

Synthesis and Composition of Tutton Double Salts: An Introductory Laboratory Project

Corissa P. McDonald, Claude H. Yoder*

Department of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania, United States of America

Abstract The synthesis and characterization of Tutton double salts is described as an ideal introduction to the synthesis and gravimetric analysis of soluble ionic compounds. The Tutton salts, with a formula of $K_2M(SO_4)_2 \cdot 6H_2O$, where M is Mg, Zn, Cu, Ni, Co, and Fe, are prepared by mixing the simple salt “constituents” and then allowing for slow evaporation of the mother liquor. After a period of one day to one week, large (0.3-0.6 cm) monoclinic plates form and can be removed either by gravity filtration or by removal with tweezers. The stoichiometry of the compound is determined by gravimetric analysis of sulfate, the divalent cation, and water. The Tutton salts are of interest because of the variation in their color depending on the divalent cation, their crystal form and size, and the formation of a hydrate with water octahedrally coordinated to the divalent cation. The compounds lend themselves to discussions of the origin of colors in the transition metals, and coordination of water to the divalent cations. The Tutton salts also have enjoyed a variety of recent applications, such as their possible utility in heat exchange and UV filters, that may merit discussion as the instructor sees fit. The simplicity of the synthesis and the ease of isolation and characterization of the product make this an excellent introduction to the synthetic process and is suitable for both secondary and college courses. The synthesis and characterization of two Tutton salts containing different divalent cations can easily be performed by groups of two students in four two-hour lab periods. The techniques that each group is exposed to include precipitation, filtration, weighing, use of the Bunsen Burner for dehydration of the salt, and conversion of a hydroxide to the oxide by ignition in a crucible.

Keywords Secondary chemistry laboratory, Introductory General chemistry, Individual or group experimental lab project, Double salts, Synthesis and characterization of double salts, Gravimetric analyses, Determination of water of hydration by heating

1. Introduction

Many inorganic materials can be categorized as double salts; that is, as an ionic compound that contains two or more different types of cations or two or more different types of anions. The common ore of copper, malachite, contains one type of cation and two different anions--hydroxide and carbonate ($Cu_2CO_3(OH)_2$). Alums, with the general formula $MAI(SO_4)_2 \cdot 12 H_2O$ contain two different cations--generally an alkali metal cation (M) and an aluminum ion-- and only the sulfate anion. Many of the minerals in the earth's crust are double salts.

In the early 1900s, the British crystallographer Alfred Edward Howard Tutton [1] studied a series of double salts that contains two different cations, generally an alkali metal cation (A^+), a doubly charged cation (M^{2+}), and the sulfate or selenate anion [2]. The monovalent cations (A^+) are generally the relatively large alkali metal cations (potassium,

rubidium, cesium) and the ammonium ion, while the divalent cations are usually the first-row transition metal +2 ions or Mg^{2+} . Although the lighter alkali metal cations are present in double salts such as krohnkite ($Na_2Cu(SO_4)_2 \cdot 2H_2O$) and bloedite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$) they appear not to form salts with the Tutton salt stoichiometry [3]. The general empirical formula for the Tutton salts, $A_2M(SO_4)_2 \cdot 6H_2O$, where A is the monovalent cation and M is the divalent cation, can also be written as $A_2M(H_2O)_6(SO_4)_2$, which emphasizes the association of the water molecules with the divalent cation.

Several of the Tutton salts occur at geological features such as fumaroles, geysers, evaporite deposits, and ore tailings [4]. Their presence on Europa has been proposed [5] and picromerite, $K_2Mg(H_2O)_6(SO_4)_2$, has been considered as a model of the primordial hydrosphere on Mars [6]. The mineral cyanochroite, $K_2Cu(H_2O)_6(SO_4)_2$, has been the subject of several recent studies of the Jahn-Teller effect [7,8]. The easy synthesis, stability, and reversible endothermic removal of water of hydration of Tutton salts also makes them candidates for waste heat removal and recovery [9,10].

One of the most interesting structural features of these salts, prepared in aqueous solution, is the coordination of water molecules to the divalent cation. The structure of

* Corresponding author:
cyoder@fandm.edu (Claude H. Yoder)

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cyanochroite (Figure 1), shows a monoclinic crystal with four potassium ions and four sulfate ions in the unit cell, which can be written as $\text{K}_4\text{Cu}_2(\text{H}_2\text{O})_{12}(\text{SO}_4)_4$; that is, as twice the empirical formula. (Because the copper ions are shared with a number of other unit cells, the partial occupancy of the copper ion must be considered when determining the number in the unit cell). The number of water molecules coordinated with each copper ion is not obvious from Figure 1. This is more clearly indicated by Figure 2, where the octahedral arrangement of the six water molecules about each copper ion is shown as an octahedron.

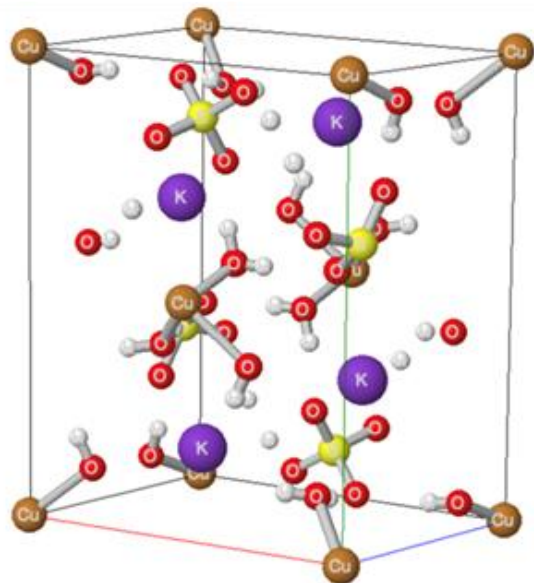


Figure 1. The structure of cyanochroite, $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$. Taken from mindat [11] using data from Bosi [4]. The purple spheres represent K^+ , copper-colored spheres represent Cu^{2+} , yellow and red represent sulfur and oxygen, respectively

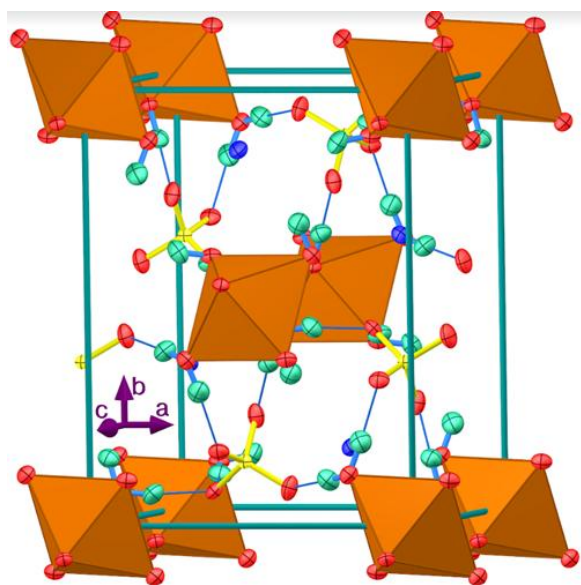


Figure 2. The structure of cyanochroite, $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$, using copper-colored octahedra to portray the coordination of six water molecules around each copper ion [7]

Although it may not be obvious from the figures above, the distances between the copper ions are large, at least partially because of the interposition of the coordinated water molecules. As a result of these large distances, this salt has been studied as an example of weakly-interacting copper ions and the Jahn-Teller distortion in the aqueous coordination sphere [7,8].

2. The Project

We have found that the synthesis and analysis of Tutton salts make an excellent multi-period laboratory project suitable for both secondary and college chemistry courses. When the divalent cation is a transition metal cation, the salts, except for those of Zn^{2+} , are colored. These salts provide a way to describe and discuss a number of interesting concepts and techniques. For example, the colors of the salts can be discussed at a variety of levels, from the simple observation that many transition metal compounds are colored to a rationalization of color using electron configuration and energy levels.

The coordination of water molecules to the divalent cation is particularly interesting and invites a discussion of electron-sharing (Lewis acid-base) reactions and the models used to describe those interactions. Of course, the level at which this coordination is discussed will depend on the course and the instructor but could certainly involve the valence bond model with hybridization of orbitals, or, in some courses, the use of the crystal field model might be desirable, particularly as an alternative model.

After the compound is synthesized, the composition; that is, the identity of the ions and their stoichiometry in the solid, crystalline compound must be established before the bonding within the compound and its physical properties can be adequately described. Techniques such as X-ray diffraction (XRD) and infrared spectroscopy (IR) are frequently used to determine the identity of groups within the structure and to establish that the compound obtained in the synthesis is not a mixture of starting materials and has been previously described in the chemical literature.

The XRD line pattern of the potassium/copper (cyanochroite) Tutton salt and XRD patterns of the simple salts used to prepare the Tutton salt are shown in Figure 3. Although cyanochroite, $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$, could be imagined as a double salt consisting of K_2SO_4 and CuSO_4 (and 6 H_2O), the XRD pattern of the Tutton salt is different from that of these simple salt “constituents.” The internal structure of the double salt therefore is not simply a mixture of simple salts.

The composition and empirical formula can also be obtained using wet chemical methods of analysis, such as gravimetric analysis, and the acquisition of physical characteristics like flame color and behavior on heating. In the present case, cyanochroite is characterized by gravimetric analysis of copper and sulfate, the color of the flame presented by potassium, and quantitative evolution of water on heating.

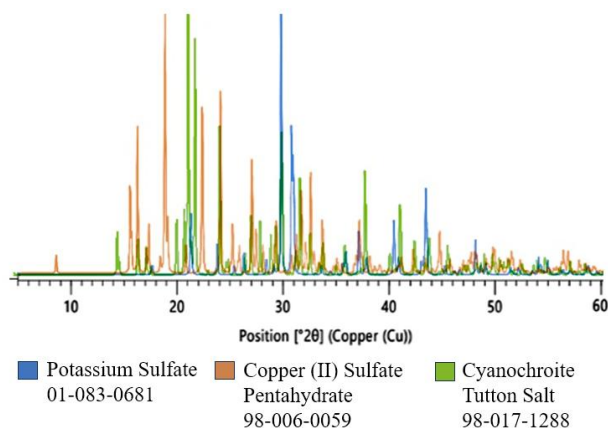


Figure 3. XRD patterns of cyanochroite, $K_2Cu(H_2O)_6(SO_4)_2$ (green), and the simple salts K_2SO_4 (blue) and $CuSO_4 \cdot 5H_2O$ (orange). The differences in the literature line patterns of the simple salts compared to the Tutton salt shows that the Tutton double salt is not merely a mixture of the simple salts used to prepare it

2.1. Synthesis

The Tutton double salts are prepared by simply mixing saturated solutions of the simple salts and allowing slow evaporation of the water in the mixture to produce large (ca. 0.2–0.5 cm) monoclinic crystals. The crystals of $K_2Cu(H_2O)_6(SO_4)_2$ and $K_2Co(H_2O)_6(SO_4)_2$ are shown in Figure 4. The dry crystals are stable and can be easily dissolved for analysis. Purification of the prepared salts is difficult, however, due to the high solubility of the double salts. The immediate removal of the crystals upon formation from the simple salt mixture serves as the most consistent regulation of purity. In our experience, purification is not necessary for the accuracy of the compositional analyses.

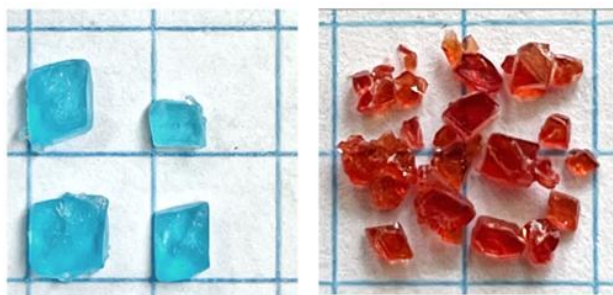


Figure 4. Crystals of $K_2Cu(H_2O)_6(SO_4)_2$ (left) and $K_2Co(H_2O)_6(SO_4)_2$ (right) obtained by slow evaporation of mixtures of the simple salts. Background grid line separations are 1 cm

Many Tutton salts are described in the literature [4,5,8] and we have prepared a total of six salts that have the general formula $K_2M(H_2O)_6(SO_4)_2$. Each of these salts contains one of the following divalent cations: copper, cobalt, magnesium, zinc, nickel, or iron. We have also synthesized double salts containing other monovalent cations such as rubidium, cesium, and ammonium with copper and cobalt as the divalent cation. Synthesis of Tutton salts containing ammonium is straightforward, but because of the additional complication of the

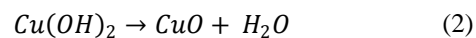
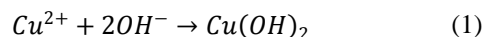
decomposition of the ammonium ion on heating, we have included only the potassium salts in this experiment.

2.2. Composition

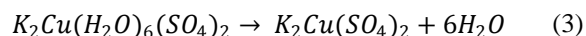
The composition of the salts can be determined using quantitative analyses followed by a classroom discussion of the difference between an empirical formula and a structural formula. For example, the analyses should allow a student to determine that the empirical formula of cyanochroite is approximately $K_2Cu(H_2O)_6(SO_4)_2$, but these techniques cannot establish the coordination of the six water molecules to the copper cation.

The characterization procedures for these compounds are illustrated below for cyanochroite:

(1) Determination of the percentage of the divalent cation by precipitation of the divalent hydroxide followed by conversion of the hydroxide to the oxide by heating (2):



(3) Determination of the percentage of water by heating in a Bunsen flame



(4) Determination of the percentage of sulfate by precipitation of $SrSO_4$,



as well as qualitative determination of the presence or absence of the potassium ion using the flame test.

2.3. Laboratory Time Requirements

At least three laboratory periods are required for this project. The Tutton salt is synthesized in the first laboratory period. The time required for the synthesis is controlled by the amount of time required to make a saturated solution of the individual simple salts. Table 1 provides a guide to the solubility of the simple salts and with gentle warming the time required can be as low as 30–45 minutes to prepare and mix the simple salts. The formation of the double salt requires several hours to one week of slow evaporation, depending on the nature of the cation. Isolation of the double salt with drying on filter paper requires no more than 30 minutes. Depending on the nature of the laboratory course, students may prepare double salts in one laboratory period and isolate the crystals from the mother liquor a week later.

The total time required for characterization, including both gravimetric determinations of sulfate and the divalent cation, is approximately four hours. Because the strontium sulfate precipitate requires a week to dry and the copper oxide must be cooled to room temperature, a third laboratory period may be utilized to perform tests such as determination of water (one hour), the flame test for potassium and divalent cation (15 minutes), the ammonia complex test for copper (II) (15 minutes), and calculation of the empirical formula.

3. Methods and Materials

3.1. Syntheses

All simple salt solutions were prepared using Milli-Q deionized water and ACS Reagent grade reagents with purities above 97%. The simple salts were mixed in a 1 to 1 mole ratio, which in our experience minimizes contamination of the product. The amounts of these reactants were determined from their solubilities in water at 20°C (Table 1).

Table 1. Synthesis reagents. Formula weights, solubilities at 20°C in grams per 100 mL, and LD50s for rats in mg per kg are included. Toxicity data obtained from Fischer Scientific Data Sheets

A ⁺ or M ²⁺	Simple Salt	Formula Weight (g)	Solubility in H ₂ O at 20°C (g/100 mL)	Toxicity (mg/kg; oral rat)
A ₂ SO ₄	K ₂ SO ₄	174.26	12.0	6600
MSO ₄	CuSO ₄ · 5H ₂ O	249.68	20.8	300
	CoSO ₄ · 7H ₂ O	173.01	37.4	582
	MgSO ₄ · 6H ₂ O	228.46	71	2217
	ZnSO ₄ · 7H ₂ O	287.54	53.8	1710
	NiSO ₄ · 6H ₂ O	262.84	62.5	264
	FeSO ₄ · 7H ₂ O	278.01	25.6	319

The data in Table 1 was used to prepare saturated solutions of two sulfate simple salts, K₂SO₄ and MSO₄, in 25-50 mL beakers using a 10 mL graduated cylinder to add the required amount of distilled water. Each mixture was then stirred magnetically until the solution was clear. In some cases, an additional 1-2 mL of water was required to dissolve all solids.

The two clear solutions of the simple salts were then combined in a 50 mL beaker, gently heated (ca. 50-60°C), and stirred for about 10 minutes with a stirring rod. Gentle heating was useful in optimizing crystal growth with no effect on crystallization time. The solution was cooled to room temperature before transferring to a crystallizing dish or 250 mL beaker and allowed to sit undisturbed until crystals of the double salt formed. The amount of time required for crystallization depended on the double salt and varied from 1 to 4 days. To slow crystallization, the recrystallizing dish was covered almost entirely with a watch glass. For most preparations, a thin aqueous layer of the Tutton salt mixture remained in the recrystallizing dish as shown in Figure 5. Any crystals that formed were immediately filtered and washed with the thin aqueous layer and left to dry on a filter paper. The aqueous layer was transferred back to the recrystallizing dish for further crystallization. In some cases, the formation of large (2-6 mm) crystals was preceded by the formation of smaller, impure crystals that were removed.

The size and shape of the crystals obtained depends on how close to saturation the simple salt solutions are for the double salt being prepared. For cyanochroite, about 10 roughly four centimeter-size blue plates, that appear to be almost square, but are actually slightly oblique rhombohedra, were obtained (Figure 4). These crystals were removed from the thin aqueous layer with tweezers and placed on a piece of

11 cm filter paper to dry. After a day, the crystals were ground in a mortar and the powder stored in a properly labeled vial.



Figure 5. Crystals of two potassium double salts two days after synthesis. For each salt, a thin aqueous layer of solution remains. The colorless zinc salt and blue copper salt are shown from left to right

4. Characterization

4.1. Color

Crystals were ground into a powder before analysis. The colors of the potassium salts are shown in Table 2.

Table 2. Observed colors of representative Tutton Salt crystals

Tutton Salt	Color
K ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	blue
K ₂ Co(H ₂ O) ₆ (SO ₄) ₂	red
K ₂ Mg(H ₂ O) ₆ (SO ₄) ₂	white
K ₂ Zn(H ₂ O) ₆ (SO ₄) ₂	white
K ₂ Ni(H ₂ O) ₆ (SO ₄) ₂	teal
K ₂ Fe(H ₂ O) ₆ (SO ₄) ₂	yellow-green

4.2. X-Ray Diffraction

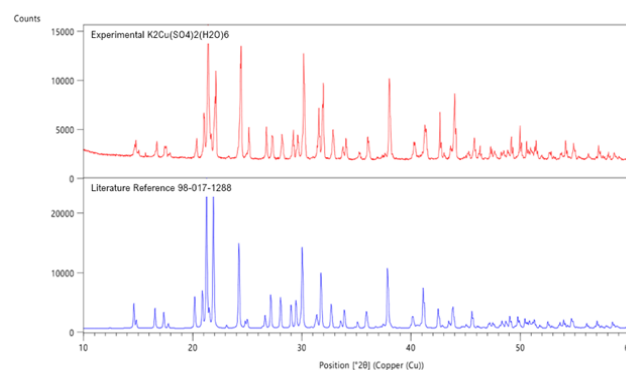


Figure 6. XRD pattern for the prepared, K₂Cu(H₂O)₆(SO₄)₂ (top) and comparative literature [15] pattern (bottom)

Double salts were characterized by X-ray diffraction using a PANalytical X'pert PRO Multipurpose diffractometer Theta-Theta System with CuKα radiation ($\lambda = 1.54060 \text{ \AA}$). The results were analyzed using the PANalytical program X'Pert Highscore Plus. The diffraction pattern of cyanochroite is shown in Figure 6, along with the best literature match. Simple sulfate salt diffraction patterns were shown previously in Figure 3.

4.3. Qualitative Identification of Ions Present in the Tutton Salt

The ions present in the Tutton salt can be identified using a few simple procedures. The presence of potassium and copper can be identified with a flame test, while the presence of sulfate can be determined by precipitating SrSO_4 using a 0.1 M $\text{Sr}(\text{NO}_3)_2$ solution from an aqueous solution of the Tutton salt. The presence of water in the dry salt can be ascertained by heating the salt in a test tube over a Bunsen flame. In each test, the results of a control test should be compared to the target analysis. This is particularly important in the flame test where impurities such as the ubiquitous sodium ion produce an orange flame, which obscures the flame of the target ion or produces a misleading color.

4.4. Quantitative Analysis of Water of Hydration

A small sample (0.1-0.25g) of finely powdered crystal was weighed into a 100 mm test tube and the test tube (and contents) were reweighed. The test-tube, held in a test-tube holder, was heated in a relatively hot (inner blue cone present) Bunsen flame to drive off the water present in the crystal. To remove all the condensate, the test tube was held at about a 45° angle and moved slowly through the flame for 10-15 seconds. During this time, the test tube was moved up and down to heat all parts of the tube. This heating process was repeated several times to ensure that the water was removed from both the powder and the tube. After the test tube cooled slightly, it was capped with a cork and cooled to room temperature and reweighed without the cork.

The percentage of liberated water was then compared to the theoretical percentage of water derived from the empirical formula for each salt. Duplicate measurements on cyanochroite gave an average of 1 percent error relative to the theoretical. The average percentage error for all the Tutton salts as reported in Table 3 is 5.3.

Table 3. Quantitative determination of the waters of hydration for six Tutton Salts. Three representative trials

	$\text{K}_2\text{M}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ where M = (Cu, Co, Mg, Zn, Ni, Fe)					
	Cu	Co	Mg	Zn	Ni	Fe
Theoretical (%)	24.5	24.7	24.9	23.7	24.7	24.9
Trial 1 (%)	24.1	26.3	24.9	25.8	19.4	18.5
Trial 2 (%)	24.2	24.7	19.8	23.4	30.6	20.6
Trial 3 (%)	24.5	22.4	21.9	23.9	24.1	23.3
Average (%)	24.3	24.5	22.2	24.4	24.7	20.8
Average Deviation from Mean (%)	±0.2	±2.0	±2.6	±1.3	±5.6	±2.4

4.5. Qualitative Analysis of Sulfate

The standard gravimetric procedure for the analysis of sulfate involves the precipitation of the low solubility BaSO_4 . Because SrSO_4 is only slightly less insoluble ($K_{\text{sp}} = 10^{-7}$ compared to 10^{-10} for BaSO_4), and $\text{Sr}(\text{NO}_3)_2$ is less toxic

(LD50 1892 mg/kg oral rat) than $\text{Ba}(\text{NO}_3)_2$ (LD50 355 mg/kg oral rat) the precipitation of $\text{Sr}(\text{NO}_3)_2$ was used.

A sample (0.450-0.650 g) of finely powdered double salt was added to 50 mL of distilled water in a 100 mL beaker. A hundredth mole sample of $\text{Sr}(\text{NO}_3)_2$ was dissolved in 100 mL of distilled water to prepare a 0.1 M solution. Using a 50 mL burette, approximately 25 mL of the strontium nitrate solution was added dropwise at a rate of 2 drops/s to the double salt solution while heating to about 60°C and stirring magnetically. The mixture was allowed to sit with occasional stirring with a glass stir rod for about 30 minutes before being covered with a watch glass and left undisturbed for 15 minutes or for up to one week. The mixture was then vacuum filtered through a Buchner funnel containing a previously weighed 5 cm quantitative filter paper. After drying the precipitate (on the filter paper) in a 100°C oven, the precipitate (and paper) was weighed again to obtain the mass of precipitated SrSO_4 (Table 4). The filtration can also be done by gravity. It is imperative to preserve the filtrate for further characterization analyses.

4.6. Quantitative Analysis of Copper

The percentage of the divalent cation can be determined by a variety of techniques, such as conversion to the oxide and colorimetry, but a simpler method makes use of the insolubility of the hydroxide. Because of the high solubility of the double salt, a hydroxide solution can be added directly to a weighed amount of the double salt until the hydroxide is completely precipitated as indicated by a change in pH from that of the slightly acidic (ca pH = 5) double salt solution to the basic solution produced after total precipitation of metal hydroxide. In the case of some cations, the product may also be a double salt containing the anion present during the precipitation. This is the case with copper (II) sulfate double salts, for which the addition of hydroxide, under some conditions, produces brochantite, $\text{Cu}_4\text{SO}_4(\text{OH})_6$ [12,13]. To alleviate this problem, 0.10 M NaOH hydroxide is added after the removal of the sulfate ion by precipitation of SrSO_4 .

Following the removal of sulfate, the filtrate (see above) is stirred magnetically in a 250 mL beaker. 25-30 mL of 0.1 M hydroxide solution is added to the filtrate with a burette using a drop rate of about 2 drop/s. After 15 minutes, the mixture is vacuum filtered through a Buchner funnel using a previously weighed 5 cm quantitative ashless filter paper. The precipitate and filter paper are then placed in a porcelain crucible and heated strongly over a Bunsen flame to convert the precipitated hydroxide to the more stable oxide, which is then weighed. Ashless filter paper is strongly recommended for the most accurate quantitative determinations.

The copper and sulfate results are compared with the theoretical percentages based on the empirical formula for cyanochroite in Table 4. Uncertainties reported are the average deviations from the mean of duplicates, given as a percent of the mean. Separate portions of the same sample must be used for all three quantitative tests.

Table 4. Quantitative determination of the percent sulfate and copper for cyanochroite

Sulfate		Copper	
Mass Tutton (g)	Experimental Percent Sulfate (%)	Mass Tutton (g)	Experimental Percent Copper (%)
0.496	39.3	0.614	13.4
0.496	40.3	0.504	15.0
0.504	41.3	0.499	13.4
0.498	39.8	0.498	14.9
0.504	39.2	0.504	14.3
Average Experimental Percent (%)	40.0	Average Experimental Percent (%)	14.2
Average Deviation from Mean (%)	±0.9	Average Deviation from Mean (%)	±0.8
Theoretical Percent (%)	43.5	Theoretical Percent (%)	14.4
Percent Error Relative to Theoretical (%)	8.0	Percent Error Relative to Theoretical (%)	1.6

4.7. Calculation of Formula

The composition of the cyanochroite Tutton salt can be determined from the three quantitative analyses (Cu, SO₄ and H₂O) by assuming that the remainder of the double salt is potassium. The number of moles of K⁺, Cu²⁺, SO₄²⁻ and H₂O in 100 g of cyanochroite as determined from the experimental and theoretical percentages is shown in Table 5.

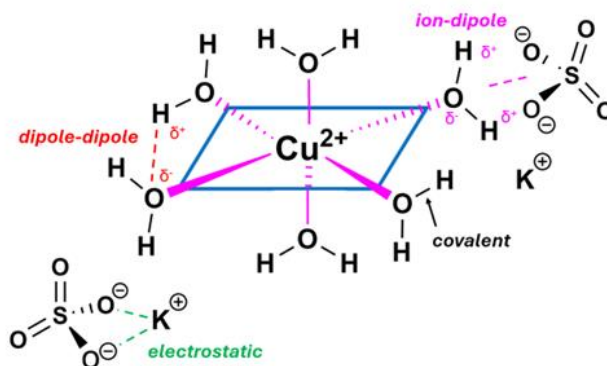
Table 5. Determination of the empirical formula of cyanochroite from the experimental analyses for copper, sulfate, and water. Percentages determined for potassium are calculated by differences of copper, sulfate, and water

	Cu ²⁺	SO ₄ ²⁻	H ₂ O	K ⁺
Theoretical Percent (%)	14.4	43.5	24.5	17.7
Average Experimental Percent (%)	14.2	40.0	24.3	21.3
Moles in 100 g Tutton Salt (mol)	0.223	0.416	1.35	0.545
Ratio of Moles Relative to the Smallest Number of Moles	1.00	1.87	6.05	2.44

5. Discussion

The objective of the project is to synthesize and determine the composition of the synthesized Tutton salt. This composition is expressed by the empirical formula of the compound, which provides the molar relationship between the elements and groups that constitute the compound. The Tutton salts are especially interesting because of the location of the water molecules in the compound. That location is not expressed by the empirical formula, but rather by the structural formula, which indicates the connections between the elements or groups. Such information must be derived from other techniques such as infrared or nuclear magnetic resonance spectroscopy.

The relationship between the empirical formula and the structural formula can be extracted by the question—where are the water molecules in the solid compound? This question should evoke discussions of the interactions in an ionic compound: electrostatic forces expressed by the Coulomb relationship. In a hydrate, however, there are additional interactions brought about by the dipoles and hydrogen bonding of the water molecules, as well as the very real possibility of covalent interactions between the water molecules and the ions. Thus, in an ionic hydrate such as the Tutton salts, the student should envision the forces that are present in the solid as ion-ion interactions, dipole-dipole interactions among the water molecules, dipole-ion interactions between the ions and water molecules, possible covalent interactions between the ions and water molecules, as well as the ubiquitous van der Waals forces. After this variety of forces is expressed, the question of how the water molecules might interact with the ions can be addressed (see Figure 7).

**Figure 7.** Typical electrostatic and covalent interactions in a Tutton Salt. Hydrogen-bonding between hydrogen and lone pairs of electrons on the oxygens of neighboring species, and Van der Waals (dispersion) forces are not shown

6. Supplementary Material: For the Instructor and Student

All samples should be prepared using distilled or deionized water and ACS Reagent grade reagents with purities above 97%. For the synthesis of the Tutton salt, students should have access to two 30-50 mL beakers, a crystallizing dish, a 60 mm wide polystyrene or glass funnel or Buchner funnel, 50- and 110-mm filter paper, 125-250 mL Erlenmeyer flask, 10 mL graduated cylinder, and a glass stirring rod. A hot plate will facilitate the dissolution of the simple sulfates. The materials needed for characterization tests are listed in subsequent sections.

6.1. Synthesis of a Tutton Salt

Instructors may find it helpful to have students use the solubility data given in Table 6 to determine the amounts of reagents to use to prepare saturated solutions. The data in the 'Mass reagents' and 'Volume' columns of Table 6 are the masses of the A₂SO₄ and MSO₄ reagents and the volume of

water that we recommend for the preparation of the saturated solutions. The column “mole reactant” shows that the 1:1 mole ratio between the monovalent and divalent sulfate reactants must be maintained.

Table 6. Representative synthesis reactant amounts determined from their solubilities in water (Table 1) based on a hundredth mole amount of potassium sulfate

	Volume of Water Added (mL)	
	K ₂ SO ₄	M ₅ O ₄
K ₂ Cu(H ₂ O) ₆ (SO ₄) ₂	14	12
K ₂ Co(H ₂ O) ₆ (SO ₄) ₂	15	7.3
K ₂ Mg(H ₂ O) ₆ (SO ₄) ₂	14	3.2
K ₂ Zn(H ₂ O) ₆ (SO ₄) ₂	15	5.3
K ₂ Ni(H ₂ O) ₆ (SO ₄) ₂	15	4.2
K ₂ Fe(H ₂ O) ₆ (SO ₄) ₂	15	11

It is difficult to overemphasize the importance of the careful preparation of the saturated reactant salts. The use of magnetic stirring and gentle heating is recommended. The addition of a small amount (1-2 mL) of water may be necessary in some cases to obtain a clear solution, but this should be done only if solid remains after stirring for 15 minutes.

The saturated solutions should be carefully mixed using a stirring rod over gentle heating (50-60°C). After 15 minutes, the beaker must be cooled to room temperature. Once the mixture is placed in the crystallizing dish, it should be left undisturbed and covered almost entirely with a watch glass or parafilm until crystals form. Any crystals that form immediately (< h) after combination of the two simple salt mixtures should be filtered or manually removed immediately.

Crystals are removed from the thin aqueous layer by filtration or by manual removal with tweezers. Large (3-6 mm) crystals are transferred to a piece of filter paper laid on a watch glass for 4-6 hours. Larger crystals should be turned over using a tweezers to ensure that both sides of the generally flat crystals are dry. The larger crystals in a given preparation are generally purer and the students should not be encouraged to scrape the bottom of the recrystallizing dish. Smaller crystals are filtered through a Buchner funnel and allowed to dry.

6.2. Characterization: Qualitative Tests

6.2.1. Flame Test and Sulfate Test

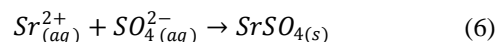
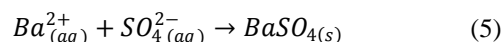
The air collar of a Bunsen burner should be opened to provide an inner blue cone of flame. A six-inch Nichrome wire can be used for the flame test but must either be inserted in a glass tube by melting the tube around the end of the wire or attached to a spatula by winding about 2 inches around the end of the spatula. It may be desirable to make a small loop at the end of the wire to allow the wire to retain powders more easily. The last one inch of the Nichrome wire must be cleaned by heating it at the tip of the inner blue cone of the Bunsen flame. This will require a minute or two of heating if badly contaminated. The cleaning process can be hastened

by dipping the wire into a few drops of 3 M HCl and then reheating.

A small sample (as a powder) of the Tutton salt should be placed in a beaker or spot plate. The Nichrome wire is then dipped into the Tutton salt powder and then placed into the top portion of the Bunsen flame. If potassium is present, a pale violet color will develop in the flame after a few seconds. If copper is present, a blue-green flame will develop. Other divalent ions in Tutton salts do not produce readily visible colors in the flame. A bit of sparkling does not indicate the presence of a particular ion.

It is always good practice to run a control test. For example, if copper is suspected, the flame test should be run on a sample of CuSO₄ or some other known copper salt. Because the flame may be contaminated by other ions, a control should also be run with distilled water, which should impart no color to the flame. Note: A drop of 3 M HCl will enhance the flame because of the greater volatility of the chlorides of the dipositive metal ions.

The same sample of the Tutton salt can also be used to determine if the sulfate ion is present. Sulfate will react with either Ba²⁺ or Sr²⁺ to form insoluble BaSO₄ (5) or SrSO₄ (6).

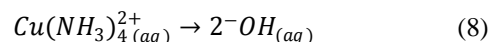
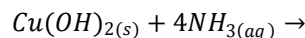
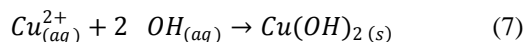


The addition of a drop or two of a 0.1 M BaCl₂ solution, or a 0.1 M Sr(NO₃)₂ solution, to a solution of the Tutton's salt should produce a white precipitate. Controls for this test could include both distilled water and a diluted solution of potassium sulfate.

6.2.2. Ammonia Complex Test

If the salt contains a divalent cation that forms an ammonia complex, the addition of 3 M ammonia (NH₃ gas dissolved in water) will initially form the solid hydroxide and then, upon addition of more ammonia, will dissolve the hydroxide and form an ammonia complex. This Lewis acid-base reaction occurs with Cu²⁺ even when the ammonia solution is fairly dilute (like 3 M NH₃), and with Co²⁺ when 6 M NH₃ is used. With both ions, the first stage of the reaction is the formation of hydroxide, followed by dissolution of hydroxide to form the complex ion. These Lewis complexes are soluble in water and strongly colored: (Cu(NH₃)₄)²⁺ is dark violet-blue and Co(NH₃)₆²⁺ is blue. The Co²⁺ ion oxidizes easily in air.

For the copper cation, the reactions are shown below (7,8)



Place a small spatula-full of powdered Tutton salt in a 100 mm test tube. Add about 0.5 mL of water and stir to dissolve the sample. Add 1 drop of 3 M NH₃ and carefully observe the reaction. Continue to add 3 M NH₃ drop wise with stirring until the solid that has formed in the test tube dissolves. If the divalent cation does not form a soluble ammonia complex

the solid will not dissolve, nor change color. Among the cations used in this project Cu^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+} form an ammonia complex. The Zn ammonia complex is colorless.

6.2.3. Waters of Hydration

Place a small spatula-full of Tutton salt in a 100 mm test tube and heat gently in a Bunsen flame. The gas jet should be regulated to produce a flame that extends about 3 to 4 inches. The air-inlet collar of the Bunsen burner should be opened enough to create an inner blue cone. Using a test tube holder to hold the test tube, move the tube into the edges of the flame to see if any water gathers at the crystals. Almost all hydrates will decompose with heating into the anhydrous salt and water.

6.3. Characterization: Quantitative Procedures

6.3.1. Quantitative Analysis of Sulfate:

Precipitation of SrSO_4

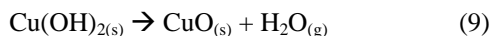
A 0.45-0.65 g sample of finely powdered double salt is used for both sulfate and copper quantitative analyses. This sample is dissolved in 50 mL of distilled water in a 100 mL beaker. The amount of the sulfate ion in the sample can be obtained by the precipitation of strontium sulfate as shown below.

Instructors may prepare a 0.100 M $\text{Sr}(\text{NO}_3)_2$ solution in advance or ask students to prepare a 50 mL solution themselves. Students should fill a 50 mL burette with approximately 30-35 mL of the tenth molar solution, which is added dropwise to the Tutton salt mixture. Following the transfer of the precipitate, it is necessary to preserve the filtrate for further analyses. If the filtrate is discarded, students cannot complete the gravimetric determination of copper.

6.3.2. Quantitative Analysis Divalent Cation

The amount of the divalent cation in the sample can be obtained by the slow addition of hydroxide to the filtrate obtained in the determination of sulfate (above). Instructors should prepare the 0.10 M NaOH solution in advance and convey the hazards involved in working with a strong base to the students. The amount of hydroxide added is determined by the 1:2 stoichiometric ratio between Cu^{2+} and OH^- in $\text{Cu}(\text{OH})_2$.

In the final step, the $\text{Cu}(\text{OH})_2$ precipitate is ignited in a crucible using a Bunsen flame to convert the copper hydroxide to the more stable copper oxide. The reaction is shown below.



6.3.3. Water of Hydration

A sample of 0.1-0.25 g of the finely powdered crystal was weighed (to three decimal places) into a 100 mm test tube. The test tube and contents must then be reweighed. A Bunsen burner flame should be adjusted so that it is no more than 4 inches high with an inner darker blue cone. The inner

cone is controlled by the amount of air admitted through the Bunsen collar.

Students should be trained in the use of an open flame with appropriate cautions about loose hair and other flammables. The test tube containing the crystal sample should then be placed at the outer edges of the flame to heat the sample gently. When moisture is seen inside the tube, the tube should be moved closer to the middle of the flame for several seconds and then the entire tube must be heated from bottom to top so that all of the water that condenses in the tube is driven off. The whole heating process should not take longer than about 2 minutes. The process of removing the condensate should then be repeated at least one more time. After the tube has cooled somewhat it should be capped with a cork to prevent moisture from entering.

After the test tube and contents have returned to room temperature the test tube (and contents) is reweighed (without the cork). To ensure all water has been removed, the test tube may be heated again, cooled to room temperature, and reweighed. Students may repeat this process until a constant weight is obtained; however, the procedure previously outlined (See Materials and Methods 4.4) requires only one heating for driving off all waters of hydration. Instructors may opt to use a crucible for larger amounts of sample, although the small test tube is optimal for safe heating of less than 150 mg. The mass of the anhydrous salt, the mass of the evolved water, and the percentage of water in the double salt can then be determined. This percentage should be compared to the theoretical percentage of water in the Tutton salt according to its formula. If a drop of water is added to the anhydrous product the product will return to its initial state.

6.3.4. Calculation of Formula

The composition of the salt can be determined from the three quantitative analyses (copper, water and sulfate-) by assuming that the remainder of the double salt is potassium. If the laboratory results give 40% SO_4 , 14% Cu and 25% H_2O , these can be converted into moles per hundred grams:

Copper	Sulfate	Water	Potassium
14 g / 63.5 g = 0.22 mol	40 g / 96.1 g = 0.42 mol	25 g / 18.0 g = 1.4 mol	21 g / 39.1 g = 0.54 mol

This can be used to obtain the ratio of moles of each species relative to copper (II).

Copper	Sulfate	Water	Potassium
0.22 mol Cu^{2+} / 0.22 mol = 1 Cu^{2+}	0.42 mol SO_4 / 0.22 mol = 1.9 SO_4^{2-}	1.4 mol H_2O / 0.22 mol = 6.4 H_2O	0.54 mol K^+ / 0.22 mol = 2.5 K^+

Rounding the ratio of moles within the uncertainty of the work:

Copper	Sulfate	Water	Potassium
1	2	6	2

Thus, the formula is $\text{K}_2\text{Cu}(\text{H}_2\text{O})_6(\text{SO}_4)_2$ which is consistent with the empirical formula of cyanochroite.

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DISCLOSURE

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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