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Hydrothermal Synthesis and Characterization of a Metal–Organic Framework by Thermogravimetric Analysis, Powder X-ray Diffraction, and Infrared Spectroscopy: An Integrative Inorganic Chemistry Experiment

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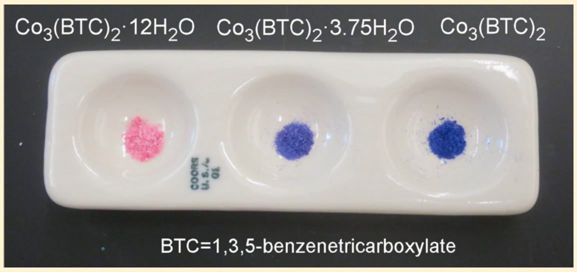
Supporting Information

ABSTRACT: This advanced undergraduate laboratory experiment involves the synthesis and characterization of a metal–organic framework with microporous channels that are held intact via hydrogen bonding of the coordinated water molecules. The hydrothermal synthesis of $Co_3(BTC)_2 \cdot 12H_2O$ (BTC = 1,3,5-benzene tricarboxylic acid) is carried out using one of four different reactors (stainless steel, microwave, polypropylene bottle, or sealed glass ampules) and the products are evaluated and compared using thermogravimetric analysis, powder X-ray diffraction, and IR spectroscopy. Powder X-ray diffraction is also used to monitor the changes in structure of the framework during the partial or complete removal of the associated water molecules, as well as after reabsorption of water.



KEYWORDS: *Upper-Division Undergraduate, Inorganic Chemistry, Laboratory Instruction, Gravimetric Analysis, Hydrogen Bonding, IR Spectroscopy, Materials Science, Thermal Analysis*

Metal–organic frameworks (MOFs)[1] are a literal and figurative extension of coordination chemistry.[2] These crystalline materials employ organic substituents (ligands) to link multiple metal centers together. By adjusting the length of the organic ligand, the size of the formed cavity or pore can be controlled. Not only can the pore *size* be controlled with chemical synthesis, but the *shape* of the pore can also be specifically designed by employing organic ligands with different functionalities or different metal centers. Metals have preferred coordination geometries (octahedral, tetrahedral, square planar, etc.); therefore, they direct the assembly of the framework. Secondary interactions, such as hydrogen bonding or π–π stacking, may also contribute to the architecture of the structure. Metal–organic frameworks can be custom-tailored for specific purposes, such as small molecule storage and transport, size- or shape-selective separation, and catalysis, and have potential in other areas, such as drug delivery and diagnostics. Special thematic issues[3] in *Chemical Reviews*, *Chemical Society Reviews*, and the *New Journal of Chemistry* provide an excellent background on the advances in MOF chemistry.

The experiment described here includes the synthesis of a MOF and the characterization of the structure using thermogravimetic analysis (TGA), powder X-ray diffraction (XRD), and IR spectroscopy. Although TGA and XRD are important techniques in chemistry and materials science, they are not commonly used by chemistry undergraduates. Previously published laboratory experiments that involve MOFs have focused on the measurement of the internal surface area[4] and investigating the host–guest relationship.[5] The unique aspect of the system reported herein is that the water molecules associated with the framework are not simply guest molecules, but are important in maintaining structural integrity of the framework. Students use TGA, IR spectroscopy, and XRD in an integrative fashion to learn how the removal of some or all of the water (and subsequent rehydration) affects the overall stability of the framework.

Another important aspect of this experiment is that it highlights the differences in the synthetic conditions required to produce a MOF versus a discrete coordination complex. Students have most likely encountered traditional synthetic techniques to prepare discrete complexes; however, to produce stable metal–ligand bonds *throughout* the framework, harsher synthetic conditions (such as hydrothermal synthesis) are generally required to obtain the most robust thermodynamic product.[2] Hydrothermal synthesis involves the extended heating of the reactants in water at elevated temperatures and pressures.

Over the past 12 years, this experiment has developed into a multiperiod synthesis, characterization, and analysis experiment that encourages upper-level undergraduates in Inorganic Chemistry or an Advanced Laboratory to review the literature, search the crystallographic database, and critically interpret the combined output from the analytical techniques to describe the

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effects of the dehydration/rehydration process. This experiment generates a tremendous amount of data, so during the course of the data collection, the students discuss what information the data provide about the product. Students are then assigned focused discussion topics in which they use the appropriate data, literature, and so forth to organize and write a more scientific-style Results and Discussion section (as opposed to a standard lab report).[6] This nontraditional lab experiment transitions students from a "cookbook" experiment to a more research-style laboratory scenario.

■ EXPERIMENTAL OVERVIEW

In 1996, porous solids of the formula $M_3(BTC)_2{\cdot}12H_2O$ (M = Co, Ni, Zn) were produced by reacting M(II) acetate hydrate with 1,3,5-benzenetricarboxylic acid (H_3BTC) in a hydrothermal fashion.[7] Hydrothermal synthesis is a common preparation technique of MOFs that normally entails heating an aqueous mixture of reactants in a stainless steel vessel/autoclave to temperatures well above the boiling point of water (120−350 °C). Stainless steel vessels (Parr reactors) are the safe and accepted containers for hydrothermal synthesis; however, they are expensive. Microwave reactors are becoming more common place in the undergraduate laboratory,[8] so a synthetic method was designed using a microwave reactor. Additionally, some commonly available equipment—narrow mouth polypropylene bottles and vacuum-sealed glass tubes—can safely and effectively serve as reactors for the hydrothermal synthesis of $Co_3(BTC)_2{\cdot}12H_2O$. (Although we have studied the nickel and zinc analogues, we have most extensively worked with the cobalt complex due to the distinctive color change associated with the dehydration of the material.)

The resulting open framework structure of $Co_3(BTC)_2{\cdot}12H_2O$ is constructed from both covalent interactions and hydrogen bonding interactions resulting in channels that are 4 × 5 Å, and it is these hydrogen bonding interactions that help assemble the coordination polymer into a porous framework.[7] Figure 1 highlights a portion of the $Co_3(BTC)_2{\cdot}12H_2O$ unit of the coordination polymer. (A coordination polymer is defined as "a coordination compound with repeating coordination entities in 1, 2, or 3 dimensions." MOFs are considered a subclass of multidimensional coordination polymers.[1])

With this experiment, students experience a different synthetic technique and observe how the synthetic conditions affect the properties of the product. Students integrate data from multiple instrumental techniques, and work in a research-like setting to determine what each piece of data provides to the overall picture of structure and bonding within this material, and they learn the limits of what conclusions can be drawn from each analytical technique.

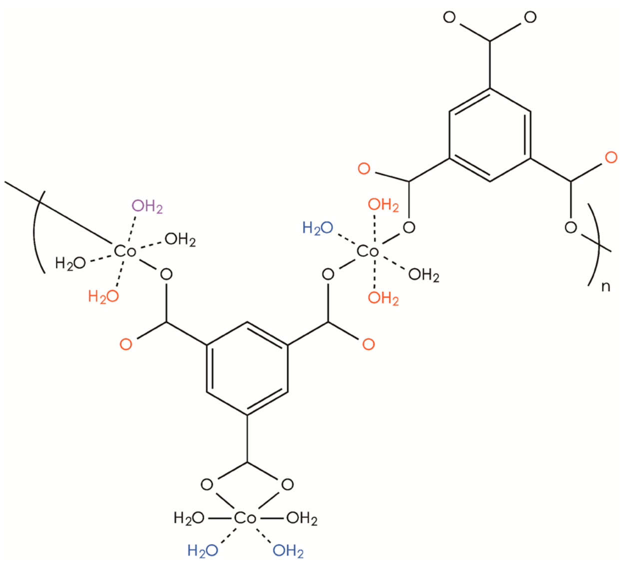

Figure 1. $Co_3(BTC)_2{\cdot}12H_2O$ repeating unit of the coordination polymer strand. Different water molecules (differentiated by color) can form different hydrogen bonding interactions: (in red) water molecules that form hydrogen bonds to adjacent BTC units within the single coordination polymer strand that is shown; (in blue) water molecules that form hydrogen bonds to water molecules on an adjacent coordination polymer strand; and (in purple) the water molecule that can hydrogen bond in either mode. Hydrogen atoms on the BTC unit have been omitted for clarity. Data from ref 7.

■ EXPERIMENT

This advanced laboratory experiment has been typically performed in three separate 4-h lab periods but may be performed in two lab periods if individual student groups carry out the analysis of one technique and collaborate with other groups on their findings. Students work in pairs to prepare $Co_3(BTC)_2{\cdot}12H_2O$ by heating an aqueous mixture of cobalt(II) acetate and H_3BTC in one of the four reactors. Detailed safety precautions and the experimental methods utilized for each hydrothermal reactor are provided in the Supporting Information. Formation of the product is verified by IR spectroscopy and powder XRD, and the solubility of the product is tested and compared to the starting materials. Thermogravimetric analysis is performed to determine the amount of water removed at a given temperature, and XRD is used to monitor the changes to the structure of the framework during the partial or complete removal of the associated water molecules, as well as after reabsorption of water.

■ HAZARDS

Cobalt(II) acetate tetrahydrate is a suspected carcinogen. Cobalt(II) acetate tetrahydrate and 1,3,5-benzenetricarboxylic acid are known skin and respiratory irritants. Proper eye protection and nitrile gloves should be worn and work should be done in a fume hood to minimize exposure. The hazards of the product, $Co_3(BTC)_2{\cdot}12H_2O$, have not been assessed; however, it is handled in a similar fashion as the reactants.

The hydrothermal process is carried out by heating an aqueous mixture in a ***closed*** container. The elevated pressures inside the container may cause catastrophic failure of the container. Goggles and insulated gloves should be worn when handling the reaction container.

■ RESULTS AND DISCUSSION

Synthesis

Average yields of $Co_3(BTC)_2{\cdot}12H_2O$ were 63% (glass ampule), 78% (polypropylene bottle), 81% (microwave), and 82% (stainless steel vessel). The low yield associated with the glass ampule was most likely a result of the reactants not mixing very well in the narrow tube during the synthesis, yet attempts to mix the reactants before sealing the tube did not statistically improve the yield. In the stainless steel reactor, the crystalline product was obtained after heating the sample at 140 °C for less than 2 days. Hydrothermal reactions performed in the polypropylene bottles were carried out at a lower temperature

(105 °C), but this did not have a significant effect on the yield or the phase purity of the material. The microwave reactor proved to be the quickest, most efficient method (30 min at 80 °C) to produce $Co_3(BTC)_2{\cdot}12H_2O$. The most notable difference between the $Co_3(BTC)_2{\cdot}12H_2O$ samples was that dark pink crystals formed in the stainless steel vessel, whereas pink powdery products were isolated by the other methods; only the former method utilized a slow temperature cool down, which tended to favor crystalline growth.

Characterization

The Supporting Information provides IR, TGA, and XRD data collected by students that demonstrate that $Co_3(BTC)_2{\cdot}12H_2O$ is produced independent of the hydrothermal reactor employed. A unique characteristic of $Co_3(BTC)_2{\cdot}12H_2O$ is that the sample undergoes a distinct change in color during dehydration. The fully hydrated sample is dark pink and transitions through purple when partially dehydrated to blue when completely dehydrated. This color change is similar to that observed in humidity detection strips that are impregnated with hydrated cobalt(II) chloride; the hydrated octahedral complex is pink, whereas the (nearly) anhydrous cobalt(II) chloride tetrahedral complex is blue.[9]

A thermogram of $Co_3(BTC)_2{\cdot}12H_2O$ collected by students (Figure 2) outlines the weight loss due to dehydration of the coordinated water molecules. At 100 °C, the weight loss of 2.5% corresponds to the loss of 1.1 water molecules per formula unit, and by 200 °C, the weight loss corresponds to the loss of almost 11.5 H_2O molecules. The sample is fully dehydrated (−12 H_2O) above 290 °C, which is lower than reported;[7a] this is likely due to different heating rates. Because the only thermal event for $Co_3(BTC)_2{\cdot}12H_2O$ is loss of water, the determination of the amount of water removed at a particular temperature could be performed using traditional gravimetric analysis methods with careful, repetitive analytical weighing before and after heating a sample.

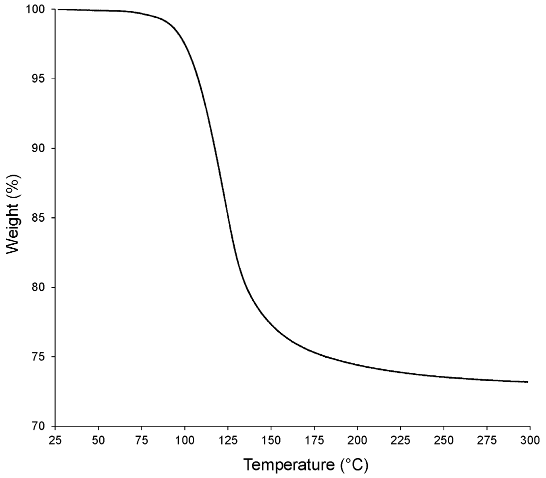

Figure 2. Thermogram for $Co_3(BTC)_2{\cdot}12H_2O$ under a nitrogen flow with a heating rate of 5 °C/min to 300 °C.

The IR spectrum of $Co_3(BTC)_2{\cdot}12H_2O$ (Supporting Information) matches that reported[7a] and can be compared to that of the starting material (1,3,5-benzenetricarboxylic acid). The lack of the 1730−1690 cm^{-1} absorption band in $Co_3(BTC)_2{\cdot}12H_2O$ indicates that the BTC unit was deprotonated to form carboxylate. The broad absorption bands between 3467−3125 cm^{-1} indicate the presence of water in the complex and these absorption bands diminish with the partial and complete dehydration of the complex.

Powder X-ray diffraction is utilized to determine the phase purity of $Co_3(BTC)_2{\cdot}12H_2O$, as well to monitor the crystallinity of the structure as the water molecules are partially or completely removed and reabsorbed. Figure 3 shows representative student-acquired powder XRD patterns of $Co_3(BTC)_2{\cdot}12H_2O$ that highlight the changes in the crystallinity during the partial dehydration and rehydration process. The lowest pattern in Figure 3 is obtained from the prepared $Co_3(BTC)_2{\cdot}12H_2O$ and indicates that the material has long-range atomic order with three low angle major reflections at 17.3, 18.4, and 26.7 2θ (deg). When the material is partially dehydrated, the *broadening* in the diffraction pattern indicates that deformation in the crystalline lattice is occurring (Figure 3, middle patterns). Due to the lower intensity of these diffraction patterns in comparison to the original product, they appear flat in the overlay; however, for a better view of the broadening, see Figure S8 in the Supporting Information. After the sample is rehydrated by soaking in water for 5−10 min, the original diffraction pattern is nearly restored with only minor changes in the position or intensity of the reflections (Figure 3, top). A deformation in the crystalline lattice—versus a complete loss of crystallinity—during the partial dehydration is supported because the rehydration process occurs instantly without the sample dissolving and recrystallizing. The rehydration of partially dehydrated samples containing varying amounts of water ($Co_2(BTC)_3{\cdot}(1-11)H_2O$) has been investigated, and in all cases, the crystallinity of the framework is reestablished as determined by XRD. However, when a *completely* dehydrated sample is rehydrated, the original structure is not restored, indicating a collapse in the structure and the loss of crystallinity in the framework (see Figure S10 in Supporting Information). Therefore, the reversibility of the dehydration−rehydration process is contingent upon having at least one water molecule (per formula unit) present as part of the framework to provide the hydrogen bonding interactions necessary to maintain the integrity of the framework. This allows water molecules to reenter the voids that form during dehydration. To view the bonding, students may refer to Figure 1 (or the handout in Supporting Information). In order to view

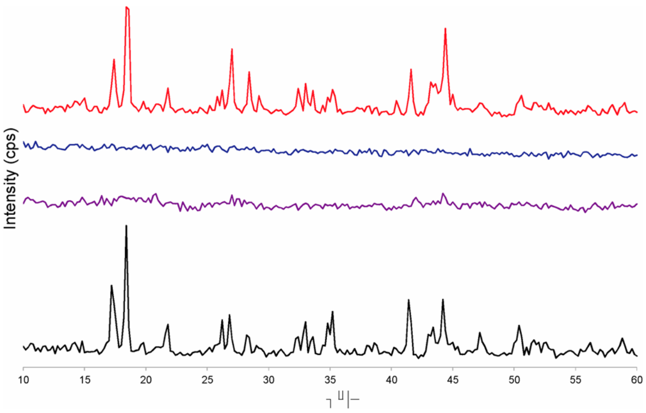

Figure 3. Powder XRD patterns of $Co_3(BTC)_2{\cdot}12H_2O$ during different stages of dehydration and reabsorption of water. The bottom pattern (black) is for the "as prepared" sample synthesized via the stainless steel reactor; the middle patterns are for partially dehydrated samples, $Co_3(BTC)_2{\cdot}7.3H_2O$ (purple) and $Co_3(BTC)_2{\cdot}3.75H_2O$ (blue); the top pattern (red) is for the fully rehydrated sample.

the channels in the crystal structure, students may refer to the original article,[7] or they may obtain the crystallographic information file (.cif) through the Cambridge Structural Database and view on software made available from the site.[10] This illustrates to students that the role of water in the $Co_3(BTC)_2$ framework is more than that of a guest; it is critical in stabilizing the framework (via hydrogen bonding).

Guest dependent pore stability has been observed to a lesser extent during the dehydration of different BTC-containing MOFs, $[M(HBTC)(H_2O)_2]\cdot 0.5H_2O$ (M = Sr or Ba).[11] Although the resulting channels in $[M(HBTC)(H_2O)_2]\cdot 0.5H_2O$ are almost double in size of $Co_3(BTC)_2\cdot 12H_2O$, the observed deformation of the former structure during dehydration is minimal due to the fact that fewer water molecules per cation are being liberated than in the $Co_3(BTC)_2\cdot 12H_2O$ structure.

■ SUMMARY

$Co_3(BTC)_2\cdot 12H_2O$ can be safely and effectively prepared by hydrothermal synthesis using a variety of reactors. Thermogravimetric analysis provides the temperature range through which dehydration occurs. Structural changes to the framework that occur during the partial dehydration and reabsorption of the included water molecules are monitored with powder X-ray diffraction. With this experiment, students learn new synthetic and instrumental techniques and integrate their findings in order to explain factors that affect the reversibility of the dehydration−rehydration process of this MOF. The students' level of understanding and ability to consider data from multiple sources are mainly assessed through discussions with them in the laboratory and by reading their journal-style Results and Discussion report.

Students have investigated the synthesis or the dehydration process beyond the basic experiment and such further studies have included: optimizing the reaction conditions with alternative hydrothermal reactors[12] to produce $Co_3(BTC)_2\cdot 12H_2O$; investigating the inclusion of ammonia[7a] into a partially dehydrated sample of $Co_3(BTC)_2\cdot xH_2O$; and the (hydrothermal, solvothermal, or traditional) synthesis and characterization of other metal−BTC materials.[11,13] These studies are briefly outlined in the Supporting Information. Although this experiment has been presented as an advanced experiment, it could be easily tailored to introduce inorganic materials and simple gravimetric analysis at the introductory level.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

This section includes experimental details for students along with safety precautions, instructor notes with purchasing information, ideas for further studies, and additional data collected by students. This material is available via the Internet at http:/pubs.acs.org.

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The authors declare no competing financial interest.

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