Design of Crystalline Solids via Solid-State Reaction

A Major Qualifying Project Report

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by

Marshall McGoff

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Professor John C. MacDonald, Advisor

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Abstract

We are investigating methods to prepare porous crystalline solids based on metal-organic frameworks (MOFs) composed of organic molecules and metal ions. MOFs form channels that permeate the crystal, resulting in solids that are porous. Consequently, MOFs are new functional materials that are now being used in a range of applications that include storage of gases (e.g., hydrogen), delivery of drugs, catalysis of organic reactions, and molecular separations. Although research has focused on using solution-based hydrothermal methods to prepare MOFs at elevated temperatures in order to form crystalline MOFs, decreasing solubility of the product as MOFs form in solution remains a major hurdle for synthesizing MOFs. Therefore, there is a growing need to develop new approaches to generate MOFs. Toward this goal, we are investigating using solid-state synthesis to synthesize MOFs by grinding organic ligands and transition metal salts together in the absence of solvents. Here we report the attempts at room temperature and hydrothermal synthesis along with the successful solid-state synthesis and characterization of a MOF composed of urocanic acid (3-(3*H*-imidazol-4-yl)prop-2-enoic acid) and copper (II) nitrate.

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1. Introduction

1.1 Porous materials

Porous materials are simply any materials that have holes in them. There are various kinds of porous materials and in general there are inorganic zeolites, organic polymers, and metal organic frameworks (MOFs). Zeolites are hydrated aluminosilicate minerals that have a microporous structure and occur in various forms in nature. These materials are mostly used for sized based separation in industrial applications and can function as molecular separators. One of the biggest advantages of using zeolites is the principal raw components are silica and alumina, two of the most abundant minerals on earth. The drawback to the synthesis of zeolites is that the synthetic zeolites often have smaller pore sizes than their natural counterparts.

Organic polymers are substances composed of molecules with large molecular mass composed of repeating structural units connected by covalent bonds. Polymers are also found in nature but the most important, PVC and nylon, are synthetically produced. These synthetic polymers are relatively easy to construct from their monomers, which makes them attractive because they are able to be designed around structural parameters. One of the disadvantages to using polymers is that they have no defined structure and therefore the exact pore size and void volume cannot be determined easily.

Zeolites and organic polymers are quite different than MOFs, which have a well defined rigid structure because of the rigidity of the metal to organic ligand bond. MOFs also generally form solids that are ordered and crystalline; thus the crystal structures and molecular packing of them can be characterized using x-ray diffraction. MOFs are modular in that they contain both metal ions and organic ligands. The structures and connectivity of MOFs can be varied based on the preferred coordination geometry of the metal ion (e.g. linear, trigonal, tetrahedral, octrahedral, etc) and the structure of the organic ligand (e.g. linear, bent, etc) and the number and type of functional groups capable of binding to metal ions. This modularity allows MOFs with a variety of structures and connectivity to be targeted. For example, metal ions such as Cd (II) that prefer tetrahedral coordination frequently form MOFs with an extended diamond motif, whereas metal ions such as Co(II) that prefer octahedral coordination often form MOFs with an extended cubic motif.

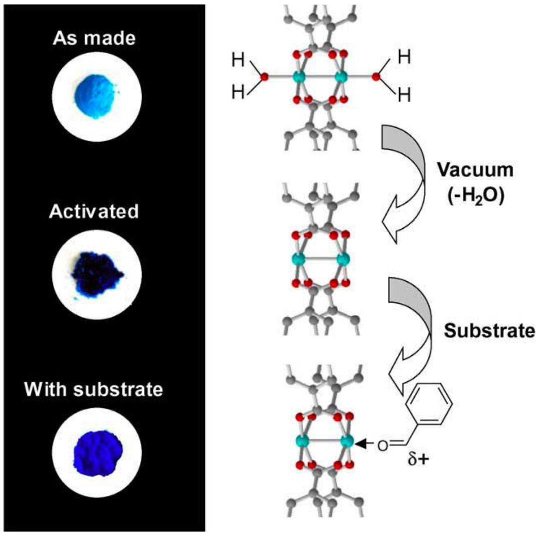
The structures of organic ligands can be modified through organic synthesis to tailor the structures and properties of MOFs. For example, the dimensions of open pores or channels in MOFs can be expanded or contracted by increasing or decreasing the corresponding distance between the functional groups that bind the metal ions on the organic ligand. MOFs usually form robust porous solids because organic ligands coordinate to metal ions by forming covalent bonds. The resulting 3-D structures of MOFs are covalent networks solids that generally can withstand the removal of guest molecules such as solvent that fill the empty spaces in the pores or channels. The fact that trapped solvent can be removed easily by heating or under vacuum while maintaining the structure of the MOF is what renders MOFs ideal as materials for constructing porous solids.

There are drawbacks to using MOFs as porous solids. One of the biggest problems is that MOFs can interpenetrate as they form in solution so that independent frameworks grow through one another. This interpenetration greatly reduces the amount of void space in pores or channels. MOFs also tend to become insoluble due to the rapid increase in molecular weight as metal ions and organic ligands add to the framework. As a result, MOFs often crash out of solution during growth as insoluble precipitates before MOFs are able to form crystalline solids. Thus high temperature hydrothermal synthesis frequently is required in order to prepare crystalline MOFs.

1.1 Uses of MOFs

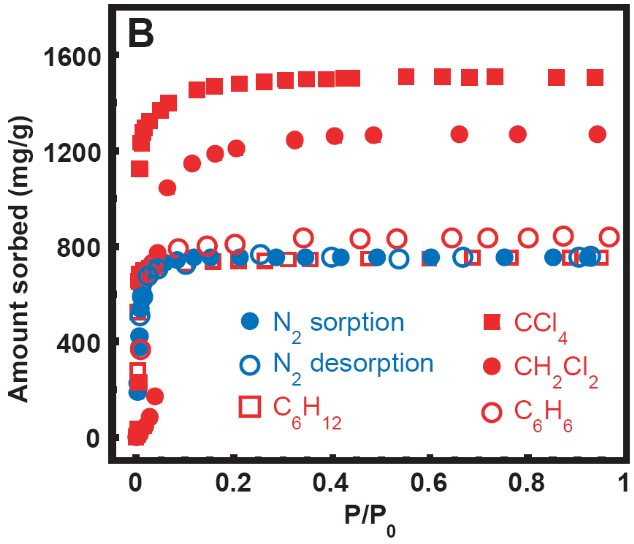
The utility of MOFs are one of the greatest strengths to using such materials. MOFs can be used for many practical applications such as for sensors for molecules. For example, a MOF composed of copper and trimesic acid has been developed to detect the presence of organic aldehydes as shown in Figure 1. This material provides a visual response in that the removal of the bound water molecules under vacuum changes the color of the crystal. Subsequent exposure of the MOF to a substrate consisting of an organic aldehyde causes a further change in the color of the crystals allowing the MOF to be used as a sensor[1].

Figure 1 - MOFs as sensors



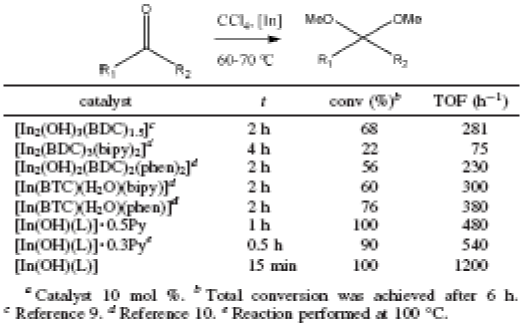
Another important use of MOFs is molecular storage. It has been shown in previous research that molecules such as methane or hydrogen gas can be stored inside of the framework of a family of MOFs composed of metal dicarboxylates that crystallize as cubic frameworks. Omar M. Yaghi reported absorption of such gases as N_2, CCl_4, C_6H_{12}, CH_2Cl_2, and C_6H_6 into the framework of these MOFs after trapped solvent molecules were removed under vacuum overnight.[2] Gas storage inside the framework of MOFs is an increasingly important field of study in the development of fuel cell technology as MOFs show tremendous potential for storing high densities of hydrogen gas.[3]

Figure 2 - Gas sorption in a MOF



MOFs have also been used as recyclable Lewis acid catalysts and it has been shown that the catalysis can occur in the pores of MOFs. For example, Gándara et al. report that their MOFs are active and selective catalysts for acetalization of aldehydes.[3] As shown in Figure 3, the reaction for the acetalization of aldehydes occurs with extremely high yields in little time using these MOFs as a catalyst.

Figure 3 - MOF as an acid catalyst



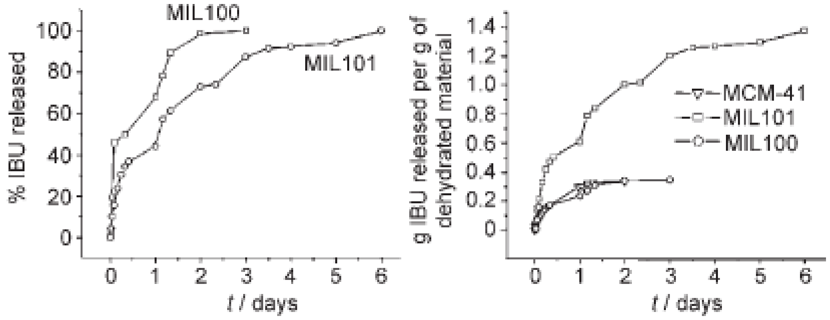
catalyst	t	conv (%)[b]	TOF (h^{-1})
$[In_2(OH)_3(BDC)_{1.5}]$[c]	2 h	68	281
$[In_2(BDC)_3(bipy)_2]$[c]	4 h	22	75
$[In_2(OH)_2(BDC)_2(phen)_2]$[d]	2 h	56	230
$[In(BTC)(H_2O)(bipy)]$[d]	2 h	60	300
$[In(BTC)(H_2O)(phen)]$[d]	2 h	76	380
$[In(OH)(L)]\cdot 0.5Py$	1 h	100	480
$[In(OH)(L)]\cdot 0.3Py$[e]	0.5 h	90	540
$[In(OH)(L)]$	15 min	100	1200

[a] Catalyst 10 mol %. [b] Total conversion was achieved after 6 h. [c] Reference 9. [d] Reference 10. [e] Reaction performed at 100 °C.

Size selective molecular separation based on the dimensions of channels and pores is another important use of MOFs as materials. Preferential adsorption of a variety of molecules by MOFs based on size has been reported recently. For example, Zhong et al demonstrated that the size of the pores in MOFs composed of manganese formate play a critical role in the ability of those materials to delectively adsorb and effectively separate CO_2 from alkane mixtures.[5]

The porous properties of MOFs make these materials ideally suited for several applications in medicine. For instance, storage and release of guest molecules has been applied to pharmaceuticals for time-released drug delivery. MOFs are ideal for that purpose because of their well defined porosity, which allows for a highly controllable rate of release, and because of their drug-loading capacity. A recent study showed that Ibuprofen can be absorbed into the framework of MOFs that contain chromium and trimesic acid or terephthalic acid.[5] This study established that Ibuprofen could be delivered over several days as shown in Figure 4.

Figure 4 - Release of Ibuprofen in a MOF



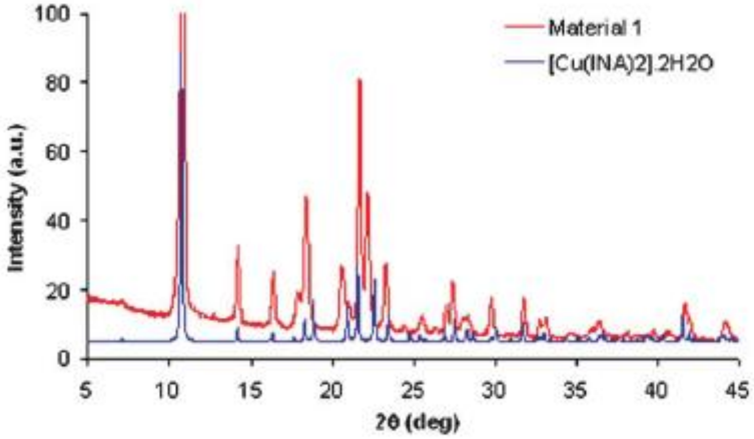
1.2 Known Methods Used to Prepare MOFs

There are three methods that have been reported for the synthesis of MOFs. While two of them are used to prepare the bulk of MOFs, the third method, solid-state grinding, has recently been shown to be a viable method for the construction of MOFs. One of the typical methods used to prepare MOFs is classified as room temperature synthesis whereby the metal ion and organic ligand are allowed to react in aqueous or organic solvent. A variety of MOFs have been constructed using this relatively simple approach. Room temperature synthesis generally requires that the metal is dissolved into a water solution with the ligand being dissolved into water or alcohol. The two solutions are mixed allowing the two components to react at room temperature. The solution is then set aside until crystals form in solution typically after several hours of days. This method is preferred when feasible because of its simplicity. The primary drawback of room temperature synthesis in this manner is a general low solubility of the MOFs, which frequently crash out of solution as insoluble precipitates instead of forming crystals. Another common problem arises from mutual insolubility of the metal salt and organic ligand in the solvent system For example, metal salts generally dissolve only in aqueous solvents in which organic ligands are insoluble; as a result, the reaction simply will not occur. Porous crystalline solids that can be prepared using room temperature synthesis generally contain significant amounts of water or aqueous solvent mixtures that are trapped in the channels of pores during growth of MOFs in solution.

Hydrothermal synthesis can greatly help to increase the solubility of the ligand or metal in solution by raising the temperature of the solution past the boiling point of the solvent. These reactions generally occur over a period of a few days and require great precision in determining the concentrations of the metal and ligand. Another possible problem is that a change in the solvent can oftentimes result in no product being formed or poor experimental results. Thus, there must be great care taken to ensure that the reaction conditions are ideal for each reaction. Some organic ligands are prone to decomposition at such high temperatures and pressures, which leads some to search for an alternative to hydrothermal synthesis.

A recent report demonstrated that a MOF can be synthesized by solid-state synthesis (grinding) that is identical to that produced hydrothermally. An article published in CrystEngComm reported that the microporous MOF $[CU(INA)_2]$ (INA = isonicotinic acid) can be obtained by grinding a quantitative amount of the starting materials together in a ball mill.[6] The reaction is followed using XPD and compared to that of the simulated XPD of the crystals grown hydrothermally. They also show that the product can be obtained by hand grinding the materials together but takes a longer amount of time to accomplish. As shown in the XPD on the left, the material ground together is identical to that grown from solution hydrothermally. Another advantage to using solid-state synthesis, besides the obvious lack of solubility being an issue in the absence of solvents, is that this chemistry is considered green. In an ever increasing environmentally conscious world, this type of chemistry is more of what the world is looking for. The other advantage of using solid-state synthesis is that the reaction is run at room temperature and there is no need to be concerned about the decomposition of the ligands.

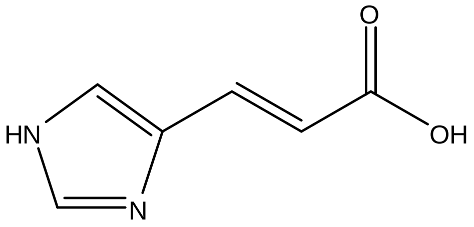
Figure 5 - XPD comparison of grinding product versus hydrothermal product



There are a few unknowns about the use of solid-state synthesis such as the incorporation of guest molecules. Most of the metal salts used are hydrates and therefore it is possible that the water molecules attached will be released and absorbed into the framework of the forming MOF. There is also the possibility that the anion (acetate for instance) attached to the metal will escape the reaction as a gas (acetic acid) but it could also become trapped into the framework. One of the biggest unknowns about the use of grinding is simply if the materials will react in the solid state at room temperature to produce a MOF.

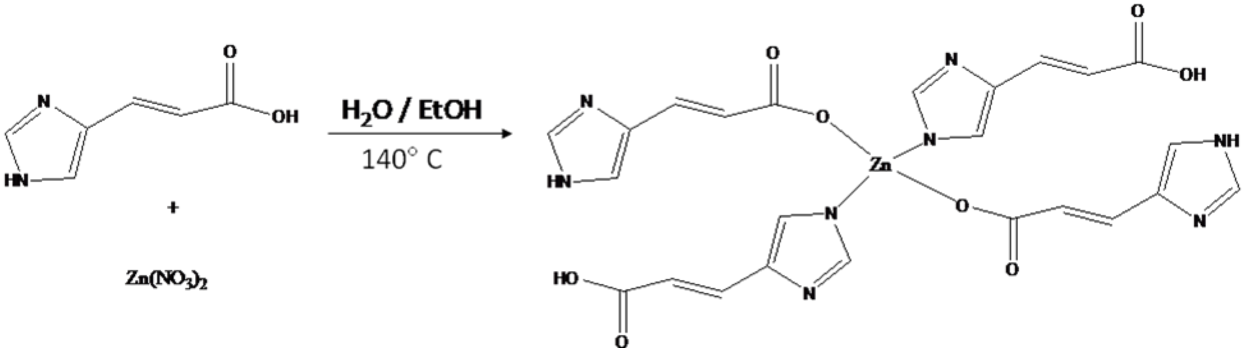
1.3 Coordination of Urocanic Acid to Transition Metals

Figure 6 - Urocanic acid



The ligand being studied in this project is urocanic acid. This ligand was picked for a variety of reasons. First, as seen in the structure, it contains an imidizole ring and a carboxylic acid. Both of these are known to bind to metal sites and it was unsure which would preferentially bind. According to previous research done with urocanic acid, it would bind with transition metals Co, Mn, Zn and Cd. A recent paper from Microporous and Mesoporous Materials shows the following reaction occurring under hydrothermal conditions:

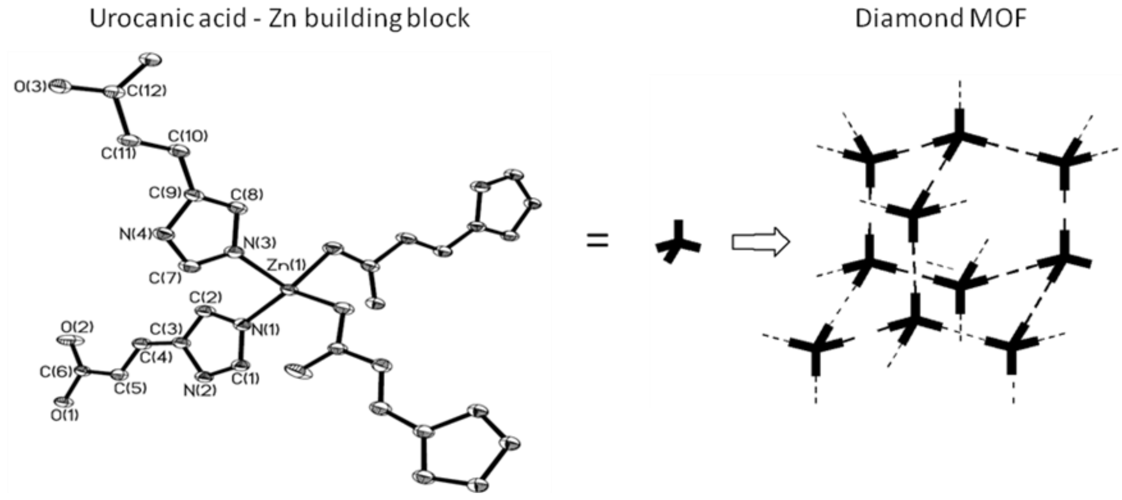
Figure 7 - Hydrothermal reaction between zinc nitrate and urocanic acid



According to the crystallographic data, the Zn complex binds both the nitrogen on the imidazole ring and the oxygen from the carboxylic acid. The crystallographic data also shows the building unit for this MOF as being tetrahedral when it forms.[8]

Water is detected in the channels using single crystal x-ray diffraction. This MOF is extremely porous, with approximately 18% weight loss observed when heated to 160°C using thermogravimetric analysis (TGA).

Figure 8 - Urocanic acid - zinc MOF crystal data



There are various ways in which the water can be incorporated. The three most common examples are listed below.

1. Coordination to the metal

Figure 9 - Tetrahedral

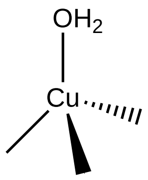


Figure 10 - Square planar

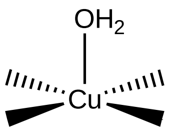
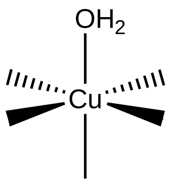
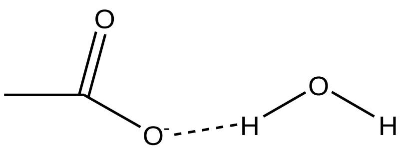


Figure 11 - Octahedral



2. Hydrogen bonding

Figure 12 - Hydrogen bond



3. Trapped in a porous channel

For this project, copper (II) nitrate was used as a metal salt for a few reasons. Most importantly, there has been no data to suggest that a copper – urocanic acid MOF has been constructed or that it would be impossible to do so. The nitrate was used because it would parallel many of the current transition metal – urocanic acid MOFs, which have already been published. It is known that copper (II) nitrate forms a trihydrate, which makes it easy to work with at room temperature in open air. In the end, it was a good choice to use copper (II) nitrate as it will be shown later in this report that a different anion does not result in the same product if any.

2. Methodology

2.1 Objectives

The initial goals of this project were to construct a MOF containing europium and urocanic acid so that it could be used as a fluorescent sensor. If europium was not a suitable metal, other lanthanides would be tested before transition metals because of the desired fluorescence. The MOF was to be grown using hydrothermal synthesis and then tested for fluorescence and adsorption of gases. If hydrothermal synthesis was not possible, then room temperature or solid-state synthesis would be used. Another goal was to determine if the urocanic acid would preferentially bind to the metal through the nitrogen in the imidazole ring or through the carboxylic acid group. The single-crystal data for the MOF could be used to obtain the structural data, which would be able to prove the mode of binding. The MOF would also be tested for its porosity and its ability to reabsorb solvent after being dehydrated. If solid-state grinding proved to be the only viable method then recrystallization would be necessary to gather the single-crystal information.

2.2 Hydrothermal

The initial stages of the project focused on using hydrothermal synthesis to attempt to obtain a product. In each of the experiments listed below, the volume of solvent used was 5mL unless noted otherwise. In each experiment, the urocanic acid and the metal were simply added into the hydrothermal vial and the solvent system was added in. The vial was then capped and placed into the oven for the predetermined amount of time. Table 1 lists all of the different attempts using hydrothermal synthesis with urocanic acid and various lanthanide metals:

Table 1:

Attempt	Metal	Solvent system	Concentration		T (°C)	Duration*
			Urocanic acid	Metal		
1	Europium acetate	5mL DMSO	$8*10^{-3}$ mM	$4*10^{-3}$ mM	120	4 days
2	Europium acetate	5mL 2:1 DMSO : MeOH	$8*10^{-3}$ mM	$4*10^{-3}$ mM	120	4 days
3	Europium acetate	5mL 2:1 DMSO : toluene	$8*10^{-3}$ mM	$4*10^{-3}$ mM	120	4 days
4	Europium acetate	5mL 2:1 H_2O : DMSO	$8*10^{-2}$ mM	$4*10^{-2}$ mM	120	4 days
5	Europium acetate	5mL 2:1 H_2O : DMSO	$8*10^{-2}$ mM	$2.7*10^{-2}$ mM	120	4 days
6	Europium acetate	5mL 3:1 H_2O : EtOH	$7.2*10^{-2}$ mM	$2.4*10^{-2}$ mM	85	4 days
7	Europium acetate	5mL 3:1 H_2O : EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	85	4 days
8	Europium acetate	5mL H_2O	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	160	4 days
9	Europium acetate	5mL 3:1 H_2O : DMF	$7.2*10^{-2}$ mM	$2.4*10^{-2}$ mM	120	4 days
10	Europium acetate	5mL 3:1 H_2O : DMF	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	4 days
11	Europium acetate	6mL DMF : MeOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	4 days
12	Europium acetate	5mL 4:4:2:1 EtOH : DMF : glycol : H_2O	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	4 days
13	Europium acetate	5mL H_2O	$1.5*10^{-1}$ mM	$5*10^{-2}$ mM	120	2 days
14	Europium acetate	5mL H_2O	$1.5*10^{-1}$ mM	$7.5*10^{-2}$ mM	120	2 days
15	Lutetium (III) acetate	5mL H_2O	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
16	Cerium (III) acetate	5mL H_2O	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
17	Lutetium (III) acetate	5mL H_2O / EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days

18	Cerium (III) acetate	5mL H_2O / EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
19	Cerium (III) acetate	5mL H_2O	$1.5*10^{-1}$ mM	$7.5*10^{-2}$ mM	120	2 days
20	Cerium (III) acetate	5mL H_2O / EtOH	$1.5*10^{-1}$ mM	$7.5*10^{-2}$ mM	120	2 days
21	Cerium (III) acetate	2:1 H_2O : EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
22	Cerium (III) acetate	3:1 H_2O : EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
23	Cerium (III) acetate	1:2 H_2O : EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
24	Cerium (III) acetate	1:3 H_2O : EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days

*Note: all tests were run in the same fashion. The oven was set to heat to the maximum temperature over 2 hours and remain at this temperature for the duration listed in the table. Then it was set to cool down over the period of 24 hours to 30°C.

After these tests were determined to have been unsuccessful, the next step was transition metals. Listed in Table 2 are the attempts using various transition metals:

Table 2:

Attempt	Metal	Solvent system	Concentration		Max Temperature	Duration
			Urocanic acid	Metal		
1	Nickel (II) nitrate	5mL H_2O	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
2	Copper (II) acetate	5mL H_2O	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
3	Copper (II) acetate	5mL H_2O / EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
4	Nickel (II) nitrate	5mL H_2O / EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
5	Copper (II)	5mL H_2O / EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$	120	2 days

	acetate			mM		
6	Nickel (II) nitrate	5mL H_2O / EtOH	$7.2*10^{-2}$ mM	$3.6*10^{-2}$ mM	120	2 days
7	Copper (II) nitrate	10ml H_2O, 10mL 5:1 EtOH / H_2O	2 mM	1 mM	140	4 days

As previously noted, all of these experiments were deemed failures and the only logical step was to abandon hydrothermal synthesis and attempt room temperature synthesis.

2.3 Room Temperature

These experiments were run at room temperature and were only heated above room temperature to increase solubility when noted. Each experiment was run similarly with the urocanic acid being dissolved into the solvent system and then the metal, which had been dissolved into the same solvent, was added slowly into the vial. The solution was left to sit overnight and monitored until it was close to complete evaporation. Table 3 lists the attempts made using various metals both lanthanides and transition metals:

Table 3:

Attempt	Metal	Solvent system	Concentration	
			Urocanic acid	Metal
1	Europium acetate	5mL 2:1 H_2O : DMSO	$8*10^{-2}$ mM	$4*10^{-2}$ mM
2	Europium acetate	5mL 2:1 H_2O : DMSO (plus a drop of KOH)	$8*10^{-2}$ mM	$4*10^{-2}$ mM
3	Europium acetate	10mL 2:1 H_2O : DMSO	$4*10^{-2}$ mM	$2*10^{-2}$ mM
4	Europium acetate	10mL 2:1 H_2O : DMSO	$5.5*10^{-2}$ mM	$2*10^{-2}$ mM
5	Europium acetate	10mL 3:1 H_2O : EtOH	$5.5*10^{-2}$ mM	$2*10^{-2}$ mM
6	Europium acetate	10mL 3:1 H_2O : EtOH	$2.2*10^{-1}$ mM	$7.2*10^{-2}$ mM
7	Europium acetate	10mL 3:1 H_2O : EtOH	$2.9*10^{-1}$ mM	$9.7*10^{-2}$ mM
8	Europium acetate	10mL 3:1 H_2O : EtOH	$3.6*10^{-1}$ mM	$1.2*10^{-1}$ mM
9	Europium acetate	10mL 3:1 H_2O : EtOH	$5.4*10^{-1}$ mM	$1.8*10^{-1}$ mM
10	Europium acetate	10mL 3:1 H_2O : ethyl acetate	$2.2*10^{-1}$ mM	$7.2*10^{-2}$ mM
11	Europium acetate	10mL 3:1 H_2O : DMF	$2.2*10^{-1}$ mM	$7.2*10^{-2}$ mM
12	Europium acetate	10mL 4:4:2:1 EtOH : DMF : glycol : H_2O	$2.2*10^{-1}$ mM	$7.2*10^{-2}$ mM
13	Europium acetate	10mL 4:4:2:1 EtOH : DMF : glycol : H_2O	$2.2*10^{-1}$ mM	$7.2*10^{-2}$ mM
14	Europium acetate	12mL 5:1 DMF : MeOH	$2.2*10^{-1}$ mM	$7.2*10^{-2}$ mM
15	Europium acetate	25mL 3:1 H_2O : DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
16	Europium acetate	5mL H_2O	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
17	Europium acetate	10mL H_2O	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
18	Europium acetate	9mL H_2O : 1mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
19	Europium acetate	8mL H_2O : 2mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
20	Europium acetate	7mL H_2O : 3mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
21	Europium acetate	6mL H_2O : 4mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
22	Europium acetate	5mL H_2O : 5mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
23	Europium acetate	4mL H_2O : 6mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
24	Europium acetate	3mL H_2O : 7mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
25	Europium acetate	2mL H_2O : 8mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM

26	Europium acetate	1mL H_2O : 9mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
27	Europium acetate	10mL DMF	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
28	Europium acetate	10mL MeOH	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
29	Europium acetate	10mL H_2O	$7.2*10^{-1}$ mM	$2.4*10^{-1}$ mM
30	Europium acetate	10mL H_2O	$7.2*10^{-1}$ mM	$3.6*10^{-1}$ mM
31	Lutetium (III) acetate	10mL H_2O	$7.2*10^{-1}$ mM	$3.6*10^{-1}$ mM
32	Cerium (III) acetate	10mL H_2O	$7.2*10^{-1}$ mM	$3.6*10^{-1}$ mM
33	Nickel (II) nitrate	10mL H_2O	$7.2*10^{-1}$ mM	$3.6*10^{-1}$ mM
34	Copper (II) acetate	10mL H_2O	$7.2*10^{-1}$ mM	$3.6*10^{-1}$ mM
35	Copper (II) nitrate	10mL H_2O	$7.2*10^{-1}$ mM	$3.6*10^{-1}$ mM
36	Copper (II) chloride	1mL DMSO, 8ml H_2O / EtOH, 1mL H_2O	$6*10^{-2}$ mM	$1*10^{-2}$ mM

After this exhaustive testing process, it was again determined that the only product crystallizing was urocanic acid. A recent article in CrystEngComm reported that it was possible to obtain a microporous MOF identical to that grown hydrothermally. It was unclear whether this technique could be applied to other systems but it looked quite promising and it was the only option available.

2.4 Solid-state

In these experiments, the urocanic acid and metal were simply ground together in a mortar and pestle in a quantitative amount. Copper (II) nitrate (150mg) was combined with urocanic acid (175 mg) and ground for 10 minutes. The powder was tested using IR and XPD initially and then placed into a vial and capped. The progress of the reaction was monitored every day by IR and XPD. After a week, it was determined that the reaction had completed and a thermogravimetric analysis (TGA) was conducted.

After this experiment was run, it was unclear how the nitrate anion affected the results and a variety of anions were also tested using the same procedure. Table 4 lists the other copper salts used in an attempt to obtain the same product as that with nitrate.

Table 4:

Anion	Mass	
	Urocanic acid (mg)	Metal (mg)
Copper (II) bromide	186	150
Copper (II) acetate	208	150
Copper (II) sulfate	166	150

2.5 Recrystallization attempts

One of the goals of the project was to obtain a single crystal suitable for single-crystal x-ray diffraction in order to determine the exact structure of the MOF. The problem with using solid-state grinding is that the product is a powder and therefore very difficult to recrystallize. Two different methods were attempted to recrystallize the powder but neither were successful. The first method was to dissolve a small amount of the powder into a solution and have it evaporate and crystallize slowly. Among the solvents tested were methanol, ethanol, isopropanol, acetone, and H_2O with the powder only being soluble in the H_2O. Eventually the H_2O evaporated but the powder did not crystallize and crashed out of solution as a powder.

The second method to recrystallize was called the hanging drop method. A drop of the powder dissolved into water was placed on the inside of the lid of a container. The container was filled with ~10mL of isopropanol and the lid was placed on top with the drop hanging down over the isopropanol. The goal of this experiment is to have the isopropanol slowly replace the water in the drop until it becomes less soluble and the product crystallizes out. This experiment failed but seemed quite promising as the powder was soluble in water.

2.6 Hydration experiment

One of the properties of MOFs is their porous behavior and a simple way to determine the porosity of a MOF is by measuring how much mass it loses while being heated. A plot of the mass lost as a function of temperature is given by the TGA and it is easy to determine the percent lost by analyzing this graph.

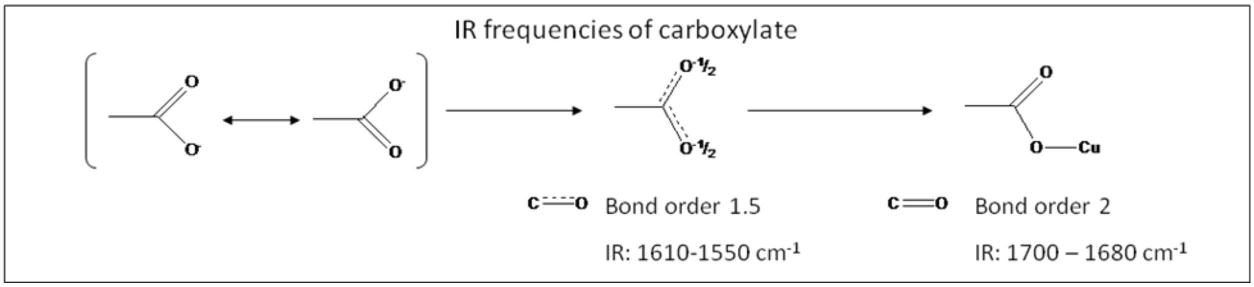
The powder from the copper (II) nitrate and urocanic acid grind was placed onto an XPD slide and heated to 150°C. It was then left in an empty dessicator with a petri dish of water placed inside. The powder was left in the dessicator for a week and then removed carefully. A portion of the powder was placed in the TGA to determine the amount of water reabsorbed. Another portion of the powder was used for IR analysis and the slide was then placed in the XPD for analysis.

3. Results

3.1 IR spectra

All of the IR spectra were collected using the Bruker VERTEX 70 with 4cm^{-1} resolution from 4000cm^{-1} to 600cm^{-1} and 16 scans each. The results of this project are very noticeable by analysis of the IR spectra obtained throughout the week long experiment testing the reaction progress. In the following series of spectra, the absorption indicated by the arrow becomes more intense over time. This phenomenon is explained in Figure 13.[9]

Figure 13 - Carboxylate resonance and its effect on IR



As shown in the illustration, the new absorption is at a higher wavenumber than previously, which indicates that the urocanic acid has become bound to the copper via the oxygen on the carboxylic acid. The following Figures (15-18) are IR spectra of the copper (II) nitrate and urocanic acid grind over the course of a few days. Also, Figure 14 indicates the color scheme for all of the IR spectra and includes a picture of the final product.

Figure 14 - Urocanic acid - copper MOF reaction

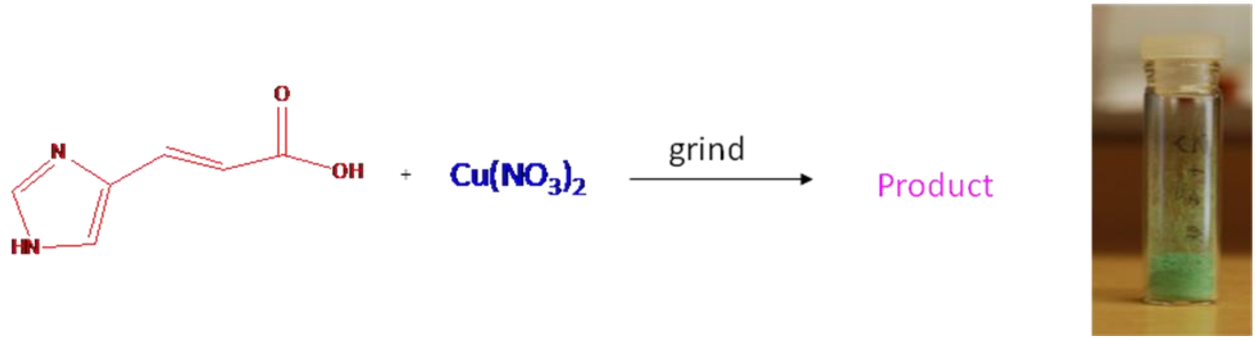


Figure 15 - Initial mixing of copper nitrate and urocanic acid

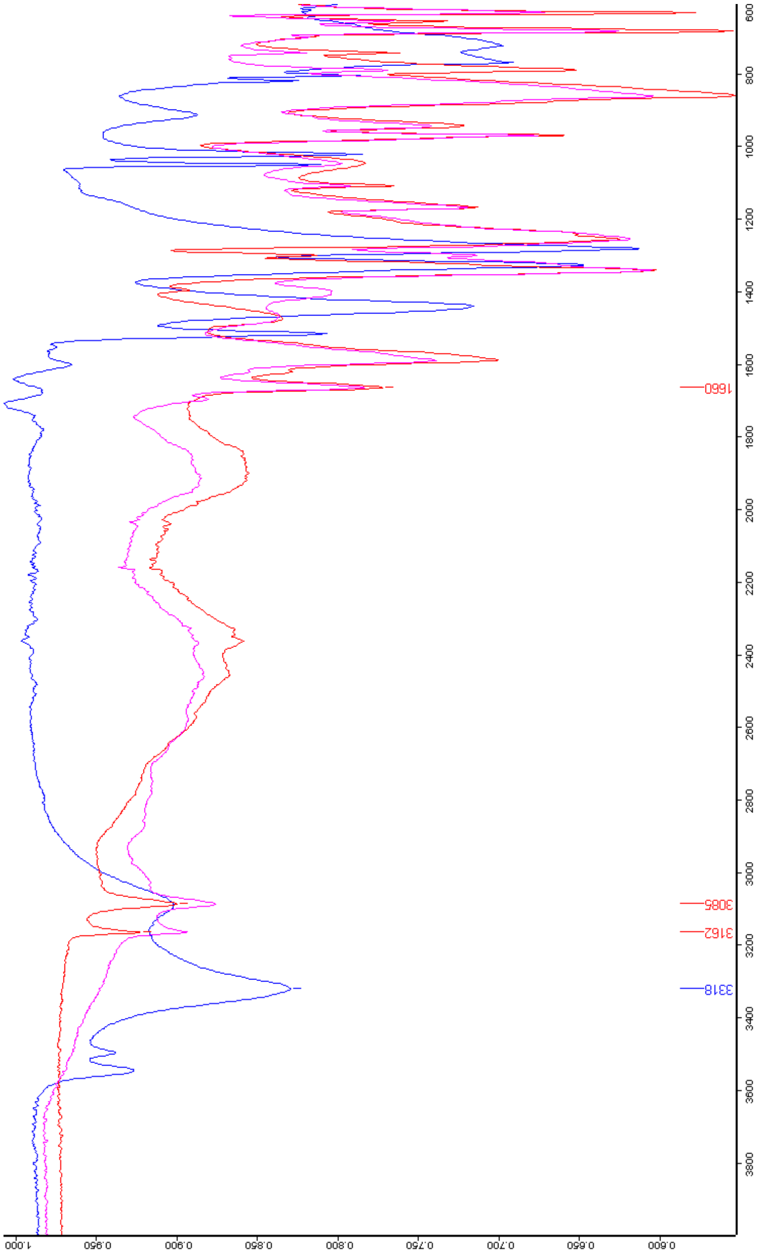


Figure 16 - 24 hours after initial mixing of copper nitrate and urocanic acid

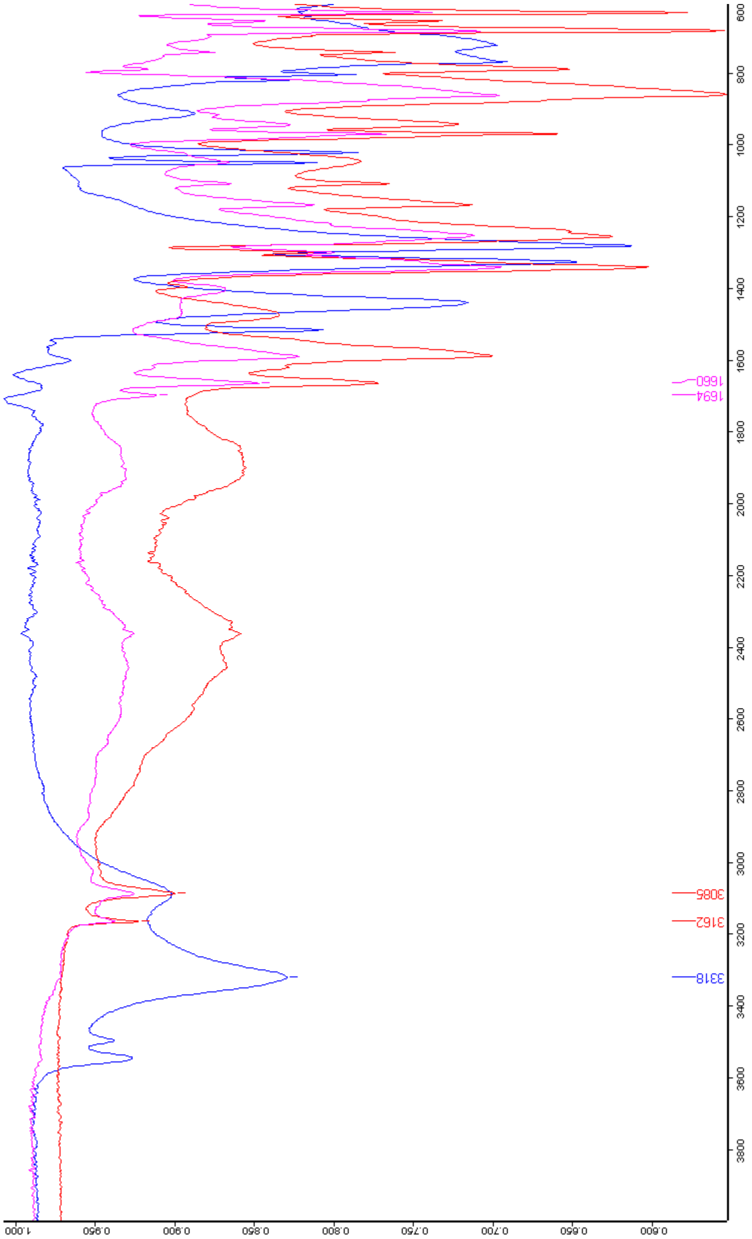


Figure 17 - 48 hours after initial mixing of copper nitrate and urocanic acid

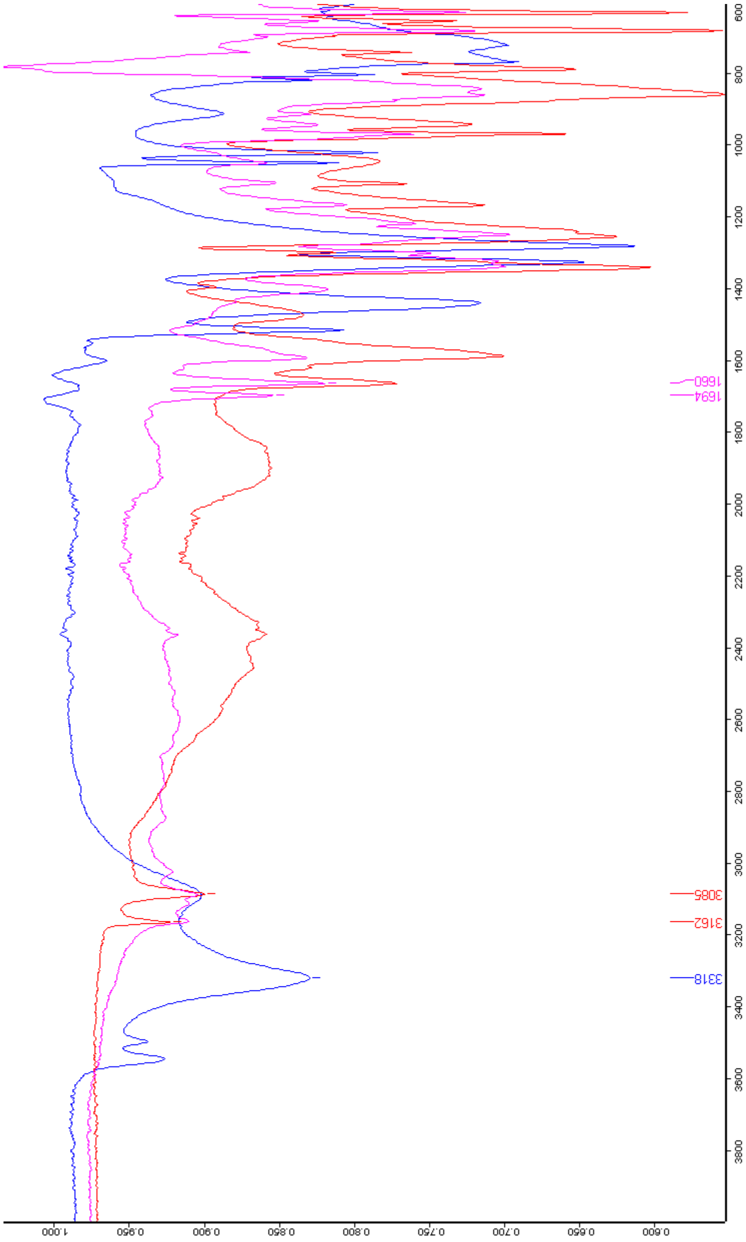
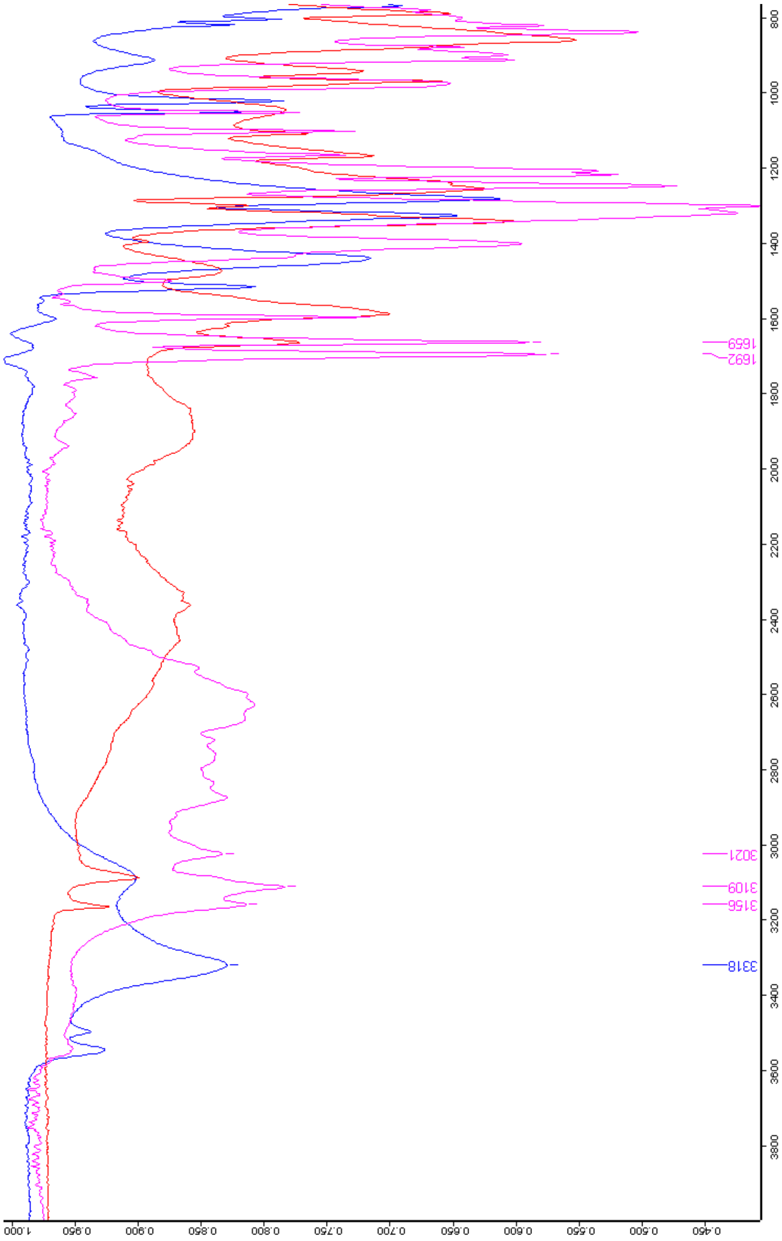


Figure 18 - Urocanic acid - copper MOF



This spectrum is the final product of the reaction from copper (II) nitrate and urocanic acid taken 7 days after the initial mixing. As seen in this spectrum, the new absorption at 1692 cm^{-1} is the same intensity as the band at 1660 cm^{-1}, which is also present in the urocanic acid.

3.2 Effect of Different Anions

The following Figures are IR spectra from the various copper salts that were used to attempt to get the same product as that from the nitrate. Figures 19-21 show the reaction mixtures after a week from the initial mixing. Figures 22-24 show the IR data for each of these reaction mixtures.

Figure 19 - Copper acetate

Figure 20 - Copper sulfate

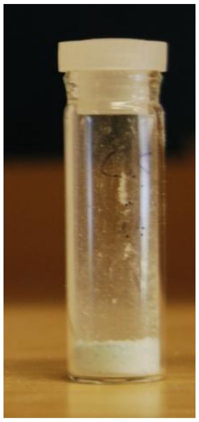
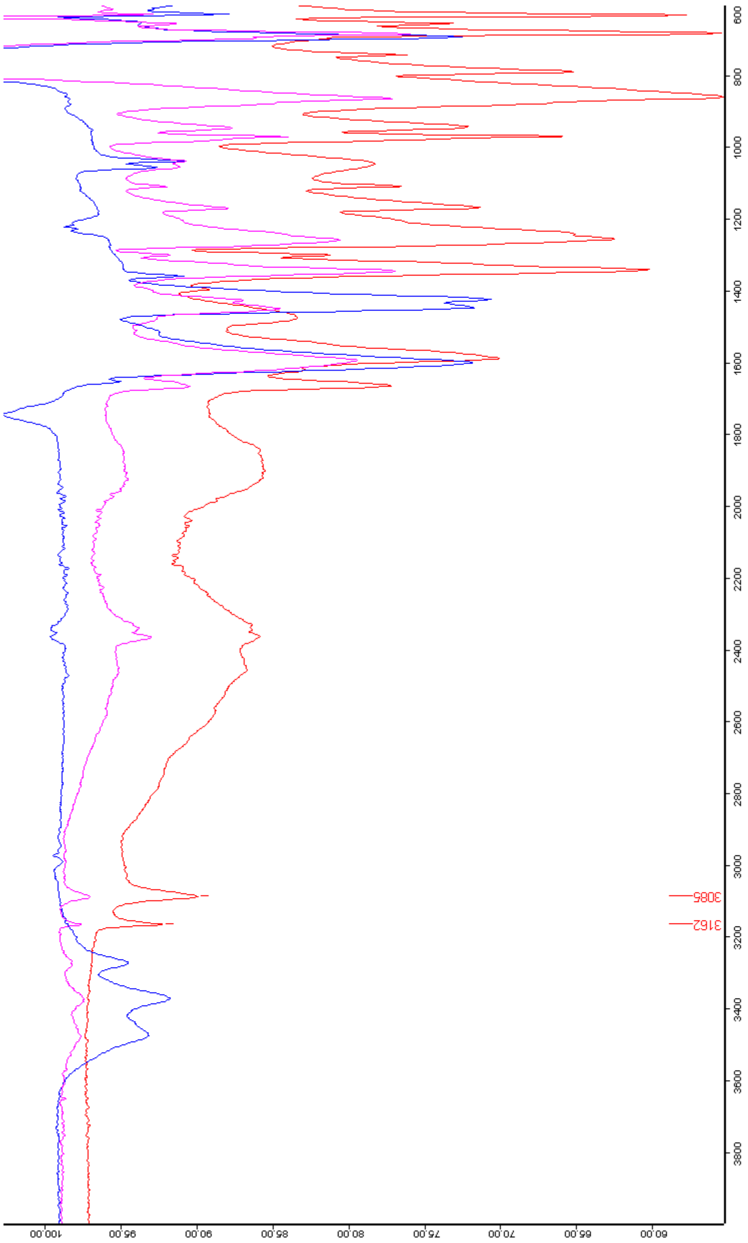


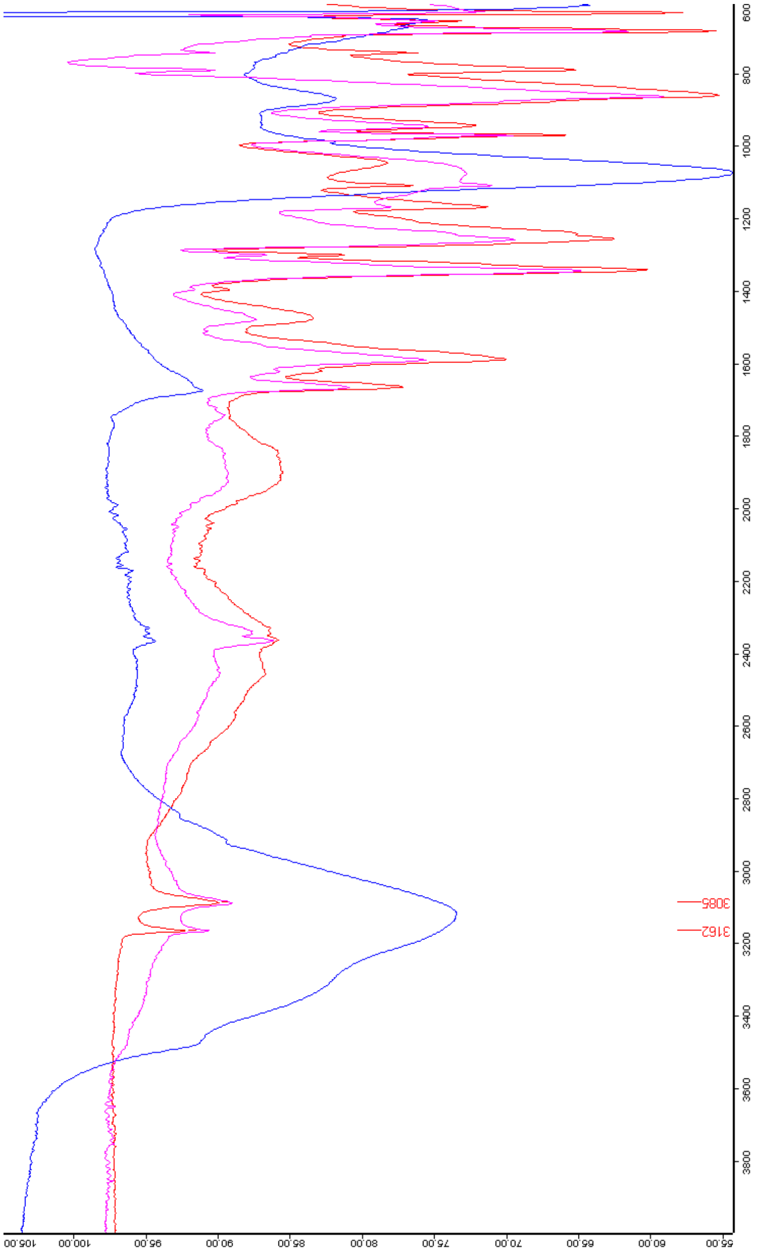
Figure 21 - Copper bromide

Figure 22 - Urocanic acid and copper acetate



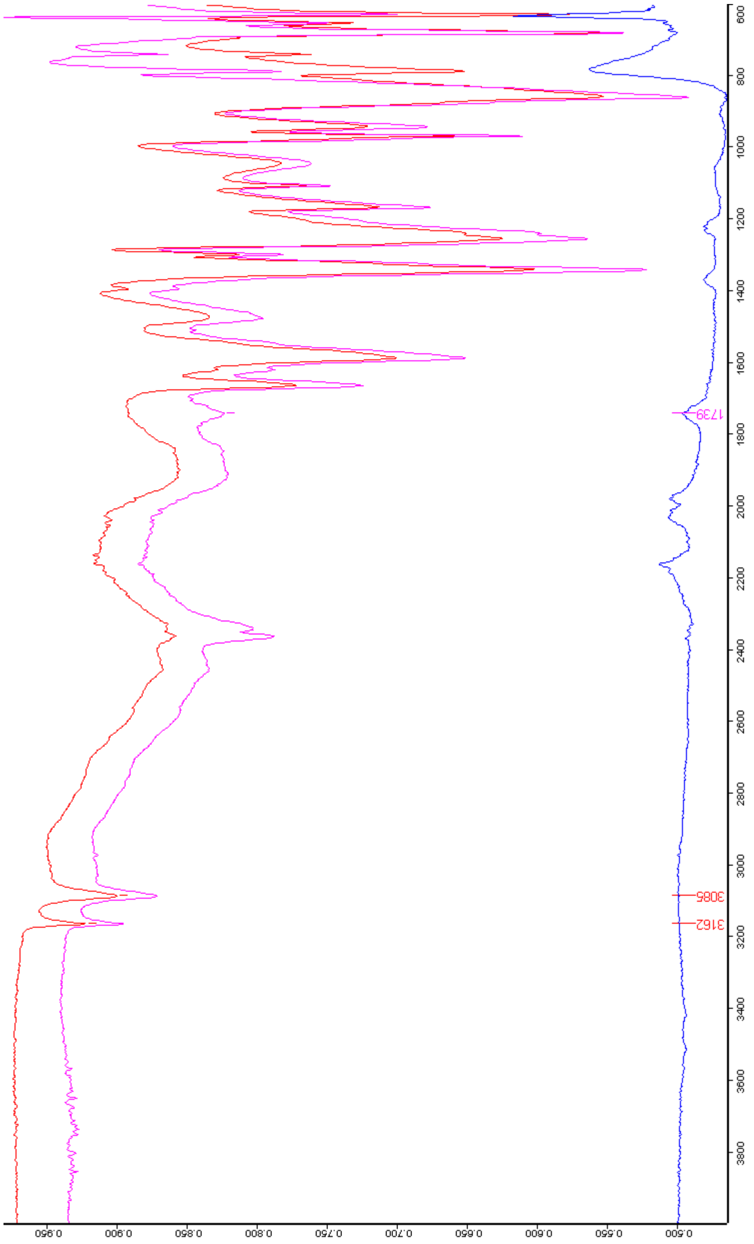
The red spectrum is the urocanic acid and the blue represents the copper (II) acetate. The purple spectrum is that of the reaction mixture, which is clearly just an overlapping of the starting materials. Thus, no reaction occurred.

Figure 23 - Urocanic acid and copper sulfate



The red spectrum is the urocanic acid and the blue represents the copper (II) sulfate. The purple spectrum is that of the reaction mixture, which is clearly just an overlapping of the starting materials. Thus, no reaction occurred.

Figure 24 - Urocanic acid and copper bromide



The red spectrum is the urocanic acid and the blue represents the copper (II) bromide. The purple spectrum is that of the reaction mixture, which is clearly just an overlapping of the starting materials. Thus, no reaction occurred.

3.3 XPD traces

All of the x-ray powder diffraction traces were collected on Bruker AXS D8 Focus from 5 to 45 2θ with 0.05 step size and 2 seconds per step. The XPD traces are harder to follow the reaction progress but over time it is clear that the product is fundamentally different than the starting materials. If it was simply a mixture of the starting materials, the XPD would be an overlay. As shown in the following traces (Figures 26-29), the peaks where 2θ is 36.5 and 39 disappear over the course of the week long experiment, which indicates the formation of the product. Also, Figure 25 explains the color scheme for all of the XPD spectra and includes a picture of the final product.

Figure 25 - Urocanic acid – copper MOF reaction

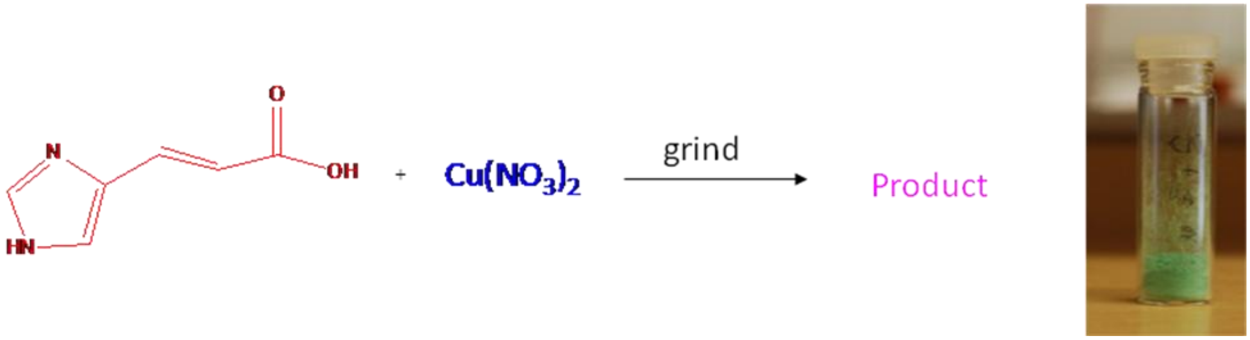


Figure 26 - Initial mixing of copper nitrate and urocanic acid

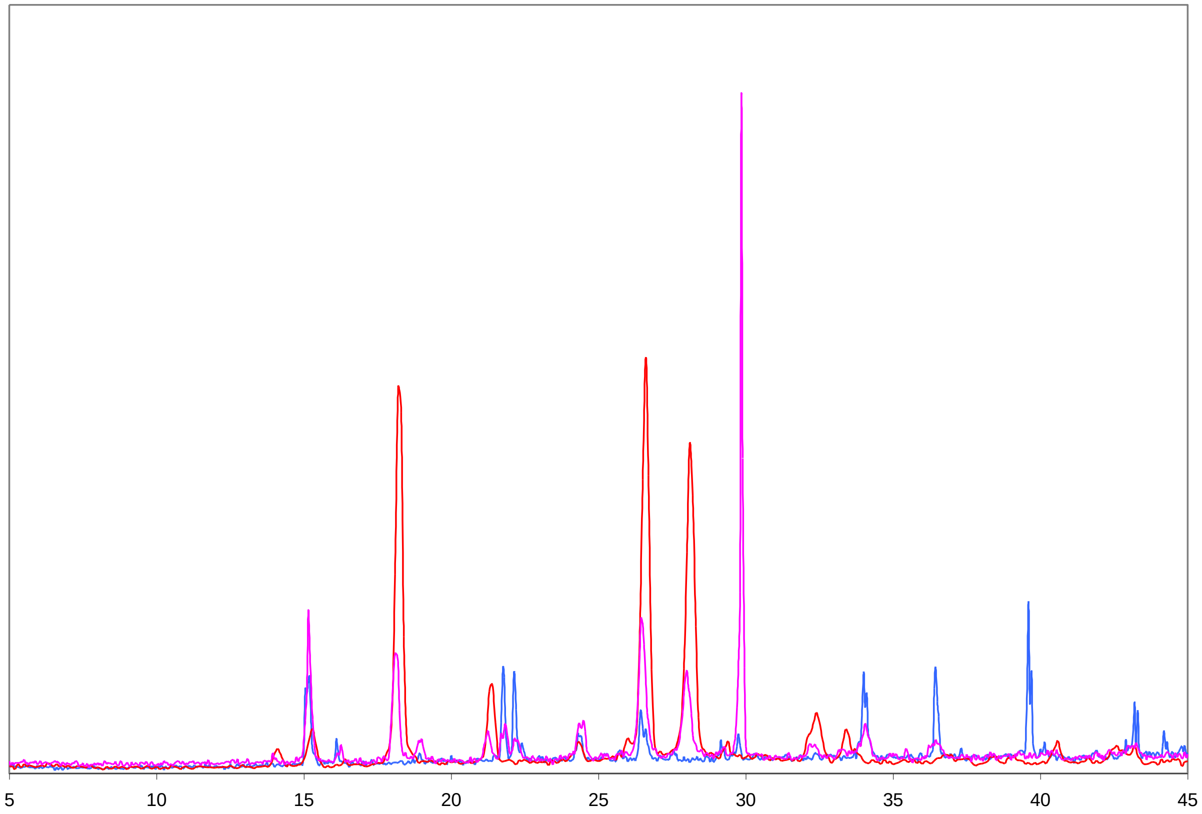


Figure 27 - 24 hours after initial mixing of copper nitrate and urocanic acid

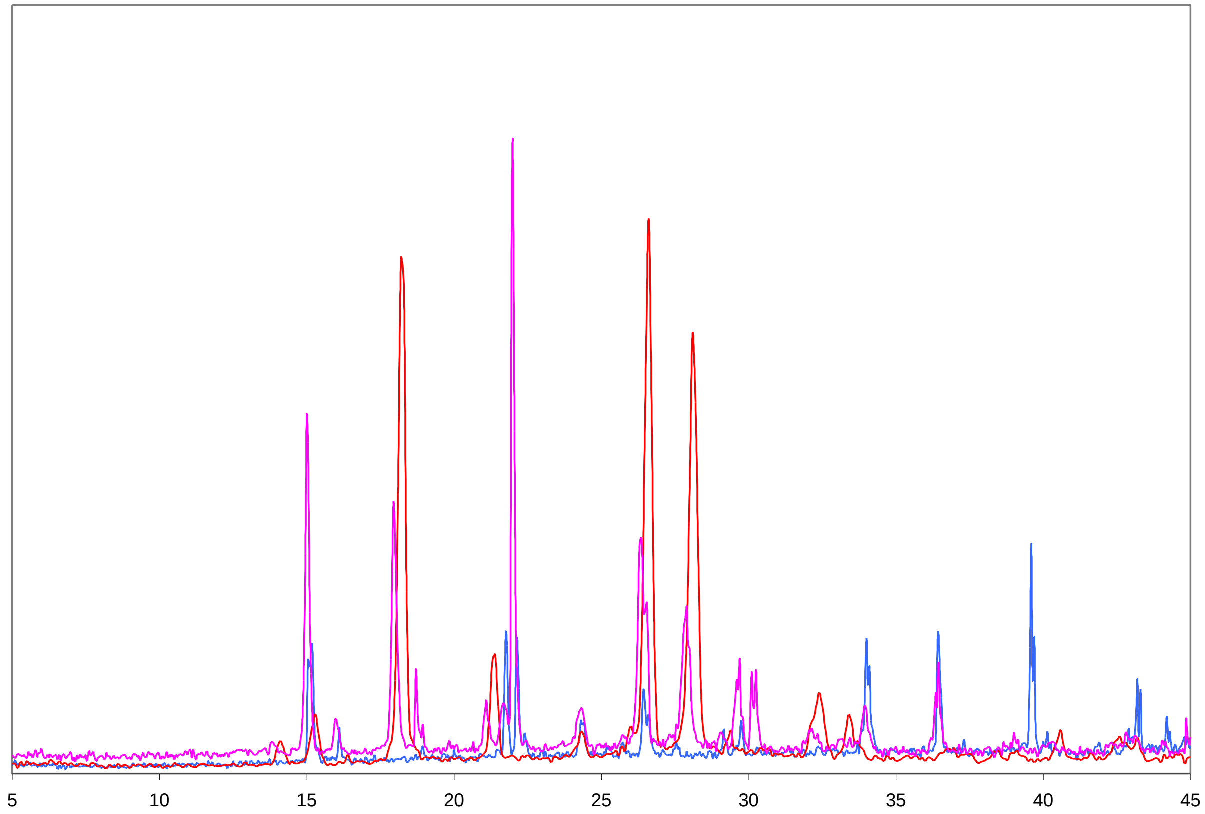


Figure 28 - 48 hours after initial mixing of copper nitrate and urocanic acid

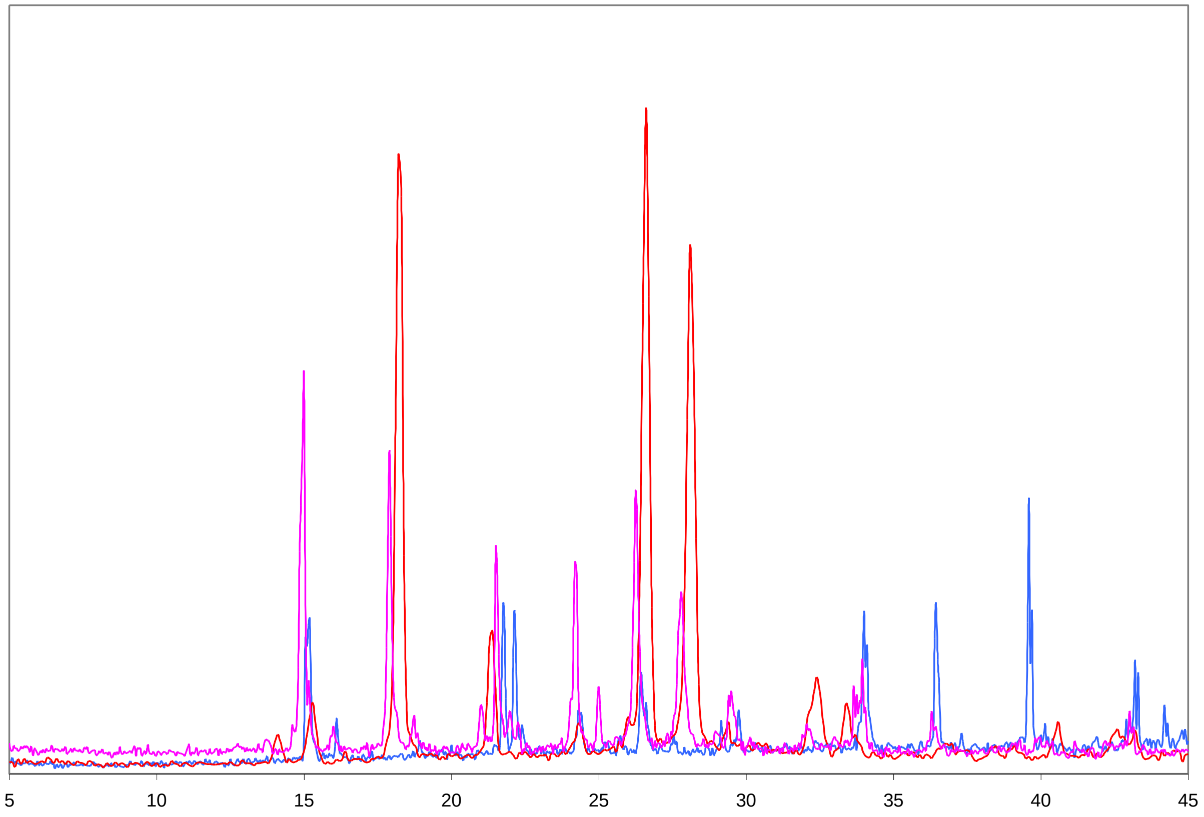
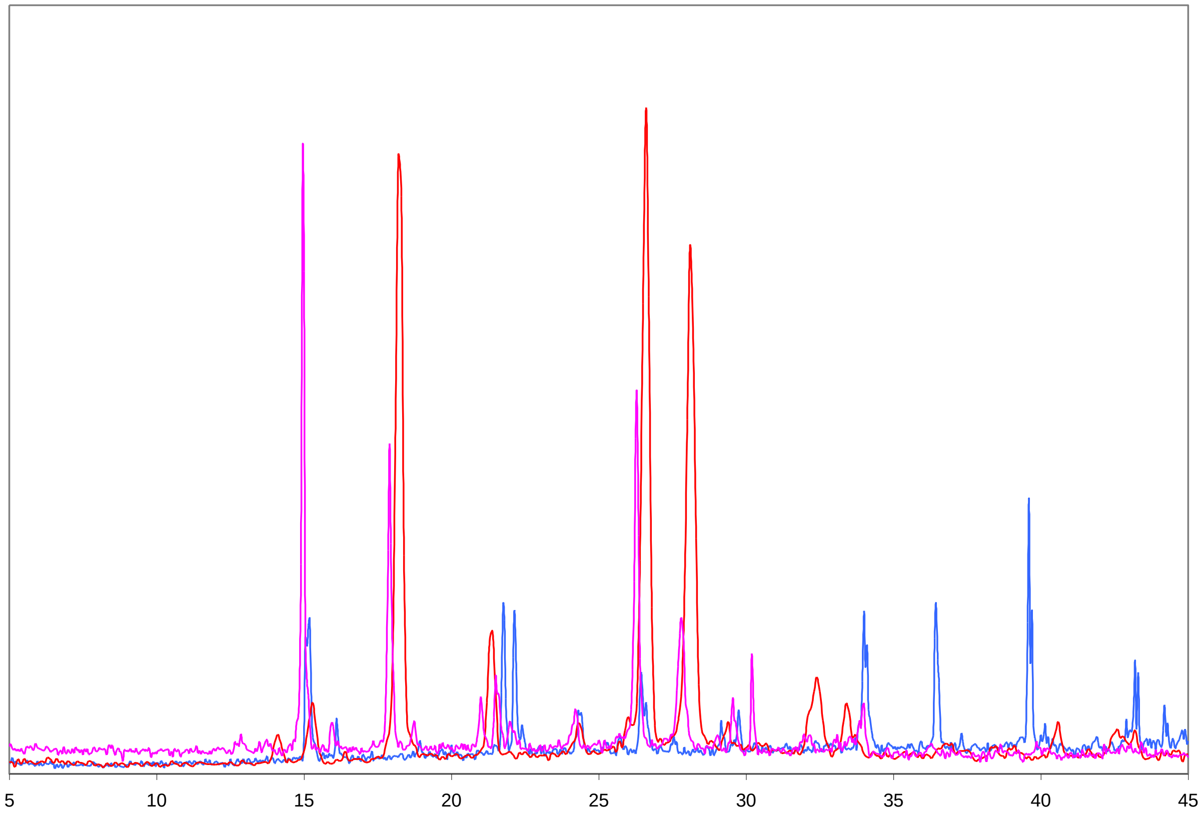


Figure 29 - Urocanic acid - copper MOF

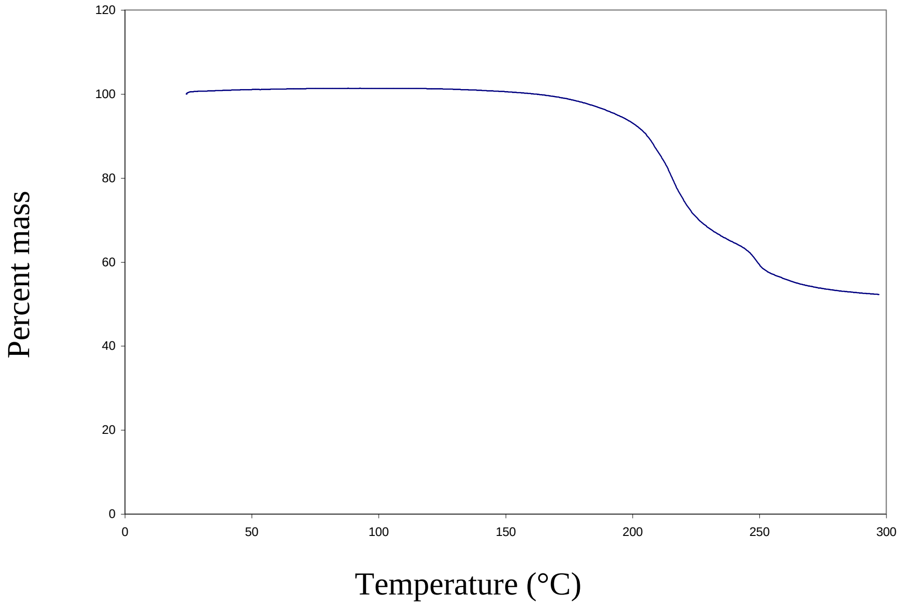


This trace is from the final product of the reaction between copper (II) nitrate and urocanic acid taken 7 days after the initial mixing. Note the disappearance of the peaks where 2θ is 36.5 and 39 over time indicating the formation of the product.

3.4 TGA

All of the TGA data was collected on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer. Figure 30 is a TGA of the product from the reaction between copper (II) nitrate and urocanic acid was taken after 7 days from the initial mixing.

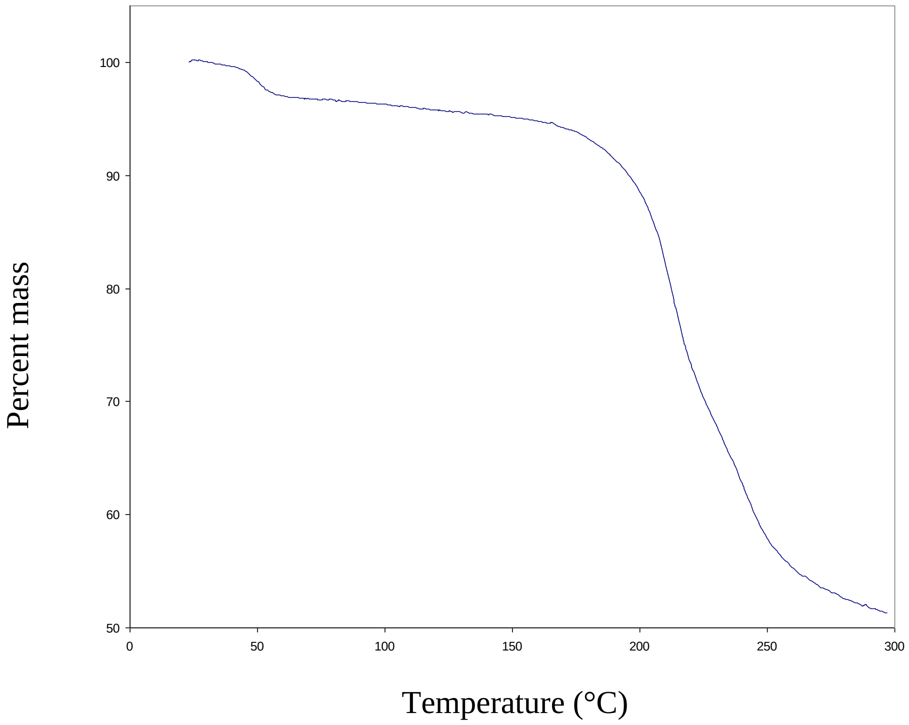
Figure 30 - TGA data for urocanic acid - copper MOF



It indicates that there is no weight loss until around 200°C, which is due to the decomposition of the ligand. The lack of weight loss also indicates that there are no guest molecules trapped in the framework of the MOF initially.

After the week long hydration experiment, another TGA (Figure 31) was taken of the powder.

Figure 31 - TGA data for urocanic acid - copper MOF after week long hydration



As indicated by the graph, there is ~3% weight loss, which indicates that the MOF is most likely non porous. It could be hydrogen bonded or possibly bound directly to the metal.

4. Conclusions

The goal of this project was to examine possible MOFs made by combining urocanic acid with various metals. Initially the metals were lanthanides hydrothermally because of their possible use as a sensor but all attempts failed. Room temperature synthesis using lanthanides also failed and transition metals were used hydrothermally with no results as well. Room temperature synthesis with transition metals failed as well and solid-state grinding was attempted using copper (II) nitrate. The powder generated from the grinding has been determined to be a MOF through IR and XPD analysis. There is no single-crystal data available so the exact structure of the MOF is not known. The effect of different anions was also tested and proved to have a great impact on the reaction as shown by IR analysis.

5. References

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6. Appendix

6.1 IR Spectra

Figure 32 - Copper acetate

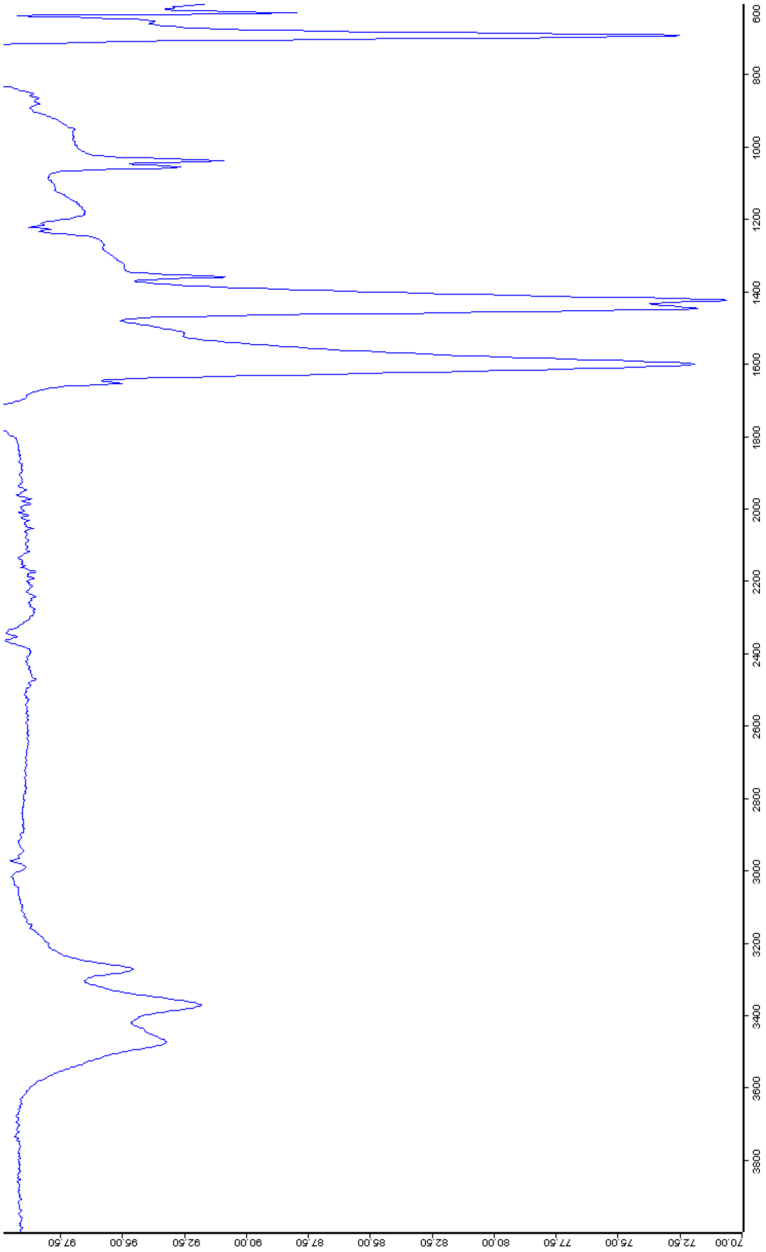


Figure 33 - Copper bromide

Figure 34 - Copper nitrate

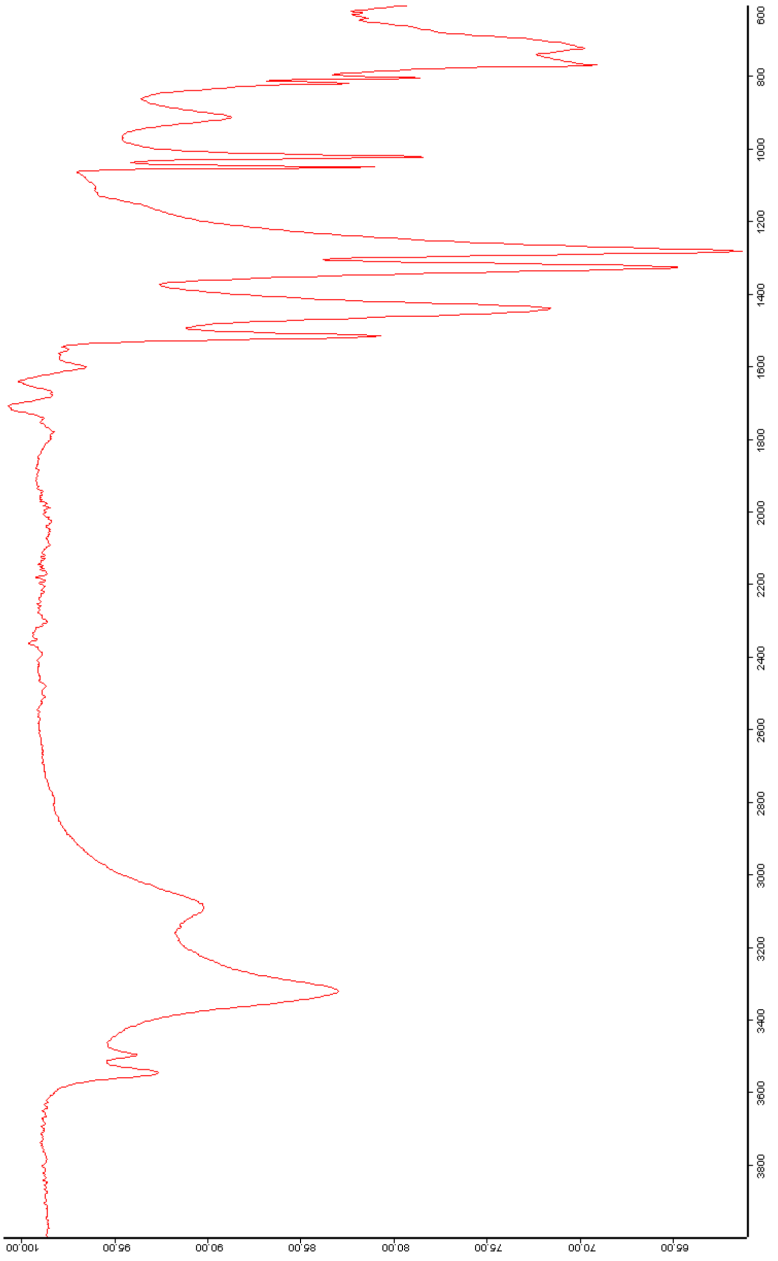


Figure 35 - Copper sulfate

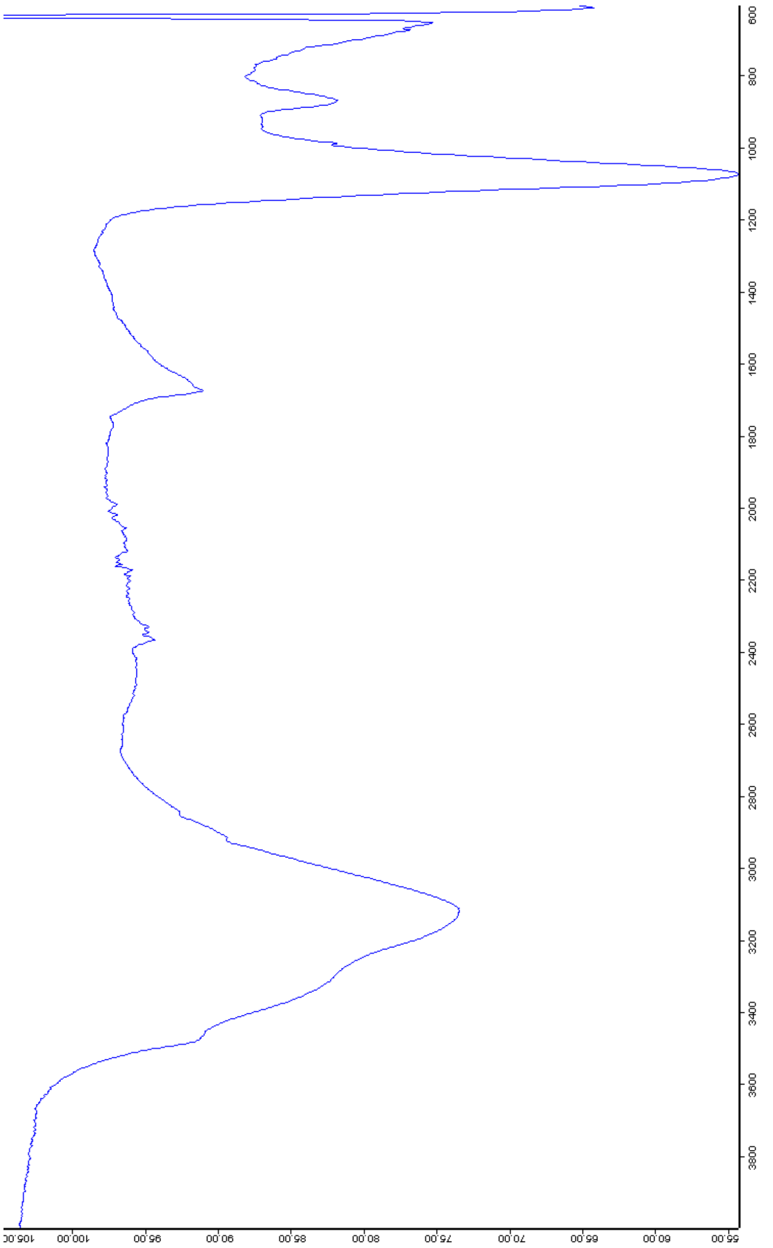
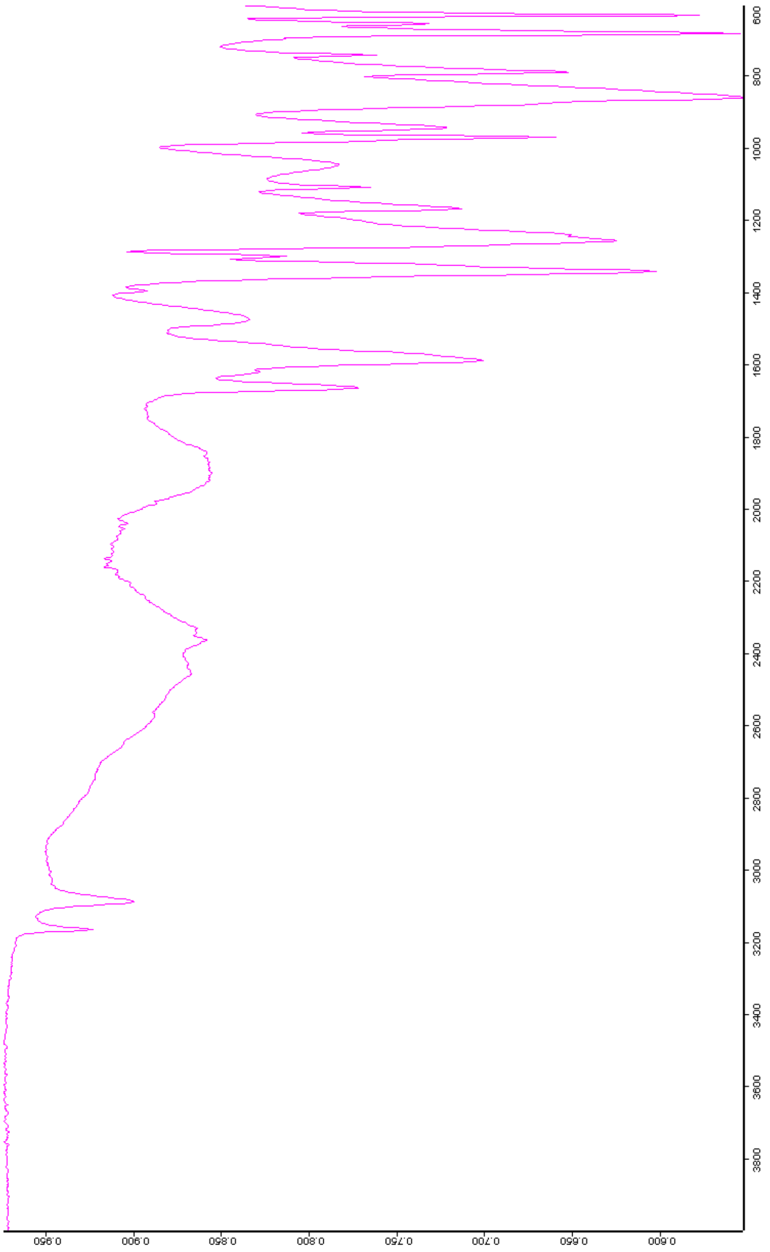


Figure 36 - Urocanic acid



6.2 XPD traces

Figure 37- Urocanic acid

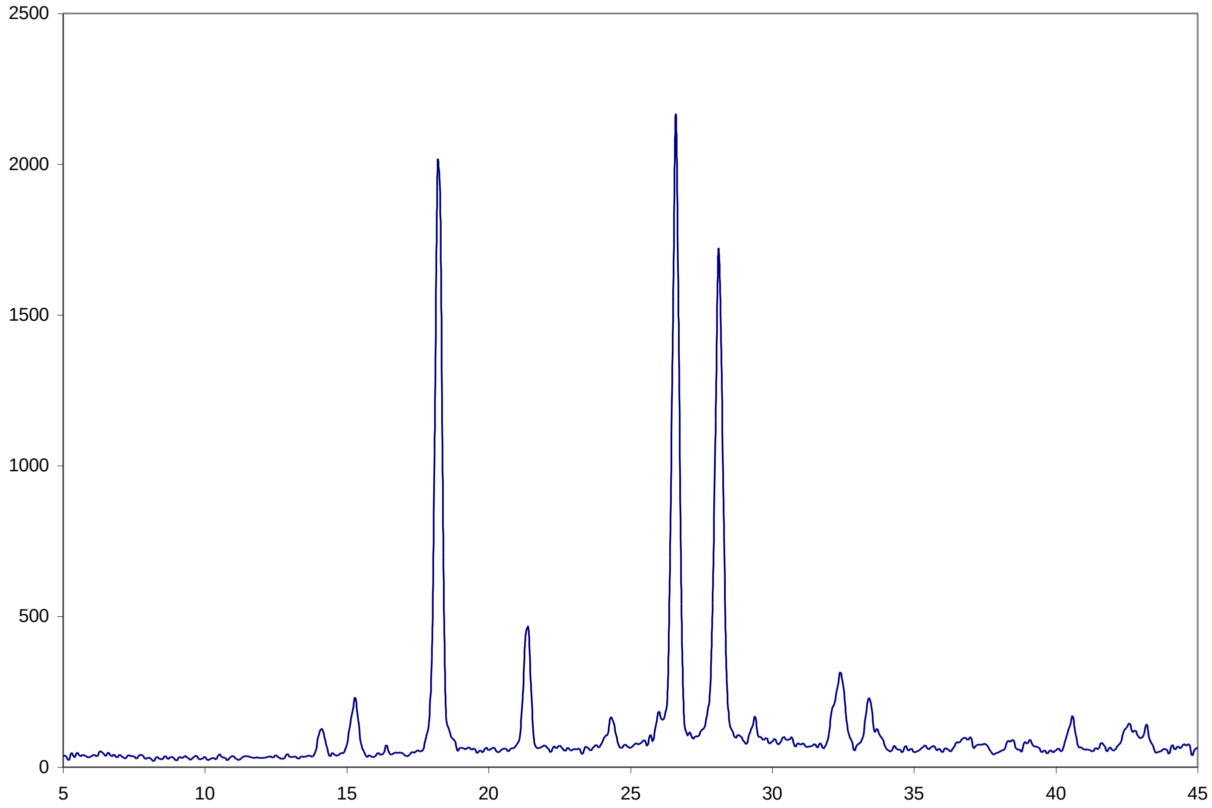


Figure 38 - Copper sulfate

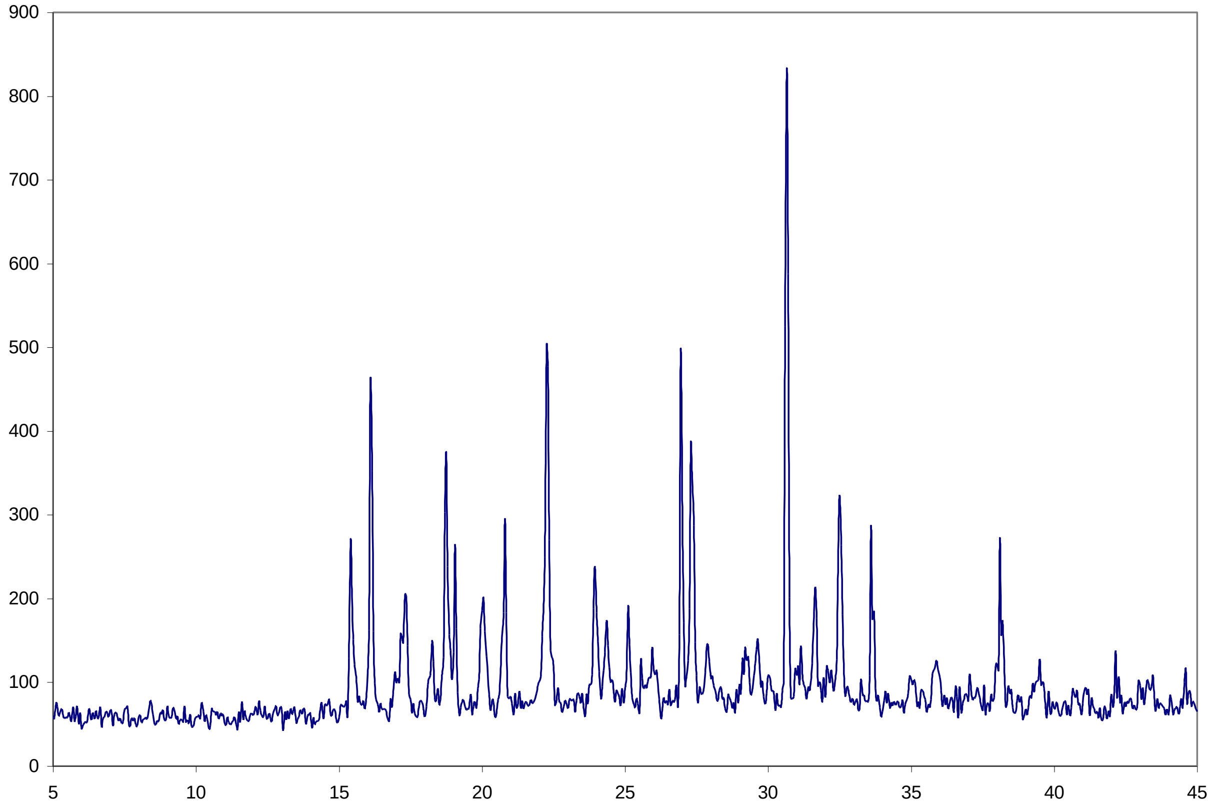


Figure 39 - Copper acetate

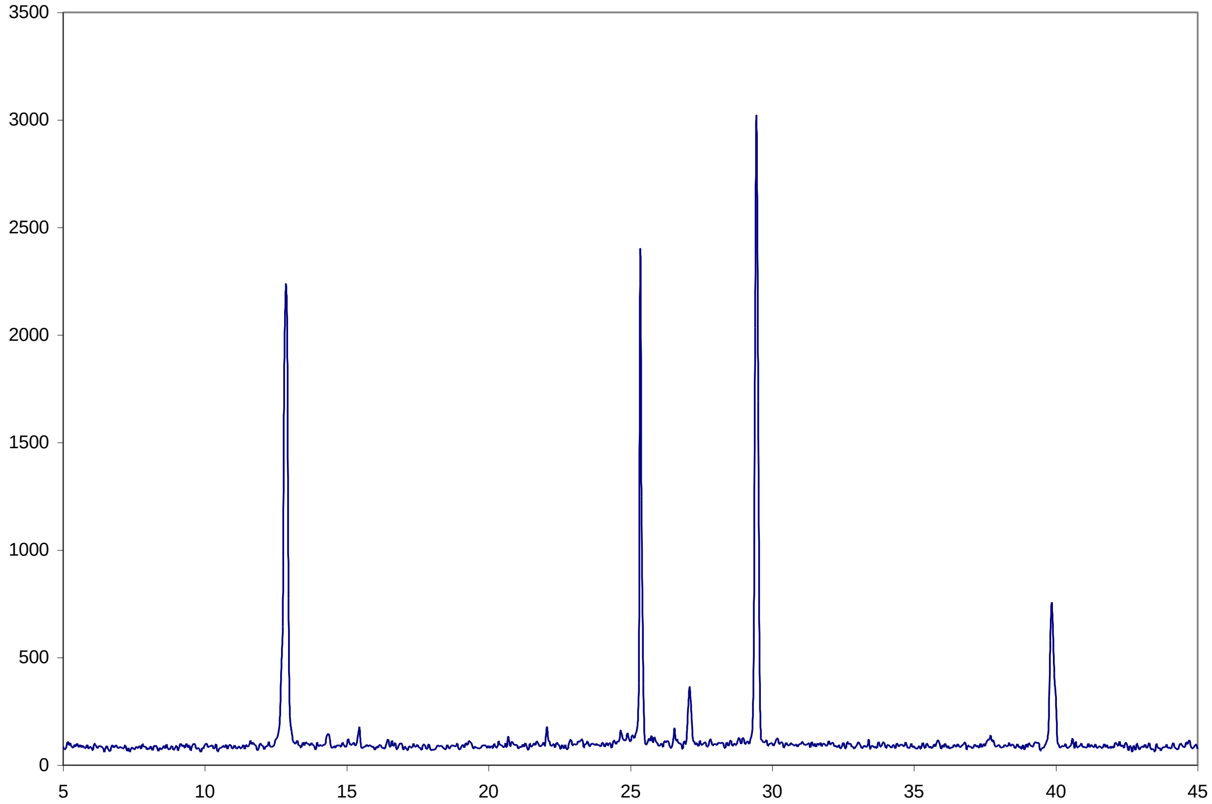


Figure 40 - Copper bromide