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A POROUS METAL-ORGANIC FRAMEWORK BASED ON BIS[4-(IMIDAZOL-1-YL)BENZOATE]CU(II)

A Major Qualifying Project Report:

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By

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Abstract

We are investigating the design of porous crystalline solids based on metal-organic frameworks (MOFs) composed of organic molecules and metal ions. MOFs derive their porosity by forming channels that permeate the crystal. As such, MOFs represent an important new class of functional materials that show fantastic potential for a range of applications that include storage of gases (e.g., hydrogen), delivery of drugs, catalysis of organic reactions, and molecular separations. To date, research on MOFs has focused primarily on using dicarboxylic acids as the organic component. Consequently, there is a need to explore organic ligands other than dicarboxylic acids in an effort to develop new MOFs that exhibit porous behavior. Toward that goal, we have prepared and investigated a novel MOF utilizing 4-(imidazol-1-yl)benzoic acid and Cu(II) ions. Here we report the synthesis, structure and porous properties of this system.

Acknowledgements

I would to thank Professor John C. MacDonald of the Chemistry and Biochemistry Department at Worcester Polytechnic Institute in Worcester, MA for all his help and time advising me in this project. I also wish to thank his graduate students Lisa Lee and Pranoti Navare for their help and guidance.

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1. Introduction

In recent years the study of metal-organic frameworks (MOFs) has received considerable attention due to the functional utility of MOFs as materials for applications in a variety of fields.[1] MOFs are three-dimensional coordination polymers consisting of metal ions bonded to organic linkers, called ligands, which create rigid frameworks permeated by open channels. These molecular frameworks have structures analogous at a macroscopic level to the skeletal steel frameworks used to construct buildings. Scientists are especially interested in the inherent porous nature of MOFs and to better understand the ability of these materials to adsorb and release molecules. To date, the majority of MOFs that have been studied rely on ligands consisting of symmetrical dicarboxylic acids that form cubic frameworks. As such, there is a need to develop and investigate new types of ligands that generate MOFs with alternative architectures (e.g., diamond).

Toward this goal, this project focused on creating new frameworks by using ligands other than dicarboxylic acids. This research focused on the ligand 4-(imidazol-1-yl)benzoic acid. We focused on this ligand for the following reasons: (1) imidazole and carboxylic acid functional groups are known to bind to transition metal ions strongly through monodentate and bidentate coordination, respectively; (2) the ligand features a rigid backbone; (3) the imidazole and carboxylic acid groups are oriented in a slightly bent arrangement at opposite ends of the ligand. The hope was that this ligand would coordinate to Cu(II) metal ions in a tetrahedral packing arrangement that, in combination with the curvature of the ligand, would lead to frameworks with a diamond architecture. Unlike cubic structures, which have linear channels exposed at six open faces for solvent to enter, these diamond structures have nonlinear channels exposed at four open faces for solvent to enter. We expected that such diamond frameworks would result in larger channels that would impart greater overall porosity than cubic frameworks.

Larger pores in the structure would be beneficial for several reasons. Currently hydrogen gas is stored under high pressure in thick-walled vessels; if MOFs can be developed that feature large surface areas and pore volumes, greater amounts of hydrogen gas can be stored under a lower pressure.[2] Thus, solid materials constructed from diamond MOFs would be safer due to the reduction in pressure and also less expensive because they would not have to be stored in thick-walled containers. With larger cavities it would be possible to create sensor materials useful for detecting organic compounds used as explosives.[3] Thus, one of our goals was to develop porous MOFs with channels large enough to absorb nitrated aromatic compounds used commonly as explosives such as trinitrotoluene.

2. Background

MOFs are just one of several different types of porous materials currently being developed. The sections that follow introduce different types of porous materials, highlight some differences in these materials compared to MOFs, and provide background information on why we chose to work with MOFs and our specific ligand.

2.1 What are Porous Materials?

Porous materials such as those shown in Figure 1are solids that have holes and channels worked into their structure allowing gases and liquids to pass through.[4] Zeolites are one of the oldest known porous materials and are believed to have been discovered in

1756 in Sweden.[5] “Zeolites are hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra (T = tetrahedral atom, e.g., Si, Al); each apical oxygen atom is shared between two adjacent tetrahedra. The term tectoaluminosilicate designates that all the oxygen atoms bridge two tetrahedral atoms. [5]

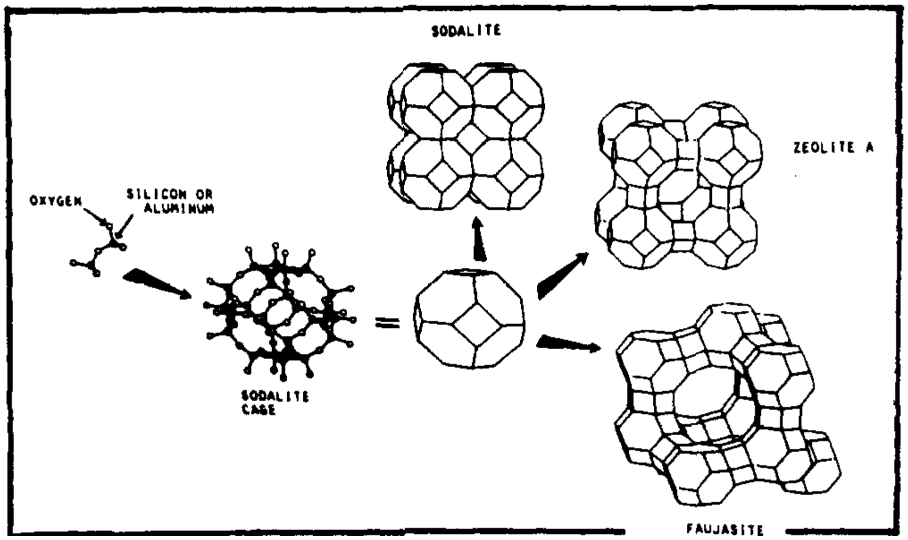

Figure 1: Schematic of Zeolite Frameworks

This figure taken from Davis and Lobo shows us that zeolites form a cage-like structure. While these cavities may have a large volume, the openings are significantly smaller and therefore could not fit large molecules but many small molecules. These materials differ from MOFs in that zeolites are composed of Group I and II metal ions (Li, K, Be, Mg etc), whereas MOFs generally include transition metals (Cu, Zn, Co) and lanthanide metals (Eu, Tb, etc). Zeolites are also capable of ion exchange which makes them appropriate for use in laundry detergents and water softeners removing unwanted ions in the water.[6] Molecular sieves are zeolites that have much smaller pores (4-13 Å).[5]

These materials are typically used in molecular separations of small molecules by selecting an appropriate sieve with an adequate pore size to bind a particular molecule such as water.

The structures and stability of MOFs can vary considerably depending on the nature of the interactions between molecules in the frameworks. For example, MOFs involving hydrogen bonding have been investigated, but have not received much attention. Omar Yaghi's group was successful in synthesizing a MOF using 1,3,5-benzenetricarboxylic acid that contained covalent bonds and also 56 hydrogen bonds per formula unit of material.[7] Even though this MOF featured small pores, 4-5 Å, it was demonstrated that guest solvent could be reversibly added and removed without changing the original framework.

2.2 Examples of Metal-Organic Frameworks

MOFs generate considerable attention in the science community because of their potential for gas storage and molecular sensors. Researchers today are looking towards hydrogen fuel cells as the future for production of energy. Development of fuel cell technology for commercial use has been difficult to accomplish because the only feasible way to store hydrogen gas is to compress it under high pressures in thick-walled cylinders. There is some evidence that MOFs will allow higher densities of hydrogen gas to be stored in containers packed with MOFs by binding hydrogen gas at free metal-binding sites within the structure making the gas more ordered and thus occupying less volume. Yaghi also demonstrated that by using different organic linkers to connect the metal ions, the dimensions of pores could be controlled predictably to create MOFs with a range of porosity.[8] The porosity and ability of those frameworks to store hydrogen gas was characterized by measuring how much methane they could reversibly absorb. Examples of several MOFs composed of zinc complexes with dicarboxylic acids developed by Yaghi are shown in Figure 2. This work established that cubic frameworks with a range of dimensions could be created and enlarged using the same template with a range of substituted benzenes (bottom row in Figure 2). This strategy provides new avenues for binding and linking a structurally related family of ligands not previously studied. The extreme to which the size of pores could be increased is illustrated by the MOFs shown in the top row of Figure 2, where the remarkable pore at the far right features an interior diameter of 28.8 Å and has 91.1% free volume.[8]

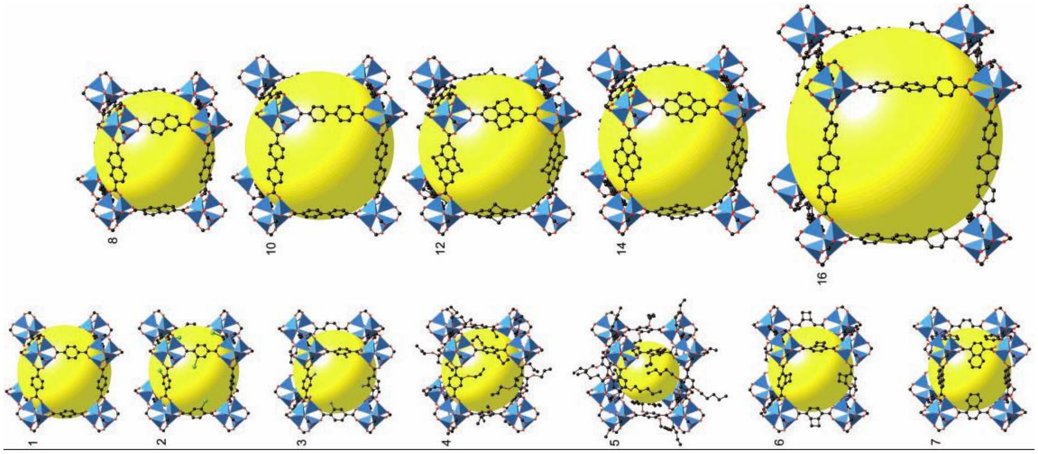

Figure 2. Single crystal x-ray structures of MOF-n (n=1-7, 8,10, 12, 14, 16).[8]

Another application that has benefited from MOFs is molecular catalysis. Catalysis within a MOF necessarily requires that the MOFs selectively bind a molecule of reactant in the pores of the framework in an arrangement that allows another molecule to react with it. Catalysis in this manner was shown in the research done by So-Hye Cho's group.[9] Utilizing a MOF called (R,R)-(2)-1,2-cyclohexanediamino-

N,N9-bis(3-tert-butyl-5-(4-pyridyl)salicylidene)MnIIICl, shown in Figure 3, they were able to catalyze the enantioselective epoxidation reaction shown in Figure 4. It was observed that without the MOF the reaction ceased after several minutes and stopped after several hours. A drastic increase in the amount of product formed was observed in the presence of the MOF when the reaction was stopped after three hours. The catalyst could be recycled for additional runs with no decrease in the enantioselective properties and only a slight loss in activity.[9]

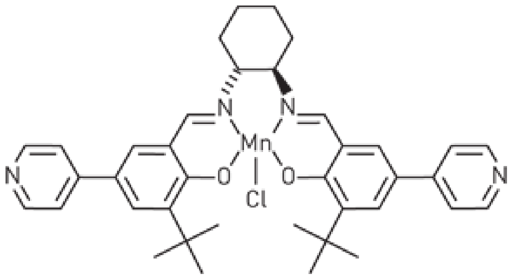

Figure 3. MOF with paddlewheel structure used in catalysis.

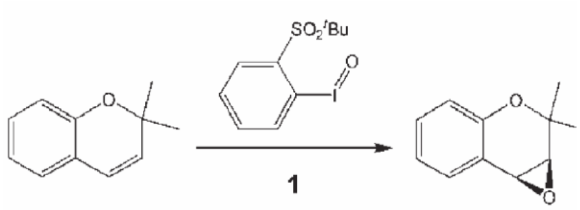

Figure 4. Reaction catalyzed by paddlewheel MOF.

One last application of MOFs is the design of sensors that respond optically or physically to presence or absence of guest molecules in the channels. For example, Stefan Kaskel used the MOF consisting of benzenetricarboxylic acid and copper ions as shown in Figure 5. They discovered that there were water molecules bound to the axial sites of the copper ions, and that once the water was removed under vacuum, the copper ions could bind other molecules in the cavity. During this process it was observed that the crystals changed color from light to dark blue when the water molecules were removed by heating in a vacuum and then finally to a brilliant blue when benzaldehyde was introduced.[10] One of our aims in this research is to develop a MOF that shows similar behavior in the presence of nitrated aromatic molecules in order to develop new types of sensors to detect explosives.

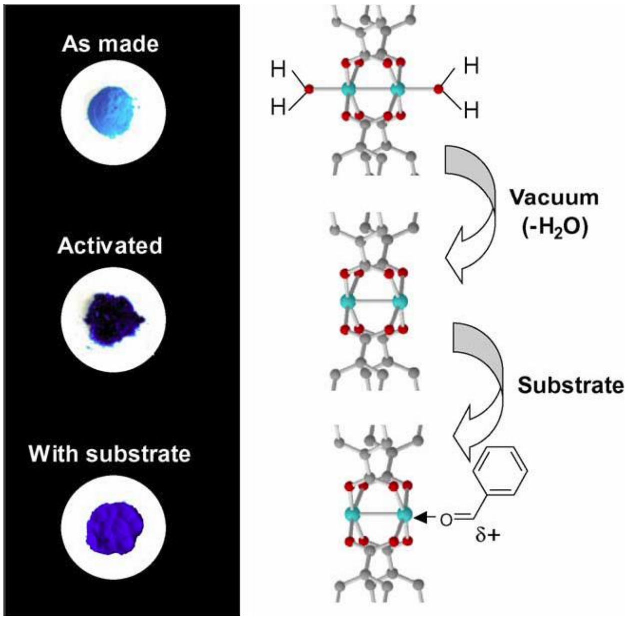

Figure 5. Color changes when dehydrating and re-solving a MOF.[10]

3. Strategy for Selecting a New Organic Ligand to Obtain Non-cubic MOFs

We chose to focus on preparing porous solids composed of MOFs instead of zeolites because MOFs exhibit significantly larger pore volumes that can accommodate large organic guests.[11] In addition, MOFs offer the advantage that the structure and properties of the organic linker can be tailored easily through organic synthesis. Considering the variety of organic ligands that are known, the most variable part of creating a MOF is selecting an appropriate organic ligand to link the metal ions. The choice of ligand is particularly important because the structure and length of the ligand will directly affect the size and architecture of the framework. Figure 6 illustrates just a few examples of organic ligands that have been utilized in synthesizing MOFs.[6] Each of those ligands contains nitrogen atoms or carboxylate groups that bind to an available metal ion. Features common to these linkers are that they are either symmetrical or the binding sites are in a linear orientation. Ligands with this linear orientation are known to generate square planar or cubic MOFs in the presence of transition metal ions. Many MOFs reported in the literature have a cubic architecture composed of orthogonal intersecting channels exposed at the faces of the cube through which guest solvents can pass. Consequently, we specifically sought to investigate newer architectures for MOFs based on diamond motifs that have fewer openings but larger pore volumes.

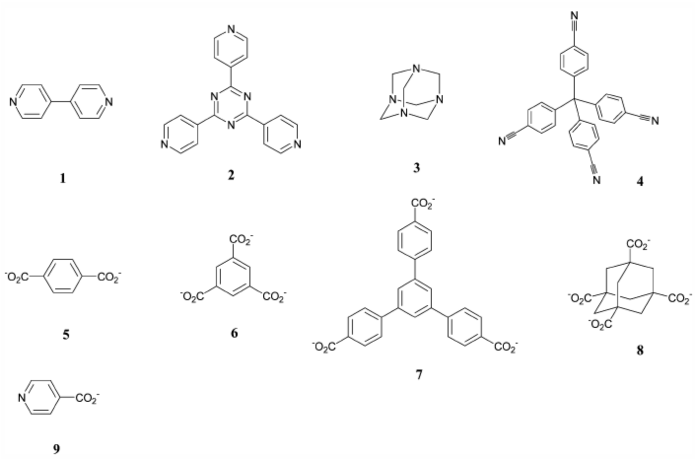

Figure 6. Examples of Rigid Ligands Used in the Synthesis of Coordination Polymers.[6]

Previous work in our group suggested that 4-(imidazol-1-yl)benzoate was a good candidate for that purpose. The structure of that ligand is shown in Figure 7 4-(Imidazol-1-yl)benzoate features a carboxylate group that can act as either a monodenatate or a bidentate binding site and a nitrogen atom on the opposite side acting as a monodentate binding site. The orientation of the imidazole group at one end with the nitrogen atom aligned off-center from the long axis of the molecule necessarily creates a slight bend in the molecule between the binding sites, highlighted by the red lines in Figure 7. Considering that carboxylate groups most commonly bind to metal ions via bidentate coordination, we expected 4-(imidazol-1-yl)benzoate to bind a metal ions such as copper(II) in one of two arrangements, shown in Figure 8. The arrangement on the left with the four oxygen atoms coplanar necessarily leads to a 2-D MOF forming a square grid, while the arrangement on the right where the four oxygen atoms are not coplanar creates a distorted tetrahedral geometry that necessarily leads to a 3-D MOF with a diamond motif.

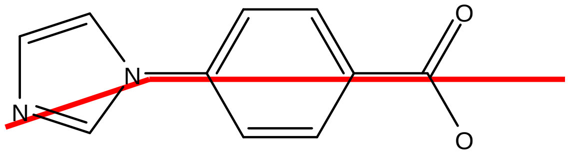

Figure 7. Structure of 4-(imidazol-1-yl)benzoate showing curvature in binding sites

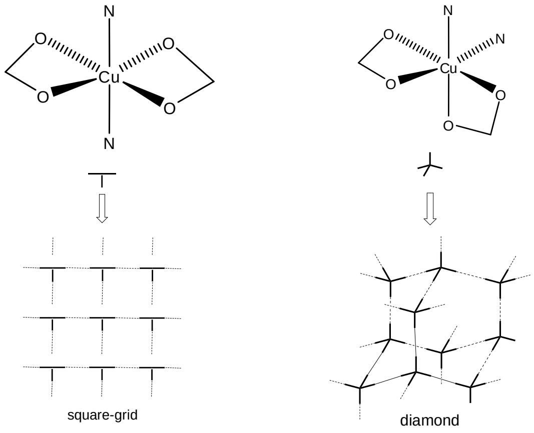

Figure 8. Illustration of 2-D square grid MOFs or 3-D diamond MOFs that can result from coplanar or non-coplanar coordination of carboxylate groups to copper(II).

The next step in designing a MOF was to select a metal ion that can bind carboxylate and imidazole groups in one of the two octahedral binding arrangements shown in Figure 8. Copper(II) was attractive because it is known (1) to coordinate strongly to imidazole and carboxylate groups; (2) to coordinate ligands in octahedral as well as square pyramidal and tetrahedral arrangements; and (3) to form stable coordination complexes under ambient conditions when exposed to air. Given these properties of copper(II), our goal was to react copper(II) with 4-(imidazol-1-yl)benzoate in the hope of generating a framework that would resemble the 3-D diamond motif shown in Figure 8.

4. Statement of Goals

The main goal of this research was to determine if it was possible to obtain a crystalline porous framework utilizing 4-(imidazol-1-yl)benzoate and Cu(II). Once synthesized the next step would be to determine the molecular building block and crystal structures using single crystal X-Ray diffraction and see if they match the predictions from Figure 8. From this diffraction it would be possible to see what solvent, if any, is present in any existing pores. Thermogravimetric Analysis could then be performed to determine how much solvent the framework contains followed by another single crystal or powder X-Ray analysis to see if the framework withstands guest loss. If the framework is stable enough to lose guest it is possible to see if it can re-absorb guest and in what amounts.

5. Experimental

5.1 Materials and Methods

Copper(II) nitrate trihydrate was purchased from Acrōs Organics. The 4-(imidazol-1-yl)benzoic acid ethyl ester was synthesized by Yu Wang, a post doctoral fellow in the MacDonald group. 200 Proof ACS/USP Grade ethanol was purchased from Pharmco-AAPER. A Yamato DKN 400 Mechanical Convection Oven was used to carry out hydrothermal synthesis of all products. TGA data was collected on a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) under a nitrogen atmosphere at a rate of 10°/min. Single crystal X-Ray data was collected using a Bruker AXS Kappa Apex II with a Mo source. The X-Ray Powder data was collected with a Bruker AXS D8 Focus with a Cu source.

5.2 Synthesis and Crystallization of Bis[4-(imidazol-1-yl)benzoate]Cu(II) (MOF-1)

Synthesis of bis[4-(imidazol-1-yl)benzoate]Cu(II), hereafter referred to as MOF-1, and subsequent crystallization of the MOF-1 were carried out according to the following procedure. A 150 mL thick-walled high-pressure reaction flask was equipped with 0.108 g (0.005 mol) of ethyl 4-(imidazol-1-yl)benzoate and 0.0604 g (0.0025 mol) of $Cu(NO)_2$ trihydrate in 100 mL of 1:1 ethanol/water (v/v) and sealed. The solution was then placed into a programmable oven and heated to 120 °C over 3 hours, held at 120°C for 48 hours, and then cooled to RT over 24 hours. The resulting clear solution contained light blue needles approximately 1/10th of a millimeter in length when removed from the oven. Dark blue crystals (MOF-1) formed slowly in solution when the flask was left unopened and undisturbed at RT over two weeks. The crystals were left in solution to prevent loss of solvent in the event that crystals formed porous MOFs. The light blue and dark blue crystals were separated by hand and then isolated and dried briefly on filter paper immediately prior to characterization.

The light blue and dark blue crystals were characterized by optical microscopy to determine the homogeneity of individual batches of crystals. The light blue crystals formed thin tiny needles too small to be suitable for single crystal structure determination using X-ray diffraction. The dark blue crystals formed plate-like crystals approximately 1/5th mm in length and roughly the same width. Upon removal from solvent, the light blue crystals did not change in appearance, while the dark blue crystals developed cracks, became very brittle, and began turning a lighter blue color at the exposed outer regions within several minutes.

To evacuate guest from crystals, samples of roughly 4 mg were placed on a TGA pan and heated to 170ºC at a rate of 10º/min. For resolvation experiments these evacuated crystals were taken from the TGA pan and placed on weighing paper in a Petri dish in a desiccator. The desired solvent was placed at the bottom of the desiccator, the container was closed and the air was pumped out using a vacuum. The crystals remained in this atmosphere either 1 week or 1 month until re-absorbed solvent loss could be measured in the TGA.

6. Results and Discussion

6.1 Crystalline Products

As in the experimental section, hydrothermal synthesis yielded two crystalline products; light blue crystals and dark blue crystals (MOF-1), shown in Figure 9. Initial experiments using 0.1 M of the ligand and 0.05 M of the metal yielded roughly equal amounts of light and dark blue crystals. Decreasing the concentrations by half yielded the dark blue crystals as the predominant product. The observation that the light blue crystals were immediately visible upon taking the vial out of the oven, while the larger dark blue crystals did not form in appreciable amounts until days later with no reduction in the amount of light blue crystals indicates that both products are stable, but that the light blue product is favored kinetically under the reaction conditions used. The fact that the relative ratio of light blue to dark blue crystals switched to favor the dark blue product by simply decreasing the concentration of the reactants indicates that the dark blue product likely is thermodynamically favored and that formation of the light blue product occurs first because that product is less soluble.

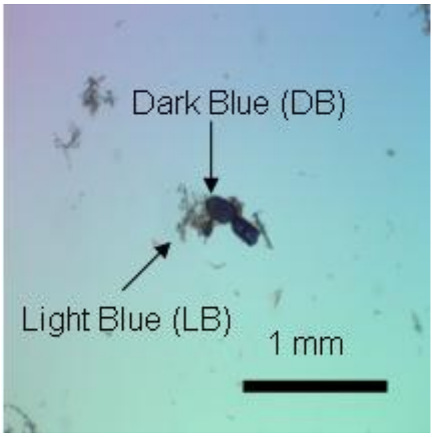

Figure 9. Picture of Light Blue (LB) and Dark Blue Crystals (DB).

6.2 Structure of MOF-1

As reported previously, single crystals of the dark blue product suitable for X-ray diffraction were isolated, X-ray data collected and the crystal structure solved. The unit cell data for the dark blue crystals is as follows:

Axis	Length	Angle
A	19.9773	90º
B	19.9773	90º
C	12.8187	90º

Table 1: Unit Cell data for DB crystal

This type of unit cell correlates to tetragonal packing because all the angles between axes are 90º apart and two of the lengths are equal. From the crystal structure, it was determined that ligand and Cu(II) reacted to form the coordination complex, bis[4-(imidazol-1-yl)benzoate]Cu(II), consisting of two ligands bound to the central Cu(II) ion. We found that hydrothermal synthesis effectively converted the ligand from the ethyl ester to the free carboxylic acid. Moreover, the crystal structure showed that the copper ion did not exclusively bind just oxygen or just nitrogen; it coordinated to them both. The carboxylate group formed two bonds with the metal on two sides and two nitrogen atoms formed one bond each. Thus, the ligands coordinate the central Cu(II) ion in an overall six-coordinate octahedral arrangement in which attached ligands are oriented in a distorted tetrahedral arrangement corresponding to the coordination shown on the top right in Figure 8. Contrary to the 2-D square grid packing predicted in the lower left of Figure 8, molecular packing in MOF-1 leads to a 3-D network with an unexpected structure rather than a 2-D network.

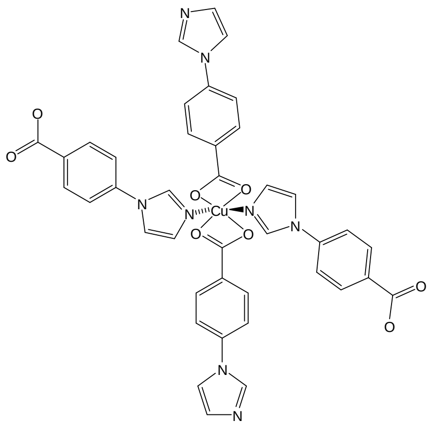

Figure 10. The binding arrangement of ligands around the central Cu(II) ion.

Shown in Figure 11 and Figure 12 are views of crystal packing that show the extended 3-D structure of MOF-1 that forms from the bis[4-(imidazol-1-yl)benzoate]Cu(II) building block (Figures 12a and 13a) and the void spaces (in yellow) that form open channels within MOF-1 (Figures 12b and 13b). Molecules of solvent trapped in the channels are not shown in these figures because it was too mobile in the pores to be resolved in crystal structure by X-ray diffraction. The shape of the channels shown in yellow in Figures 12b and 13b represents the solvent-accessible spaces where a spherical probe molecule with a 1.2 Å radius could fit. The crystal structure shows unambiguously that MOF-1 forms a 3-D coordination network with tetragonal symmetry. The resulting porous framework does not have a diamond structure as predicted, but rather features smaller symmetry-equivalent channels oriented along the a and b axes and larger channels oriented along the c axis in the crystal.

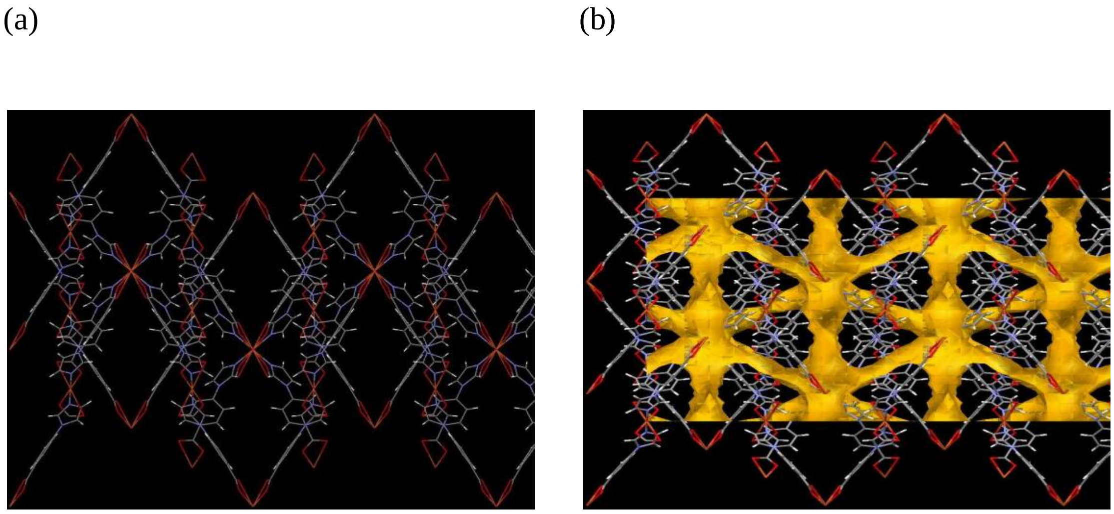

Figure 11. (a) Crystal packing looking down the a axis. (b) Void spaces of channels highlighted in yellow.

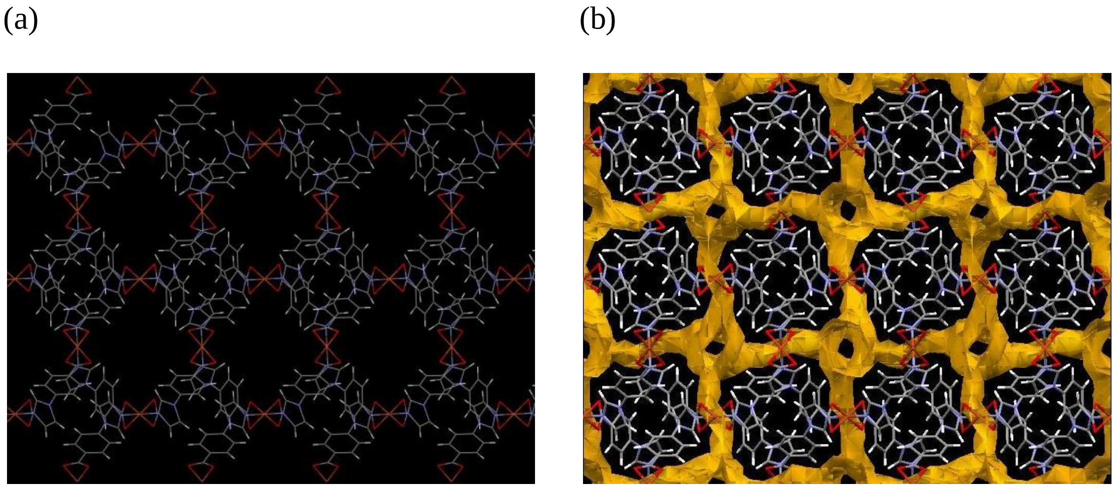

Figure 12. (a) Crystal packing looking down the c axis. (b) Void spaces highlighted in yellow.

6.3 Porous Behavior

Once we were successful in determining from the crystal structure that the dark blue crystals of MOF-1 had pores, we investigated the thermal behavior of both the light blue and dark blue crystals using thermogravimetric analysis (TGA) to determine if either material lost solvent as a function of heating, and to determine the relative percent mass of the bulk crystals contributed by guest solvent that was lost. Samples were removed from solvent, blotted dry and immediately placed into the TGA instrument, and heated from RT to 170°C at a heating rate of 10°C/min.

These spectra can be found in Figure 13. The results from the TGA experiments are summarized in Figure 17. The dark blue crystals lost 19-22% of their mass based on 5 different runs, whereas the light blue crystals lost no more than 4% of their mass. Using the molar masses of ethanol and water we attempted to fit the composition of the solvent lost to the experimentally determined loss of 19-22% mass in the dark blue crystals. A 19-22% loss corresponds to a loss of four molecules of water and one molecule of ethanol per building unit of the framework (i.e., 2:1 ligand:Cu). Close examination of the TGA traces revealed a change in slope after a 6% loss in mass. This change in slope can be explained by ethanol being lost initially at lower temperatures, 30-60ºC since ethanol boils at lower temperature than water and should form weaker intermolecular interactions within the channels of MOF-1 than molecules of water. One molecule of ethanol being lost equals a 6% loss in mass, which correlates well with the calculated solvent composition of 4:1 water/ethanol. Thus it appears reasonable that the initial loss of mass is a loosely bound ethanol in the structure leaving at lower temperatures. The light blue crystals lost 4% mass, which is a loss in mass too small to indicate a porous solid. Based on analysis of the molar mass of the building unit in MOF-1 (2:1 ligand:Cu(II)), it is likely that the light blue crystals form a nonporous hydrate.

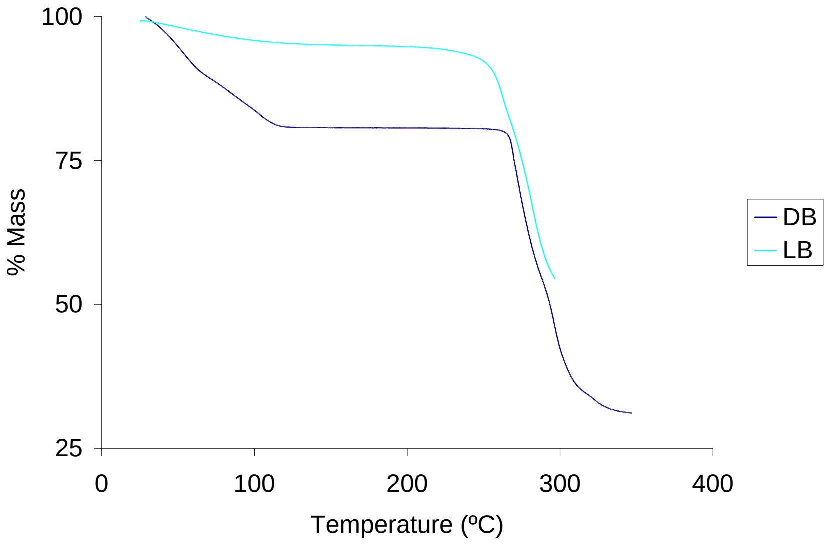

Figure 13: TGA data for LB and DB crystals

X-Ray Powder diffraction (XPD) data was collected on the dark blue crystals out of solution and after heating the sample to 170ºC to drive off all the guest solvent in order to determine if the framework could withstand losing guest. The XPD traces are shown in Figure 14. The XPD traces for the light blue crystals were also shown for comparison to the traces for the dark blue crystals after heating. This data shows that the dark blue crystals undergo a phase change to a new solid form that differs both from that of the dark blue crystals prior to heating and to that of the light blue crystals. These results indicate that MOF-1 likely undergoes a change in structure upon loss of solvent to a new MOF that differs in packing from that in the dark blue and also the light blue crystal. Attempts to collect single crystal X-ray data of this new form by taking a crystal from solution and heating it on the diffractometer were unsuccessful and showed that a single dark blue crystal either became polycrystalline or lost crystallinity upon loss of solvent

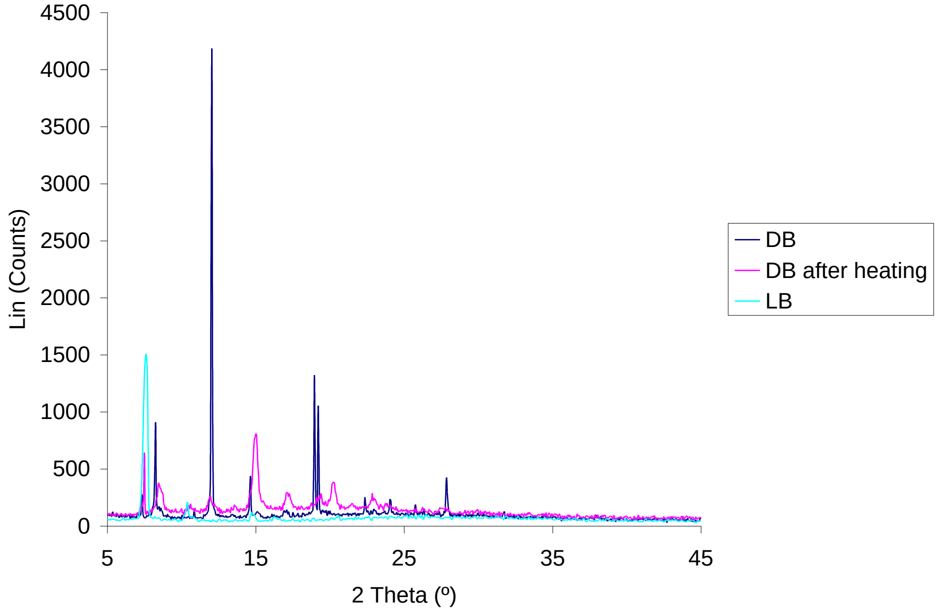

Figure 14: XPD data for DB, LB and DB after heating

6.4 Stability of the Dark Blue Crystals at RT

As stated previously, the dark blue crystals lost between 19-22% of their mass when heated. The exact loss in mass varied from run to run depending on how quickly the sample was dried and placed in the TGA instrument for analysis. We hypothesized that this range occurred because the crystals lose guest solvent quickly even at RT. To test this hypothesis, crystals were placed in the TGA and equilibrated isothermally at 25ºC and loss in mass was recorded as a function of time. The results of this experiment are shown in Figure 15. Surprisingly, the data clearly shows that the crystals lost 5% of their mass after only 15 minutes sitting at 25°C. These findings indicate that loss of solvent from the dark blue crystals begins immediately upon removal of the crystals from solution and that the amount of solvent actually contained the channels of MOF-1 likely exceeds 19-22% by mass.

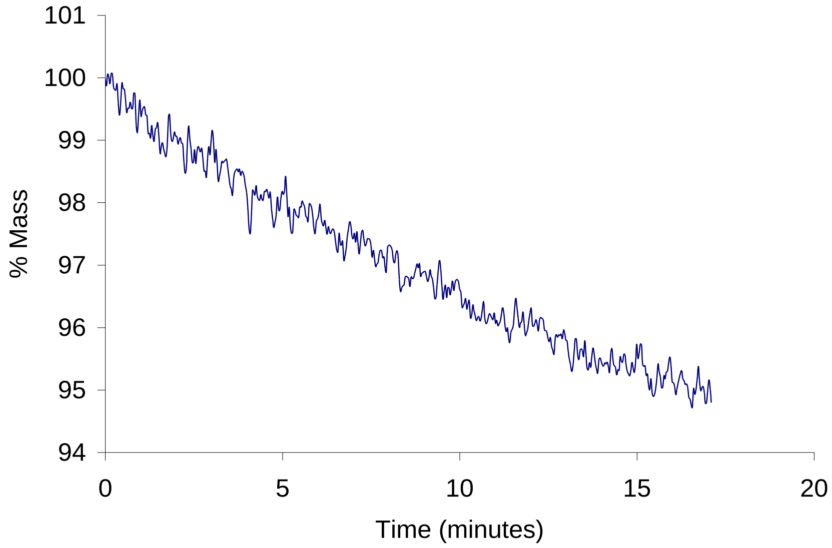

Figure 15: DB crystals losing mass at RT

6.5 Reversibility of Guest Loss

We have shown that MOF-1 forms crystals that are porous and can lose significant amounts of solvent very quickly. We next wanted to determine if the unknown new solid phase present in evacuated (heated) samples of the dark blue crystals was still porous and would continue to take up guest. Accordingly, the dark blue crystals were heated to 170ºC to drive off solvent, and then placed in a desiccator with the desired solvent in an open container, the pressure reduced under vacuum inside the dessicator, and the crystals allowed to sit in the presence of the solvent vapor. Samples were exposed separately to ethanol, water, and 1:1 ethanol/water (v/v) for 1 week; in addition, one sample was exposed to 1:1 ethanol/water (v/v) for one month. The TGA traces for those experiments are shown in Figure 16. The TGA data is tabulated graphically in Figure 17.

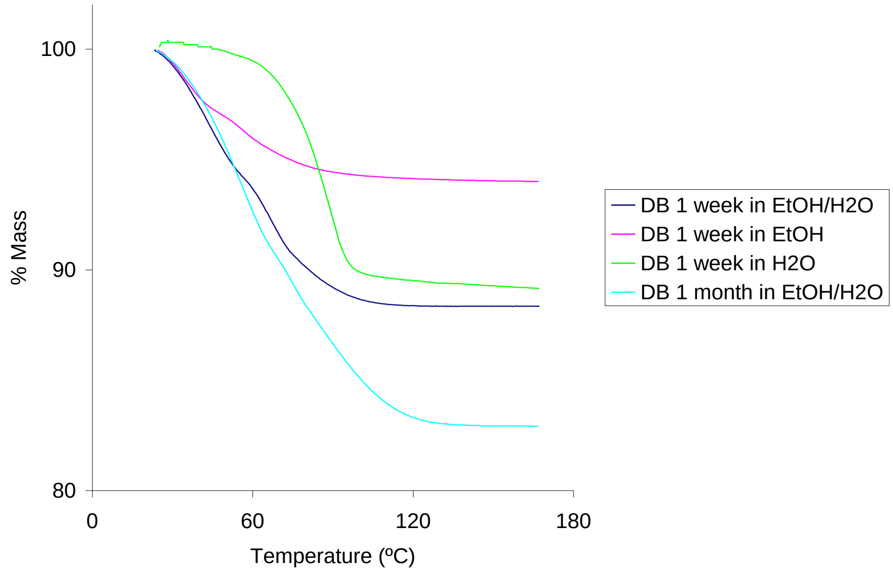

Figure 16: TGA data for resolvation experiments

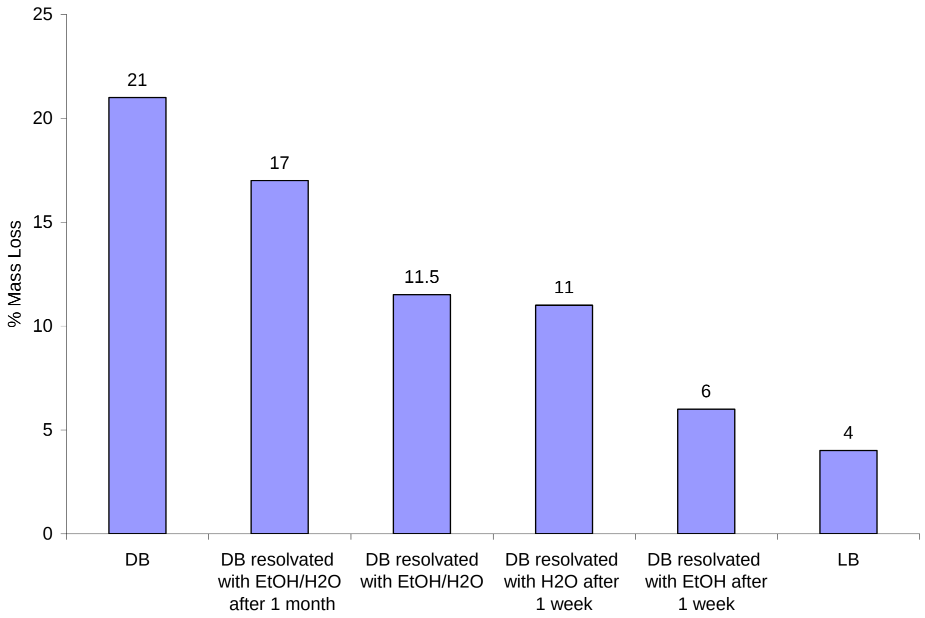

Figure 17. Summary of % mass lost from DB, LB and heated dark blue crystals after exposing them to guest solvent.

The TGA data show that the unknown solid phase in preheated blue crystals reabsorbed solvent equivalent to 11% of their mass after exposure to 1:1 ethanol/water after one week and solvent equivalent to 17% of their mass after exposure for one month. It is interesting to note that an equivalent mass of solvent was absorbed (11%) when the samples were exposed to1:1 ethanol/water or pure water for 1 week, whereas just 6% by mass of ethanol was absorbed over the same period. It is interesting to note that the sum of 11% water and 6% ethanol absorbed independently matches the total mass of solvent absorbed from 1:1 ethanol/water after one month. Moreover, the absorption of 6% by mass observed for ethanol matches the amount of mass lost from the original sample of dark blue crystals before the slope changes and becomes less steep. Taken together, these results suggest that the unknown solid phase present in the heated dark blue crystals certainly contains a MOF that is porous and that selectively absorbs nearly double the mass of water when compared to ethanol. We suspect that the structure of the MOF present in the unknown phase is similar or identical to that present in the dark blue crystals of MOF-1 and that similar to MOF-1, the unknown phase preferentially absorbs more water than ethanol. On the basis of the slope in the TGA data, it is likely that the porous behavior of the two materials is essentially the same. The unknown framework may in fact rise from a relaxation in the original framework in MOF-1, which would explain the ability of the unknown MOF to take up a mass of solvent similar to that present in MOF-1. To test this hypothesis and to determine whether the unknown MOF would return to the original structure of MOF-1 when re-solvated, crystals of MOF-1 were evacuated then re-hydrated in a humidified atmosphere for two days and the XPD trace compared to that from the dark blue crystals of MOF-1. The XPD trace from that experiment is shown in Figure 18. The XPD traces from the two samples do not match, indicating that the framework in the rehydrated sample differs from that of MOF-1. This finding does not rule out the hypothesis that the two MOFs are similar in structure.

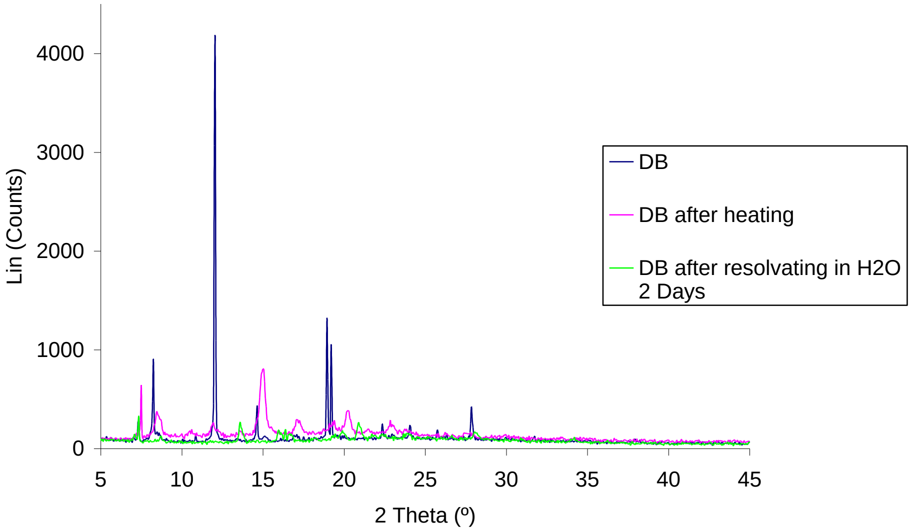

Figure 18: XPD for rehydration of DB crystals

7. Conclusions

The goal of our research was to synthesize a metal-organic framework, MOF-1, which packed in an arrangement other than cubic. Our framework consisting of 4-(imidazol-1-yl)benzoate and copper ions packed in a novel 3-D arrangement. We were able to show it is porous, losing between 19% and 22% of total mass as guest solvent included in the open channels. The crystals lose solvent quickly just sitting in air--roughly 5% mass in 15 minutes—reflecting the porous nature and large size of the channels in MOF-1. This system, even though it undergoes a change in structure after heating, is still able to absorb as much as 17% of its mass as guest solvent when exposed to solvent in a saturated atmosphere for one month.

8. References

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