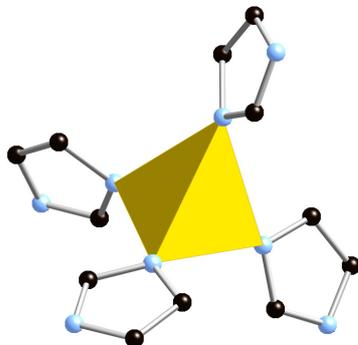


A Search For Magnesium
Imidazolate Zeolitic Frameworks



by

Nicholas Stadie

Arizona State University

Department of Chemistry and Biochemistry

April 2007

Introduction

The progress of science throughout history parallels man's insatiable pursuit of knowledge. The direction of this pursuit evolves continually, especially in the field of science. As current theories adapt, change the direction of, and shed light on new theories, a general progression is established. But the individual studies themselves change with time like fashionable clothing. It so happens that the way of knowledge is directed by the needs of society.

Today's fashions in the realm of inorganic chemistry include such topics as molecular machines, conductive polymers, alternative energy solutions, nanoscale systems (nanotubes for example), among many others. A particularly relevant such topic to the modern world is the exploration of hydrogen as a potential replacement for waning and destructive fossil fuels.

A wealth of problems arise at this proposition of a *hydrogen economy*, in production, storage, cost, and infrastructure necessary to afford the possibility of replacing current technology. Of course, hydrogen exists as a diatomic gas at standard conditions, and a highly explosive one at that. Storage of this fuel by liquefaction requires an excess of energy and is very inefficient in that way. It has been surmised that porous solid state materials among many other alternatives may be suitable as a solution to the storage problem; hydrogen molecules densely integrated into the cavities of an extended crystal framework would be less dangerous and more efficiently stored than the free gas.

In the ultimate goal of understanding the complexities of solid state chemistry, this search for a suitable hydrogen storage material presents a fitting medium by which the broader advancement of science may be achieved.

Zeolites

Since the early 1950s, zeolites and other molecular sieves have found widespread applications in many diverse areas and have subsequently become very important inorganic compounds with a large international market.¹ It is estimated that crystalline microporous zeolites make up about \$350 billion of the global economy in such broad areas as petrochemical refinery, ion-exchange treatment, water purification, and gas separation.² Traditionally, these solids proved to have outstanding physical properties such as high porosity. Therefore, zeolite-type materials may be explored as a model for promising materials which may be suitable for hydrogen storage.

Many zeolites are natural products; some of these have never been synthesized in a laboratory and conversely, there exist many synthetic zeolites which are not found in nature. Natural zeolites had been either harvested from natural sources or produced commercially where possible. Others were begotten simply by *discovery based synthetic chemistry*, a work of intensive trial and error procedure directed only by empirical results. In this way, a number of syntheses are explored and fine-tuned in a repeated cycle based on what is observed to produce better products; this is arduous and time consuming.

Technically speaking, zeolites are microporous solids that are defined as follows: hydrated crystalline tectoaluminosilicates constructed from TO_4 tetrahedra. The tetrahedral atoms may be any combination of silicon and aluminum, and each oxygen atom is shared by exactly two adjacent tetrahedra (see *Figure 1*). The International Zeolite Association, which presides over all matters related to zeolite chemistry, also includes structures containing phosphorous tetrahedral sites in this definition.

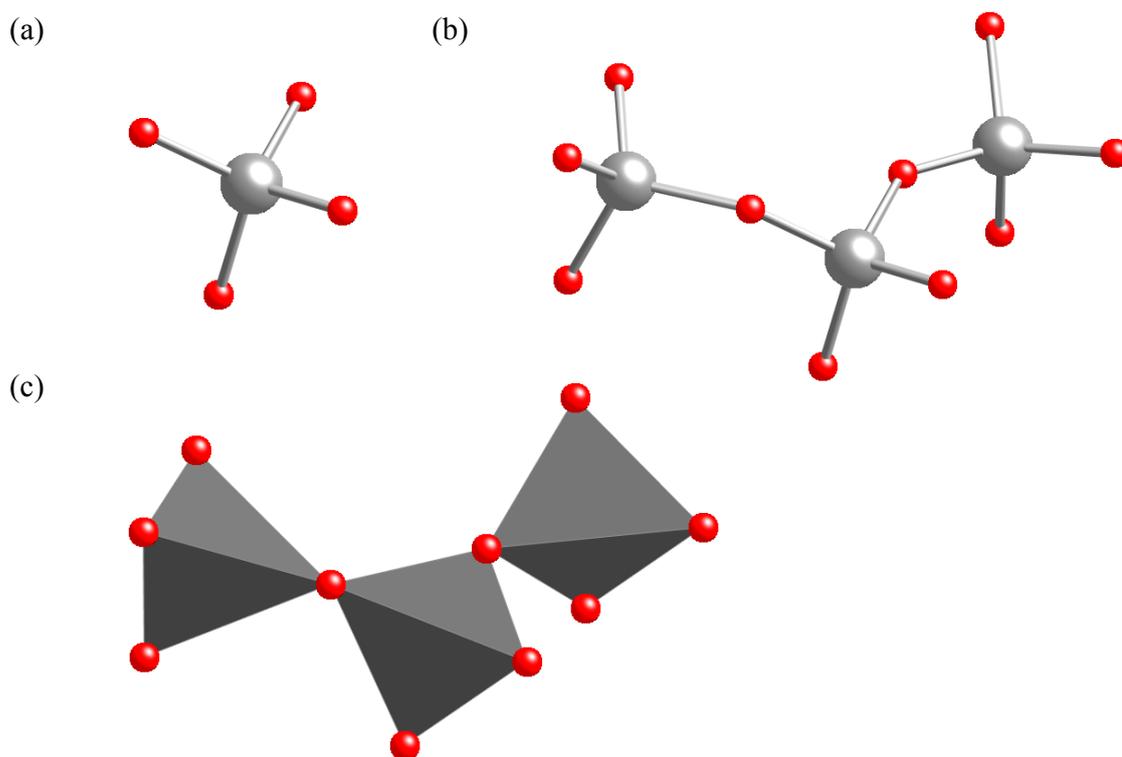


Figure 1. TO_4 tetrahedra represented as (a) a single ball and stick unit, (b) multiple ball and stick units, and (c) multiple polyhedral units. Silicon or aluminum T sites are shown in gray and oxygen in red.

Faujasite is an important example of a naturally occurring zeolite. Denoted by its three letter symbol FAU, its framework structure is characterized by the arrangement of SiO_4 tetrahedra such that they enclose a large a-cage cavity which is entered through a 12-ring window (7.4\AA in diameter). This makes faujasite the most “open” of all zeolite topologies, and a mathematically important zeolite framework.

Typically, zeolites are prepared by *solvothermal methods* wherein non-molecular building blocks of alumina and silica (usually salts) are combined with some alkali metal hydroxide and water, and reacted in an enclosed environment at a high temperature for a specific duration of time. This type of synthesis is not grasped by chemists at the same level of understanding as synthetic organic chemistry. The zeolite is thought to be

assembled through a series of spontaneous molecular recognition events that cannot be defined by the same dot-and-arrow schematics that traditional synthetic organic chemistry is founded on. In some cases, organic chemicals are added to the synthesis to tailor the subsequent assembly of the zeolite toward a desired product: these additives are aptly referred to as *structure directing agents*. The mechanism of their involvement is also very obscure, but lends to the wealth of knowledge that can be gained from further exploration of such systems.

In summary, zeolites have the physical qualities necessary for a promising storage model but present very obvious obstacles in the directed design of materials specific to the hydrogen purpose. A more logical design approach must be taken.

Metal Organic Frameworks

In the 1990s, it was found that a much more rational and flexible design of new materials could be conceived by linking inorganic metal clusters with rigid organic building blocks to produce materials exhibiting desired macroscopic properties.³ These materials have since been referred to as metal-organic frameworks, or MOFs.

In designing MOFs, there are a number of inorganic clusters and organic linkers at one's disposal. The clusters serve as vertices and the linkers as edges in one type of representation of these frameworks. Vertices may be represented by their polyhedron equivalent and edges by a simple geometric figure as well. In this way, the architecture of a three-dimensional MOF structure may be portrayed as an embedding of a three-periodic net; a complex solid-state system may be controlled and manipulated by knowing and applying the tenets of reticular chemistry.

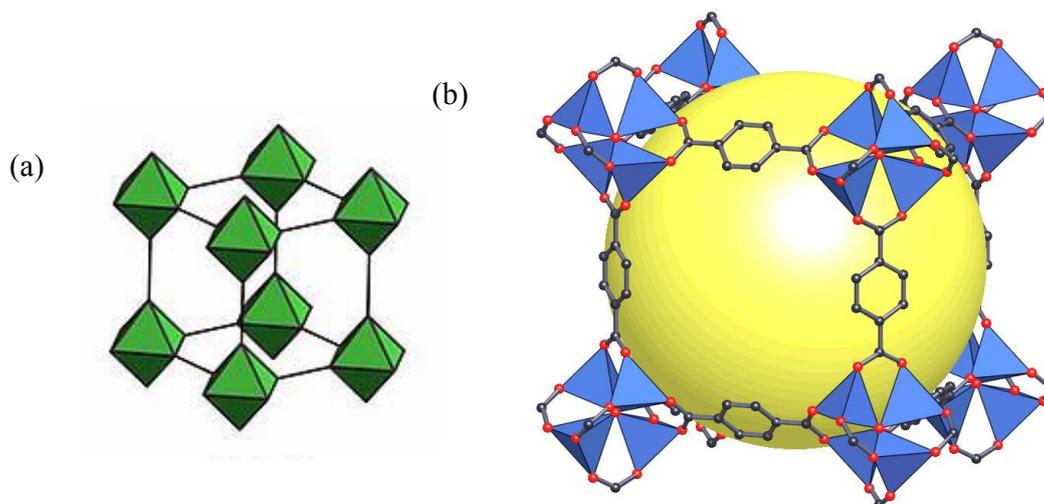


Figure 2. A metal-organic framework, referred to as MOF-5, is constructed from octahedral zinc carboxylate clusters connected by benzene dicarboxylate linkers. The resulting structure may be represented as (a) octahedral vertices connected by straight edges in the *pcu net*, or as (b) a unit cell constituting eight zinc clusters and twelve copolymerized linkers enclosing a large cavity, shown here as a yellow sphere of diameter 18.5Å. Zinc is shown in blue, oxygen in red, and carbon in black.¹³

A wide variety of metal-organic frameworks have been reported, but the rational design of such materials has been most thoroughly exhibited by Professor Omar Yaghi and his group, now at UCLA. Many of these structures have been said to resemble “molecular scaffolding,” and indeed the same joints may be connected with varying lengths of organic linkers to create different sized channels in the crystalline material. Yaghi has called these related structures *isoreticular metal-organic frameworks* and sees no limitations restricting the possible length of the linkers and the subsequent pore size exhibited.³ Of course, some obstacles have stalled the realization of this theory, especially in dissolving and properly reacting exceptionally long benzene chains.

Not only is it possible to simplify various MOFs to a geometrical construction, it is also possible to logically predict the outcome of a synthesis by knowing its reticular components. Knowing which inorganic components are present, one can enumerate the

different types of vertices that may result. In the same way, knowing all complimentary organic linkers present, one can enumerate the different types of edges that will result. If this is sufficiently simplified, one can surmise the most likely resulting crystalline products (assuming proper form and reaction of all reagents) by using simple geometry to predict the likeliest related nets. Therefore, a desired framework may be pursued by combining the necessary building blocks for the associated net of that framework.

For example, in a very simple case: if only one type of six-coordinated inorganic cluster and only one type of straight linker are present in the synthesis, then the allowed respective nets will also only have one type of six-coordinated vertex and one type of regular edge. This gives 9 total possibilities, of which 3 are related by symmetry, leading to 6 unique possible nets. Although the underlying chemistry of the complex reaction may not be understood, it is still possible to narrow the likely products down to only six different outcomes! Of course, with further restraints placed on the reaction or more specific knowledge of the reagents, this may be even further simplified. Of the six outcomes possible, only the primitive cubic lattice (pcu) net has vertex symmetry which is consistent with an octahedral inorganic cluster. Since it is known that Zn^{2+} in the appropriate carboxylic acid readily forms such an octahedral oxide-centered cluster, a coupling of this reagent with a rigid, straight, dicarboxylic benzene linker may be hypothesized to adhere to a crystalline product in the pcu net. This is, in fact, the experimental result (see *Figure 2*).

Employment of this strategy has yielded a myriad of new materials with open frameworks that can accommodate the adsorption of a wide spectrum of molecules, even as large as C_{60} . These materials are very promising as candidates for hydrogen storage.¹⁴

Zeolite Analog Frameworks

Considerable efforts have been focused on the synthesis of crystalline materials whose structures resemble zeolite frameworks, in pursuance of products which render the same desirable macroscopic properties. This is no more apparent than in the study of metal-organic frameworks which display zeolite-like topologies, due to the flexible and logical approach which can be taken in the synthesis of such materials. In theory, zeolite-like structures which have an organic component are superior to traditional zeolites in that they could potentially exhibit the same attractive characteristics but would also be adjustable by known techniques of organic chemistry. Pore size, shape and character, for instance, may be manipulated with ease by the functionalization or transformation of the organic component.

The only two defining characteristics of zeolite frameworks which must be imitated to create a zeolite analog framework are (a) the tetrahedral nature of the TO_4 sites and (b) the bonding angle of oxygen. Thus, in respect to MOF equivalents, the system required is very simple: (a) the inorganic component must be four-coordinated and take tetrahedral geometry and (b) the organic linker must have only two binding sites which mimic the Si-O-Si bonding angle found in most zeolites.

For the inorganic component, a single metal atom may be used as a tetrahedral building block to replace the silicon or aluminum sites in the zeolite analog framework. Of course, a cluster species may be designed and adopted for this purpose as well, but for simplification purposes, the former is the preferred substitute. There are a large number of metal atom candidates which can be shown to choose tetrahedral coordination in crystalline solids. More must then be known about the linker to narrow one's choices.

The essential bond in most zeolites which is to be imitated by the organic linker is the Si-O-Si bond, exhibiting a bond angle of typically 145° .⁵ Thus, an organic molecule is needed which has two sites for coordination that are bent at a similarly large bonding angle of roughly 145° . This molecule should be planar to avoid any ambiguity in its crystalline conformation; aromatic rings work suit this purpose quite well. It was discovered that the five-membered heterocyclic imidazole ring may bridge two metal atoms by way of its nitrogen sites, which are positioned at an angle of 143° from the centroid of the ring.⁹ Therefore, this rigid aromatic ring satisfies the requirements for a suitable organic linker in zeolite analog frameworks (such species are referred to as *zeolitic imidazolate frameworks*, or ZIFs).

In a zeolitic MOF incorporating imidazole as a linker, a good metal site candidate would be one that is known to take a tetrahedral geometry in coordination with that linker. It so happens that, as in many scientific problems, nature has a suitable design model from which to start. There exist a number of biological examples which present such complexes as zinc, copper, and cobalt in tetrahedral configuration when surrounded by imidazolate ligands.^{10,11} For instance, the copper site in methanobactin, an important molecule for copper transport in methane-oxidizing bacteria, is found by x-ray crystallography to be tetrahedral in geometry. This example, in particular, suggests copper as a promising candidate for zeolite analog imidazolate frameworks.

Another approach to selection of an appropriate metal site for ZIFs is to examine homogeneous nitride structures which have tetrahedral metal sites, since the immediate bond to each nitrogen atom mimics that of an imidazolate bond. Examples of such tetrahedral configurations occur in the nitrides of gallium, aluminum, and indium (in the

common *wurtzite* structure) as well as for a number of other metals: magnesium in Mg_3N_2 , calcium in Ca_3N_2 , cobalt in Co_2N , zinc in Zn_3N_2 , and germanium in Ge_3N_4 .

For the nine potential candidates reasoned above, ZIFs have been reported only for copper, cobalt, gallium, zinc, and indium. These metals show an extraordinary ability to make zeolite analog frameworks as postulated. The first ever report of a crystalline compound whose structure was characterized by exclusively metal-imidazolate bonding was a cobalt such structure in 1975, much preceding the establishment of metal-organic framework chemistry.¹² Many others have followed, notably the zinc imidazolates reported by Yaghi et. al. in 2006 which were shown to conform to numerous different zeolite and zeolite-like topologies, depending only on slight variations in the conditions of synthesis.⁵⁻⁷ Interestingly, one important zeolite framework which has not been reproduced as a ZIF is faujasite, perhaps the most desirable of all zeolite topologies.

N-45, A Zinc Imidazolate

To better understand the science of designing and creating zeolite analog imidazolate frameworks, I performed a number of experiments with synthetic conditions that mimicked experimental procedures reported in literature. Zinc imidazolates had shown highly successful outcomes, and from this starting point, my first set of experiments coupled a zinc reagent with imidazole. One such experiment, referred to as N-45, is given below:

N-45: A solid mixture of zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, (0.104g, 3.50×10^{-4} mol) and imidazole (0.154g, 2.26×10^{-3} mol) was dissolved in 10mL of dimethylformamide in a 50mL polypropylene centrifuge tube. The tube was capped and heated at a rate of 5°C per minute to 85°C in a programmable oven; this temperature was held constant for 48 hours. The oven was then fan-cooled to room temperature at an average rate of 0.5°C per minute. The crystals were photographed under magnification while in solution. The mother liquor was

decanted off following centrifuge and the sample washed with DMF (10mL \times 3). The remaining solvent was allowed to evaporate and the colorless octahedral crystals were analyzed by single crystal x-ray diffraction.

Under magnification, the crystals produced were noted to be colorless and fairly uniform in size. Many of the crystals were found to exhibit distinct octahedral shape, especially those that were smallest, and were noted to be physically robust; they did not dissolve in the presence of water, ethanol, or open air. The crystals “blinked” when rotated under polarized light, indicating non-cubic periodic structure.

A single crystal was harvested which was about 70 \times 70 \times 100 microns in size. It was mounted on the tip of a glass fiber, fitted to a goniometer head, and inserted into an x-ray diffraction instrument for data collection. The diffraction data showed that the framework was marked by orthorhombic (Pbca) symmetry. Dr. Thomas Groy aided in determining the solution of the atomic structure which was shown to have the molecular formula: $\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2 \cdot (\text{DMF})(\text{H}_2\text{O})$. As expected, the imidazolate ligand was present in a 2:1 ratio with zinc. Dimethylformamide molecules leftover from solvent were discovered to be present in the pores. Upon further analysis, the three-dimensional framework of zinc and imidazolate was found to be topologically equivalent to the cag zeolite-like framework. A representation of this may be shown by connecting the zinc tetrahedra and the centroid of each imidazolate ligand (see *Figure 3*).

This cag imidazolate is among many other known zeolite-like frameworks incorporating zinc as a metal site. The reagent used, zinc nitrate hexahydrate, reacted with imidazole simply upon contact, forming an immediate liquid; its ease of use and high tendency to coordinate with imidazole even in a solvent-less environment is evident. The low temperature required of the synthesis also shows that little energy is required to break and build the appropriate bonds. The pH of this environment did not need to be

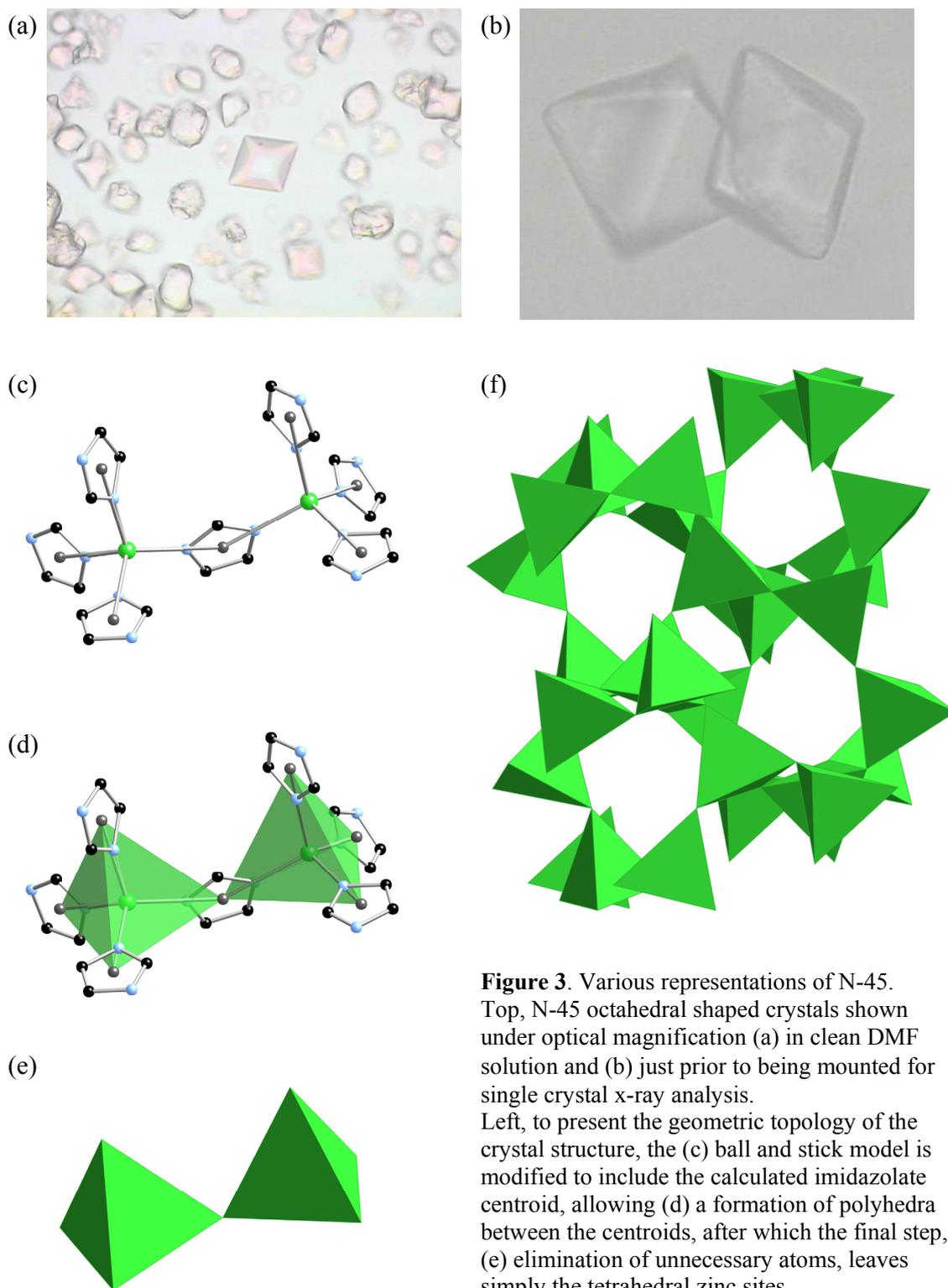


Figure 3. Various representations of N-45. Top, N-45 octahedral shaped crystals shown under optical magnification (a) in clean DMF solution and (b) just prior to being mounted for single crystal x-ray analysis. Left, to present the geometric topology of the crystal structure, the (c) ball and stick model is modified to include the calculated imidazolate centroid, allowing (d) a formation of polyhedra between the centroids, after which the final step, (e) elimination of unnecessary atoms, leaves simply the tetrahedral zinc sites. Right, in this way, (f) cag topology is realized. Zinc is shown in green, nitrogen in blue.

modified to motivate this reaction, another simplicity which lends good reason to the extensive list of related zinc imidazolates. Indeed, zinc is an excellent candidate for this type of zeolitic metal-organic framework built on a single metal coordination site and an imidazolate linker. However, the search for better and more efficient ZIFs continues.

Magnesium Imidazolates

In addition to transition metal imidazolates, it has been demonstrated that similar coordination networks can be made with alkali and alkali-earth metals.¹⁶ These smaller s-block metals are appealing because they have the potential advantage of creating particularly lightweight MOFs. Most are abundant and readily available at affordable costs. Finally, s-block metals have been shown to be attractive candidates for materials with high storage capacities for hydrogen and methane.¹⁷

Magnesium is an s-block metal that is found in tetrahedral coordination symmetry in its nitride crystal structure, Mg_3N_2 . The molar mass of pure magnesium metal is 24.3g, less than half that of even the smallest transition metals for which imidazolate structures have been reported. The largest transition metal with which an imidazolate has been synthesized is indium, which has a molar mass of 114.8g. Magnesium is the lightest industrial metal and costs about the same price as aluminum, at \$1.60 per kg. It is found in great abundance (the 8th most abundant element in the universe) and makes up roughly 2.5% of the earth's crust. Its metal is not found in nature, but it is the 3rd most plentiful ion found in sea water and is essential to all known living organisms.

It is also known that magnesium dicarboxylate complexes have been reported which show high porosity and a relatively good binding affinity for H_2 .¹⁸

Therefore, it is apparent that magnesium displays many desirable attributes and all of the necessary attributes of a metal candidate for a zeolitic MOF. It was found that no magnesium ZIFs had ever been reported, and it was the purpose of my research to either accomplish this or to understand why.

Synthesis Techniques

From the experimental information reported for existing metal imidazolate frameworks, the following were components considered in the design of a synthesis for new magnesium imidazolates:

1. Solvothermal Synthesis: the solvent plays a role in dissolving the reagents, adequately directing the structure of the crystal, and setting the system's foundational pH.
2. Integral Reagent Ratios: small number, whole value proportions of imidazole to metal ions have given successful syntheses in sometimes illogical ratios (not necessarily 2:1).
3. Mild Temperature: chemical interaction is motivated, but conditions do not radically alter the character of the reagents or the solvent.
4. Varied Reaction Times: the duration of time spent at elevated temperature is generally on the order of days, but is inconsistent from synthesis to synthesis.

It was understood that magnesium would likely interact much differently with imidazole than in previously reported experiments involving transition metals. These considerations were, nonetheless, the best available insight to our group.

For the first experiments, the following solutions were given to the considerations discussed above. These were to be applied in as many different combinations as possible to investigate their role in synthesis:

1. Solvent: dimethylformamide (DMF)
2. Reaction Vessel: 50mL disposable polypropylene centrifuge tubes
3. Magnesium Reagent: magnesium acetate tetrahydrate
4. Imidazolate Reagent: crystalline imidazole
5. Reagent Ratios: 2:1, 1:1, 2:1, 3:1, 4:1 (Mg:Im)
6. Oven Temperature: 75-140°C
7. Reaction Duration: 1-4 days

These conditions were altered and modified to yield the highest quality and quantity of crystalline product.

N-70 Magnesium Acetate Cluster

The first successful synthesis which produced single crystals whose structure was characterized to show a magnesium imidazolate coordinative bond is referred to as N-70.

The experimental detail is as follows:

N-70: A solid mixture of magnesium acetate tetrahydrate, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, (0.670g, 3.12×10^{-3} mol) and imidazole (1.546g, 2.27×10^{-2} mol) was dissolved in 20mL dimethylformamide in a 50mL centrifuge tube. The tube was stirred for 30 minutes until all reagents were well dissolved, capped, and heated at a rate of 5°C per minute to 85°C in a programmable oven; this temperature was held constant for 48 hours. The oven was then fan-cooled to room temperature at an average rate of 0.5°C per minute. The mother liquor was decanted off following centrifuge and the sample was washed with DMF (10mL \times 3). The colorless plate-like crystals in solution were photographed under magnification and harvested for analysis by single crystal x-ray diffraction.

Under magnification, the crystals produced were noted to be colorless and plate-like in shape. The smaller crystals took distinct geometric shapes, predominantly trapezoids and elongated hexagons. The crystals were remarkably fragile as well; they were often layered and could be separated and destroyed with ease. Under intense light, the smaller layered crystals showed brilliant patterns and colors (see *Figure 4*).

A single trapezoidal plate crystal was harvested and measured to be $120 \times 100 \times 50$ microns in size. The diffraction data collected from this crystal showed the framework was characterized by orthorhombic (*Aba2*) symmetry and gave a molecular formula of: $[\text{Mg}(\text{C}_3\text{H}_3\text{N}_2)_2(\text{CH}_3\text{COO})]_2(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. After obtaining a solution for the crystal structure of N-70, it was found that the repeating unit was a non-connected molecule of two magnesium atoms and predominantly oxygen-containing ligands. Each magnesium atom is six-coordinated: with two terminal imidazoles, two shared “bridging” acetates, one terminal acetate, and a single water molecule that lies at the center of the cluster. These six ligands complete the distorted octahedral geometry of each magnesium atom.

Of particular note, the first magnesium imidazolate bond had been successfully synthesized. However, it is more than obvious that this structure does not satisfy the goal of achieving a magnesium ZIF for the following main reasons:

1. Non-dimensional: the structure is not connected along any spatial axis, simply forming an array of independent dimagnesium clusters.
2. Terminal Imidazolate Ligands: the imidazolate rings did not copolymerize with the magnesium sites to serve the role of a linker.
3. Linking Acetate Ligands: the acetate groups left over from the reagent are still present in majority and serve in primary linking function.

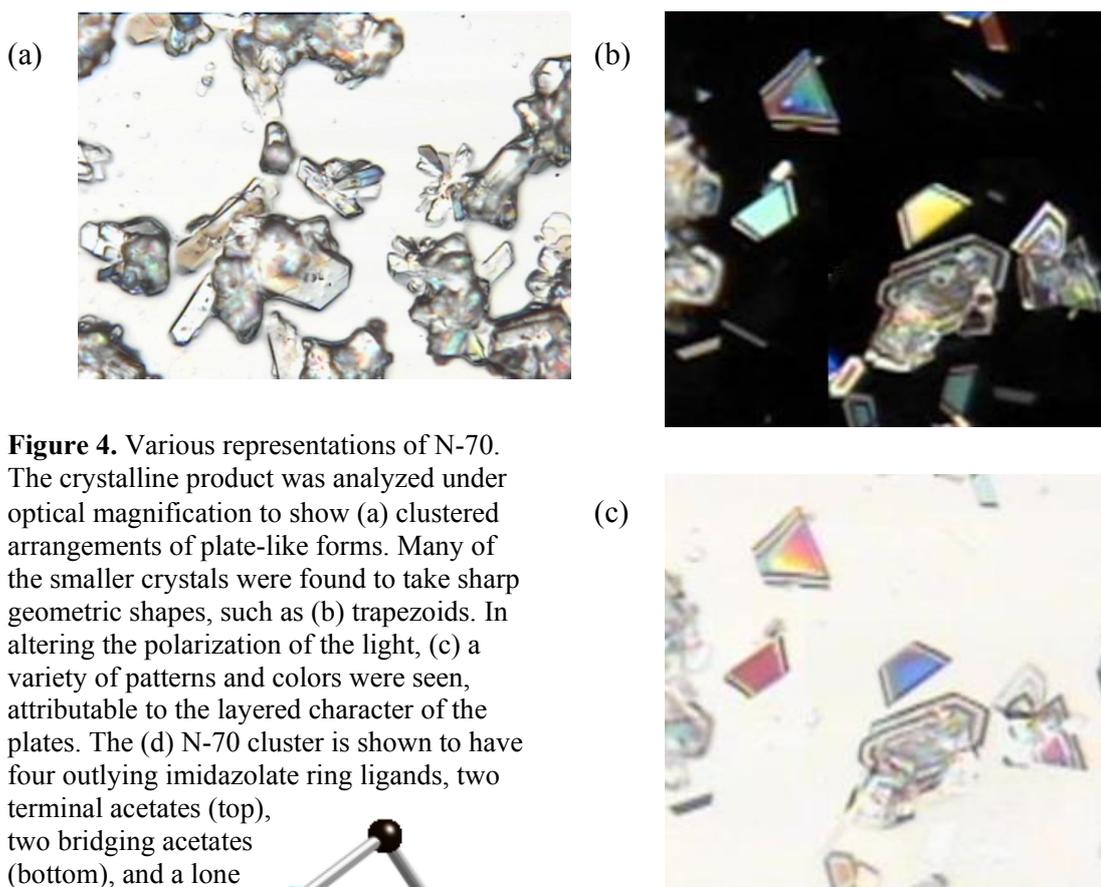
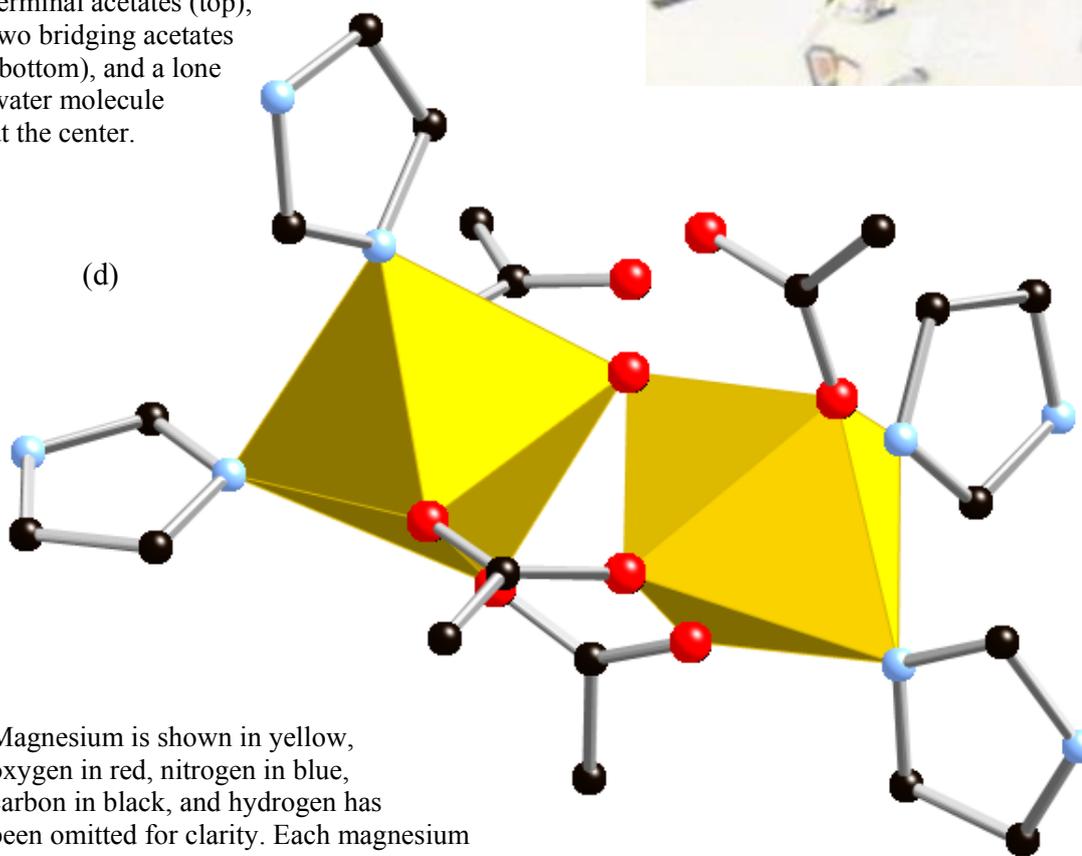


Figure 4. Various representations of N-70. The crystalline product was analyzed under optical magnification to show (a) clustered arrangements of plate-like forms. Many of the smaller crystals were found to take sharp geometric shapes, such as (b) trapezoids. In altering the polarization of the light, (c) a variety of patterns and colors were seen, attributable to the layered character of the plates. The (d) N-70 cluster is shown to have four outlying imidazolate ring ligands, two terminal acetates (top), two bridging acetates (bottom), and a lone water molecule at the center.



Magnesium is shown in yellow, oxygen in red, nitrogen in blue, carbon in black, and hydrogen has been omitted for clarity. Each magnesium atom is represented as a coordinative polyhedron.

4. Octahedral Magnesium Sites: tetrahedral coordination of the metal site was not achieved, a primary objective in creating a zeolitic framework.

None of the sought-after characteristics of a connected magnesium imidazolate framework were realized. However, a new and interesting magnesium-oxygen cluster was prepared. For this reason, N-70 is pending publication with Acta Crystallographica Section E.

N-111 Magnesium Acetate Chain

The second successful synthesis which produced single crystals whose structure was characterized to show a magnesium imidazolate coordinative bond is referred to as N-111. The experimental detail is as follows:

N-111: A solid mix of magnesium acetate tetrahydrate, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, (0.786g, 3.67×10^{-3} mol) and imidazole (0.334g, 4.91×10^{-3} mol) was dissolved in 20mL dimethylformamide in a 50mL centrifuge tube. The tube was thoroughly stirred to dissolve all reagents, capped, and heated at a rate of 5°C per minute to 85°C in a programmable oven; this temperature was held constant for 48 hours. The oven was then fan-cooled to room temperature at an average rate of 0.5°C per minute. The mother liquor was decanted off following centrifuge and the sample washed with DMF (10mL \times 3). The crystals were photographed under magnification while in solution. The colorless plate-like crystals harvested from solution were analyzed by single crystal x-ray diffraction.

Optically, the crystals produced were noted to be colorless and plate-like, very similar to those produced in the N-70 synthesis previously. Most of the crystals were observed to be much longer in one dimension than those seen for N-70, almost tending toward needles. These had the same basic hexagonal and trapezoidal shape as the previous crystals, but were simply elongated. This fact indicated that there was likely to be a longer unit cell in one dimension, or that the structure was connected along one or more axis.

A single crystal was harvested and measured to be $180 \times 100 \times 50$ microns in size. The diffraction data collected from this crystal showed that the framework was marked by orthorhombic (Pnn2) symmetry and gave a molecular formula for the compound as: $\text{Mg}_3(\text{C}_3\text{H}_3\text{N}_2)_2(\text{CH}_3\text{COO})_6 \cdot \text{H}_2\text{O}$. Upon further analysis, the structure was indeed discovered to be closely related to the N-70 cluster; however, in N-111, the magnesium octahedra were connected in one dimension to give straight “chains” along one axis. Also, there were found to exist two different magnesium environments in this structure, as opposed to the one magnesium site in N-70 that was simply related to its complement by symmetry (see *Figure 5*).

As with N-70, a three-connected magnesium imidazolate had not been achieved. In regards to the four considerations made for the previous structure, N-111 only showed one improvement:

1. One-dimensional: the chain structure is only connected along one axis.
2. Terminal Imidazolate Ligands: the imidazolate rings did not interact with magnesium at both nitrogen sites.
3. Linking Acetate Ligands: the acetate groups left over from the reagent are still present in majority and primary linking function.
4. Octahedral Magnesium Sites: the desired tetrahedral coordination of the metal site was not achieved.

A step had been made in the right direction, but it is quite clear that N-111 is far from exemplifying the desired characteristics of a magnesium ZIF. Again, a new and interesting magnesium-oxygen structure was prepared, and thus, N-111 is pending publication with *Acta Crystallographica Section E*.

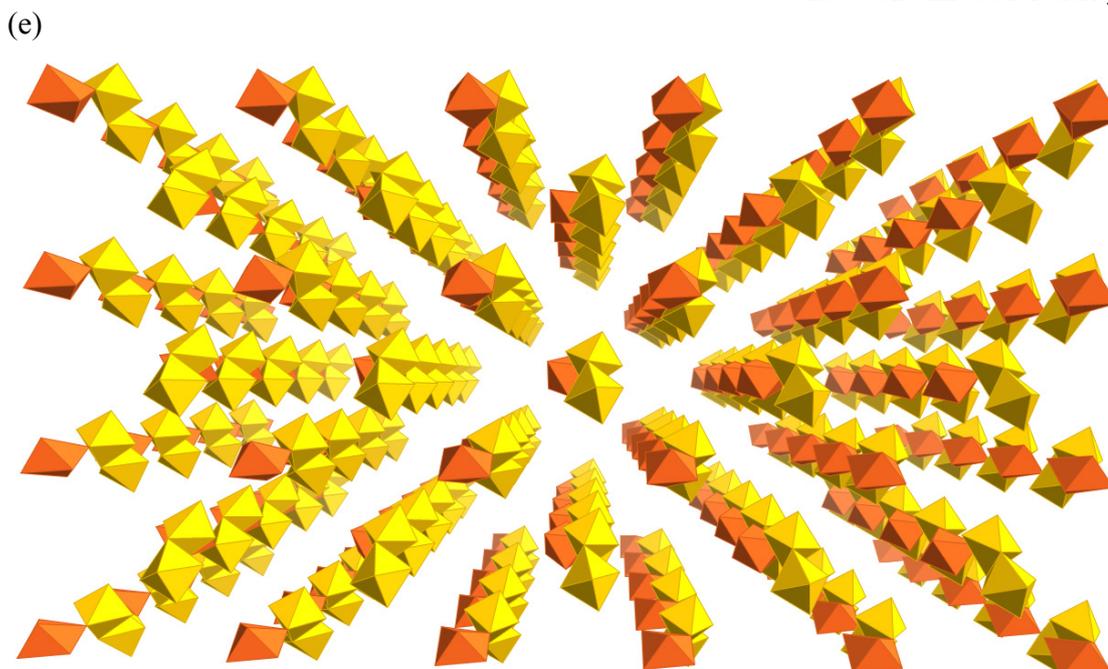
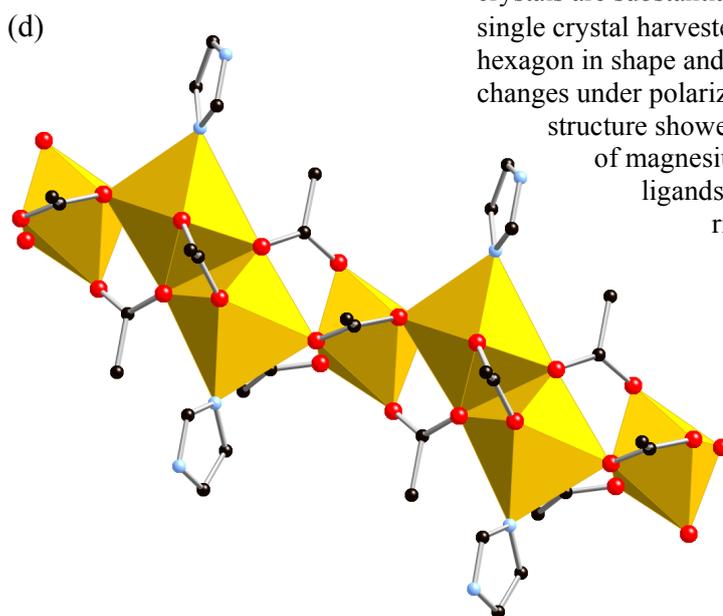
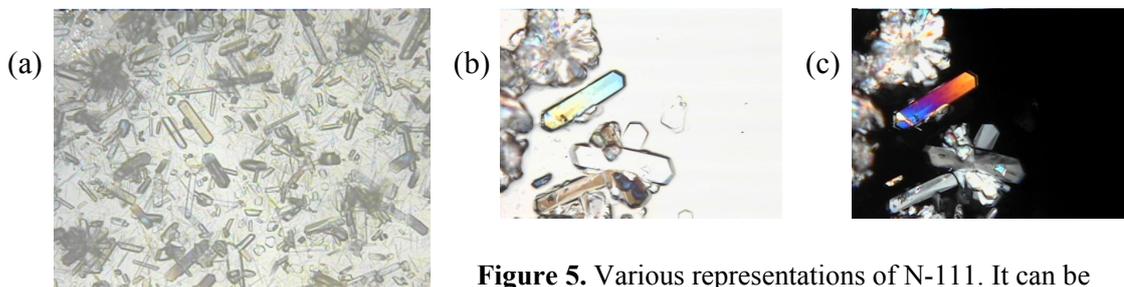


Figure 5. Various representations of N-111. It can be seen under optical magnification that (a) the plate-like crystals are substantially longer for this compound. The single crystal harvested for data collection was (b) a long hexagon in shape and (c) was found to exhibit vast color changes under polarized light. The resulting crystal structure showed (d) a periodicity in one direction of magnesium octahedra linked by acetate ligands and showing terminal imidazolate rings normal to the direction of the chain. The two unique Mg sites are distorted octahedra of similar size. The periodicity of the structure may be seen when (e) viewed down the axis of connected atoms.

Magnesium is shown in yellow and orange, oxygen in red, nitrogen in blue, and carbon in black. Hydrogen has been omitted for clarity.

Toward Magnesium Frameworks

Of the shortcomings in the results produced by N-70 and N-111, the most important are: (a) the failure to fully deprotonate the imidazolate linker and achieve copolymerized linking capability, and (b) the inability to rid the magnesium of its existent oxygen-containing carboxylate ligands.

To entice the imidazole ring to link magnesium atoms at both nitrogen sites, it is clear that the reaction conditions must be suitably alkaline to deprotonate the trivalent nitrogen. For syntheses involving zinc, the conditions present were sufficiently basic to allow imidazolate to form and serve as a proper linker. To be sure that this was not the main obstacle in realizing a three-dimensional magnesium imidazolate, experiments were undertaken which incorporated a number of high pH reagents. Strong laboratory bases (concentrated NaOH and aqueous ammonia), strong amine bases (trimethylamine and (iso)propylamine), as well as weak amide bases (formamide and dimethylformamide) were added in various quantities to syntheses which had shown promising results in the absence of base.

The results from these trials were mixed. Crystals were never formed for the strongly basic additives to the mixture. Strange solidification reactions and unusable products occurred for experiments with amine bases. It was hypothesized that these harsh organic chemicals may have been reacting with the polypropylene centrifuge containers at high temperatures. DMF alone was not alkaline enough to fully deprotonate the imidazole, as exemplified in N-70 and N-111. However, experiments with formamide yielded some enlightening results.

N-139 Magnesium Formate Framework

In formamide solution, a similar synthesis to those discussed above yielded a large quantity of single crystals, referred to as N-139. The experimental detail is as follows:

N-139: A solid mix of magnesium acetate tetrahydrate, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, (0.991g, 4.61×10^{-3} mol) and imidazole (0.317g, 4.66×10^{-3} mol) was dissolved in 10mL formamide in a 50mL centrifuge tube. The tube was stirred for 30 minutes until all reagents were well dissolved, capped, and heated at a rate of 5°C per minute to 95°C in a programmable oven; this temperature was held constant for 72 hours. The oven was then fan-cooled to room temperature at an average rate of 0.5°C per minute. The mother liquor was decanted off following centrifuge and the sample was washed with formamide (10mL \times 3). The colorless plate-like crystals in solution were photographed under magnification and harvested for analysis by single crystal x-ray diffraction.

Under optical magnification, the crystals produced were noted to be colorless and in tight clustered units. The crystals which had escaped the cluster formation were block-like and quite sturdy. Some resembled geometric shapes, notably octahedra, but most exhibited a non-symmetric appearance. Some of the longer blocks at first resembled the plate-like crystals evident in both N-70 and N-111, though did not show the same layered character and were remarkably less fragile. This indicated a more robust, connected framework had likely been achieved.

Many single crystals were available for harvesting; a particularly homogeneous block of material was mounted and analyzed by x-ray diffraction. The data collected showed that the framework was marked by orthorhombic (Pnna) symmetry and that the molecular formula of the compound was $[\text{Mg}(\text{HCOO})_3] \cdot \text{HCONH}_2$.

Of course, this is a very surprising result: imidazolate was not present *at all* in this compound, seemingly showing a further deviation from the path toward magnesium imidazolate frameworks. However, upon further analysis, it became apparent that the

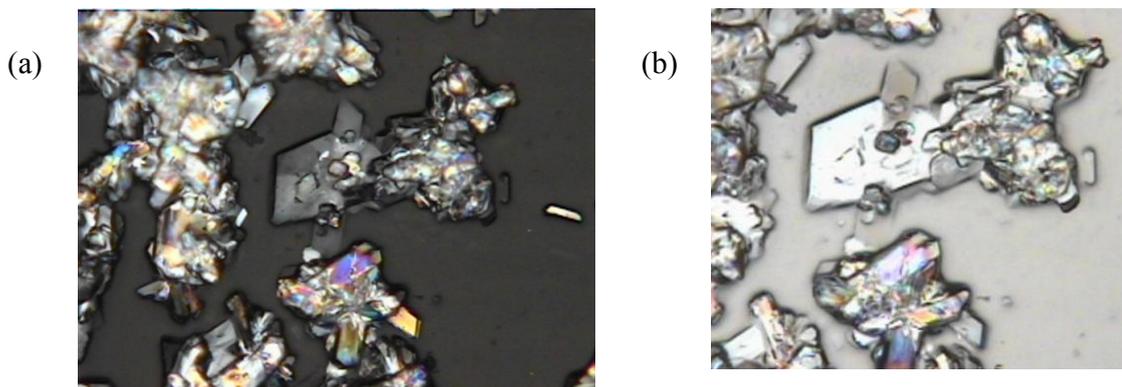
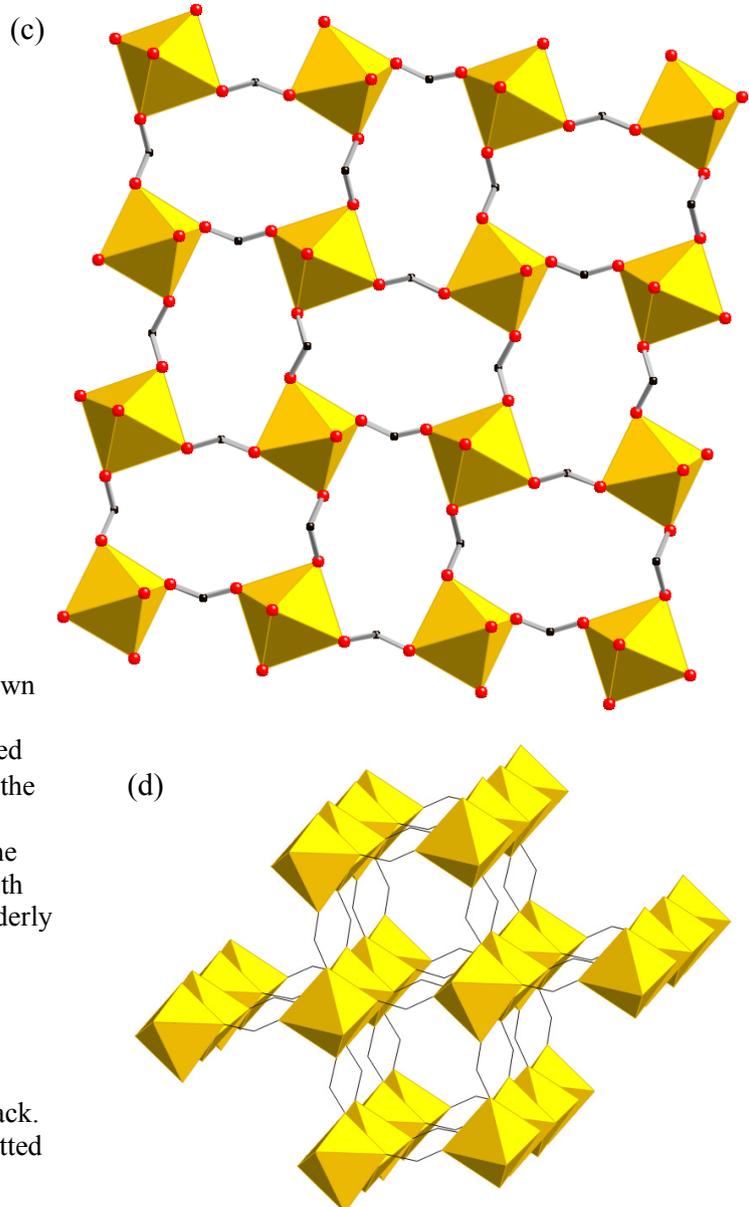


Figure 6. Various representations of the N-139 synthesis. Under optical magnification and rotated polarized light, (a) the N-139 crystalline product exhibited brightly colored clusters and some separate single blocks of material in surrounding solvent. One such example is shown (b) at higher zoom and takes the shape of a trapezoid. However, unlike N-70 and N-111 trapezoidal plates, these crystals were found to be in much more resilient block-like form. The resulting crystal structure is found to be (c) a three-dimensional array of magnesium sites linked by formate ligands. The “checkerboard” pattern shown is also connected along the axis normal to the plane of disoriented octahedra. Upon elimination of the atoms and replacement by wire bonds, (d) it is possible to see the resemblance of this structure with the pcu net. However, the disorderly arrangement of the octahedral vertices prevents such a valid representation.

Magnesium is shown in yellow, oxygen in red, and carbon in black. Hydrogen atoms have been omitted for clarity.



resulting crystal structure was fundamentally connected in three dimensions to produce a lattice of magnesium-oxide octahedra in a near pcu configuration (see *Figure 6*).

Despite its obvious lack of success, N-139 unveiled useful information about the tendency of magnesium to form oxygen-coordinative bonds in preference to a nitrogen equivalent. Its evaluation, in regards to the original remarks made of N-70, gives the following observations:

1. Three-dimensional: the framework is in this case fully connected.
2. Imidazole Not Present: the imidazole reagent had no apparent interaction with magnesium in the major product.
3. Linking Formate Ligands: formate groups were present in primary linking function.
4. Octahedral Magnesium Sites: the desired tetrahedral coordination of the metal site was still not achieved.

Only one notable improvement over N-111 was accomplished: the extension of connected units to three dimensions. Again, a new and interesting magnesium-oxygen structure was prepared and thus, may be reported to Acta Crystallographica.

Discussion

It has been the trend of the results produced from experiments N-70, N-111, and N-139 that magnesium is extremely prone to coordinative bonding of oxygen-containing ligands, especially carboxylates. Therefore, in the successful synthesis of a magnesium imidazolate framework, either (a) these extraneous ligands must be exempt from any presence at all in the initial mixture or (b) a linker must be devised which is preferred.

In attempting to eliminate all oxygen-containing elements of the reaction, a complication is introduced which is extensive and problematic. Of course, a reaction may be designed which couples an anhydrous magnesium reagent (such as MgCl_2 perhaps) with imidazole in an oxygen-less solvent, reacted in a nitrogen environment. This is possible, but undermines the simplicity of the experiment to begin with.

It is therefore a more suitable solution to look toward a linker which is based on oxygen as the most probable pathway to a magnesium framework. Formate presents an apparent candidate, although its bonding angle is difficult to control, as with many other oxygen-containing compounds. Of course, a dicarboxylate could be imagined, potentially based on cyclopentadiene to give it the appropriate bonding angle, but a new tetrahedral inorganic cluster would be an essential requirement to that alternative. Of the plethora of clusters enumerated by Yaghi et. al., none exhibits tetrahedral geometry for carboxylate linkers. It might be possible, with the aid of an organic chemist, to devise an appropriate linker which mimics the character of imidazole, but such a molecule is hard to imagine.

In all, it appears that magnesium has proven to be a difficult candidate for zeolitic imidazolate MOFs; however, along the way, some new and interesting compounds were prepared and innovations have resulted which beg new questions of the application of magnesium to other similar solid-state systems.

Conclusions

While pursuit of knowledge merely for knowledge sake is the true impetus of the work of scientific scholars the world around, a certain justification of one's direction is always a requirement. This broader purpose is sometimes finalized in a successful way

and many times altered or abandoned as new discoveries are uncovered. Nonetheless, it must always be realized, especially in the light of seeming failure, that a noble purpose of any research is simply to familiarize and understand the physical world around us. In this sense, so long as even the simplest new understanding is achieved, an endeavor may never be marked as a defeat.

References

1. Sherman, J. D. Synthetic Zeolites and Other Microporous Oxide Molecular Sieves. *PNAS* **96**, 7 (1999).
2. Van Bekkum, H. *et al.* *Introduction to Zeolite Science and Practice* (Elsevier, Amsterdam, 1991).
3. Rowsell, J. L. C. *et al.* Metal-Organic Frameworks: A New Class Of Porous Materials. *Microporous and Mesoporous Materials* **73** (2004).
4. Huang, X. *et al.* A Metal-Organic Open Framework With Sodalite Topology. *Chinese Science Bulletin* **48**, 15 (2003).
5. Park, K. S. *et al.* Exceptional Chemical and Thermal Stability of Zeolitic Imidazolate Frameworks. *PNAS* **103**, 27 (2006).
6. Tian, Y. Q. *et al.* A Layered Bimetallic Imidazolate Polymer, the First Hybridized Cobalt(II) Imidazolate. *Anorg. Allg. Chem.* **630** (2004).
7. Huang, X. C. *et al.* Ligand Directed Strategy for Zeolite Type Metal-Organic Frameworks: Zinc(II) Imidazolates with Unusual Zeolitic Topologies. *Angew. Chem.* **45** (2006).

8. Irish, D. E. *et al.* Structure of Magnesium Diacetate Tetrahydrate. *Acta Cryst.* **C47** (1991).
9. McCullen, R. K. *et al.* The Crystal Structure of Imidazole at 103 K by Neutron Diffraction. *Acta Cryst.* **B35** (1979).
10. Hyung, J. K. *et al.* Methanobactin, a Copper-Acquisition Compound from Methane-Oxidizing Bacteria. *Science* **305** (2004).
11. Lu, Y. *et al.* New Type 2 Copper-Cysteinate Proteins: Copper Site Histidine to Cysteine Mutants of Yeast Copper-Zinc Superoxide Dismutase. *Inorg. Chem.* **35**, 6 (1996).
12. Sturm, V. M. *et al.* Die Kristallstruktur von Diimidazolylkobalt. *Acta Cryst.* **B31** (1975).
13. Li, H. *et al.* Design and Synthesis of an Exceptionally Stable and Highly Porous Metal-Organic Framework. *Nature* **402** (1999).
14. Rosi, N. L. *et al.* Hydrogen Storage in Microporous Metal-Organic Frameworks. *Science* **300** (2003).
15. Tian, Y. Q. *et al.* Two Polymorphs of Cobalt(II) Imidazolate Polymers Synthesized Solvothermally by Using One Organic Template. *Inorg. Chem.* **43**, 15 (2004).
16. Chen, B. *et al.* Strategies for Hydrogen Storage in Metal-Organic Frameworks. *Angew. Chem. Int. Ed.* **44** (2005).
17. Dinca, M. *et al.* Strong H₂ Binding and Selective Gas Adsorption Within the Microporous Coordination Solid Mg₃(O₂C-C₁₀H₆-CO₂)₃. *J. Am. Chem. Soc.* **127** (2005).

18. Rood, J. A. *et al.* Synthesis, Structural Characterization, Gas Sorption, and Guest Exchange Studies of the Lightweight, Porous Metal-Organic Framework $\text{Mg}_3(\text{O}_2\text{CH})_6$. *Inorg. Chem.* **45**, 14 (2006).