compound–that the compound that they are preparing is theirs.

The preparation and analysis of copper (II) carboxylates has the following advantages:

1. a variety of carboxylates are prepared easily from numerous carboxylic acids,
2. the compounds generally do not need extensive purification,
3. because the compounds contain a colored ion (Cu^{2+}) and are decomposed easily by heat, they can be analyzed for copper in two different ways—gravimetrically by decomposition to CuO and by colorimetry, and
4. most of the carboxylates contain water of hydration, which can be determined easily by gravimetric thermal analysis.

Although there are a variety of methods for the synthesis of metal carboxylates, three methods have been used widely for the synthesis of copper carboxylates in aqueous solution:
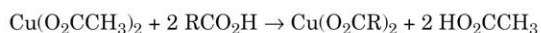
1. reaction of basic copper (II) carbonate ($Cu_2CO_3(OH)_2$) with a carboxylic acid.

$$2\ RCOOH + Cu_2CO_3(OH)_2 \rightarrow Cu(O_2CR)_2 + 2\ H_2O + CO_2$$
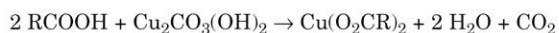
2. reaction of the sodium salt of the carboxylic acid with copper (II) sulfate.

$$2\ RCOONa + CuSO_4 \rightarrow Cu(O_2CR)_2 + Na_2SO_4$$
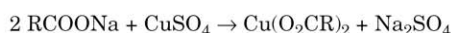
3. reaction of copper (II) acetate with the carboxylic acid in ethanol–water solution.

$$Cu(O_2CCH_3)_2 + 2\ RCO_2H \rightarrow Cu(O_2CR)_2 + 2\ HO_2CCH_3$$

These methods are particularly appropriate for the first-year course because they exemplify Lowry–Brönsted (1 and 3), Lewis (3), and ion combination (2) reactions. Each method has its advantages. The copper carbonate route is probably the most general and has been used to prepare all of the compounds described below. However, the use of water–insoluble acids requires that excess acid be re-

moved by washing the product with ethanol. The copper acetate method works best when the carboxylic acid is insoluble in water (but soluble in ethanol); whereas, the copper sulfate synthesis is most appropriate when the acid is soluble in water and the copper carboxylate is relatively insoluble in water. The yields vary considerably, depending on the compound and method employed, but in general are between 30 and 80%.

The percent of water of hydration can be obtained by heating the compound in an oven at 110–120 °C for at least 2 h. The percent of copper can be obtained either gravimetrically by thermal decomposition of the carboxylate to CuO or by colorimetry using a Spectronic 20 or a simple homemade LED photometer (1). The colorimetry can be done several ways:

- the sample can be dissolved in acid and the percent copper determined from a calibration curve prepared using copper acetate and HCl,
- or the sample can be dissolved in ammonia to give the ammonia complex (the actual composition of the ammonia solution will depend upon the concentration of ammonia) using a standard curve based on copper acetate dissolved in ammonia.

The acid method was found to give good results with solutions ranging in concentration from 0.01 to 0.15 M; whereas, the ammonia method requires more dilute solutions (0.005–0.04 M) because of the greater intensity of the color of the ammonia complex. Development of color using the disodium salt of EDTA was less successful than either of these methods. Of the two colorimetry methods, the ammonia method is somewhat easier to execute and also gives results closer to the theoretical values in six out of nine cases (the palmitate and laurate were not soluble in the ammonia solution and must be dissolved in acid). The most accurate method for the determination of copper in these compounds is the gravimetric CuO method.

The preparation of the carboxylates can be pursued as an undergraduate project in a variety of ways.

First, each student can be given a different carboxylic acid and directed to try three different ways to make the carboxylate salt and determine which is best by measurement of yield, ease of preparation, ease of purification, and purity of product.

Second, each student can be given a different carboxylic acid and directed to determine the composition of the carboxylate salt.

Third, each student can be given a different carboxylic acid, directed to make the carboxylate through a specific procedure, and then determine which method of analysis for copper is best.

Fourth, each student can be given an unknown carboxylic acid, directed to make the carboxylate through a particular route, analyze for percent water and percent copper and then determine the identity of the unknown.

Finally, several of these approaches can be combined and the student can be directed to determine the best method of synthesis, an appropriate method of purification, and the best method of analysis. In each case except the use of the carboxylic acid as an unknown, the student can be expected to rationalize differences in procedure for different carboxylate acids.

The structures of the carboxylates are also of interest although perhaps too complicated for the introductory course. In most of the solid carboxylates, the carboxyl group (RCO$_2$) bridges two copper atoms with each oxygen linked to a copper atom. Cupric acetate monohydrate, for example, contains dimeric Cu$_2$(CH$_3$CO$_2$)$_4$·2H$_2$O units in which the two side-by-side copper atoms are bridged by the four acetates. In this structure each copper is also linked to a water molecule giving each copper a coordination number of six (2).

Experimental

Synthesis

Copper Carbonate Method

A sample of 2.76 g (0.0125 mol) of basic copper carbonate was placed in a 500-mL Erlenmeyer flask with 50 mL of water. A 0.05 mol sample of the appropriate carboxylic acid was dissolved in a minimum amount of water, or, if the acid was insoluble in water, it was slurried with about 50 mL of water. The acid solution (or slurry) was added slowly to the copper carbonate and stirred magnetically. After the addition was complete, the mixture was heated gently to about 60 °C; the flask was then covered with a watch glass and the mixture was heated overnight. The mixture was cooled and filtered by suction. If the product was insoluble in ethanol, the residue was washed thoroughly with 95% ethanol in several portions. After air drying, the compound was stored in a screw cap bottle. A sample of the product was tested for the presence of carbonate by the addition of 6M HCl. The absence of a visual reaction (fizzing) was taken as the absence of carbonate.

Copper Sulfate Method

When the salt was not commercially available, it was prepared by dissolving 0.05 mol of the acid in a minimum amount of water in a 250-mL Erlenmeyer flask. Sodium hydroxide (2 M) was added with stirring to make the solution just basic to litmus paper. The correct stoichiometric amount of copper sulfate pentahydrate was dissolved in a minimum amount of water in a separate 250-mL Erlenmeyer flask. The two solutions were then mixed in a beaker. If a precipitate did not form immediately, the mixture was covered and allowed to stand for 24 h. The precipitate was isolated by vacuum filtration, allowed to air dry overnight in a crystallizing dish, and stored in a screw cap bottle.

Copper Acetate Method

A sample of 5.0 g (0.025 mol) of copper acetate was dissolved in 50 mL of water in a 250-mL Erlenmeyer flask. In another flask a stoichiometric amount of the acid was dissolved in a minimum amount of ethanol. The two solutions were mixed in a 400-mL beaker. In some cases a precipitate formed only after sitting overnight. The precipitate was isolated by suction filtration, air dried, and then stored in a screw cap bottle.

Analysis

Water of Hydration

A porcelain crucible was heated to redness in a Bunsen flame, allowed to cool in a dessicator and weighed. Approximately 0.5 g of the compound, weighed to four significant figures, was added to the crucible. The crucible was placed in a crystallizing dish in a 110 °C oven for 1 h and, after cooling in the dessicator, was reweighed. The crucible was then returned to the oven for another hour, reweighed, and this process continued until constant weight was achieved.

Percent Cu by CuO

A porcelain crucible was heated to redness in a Bunsen flame, allowed to cool in a dessicator and weighed. Approximately 0.5 g of the compound, weighed to four significant figures, was then added to the crucible. The crucible was placed on a clay triangle, partly covered with the lid, and heated gently with a Bunsen burner. After about 20 min of gentle heating, the heat was increased and, finally, the crucible was heated to redness for 2 h. The crucible was

cooled in a dessicator and then weighed to determine the amount of CuO present.

Percent Cu by Colorimetry

A calibration curve was established by making 500 mL of a standard solution of 20.106 g copper acetate and 133 mL 3.0 M HCl. This solution (0.2 M in Cu^{2+} and 0.8 M HCl) was used to prepare 10 dilutions ranging in Cu^{2+} concentration from 0.01 to 0.15 M. The absorbance of each solution was determined with a Spectronic 20 at 675 nm and a Beers law plot was obtained by least squares.

The solution of the copper carboxylate in the 0.01 to 0.15 M range was prepared by dissolving an appropriate amount of the carboxylate (weighed on an analytical balance) in 3 M HCl solution. The amount of this solution was selected to provide four times the molar amount of HCl. The mixture was stirred and heated as necessary and, in those cases where the resulting carboxylic acid was insoluble, the solution was filtered and made to volume with distilled water. The concentration of Cu^{2+} was determined from the absorbance of the solution and the least squares equation derived from the calibration curve.

If the ammonia complex method is used a calibration curve must be established by making a 0.05 M solution of copper acetate (4.99 g) and 1 M ammonia (33 mL of concentrated ammonia) in a 500-mL volumetric flask. Solutions ranging in molarity from 0.005 to 0.04 were prepared from this stock solution using standard volumetric procedures. A Beers law plot was obtained at a wavelength of 600 nm. The solution of the copper carboxylate was prepared in the 0.005 to 0.04 M range by weighing out the appropriate amount of carboxylate on an analytical balance and then dissolving it in the correct amount of 1 M ammonia. The least squares Beers law plot was then used to convert absorbance to concentration and percent copper.

Results and Discussion

The table gives the data obtained for 11 carboxylates. In most cases, the experimental data for percent water and percent copper are in good agreement with the theoretical values. For most compounds the determinations were performed at least twice by two different students. The standard deviation for the CuO determinations is about 2.0%, while for the determination of water of hydration it is about 0.6%. The table contains the results of the analytical determinations, as well as the methods of synthesis attempted. The table shows that in general the percent copper by the CuO method was more accurate than that determined by colorimetry. The colorimetry is also more problematic in those cases where the insolubility of the parent acid requires filtration of the solution. On the other hand, the CuO method is also not without problems: burning is particularly a problem with the carboxylates of the long chain acids (lauric and palmitic) and must be minimized by careful heating and judicious use of the crucible lid.

All of the compounds except the citrate have a stoichiometry based upon the number of carboxyl groups in the molecule. In the case of the citrate the central hydroxyl group is sufficiently acidic to lose a hydrogen (thereby producing a trivalent anion), which makes the citrate a particularly interesting unknown. Our attempts to uncover other carboxylates with an acidic hydroxyl group were unsuccessful; for example, salicylic acid does not (apparently) lose a hydrogen from the phenolic OH (it does, however, form several hydrates and, in our experience, is not an easy compound to prepare reproducibly).

In all cases, the analytical results are sufficiently accurate to allow the student to determine the ratio of number of moles of cupric ion to moles of anion even if the wrong formula for the anion is assumed. For example, if the student assumes that the anion in copper malonate is the hydrogen malonate ion ($HC_3H_2O_4^-$), the analytical data will reveal that there is a 1 to 1 ratio between the cupric ion and the anion (the student, of course, must realize that these ratios are going to be small whole number ratios (1:1, 1:2, etc., not 27:35, and so on). Charge balance then mandates that the anion in this case has a −2 charge and is really the malonate ion ($C_3H_2O_4^{2-}$). The waters of hydration cannot be as accurately determined. This limitation is a result of errors in the other analytical data and the extent to which the sample has been carefully air-dried. A discussion of the sources of these errors and their relationship to real world (rather than lab book) analyses can be of great value to the student.

Experimental Results for Analysis of Copper Carboxylates

Cupric Salt	Formula	Syn[a]	Th % H2O	Ex % H2O	Th % Cu	Ex[b] % Cu_gr	Ex[b] Cu_c	Ex[b] Cu_n
formate	$Cu(CHO_2)_2 4H_2O$	A,B	31.9	29.6	28.2	31.6	33.7	33.8
acetate	$Cu(C_2H_3O_2)_2 H_2O$	A,B	9.02	10.3	31.8	28.0	33.2	31.8
laurate	$Cu(C_{12}H_{23}O_2)_2$	A,B,C	0	4.97	13.7	13.0	18.6	–
palmitate	$Cu(C_{16}H_{31}O_2)_2$	A,C	0	0.24	11.1	10.9	13.2	–
benzoate	$Cu(C_7H_5O_2)_2 2H_2O$	A,B,C	10.5	8.45	18.6	19.8	14.2	
malonate	$CuC_3H_2O_4 2H_2O$	A,B,C	17.9	20.2	31.8	29.4	25.2	29.6
glutarate	$CuC_5H_6O_4 2H_2O$	A,B	15.7	14.2	27.9	27.2	26.3	31.9
lactate	$Cu(C_3H_5O_3)_2 2H_2O$	A,B,C	13.0	14.1	22.9	22.8	25.2	24.4
tartrate	$CuC_4H_4O_6 3H_2O$	A,B	20.3	21.6	23.9	24.8	24.7	23.1
glycolate	$Cu(C_2H_3O_3)_2$	A,B	0	0.09	29.7	29.2	32.7	30.0
citrate	$2CuC_6H_4O_7 5H_2O$	A,B,C	12.5	6.5	35.3	30.8	35.1	29.1

[a] A= copper carbonate method, B= copper sulfate method, C=copper acetate method.
[b] gr=CuO gravimetric method, c=colorimetry using copper acetate standard, n=colorimetry using ammonia complex.

Acknowledgment

Literature Cited

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