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A General Approach to the Production and Geometry of the Square Trigonal Prismatic Crystal Net

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A General Approach to the Production and Geometry of the
Square Trigonal Prismatic Crystal Net

By

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Abstract

The development, design, and analysis of the Square Trigonal Prismatic (**stp**) crystal net by Alexander Schoedel at the University of South Florida (USF) serves as a case study for bridging mathematics and chemistry. By conducting analysis from both viewpoints alongside elaboration of field-specific concepts and terminologies, we present the approach each field takes when engineering crystal nets. For chemistry, we develop common chemical knowledge into terminology and theory specific to the field of Metal-Organic Materials (MOMs) in which **stp** was developed. For mathematics, we discuss graph theory and polyhedra and build towards the concepts of symmetry using point groups and space groups.

We present the terminology and methodology of each field to enable communication across fields and include a discussion on the various layers that disrupt easy communication across fields. These layers include misunderstandings in terminology, misconceptions and stereotypes of mathematics, and the problem of information distribution in chemistry lab. By presenting each, we hope to inspire professionals to address such barriers. With the analysis of **stp**, basic terminology, and elaboration on what is dividing the fields, we create a common ground on which mathematicians and chemists can discuss and collaborate.

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I. Introduction

The modern development of new materials focuses on predicting, designing, and synthesizing structures with certain properties. While the traditional “mix and wait” process has yielded and continues to yield interesting and important materials, it often does not result in products whose structures are predicted in advance. A newer strategy of design, the *reticular synthesis* coined by Yaghi et al (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003), has seen success in producing stable, adjustable structures which are predicted before synthesis. As applied to the field of *Metal-Organic Materials (MOMs)*, reticular synthesis has produced *Metal-Organic Frameworks (MOFs)* which are stable and porous with adjustable dimensions (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003). By the MOMs field, we mean a particularly broad field of materials composed of metal *ions* (to be defined section II) or metal clusters connected together by *organic molecules* (Perry, 2009), which is to say molecules containing hydrogen and carbon among other elements (Carter, 2007):

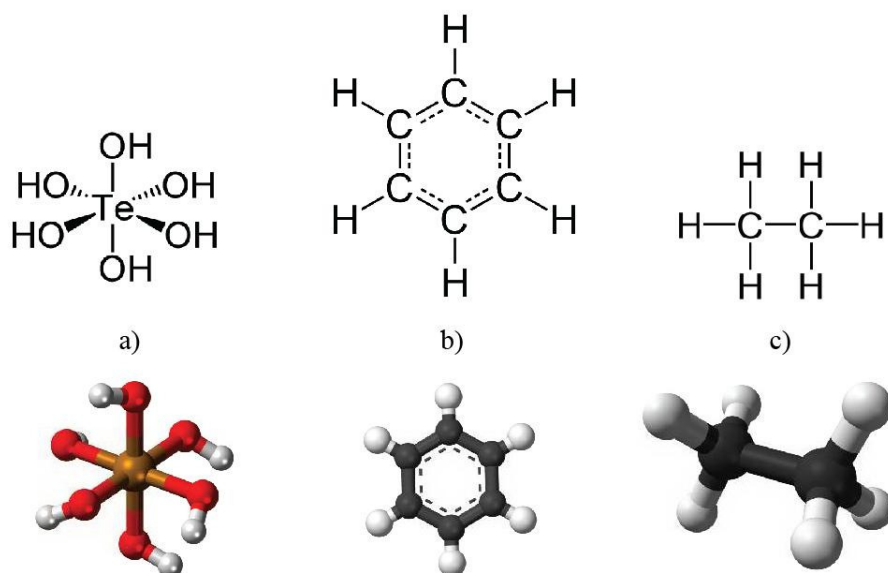


Figure 1: Two-dimensional and three-dimensional representations the molecules of a) telluric acid, b) benzene, and c) ethane. For all two-dimensional representations, bonds are represented by solid or dashed lines, and each element is represented by its notation in the periodic table (Miessler & Tarr, 2011). For all three-dimensional representations, bonds are cylinders in between spheres, hydrogen atoms are white, carbon atoms are dark grey, oxygen atoms are red, and tellurium atoms are gold. Note that b) and c) are organic, but a) is not. For all remaining three-dimensional representations of molecules, bonds will be the cylinders in between spheres. Figure 1 source: public domain, obtained from Wikimedia Commons. Figure 1.a) was dedicated to the public domain; the source is: <http://commons.wikimedia.org/wiki/File:Telluric-acid-3D-balls.png>

Yaghi et al define reticular synthesis as the “process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures (networks), which are held together by strong bonding” (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003). Accordingly, reticular synthesis utilizes *Molecular Building Blocks (MBBs)*, molecules acting as the bricks used to assemble structures that are designed beforehand. We will define MBBs and other unfamiliar terminology in sections II and III. The development of reticular synthesis has been closely related to the increasing scientific interest in the field of MOMs since Yaghi’s “Reticular Synthesis and the Design of New Materials” (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003). This is due to the real-world applications in which the MOMs field is currently involved, which we will detail in section II.

Dr. Mike Zaworotko and other researchers at the University of South Florida (USF) have made multiple developments in the field of MOMs. One in particular is the subject of this thesis: the development of the Square Trigonal Prismatic (**stp**) *crystal net* (to be defined in section III) by Alexander Schoedel, which was designed and predicted using a pre-formed trigonal prismatic MBB (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). To understand this development, we will discuss the properties and analysis of **stp** from chemistry and mathematics points of view alongside terminology and introductory concepts in the follow two sections.

II. Chemistry of stp

A. Basics of Chemistry

Before discussing the purpose, design, and synthesis of **stp**, we clarify the basic nomenclature. We presume the audience is familiar with the notions of: an *atom*, a *proton*, an *electron*, a *neutron*, an *element*, a *bond*, and a *molecule*. Additionally, a *compound* is defined here to be a substance composed of the one kind of molecule, consisting of several kinds; thus, compounds can be thought of in a larger, real-world scale. From these definitions, we will build the basic chemistry needed to understand the rest of this thesis. This description will not involve the finer physics behind how atoms function, internally or in relation to each other, but rather present the general ideas necessary for this thesis. The element an atom belongs to is determined by the number of protons in its nucleus.

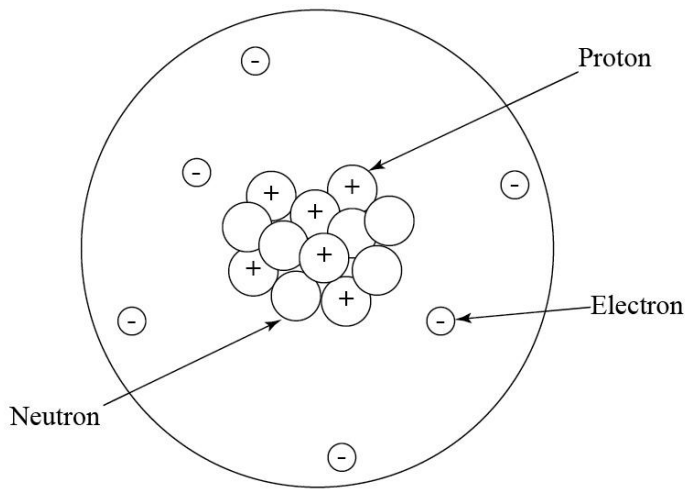


Figure 2: Two-dimensional representation of a carbon atom. The atom has six protons, six neutrons, and six electrons as per the standard in a periodic table (Miessler & Tarr, 2011). The boundary of the atom has been outlined by a circle.

An atom has an *electron cloud*, which is a group of electrons that hover around the nucleus of protons and neutrons at different distances (Carter, 2007). Electrons in the cloud that are closer to the nucleus will be more attracted to it than those further away. This electron cloud can be thought of as a layering of *shells* of electrons around the nucleus in general, with each shell having electrons that have roughly the same attraction to the nucleus (Carter, 2007). It turns out that beginning with the innermost electron shell, each shell around a nucleus can only be occupied by a certain number of electrons, regardless of which element the atom is. Excess electrons fill the more outward shells progressively until each electron is in a shell, with the outermost shell called the *valence shell* (Carter, 2007); electrons in the valence shell are called *valence electrons*.

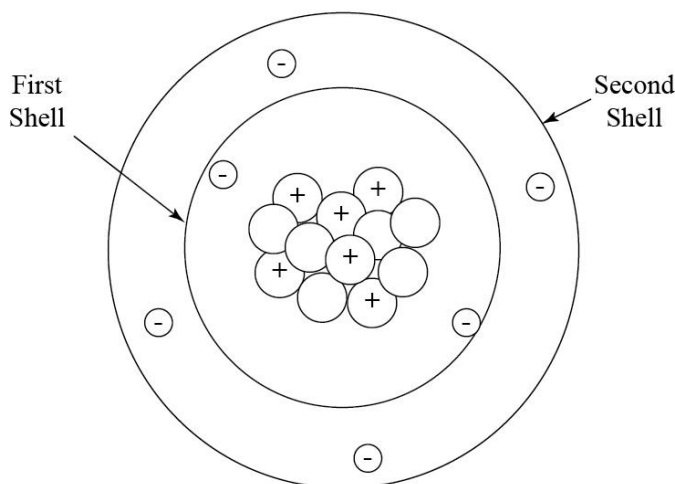


Figure 3: Two-dimensional representation of a carbon atom's electron shells. Note that the distance from the nucleus of each electron in a shell is not necessarily the exact same. Moreover, a carbon atom has only four electrons in its valence shell.

For reasons beyond the scope of this thesis, an atom's innermost shell can only hold two electrons, and each successive shell can only hold eight before it is full and another shell is formed. Furthermore, atoms are more structurally stable with completely filled or half-filled

valence shells (Carter, 2007). Accordingly, atoms will tend to form bonds in order to share, lose, or gain electrons so that their valence shells are filled.

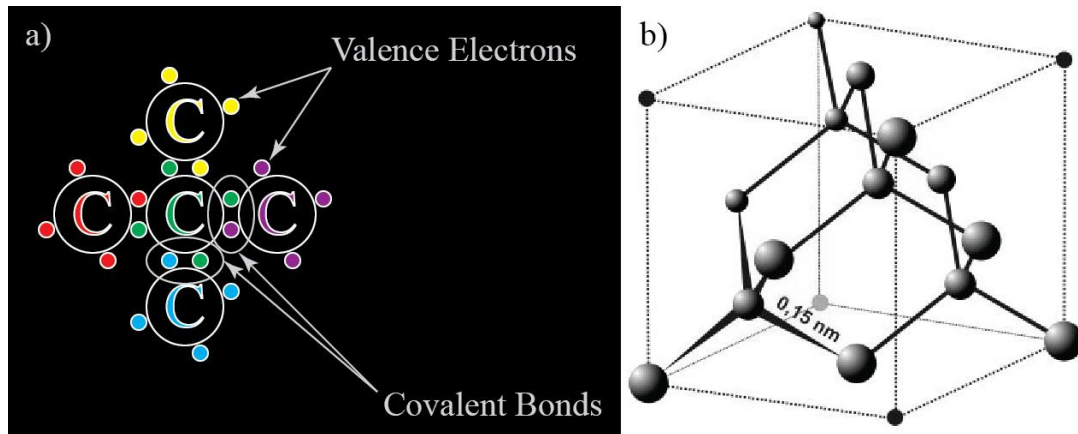


Figure 4: a) Two-dimensional representation of carbon atoms covalently bonded. In the above image, each carbon atom is represented by the letter C, and only their valence electrons are shown. Each atom represented has its own associated color. b) Three-dimensional representation of some carbon atoms connected to each other. In this case, the covalent bonds from bold lines and the carbon atoms are gray spheres. Our audience should ignore the dotted lines and non-carbon spheres. The distance in between two carbon atoms is denoted by 0.15 nanometers. The source of Figure 4.b) is http://commons.wikimedia.org/wiki/File:Diamond_and_graphite2.jpg

The most important kind of bond for this thesis is the *covalent bond*, in which two atoms or molecules share a pair of electrons in order to fill one or both of their valence shells, as shown above (Carter, 2007). In Figure 4, the central carbon atom fills its valence shell through covalent bonding. The limit on how many covalent bonds any one atom or molecule is based on the number of electrons it has. In particular, a *coordinate covalent bond* is a covalent bond in which the pair of shared electrons comes from one atom or molecule (Miessler & Tarr, 2011). Coordinate covalent bonds and *ligands* form the building blocks of chemical structures discussed in this thesis. Ligands are atoms, ions, or molecules that form coordinate covalent bonds in which they share their electron pair with a metal atom or *ion* (Miessler & Tarr, 2011),

Finally, an ion is an atom or molecule with a different number of protons than electrons in total. Specifically, *anion* has more electrons than protons and is negatively charged overall while a *cation* has more protons than electrons and is positively charged overall. (Carter, 2007) Anions typically have a “*n-*” next to their chemical formula (e.g. OH⁻) and cations typically have a “*n+*” instead (e.g. Mg²⁺) where *n* is a positive integer greater than one denoting the number of excess or absent electrons; if *n* = 1, it is not shown.

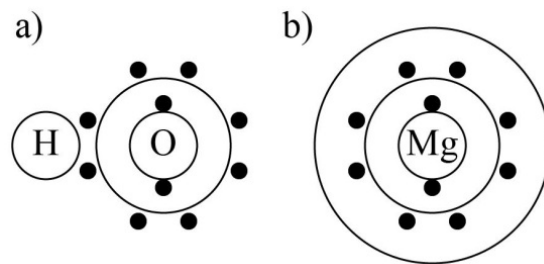


Figure 5: Two-dimensional representations of ions. An atom's nucleus is represented by its element notation in the periodic table (Miessler & Tarr, 2011), black dots are electrons, and each circle represents a shell of electrons of an atom. a) A molecule of hydroxide (OH^-); hydrogen has one proton and oxygen has eight, so the presence of ten electrons signify hydroxide is an anion. b) An atom of magnesium, which has twelve protons; the presence of ten electrons signify that these magnesium atom is a cation.

B. Purpose and Design of **stp**

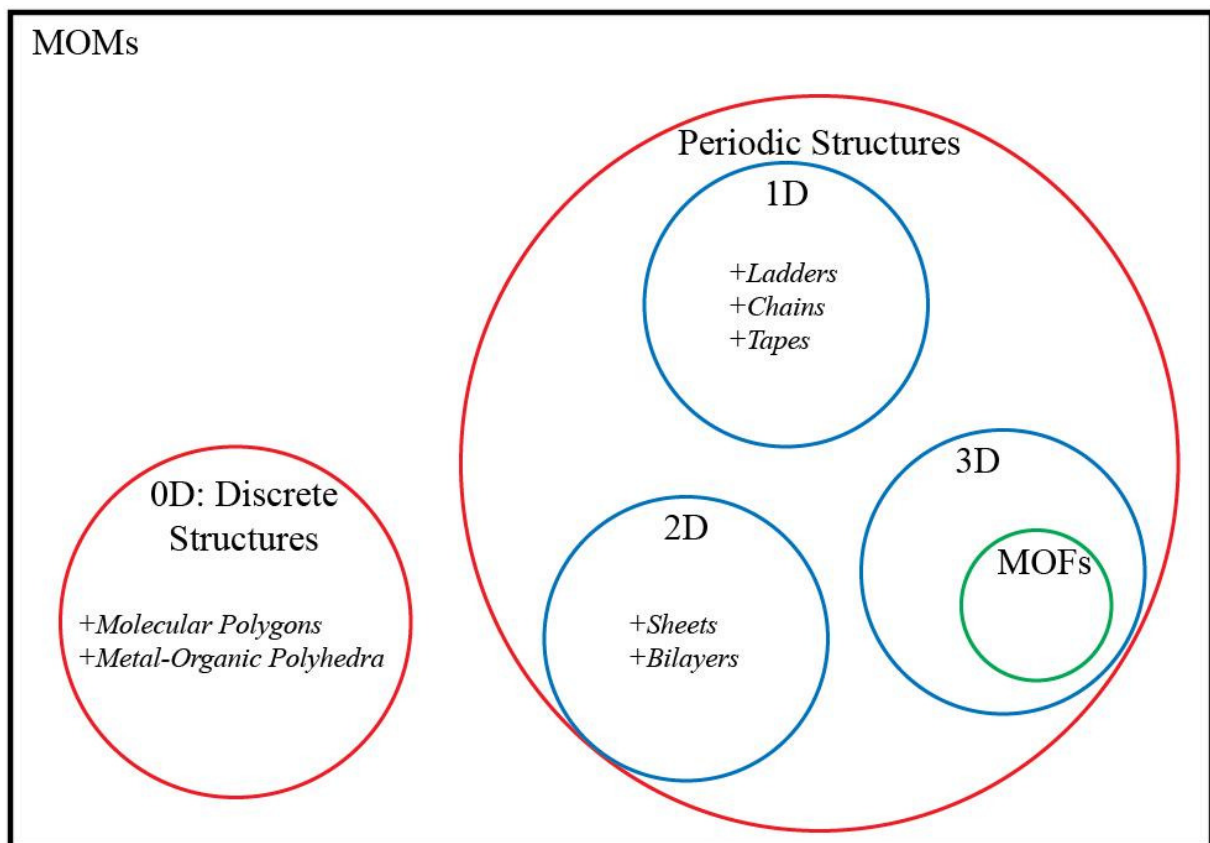


Figure 6: Venn diagram of the field of MOMs based on Perry's table (Perry, 2009).

The **stp** crystal net was designed in the context of 3-periodic MOMs and their applications. We define something as periodic if it occurs at equal, measurable intervals in a

generic space. Below is an example of the periodic occurrence of a dot along one dimension, for example the number line. Moreover, something is 3-periodic if it occurs periodically along each of the three axial dimensions in the real world. Thus a structure is 3-periodic if it occurs periodically along the aforementioned three dimensions. Below are examples of 1-periodic, 2-periodic, and 3-periodic structures:

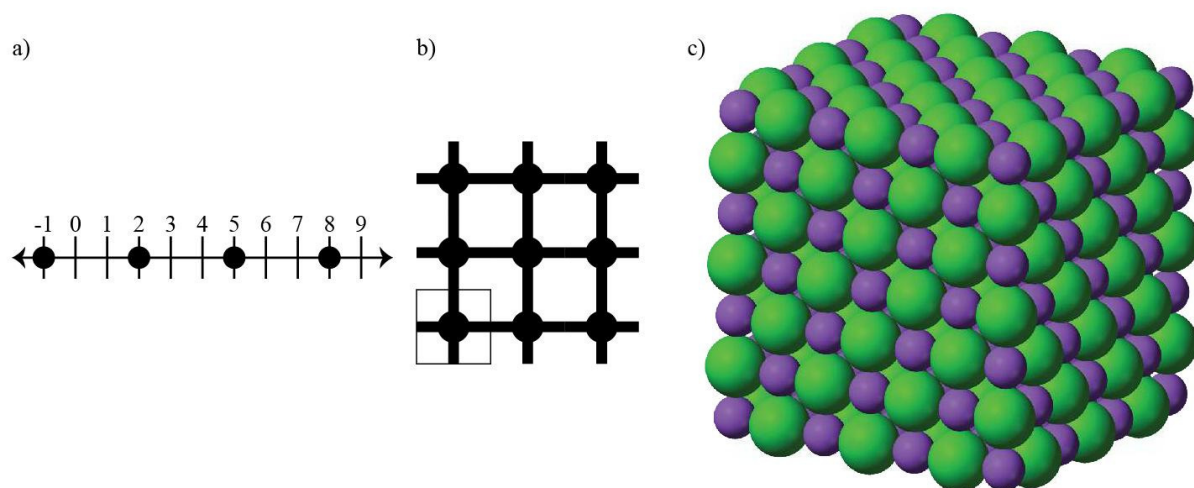


Figure 7: a) Example of the periodic occurrence of a dot on the integer number line. b) Example of the periodic occurrence of the square tile across a plane. c) Example of the periodic occurrence of sodium (Na, in purple) and chlorine (Cl, in green) atoms in salt (NaCl). **Figure 7.c source: Public Domain, obtained from Wikimedia Commons.**

A Metal-Organic Material (MOM) is typically composed of metal ions or metal clusters, which are connected to each other by organic molecules serving as ligands. Specifically, Metal-Organic Frameworks (MOFs) are 3-periodic MOMs that define the three-dimensional structures of *crystals*. (Miessler & Tarr, 2011) We define crystals to be solids whose components (e.g. atoms, ions, or molecules) are arranged in a periodic order allowing them to be extended in all three axial dimensions (Perry, 2009). Figure 7.c) is an example of a salt (NaCl) crystal in which the sodium or chlorine atoms are arranged periodically; it is visible that this three-dimensional periodic occurrence can be continued in any of the three axial directions. All the crystals we shall discuss henceforth will be MOMs.

In regards to MOMs, the organic ligands that connect metal ions or metal clusters are called *linkers*. The metal ions or clusters are referred to as *nodes* (Batten & Robson, 1998); linkers have at least two sites at which bonds can be formed to nodes. Moreover, MOFs are recognized for the empty spaces in between nodes and linkers which are often referred to as pores. Here is an example of MOM along with its building blocks:

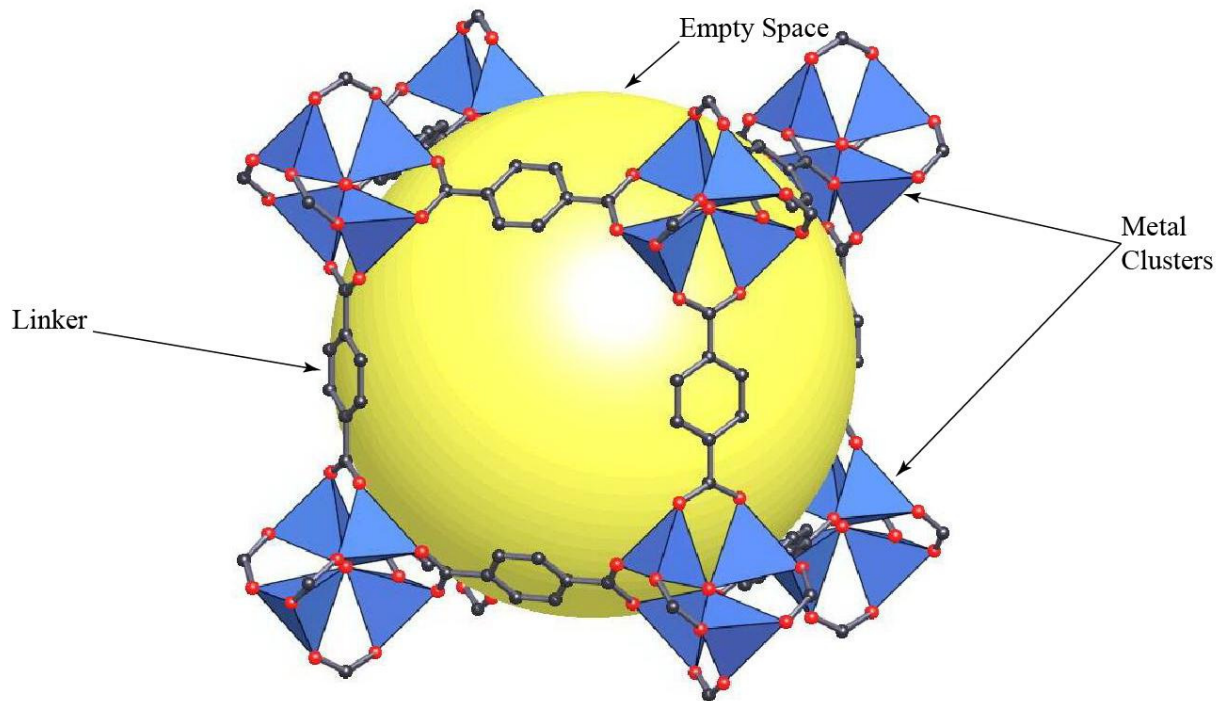


Figure 8: Three-dimensional representation of a MOF. We distinguish that metal clusters are not just the blue three-dimensional objects, but groups connected to each other by linkers. Courtesy of Dr. Michael O’Keeffe.

In the MOM seen above, the node is a cluster composed of a metal ion and oxygen atoms and is an example of an MBB. MBBs have distinct geometric arrangements defined by the points at which the MBBs can be connected to linkers, called *extension points* (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003). Nodes and linkers are classified by their *connectivity*: a node is said to be *n-connected* if there are *n* linkers attached to it and a linker is said to be *n-connected* if it connects *n* nodes (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011).

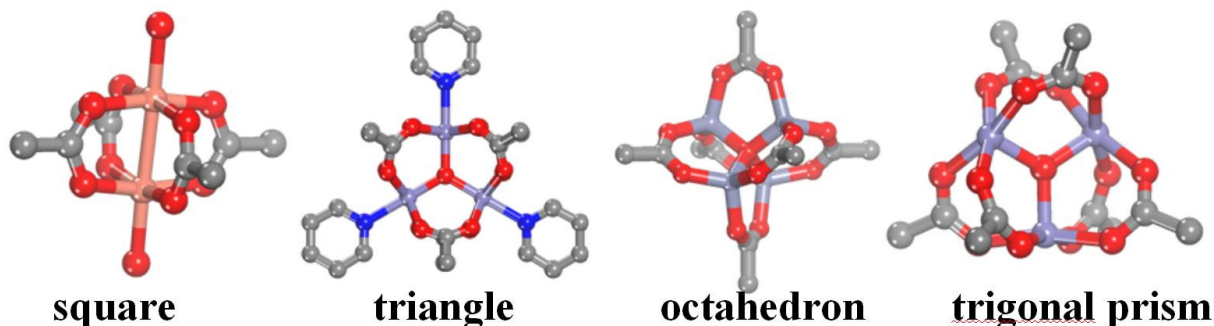


Figure 9: Four three-dimensional representations of MBBs, the names of which will be elaborated upon in section III. Light blue or light red spheres represent metal ions, gray represents carbon, and dark red represents oxygen. Courtesy of Alexander Schoedel.

The purpose of designing **stp** (O'Keeffe, Peskov, Ramsden, & Yaghi, 2008) was to construct a crystal net that used the *trigonal prismatic* Primary Molecular Building Block (tp-PMBB-1) and to create visible single crystals. A trigonal prismatic structure has the following form:

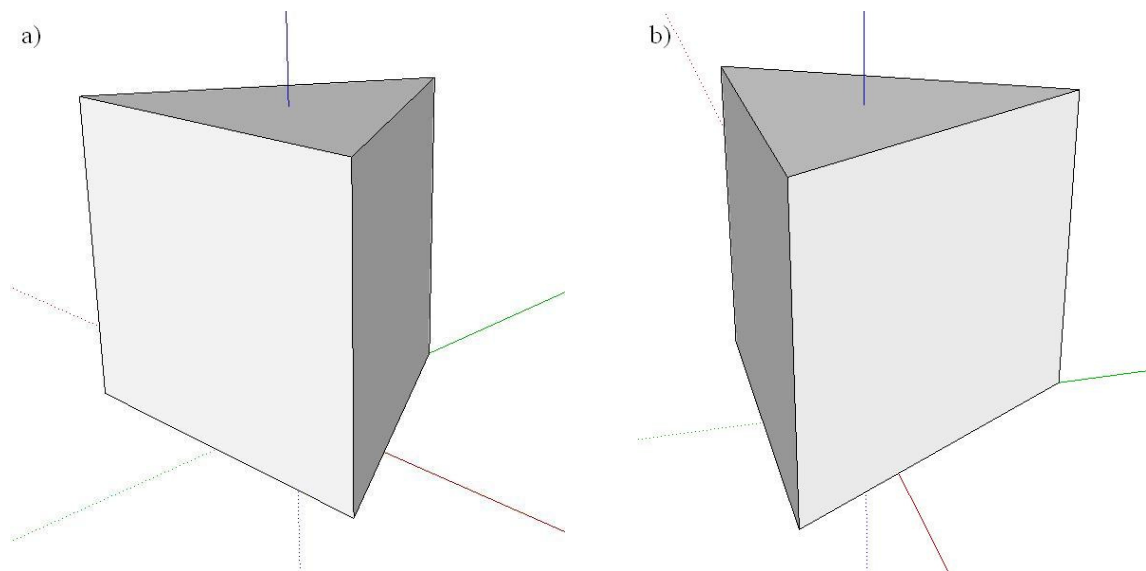


Figure 10: a) - b) Three-dimensional representations of a trigonal prism, seen from two angles. The green line represents the z-axis, blue is the y-axis, and red is the x-axis.

Researchers need MOMs to form full crystals that can exist stably without other supporting structures for most potential applications. We note this because a perfect MOM might form a single crystal; however, not all predesigned MOMs form single crystals but instead could form powders or amorphous solids. Often, predesigned MOMs either need other molecules for structural support, like solvents and anions that are present during the actual synthesis of a MOM. These are in addition to the MBBs and linkers that make up a MOM's structure; without this structural support, some MOMs are unstable so their structures tend to collapse. Up until Schoedel's research, trigonal prism MBBs based on chromium (III) had only yielded microcrystalline powders. These materials had already shown outstanding framework stability with very large *surface areas* within the "porous" crystal. In general, surface area is the area required to cover the surface (i.e. outer boundaries) of any object, as seen below:

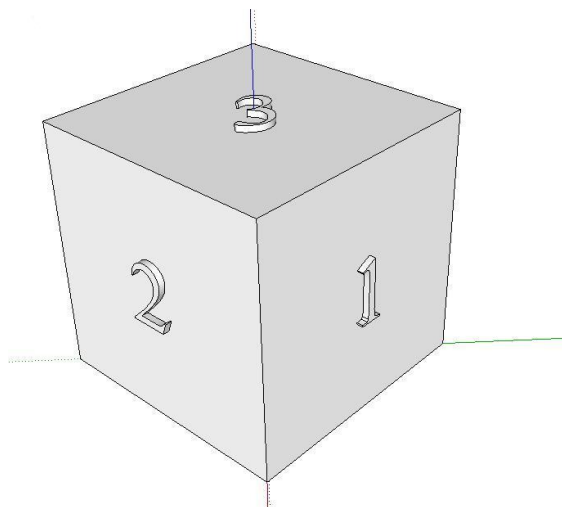


Figure 11: Three-dimensional representation of a cube with three faces labeled. The area necessary to cover each of these faces and the three unseen faces sums to be the total surface area of the cube. The green line represents the z-axis, blue is the y-axis, and red is the x-axis.

In regards to MOMs however, surface area does not just deal with exterior surfaces because MOMs behave like sponges. That is, MOMs have internal surfaces onto which other molecules and/or atoms become attached inside, much like water is attached to the interior of a sponge after entering through the sponge's pores. This explanation suffices for describing crystals as "porous," because a full discussion on the definition and qualities of pores is beyond the scope of this thesis. The interior surfaces of MOM crystals also contribute to their overall surface areas, allowing for extremely large surface areas even in small crystals. For example, at the time Yaghi et al published "Reticular Synthesis and the Design of New Materials," a MOF had been found with a surface area of 2,900 meters squared per gram (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003).

In regards to atoms and molecules, the outer boundaries are determined by the valence shell and its experimental distance from the nucleus or nuclei. For an atom, this distance is referred to as the radius of the atom. Thus, the surface area of a MOM covers all of its molecular components, taking into account atom and molecule intersections. Below is an example of the outer boundaries to be covered for an MBB:

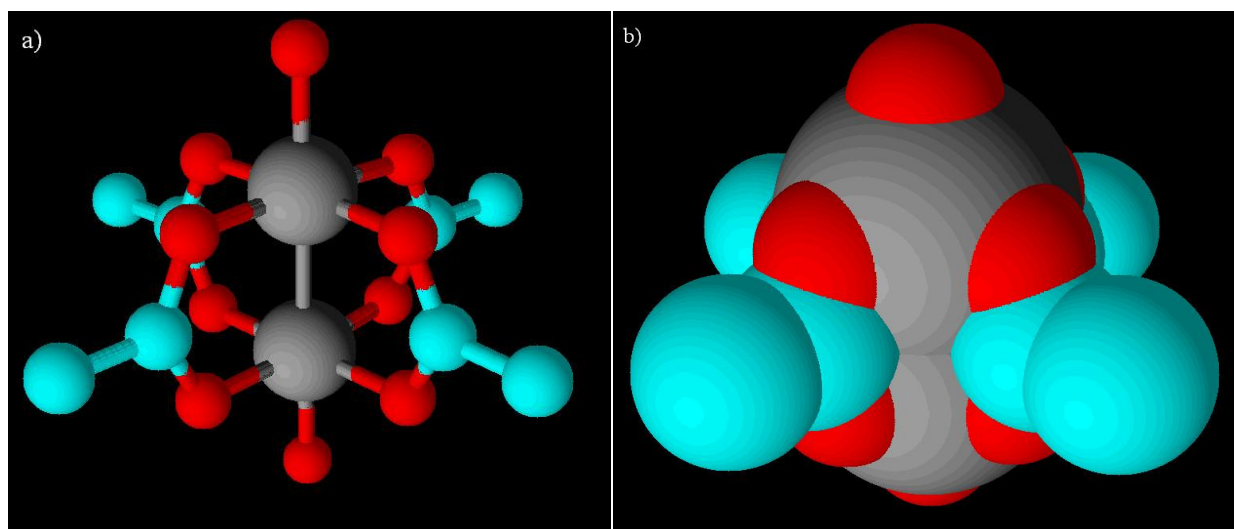
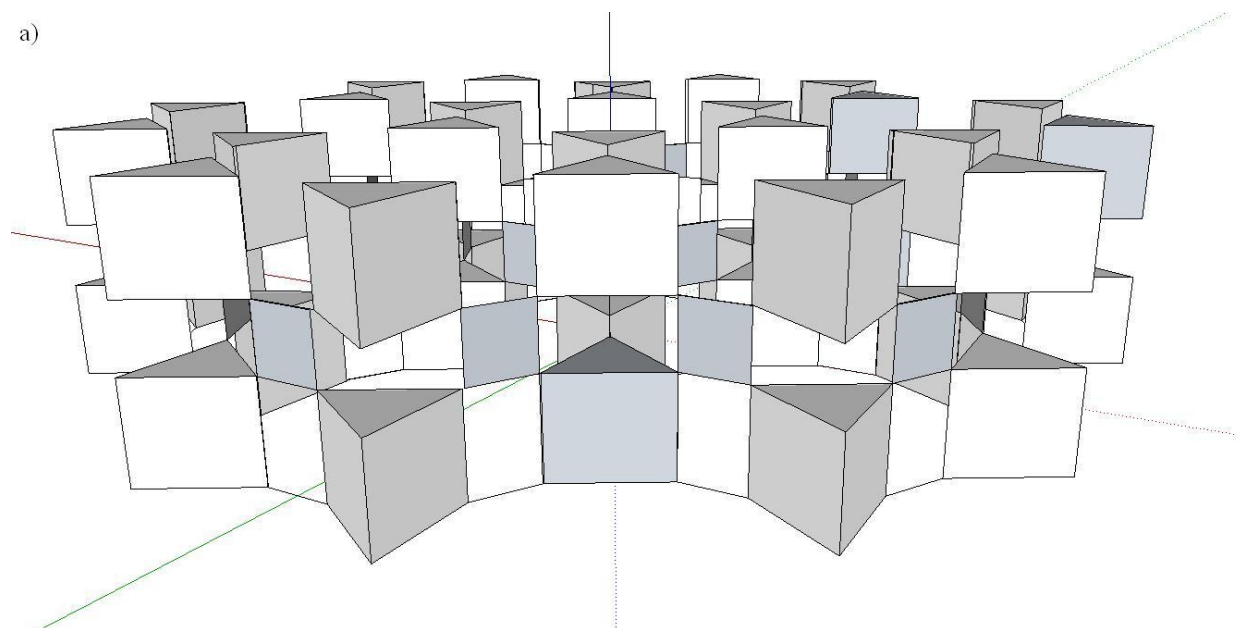


Figure 12: Two three-dimensional representations of an MBB. In both, oxygen atoms are red, carbon atoms are light blue, and metal ions are red. a) Typical “ball and stick” representation of such an MBB. b) Representation of the same MBB, but instead taking into account atoms’ radii. This representation is used to determine the MBB’s surface area.

Schoedel anticipated that trigonal prismatic MBBs could be assembled together using another MBB and form 3-periodic MOMs, which he expected to form into visible single crystals (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). The two MBBs he chose to test with the trigonal prismatic MBB were a linear MBB and a square MBB. The **stp** crystal net design resulted from the use of a trigonal prism MBB and a square MBB, as seen below.



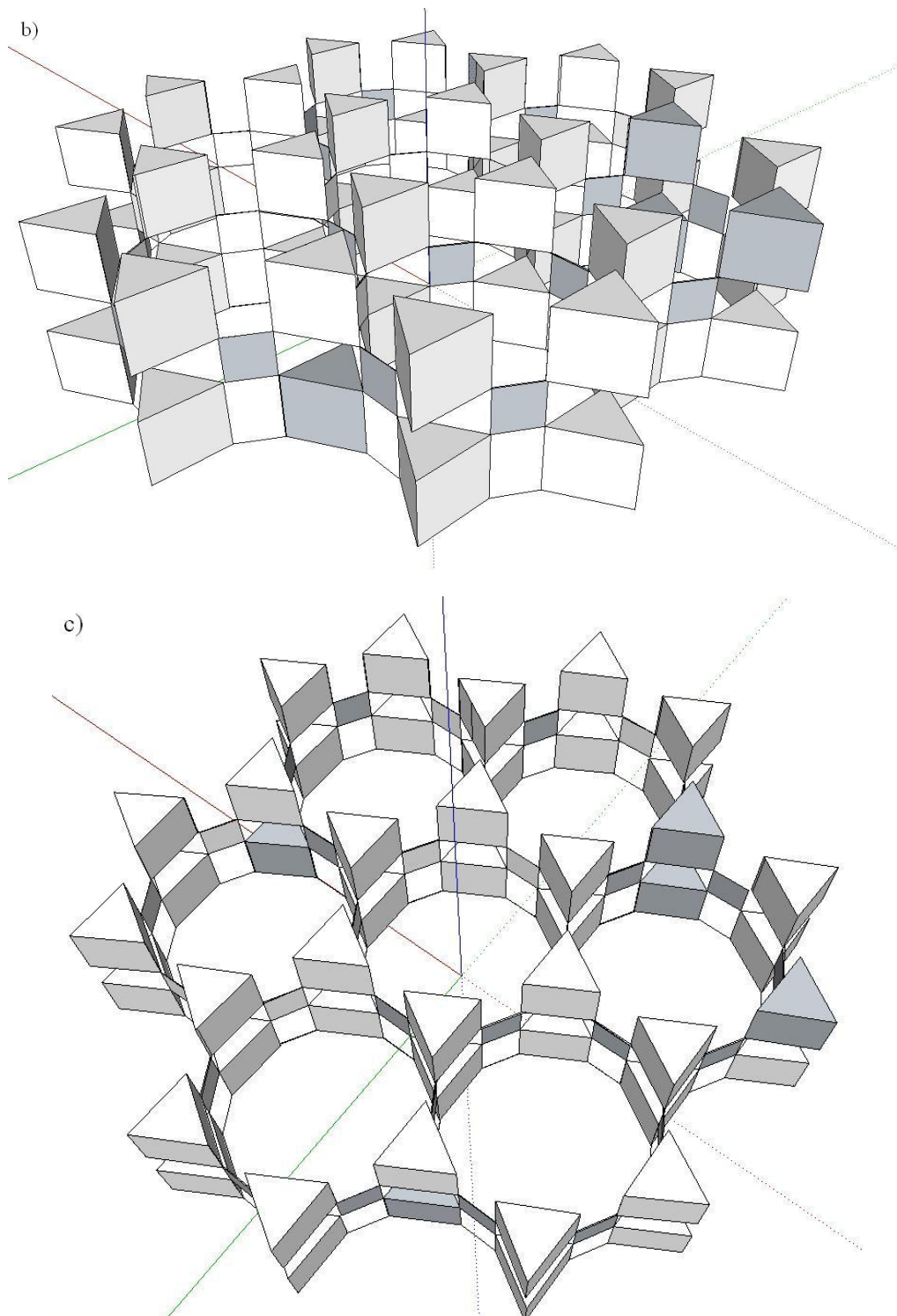


Figure 13: a) – c) Abstract three-dimensional representation of some of the stp crystal net using trigonal prism MBBs connected to each other by square MBBs. The green line represents the z-axis, blue is the y-axis, and red is the x-axis.

C. Synthesis

1. Theoretical Process

Per the application of reticular synthesis, the **stp** crystal net was predicted before the chemicals were chosen to synthesize a crystal with the **stp topology** (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). Here, we make the important distinction between the vast field of topology in mathematics and the meaning of the term “topology” in chemistry. In chemistry, a material’s topology describes properties of its atomic or molecular structure. In terms of mathematics, the chemical topology of a material describes the “isomorphism class” to which a space or figure belongs; however, further details on “isomorphisms” and “isomorphism classes” are specific to the algebra sub-field of mathematics and are beyond the scope of this thesis. Because we will not deal with topology in mathematical terms in this section, we will use the term topology in the chemical sense. Nevertheless, we detail the problems of similar terminology with vastly different meanings in section IV. We further note that the naming system we use for chemical topologies comes from the Reticular Chemistry Structure Resource (RCSR) (O’Keeffe, Peskov, Ramsden, & Yaghi, 2008).

The use of a linear MBB was expected to yield a crystal with the *6,6-connected acs* topology (Sudik, Côté, & Yaghi, 2005); however, because a linear, yet bendable MBB was used, crystals with other “*6,6-connected*” **snx** and **snw** topologies (O’Keeffe, Peskov, Ramsden, & Yaghi, 2008) were produced instead. By 6,6-connected, we mean a topology in which the only nodes that exist are two distinct kinds of 6-connected nodes. The nodes are distinct because they are not “isomorphic” to each other, which means that we cannot use one in place of the other when describing this topology. A further discussion on kinds of nodes and whether two nodes are isomorphic would once again be beyond the scope of this thesis. We will present the **snx** and **snw** topologies and elaborate upon some of the chemical process in section IV. In regards to the **stp** crystal net, the 6-connected trigonal prism MBB, henceforth referred to as tp-PMBB-1, was searched for in the Cambridge Structure Database (CSD) (Schoedel, Synthesis of stp, 2012). This database details the structures of thousands of known molecules and compounds. The constraints on the search for tp-PMBB-1 were that the trigonal prism structure was to have one kind of metal ion and isonicotinic acid, shown below.

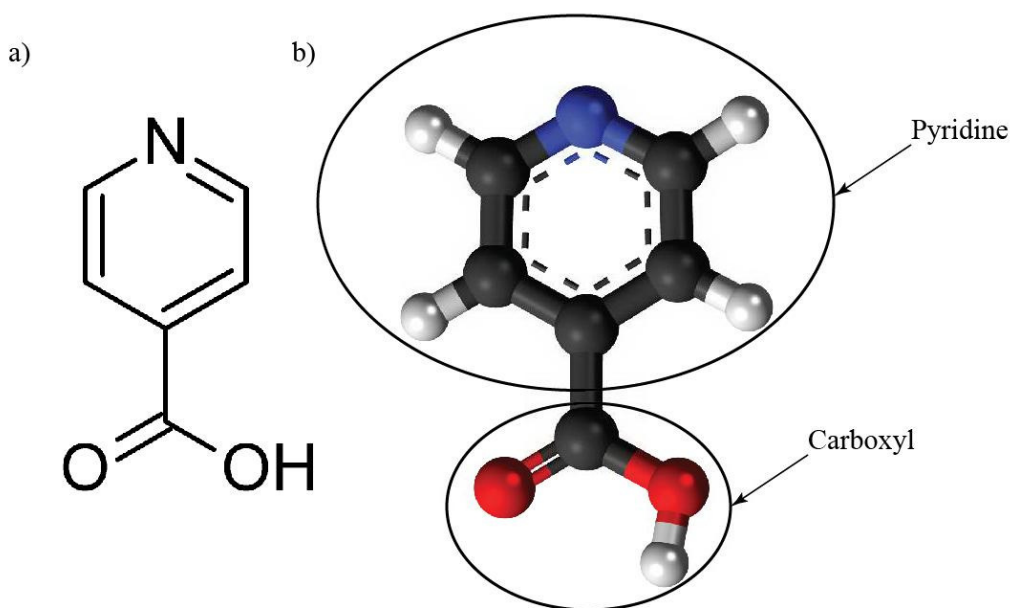


Figure 14: a) Two-dimensional representation of a molecule of isonicotinic acid. It is common to denote two covalent bonds with two lines between the same atoms; also, carbon is frequently not written in two-dimensional representations, but rather corners or which have no elements are implied to be carbon atoms. Finally, bonds to hydrogen atoms and the atoms themselves tend not to be shown in two-dimensional representations, though their presence is implied. b) Three-dimensional representation, with carbon atoms in dark grey, nitrogen in blue, oxygen in red, and hydrogen in white. Figure 14 source: public domain, obtained from Wikimedia Commons. Figure 14.b) was dedicated to the public domain; the source is: <http://commons.wikimedia.org/wiki/File:Isonicotinic-acid-3D-balls.png>

Isonicotinic acid, shown above, is composed of a carboxyl *moiety* and a pyridine, both of which are labeled above. We define moiety to be a group of atoms, ions, or sub-molecules that have a specific structure and composition (Carter, 2007). MBBs are *decorated* with moieties when sub-molecules of said moieties are connected to MBBs at their extension points (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003). Examples of two common moieties are shown below.

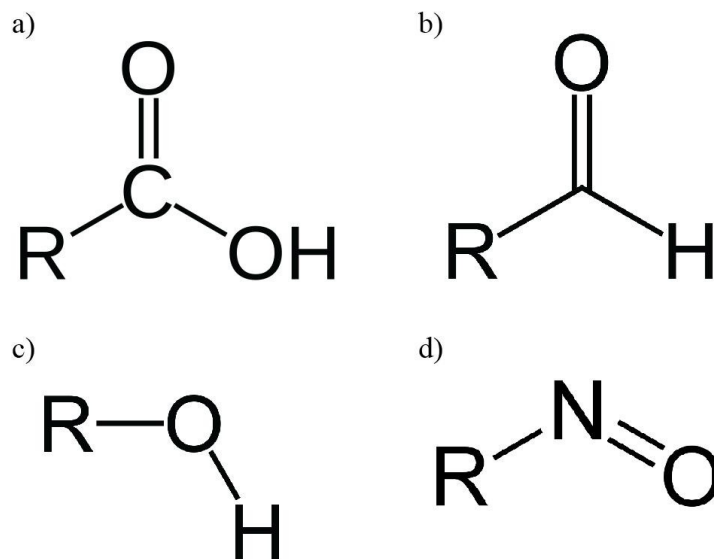


Figure 15: Two-dimensional representations of different moieties. For all moieties, R usually represents an organic molecule; but if the moiety is organic, R can be simply a hydrogen atom. a) Carboxyl moiety, b) Aldehyde moiety, c) Hydroxyl moiety, and d) Nitroso moiety. Figure 15 source: public domain, obtained from Wikimedia Commons.

The reason for having such constraints on the search for tp-PMBB-1 was that it would allow six pyridine molecules to be exposed at tp-PMBB-1's extension points so that each pyridine could serve as a linker between tp-PMBB-1 and a second metal node (MBB). Only one trigonal prism structure was found, with the chromium serving as the metal ion (Mullica, Pennington, Bradshaw, & Sappenfiled, 1992). This process is better understood in the figures below (Schoedel, Synthesis of stp, 2012).

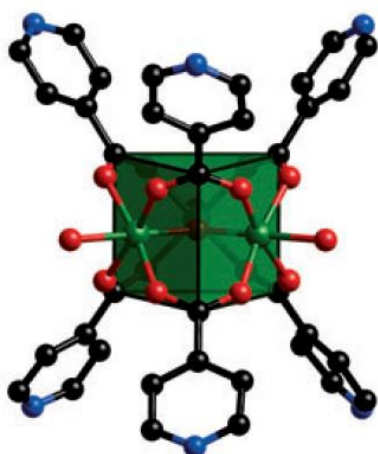


Figure 16: Three-dimensional representation of tp-PMBB-1 with a trigonal prismatic outline. Note the six exposed nitrogen (in blue) atoms. Chromium atoms are in green, oxygen atoms in red, and carbon atoms are black. Courtesy of Alexander Schoedel.

Accordingly, Schoedel then used CSD to find a 4-connected square structure composed of a metal ion and 4 pyridines. He found CdN_4 (shown in Figure 17.a), a rigid square sub-molecule of the molecule formed by connecting cadmium (II) to four pyridines, shown at the center of Figure 17.b (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). This MBB will henceforth be known as MBB-2 (Schoedel, Synthesis of *stp*, 2012).

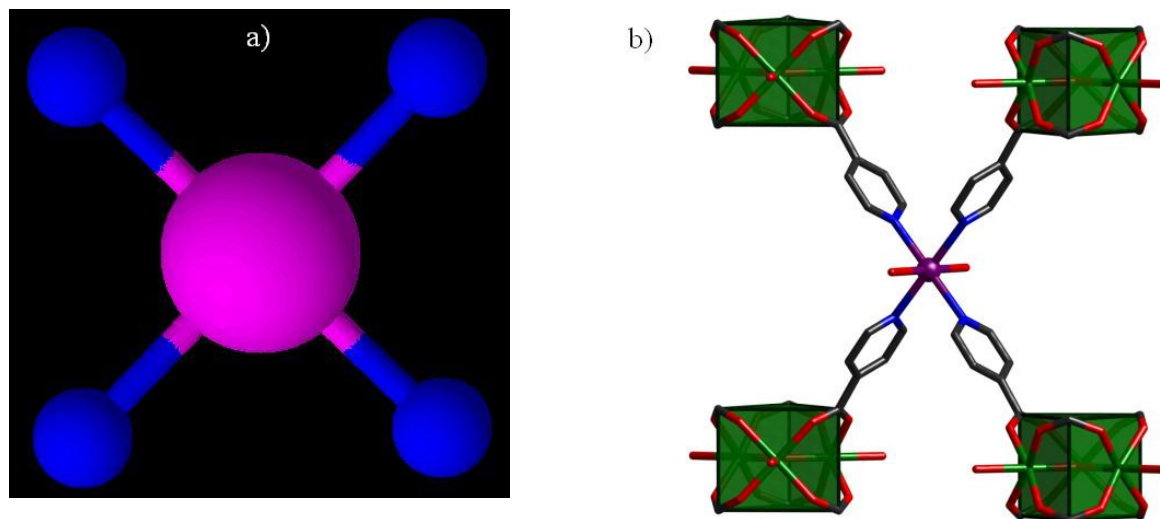


Figure 17: a) Three-dimensional representation of CdN_4 , with nitrogen atoms in blue and cadmium in magenta. Note the black square outline of this MBB. b) The assembly of MBB-2, connecting four adjacent *tp*-PMBB-1s through their exposed pyridines. Oxygen atoms are in red, chromium in green, carbon in dark grey, nitrogen in blue, and cadmium in magenta. Figure 17.b Courtesy of Alexander Schoedel.

Thus, the design of the *stp* crystal net was transferred into a theoretical chemical formula consisting of *tp*-PMBB-1 and MBB-2 as shown above, connected by pyridine linkers.

2. 2-Step Crystal Engineering

Though the synthesis of a crystal with the *stp* topology is based on the theoretical process previously described, the actual synthesis in the lab involves other stabilizing mediums and molecules. The process is first divided into two steps: 1) the construction of *tp*-PMBB-1 using chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$) and isonicotinic acid dissolved in water, and 2) the construction of MBB-2 using cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$) in a layering process which will be detailed later. We clarify that the ($\cdot n \text{H}_2\text{O}$) notation describes the ratio of a moles of a compound to n moles of water.

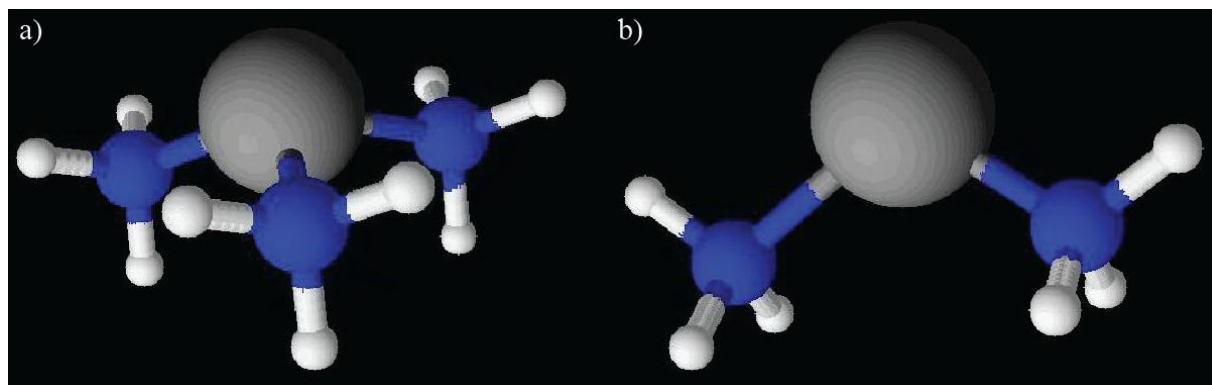
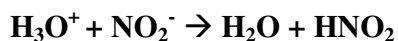


Figure 18: Three-dimensional representations of the chemical structures of a) chromium ($\text{Cr}(\text{NO}_3)_3$) and b) cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$). Note: Gray sphere represent the metal, blue nitrogen, and white hydrogen.

The division of these steps is based on the Hard and Soft Acid and Base theory (HSAB theory) developed by R. G. Pearson (Miessler & Tarr, 2011). We must first review what *acids*, *bases*, and *polarity* are. We will use the accepted Brønsted-Lowry definitions of acids and bases: “an acid is any proton donor and a base is any proton acceptor” (Carter, 2007). By this we mean that an acid reacts in such a way as to lose protons (in the form of atoms or sub-molecules) and a base reacts in such a way as to gain protons (in the aforementioned form). In the formula below H_3O^+ is the acid and NO_2^- is the base (Miessler & Tarr, 2011). The reason for this is that H_3O^+ loses a hydrogen atom, which has only one proton, and NO_2^- gains that hydrogen atom.



Next, we define polarity. Polarity occurs when the electron clouds of two atoms in a bond are drawn in either one direction or another. This is directly related to the intensity of positive attraction in each atom’s nucleus (Carter, 2007). Polarity leaves one atom in the bond with its positive nucleus more exposed and the other atom with a relative overabundance of electrons which results in a positively charged and negatively charged side, respectively. Take the covalent bond in between an oxygen atom and a hydrogen atom (shown below); in this case, side opposite of the bond is negatively charged for oxygen and positively charged for hydrogen.

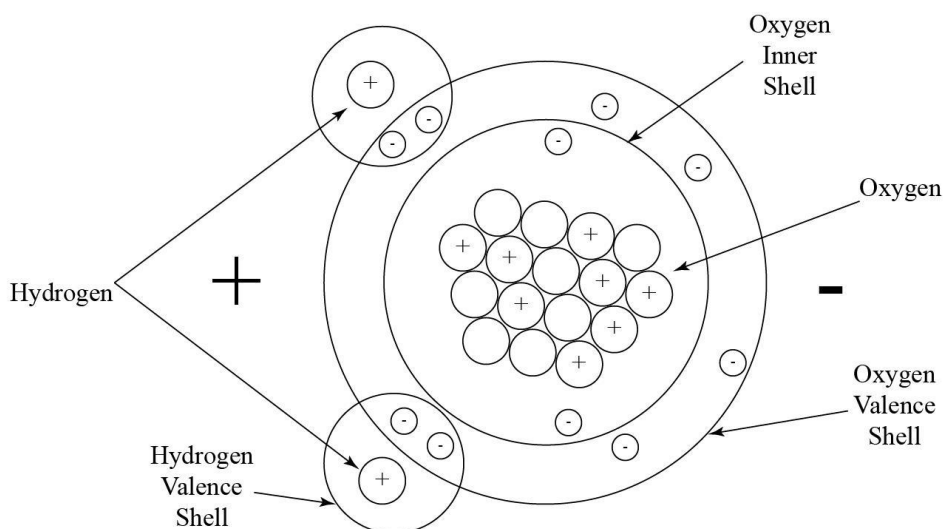


Figure 19: Two-dimensional representation of a H_2O molecule. The each intersection of the oxygen atom's valence shell with the hydrogen atoms' valence shell represents a covalent bond. Note the abundance of electrons on the right side of the molecule and the two exposed protons on the left side of the molecule.

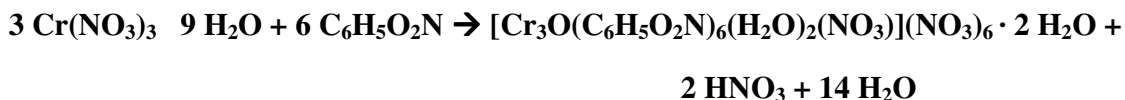
Generally, however, polarity is not isolated to just the bond between two atoms. Molecules are polar if there is overall stronger charge in the nuclei of a group of atoms than the rest of the molecule, as shown below (Carter, 2007). A molecule is said to be *polarized* if it exhibits polarity and *polarizable* if a bond can be formed which would make the molecule polarized. Finally, molecules that are polarized are simply called *polar molecules*. The H_2O molecule in Figure 19 is a polar molecule because the side on which the hydrogen atoms are connected is positively charged because of each hydrogen atom. Furthermore, the opposite side is negatively charged because of all the electrons.

Now we can understand how HSAB theory dictates the division into two steps of the synthesis of an **stp** crystal. First, HSAB theory declares that polarizable acids and bases are “soft” while non-polarizable (those that can't be polarized) acids and bases are “hard.” Moreover, it states that “hard acids prefer to bind with hard bases and soft acids prefer to bind with soft bases” (Miessler & Tarr, 2011). This means that reactions involving the same kind of acid and base (hard or soft) will occur more thoroughly and more often than those involving one hard and one soft. Further study behind the mechanisms that explain HSAB theory is beyond the scope of this thesis.

3. Synthesis

In this sub-section, we consider the components of **stp**: chromium (Cr^{3+}) is a hard acid, carboxylate is a hard base, cadmium (Cd^{2+}) is a soft acid, and pyridine is a soft base. The first step of the synthesis involves the reaction of a hard acid and hard base, which yields a stable

structure (Schoedel, Synthesis of stp, 2012), in our case the nitrate salt of tp-PMBB-1 ($\text{Cr}_3\text{O}(\text{isonicH})_6(\text{H}_2\text{O})_2(\text{NO}_3)](\text{NO}_3)_6 \cdot 2 \text{H}_2\text{O}$) seen in the chemical reaction below. The second step involves the reaction of the soft basic portion of tp-PMBB-1, the pyridines, with the soft acid cadmium. First reaction:



As mentioned before, in the first step isonicotinic acid was dissolved in hot water and reacted together with chromium nitrate, which after evaporation yielded the nitrate salt of tp-PMBB-1. In this case, the nitrate ions balance out the charge of the tp-PMBB-1s (Schoedel, Synthesis of stp, 2012). In particular, one *mole* of $\text{Cr}(\text{NO}_3)_3$ reacts with 2 moles of isonicotinic acid, so half as many moles of a chromium nitrate as isonicotinic acid are required for the reaction in the first step.

A mole is an International Systems of Units (abbreviated SI from French) unit measuring chemical amount, much like a second is the SI unit of time. Just as second is abbreviated in SI to *s*, so mole is abbreviated to *mol*. One mole of an element or a compound has approximately 6.02×10^{23} atoms of the element or molecules of the compound, respectively (Carter, 2007). Because different elements and molecules have a different number of protons, neutrons, and electrons, the weight in grams of a mole varies depending the element or compound; these weights are all catalogued by the Chemical Abstracts Service (CAS) and every individual compound has its own CAS registry number.

Using molecular weights obtained from CAS, the exact amounts, in grams, of 1 mmol (millimole or a thousandth of a mole as per SI convention) of isonicotinic acid and 0.5 mmol of chromium nitrate were calculated and measured: 123.1 mg (milligrams) and 200.1 mg respectively. Each of these was obtained from sealed containers, separated using a small spatula, and measured using a scale accurate to 0.1 mg. First, a water bath was set up on top of a hot plate utilizing a large beaker and a smaller beaker. The smaller beaker was placed inside the large one; then water was poured in the larger beaker to about half volume. This amount is arbitrary and the larger beaker with the water (i.e. the water bath) is only used in order to ensure that the isonicotinic acid and chromium nitrate are not burned during the reaction (Schoedel, Synthesis of stp, 2012). Next, 50 mL of *deionized* water, water from which the ions have been removed, were added into the smaller container. This amount is somewhat arbitrary and measured out to be enough (by experience) for the given amount of isonicotinic acid to be dissolved before adding of the chromium nitrate nonahydrate (Schoedel, Synthesis of stp, 2012). On that note, the hot plate was then set to 373 Kelvin (denoted in SI as K; 373 K are 100 degrees Celsius). Using a stirring bar, the isonicotinic acid was added and then dissolved in the 50 mL of water. After the isonicotinic acid was fully dissolved, the chromium nitrate was added.

After about two minutes in the above set-up, during which the solution in the small beaker goes from being dark green to deep blue, the temperature was set down to 353 K. The water in the smaller beaker was then evaporated over a period of two hours; as tp-PMBB-1 forms, it turns the solution back to a dark green color when only few milliliters remain at the bottom. Once the water was fully evaporated, tp-PMBB-1 was recovered in the form of a green powder, ready to be used in the next step of synthesis, or, in our case, placed in a sealed container for later use.

The second step of the synthesis involves a layering process in which different layers of solvents are used to react the cadmium nitrate with the tp-PMBB-1 product from the first step. Nitrate is once again used with the metal ion, this time cadmium, so as to balance the overall charge of the resulting framework with single kind of anion. Below is an explanation of what makes nitrate (NO_3^-) negatively charged:

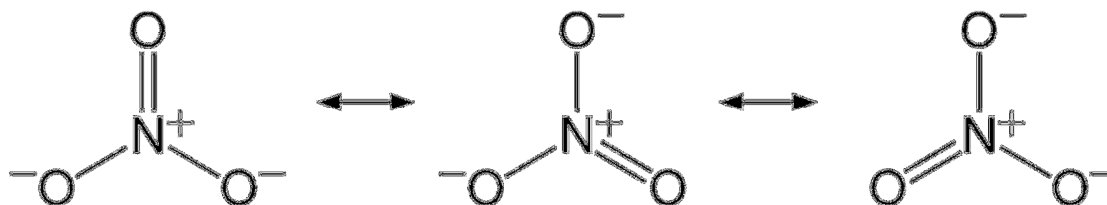
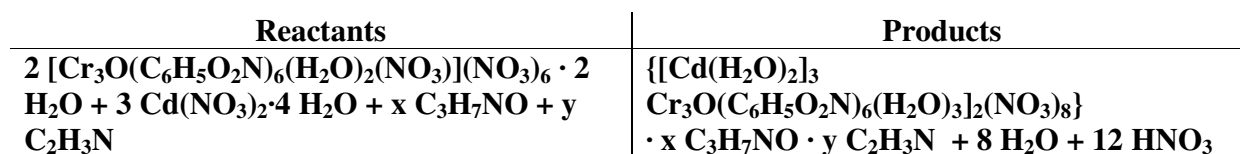


Figure 20: Three-dimensional representations, with ions labeled with their charge of the three possible states of a NO_3^- molecule. The molecule alternates among these three states for the three oxygen atoms that surround the nitrogen atom. In each case, only one oxygen atom with a double covalent bond to the nitrogen atom; the other two oxygen atoms are anions (Miessler & Tarr, 2011). We note that only the bonds that move around; the oxygen atoms in the above picture are fixed, and the molecule is not just rotating through the three states. Furthermore, in all three possibilities, the ions indicate that there is an additional electron present, and there is always one side of the molecule that is more negatively charged overall. Therefore, the nitrate molecule is negatively charged. Figure 20 source: public domain, obtained from Wikimedia Commons.

Second reaction, where x is the number of moles of DMF and y is the number of moles of MeCN:



This layering process is results from the property that *homogenous* solvents of different polarities and liquids of different densities organize themselves individually and vertically with less dense liquids progressively sitting on top of more dense liquids (Carter, 2007). A substance is homogenous if its composition is uniform all throughout (Carter, 2007). In the case of this reaction, solvents *N,N*-dimethylformamide (DMF) and acetonitrile (MeCN) were used to slowly spread the cadmium nitrate layer into the tp-PMBB-1 layer. This slow introduction is done in order to allow the **stp** crystals to grow properly into large single crystals in the middle layer, instead of a powder (Schoedel, Synthesis of stp, 2012). Moreover, the polarity of DMF is greater than that of MeCN, so mixtures of these two solvents at different ratios will have different densities and polarities. By “layering”, we mean that the different concentrations of DMF and MeCN mixtures are carefully placed one on top of the other, from lowest to greatest density.

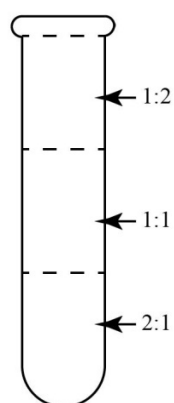


Figure 21: Diagram of the three different layers of homogenous concentrations. Each is labeled with ratios of DMF to MeCN.

In the actual synthesis, the above layering was observed with the top and bottom layers each being 3 mL in volume. Two trials were done for the middle layer: one trial had a 1 mL middle layer and the other had a 3 mL middle layer composed of a mixture of DMF and MeCN at a one to one ratio. The idea behind this was to show that a larger middle layer would give the crystals more time and space to form (Schoedel, Synthesis of stp, 2012). Each layer was measured with an electronic pipette for accuracy, mixed inside an individual test tube, and agitated using test-tube mixer that vibrates a test tube when it is pressed against the agitator. In addition, 96.3 mg of cadmium nitrate was dissolved in the test tube containing the top layer while 63.1 mg of tp-PMBB-1 was dissolved in the test tube containing the bottom layer. The layering was then carefully and slowly done in a separate test tube, with each layer being allowed to settle before the next layer was added. The final test tube was given a week to let the reaction occur, and was covered up in order to avoid the evaporation of the solvents. This temporary layering eventually became a uniform mixture, but the time for that to occur was long enough for the cadmium nitrate and the tp-PMBB-1 to slowly react and form crystals at the

middle layer, once again leaving the excess nitrate in the surrounding solution (Schoedel, Synthesis of stp, 2012).



Figure 22: Photo of crystal formation from one test tube. stp crystals are the particles at the bottom of the test tube, though the largest crystals were attached on the side of the test tube. Courtesy of Joy D'Andrea.

D. Properties and Applications

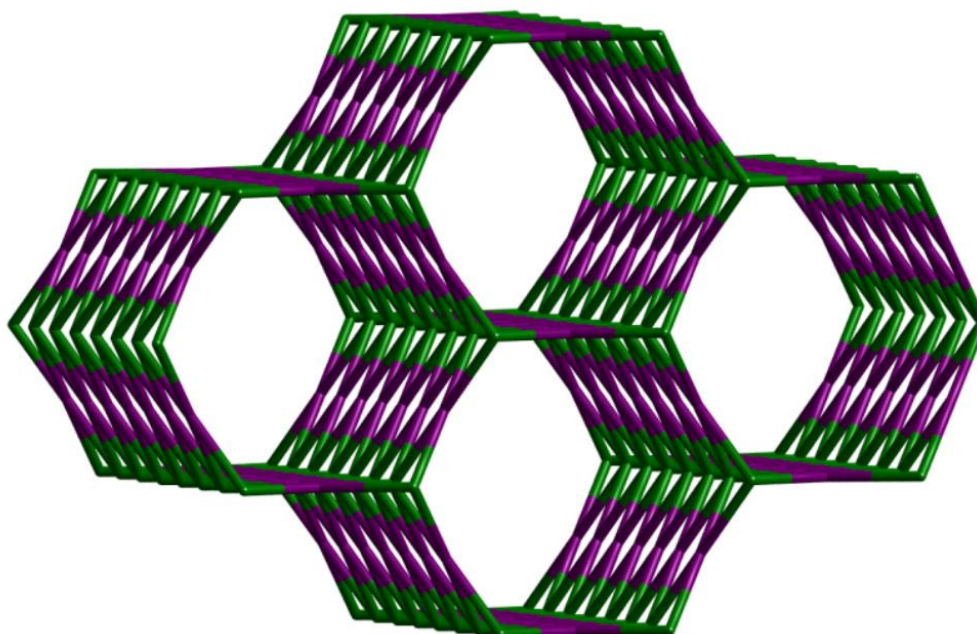


Figure 23: Simplified three-dimension representation of the top-down view of the stp crystal net. tp-PMBB-1s are represented as green intersections and MBB-2s are purple intersections. This figure is similar to Figure 13, but features MBBs as nodes instead. Courtesy of Alexander Schoedel.

Now that we have presented the concepts behind the synthesis of a crystal with the **stp** structure, we can discuss the properties and applications of this crystal and those like it. In general, the real-world applications of the MOMs field include “ion exchange, hydrogen storage, molecular sensing, drug delivery, and medical imaging” (Miessler & Tarr, 2011). The main properties of a synthesized crystal that interest the research group to which Schoedel belongs are: 1) anion exchange capability, and 2) *gas sorption*. By *sorption*, we generally mean the interaction by which two substances stick together and in the case of gas sorption, we mean the interaction by which a gas sticks to a substance. The gas sorption of a MOF, in the form of crystal, is described as gas molecules or atoms sticking to the surface area of the MOF, which again includes the inner wall channels within MOF (Nugent, 2012). If the audience is uncertain about this, it helps to think of the MOF absorbing and retaining gas as a sponge would water, keeping in mind that MOFs are inherently porous (Nugent, 2012).

Since **stp** is inherently *cationic* and possesses large hexagonal channels, it was anticipated that the charge balancing nitrate anions would be exchangeable with other anions. A substance is cationic if it has more cations than anions. Generally, anion exchange is the process by which the main anion in the structure is chemically replaced with another (Schoedel, Synthesis of **stp**, 2012). NO_3^- is the anion in our case (Figure 20) because it is the excess ion left over by each of the steps in the two-step synthesis of the **stp** crystal, remembering that it balances the overall charge of the crystal structure (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). Ideally, anion exchange does not affect the structure of a MOF. The purpose of this exchange is to measure the gas sorption of a particular MOM for a specific gas, and relate that gas sorption to the same MOM containing different anions. The hope of the research group is to correlate certain anions with particular gas sorption ranges in order to form guidelines for what anions are expected to give a MOF the most gas sorption or highest selectivity.

Increased gas sorption itself, for particular gases, is the other desired property for MOFs in general. To this end the gas sorption of a MOF is tested for specific gases, and this gas sorption is compared to that of other MOFs, for the same gases as well. The idea is to see which MOFs tend to have the most gas sorption with specific gases. In general, CO_2 at 273K (0 degree Celsius) is the first gas to be checked inside a MOF which is being studied for gas sorption, because its sorption in MOFs indicates porosity and lead to the decision if further studies will be conducted or not (Schoedel, Synthesis of **stp**, 2012).

As for the **stp** crystal produced, it could be shown that nitrate anions (NO_3^-) were successfully exchanged by tetrafluoroborate anion (BF_4^-) (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). In terms of gas sorption experiments, no significant uptakes could be achieved for **stp**. Though the crystal is itself stable inside the DMF and MeCN solution, once it is removed from the solution it tends to deform and eventually lose its structure altogether. This is caused by the flexibility of the tp-PMBB-1 which might cause shrinking upon removal of solvents inside the channels. (Schoedel, Synthesis of **stp**, 2012). In turn, this causes

the angles in between linkers to change; because the **stp** crystal structure has well defined angles, even the most remote change in the angles will cause the structure to deform.

The real importance of the synthesized **stp** crystal is to confirm that a well-formed **stp** structure can be realized for the first time in a MOM. As Schoedel et al notes, because elements other than cadmium and linkers other than pyridine can be used applying the same concepts, crystals with **stp** topology can be produced with longer or angular linkers and different metal ions (Schoedel, Wojtas, Eddaoudi, & Zaworotko, 2012). These **stp** crystals exemplify how MOMs are tunable and adjustable in their metrics and composition. Examples of these new crystals cannot be presented in this thesis, however, because their structures and design have not yet been published.

Like the original crystal, some of these different manifestations of **stp** have shown interesting single-crystal to single-crystal anion exchange properties (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). In this context other structures prepared by the 2-step approach showing the **acs** topology have also been used in various anion exchange processes. These crystals possess increased gas sorption for carbon dioxide at 273K among various trials (Schoedel, Synthesis of stp, 2012). These results, in turn, have opened up the **stp** crystal net for potential MOFs throughout the entire field.

III. Mathematics of Crystal Nets

A. Graph Theory

We start the mathematical analysis of **stp** from the view point of graph theory. First, we define a *graph* to be a diagram made up of points (i.e. *vertices*) and line segments joining pairs of these points (i.e. *edges*). Below are two such examples of the various diagrams that can be classified as graphs:

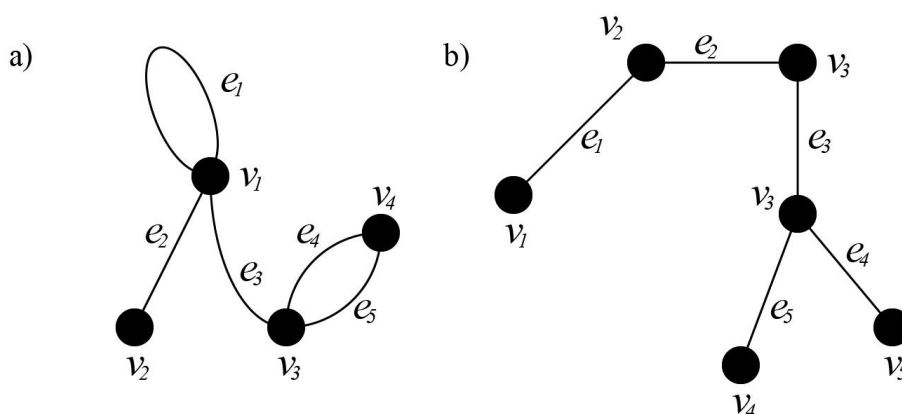


Figure 24: a) – b) Graph examples: vertices labeled v_i and edges labeled e_i , each i is an integer.

Because graphs are abstract in general mathematics, we clarify that we will be working with *simple graphs* that exist in *real space*. By simple graph, we mean a graph in which no edges join a vertex to itself (i.e. no loops) and only one edge can join any two specific vertices (Bona, 2006). An example of a simple graph can be seen Figure 24.b). We note that Figure 24.a) is not a simple graph because of e_1 is a loop and because e_4 and e_5 connect the same vertices (v_3 and v_4). By real space, denoted as \mathbb{R}^3 , we mean the three-dimensional space in which we live, where exact locations can be represented by points (i.e. vertices) and line segments (i.e. edges) represent the shortest curve between two points. The two vertices incident to an edge are its endpoints. The audience should be familiar with the Cartesian coordinate system of labeling locations in \mathbb{R}^3 , which has an x -axis, a y -axis, and a z -axis.

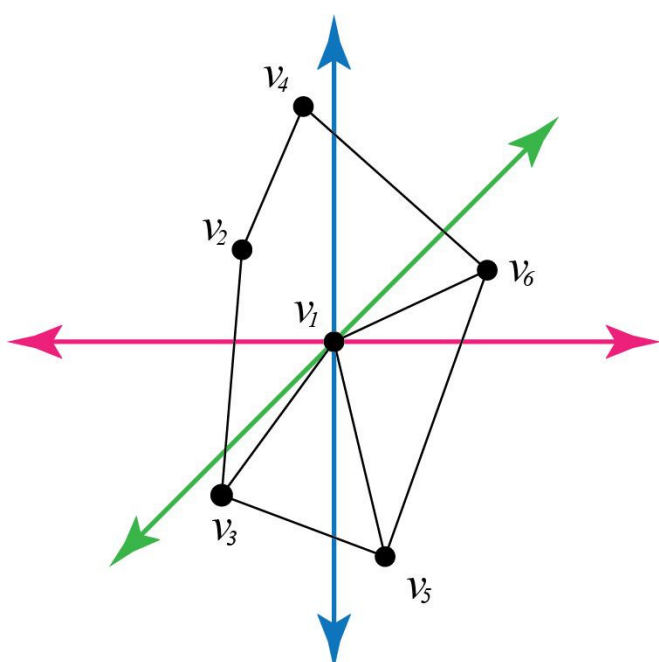


Figure 25: Example of a graph in \mathbb{R}^3 , using the Cartesian coordinate system. The green line represents the z -axis, blue is the y -axis, and red is the x -axis. The coordinates are $v_1: (0, 0, 0)$, $v_2: (-2, 0, -3)$, $v_3: (1, 10, 7)$, $v_4: (1, 6, 2)$, $v_5: (2, -4, 3)$, and $v_6: (3, 2, 0)$

We must define one last graph theory term before we can apply graph theory to chemical substances: *cycles*. First, we must define a *walk*, which is a sequence of distinct vertices and distinct edges $v_1e_1v_2e_2\dots e_kv_{k+1}$ such that for each i , the end point is of edge e_i is the starting point edge e_{i+1} (Bona, 2006). Now, we define a *cycle* to be a walk that starts and ends at the same vertex, but does not involve any other vertex more than once (Bona, 2006). Examples of these two objects are shown below:

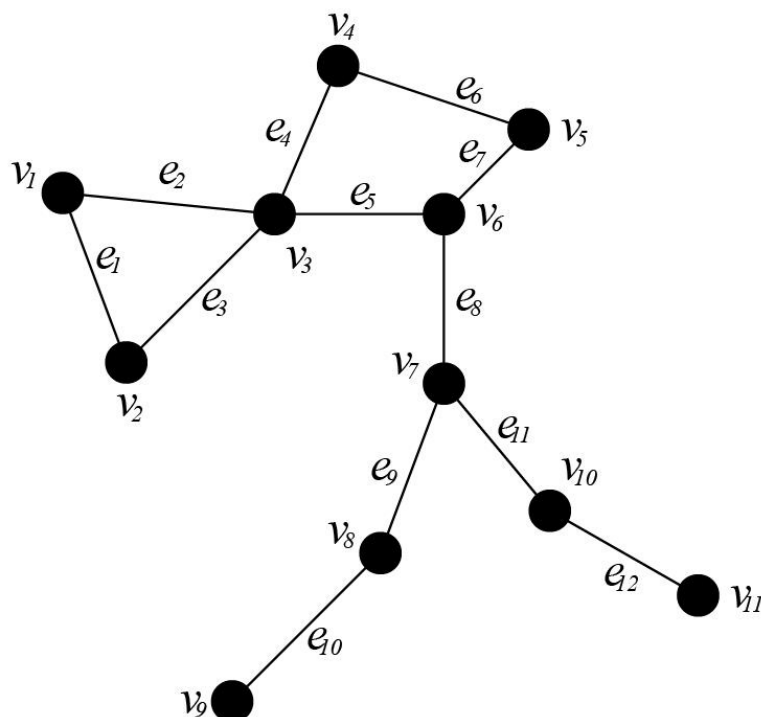


Figure 26: An example of a graph. In this graph, $v_6 e_8 v_7 e_9 v_8 e_{10} v_9$ and $v_7 e_{11} v_{10} e_{12} v_{11}$ are walks while $v_1 e_2 v_3 e_3 v_2 e_1 v_1$ and $v_3 e_4 v_4 e_6 v_5 e_7 v_6 e_5 v_3$ are cycles.

Now we can associate graphs with chemical structures by distinguishing analogues to vertices and edges. We have already discussed that we will only be working with simple graphs that exist in \mathbb{R}^3 ; because of this, associating vertices with individual atoms and edges with bonds is well within the scope of graph theory (review Figures 1, 9, 12.a), 16, 17, and 18). By the same reasoning, we can think of sub-molecules as vertices in complex molecular structures with edges still representing bonds, or nodes in MOMs as vertices with edges representing linkers. This is best exemplified by the nodes of the **stp** net in Figure 23 which represent 6-connected tp-PMBB-1s and 4-connected MBB-2s, or respectively represent vertices with six edges and vertices with four edges when the net is viewed as a graph. The *degree* of a particular vertex is the number of edges in which the vertex is one endpoint (e.g. a vertex with six edges has a degree of six). Thus, the connectivity of a node is the degree of a vertex when relating nodes to vertices (e.g. a 6-connected node has a degree of six when the node is represented as a vertex in a graph).

B. Polyhedra

There is one very important use of graphs in analyzing the MBBs of MOMs, but in order to understand it, we must first understand *polyhedra*. A polyhedron (the singular of polyhedra) is a finite three-dimensional object bounded by finitely many non-intersecting polygons, which are the polyhedron's *faces*. Here, a polygon is a two-dimensional shape bounded by finitely many line segments that enclose a certain area. In \mathbb{R}^3 , we can simply think of polygons as two-dimensional

cycles whose edges don't intersect. An example of a polyhedron is the trigonal prism in Figure 10, referred to in mathematics as a triangular prism because of its triangle base. Two other examples are shown below:

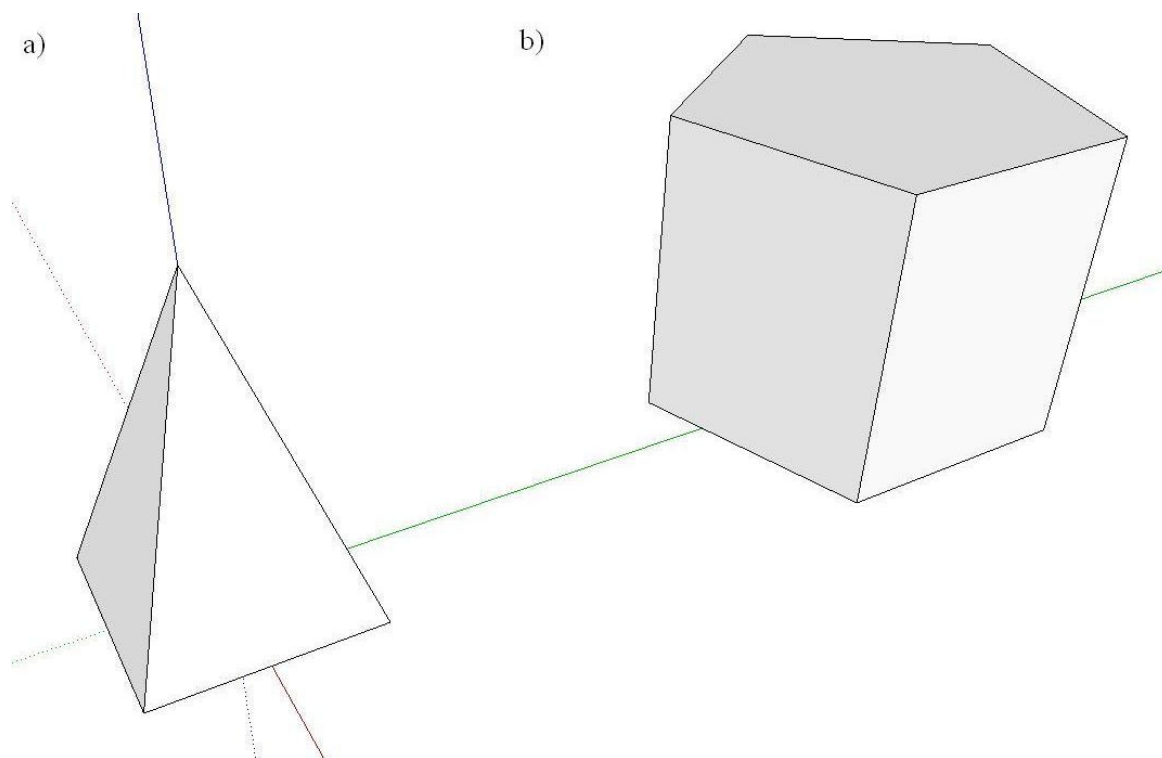


Figure 27: Polyhedra viewed on the Cartesian coordinate system: a) Square Pyramid and b) Pentagonal Prism. The green line represents the z-axis, blue is the y-axis, and red is the x-axis.

There are classes of polyhedra that are and have been of interest to the chemistry field, including the class of *platonic solids*. Platonic solids, are polyhedra whose vertices and faces are related to one another by *symmetry operations* (which will be discussed in the following subsection) and whose faces are also all *congruent* (O'Keeffe & Hyde, *Crystal Structures: I Patterns and Symmetry*, 1996), which is to say equal in all measurements and form. Below are the five platonic solids.

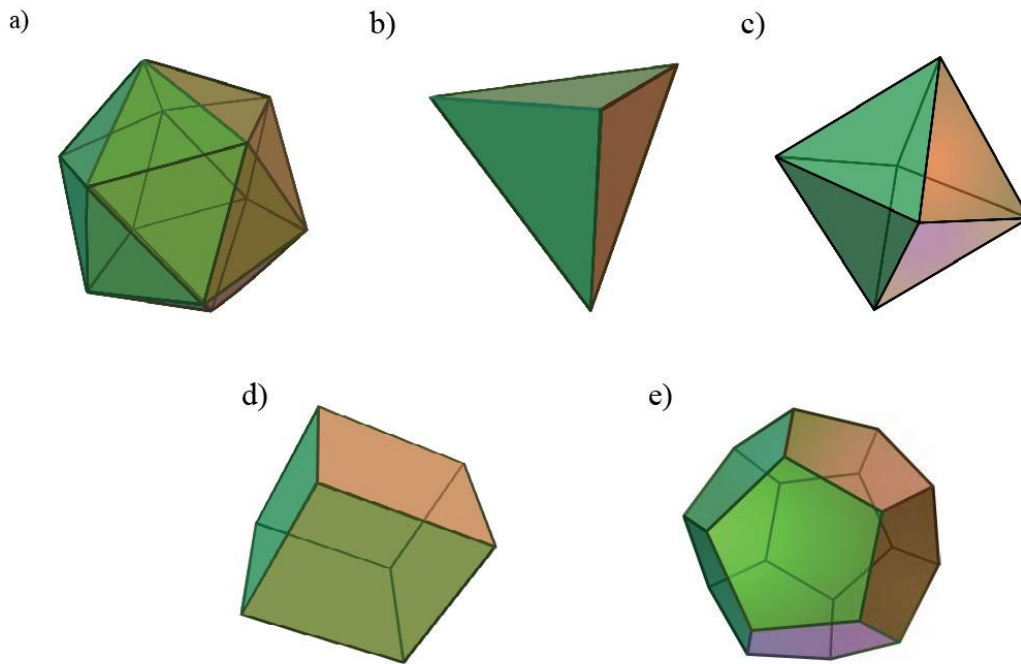


Figure 28: Representations of the five platonic solids from WikiMedia Commons. “Permission is granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.2 or any later version published by the Free Software Foundation; with no Invariant Sections, no Front-Cover Texts, and no Back-Cover Texts.”

- | | |
|----------------------|---|
| a) Icosahedron | http://commons.wikimedia.org/wiki/File:Icosahedron.svg |
| b) Tetrahedron | http://commons.wikimedia.org/wiki/File:Tetrahedron.svg |
| c) Octahedron | http://commons.wikimedia.org/wiki/File:Octahedron.svg |
| d) Hexahedron (Cube) | http://commons.wikimedia.org/wiki/File:Hexahedron.svg |
| e) Dodecahedron | http://commons.wikimedia.org/wiki/File:POV-Ray-Dodecahedron.svg |

Since the boundary of a polygon is a cycle, we can discuss MBBs as either polygons or polyhedra whose vertices are defined by their extension points. Following this, we can identify the edges of MBBs as the shortest line segments at the shortest distances in between extension points. These are selectively included such that no two edges are intersecting while every extension point has at least two edges connected to it if the MBB is represented by a polygon or at least three edges if the MBB is represented by a polyhedron. An MBB can only be a polygon if all of its extension points lie on the same plane; otherwise it must be described as a polyhedron. Below are the polygon and polyhedron outlines of the MBBs from Figure 9 which explain how each MBB was named:

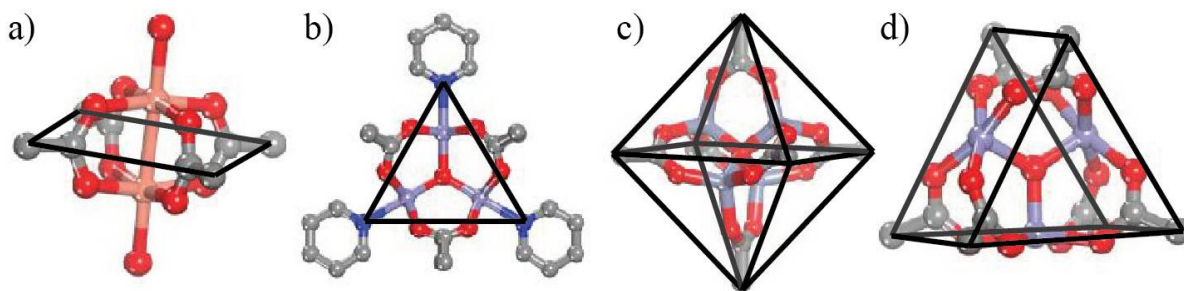


Figure 29: Three-dimensional models of MBBs with polyhedron outlines: a) Square, b) Triangle, c) Octahedron, and d) Trigonal Prism. Courtesy of Alexander Schoedel.

Using the notion of cycles as polygons, we can identify the faces of an MBB if it is represented as a polyhedron. For two-dimensional MBBs, one cycle should be formed which includes every extension point (i.e. vertex) outlining a polygon. For three-dimensional MBBs to be associated with particular polyhedra, graph representations should be used such that cycles are created, with each extension point belonging to three different cycles. In creating these cycles, bonds, atoms, and molecules which are not extension points should be ignored. Finally, the potential polyhedron should be drawn so that there is only one final space contained by the polyhedron, not multiple disjoint spaces. We recommend that researchers refer to models of polyhedra in the public domain to ensure that they are making the single polyhedron they desire for their MBB or ensure that the polyhedron they have identified for an MBB is appropriate.

It is by following the process above of identifying the two-dimensional or three-dimensional structure of MBBs that we can then access the symmetry of MBBs and the crystal nets they form. This process will be detailed in full in the following sub-section.

C. Symmetry

1. The Mathematics of Symmetry

Discussion on symmetry in \mathbb{R}^3 begins with *isometries*, which we will describe in terms of *mappings*. We assume familiarity with the notions of the Cartesian coordinate system and a mapping, which relates a set of points, the *domain*, to another set of points, the *range*, such that each point in the domain is only related to one point in the range. This constraint does not mean that each point in the range is related to only one point in the domain; adding this separate constraint would make the mapping *one-to-one*. Common examples and non-examples of mappings are shown below in two dimensions and in \mathbb{R}^3 :

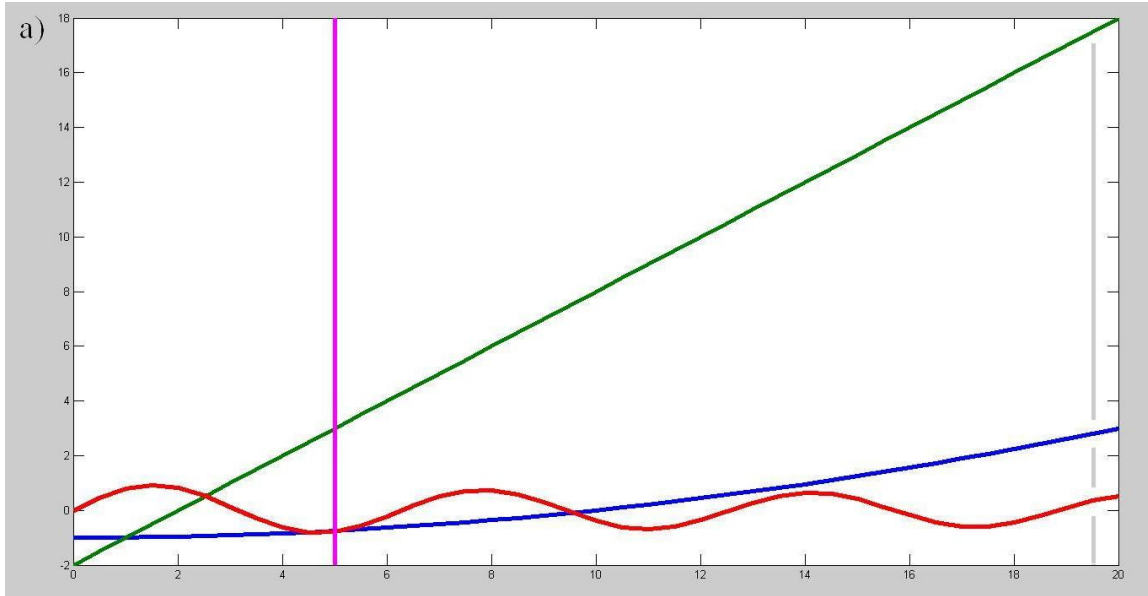
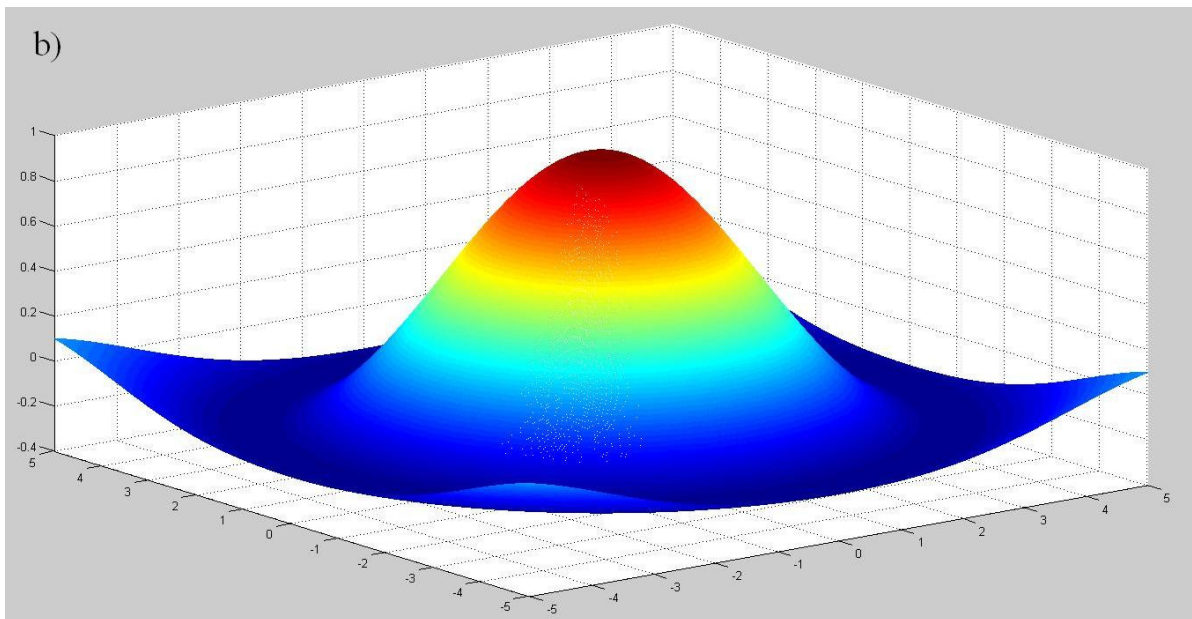


Figure 30: a) (Above) Three examples of mappings in two dimensions plotted in the Cartesian coordinate system represented by the red, blue and green lines. The domain is the set of all real numbers along one dimension, the x-axis in our case. Note that with this as our domain, the line in magenta is not a mapping because one point in this domain is related to more than one point in the range, the real numbers along the other dimension (i.e. the y-axis). Furthermore, the mappings in blue and green are one-to-one because each point in the range corresponds to a unique point in the domain and vice versa. b) (Below) An example of a mapping in \mathbb{R}^3 with varying colors to increase visibility. The domain of this mapping is the set of all ordered pairs (x, y) in two dimensions such that x and y are real numbers.



An isometry in \mathbb{R}^3 is a mapping that preserves all distances in between points. Below are an example and a counter-example in which the distances have been labeled next to the dashed lines:

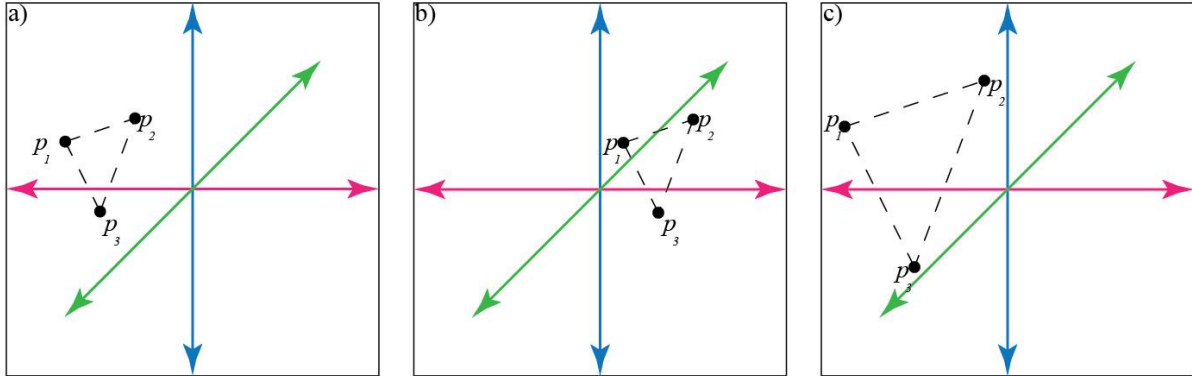


Figure 31: In each, the green line represents the z-axis, blue is the y-axis, and red is the x-axis. a) Original coordinates: p_1 (-4, 1, 0), p_2 (1, 3, 2), and p_3 (0, 2, 4). b) Example of an isometry: p_1 (1, 2, 0), p_2 (6, 3, 2), and p_3 (5, 2, 4). c) Counter-example: p_1 (-7, 4, 4), p_2 (-5, 4, 2), and p_3 (-3, 2, 6). We note that the distances between points in a) and b) are the same, but the distances in between points of a) and c) are not the same.

Because neither a mapping nor an isometry limit the number of points being mapped, isometries can map two-dimensional and three-dimensional shapes in \mathbb{R}^3 while preserving distances. Hence, an isometry will preserve the shape of any geometric figure (shown below). Furthermore, an isometry is a symmetry operation if and only if a shape (in \mathbb{R}^3) exists such that the isometry maps the shape onto itself (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996), permuting the vertices and edges.

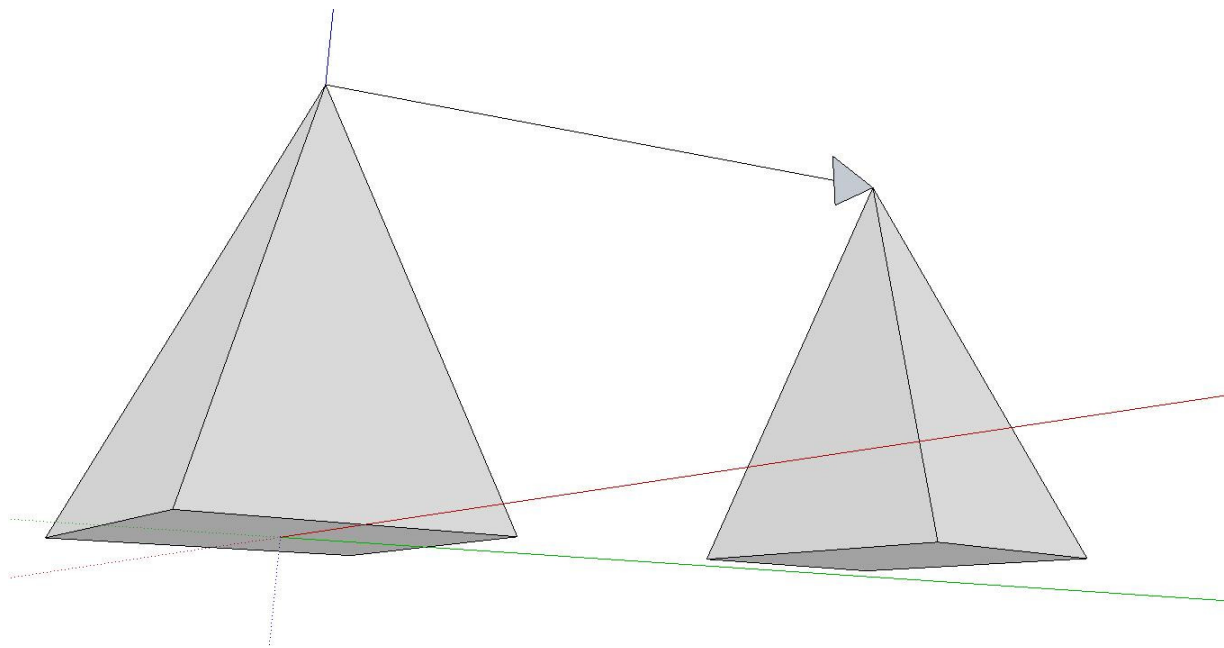


Figure 32: An example of an isometry using a square pyramid. In this case, the pyramid is moved in the direction of the arrow, but all the distances within the pyramid itself are left unchanged. The green line represents the z-axis, blue is the y-axis, and red is the x-axis.

Now we can discuss one of the most important terms for our mathematical analysis: a *point group*. We define a point group as a collection of distinct isometries closed under composition and inversion which share some *fixed point* in \mathbb{R}^3 (e.g. the intersection of multiple rotation axes) and which constitute all of the symmetry operations for a certain object in \mathbb{R}^3 (O'Keeffe & Hyde, *Crystal Structures: I Patterns and Symmetry*, 1996). An isometry has a fixed point if the isometry maps that point to itself. An object's point group can be defined in the above manner, though we note that this definition is specific to subject of crystals in this thesis. The importance of point groups lies in describing the symmetries of nodes, shown in the next section with examples. Below, the three rotations shown in Figures 33.c) to Figure 33.e) are the only symmetry operations of the object shown or than the *identity* (explained later in this section). Thus, these symmetry operations compose the object's point group, named 3 in the International Tables of Crystallography (Hahn, 1996).

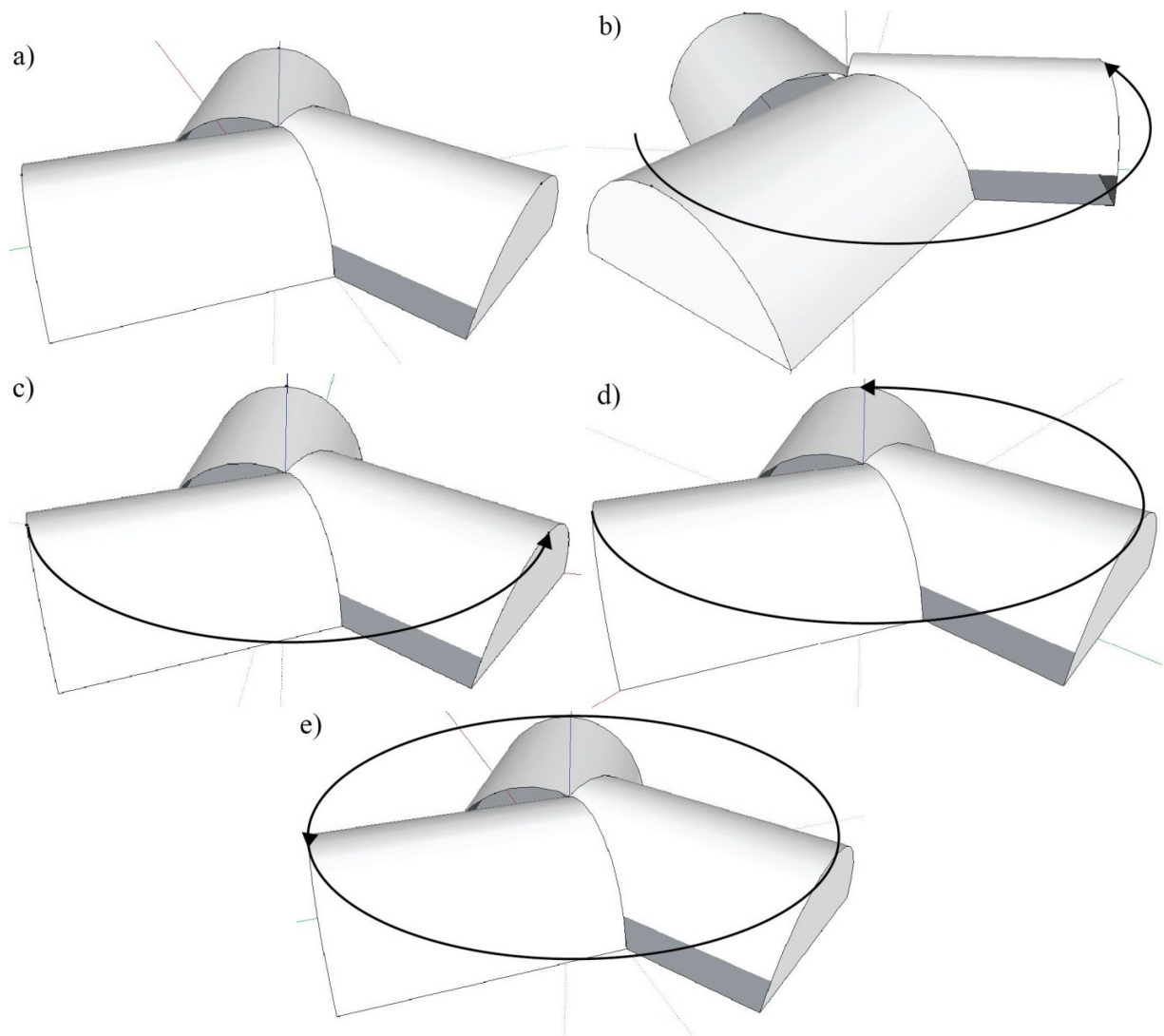


Figure 33: A three-dimensional object with three rotational symmetry operations in Cartesian coordinate system. The green line represents the z-axis, blue is the y-axis, and red is the x-axis. The four rotations are about the y-axis, each denoted by dashed lines: a) no rotation, b) 200 degree rotation, c) 120 degree rotation, d) 240 degree rotation, and e) 360 degree rotation. Note that the object appears to be in the exact same position as a) for the rotations in c), d), and e); the rotation in b) serves as a non-example of a symmetry operation.

In order to describe these point groups in detail, however, we must use *vectors*. A vector is a displacement defined by a start point to an end point in \mathbb{R}^3 . Thus a vector is said to have direction in \mathbb{R}^3 . We can think of a vector v between starting point $p_1 = (x_1, y_1, z_1)$ and end point $p_2 = (x_2, y_2, z_2)$ as described below:

$$v = \begin{bmatrix} x_2 - x_1 \\ y_2 - y_1 \\ z_2 - z_1 \end{bmatrix} = \begin{bmatrix} v_1 \\ v_2 \\ v_3 \end{bmatrix}$$

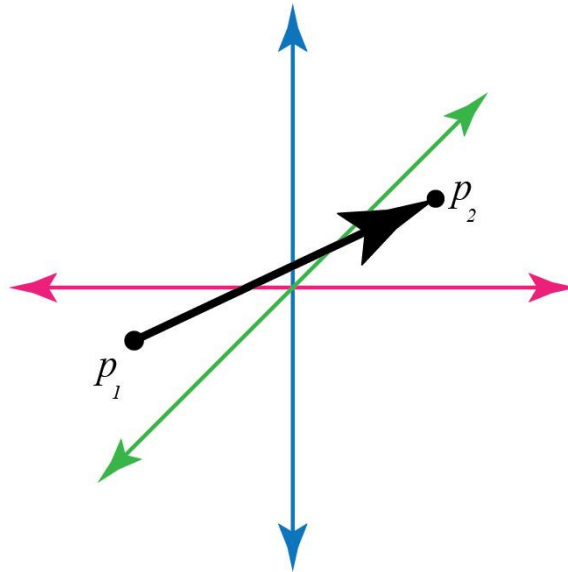


Figure 34: Drawing of an arbitrary vector from p_1 to p_2 in the Cartesian coordinate system as described above. The vector is represented by the black line segment with an arrow.

Vectors are the primary building blocks for understanding symmetry and all that follows from it. To begin, a vector x 's elements are more commonly written as follows:

$$x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}$$

The length of a vector x is (Prince, 2004):

$$|x| = \sqrt{x_1^2 + x_2^2 + x_3^2}$$

A vector can be fixed by its direction and its length (Prince, 2004). Furthermore, any two vectors a and b can be added to form vector c :

$$a + b = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} + \begin{bmatrix} b_1 \\ b_2 \\ b_3 \end{bmatrix} = \begin{bmatrix} a_1 + b_1 = c_1 \\ a_2 + b_2 = c_2 \\ a_3 + b_3 = c_3 \end{bmatrix} = c$$

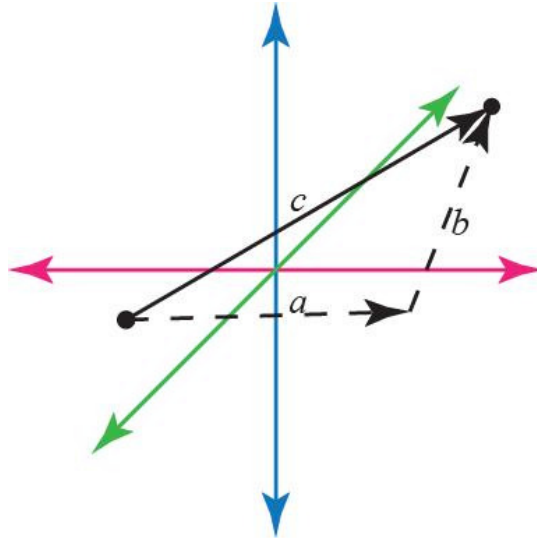


Figure 35: A drawing representing the vector addition from above in the Cartesian coordinate system, not the actual positions of component vectors a and b . Note, vectors a and b must originate from the same point to add up to vector c . Thus, they are drawn above with dashed lines, while vector c is drawn in with a solid line.

We apply vector addition to *translations*; a translation is a mapping that shifts \mathbb{R}^3 in a certain direction by a certain distance (*magnitude*), defined by a translation vector. The translation also shifts any object embedded in \mathbb{R}^3 , without affecting the shape of the object; in this way a translation is similar to a symmetry operation. In fact, a translation can actually be formulated by a fundamental kind of symmetry operation on an object and thus be thought of as symmetry operation; however, this formulation is beyond the scope of this thesis. Nonetheless, a translation is an isometry. The translation of vector x by translation vector t resulting in vector y (directed at the new end point from the same start point) is defined as follows (Hahn, 1996):

$$y = x + t = \begin{bmatrix} x_1 + t_1 \\ x_2 + t_2 \\ x_3 + t_3 \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix}$$

The next building blocks for understanding symmetry are *matrices*. For our purposes, a matrix is a two-dimensional array of real numbers with three rows and three columns (Prince, 2004). Though there are more general matrices, we will work with those that represent point group isometries. The form of a matrix is given below:

$$A = \begin{bmatrix} a_1 & a_2 & a_3 \\ a_4 & a_5 & a_6 \\ a_7 & a_8 & a_9 \end{bmatrix}$$

Here each a_i is a real number.

We will only consider matrices as representations of point group isometries, specifically symmetry operations. The *linear transformation* of a vector by a symmetry operation is the multiplication of the matrix associated with the symmetry operation and the vector. Below is the general form of a matrix multiplied with a vector (i.e. matrix multiplication), where A is a matrix, x is the original vector, and y is the resulting vector:

$$Ax = y$$

Where $Ax = y$ is defined as follows:

$$\begin{bmatrix} a_1 & a_2 & a_3 \\ a_4 & a_5 & a_6 \\ a_7 & a_8 & a_9 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} a_1x_1 + a_2x_2 + a_3x_3 \\ a_4x_1 + a_5x_2 + a_6x_3 \\ a_7x_1 + a_8x_2 + a_9x_3 \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \end{bmatrix}$$

If the linear transformation is an isometry, the resulting vector y has the same length as the original vector x (Prince, 2004). It can be shown that there is only one fundamental kind of symmetry operation, the reflection (defined below), from which all seven kinds of symmetry operations in \mathbb{R}^3 can be derived; however, this requires mathematics beyond the scope of this thesis. We will instead define five symmetry operations, the identity being one of them, and define the other two would-be symmetry operations differently later in this sub-section.

- *Identity* – a symmetry operation which maps each point in \mathbb{R}^3 to itself (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996). This is represented by the matrix (Prince, 2004):

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

- *n-Rotation* – a symmetry operation in which an object is rotated $\frac{2\pi}{n}$ radians about a line in \mathbb{R}^3 such that after n rotations, the object will return to its original state (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996). An example is an n -rotation about the z -axis in the Cartesian coordinate system (Prince, 2004), whose matrix is:

$$\begin{bmatrix} \cos \frac{2\pi}{n} & \sin \frac{2\pi}{n} & 0 \\ -\sin \frac{2\pi}{n} & \cos \frac{2\pi}{n} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Note: In order for an object to have an n -rotation as one of its symmetry operations, all n individual rotations must be symmetry operations of the object.

- *Reflection* – a symmetry operation in which an object is reflected across a two-dimensional plane in \mathbb{R}^3 (the *mirror* of the reflection) to a mirror image equidistant from

the mirror via a line through both points perpendicular to the mirror (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996). An example is a reflection through the xy -plane in the Cartesian coordinate system (Prince, 2004), whose matrix is:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Two more symmetry operations can now be defined in terms of the classes of symmetry operations above. Here we note that a composition of symmetry operations applied one after the other will result in a new symmetry operation. Furthermore, the new symmetry operation is guaranteed to be in an object's point group because the component symmetry operations are in said point group.

- *Inversion* – a sequence of three distinct reflections through three distinct planes intersecting at one point. An example is the sequence of reflecting an object through the xy -plane, then the xz -plane, and finally the yz -plane, which all intersect at the origin of the Cartesian coordinate system. This inversion, which we'll call the *traditional inversion* for the purposes of referring to it later in the thesis, results in the following matrix (Prince, 2004):

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

- *Roto-inversion* – a rotation followed by an inversion (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996). This symmetry operation is also a *roto-reflection*, a rotation followed by a reflection, though the reason for this is beyond the scope of this thesis.

The remaining would-be symmetry operations are not linear transformations but rather *affine transformations*. We define an affine transformation on a vector x , resulting in vector y as:

$$y = Ax + t$$

Where A is a symmetry operation, Ax is a linear transformation, meaning symmetry operation associated with A applied to x , and t is a translation vector, which is applied after the linear transformation.

For us it should suffice that an affine transformation will simply be a symmetry operation followed by a translation, as this still fits in the unmentioned formal definition. We will refer to what would have been the seven fundamental symmetry operations as our seven fundamental affine transformations. The last two fundamental affine transformations are:

- *Glide* – a reflection followed by a translation parallel to the reflection plane (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996).

- *Screw* – a rotation followed by a translation along the axis of rotation (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996).

Just as we describe the symmetry of finite objects such as polyhedra with symmetry operations, we can describe the symmetry of infinite objects, such as crystal nets with affine transformations. Again, a symmetry of a graph is an isometry that maps the graph onto itself, vertices to vertices and edges to edges; and the *symmetry* group of a graph is the group of its symmetries. But in order to understand what a crystal net is, we must first discuss *lattices*. A lattice is a group of vectors in n dimensions generated by n distinct translation vectors (n is an integer) such that any combination and/or repetition of these translation vectors will yield a vector in the group. Accordingly, a lattice in \mathbb{R}^3 is generated by three translation vectors; these vectors must not all lie on the same plane in order to generate a three-dimensional lattice (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996), and must also have the same start point. An example of a lattice and the vectors that generate it is shown below. The points that are added represent the endpoints of vectors in the lattice, which all share the same start point as the translation vectors. The example is in two dimensions for ease of visibility; however, the same concepts apply for \mathbb{R}^3 or any other number of dimensions.

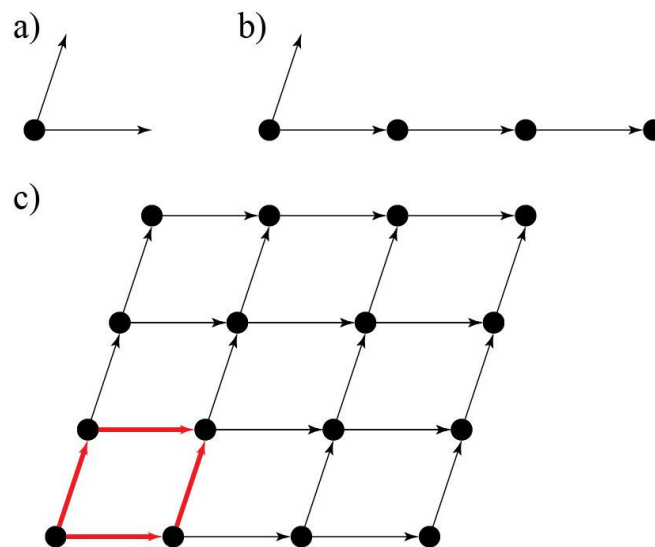


Figure 36: Generation of a lattice from two translation vectors, represented by line segments with arrows. We note that just as three translation vectors must not lie on the same plane to generate a three-dimensional lattice, two translation vectors must not lie on the same line in order to generate two-dimensional lattice. a) A starting point and two translation vectors for a lattice. b) The generation of lattice points along one dimension by repeating one vector. c) The generation of a two-dimensional lattice from the combination and/or repetition of the two translation vectors.

The highlighted structure above is called the *unit cell* of a lattice and is an n -dimensional object, where n is the number of translation vectors that define the lattice. A unit cell is defined

by its edges, which are the translation vectors of a lattice, and its ability to generate all of the vectors and space of a lattice. This generation is done by applying appropriate translations to the unit cell. This is shown for the lattice in Figure 37:

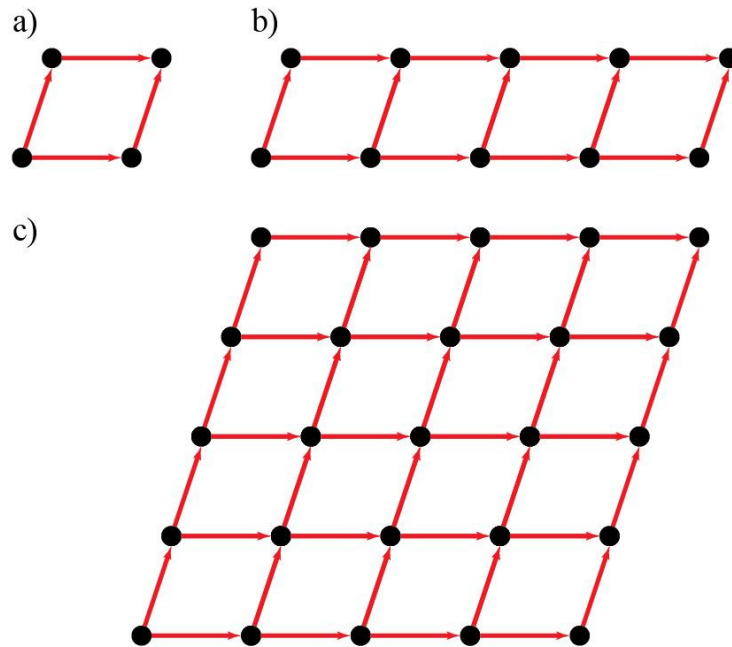


Figure 37: Generation of the lattice in Figure 36 through use of a unit cell. a) Unit cell. b) Points generated by repeating unit cell along one dimension. c) Two-dimensional lattice from Figure 36 generated by repeating the unit cell across two dimensions.

While a unit cell generates all of the space inside a lattice, not all of the smallest structures in a lattice are unit cells. Also, there is not always one unique unit cell for a lattice.

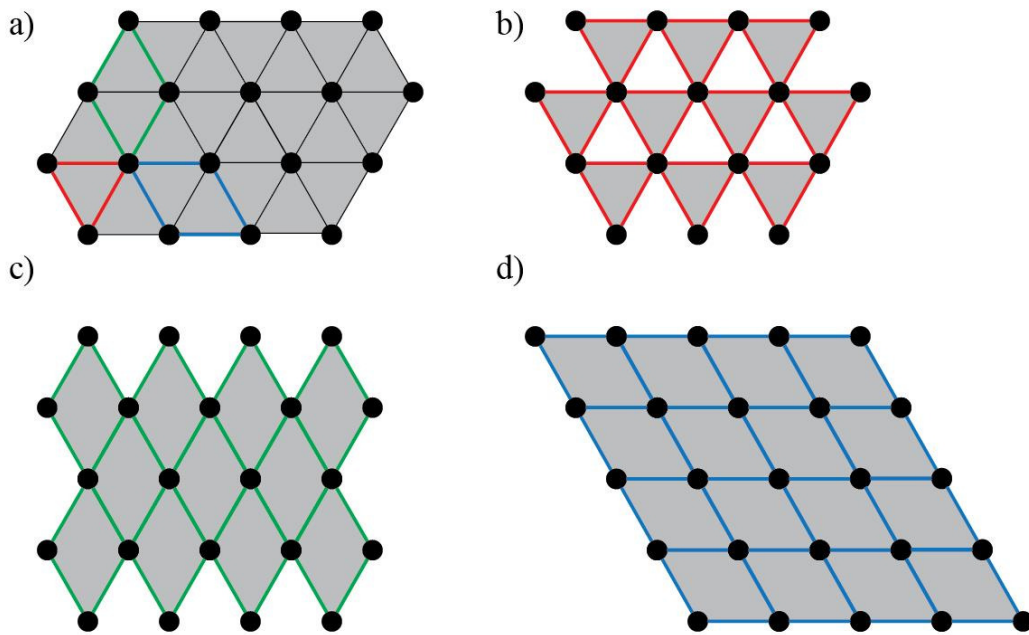


Figure 38: a) Two-dimensional lattice with three possible unit cells highlighted. The area of the lattice is shaded gray for reference. b) Attempted generation of the lattice by the red unit cell. In this case, all the points of the lattice could be generated, but not all of the area is generated. c) Lattice generated by green unit cell. Even though the shape of the portion shown is not the same, all of the points and all of the area of the infinite lattice can be generated. d) Lattice generated by blue unit cell with the same distinction on immediate shape as c).

At last, within the context of lattices and affine transformations, we may finally discuss crystal nets and *space groups*. A space group is the group of all distinct affine transformations that describe all of the symmetries of an entire crystal net (Prince, 2004). We define a crystal net as a graph of points in \mathbb{R}^3 , with line segments as edges, whose *symmetry group* includes a lattice group. The symmetry groups of crystal nets are groups of affine transformations, and each crystal net is said to have a space group. Below is an example of the NaCl crystal from Figure 7.c) placed on a lattice:

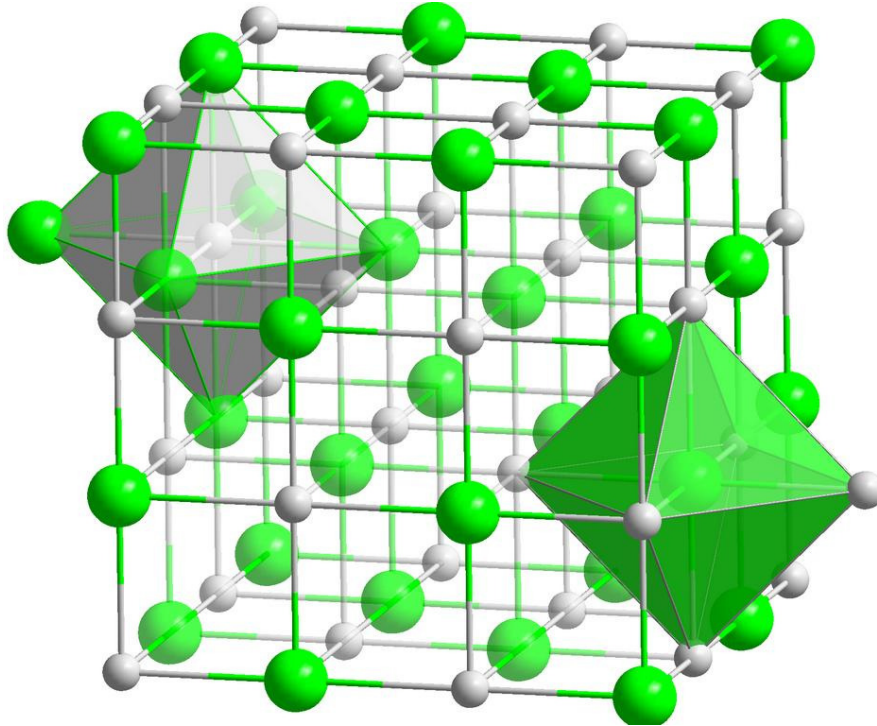


Figure 39: The crystal net of a NaCl crystal on a lattice. The two shaded octahedrons are potential unit cells for this crystal net. Chlorine atoms are in green and sodium atoms are in white. Figure 39 source: public domain, obtained from Wikimedia Commons.

Just like symmetry operations, the crystal net symmetries described above map the crystal net onto itself. Of course, just as no point group is specific to a finite three dimensional object, no space group is specific to a certain crystal net; however, finite objects have only one point group and crystal nets have only one space group.

2. The Symmetry of **stp**

We will begin the analysis of the symmetry of **stp**, by observing the point groups of **stp**'s two MBBs: the trigonal prism and the square. First, even though the square is a two dimensional object, its point group can be defined in three dimensions. This definition has a reflection whose mirror plane is the same as the plane on which the square lies. The two-dimensional point group of a square is named $4mm$ (O'Keeffe & Hyde, *Crystal Structures: I Patterns and Symmetry*, 1996), and it is represented below:

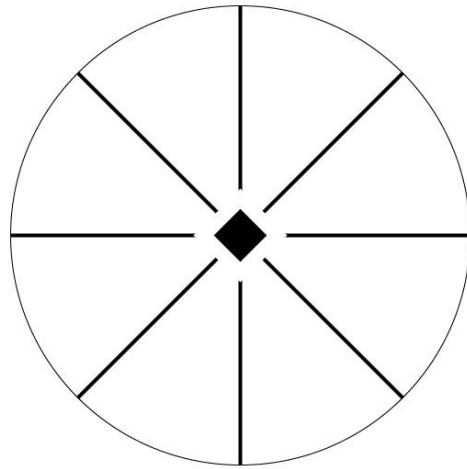


Figure 40: (Courtesy of the International Tables for Crystallography) Diagram of $4mm$

We will explain the meaning of the image above using the symbol conventions outlined in the International Tables, Volume A. However, we must first be able to place the square on this image to give the lines visible meaning. This is done below:

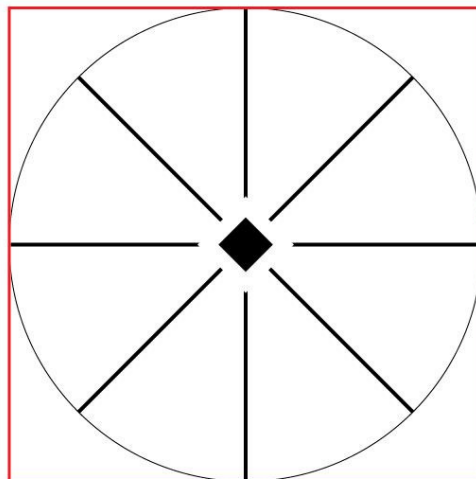


Figure 41: (Courtesy of the International Tables for Crystallography) Diagram of $4mm$ placed at the center for a square, outlined in red.

We describe now the six unique symmetry operations that form a square's point group, as observed strictly from the original drawing of the point group. First, the identity, present in all n -dimensional point groups, where n is an integer. Next is the diamond at the center of the circle, which is placed at the center of any square, signifies a 4-rotation with the center of the diamond as the axis of rotation, which is perpendicular to the plane that square is on. Naturally, any of the four rotations that comprise the 4-rotational symmetry on the square will be symmetry operations on the square. Next, the four bold line segments that cross through the diamond are all mirror

lines signifying where a mirror plane intersects the plane in which the square resides. These mirror planes perpendicular to the plane of the $4mm$ diagram signify the existence of four reflections. These reflections are also symmetry operations for a square, completing our six unique symmetry operations. (Hahn, 1996)

Next is the point group of a trigonal prism, named $\bar{6}m2$ (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). Instead of using the International Tables, Volume A, we use O’Keeffe’s and Hyde’s Crystal Structures I. Both resources are among many that provide accurate diagrams of two-dimensional and three-dimensional point groups; however, the International Tables is the formal source of all crystallographic point groups and space groups.

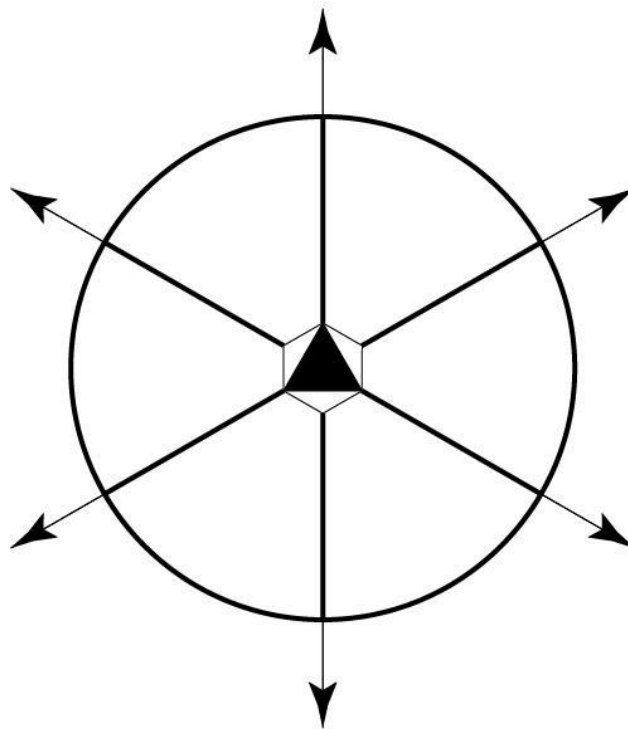


Figure 42: (Courtesy of Dr. Michael O’Keeffe) Point Group $\bar{6}m2$

Once again, we will place this image on a trigonal prism to give visible meaning. Because a trigonal prism is a three-dimensional object, the image below presents a top down view of a trigonal prism with arbitrary height and then the drawing of $\bar{6}m2$ on the prism. Though it is not visible in the drawing below, the drawing should be placed halfway up the height of the prism in order to make sense.

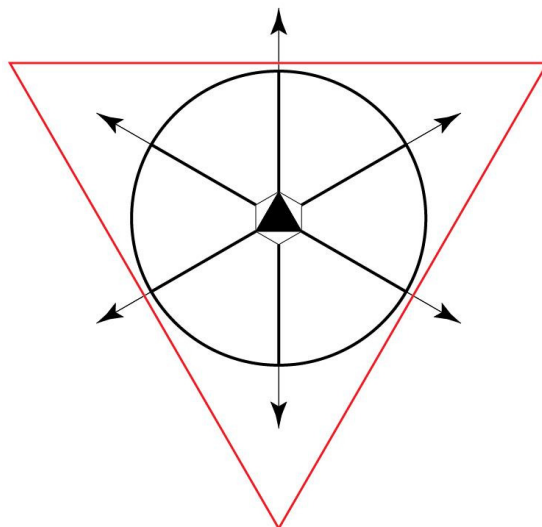


Figure 43: (Courtesy of Dr. Michael O’Keeffe) Top-down view of trigonal prism (outline in red) with point group $\bar{6}m2$ located at the center of the triangle.

This point group has twelve unique symmetry operations, and these will be discussed from the original drawing of the point group again. The symmetry operations include the identity, and three reflections; these reflections are denoted by the bold lines in Figure 42, which once again represent the intersection of mirror planes with the plane on which we are viewing the prism. However, there is another reflection whose mirror plane is the plane on which the drawing exists (O’Keeffe & Hyde, *Crystal Structures: I Patterns and Symmetry*, 1996). Notice that the drawing is half-way up the height of the prism:

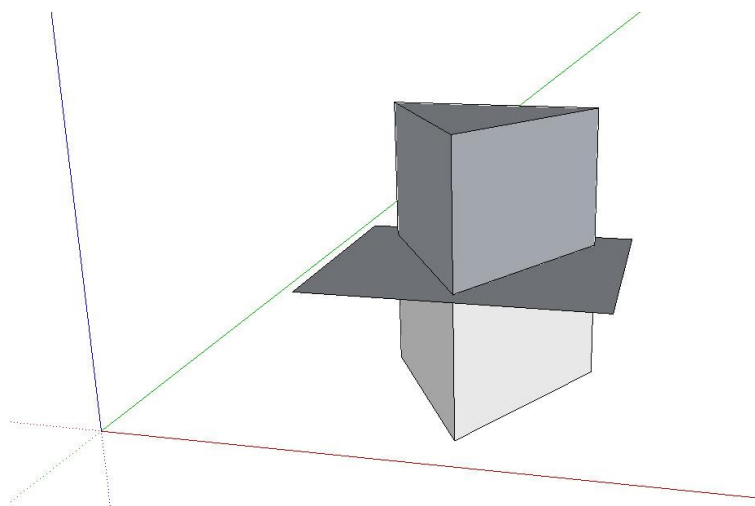


Figure 44: Three-Dimensional representation of trigonal prism with the location of the plane on which the diagram above rests. The green line represents the z-axis, blue is the y-axis, and red is the x-axis.

Next are the six 2-rotations of the trigonal prism; a 2-rotation (by 180 degrees) is denoted by an arrowhead pointing in the direction of the axis of rotation (O’Keeffe & Hyde, *Crystal Structures: I Patterns and Symmetry*, 1996). Once again, because the trigonal prism is three-dimensional, the axis of each 2-rotation actually lies on the plane; the six axes are actually all

along the bold lines in the drawing of the point group. Though this is no coincidence, explanation for this is beyond the scope of this thesis. This leaves us with the shaded triangle inside the hexagon at the center of the point group drawing. This is actually a roto-inversion named $\bar{6}$ (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996). This represents one iteration of a 6-rotation followed by the traditional inversion, repeated until the 6-rotation would complete normally (i.e. after six rotations in total) (O'Keeffe & Hyde, Crystal Structures: I Patterns and Symmetry, 1996). In the diagram, the axis of rotation is perpendicular to the diagram's plane.

With the point groups of the trigonal prism and the square described above, we can now proceed to the space group of **stp**, which is $P6/mmm$ (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). We recommend that our audience view Figures 13, 23, 45, and 46 in order to get a good understanding of the symmetries of **stp**. We include Figure 13.c) again for reference after the diagram of space group $P6/mmm$ below.

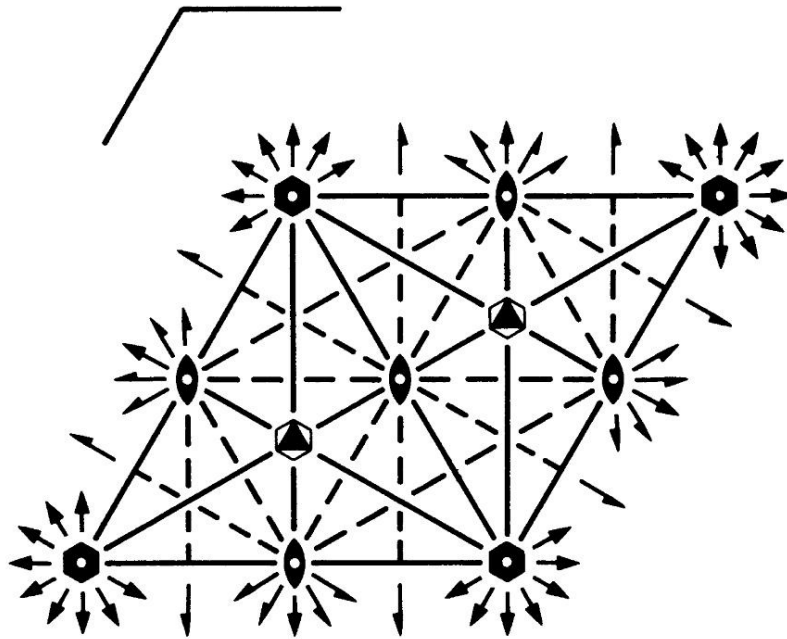


Figure 45: (Courtesy of the International Tables for Crystallography) Diagram of space group $P6/mmm$.

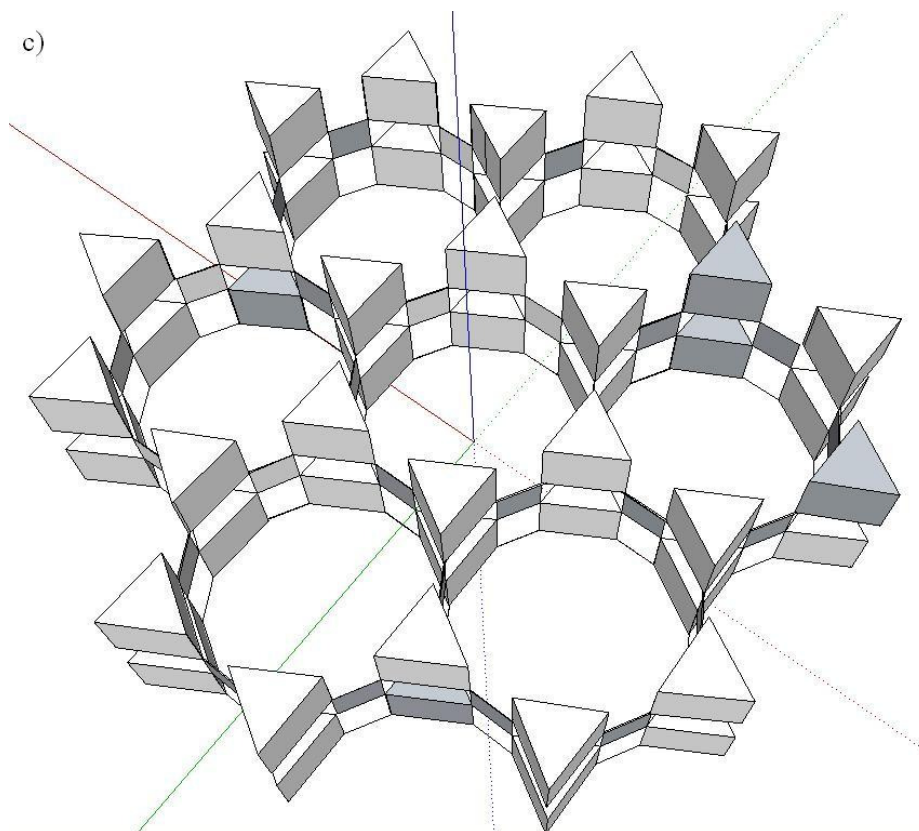


Figure 13.c): Please refer to pages 14 and 15 for all of Figure 13 if necessary.

The space group $P6/mmm$ has twenty-four distinct symmetry operations as defined by its unit cell (Hahn, 1996); however, because they are composed into numerous operations, we will just explain the notation of the symbols for visible operations in the diagram above. We note that the diagram is half-way up the height of the unit cell of **stp**; accordingly, the two line segments which meet at an angle at the top-left corner of the diagram signify that the plane on which the diagram is on is a mirror plane. Following the convention mentioned previously, the bold lines all signify reflection lines on which mirror planes intersect the diagram's plane at right angles. In the case of $P6/mmm$, all solid lines are bold. Another familiar symbol is the triangle inside of a hexagon, which the $\bar{6}$ roto-inversion whose axis is perpendicular to the plane. (Hahn, 1996)

There are three remaining unfamiliar symbols in the diagram: the four hexagons with white holes, the five ovals with white holes, and the dashed lines. The hexagons represent 6-rotations whose axes are perpendicular to the diagram's plane and are located at the center of each hexagon (Hahn, 1996). This is true for the ovals, which represent 2-rotations instead (Hahn, 1996). Furthermore, all mirror planes for reflection or glide symmetries are either perpendicular or parallel to the axes of 6-rotations. Finally, the dashed lines denote glide lines where glide planes intersect the diagram's plane at 90 degrees (Hahn, 1996). Each of these glides is composed of a reflection across the glide plane and a translation. The length of each translation

is the distance between the two symbols the glide line connects. Moreover, glide lines ending in an arrow denote that the glide goes to the appropriate symbol in the next unit cell. We show this below with four adjacent unit cells of the space group diagram:

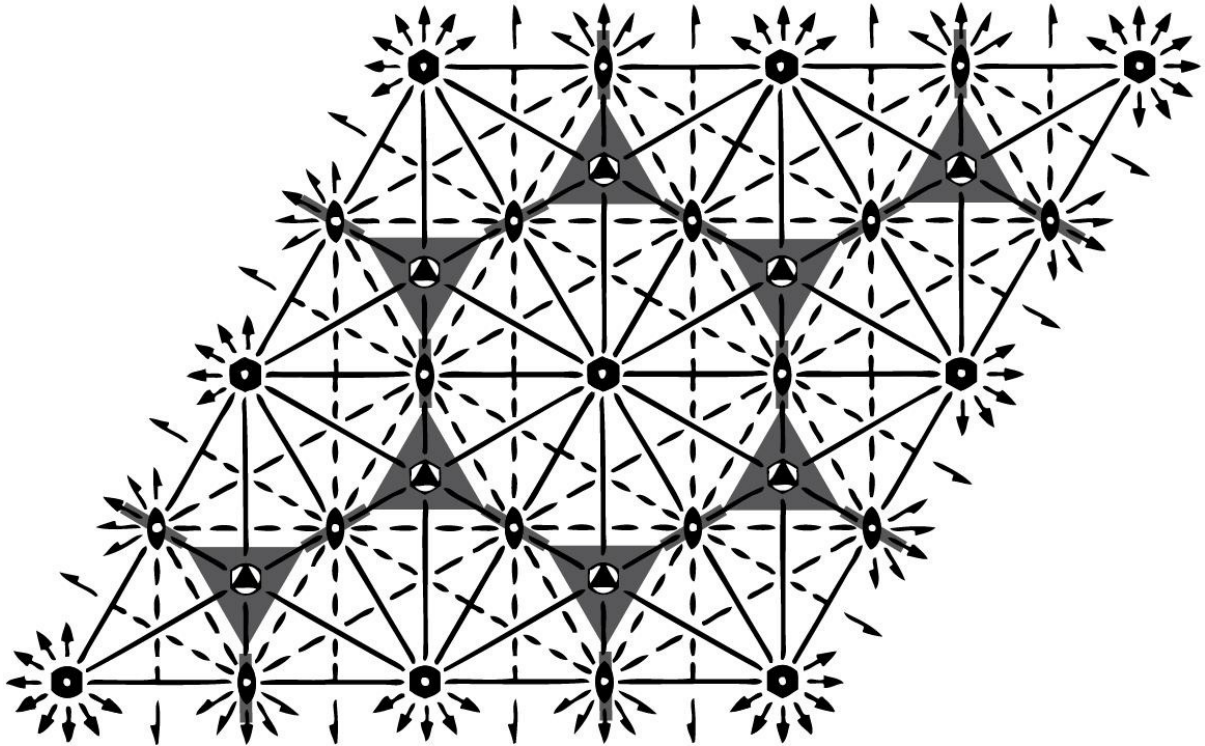


Figure 46: (Courtesy of the International Tables of Crystallography) Four adjacent unit cells of $P6/mmm$. We have included a top-down view of the model on Figure 13 as a reference to better understand the symmetry operations of $P6/mmm$. The gray triangles denote tp-PMBB-1 nodes as viewed from above, and the gray rectangles connecting these denote the MBB-2 nodes one level above and below the tp-PMBB-1 nodes. We recommend that the audience verify this visually with Figure 13.

By observing the point groups $4mm$ and $\bar{6}m2$, we can now understand the resulting space group $P6/mmm$ of **stp**. Referring to Figure 46, we see that the center of the tp-PMBB-1 nodes are located at the center of the $\bar{6}$ -rotations. Thus $\bar{6}m2$, the point group for trigonal prisms, helps explain the presence of the $\bar{6}$ operations in the space group of **stp**. Moreover, Figure 46 shows an opening formed by a cycle of six tp-MBB-1 nodes at the center of each 6-rotation. The presence of these 6-rotations now becomes easier to understand since all tp-MBB-1 nodes are exactly the same, and there are six of them evenly spaced surrounding each opening. Here we recommend strongly that our audience verify that the tp-PMBB-1 nodes are indeed evenly spaced and that the 6-rotations do belong to the $P6/mmm$. One does this by rotating the diagram on Figure 46 by $\frac{2\pi}{6}$ radians, obtained from the equation on page 39 with $n = 6$.

MBB-2 nodes are all located on 2-rotation symbols in the space group diagram, perpendicular to the plane on which the diagram resides. This is no coincidence, since an MBB-2 node is represented by a square which lies on one plane. Accordingly, the 2-rotation of these perpendicular nodes in Figure 46 is supported by the point group $4mm$, replacing a reflection in one dimension with the resulting 2-rotation symmetries in space group $P6/mmm$. Finally, the glide and reflection lines can be explained by both the reflection symmetries of tp-PMBB-1 and MBB-2 and the translation vectors of the lattice of **stp**. Once again, we recommend strongly that our audience use Figure 46 to verify this visually.

Further analysis would show how symmetries of tp-PMBB-1 in $\bar{6}m2$ and MBB-2 in $4mm$ result in **stp**'s remaining symmetry operations and their compositions in $P6/mmm$. While some of the analysis required is beyond the scope of this thesis, it is clear that the point groups of and linkers connecting tp-PMBB-1 and MBB-2 result in a crystal net with the space group of $P6/mmm$. This relationship leads to the notion that the **stp**'s symmetry is not only explained by its components in a visible manner, but that the symmetry of **stp** could be readily predicted before a crystal with the **stp** "topology" was actually synthesized. Indeed, Schoedel had the "topology" predicted (Schoedel, Synthesis of stp, 2012) mathematically; however, our point is that by understanding the concepts we have presented, chemistry researchers could predict most, if not all of the symmetries in the space group of a crystal net that they are designing.

While we recognize that not all symmetries are as visible as those in $P6/mmm$, symmetry prediction by chemists would not only give them a better idea of the crystal net they are synthesizing, but it would allow them to communicate with mathematicians in symmetry terms. This communication is important for professionals from both fields, because it would allow mathematicians to theorize crystal nets with specific nodes and find out from chemistry resources which molecules results in the nodes they want. Such communication would also chemists to be aware of symmetries, or be able to discuss these with mathematicians, during the step in which they first begin to design the kind of net they want to synthesize. We have found that this initial design process is the time at which ideas get explored or disregarded, so further knowledge or communication might lead to the formation of crystal nets that would have otherwise not been considered.

IV. Bridging Mathematics and Chemistry

A. Terminology:

In order to discuss how mathematics and chemistry might be further bridged in the context of the thesis up to this point, we must also discuss how information is distributed. For both mathematicians and chemists, the most important information is published and cited, and the coursework building up to understanding the concepts discussed in publications takes the form of textbooks. This is the case for all the ideas and terms in chemistry and mathematics. With the information presented in the previous sections, we hope to breach the *layer* of necessary

information to understand the field of MOMs and crystal nets from both view-points. By a layer, we mean an apparent communication gap preventing individuals from both fields from interdisciplinary understanding. The information presented thus far provides a common ground with not only the terms, but the tools with which the audience can build their own understanding of either field in regards to MOMs and crystal nets.

Nevertheless, we must discuss some terminology that adds difficulty to communication, even with a common ground. The most notable of these is the term topology, as discussed in section II; in mathematics, the proper term for “topology” in chemistry is “isomorphic class,” as mentioned previously. We suspect that use of the term “topology” in chemistry arose from the application of the topology sub-field in mathematics to the “isomorphism” of graphs representing molecules. Nonetheless, the term is now widely accepted in the field of chemistry as it is currently defined. Topology is not the only term that has different meanings in both fields; a trigonal prism is called a triangular prism in mathematics, mentioned in section III.

The term *default* presents another problem for interdisciplinary communication, as used in chemistry and the MOMs field in particular. While “default” chemical arrangement (e.g. positions, topologies, or compounds) seem to be readily identifiable when certain components (e.g. molecules or MBBs) are presented, the exact definition of what makes something default is hard to identify. We understand a chemical arrangement to be default for certain components if empirically those components form that arrangement most often and/or under ideal (i.e. preferred) conditions. For example, when the MBBs that Schoedel worked on yielded crystals with **snx** and **snw** “topology” instead of the expected **acs** topology, the **acs** topology was expected because it is the “default” topology based on the MBBs (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). In this case, Schoedel explains that because the linear MBB he used was bent (i.e. not ideal), the crystals did not form into the default **acs** topology as expected (Schoedel, Synthesis of stp, 2012).

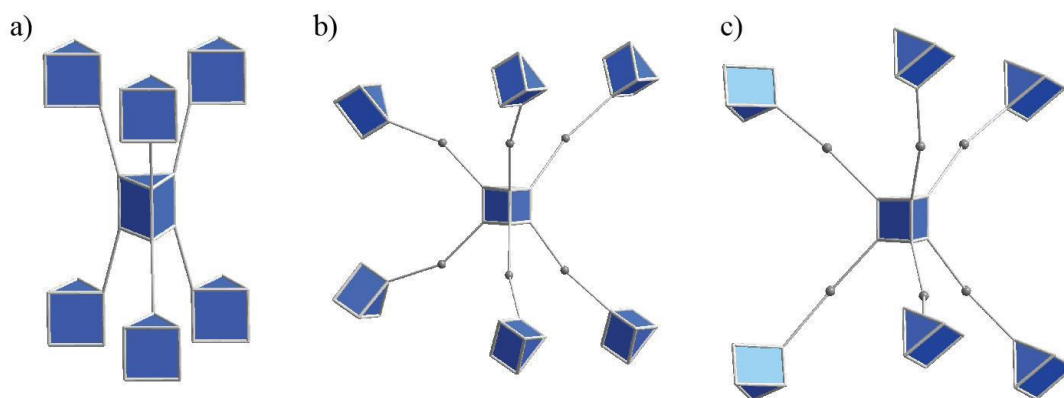


Figure 47: (Courtesy of Alexander Schoedel) Three-dimensional crystal portions composed of tp-PMBB-1s and linear (or bent) MBBs. Schoedel expected the acs “topology” formed by with linear MBBs in a), but since the MBBs were flexible, they bent to form b) snx and c) snw “topologies” during actual synthesis.

The problem with the term “default” is that the definition is constantly being updated for certain components. Thus, what is a default position currently might change if the preferred conditions change or if enough statistics point to another position. While those in the field would be aware of this constantly, this creates an uncertainty in those coming into the field.

Another terminological problem lies in the use of the term *ring* in chemistry and mathematics. The definition of a ring in mathematics is beyond the scope of this thesis, but the definition of a “ring” in chemistry refers to a cycle. Indeed, the compounds which form one or more “rings” are called *cyclic compounds*, for example Figure 1.b) and Figure 49.

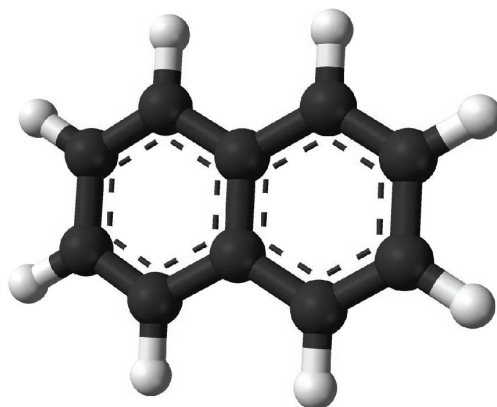


Figure 48: (Public Domain, obtained from WikiMedia Commons) Three-dimensional representation of a naphthalene molecule. If viewed as a graph, two cycles can be identified, each marked by dotted lines. The presence of these (though only one is required) makes this a cyclic compound.

Visually, we can see why these features are called rings in chemistry; nonetheless, the precise definition of a ring in mathematics causes confusion during interdisciplinary communication. To be clear, while we will not define a ring in terms of mathematics, it is nothing like a cycle from graph theory. Moreover, as is the case with all of the terms we've discussed so far, because both fields use the term “ring” concretely and often as basic knowledge, professionals from each field are defensive about their definition being the correct one. We suspect that understanding what professionals from a different field mean with their terms will at least allow better interdisciplinary communication.

B. Information Layer: Mathematics

Perceptions about mathematics or mathematicians form the next layer we discuss. Just as any other field has stereotypes or commonalities regarding its practices or its professionals, so does mathematics. These include the notions that mathematics is focused more on the abstract than the practical and that mathematicians tend to be excessively rigorous in their statements.

First, from our observation and experience, we find that professionals from other fields, or even non-professionals, believe that mathematics is far more concerned with abstract ideas and conclusions rather than anything that can be used or seen in the real world. This idea that seems to stem from the depth at which a sub-field of mathematics is taught to mathematics students before the “applications” or “shortcuts” are taught. For example, a course on partial differential equations is taught after a sequence of courses and understood through analysis, a sub-field of mathematics. Concepts are built from the general case and students are presented with partial differential equations in spaces including, but not limited to, \mathbb{R}^3 . And while the depth depends on the professor teaching the course, this amount of depth is not seen in physics or engineering courses relating partial differential equations to applications in each field.

Indeed, an engineering or physics course on partial differential equations will most likely include the most pertinent equations and “shortcuts” for finding solutions to common partial differential equations. On the other hand, a mathematics course will also involve proofs on why said “shortcuts” work and build up to understanding as many forms and solutions of equations as possible. In this manner, the engineering course is “focused on applications” while the mathematics course is “focused on abstract notions.” This is a misconception, since the abstract proofs and statements that go into mathematics courses allow mathematicians to also understand their applications, even if these applications aren't carried out in as much depth in the \mathbb{R}^3 . Moreover, just as researchers' interests in other fields vary per sub-field, so do mathematicians' interests in the sub-fields of mathematics. Subsequently, not all mathematicians focus solely on abstract concepts, though some do.

Another common belief is that the field of mathematics tends to have exceedingly rigorous statements, and thus mathematicians tend to be very precise concerning their conclusions and terminologies. This can be jarring for a professional who comes from a field that

is developing a new branch. For example, terminology and understanding about sub-atomic particles has grown over the course of the last century; in this sub-field, general ideas were pursued, altered, and adjusted as new information arrived. And while new branches in mathematics arise from new ideas and/or explanations of certain phenomena, the terminology and proofs in mathematics are precise. Thus, new branches are not formulated by observation and terminology that grows to be precise; rather new branches from mathematics arise from proofs based on established or accepted theorems and/or postulates.

Mathematicians have certainty when discussing mathematics because the statements which the field uses have been logically constructed whether the branch to which they belong is new or not. This quality causes mathematicians to demand rigor in terminology or ideas from other fields where experimentation and research point to likely conclusions, but not necessarily absolute ones. Because of this, discussion between mathematicians and professionals from other fields tend to be frustrating. We recommend that mathematicians keep in mind that other professionals tend develop fields from observation and accepted theories rather than logically proven theorems.

C. Information Layer: Chemistry

The final layer is specific to chemistry and involves the distribution of information within a chemistry lab. While our experience with this layer is specific to a particular chemistry lab, we present occurrences that seem to be common practices across chemistry labs. From what we've found, the main problem that composes this layer is the distinction among *published*, *recorded*, and *implied* information.

By published information, we mean the information that is presented in the chemistry publications. In particular, the publication that served as the main reference for this thesis, Schoedel's "Network Diversity through Decoration of Trigonal-Prismatic Nodes: Two-Step Crystal Engineering of Cationic Metal-Organic Materials," presents most common concepts and procedures published. The publication details the context of the work on **snx**, **snw**, and **stp** in regards to using the trigonal prismatic MBB. With citations, the publication briefly goes over the choices of specific chemicals and procedures, since the cited sources provide the step-by-step procedures, the evidence behind presented information (such as the crystal nets of crystal found), etc. Thus, the publication presents a root from which all recorded information can be traced.

By recorded information, we mean the specific quantitative and qualitative information that is written down by researchers in the chemistry lab. This information is recorded across various mediums, including electronic files, personal lab books, and instrument lab books (Nugent, 2012). Varied naming conventions, which are detailed when the sources of publications are traced back, are utilized. For example, in the lab in which Schoedel and his colleague Nugent work there is a practice of using an ID system to identify the lab books and files of specific

individuals, so that others might quickly find desired information regarding trials and studies, shown below (Nugent, 2012):

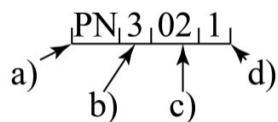


Figure 49: Identification system used in the research lab to which Schoedel and Nugent belong: a) researcher's initials, b) lab book number, c) page number in the lab book, and d) item on the page. This system is used for associated files and notes.

Nonetheless, this ID system has variations across individuals in the lab, and there is no indication that other labs have similar identification systems for their lab books and files. Moreover, the organization of the lab books at the time of this thesis was non-existent, though all of the lab books were stacked in a common area. In regards to specific chemical procedures, even though files have the same IDs as those of lab books so that observed information can be matched with measured information, there is also information that is saved at the terminal of an instrument rather than the personal terminal of the individual conducting the procedure. This results in a web of information distributed across different places that any other individual would have to traverse. This creates difficulty in following another's procedures, or reinvestigating another's trials, if the other individual is not present to explain and serve as a guide. This is not the case when information is published, because the supporting information and files are then made available. More so, it is the case when projects, such as those of undergraduates, are discontinued or specifically in this lab, when procedures are not in line with the goals of lab being discussed.

The goal of this particular lab is to produce efficient MOMs which are low-cost, are very porous, have large surface areas, and are stable outside of solvents (Nugent, 2012). This makes sense because such MOMs would have broad applications which can be developed, funded, and pursued by others. Still, the projects that don't yield such MOMs, while exhibiting other intriguing or otherwise unexplored properties, mostly fall by the wayside. An example is a table of various trials done by Nugent, to identify which chemical combinations would yield single crystals, denoted by a star (Nugent, 2012). In this table, the possibilities that didn't result in crystals, but perhaps powders, changes in color, or other visible changes are not explored because of time and resource constraint. In mentioning resource constraint, we remember that part of the aforementioned goal is to produce low-cost MOMs. Accordingly, researchers frowned upon using materials not in line with this goal, or even excessive use of expensive materials.

The limitations of a goal exist in all fields of research, since researchers can only do so much upon finding features that aren't directly related. The problem here is that because recorded information is scattered, another individual would have difficulty finding the information to begin a project with a different goal. This would mean that work or evidence

already recorded would be ignored or unused altogether, regardless of how important it may be to the imagined potential project. This is particularly problematic for individuals coming from another field, say mathematics, who are journeying into the field unaware of what others may have worked on and discarded. This entire problem is further complicated because of the widespread implied information in chemistry labs.

By implied information, we mean the information that is neither recorded nor published, but expected of individuals working in the lab. Naturally, this information constitutes the necessary background for working in the lab; however, it also includes lab practices taught to individuals. The problem with this is that these are recorded guidelines, but rather understood practices regarding common procedures. For example, when a MOF needs to be cleansed of the solvent in which it resided, it needs to go through solvent wash cycles, which aren't recorded but are implied when the solvent is said to be removed (Nugent, 2012). These are procedures which new individuals are instructed to do and that are expected to be done thoroughly. For those not in the chemistry field, however, these implied procedures are neither seen in recorded information nor in published information, so such individuals are not aware of the necessity nor practice of this procedures just by reading printed information or briefly conversing with those who work in the lab.

More importantly, the experience which guides researchers in the lab to try different chemical designs, structures, and procedures is implied as well. While working in the lab, a new individual might be made aware of things other have found to work or not work, but once again, this would not be the case for individuals who aren't members of the lab or who aren't in the field. The brief recordings of multiple trials that researchers note in their notebooks carry little more information than which chemicals and amounts yielded visible crystals, for example (Nugent, 2012). While this is in line with the goal of the lab, others reading recorded information have no information as to what caused a particular research to try a certain amount or chemical over another. And if an individual *X* is indisposed because of travel, vacation, etc. others who aren't familiar with *X* would not be able to follow the logic that led the individual to a certain reaction that proved particularly successful. This is a problem both inside the chemistry field and in cooperation with other fields, because being able to track the reasoning of researcher in how he conducts experiments might yield unnoticed information as to what practices yield and don't yield results. Unfortunately, the exact measure of how much a researcher's practices are correlated to successful outputs is beyond the scope of this thesis.

We recommend changes addressing the above issues to be discussed between chemists and professionals from other fields. We recognize that for all researchers, doing research alone consumes plenty of time. However, an interdisciplinary discussion should reveal practical solutions that would welcome work between the chemistry and mathematics fields, among others.

V. Conclusion

A. Future Work

The use of platonic solids or other well-known polyhedra is widespread in the chemistry field and particularly seen in regards to MBBs; however, the use of other polyhedra is a sub-field that merits exploration. Since the goal of MOM labs are the same as the goal of the lab mentioned in the previous section, it follows that having a wealth of new MBBs might lead to different and potentially useful crystal nets with desired attributes. By this wealth, we mean MBBs having polyhedral structure that aren't platonic solids, since these and some two-dimensional are the structures that tend to see most attention (Yaghi, Ockwig, Chae, Eddaoudi, & Kim, 2003). This is evidenced by the fact that the trigonal prism MBB is just now being explored for new crystal nets by Schoedel (Schoedel, Wojtas, Kelley, Rogers, Eddaoudi, & Zaworotko, 2011). These common structures seem to form a comfort zone for researchers, though this limits the potential crystal nets that can arise from a mathematical sense. Thus, it is our recommendation for research on crystal nets to include new polyhedra as the structures of MBBs.

B. Conclusion

There are hundreds of crystals nets which have been identified on RCSR; the information in this database describes the properties of the nets in terms of crystallography and applied mathematics. However, RCSR also distinguishes the space group for each crystal net online. Accordingly, the use of RCSR in combination with the International Tables for Crystallography, Volume A can be applied for any other crystal net. This is exemplified by our analysis of the space group of **stp**. The International Tables include an entire guideline for different notations in understand what each space group diagram means (Hahn, 1996). With our analysis as an example, we trust that researchers from both the chemistry and mathematics fields can discuss and understand the symmetries that arise in crystal nets from different nodes from a mathematic and chemical viewpoint.

Our hope is that by understanding symmetry and space groups, chemists and mathematicians might better design and synthesize nets with specific qualities. This requires the experience that chemists have in determining which nodes to use for certain connectivity and which processes might best yield certain MBBs or linkers. This also requires the extensive background mathematicians have in predicting and explaining symmetries that arise from the point groups of different nodes. In bridging chemistry and mathematics, this collaboration would no doubt allow desired MOMs to be pre-designed and synthesized efficiently, with both chemical and mathematical certainty. It might also result in the discovery of new crystal nets like **stp**, thereby increasing MOM possibilities for chemists. An increase in discoveries would also expand and detail which node combinations work and why, a matter of importance for professionals in both fields.

We believe that this thesis is the beginning of a bridge between mathematics and chemistry, at least in the interdisciplinary field of MOMs and crystal nets. With our commentary of the layers dividing the two fields and our explanations provided alongside the chemical and mathematical analysis of **stp**, we have created the beginning of a common ground for discussion. This discussion on processes, symmetries, etc. by professionals from both fields must be built upon, considering all of the applicable theories and concepts from each field that we had neither the depth nor space to cover. Nonetheless, we hope this thesis can be the first step on the path of collaboration.

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