Lightweight Magnesium Metal-Organic Frameworks

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Abstract

Magnesium metal-organic frameworks (Mg-MOFs) are a relatively new field of research. Currently, only a small number of Mg-MOFs exist, and most of them have not been studied very extensively. This work investigates three new magnesium structures made with a pre-existing ligand used for MOF synthesis.

Chapter one of this thesis details information about MOFs generally with specific focus on certain parts of their structures and capabilities. This includes a brief overview of different types of MOFs, including, multiwalled and lightweight MOFs. This is followed by a more in-depth literature review of the synthesis and applications of a number of Mg-MOFs.

Chapter two focuses on the synthesis and characterisation of the pre-existing ligand, 2-(4-carboxy-1, 1’-biphenyl)imidazo(4, 5-f)-1, 10-phenanthroline (L1). This includes the characterisation of L1 by single crystal X-ray crystallography. This was followed by the synthesis and characterisation of a new ligand 2-(3, 5-biscarboxy-1, 1’-biphenyl)imidazo(4, 5-f)-1, 10-phenanthroline (L2). The methylated version of L2 was characterised via single crystal X-ray crystallography due to the low solubility of the non-protected L2. Attempts were made to produce ruthenium-ligand complexes with L1 and L2, but these processes were unsuccessful.

Chapter three focuses on how L1 and L2 were used to create a number of new metal-organic structures. These structures were, three separate magnesium MOFs, a cadmium MOF, and two sodium coordination polymers. L1 was also used to produce a zinc MOF that had recently been published. The three magnesium-L1 MOFs were synthesised, characterised, and compared to determine why and how they were produced. The first Mg-MOF was a simple one-dimensional chain with two sets of L1 bound to each magnesium ion metal node in opposite directions (Mg-MOF-1). The second Mg-MOF formed as a two-dimensional layered sheet framework with large 1D pores. The framework was held together by secondary building units (SBUs) with four magnesium ions bound together by formate bridging ions and the carboxylate groups of L1 (Mg-MOF-2). The third Mg-MOF formed was a much more intricate 1D chain, with each chain-link comprising of multiple L1 ions and magnesium ions bound together with formate bridging (Mg-MOF-3). The structure of Mg-MOF-3 indicates that it may have been a partially formed version of Mg-MOF-2.
Chapter four presents an overview of the future work that can be investigated regarding the structures that have been made with L1 and L2. This includes a more comprehensive investigation into the materials that have been produced such as their gas adsorption and photophysical properties. It also includes the planned production and analysis of isoreticular analogues of the already produced material. Finally, it includes the synthesis of ruthenium-ligand complexes via literature methods and the potential bimetallic MOFs that could be synthesised with those complexes.
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Chapter 1: Introduction

1.1 MOF Chemistry

Metal-organic frameworks or MOFs are defined as large, ordered, repeating, metal-organic crystalline structures. MOFs are formed by the binding of organic bridging ligands with inorganic metal nodes. For this thesis these metals can include transition metals, rare earth metals, and alkaline/alkali metals but excludes sodium. The bridging ligands usually bind to two or more metal nodes and the metal nodes bind to multiple bridging ligands to form a network. The metal nodes tend to be either a single metal ion or a cluster of metal ions. These clusters of metal ions are also known as secondary building units (SBUs). MOFs are most commonly designed to have symmetrical, rational structures that are often considered to be aesthetically pleasing as well as functional. MOFs are well known for their large internal BET (Brunauer–Emmett–Teller) surface area, high porosity and their high levels of tunability. Because of these features, MOFs are able to perform several different applications such as reaction catalysis, ion exchange, drug delivery, sensing, light-harvesting, and many more. But one of the most important and useful applications of MOFs is their ability to adsorb and separate gases selectively.

Figure 1.1: Crystal structure of MOF-5 including colour coding, ZnO₄ SBU: blue, large internal pore: yellow, carbon: black, oxygen: red.
A common method of MOF synthesis involves reacting a metal salt with a carboxylic acid based bridging ligand in dimethylformamide (DMF) with heating and, if necessary, a moderator. The synthetic pathway for this particular method is straightforward. As the solution is heated, the DMF will slowly decompose (sometimes aided by a moderator) into the base dimethylamine. This process will cause the carboxylic acid groups of the ligands to deprotonate into carboxylate groups which will then bind to the positive metal ions forming the MOF. This process is designed to be relatively slow, taking up to several days of heating, allowing for the MOF crystals to form slowly. The moderator adjusts the speed of the reaction, such as an acid which would increase the rate at which the DMF decomposes.\textsuperscript{2,10,11} Another moderator that can be present in MOF synthesis is distilled/deionized water, previously shown to improve the crystallinity of the MOF at specific concentrations.\textsuperscript{12}

One common issue when working with MOFs is characterisation. Most common forms of characterisation such as nuclear magnetic resonance (NMR) spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, and mass spectrometry, require the product to be dissolved in a specific solvent before it can be characterised. This is an issue due to most MOFs being very robust, which means that they will not dissolve in most solvents. If a MOF was dissolved in solvent the framework would likely collapse or deform making characterisation by the above methods ineffective. Alternatively, the use of characterisation methods like Infrared (IR) spectroscopy or elemental analysis also has issues. IR spectroscopy would likely only show the bonds within the ligand but not between the metal and the ligand. Whereas elemental analysis would likely be impeded by the solvent molecules that had bound to the MOF. Due to the MOF’s crystalline nature, one common method of characterisation is single crystal or powder X-ray crystallography, which can determine the molecular structure of the MOF. However, this method of characterisation also has issues as the disordered solvent molecules that remains within the pores of the MOF reduce the accuracy of the measurements.\textsuperscript{13}

The synthesis of a new MOF is often performed via reticular synthesis. Reticular synthesis involves the reaction between a metal ion or SBU and a predesigned bridging ligand to produce a MOF with a predicted/designated topology.\textsuperscript{14} But for this to occur, the bridging ligand must be relatively rigid and stable so as not to bend or twist in unexpected ways during the synthesis of the MOF.\textsuperscript{15} In most cases predicting the topology of a MOF is not an easy task so methods like reticular synthesis are beneficial. The overall structure of a MOF can vary wildly depending on the potential coordination geometry of the metal ion/SBU and the ligand’s binding capabilities. Additionally, the introduction of moderators into the synthesis reaction can lead
to said moderators being incorporated in the framework leading to a very different MOF topology than predicted.\textsuperscript{16} Overall, the ability to predict and design the topology of a MOF is important because the topology of the MOF determines the pore size and shape. This, in turn, determines the MOFs capacity to adsorb guest molecules within itself.\textsuperscript{17} Another unique factor of MOF topology is interpenetration. Interpenetration is when a single network has large enough pores that another identical network can be formed woven into the first network, i.e., one network’s bridging ligands and metal nodes can penetrate another network and vice versa. Interpenetration has two major effects in MOF structures, it decreases the size of the pores and increases the structure’s overall stability. The decrease in pore size is straightforward, the space in the pores of one network is being taken up by another network, the increase in stability is caused by the reinforcement that this causes. If a part of a non-interpenetrated MOF is damaged or removed, the overall structure is more likely to collapse. Whereas if a part of one network in an interpenetrated MOF is damaged the damaged network can still be held together by the other network. Additionally, an interpenetrated MOF can have more than two networks, it is possible for multiple networks to be interwoven to form a more stable MOF overall.\textsuperscript{18}
1.2 Gas Storage and Separation

Gas adsorption and storage are an ever-increasing field of interest regarding environmental protection. The ability of a substance to selectively capture greenhouse gases would make that substance incredibly useful and valuable.\textsuperscript{19,20} There are several different gases present in the atmosphere that it would be beneficial to be able to take from the air easily and selectively. Such gases are usually either harmful or negatively impact the environment in large quantities, such as carbon dioxide (CO\textsubscript{2}) or methane (CH\textsubscript{4}).\textsuperscript{21,22} Also, capturing certain gases for later use would be incredibly beneficial, such as oxygen (O\textsubscript{2}), nitrogen (N\textsubscript{2}) or carbon dioxide (CO\textsubscript{2}) gas. Although not normally found in the atmosphere naturally, one of the most sought-after gases is hydrogen gas (H\textsubscript{2}). If a method of reliably capturing, storing, and releasing H\textsubscript{2} when needed was developed, it could serve as a safe, clean energy source.\textsuperscript{20,23}

The high level of porosity and the relatively large internal surface area of many MOFs is instrumental in their ability to capture, separate, and store gases selectively. Furthermore, the high level of tunability that MOFs are also known for allows for the capture and separation of gases to be highly specific and very tailorable depending on the components used in the production of the MOF. Thus, it is possible to influence what type of gas and how well it is collected by either increasing or decreasing the size of the pores of a MOF or by changing the size or shape of the structure’s bridging ligand.\textsuperscript{20} Adding or changing the metal ion used also alters the gas adsorption properties of a MOF. Adding a second metal ion in the synthesis of a MOF makes it possible to produce a bimetallic MOF. Such a MOF has been shown to be more capable of binding than its single metal analogue.\textsuperscript{1} The other method of altering gas adsorption properties is to produce an isoreticular analogue of the MOF. Changing the metals and keeping the ligands the same the gas adsorption capacity and selectivity of the MOF can potentially be tuned without the overall topology of the MOF being altered.\textsuperscript{24,25} MOFs have also been separated into four different categories depending on their capacity to adsorb and desorb gases and other guest molecules (Figure 1.2).\textsuperscript{26}
Figure 1.2: Gas adsorption and desorption properties of different types of MOFs. First generation collapse upon removal of guest. Second generation is unaffected by adsorption/desorption of guest molecules. Third generation flexes to accommodate adsorption/desorption of guest molecules.²⁶
1.3 MOF Sensing Capabilities

While gas adsorption has attracted a large deal of interest, various MOF’s can have several other applications. A fascinating application that MOFs can be designed and used for is chemical sensing. MOFs can be tailored to sense a variety of different materials from something as simple as a specific metal ion, to slightly larger materials like gas molecules, to larger relative complex molecular materials such as pesticides and antibiotics.

How different MOFs are used to sense a particular molecule can vary, but a number of commonly used methods rely on the UV-vis/fluorescence properties of the MOF. First is fluorescence quenching in which a MOF has a strong/distinct fluorescence spectrum, and when it is in the presence of specific molecules, the level of fluorescence drops dramatically to a zero/near-zero level. This method can be useful for highly sensitive detection, i.e., parts per billion (ppb) detection levels. This method can be used to accurately measure concentration of the measured substance at low concentration. The second method involves taking a MOF that is not photoactive in the visible spectrum or is only weakly photoactive (usually a white/off-white solid) and introducing it to the molecule it is supposed to be sensing. Doing so would move existing UV peaks into the visible spectrum and potentially increase the intensity of the fluorescence peaks (Figure 1.3). This can also be used to measure concentration but usually only at low concentrations as the increase in intensity will plateau after a certain point. Most forms of chemical detection via MOF fluorescence can detect even trace amounts of a specific molecule and can be used to calculate its concentration.

Figure 1.3: Example of chemical sensing MOF under 254 nm UV light in the presence of europium(III) ion (left), dysprosium(III) ion (centre) and terbium(III) ion (right).
1.4 Isoreticular MOF Chemistry

MOFs have been shown to have a very high degree of tunability regarding topology and porosity. Because of this, a particular subset of MOF chemistry known as isoreticular MOF chemistry has been shown to be useful for predictably synthesising a MOF with an expected topology. This involves synthesizing a particular MOF then synthesizing different MOFs with similar topologies. This is usually done by substituting the bridging ligand with a similar ligand. Usually, a ligand that is either shorter or longer and has the same binding capabilities while not altering the metal that is used. Alternatively, it can also be done by substituting the original MOF’s metal ion/SBU used with another metal ion/SBU that has the same or similar binding capabilities and configuration e.g. the same charge, same coordination geometry. While the overall topology will stay the same the size of the isoreticular MOFs can change dramatically depending on the length of the bridging ligands (Figure 1.4). If the general shape of the ligand and the donor groups at each end of the ligand are not changed, then the overall topology of the MOF would be expected to stay the same, then it can be considered an isoreticular Metal-Organic Framework (IRMOF). A significant consequence of synthesizing IRMOFs is the change in gas adsorption properties of the MOF. This change results from either the change in the length of the bridging ligand altering the framework’s pore sizes, or the change in the metal to a metal with different gas adsorption properties. As well as having different gas adsorption properties, isoreticular analogues of various MOFs could also prove to be more capable as catalysts or chemical sensors depending on the metal or ligand change. Additionally, it could also be possible to alter the binding properties of the MOF by adding functional groups to the ligand that could selectively bind different materials. If the new framework had the same or a similar topology it would then be considered an IRMOF.
Figure 1.4: Illustration of isoreticular MOFs of MOF-5. MOF-5 is shown as IRMOF-1 (top left), IRMOF-n (n = 1-8, 10, 12, 14, 16) are all non-interpenetrating IRMOFs. Including colour coding, ZnO₄ SBU: blue, large internal pore: yellow, carbon: black, oxygen: red. 4,31
1.5 Structural Strength of MOFs

One of the most significant problems when it comes to working with MOFs is framework collapse. This is when the structure of the MOF is not sturdy enough and collapses spontaneously (often when the framework is removed from the solvent it was synthesized in) or due to external forces. In most cases, framework collapse happens when guest molecules are removed from the pores of the framework (also known as activating the MOF), causing the structure to degrade in quality or fall apart rapidly (Figure 1.5).\textsuperscript{34,35} This is a problem as repeatedly capturing, storing, and releasing guest molecules is one of the primary purposes of the majority of MOFs’. Therefore, the tendency of certain MOFs to collapse when the guest molecules are removed greatly diminishes that MOF’s usefulness. Additionally, when MOFs are synthesized in solution, they usually form with the solvent they were produced in adsorbed inside their pores which can make them very difficult to remove as the solvents that are often used to synthesize MOFs are usually high boiling point solvents such as dimethylformamide (DMF), diethylformamide (DEF), or dimethylsulfoxide (DMSO).\textsuperscript{6}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure15.png}
\caption{Potential outcomes of solvent removal, including successful removal (top), partially successful removal (right), formation of partially collapsed partially crystalline structure (bottom right), the collapse of outer structure with crystalline inner structure (bottom left) and formation of fully collapsed structure (left).\textsuperscript{35}}
\end{figure}
Due to the high boiling point of common solvents used to synthesise MOFs, only some specific methods can be used to remove them from the MOFs they are bound within. The first and arguably simplest method of solvent removal is heating under a vacuum. Due to the propensity of MOFs to decompose at high temperatures, simply heating a MOF to the solvents boiling point is not a viable strategy. As such, heating the MOF under vacuum is a relatively straightforward procedure, as applying a vacuum to the MOF will drop the solvents boiling point to a more reasonable temperature. The second method is a solvent exchange in which the MOF is washed in a more volatile solvent with a much lower boiling point than the solvent that was used in the MOF synthesis. After being sufficiently washed with the more volatile solvent, all the original solvent should be removed from the MOF and replaced with the new solvent. This more volatile solvent can then be removed via heating or vacuum drying or a combination of the two (Figure 1.6). While those are two relatively simple solvent removal methods used in MOF activation, other more complicated methods can be used if the first two methods are unsuccessful in solvent removal or cause the framework to collapse. Some of the other more complicated methods of solvent removal include the use of supercritical (high temperature and high pressure) CO₂, soaking the MOF in benzene and freeze-drying it repeatedly, and specific chemical treatment in which a specific material such as a strong acid is required to remove the solvent from the framework.6

![Figure 1.6 Solvent removal through method 2: solvent exchange and evacuation.](image-url)
The potential solutions to the problem of MOF collapse due to solvent removal are either use a method of guest removal that is non-destructive, of which there are a number of approaches or to develop MOFs with a higher level of robustness. Personalizing the method of guest molecule removal for each MOF is an inefficient method of creating and activating useful MOFs, whereas developing MOFs that can withstand the necessary environments and stimuli used to remove guest molecules from the MOF’s pores is a much more sustainable method of creating MOFs for long-term use. One such method of forming a more robust MOF is to synthesise a MOF formed out of multiple interpenetrated networks. This would be useful if part of one of the networks were damaged when removing guest molecules, since the overall structure would remain stable.¹³ Although it may be difficult to restrict the level of interpenetration, which may decrease the size of the MOF’s pores too much for it to be useful.¹⁸
1.6 Multi-Walled MOF Chemistry

Another possible way to increase the stability of a framework is to produce a multi-walled (usually double-walled) MOF. The synthesis of multi-walled MOFs is a fairly new approach in MOF chemistry, with the first double-walled MOF being synthesised as recently as 2010.37 Normally, MOFs are formed in such a way that the pores within the MOF are separated by a single bridging ligand, therefore a multi-walled MOF would have multiple ligands parallel to each other separating the pores. The pores of the MOFs tend to be smaller Due to the extra layers, making them less capable of capturing larger gases, but also making the MOFs more stable and robust, meaning that they are less likely to collapse when their guest molecules are removed.18,38 The increase in the structural stability of multi-walled MOFs is stated to be similar to that of interpenetrated MOFs.38 The presence of a multi-walled structure within a MOF will also reduce flexibility by a great degree ensuring that the MOF will be a robust structure but not a flexible one. This method will likely be more controlled than interpenetration as a framework can be interpenetrated multiple times over, which can greatly decrease the volume of the MOF’s pores. Due to steric hindrance and the limits of the binding capacity of a metal ion/SBU, it would be almost impossible for a framework to be more than triple-walled.18 In the past the Hanton-Morrati group has worked with and produced double-walled MOFs (Figure 1.7).5

![Figure 1.7 View down the c-axis of isoreticular double-walled lithium MOFs, LiMOF12 (left), LiMOF30 (middle) and LiMOF50 (right).5](image-url)
1.7 Lightweight Metal-Organic Frameworks

While most MOFs are designed with transition metals as the metal nodes that the bridging ligands bind to, it is also possible for MOFs to be synthesised with the lighter “s block” metals. Currently MOFs have been produced using lithium\textsuperscript{5,39}, magnesium\textsuperscript{29,40} and calcium\textsuperscript{41}. One of the goals of using lightweight metals for MOF synthesis is to produce lightweight MOFs to determine what they can compare to the heavier ones made with transition metals. The purpose of synthesising lightweight MOFs is to exploit the high surface area and large pores that MOFs possess while forming lightweight low-density MOFs with high volumetric and gravimetric capacities.\textsuperscript{42} The smaller s-block metals take up less space allowing for more empty space between metal nodes (i.e. larger pores). Plus the lightness of s-block metals means that the overall weight of the framework would be lower, allowing for a higher ratio of gas adsorption by mass than MOFs synthesised using transition metals.\textsuperscript{28}

Selective adsorption of lightweight gases such as hydrogen and methane has drawn considerable attention with respect to MOFs. Because of this, lightweight MOFs with small ligands and metal ions are of particular interest as they are attractive candidates to adsorb and store lightweight gases.\textsuperscript{11} Furthermore unlike certain transition metals most lightweight s-block metals, excluding beryllium, are nontoxic and even biologically active in some cases, which makes them preferable materials to handle.\textsuperscript{29}
1.8 Calcium Metal-Organic Frameworks

Calcium MOFs are particularly rare for several reasons. First, there is a general lack of lightweight alkali metal-based MOFs. Second, reticular synthesis of MOFs is based on predictability, i.e., the ability to compare a pre-existing MOF to a potential new MOF and, with a practical level of accuracy, determine the structure/topology of the new MOF. Calcium is problematic for use in reticular MOF synthesis due to its high coordination number and variable coordination geometry.\(^4^1\) Calcium ions have been shown to form a wide variety of number of bonds and that its coordination number can go as high as nine; this is problematic when attempting the synthesis of a MOF with a predetermined design.\(^4^3\) The variability in the number of bonds leads to a highly unpredictable structure, and the high number of potential bonds would likely cause a large amount of interference between the up to nine ligands attempting to bind to the calcium, especially if any of the ligands are particularly large (such as if they possess aromatic groups). This would likely lead to the MOF being too cluttered and dense to be sufficiently porous, making Ca-MOFs less capable of adsorbing guest molecules and therefore less efficient at many processes MOFs are used for.

Despite the drawbacks and difficulties of producing a calcium MOF there are several advantages to producing Ca-MOFs, and there have been a handful of Ca-MOFs made so far.\(^4^1, 4^4, 4^5\) Calcium, unlike certain metals commonly used in MOFs, is non-toxic,\(^4^6\) environmentally friendly,\(^4^1\) and is the 7th most abundant element on earth by mass, making it easy and cheap to source.\(^4^7\) Due to the low toxicity of calcium, efforts have been made to design and produce Ca-MOFs that are stable in aqueous/biological environments for drug delivery (Figure 1.8). This is because the same traits that make MOFs desirable for things like capture, storage and induced release of gases can also be used for the administration of medicine and calcium is a bioactive metal so it can be used in the production of bio-applicable MOFs.\(^4^4\)
Figure 1.8: The crystal structure of a water stable calcium MOF, PFC-41. Including colour coding, carbon: black, oxygen: red, calcium green, phosphorus purple.\textsuperscript{44}
1.9 Lithium Metal-Organic Frameworks

Lithium-based MOFs are of particular interest in producing lightweight MOFs, as lithium is the lightest metal there is and therefore is the lightest material that can be used in the formation of lightweight metal-organic frameworks.

Lithium in particular is a source of interest regarding capturing hydrogen gas. Specifically MOFs that have lithium ions bound to them, i.e. Li$^+$ doped/decorated MOFs have shown an increased ability to adsorb H$_2$ compared to non-doped versions of the same MOF. This is because the lithium ions are very deprotected and positively charged whenever they are bound to organic molecules, therefore, they are capable of binding H$_2$ molecules via electrostatic interactions.

While there are some MOFs that have lithium ions added to the framework to increase hydrogen storage capabilities, there are very few MOFs in which lithium ions are used as the metal nodes. This is because it is quite challenging to form MOFs around lithium ions due to their relatively low and inconsistent coordination number (4-6). As well as the fact that lithium ions tend to only be able to coordinate to other molecules weakly. These two facts make it fairly difficult to predictably synthesise a lithium-based MOF. Despite the difficulties a number of people have managed to produce and characterise various forms of lithium MOFs (Figure 1.7 & 1.9). MOFs with lithium nodes tend to have comparably low framework densities due to the small size of the metal, which tends to be favourable in terms of gas adsorption. Lithium MOFs possess both low density frameworks and the ability to bind H$_2$ molecules to any lithium ions that are not fully bound (i.e. when a lithium ion is coordinated to less than 4-6 ligands). As such, Li-MOFs prove to be a potential source of interest for adsorbing hydrogen and other useful gases under practical conditions (i.e., near room temperature and atmospheric pressure).
Figure 1.9: The crystal structure of a Li-MOF, IMP-22. Including colour coding, carbon: black, oxygen: red, lithium: blue.\textsuperscript{42}
1.10 Magnesium Metal-Organic Frameworks

Magnesium-based metal-organic frameworks (Mg-MOFs) are particularly interesting even compared to the other “s-block” based MOFs with a particular research focus on Mg-MOF-74 (Figure 1.10).\textsuperscript{51-55} Despite this interest, “s-block” based MOFs are a relatively new field of study. As such there is a limited amount of information about Mg-MOFs and the other “s-block-metal” MOFs. Magnesium ions are $2^+$ ions meaning they are capable of binding to two separate, negatively charged ligands. While it has been shown that MOFs can be synthesised with $1^+$ metals,\textsuperscript{28} the ability to form more than one strong bond between a positively charged metal ion and negatively charged bridging ligands greatly increases the variety of MOFs that can be produced and the stability of those MOFs.\textsuperscript{30} Mg ions have been shown to bind strongly to both charged ions and neutral atoms, meaning that Mg-MOFs could be formed with a wide variety of charged and neutral ligands assuming the overall charge is balanced with a counter-anion when necessary.\textsuperscript{25} Additionally, magnesium is an octahedrally coordinated metal ion meaning it can form up to six bonds and thus should be able to produce three-dimensional MOFs easily. Due to the strength of the magnesium-oxygen bonds and the fact that carboxylate groups are often used in the metal-ligand bonds used to form MOFs magnesium likely offers the greatest flexibility in terms of the s-block metals used to form MOFs.\textsuperscript{56}

![Mg-MOF-74](image)

Figure 1.10: The crystal structure of activated Mg-MOF-74. Including colour coding, carbon: black, oxygen: red, magnesium: blue.\textsuperscript{55}
1.11 Magnesium MOF Literature Review

In 2005 the first-ever published magnesium MOF was synthesised. It was formed by reacting magnesium nitrate (Mg(NO$_3$)$_2$•6H$_2$O) with 2,6-naphthalene-dicarboxylic acid (H$_2$NDC) in DEF. It was made alongside a zinc analogue using different solvents. The structure of the Mg-MOF was also an analogue of a pre-existing nickel-based MOF, which likewise had naphthalene-dicarboxylate bridging ligands. The 3D structure that was formed had three magnesium ions within the asymmetric unit, the central magnesium was bound to six carboxylate groups while the outer two magnesium ions were bound to four carboxylate groups and two DEF molecules (Figure 1.11 top). Each magnesium ion formed a distorted octahedral geometry. The compound then had the residual solvent guest molecules removed via heating the framework to boil off the DEF forming the pure MOF Mg$_3$(NDC)$_3$ (Figure 1.11 bottom). It was found that removing the solvent molecules also alters the structure of the MOF. The structure was shown to revert to its original form when exposed to DEF but was stable in either configuration. The de-solvated MOF had a relatively low capacity for hydrogen gas adsorption between 0.42 wt. and 0.60 wt. % at 77 K. It was also determined to have a nearly non-existent gas adsorption capacity for either carbon dioxide or nitrogen gas. The MOF’s low gas capacity was determined to likely be due to the relatively small pore sizes that the de-solvated MOF possessed. However, it had a relatively high capacity for oxygen gas adsorption compared to the other gases (potentially due to magnesium’s oxophilic nature) and was thought to be useful for separating oxygen and nitrogen gas from the air.\textsuperscript{25}
Figure 1.11 Structure of MOF [Mg₃(NDC)₃(DEF)₄] upon synthesis focused on Mg centres [top] and full Mg-MOF with solvent molecules removed [bottom].
The specific interest in lightweight MOFs led to a study into the synthesis of a MOF using one of the lightest metals, magnesium, as the node and the lightest carboxylic acid, methanoic acid (formic acid), as the bridging ligand. This reaction was performed by reacting magnesium nitrate and formic acid in DMF, in a sealed unit, at 110 °C for 40 hours. This produced a magnesium formate MOF with DMF held within its pores \([\text{Mg}_3(\text{O}_2\text{CH})_6\text{•DMF}]\) (Figure 1.12). The structure of the MOF is reminiscent of adamantane, and it was shown that within the MOF, the magnesium ion could take one of four subtly different binding configurations. Attempts were made to produce similar frameworks with calcium, strontium, and barium, of which only the barium product was similar to the Mg-MOF. Despite the similarity, the Ba-MOF was not an isoreticular analogue of the magnesium formate MOF due to the residual nitrate that remained partially bound to the metal. Once the Mg-MOF had been produced and analysed, the solvent bound within the MOF was removed via heating at under vacuum. This process showed that the magnesium formate MOF did not decompose or deform when the solvent was removed. Once the solvent had been removed, the MOF was tested for its ability to adsorb other solvents. The desolvated MOF was soaked in a number of solvents, including acetone, benzene, cyclohexane, diethyl ether, DMF, ethanol, methanol, and tetrahydrofuran. Mg-MOF was able to adsorb every solvent tested, except for cyclohexane showing that the MOF can bind a wide variety of organic solvents. The gas adsorption capacity of the MOF was also tested and was shown that at low temperatures (approximately 70 K) the Mg-MOF could adsorb hydrogen and nitrogen gas, but only moderately when compared to other pre-existing MOFs. Finally, a thermogravimetric analysis (TGA) was taken of \(\text{Mg}_3(\text{O}_2\text{CH})_6\text{•DMF}\) and was found that the solvent evaporated between 150 and 200 °C and the desolvated framework decomposed at approximately 400 °C. This was compared to transition metal analogues of the MOF including manganese, iron and cobalt analogues that all decomposed at temperatures less than 300 °C. Overall, it was determined that \(\text{Mg}_3(\text{O}_2\text{CH})_6\) is a fairly stable MOF that can bind guests relatively well such that the pores of the MOF will increase in size to accommodate larger guest molecules and that the framework will remain stable when the guest molecules are removed.\(^{11}\)

![Figure 1.12 Part of magnesium formate MOF with bound DMF molecules \([\text{Mg}_3(\text{O}_2\text{CH})_6\text{•DMF}]\). Mg\(^{2+}\) ions shown as green spheres, carboxylate linkers shown as grey rods.\(^{11}\)](image)
The magnesium MOF Mg-MOF-74 was synthesised and had its gas-adsorption characteristics analysed. Mg-MOF-74 was an isoreticular analogue of MOF-74, which was primarily synthesised with zinc. The MOF was synthesised via a reaction between magnesium nitrate hexahydrate and 2,5-dioxidoterephthalate (DOT) in DMF, then the residual DMF molecules adsorbed to the magnesium ions within the framework were flushed out via a methane gas flow (Figure 1.13). The MOF’s ability to selectively adsorb gases was measured via pumping a mixture of methane gas and carbon dioxide through the framework and measuring the gas levels on the other side of the framework at 40 °C. It was determined that Mg-MOF-74 effectively adsorbs carbon dioxide while allowing the methane gas to pass through. Mg-MOF-74 only captured a negligible amount of methane gas, and this continued until the MOF was saturated with carbon dioxide. It was determined that the MOF was able to adsorb carbon dioxide up to a value of 8.9 mass percentage (8.9 wt. %) which at the time of publication was the best selective CO₂ adsorption capacity of any MOF known. It was also able to release all the CO₂ under gentle prompting (methane gas flow at 80 °C) and still retained functionality after purging. It also retained functionality when exposed to water vapour that would be common under a standard atmosphere. The main takeaway this paper gives is that having an exposed metal ion i.e. a metal ion that is not fully coordinated within a MOF greatly increases selectivity and adsorption capacity.\(^\text{55}\)

![Figure 1.13: Synthesis and solvent removal of Mg-MOF-74. Including colour coding, carbon: black, oxygen: red, magnesium: blue, DMF solvent molecules: red.\(^\text{55}\)](image-url)
While there is considerable interest in the using MOFs in environmental protection, there is paradoxically a rather large issue regarding MOF synthesis. Many MOFs are designed using toxic transition metals, like cobalt, and often, the solvents used in MOF synthesis, such as DMF are damaging to the environment. Because of this, there is interest in MOFs that can be synthesised in aqueous conditions with less toxic metals such as magnesium. The MOF Mg-CUK-1 was synthesised via a reaction with magnesium nitrate hexahydrate and 2,4-pyridinedicarboxylic acid (2,4-pdc) in an aqueous solution with heating via microwaving for approximately 30 mins. Mg-CUK-1 is an isoreticular analogue of the cobalt-based MOF CUK-1, which was synthesised via conventional heating methods, i.e. heating in an oven for 15 hours.55 Upon synthesis, Mg-CUK-1 had the same topology as CUK-1 but crystallised in a different space group due to the large number of well-ordered water molecules within the MOF’s pores (Figure 1.14). The water was removed via gentle heating, causing Mg-CUK-1 to adopt the same space group as CUK-1. Mg-CUK-1 was able to adsorb gases selectively and showed a preference towards CO₂. Mg-CUK-1 was also able to adsorb specific hydrocarbons, mainly aromatic hydrocarbons. One interesting part of its ability to bind aromatic hydrocarbons is its ability to specifically bind disubstituted aromatic compounds that exist in the para configuration, specifically, xylene and divinylbenzene (DVB). The MOF’s ability to selectively bind p-divinylbenzene is especially useful as commercial-grade DVB exists as a mixture of para- and meta-DVB as well as a smaller amount of para- and meta-diethyl-benzene (DEB). Due to the relative ease that Mg-CUK-1 can be produced and its ability to purify DVB mixtures into p-DVB, the new magnesium analogue Mg-CUK-1 already has an industrial use.58
Figure 1.14: (A) Mg-CUK-1 upon synthesis, including colour coding, carbon: green, nitrogen: blue, oxygen: red, magnesium: grey, guest water molecules yellow. (B) Well-ordered water molecules that form a 1D chain within Mg-CUK-1. (C) Space-filling view of water molecule chain.
The MOF Mg(pdda)(DMF) was synthesised via the reaction of magnesium nitrate hexahydrate with 2,6-di(4-carboxyphenyl)pyrazine (H₂pdda) in a 1:1 mixture of DMF and water with heating under autogenous pressure. The MOF formed had a complex structure, as within the structure, each ligand had bound to five separate Mg²⁺ ions, and each Mg²⁺ ion had bonded to five separate ligands as well as a single DMF molecule each, to fill out the Mg²⁺ ion’s coordination geometry. Overall, the structure the MOF takes is a 3D double-walled framework with diamond-shaped pores and DMF molecules coordinated to the Mg²⁺ ion (Figure 1.15). The MOF was thermogravimetrically analysed to find that all the coordinated solvent is released at 300 °C and the framework itself is thermally stable up to 530 °C. Once the MOF has been activated i.e., the solvent was removed via heating under a N₂ atmosphere, the activated MOF (Act-MOF) was reacted with three lanthanides to determine how well it can sense specific lanthanides. The activated MOF was reacted with europium (Eu³⁺), dysprosium (Dy³⁺), and terbium (Tb³⁺) ions. There was very little shift in photoluminescence in the presence of dysprosium and terbium cations. Whereas there was a very noticeable increase in photoluminescence of the Act-MOF when in the presence of europium ions. So much so that under a UV light, the europium coordinated MOF (Eu³⁺@Act-MOF) shone bright pink, even to the naked eye. Additional investigation into the sensing ability of the Act-MOF found that it was also able to strongly detect europium under various levels of acidity (pH = 3-9) or when the Eu³⁺ ion was part of a mixed solution of other ions. Overall, Mg(pdda)(DMF) was a thermally stable, robust Mg-MOF that could strongly sense europium ions under a variety of conditions. ²⁷
Figure 1.15 (a) Unit cell of Mg-MOF (Mg(pdda)(DMF)), (b) 3D structure of activated Mg-MOF, (c) 2D plane view of the Mg-MOF showing solvent removal and the 1D chain formed by magnesium ions, yellow balls indicate pore volume/empty space.
As energy demands increase, there has been an increased demand to produce more efficient electrolyte materials for fuel cells. The ability to design and tune MOFs has led to their use in acting as a proton-conducting material. Proton conducting metal-organic frameworks (PCMOFs) exist as either hydrated materials that work at low temperature (< 100 °C) or anhydrous materials that are designed to work at high temperatures. For the low temperature hydrated PCMOFs to be useful, they need to be stable in water. The MOF titled PCMOF10 was synthesised via a reaction between Mg(NO$_3$)$_2$•6H$_2$O and 2,5-diphosphonoterephthalic acid (H$_6$L) in a water/methanol solution. The MOF formed a distorted ladder-like structure with a chain of alternating four-membered and eight-membered rings with the aromatic ligands acting as the bridge between each chain (Figure 1.16). PCMOF10 strongly adsorbs water such that upon synthesis, almost 20 % of the weight of the frameworks was coordinated water molecules. PCMOF10’s ability to conduct protons was measured as synthesised, and it was found that at high relative humidity (95 % RH) and moderate temperature (70 °C), it was able to conduct protons more efficiently than almost any other PCMOF. Additionally, unlike other PCMOFs, this framework has been shown to be very stable in water. PCMOF10 was also shown to retain its structure and proton conductivity after multiple cycles. PCMOF10 therefore is a new, unique framework capable of highly efficient proton conduction without loss of functionality making it a useful MOF in terms of producing more efficient fuel cells.59
Figure 1.16: (a) Crystal structure of PCMOF10, (b) hydrogen bonding between coordinated water molecules and the MOF.\(^\text{59}\)
It was determined that an efficient method of decreasing power usage in residential buildings was an overhaul of building heating and cooling systems. That investigation put forward the idea of using thermal batteries, but water-based thermal batteries would not be efficient due to the high boiling point and high heat capacity of water. As such, the idea of methanol-based thermal batteries was raised. As part of that study, a series of MOF’s were designed and synthesised using a modified version of a method used to synthesise MOF-74. Six MOFs were synthesised with three being made via a reaction between divalent metal ions magnesium (Mg$^{2+}$), nickel (Ni$^{2+}$) and cobalt (Co$^{2+}$) with 4,4’-[1,4-phenylenebis-(carbonylimino)]bis(2-hydroxybenzoic acid)] (H$_4$TDA) to form M$_2$(TDA)(H$_2$O)$_2$ (M-VNU-74-I). The same process was used to form the MOF series M-VNU-74-II with the ligand being replaced with 4,4’-[oxalylbis(imino)]bis(2-hydroxybenzoic acid)] (H$_4$ODA) which formed M$_2$(ODA)(H$_2$O)$_2$ (Figure 1.17). The MOFs formed with honeycomb-like structures that had large hexagonal pores. They were all isoreticular analogues of both each other as well as MOF-74. Unfortunately, the MOF series M-VNU-74-I was not useful for its intended purpose, as when it was used for methanol adsorption, the structure collapsed. However, the MOFs in series M-VNU-74-II were exceptionally capable of methanol adsorption and delivery, even compared to other MOFs. All three MOFs had high gas capacities, with the MOF Mg-VNU-74-II having the highest capacity by weight, likely because it would be considered a lightweight MOF and would have the lowest density in the MOF series. Further studies into the methanol adsorption and desorption of Mg-VNU-74-II showed that there was a slight decrease in efficiency after the first cycle. But aside from the first cycle, the MOF remained incredibly stable. The information gathered about the M-VNU-74-II MOFs indicates that they were capable of use for their intended means. 
Figure 1.17: Ligand structures of TDA and ODA (left), crystal structures of MOFs M-VNU-74-I and M-VNU-74-II (right).
A new amino acid-based ligand, 4,4’-(4-aminopyridine-3,5-diyl)dibenzoic acid (H$_2$APDA) was synthesised (Figure 1.18) and was used to form a new magnesium MOF. The ligand was reacted with magnesium nitrate in a mixed solution of N, N-dimethylacetamide (DMA), ethanol, and water with heating and formed the photoactive metal-organic framework (Photo-MOF) Mg-APDA. The resulting MOF was a multi-layered 2D framework that had two magnesium ions acting as the secondary building unit, which bound to both the ligand’s carboxylate groups and the nitrogen atom within the pyridine ring. The framework possessed a double-walled structure and pores that formed 1D hexagonal channels with the ligand’s amine group pointing inwards towards the channel (Figure 1.19). This Mg-MOF was synthesised to test its sensing capabilities firstly of iron(III) ions and antibiotics and pesticides later in the study. Mg-APDA itself was highly fluorescent. To determine what guest molecule it bonded to most preferentially, it was suspended in DMF and had various materials (ions, antibiotics, and pesticides) introduced to the solution. It was determined what it would bind to by observing which materials most clearly quenched the Photo-MOF’s fluorescence. Compared to more than a dozen other metal ions which partially quenched the Photo-MOF, Fe(III) decreased the fluorescence of the Photo-MOF to a negligible intensity. The same test was performed with nine popular antibiotics, and it was found that both nitrofurazone (NZF) and nitrofurantoin (MFT) which are both nitrofuran (NF) class antibiotics were the most effective at quenching the fluorescence of the Photo-MOF by a large margin. The success of these experiments encouraged the researchers to test the Photo-MOF’s capacity to sense pesticides as well. Five commonly used pesticides were introduced to the solution, and it was found that 2,6-dichloro-4-nitroaniline (DCN) was the pesticide that most strongly quenched the MOF’s fluorescence again by a large margin. Overall, it was determined that the sensing capabilities of the MOF were excellent. For the substances listed above, the minimum sensing limit was between one hundred and two hundred parts per billion (100-200 ppb). Mg-APDA was also compared to other MOFs in terms of their sensing abilities in regard to each of the listed materials and was determined to be comparable if not more effective than almost every other MOF.\textsuperscript{29}
Figure 1.18: 4,4′-(4-Aminopyridine-3,5-diyl)dibenzoic acid (H₂APDA).²⁹

Figure 1.19: (a) Unit cell of Mg-MOF (Mg-APDA), (b) top-down perspective of 3D structure of Mg-APDA (c) side-on view of 1D channel in Mg-APDA, (d) Mg-MOF topology.²⁹
Since CO₂ emissions are a common by-product of various industrial processes, there is a large amount of interest in using that CO₂ to produce more useful, less environmentally harmful materials.⁶¹ One such method is the reaction of three-membered epoxide rings with CO₂ to form cyclic carbonates, but this reaction requires a catalyst. Unfortunately, even with catalysts, most reactions will only occur with harsh conditions, i.e., high pressure of CO₂ and high temperature. The catalyst can sometimes be very difficult to remove from the product when the reaction is completed, making currently used catalysts not a very attractive option.⁶² In an attempt to produce a catalyst that can facilitate the reaction occurring with less harsh conditions a series of MOFs were designed and synthesised. The MOF series developed was called M-MOF-184, in which the M represented a number of 2+ metal ions including Mg²⁺, Co²⁺, Ni²⁺ and Zn²⁺. Attempts were made to produce Fe-MOF-184 and Cu-MOF-184 but could not produce suitable crystals for analysis or use as a catalyst. The MOFs were designed to possess large pores and a high surface area as well as acidic and basic sites to facilitate the binding of the reactants and allow the reaction to occur within the MOF (Figure 1.20). Once Mg-MOF-184, Co-MOF-184, Ni-MOF-184, and Zn-MOF-184 were all produced and were activated, catalytic studies began.

The reaction involves combining the MOF-184 crystal and tetrabutylammonium bromide (a phase transfer catalyst) with the liquid epoxide styrene oxide in a CO₂ atmosphere (approximately 1 atm) and heating the mixture to 80 °C with stirring. The products were then separated from the catalysts to determine the product yield, as well as the conversion rate and selectivity that the MOFs possessed. After which the MOFs were activated again for reuse. Each MOF was used three times to determine their effective lifetime and gain a more accurate measure of their individual selectivity and conversion rates. This method was repeated with a number of other epoxides at room temperature, all of which showed reasonable yields. Overall, it was determined that the MOF Zn-MOF-184 was the most efficient catalyst. As it had the highest conversion when heated, compared to its other MOF-184 analogues, and compared to other MOF catalysts like Zn-MOF-74. Mg-MOF-184 showed excellent CO₂ uptake comparable to that of the other two MOFs at room temperature and standard atmospheric pressure. Overall, the four MOFs produced all showed to be very effective catalysts allowing the reaction to occur at much more easily obtained conditions.²⁴
Figure 1.20: Structure of Catalytic MOF M-MOF-184 and diagram of catalytic synthesis of carbonate ring via the reaction of epoxides and CO$_2$.\textsuperscript{24}
1.12 Scope of the Thesis

The original scope of this thesis was loosely based around already existing work by Macreadie et al. regarding the synthesis of various MOFs containing the same or similar ligands. The general structure of these ligands involves a phenanthroline group bound to a carboxylic acid-containing benzene ring with an imidazole group as the intermediary. As such, a series of potential ligands were discussed as possible areas of research (Figures 1.21-1.24). These ligands would be synthesised and characterised as time permitted since the most significant limiting factor for this thesis was the relatively short timeframe.

Figure 1.21: Ligand 1 (L1) [2-(4-carboxy-1, 1’-biphenyl)imidazo(4, 5-f)-1, 10-phenanthroline] (HNCPP)

Figure 1.22: Ligand 2 (L2) [2-(3, 5-biscarboxy-1, 1’-biphenyl)imidazo(4, 5-f)-1, 10-phenanthroline]
Once a ligand was produced it would be fully characterised, including NMR, IR and UV-vis spectroscopy, mass spectrometry, elemental analysis, and crystallographic analysis.

Using phenanthroline as the base of the ligands allows for a high level of stability and a great degree of flexibility in the types of ligands that can be synthesized. Phenanthroline is a chelating molecule allowing for strong binding between the ligand and various metals.\textsuperscript{10,63} Carboxylic acid groups are also commonly used as metal-binding groups in MOF synthesis reactions.\textsuperscript{17,55,64} Due to the strong binding capacities of both ends of the planned ligands, a series of metals were introduced to the synthesised ligands to produce various new MOFs. The resulting MOFs were characterised via single crystal X-ray crystallography.
The first MOF attempted to be synthesised was an isoreticular analogue of a bimetallic ruthenium-cobalt Photo-MOF synthesised by Macreadie et al.\textsuperscript{2} Unfortunately, the process required a two-step reaction involving complexing the ligand with ruthenium before reacting it into a MOF. Issues with forming the complete complex meant that attempts to produce a ruthenium-cobalt MOF crystal failed. Powder analysis of the presumed MOF product gave no additional information. Additionally, attempts to measure the gas adsorption properties of said power were also fruitless.

Scheme 1.1: General synthesis of single metal L1 MOF

Difficulties in synthesising a bimetallic MOF from a ruthenium metallo-ligand complex led to attempts to produce single metal MOFs. A variety of metals were reacted with L1 to form several MOFs, including a brand new cadmium MOF, a zinc MOF that had recently been published by Macreadie et al.\textsuperscript{10} and most interestingly a series of magnesium MOFs. Due to the rarity and general interest in magnesium MOFs more extensive study was undertaken into the three new magnesium frameworks, as well as one already published magnesium-formate MOF.\textsuperscript{11} Unfortunately, due to time restraints that were exasperated by the lockdown caused by the COVID-19 pandemic and lack of bulk MOF product more extensive study of the magnesium-L1 MOF structures and other magnesium structures could not be undertaken.
Chapter 2: Ligand Chemistry

2.1 Phenanthroline Based Compounds

In the past, it has been shown that phenanthroline based metal complexes and substituted phenanthroline compounds possess photoactive properties. Due to this, they, have been used as photoactive materials in various capacities. One particular subset of phenanthroline based compounds that have been used relatively commonly is imidazo[4,5-f][1,10]phenanthroline (Figure 2.2), as it can be used as the basis for many different compounds.

Figure 2.1: 1, 10-Phenanthroline

Figure 2.2: Imidazo[4,5-f][1,10]phenanthroline

There has also been some interest in phenanthroline-based ligands in MOF synthesis due to two major factors. First, 1,10-phenanthroline and its derivatives contain a bidentate group which can form a strong bond between the ligand and a metal ion. Second, it is relatively easy to carry out reactions with phenanthroline to add any number of different groups to the molecule, such as adding an intermediary imidazole group via the Debus-Radziszewski reaction which can also be designed to bind to a metal ion. These two factors allow phenanthroline based ligands to be used to form a wide variety of MOFs.
2.2 Spectroscopic Properties of Phenanthroline and its Substituents

Phenanthroline exists as a white crystalline material and is itself a weakly emissive molecule. However, when phenanthroline is reacted with other materials, the resulting products can have much more varied spectroscopic properties. Due to the large number of ways that phenanthroline can be substituted the resulting products can have strong emission peaks from the ultra-violet region to the near infra-red region.\textsuperscript{10}

In addition, purely organic phenanthroline compounds being photoactive, many different metal-ligand complexes involving phenanthroline are capable of various forms of photoactivity. The photoactivity of a metal-phenanthroline can be modified by both the organic substituent group of the phenanthroline and what metal the organic ligand is bound to. Due to this, various metal-phenanthroline complexes have been used as fluorescent sensors of specific chemicals and as light-activated cancer medication (Figure 2.3).\textsuperscript{67-69}

![Figure 2.3: UV-vis spectra of biphenyl-imidazole phenanthroline ligand (4), rhodium-ligand complex (6) and the rhodium-ligand complex in the presence of the antibiotic amoxicillin (6: amoxicillin).\textsuperscript{67}}

As well as standard metal-phenanthroline complexes being shown to be photoactive, metal-organic frameworks containing a phenanthroline binding group have been shown to be photoactive. This can be done by binding the phenanthroline group to a photoactive metal ion on a MOF.\textsuperscript{2} Otherwise this can be done by forming a photoactive ligand that contains phenanthroline and using said ligand to form a MOF.\textsuperscript{10}
2.3 Biological and Pharmaceutical Applications of Phenanthroline Compounds

Both phenanthroline based organic compounds and phenanthroline based metal-organic complexes have been shown to be biologically active. Phenanthroline compounds have been shown to be viable as pharmaceuticals due to their ability to interchelate and interact with DNA. In particular, both purely organic imidazo[4,5-f][1,10]phenanthroline based compounds, and metal-organic complexes, have been explored in regard to their viability as anticancer drugs.\textsuperscript{68,69} For example, in a recent case, a set of substituted phenyl-imidazo(4, 5-) -1, 10 phenanthroline molecules were synthesised and their capacity to selectively target cancer cells of the liver was analysed (Figure 2.4). It was determined that the hydroxy-substituted molecule possessed the highest anticancer potential due to its capacity to provoke cell apoptosis (programmed cellular destruction).\textsuperscript{68}

![Figure 2.4: Synthesis of substituted phenanthro-imidazole molecules studied regarding their capacity for combating Hepatocellular carcinoma (Liver cancer).\textsuperscript{68}](image)

As well as acting as pharmaceuticals, phenanthroline compounds can be used as detectors of other materials. While phenanthroline itself is not particularly photoactive, specific phenanthroline compounds can be highly photoactive.\textsuperscript{10} Due to this, both organic and metalloorganic phenanthroline based compounds can be used as photoactive detectors based on what materials interact with the compound and how they affect the spectroscopic properties of the material, (e.g. fluorescence quenching, shifts in relative absorbance intensity, or change in the wavelengths of the absorbance bands that the compound possesses). One case of this is a rhodium based metal-organic complex used to detect the presence and concentration of amoxicillin, a common antibiotic (Figure 2.3).\textsuperscript{67}
2.4 Metal-Phenanthroline Complexes and MOFs

Phenanthroline and phenanthroline based molecules can form a wide variety of metal-ligand complexes. The chelating group of two nitrogen atoms is very attractive to several different metal ions. Phenanthrolines strong binding properties allow it to form complexes with rare earth metals,\textsuperscript{70} many transition metals,\textsuperscript{65} and even certain s-block metals.\textsuperscript{71} Phenanthroline is a neutral ligand that bind very strongly to different metals. Because of this metal-phenanthroline complexes need to either include a charged ligand bound to the metal group or a non-coordinated counter anion to balance the overall charge of the complex. The charged ligand can be a separate ligand or a diffident functional group in a ligand with a phenanthroline functional group.\textsuperscript{2,72}

On top of phenanthrolines ability to form various metal-ligand complexes, its various properties also make it an ideal molecule to design MOFs. Because phenanthroline is capable of binding metal ions on its own and can be substituted with a functional group that would strongly bind a metal ion, such as a carboxylate group, there are various MOFs that could be formed with phenanthroline as the base. Depending on the method used, it is possible to synthesise either a single metal or a bimetallic MOF. Forming a single metal MOF would simply require the phenanthroline to be substituted with a functional group that easily binds metal ions. Then react the ligand with a metal that would bind to both the new functional group and the phenanthroline group.\textsuperscript{10,63} To form a bimetallic MOF would require a slightly more complex process. This could be done by reacting phenanthroline-dione with a nitrophilic metal (\(M_1\)) that would form a bidentate bond between the metal and the nitrogen atoms of the phenanthroline-dione. Then substituting the complex with an \(R\) group that would bind a different type of metal. After which the metal complex would be reacted with a different metal (\(M_2\)) which binds to the new exposed functional group forming the bimetallic MOF (Scheme 2.1).\textsuperscript{2}
Figure 2.5: SCNU-1 (Copper(II) 4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol MOF).\textsuperscript{63}

Scheme 2.1: General synthesis of Bimetallic phenanthroline-based MOFs.\textsuperscript{2}
2.5 Ligand Chemistry Literature Review

One area of interest in MOF chemistry is the photoactive properties that some MOFs have. Interestingly, despite a large amount of interest in Ru$^{2+}$-phenanthroline complexes, there has been very little interest in MOFs which use Ru$^{2+}$-phenanthroline complexes as SBUs. Ruthenium complexes have a tendency to be luminescent under conventional conditions, and phenanthroline has been shown to be an excellent facilitator in creating a photoactive substance.\textsuperscript{10} To produce a ligand capable of forming a MOF with a Ru$^{2+}$-phenanthroline SBU, the bridging ligand of the structure was a bifunctional ligand with a carboxylic acid group and a phenanthroline group. As such the ligand 2-(4-carboxyphenyl)imidazo(4, 5-f)-1, 10-phenanthroline (HNCP) was produced and reacted with ruthenium to form the ruthenium-ligand complex (Figure 2.6 d). This ruthenium-ligand complex was reacted with cobalt nitrate in a solvothermal reaction with trifluoracetic acid (TFA) as the moderator under autogenous pressure to form the MOF [Co$^{II}$L$^\text{Ru}$]TFA (Figure 2.6 a, b & c). A series of photophysical studies were done on both the ruthenium-HNCP complex and the produced Photo-MOF. It was shown that the MOF and the ruthenium complex both had similar absorption properties, with the MOF having a slightly higher absorption intensity. The two materials also had a similar photoluminescence spectrum except that the MOF had a much sharper increase in photoluminescence than the ruthenium complex, starting at near-zero around 550 nm and reaching its peak at approximately 620 nm. Further attempts were made to determine the two structures fluorescent properties, but when the ruthenium complex was excited by a high energy laser, the product degraded rapidly. The Photo-MOF, on the other hand did not degrade when excited by the same laser. TGA of the MOF determined that it was thermally stable up to 250 °C. Additionally, the MOF was shown to adsorb CO$_2$ preferentially over N$_2$, even at room temperature. Overall, it was shown that it was possible to produce a photo-active MOF that can preferably adsorb specific gases at room temperature using a bifunctional ligand containing a phenanthroline group and a carboxylate group.\textsuperscript{2}
Figure 2.6: Crystal structure of the Photo-MOF [Co$^{III}$L$^{Ru}$]TFA, (a) single hexagonal channel with a diameter of approximately 2.1 nm, (b) symmetry elements of the structure, (c) expanded view of the multi-layered 2D crystal structure with hexagonal pores, (d) structure of the ruthenium metal-ligand complex.$^{2}$
MOFs with photophysical and luminescent properties have become an area of increased interest, particularly the use of photoactive MOFs in sensing. Thus, the use of photoactive ligands or ligands that become photoactive when complexed, in the synthesis of MOFs is a method worth investigating. While phenanthroline by itself is weakly emissive, its derivatives, and complexes that are made with it, have shown to be quite photoactive. In this case, the phenanthroline containing ligand that was studied was 2-(4-carboxy-1, 1’-biphenyl)imidazo(4, 5-f)-1, 10-phenanthroline (HNCPP). HNCPP was reacted with manganese and zinc under identical conditions to form two MOFs with quite different structures. The two MOFs were formed by combining HNCPP with the respective metal salt in a solution of DMF and formic acid and heating the solution under autogenous pressure. The manganese MOF (Mn-MOF) formed a relatively straightforward 3D structure in which the manganese ions are all pseudotetrahedrally bound to four separate NCPP* ligands (Figure 2.7, a, b). The structure was six-fold interpenetrated but still had relatively large 1D pores down the a axis (Figure 2.7, c). The manganese structure was also shown to be thermally stable up to approximately 380 °C. The zinc MOF formed a more complicated structure. Within the zinc MOF (Zn-MOF), two crystallographically distinct zinc ions exist, as well as the NCPP ligands and bridging formate groups which bind the zinc ions together (Figure 2.7, d). The overall structure of the zinc MOF was a two-fold interpenetrated 3D structure with large pore channels running down the a axis (Figure 2.7, e, f). The zinc MOF was shown to be thermally stable up to approximately 325 °C. Gas adsorption and photophysical studies were done of the two structures. They were both shown to be able to adsorb CO₂ at normal room temperatures (0-25 °C) relatively well. The photophysical properties of the two MOFs were compared to HNCPP. It was found that the maximum absorptions of the two MOFs were very similar to that of the ligand with a small shift of 9 nm downfield in the Mn-MOF and 5 nm downfield in the Zn-MOF from the ligand’s absorption maxima. The manganese MOF also had an adsorption peak at 416 nm, which was likely an interaction between the manganese ion and the ligand. The photoluminescence of the ligand and the Mn-MOF were shown to be almost identical, whereas the photoluminescence peak of the Zn-MOF had moved downfield approximately 50 nm. Overall, both MOFs show interesting properties in both their photophysical activities and their gas adsorption abilities. This shows that MOFs made with phenanthroline based ligands could be very useful for several reasons in the future.¹⁰
Figure 2.7: Different views of the crystal structure of the manganese MOF (a, b, and c) and the zinc MOF (d, e, and f).  

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2.6 Synthesis of L1

Both L1 and L2 were synthesized from a modified literature method,\(^2\) plus, one of the components of L2 was synthesized via another literature method.\(^73\) Both ligands were synthesised via the Debus-Radziszewski Imidazole Synthesis Reaction, which involves reacting a dicarbonyl, an aldehyde, and ammonia to form an imidazole ring binding the dicarbonyl and aldehyde into a molecular chain with the imidazole ring as the intermediary (Scheme 2.2).\(^66\)

![Scheme 2.2: General Synthesis of Imidazole via the Debus-Radziszewski Reaction.\(^66\)]

Firstly, 1,10-phenanthroline monohydrate was oxidised into 1,10-phenanthroline-5,6-dione. There are two potential methods to synthesise 1,10-phenanthroline-5,6-dione. Both involve the oxidation of 1,10-phenanthroline via strong acids with bromine as the intermediary. The first method involves heating 1,10-phenanthroline in a mixture of nitric and sulfuric acid while adding liquid bromine (Br\(_2\)) intermittently (Scheme 2.3, left). The second method is fairly identical, with potassium bromide (KBr) replacing the bromine, but the materials used had to be combined slowly at low temperatures (~0 °C) before heating (Scheme 2.3, right, mechanism included in Scheme 2.4).\(^74\) Both methods were tested, and method two was preferable as it produced a higher, more consistent yield of ~35 % and did not require the use of highly toxic liquid bromine.

![Scheme 2.3 Synthesis of 1,10-phenanthroline-5,6-dione bromine method (left), synthesis of 1,10-phenanthroline-5,6-dione potassium bromide method.\(^74\)]
Once the phenanthroline had been oxidised to phenanthroline dione synthesising L1 was a relatively straightforward process. The biphenyl precursor to L1 4'-formyl-[1,1'-biphenyl]-4-carboxylic acid is commercially available, so the synthesis of L1 is simply a reaction between that and the newly formed phenanthroline dione. The reaction involves 1, 10-phenanthroline-5, 6-dione, 4'-formyl-[1,1'-biphenyl]-4-carboxylic acid and ammonium acetate, all reacting with heating and stirring in a solution of acetic acid before being quenched with water, neutralized with an ammonium hydroxide solution, washed and dried thoroughly (Scheme 2.5). The acetic acid cleaved the ammonium acetate into ammonia which then allowed the Debuss-Radziszewski reaction to occur. Once the ammonia had formed, it reacted with the phenanthroline-dione via a condensation reaction to form a diimine intermediary. Then the diimine intermediary reacts with the aldehyde group of 4'-formyl-[1,1'-biphenyl]-4-carboxylic acid via a condensation reaction to form L1 (Scheme 2.6, mechanism included in Scheme 2.7).^{10,66}

**Scheme 2.4: Synthesis of 1, 10-phenanthroline-5, 6-dione potassium bromide method mechanism.**

**Scheme 2.5: Synthesis of L1.**^{2,10}
Scheme 2.6: Two step synthesis of L1 via the Debus-Radziszewski Reaction.\textsuperscript{66}

Scheme 2.7: Predicted reaction mechanism of two-step synthesis of L1.
2.7 Synthesis of L2

The synthesis of L2 proved to be slightly more difficult since the biphenyl precursor to L2 was not commercially available. There were also very few sources regarding the synthesis methods of 4'-formylbiphenyl-3, 5-dicarboxylic acid. The first reaction method that was found was a palladium cross-coupling reaction between 3, 5-dicarboxyphenylboronic acid and 4-bromo benzaldehyde. This reaction was done in a solution of para-dioxane and water using [1, 1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) as the catalyst and potassium carbonate as the base (Scheme 2.7).\(^7\)

\[\text{Scheme 2.7: Synthesis of 4'-formylbiphenyl-3, 5-dicarboxylic acid p-dioxane/water method.}\]

Multiple attempts were made to synthesise 4'-formylbiphenyl-3, 5-dicarboxylic acid via this method but the resulting product was usually very impure and unusable. Attempts were made to purify the product via column chromatography, but the results were not much better. After being run through the column, the purity of the product was only moderately better than before, and the yield was negligible, usually only enough for a single NMR analysis.

To decrease the possibility of the two molecules binding the wrong way, (i.e., the bromobenzaldehyde binding to one of the carboxylic acid groups), the carboxylic acid groups in dicarboxy-phenylboronic acid were protected by methylating the carboxylic acid groups into methyl esters (Scheme 2.8). Then the cross-coupling reaction took place the same way as before (Scheme 2.9).
Scheme 2.8: 3, 5-Dicarboxyphenylboronic acid protection reaction.\textsuperscript{76}

Scheme 2.9: Synthesis of 4’-formylbiphenyl-3, 5-bismethoxycarbonyl p-dioxane/water method.\textsuperscript{75}

Unfortunately, this reaction also produced an impure, mixed product. Also, the yield was so low that purification via column chromatography was not viable, so a new method was found.

The next attempted reaction method was also a palladium cross-coupling reaction between 3, 5-dicarboxyphenylboronic acid and 4-bromo benzaldehyde. However, this reaction used tetrakis(triphenylphosphine) palladium(0) as the catalyst, sodium hydrogen carbonate as the base and was reacted in a 1:1 solution of toluene and ethanol (Scheme 2.10). The product was filtered through a layer of Celite (diatomaceous earth) and washed with brine while still in solution. The final product was obtained via taking the organic phase and removing the solvent but upon analysing the product, it was found to be an impure product again.
Scheme 2.10: Synthesis of 4’-formylbiphenyl-3, 5-dicarboxylic acid ethanol/toluene method

The final method that was found that was successful was a palladium cross-coupling reaction between dimethyl-5-bromoisophthalate and 4-formyl-phenylboronic acid. This reaction used tetrakis(triphenylphosphine) palladium(0) as the catalyst, potassium carbonate as the base, and reacted in degassed DMF under a N₂ atmosphere (Scheme 2.12). Dimethyl 5-bromoisophthalate is the protected form of 5-bromoisophthalic acid, formed via refluxing in methanol with a small amount of sulfuric acid present (Scheme 2.11). The carboxylic acids in 5-bromoisophthalic acid were protected to avoid unwanted side products.

Scheme 2.11: 5-Bromoisophthalic acid protection reaction.

Scheme 2.12: Synthesis of 4’-formylbiphenyl-3, 5-bisethoxycarbonyl DMF method.
This synthetic method proved to be much more reliable and was able provided a reasonable yield of about 30% with good purity after a very straightforward purification of recrystallising the crude product in ethanol. The purity of the product was determined with a $^1$H NMR spectrum that was identical to the literature.\textsuperscript{73}

Once the methylated biphenyl precursor to L2 had been synthesised, it was reacted with 1, 10-phenanthroline-5, 6-dione to form methylated-L2. This reaction was identical to the synthesis of L1 (Scheme 2.13, 2.14).\textsuperscript{10,66}

Scheme 2.13: Synthesis of methylated-L2.\textsuperscript{2,10}

Scheme 2.14: Two-step synthesis of methylated-L2 via the Debus-Radziszewski Reaction.\textsuperscript{66}
The final step in this synthetic pathway is to deprotect the methylated-L2 by cleaving the methyl ester groups off the ligand and turning them back into carboxylic acid groups. This is done by dissolving the methylated-L2 in a solution of ethanol and aqueous sodium hydroxide and refluxing for three hours. After cooling the solvents are removed via rotary evaporation at reduced pressure. The product is then dissolved in water and neutralized with hydrochloric acid until it precipitates and is thoroughly washed with water to remove excess base/acid (Scheme 2.15).

Scheme 2.15: Deprotection reaction of methylated-L2 to L2.

Upon discovering a way to produce the methylated biphenyl precursor to L2 reliably, the process of synthesising L2 became relatively simple and straightforward. This allowed the production of L2 to be carried out with a reasonably high yield and purity.
2.8 Synthesis and Characterisation of Ru-L1 Complex

The ruthenium metallo-ligand complex (Ru-L1) was synthesised via a modified literature method. The literature method involved reacting tetrakis-(DMSO)-dichloro-ruthenium(II) with 1, 10-phenanthroline-5, 6-dione to form a metal complex (Scheme 2.16). Then reacting that metal complex with an aldehyde containing substance to form the ruthenium metallo-ligand complex. As part of this reaction, the counter-anion was changed from chlorine to hexafluorophosphate. The literature also included a deprotection step, as the carboxylic acid in the phenyl precursor to the literature ligand was protected with methyl groups (Scheme 2.17).

![Scheme 2.16: Synthesis of [Ru(phenanthroline-dione)₃]Cl₂ literature method]

The modified method involved synthesising L1 first then reacting it with tetrakis-(DMSO)-dichloro-ruthenium(II). This reaction took place the same way the first step of the literature synthesis of metallo-ligand took place, L1 and the ruthenium complex were refluxed in a water/ethanol solution. The product was then dissolved in methanol and a saturated aqueous solution of ammonium hexafluorophosphate was added to replace the chloride counter-anions with hexafluorophosphate (Scheme 2.18).
The resulting product was not the trisubstituted ruthenium complex, but a mixture of complexes. Due to the low solubility of the Ru-L1 complex, partially substituted products tended to precipitate as the reaction continued (Figures 2.8, 2.9). Thus, the product of the reaction was a mixed solution of partially reacted materials, including some unreacted ligand. NMR analysis of the product was attempted, but since the product could only be dissolved in DMSO the residual bound DMSO molecules were masked by the DMSO solvent peak in the spectra giving inaccurate results. Additionally, because $^1$H NMR spectroscopy only shows the relative abundance of protons, it could not be used to accurately determine by what degree the ligand(s) had bound to the ruthenium ion. However, $^1$H NMR was able to show that L1 had bound to the ruthenium metal due to small shifts in proton peaks of the phenanthroline protons. Because the $^1$H NMR spectra of the product indicated that the ruthenium complex had been produced further experiments took place using the partially substituted Ru-L1 complexes.
Due to the low solubility of the product, it was difficult to determine the size of the product via mass spectrometry. After multiple attempts, an accurate mass spectrum of the product was produced and showed that the result was an impure mixed product. Because the Ru-L1 complex was a mixed product elemental analysis did not produce helpful results in characterising the product.

![Figure 2.8: Mono-substituted ruthenium metallo-ligand complex found by mass spectrometry analysis](image)

![Figure 2.9: Di-substituted ruthenium metallo-ligand complex found by mass spectrometry analysis](image)

Potential variations in the Ru-L1 complex synthesis were briefly entertained but were sidelined due to interest in MOF synthesis via reactions between other metal ions and non-complexed L1.
2.9 Attempted Synthesis of Ru-L2 Complex

An attempt was made to synthesise a Ru-L2 complex like the Ru-L1 complex. In this case, the reaction was between the methylated-L2 and tetrakis(DMSO)dichloro-ruthenium(II).

Scheme 2.19: Synthesis of [Ru(L2)$_3$][PF$_6$]$_2$ experimental method$^2$

The first two steps worked relatively well, producing a Ru-methylated-L2 complex with a moderate yield (~ 70 %). However, the third step (the deprotection reaction to remove the methyl ester groups and convert them back to carboxylic acid groups), caused the structure to change dramatically. The NMR spectrum of the product was very different from expected results and from the NMR spectra of the ligands. Additionally, attempts to purify the product via recrystallisation caused the yield to drop to < 1%. Due to the difficulty to produce L2 compared to L1 and the interest in MOFs made with L1, further work with the Ru-L2 complex was not undertaken.
2.10 Characterisation of L1 and L2

Both L1 and L2 were characterised using a number of different methods. The products' proton and carbon environments were confirmed through a combination of 1D $^1$H and $^{13}$C NMR spectroscopy. As well as 2D corelated (COSY), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond correlation (HMBC) NMR spectroscopy. IR spectroscopy showed that the correct types of bonds were present in the products. Mass spectrometry was used to determine the molar mass of the molecules. However, due to the low solubility of L2 it had to be deprotonated by adding a small amount of base to the solution before it could be measured via mass spectrometry. Elemental analysis of L1 was taken and shown to be with expected values as well. Crystal structures of L1 and L2 were attempted to be produced; however, due to the strong binding capacity of the products, only structures of L1 and methylated-L2 were obtained. Lastly due to the relatively low solubility of the products (especially L2), a solid-state UV-vis spectrum was taken of two products and compared with the spectrum of 1, 10 phenanthroline (Figure 2.10).

![Figure 2.10: Absorbance spectrum taken of solid state 1, 10 phenanthroline, L1 [2-(4-carboxy-1,1′-biphenyl)-imidazo(4,5-f)(1,10)phenanthroline], and L2 [2-(3, 5-biscarboxy-1,1′-biphenyl)-imidazo(4,5-f)(1,10)phenanthroline.](image-url)
The introduction of the imidazole, biphenyl and carboxylic acid groups caused the absorbance peaks shown in phenanthroline to move downfield (towards higher wavelengths). Looking only at the absorbed visible light, L1 absorbs from 400 nm to 500 nm, where its intensity drops to near zero. This means that it absorbs light in the blue to the violet spectrum of visible light. This result makes sense considering the light yellow-orange colour of solid L1. L2 absorbs from 400 nm to approximately 600 nm, where its intensity drops to near zero. This means that it absorbs light in the yellow to violet spectrum of visible light. This result also makes sense as solid L2 is a much darker reddish-brown colour. This experimental data corresponds well with the literature in which phenanthroline is only photoactive in the visible spectrum when it is bound to other compounds. Due to the impure nature of the ruthenium metallo-ligand a UV-vis spectrum was not taken of it.
2.11 Crystal Jars of L1 & L2

Multiple attempts were made to produce crystals of L1 and L2 at room temperature via the evaporation method or the diffusion method. But due to the low solubility of the two ligands, those methods did not work. While L1 is soluble in ethanol at room temperature, it tended to precipitate as a powder within a few hours to a day. L2 was even less effective as it is insoluble in most solvents, even in DMF at room temperature, although the methylated-L2 was relatively soluble in ethanol and DMF. Because of this crystal jars were set up like the jars used to synthesise MOFs. L1 and L2 were each dissolved in DMF with formic acid as a moderator for L1 and ammonium hydroxide as the moderator for L2 (to deprotonate L2 and make it more soluble). The solutions were sealed in golden capped jars, and heated for 72 hours at 140 °C.

This process was repeated with ethanol as the solvent and the methylated-L2 was also crystallised in this reaction. The solutions were again sealed in golden capped jars and heated for this process, but only for 24 hours at 90 °C. Crystals were produced from these jars and were taken and analysed via single crystal X-ray crystallography with varying results.
2.12 Crystal structures of L1 & L2

All the figures in this section were produced in Mercury. They follow the colour code carbon: grey, nitrogen: blue, oxygen: red, hydrogen: white. Hydrogen bonds will be shown as black dotted lines.

**Ligand 1 (L1)**

![Figure 2.11: An X-ray crystal structure of the asymmetric unit of L1 formed in DMF solvent.](image)

L1 was crystallised in DMF in the monoclinic space group $P2_1/c$. The asymmetric unit is comprised of one complete L1 molecule and one DMF solvent molecule. The phenanthroline group and first benzene ring are essentially planar, and the second benzene ring is twisted 39.1° with respect to the phenanthroline moiety. This is likely due to the hydrogen bonding of between the oxygen of the DMF solvent molecule and the adjacent hydrogen atoms of L1. The DMF solvent molecule is bound to the imidazole ring via hydrogen bonding with an $O_{\text{DMF}}$–H-$N_{\text{im}}$ distance of 2.03 Å corresponding to an $O_{\text{DMF}}$–$N_{\text{im}}$ distance of 2.883(3) Å.
Figure 2.12 An X-ray crystal structure of a 1D chain of L1 formed in DMF solvent.

L1 forms a head-to-tail 1D chain running along the [1 0 1] diagonal axis via hydrogen-bonding (H-bonding) between the carboxylic acid group and one of the N atoms of the phenanthroline group. Along the chain L1 is rotated 180° with respect to adjacent molecules such that the H-bonded DMFs are on alternating sides of the chain. The COOH…Nphen distance is 1.88 Å corresponding to a COO…Nphen distance of 2.700(3) Å.

Figure 2.13 An X-ray crystal structure of L1 stacking mode down the b axis. DMF solvent molecules removed for clarity.

Additionally, there was some weak π-π stacking between the imidazole ring and the central ring of the phenanthroline in the ligand with a distance of 3.72 Å. This causes the chains to stack leading to a 2D sheet in the (ac) plane.
Figure 2.14: An X-ray crystal structure of the asymmetric unit of methylated-L2 formed in ethanol solvent.

Methylated-L2 was crystallised in ethanol in the monoclinic space group $P2_1/c$. The asymmetric unit is comprised of two complete methylated-L2 molecules and two ethanol solvent molecules. In contrast to L1, the phenanthroline group and second benzene ring of methylated-L2 are essentially planar, and the first benzene ring is twisted by 25.7° (N1, N2) and 27.8° (N5, N6) with respect to the phenanthroline groups. Methylated-L2 forms a 1D chain running along the $a$ axis via H-bonding between the imidazole groups, the ethanol solvent and one of the N atoms of the phenanthroline group. The ethanol solvent molecule is bound to the imidazole ring via hydrogen bonding with an $O_{\text{EtOH}}$...H-N$_{\text{im}}$ distance of 2.01 (N3-O10) Å corresponding to an $O_{\text{EtOH}}$...N$_{\text{im}}$ distance of 2.865(7) Å. As well as $O_{\text{EtOH}}$...H-N$_{\text{im}}$ distance of 1.98 (N8-O9) Å corresponding to an $O_{\text{EtOH}}$...N$_{\text{im}}$ distance of 2.831(6) Å.
Methylated-L2 forms a 1D chain running along the $a$ axis via H-bonding between the imidazole groups, the ethanol solvent and one of the N atoms of the phenanthroline group. The ethanol solvent molecule is bound to the phenanthroline ring via hydrogen bonding with an O-$\text{EtOH}$...$N_{\text{phen}}$ distance of 2.39 (O9-N1) Å corresponding to an $\text{O}_{\text{EtOH}}$...$N_{\text{phen}}$ distance of 2.926(7) Å. As well as O-$\text{EtOH}$...$N_{\text{phen}}$ distance of 2.45 (O9-N2) Å corresponding to an $\text{O}_{\text{EtOH}}$...$N_{\text{phen}}$ distance of 3.224(7) Å. Finally, O-$\text{EtOH}$...$N_{\text{phen}}$ distance of 2.22 (O10-N5) Å corresponding to an $\text{O}_{\text{EtOH}}$...$N_{\text{phen}}$ distance of 2.995(8) Å.

The methylated-L2 molecules stack in a head to tail configuration with weak $\pi$-$\pi$ stacking between the molecules with a distance between the molecules of 3.711-3.986 Å.
2.13 Conclusion

In this chapter L1 was produced via a modified literature method with relative ease and was fully characterised. Attempts were made using L1 to produce a trisubstituted Ru-L1 complex. The low solubility of the produced ruthenium L1 complex cause difficulties in characterisation. $^1$H NMR spectroscopy indicated that a Ru-L1 complex had formed. Because the only solvent that dissolved the product at room temperature was deuterated DMSO, the residual DMSO molecules bound to the Ru$^{2+}$ ion were masked. It was found using mass spectrometry that the ruthenium complex was a mixture of mono- and di-substituted Ru-L1 complexes. The focus of the study had moved from MOF synthesis with the metallo-ligand complex to MOF synthesis using L1.

During this time, attempts to produce L2 were also taking place; however, synthesising L2 was much more difficult than synthesising L1. This was because the biphenyl precursor to L2 containing two carboxylic acid groups on one ring and an aldehyde group on the other (4’-formylbiphenyl-3, 5-dicarboxylic acid) was not commercially available. As such, the precursor had to be produced using a palladium cross-coupling reaction. Multiple attempts were made using various reaction conditions before a successful method was found. The successful reaction involved protecting the carboxylic acid groups by methylating them before the reaction took place then heating the two reactants in a solution of degassed DMF under a N$_2$ atmosphere. Once the biphenyl L2 precursor was made, producing then deprotonating L2 was relatively straightforward. Once L2 was produced, it was characterised, and the attempts to form MOFs with it began.
2.14 Experimental

**General Information**

**Product Synthesis**

All starting materials used were purchased from commercial suppliers and used as received with no further purification required. All solvents were also used as received and were of LR grade or better. For the product compounds which have been previously reported characterisation was used only to determine their successful synthesis.

**Physical data collection**

IR analysis was carried out using a Bruker Alpha FT-IR spectrometer. Solid-state UV-vis analysis was carried out using a PerkinElmer Lambda 950 UV/Vis/NIR Spectrometer. Microanalysis was carried out in the Campbell Microanalytical Laboratory, University of Otago. All microanalysis results collected had an associated uncertainty of no more than ±0.5%. $^1$H-NMR, $^{13}$C-NMR and 2-dimensional spectra were collected on either a 400 or 500 MHz Varian UNITY INOVA NMR spectrometer in DMSO-d$_6$. Spectra were referenced to the internal solvent signal and chemical shifts reported in δ (ppm). Electro-spray mass spectrometry (ESMS) was carried out on a Bruker micro TOFQ instrument (Bruker Daltronics, Bremen, Germany). Samples were introduced using direct infusion into an ESI source in positive mode and sampling averaged for two minutes over an m/z range of 50 to 3000 amu. Mass was calibrated using an external calibrant of sodium formate clusters, 15 calibration points from 90 to 1050 amu, using a quadratic plus HPC line fit. ESMS spectra were processed using Compass software (version 1.3 Bruker Daltronics, Breman, Germany).
X-ray Crystallography

Single crystals were mounted in paratone-N oil on a nylon loop. Single crystal X-ray data were collected on an Agilent Technologies Supernova system at 100 K at the University of Otago using mirror monochromated Mo Kα (λ = 0.71073 Å) radiation. The data were treated using CrysAlisPro software and Gaussian absorption corrections were applied. Intensities were corrected for Lorentz and polarization effects and a multi-scan absorption correction was applied. The structures were solved by direct methods SHELXT\textsuperscript{78} and refined on F2 using all data by full-matrix least-squares procedures SHELXT interfaced through the program WINGX.\textsuperscript{79} Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in ideal positions unless specified in special refinements. All calculations were performed using the WinGX interface.\textsuperscript{79} Detailed analyses of the extended structure were carried out using Mercury (Version 3.5.1).\textsuperscript{80} The CIF file generated from single crystal X-ray crystallography has been CIF checked and is of the standard required for publication.
Synthesis of 1, 10-Phenanthroline-5, 6-Dione Bromine method

1, 10-Phenanthroline monohydrate (1.0088 g, 5.0893 mmol) and bromine (0.65 mL, 12.61 mmol) were added in sequence to an ice-cold mixture of sulfuric acid (10 mL) and nitric acid (5 mL). The solution was stirred for 5 hours at 95 °C with additional bromine (3 × 0.17 mL) added at hours 2, 3, and 4. The solution was cooled to room temperature and poured into ice (100 g). The solution was neutralized with a 30 % aqueous sodium hydroxide solution. The products were extracted with dichloromethane (200 mL), dried with sodium sulfate, and filtered via vacuum filtration. The filtrate was taken, and the solvent was removed via rotary evaporation and the product was recrystallized with methanol. The product was obtained as yellow needle-like crystals (0.2829 g, 27 %). \(^1\)H NMR (400 MHz, DMSO-d\(^6\)) δ 8.99 (s, 2H, H\(_3\), H\(_{12}\)), 8.39 (s, 2H, H\(_5\), H\(_{10}\)), 7.67 (dd, J = 7.8, 4.7 Hz, 2H, H\(_4\), H\(_{11}\)).

Synthesis of 1, 10-Phenanthroline-5, 6-Dione Potassium Bromide method

1, 10-Phenanthroline monohydrate (1.0000 g, 5.045 mmol) and potassium bromide (4.4424 g, 37.331 mmol) were combined in a 3-neck 100 mL round bottom flask. Ice-cold sulfuric acid (18 mL) and nitric acid (7 mL) was added to the mixture dropwise slowly. The solution was stirred for 1.5 hours at 80 °C then for 3.5 hours at 100 °C. The solution was cooled to room temperature and poured into ice (approximately 100 g). The solution was neutralized with a 30 % aqueous sodium hydroxide solution. The products were extracted with dichloromethane (200 mL), dried with magnesium sulfate, and filtered via vacuum filtration. The filtrate was taken, and the solvent was removed via rotary evaporation. The product was obtained as a yellow-orange powder (895.9 mg, 84 %). The product was recrystallised with methanol. The product was obtained as yellow crystals (386.9 mg, 36 %). \(^1\)H NMR (400 MHz, DMSO-d\(^6\)) δ 8.99 (dd, J = 4.7, 1.8 Hz, 2H, H\(_3\), H\(_{12}\)), 8.39 (dd, J = 7.8, 1.8 Hz, 2H, H\(_5\), H\(_{10}\)), 7.67 (dd, J = 7.8, 4.6 Hz, 2H, H\(_4\), H\(_{11}\)). \(^{13}\)C NMR (101 MHz, DMSO-d\(^6\)) δ 177.76 (C7, C8), 154.34 (C1, C14), 152.29 (C3, C12), 135.66 (C5, C10), 129.08 (C6, C9), 125.22 (C4, C11). ES-MS found (m/z): 211.05; calc (m/z): 211.05 [C\(_{12}\)H\(_6\)N\(_2\)O\(_2\)]\(^+\).
Synthesis of Ligand 1 (L1) \(^{2,10,81}\)

1, 10-Phenanthroline-5, 6-dione (400.0 mg, 1.903 mmol) and ammonium acetate (4.000 g, 51.894 mmol) was dissolved in glacial acetic acid (20 mL). While stirring 4’-formyl-[1, 1’-biphenyl]-4-carboxylic acid (430.5 mg, 1.903 mmol) dissolved in acetic acid (8 mL) was added to the solution. The solution was stirred for 4 hours at 95 °C and was quenched with water (200 mL); the solution was neutralized with a 30 % aqueous ammonium solution until the product precipitated. The precipitate was collected via vacuum filtration and washed with cold water and cold acetone then oven dried at 60 °C. The product was obtained as a yellow-orange powder (438.3 mg, 55 %). \(^1\)H NMR (400 MHz, DMSO-d\(^6\)) \(\delta\) 9.04 (dd, \(J = 4.3, 1.7\) Hz, H\(_2\), H\(_{25}\)), 8.95 (dd, J = 8.2, 1.8 Hz, 2H, H\(_6\), H\(_{22}\)), 8.42 (d, J = 8.1 Hz, 2H, H\(_{10}\), H\(_{19}\)), 8.08 (d, J = 8.1 Hz, 2H, H\(_{14}\), H\(_{17}\)), 7.93 (d, J = 8.1 Hz, 2H, H\(_{13}\), H\(_{18}\)), 7.85 (dd, J = 8.1, 4.3 Hz, 2H, H\(_3\), H\(_{24}\)); \(^{13}\)C NMR (101 MHz, DMSO-d\(^6\)) \(\delta\) 167.20 (C\(_{16}\)), 150.05 (C\(_7\), C\(_8\)), 147.90 (C\(_2\), C\(_{25}\)), 143.68 (C\(_1\), C\(_{26}\)), 143.20 (C\(_6\), C\(_{21}\)), 139.80 (C\(_{11}\), C\(_{12}\)), 130.33 (C\(_{15}\)), 130.02 (C\(_{14}\), C\(_{17}\)), 129.72 (C\(_4\)/C\(_{23}\)), 129.67 (C\(_4\)/C\(_{23}\)), 127.53 (C\(_9\), C\(_{20}\)), 126.83 (C\(_{10}\), C\(_{19}\)), 126.76 (C\(_{13}\), C\(_{18}\)), 123.33 (C\(_3\), C\(_5\), C\(_{22}\), C\(_{24}\)). ES-MS found (m/z): 417.13; calc (m/z): 417.13 [C\(_{26}\)H\(_{16}\)N\(_4\)O\(_2\)]\(^+\). IR: \(\nu\)\(_{\text{OH}}\) 3258 cm\(^{-1}\), \(\nu\)\(_{\text{CH}}\) 1923 cm\(^{-1}\), \(\nu\)\(_{\text{NH}}\) 1608 cm\(^{-1}\), \(\nu\)\(_{\text{OH}}\) 1424 cm\(^{-1}\), \(\nu\)\(_{\text{CN}}\) 1314 cm\(^{-1}\), \(\nu\)\(_{\text{Ben}}\) 693 cm\(^{-1}\). Product was recrystallised in ethanol and collected via vacuum filtration. The product was obtained as a yellow/off-white powder (373.7 mg, 47 %). Elemental analysis found: C 71.20, H 4.39, N 12.87; calc for C\(_{26}\)H\(_{16}\)N\(_4\)O\(_2\)-[H\(_2\)O]: C 71.88, H 4.18, N 12.90.
Synthesis of Tetrakis(dimethylsulfoxide)dichloro-ruthenium(II)  

Ruthenium chloride (843.4 mg, 4.0659 mmol) was dissolved in DMSO (10 mL) in a 50 mL round bottom flask. The solution was refluxed for approximately an hour at approx. 190 °C and left to cool to room temp. Ice-cold acetone (200 mL) was added to the solution and the mixture was left in the freezer overnight. The precipitate formed was collected via vacuum filtration. The product was obtained as a light-yellow powder (603.0 mg, 30%). ¹H NMR (400 MHz, CDCl₃) δ 2.72 (s, 3H, DMSO).
Partial Synthesis of Ruthenium Metallo-Ligand 1 (Ru-L1) Complex 2

Tetrakis(dimethylsulfoxide)dichloro-ruthenium(II) (76.3 mg, 0.1575 mmol) and Ligand 1 (232.0 mg, 0.5571 mmol) was dissolved in a water/ethanol solution (1:1 6 mL). The solution was refluxed at 100 °C for 6 hours with stirring, then cooled to room temp, and then the solvent was removed via rotary evaporation. The product was obtained as a brown oil (319.8 mg, 126 %). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.06 (d, J = 4.2 Hz), 8.98 (t, J = 7.4 Hz), 8.45 (dd, J = 12.6, 8.1 Hz), 8.12 – 7.89 (m), 2.54 (s, residual bound DMSO). ES-MS found (m/z): 1047.14; calc (m/z): 1047.14 [Ru(C$_{26}$H$_{16}$N$_4$O$_2$)$_2$(C$_2$H$_6$SO)Cl]$^+$; ES-MS found (m/z): 969.13; calc (m/z): 969.13 [Ru(C$_{28}$H$_{16}$N$_4$O$_2$)$_2$Cl]$^+$; ES-MS found (m/z): 787.04; calc (m/z): 787.04 [Ru(C$_{28}$H$_{16}$N$_4$O$_2$)(C$_2$H$_6$SO)$_3$Cl]$^+$; ES-MS found (m/z): 709.03; calc (m/z): 709.03 [Ru(C$_{28}$H$_{16}$N$_4$O$_2$)(C$_2$H$_6$SO)$_2$Cl]$^+$; The product was dissolved in methanol (25 mL) then a saturated ammonium hexafluorophosphate aqueous solution (1.5 mL) was added dropwise until the product had precipitated. The product was filtered via vacuum filtration and washed with methanol. The product was obtained as a red-brown powder (245.7 mg, 97 %). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.10 – 9.02 (m), 8.97 (d, J = 8.2 Hz), 8.43 (d, J = 8.3 Hz), 8.11 – 7.93 (m), 7.93 – 7.82 (m), 4.09 (s), 3.51 – 3.41 (m), 3.17 (s), 2.54 (s), 1.05 (t, J = 7.0 Hz). The product was then attempted to be recrystallised in methanol. The product was obtained as a red-brown powder (83.0 mg, 33%). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.05 (dd, J = 4.3, 1.7 Hz), 8.96 (dd, J = 8.1, 1.8 Hz), 8.43 (d, J = 8.2 Hz), 8.06 (dd, J = 18.9, 8.1 Hz), 7.95 (d, J = 8.1 Hz), 7.87 (d, J = 12.2 Hz). IR: ν$_{NH}$ 3335 cm$^{-1}$, ν$_{OH}$ 3287 cm$^{-1}$, ν$_{CH}$ 1989 cm$^{-1}$, ν$_{CN}$ 1313 cm$^{-1}$, ν$_{ben}$ 692 cm$^{-1}$. Elemental analysis found: C 57.97, H 3.80, N 10.72; calc for RuC$_{78}$H$_{48}$N$_{12}$O$_6$P$_2$F$_{12}$: C 57.11, H 2.95, N 10.25.
Attempted Synthesis of 4’-Formylbiphenyl-3, 5-dicarboxylic acid

3, 5-Dicarboxylphenylboronic acid (501.7 mg, 2.3896 mmol) and 4-Bromobenzenaldehyde (449.4 mg, 2.4289 mmol) was dissolved in a para-dioxane/water solution (4:1, 107 mL). Potassium carbonate (825.3 mg, 5.9716 mmol) and [1, 1’-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) (168.5 mg, 0.2303 mmol) were added to the solution and the mixture was heated and stirred under reflux for between 3 and 18 hours. The reaction was monitored via TLC. The solution was left to cool to room temperature and was extracted with water and dichloromethane twice. The aqueous phase was washed with dichloromethane, and then the organic phase was dried with sodium sulfate then was filtered and the solvent was removed via rotary evaporation. Product was collected as a yellow-brown oil (95.9 mg, 15 %). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.09 (s), 8.03 (q, J = 8.5 Hz), 7.92 (d, J = 7.5 Hz), 7.65 (t, J = 9.8 Hz), 7.56 (d, J = 8.1 Hz), 7.53 (s), 7.50 (s), 7.47 (d, J = 6.7 Hz), 4.56 (s), 4.49 (s), 4.22 (s), 4.09 (s), 3.57 (s), 2.68 – 2.57 (m), 2.19 – 2.06 (m), 1.48 (s), 1.23 (s), 1.17 (s), 0.87 – 0.77 (m). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 130.71, 130.19, 128.53, 128.42, 127.92. The product was then absorbed on silica gel (SiO$_2$) and subjected to column chromatography (petroleum ether: EtOAc ~100:8) to give the product as a white/off-white solid. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.08 – 7.97 (m, 3H), 7.80 – 7.39 (m, 4H).
Synthesis of [3, 5-Bis(methoxycarbonyl)phenyl] Boronic acid

3, 5-dicarboxyphenyl boronic acid (196.6 mg, 0.9364 mmol) was dissolved in methanol (6 mL) then conc. sulfuric acid (0.1 mL) was added slowly to the solution. The solution was refluxed with stirring for 8.5 hours then left to cool to room temperature. The excess methanol was removed via rotary evaporation and the resulting product was combined with water (6 mL). The product was obtained as a white powder (228.9 mg, 127 %). The product was recrystallised in water. The product was obtained as a white powder (101.6 mg, 45 %).$^{1}$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.66 – 8.62 (m, 1H, H$_6$), 8.50 (d, $J = 7.0$ Hz, 2H, H$_2$, H$_{10}$), 3.90 (s, 6H, H$_5$, H$_9$).$^{13}$C NMR (101 MHz, DMSO-d$_6$) $\delta$ 165.74 (C$_4$, C$_8$), 139.16 (C$_1$, C$_2$, C$_{10}$), 131.13 (C$_6$), 129.41 (C$_3$, C$_7$), 52.38 (C$_5$, C$_9$). ES-MS found (m/z): 237.06; calc (m/z): 237.07 [C$_{10}$H$_{11}$O$_6$B(-H)].
Attempted Synthesis of 4’-Formylbiphenyl-3, 5-bismethoxycarbonyl

[3, 5-Bis(methoxycarbonyl)phenyl] boronic acid (80 mg, 0.3361 mmol) and 4-Bromobenzenaldehyde (62.2 mg, 0.3362 mmol) was dissolved in a para-dioxane/water solution (4:1, 15 mL). Potassium carbonate (118.2 mg, 0.8553 mmol) and [1, 1’-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) (24.3 mg, 0.0332 mmol) were added to the solution and the mixture was heated and stirred under reflux for between 3 and 18 hours. TLC monitored the reaction. The solution was left to cool to room temperature and was extracted with water and dichloromethane twice. The aqueous phase was washed with dichloromethane, and then the organic phase was dried with sodium sulfate then was filtered and the solvent was removed via rotary evaporation. The product was obtained as a brown oil (23.8 mg, 24%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.09 (d, $J = 3.1$ Hz), 8.08 – 7.97 (m), 7.97 – 7.80 (m), 7.70 – 7.55 (m), 7.55 – 7.51 (m), 7.51 – 7.38 (m), 7.33 (dd, $J = 13.6, 7.6$ Hz), 7.31 – 7.13 (m), 4.49 (q, $J = 1.7$ Hz), 4.22 (q, $J = 1.9$ Hz), 3.94 (d, $J = 4.5$ Hz), 3.86 (s), 2.63 (ddt, $J = 24.9, 17.0, 8.7$ Hz), 2.32 – 2.20 (m), 2.15 (q, $J = 8.1, 7.7$ Hz), 1.98 – 1.83 (m), 1.73 (s), 1.23 (s), 0.84 (d, $J = 6.9$ Hz).
Alternate attempted Synthesis of 4’-formylbiphenyl-3, 5-dicarboxylic acid

4-Bromobenzenaldehyde (210.0 mg, 1.1350 mmol) was dissolved in an ethanol/toluene solution (1:1, 16 mL). Tetrakis(triphenylphosphine) palladium (0) (4.8 mg, 0.0042 mmol) was added, and the solution was stirred for 15 minutes. 3, 5-Dicarboxylphenylboronic acid (275.9 mg, 1.3141 mmol), sodium hydrogen carbonate (370.0 mg, 4.4042 mmol), and water (5 mL) was added sequentially to the solution. The solution was heated under reflux for 23 hours then left to cool to room temp. The solution was filtered via vacuum filtration through a thin layer of Celite and a sintered glass funnel and the filtrate was washed with brine. The organic phase was separated out and dried with sodium sulfate, then the solution was filtered via vacuum filtration. The filtrate was collected, and the solvent was removed via rotary evaporation. Product was collected as a yellow-brown oil (19.2 mg, 7%). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.09 – 7.71 (m), 7.66 – 7.50 (m), 7.37 – 7.16 (m), 1.91 – 1.75 (m), 1.23 (s).
Synthesis of Dimethyl 5-Bromoisophthalate

5-Bromoisophthalic acid (1.000 g, 4.081 mmol) was dissolved in methanol (17 mL). Conc. sulfuric acid (0.4 mL) was added slowly, and the solution was refluxed with stirring at 65 °C for 18 hours. The excess methanol was removed via rotary evaporation, the residue was mixed with water (3 × 10 mL), and the precipitate was collected via vacuum filtration. The product was recrystallised in water and the precipitate was collected via vacuum filtration. The product was obtained as a white powder (0.8207 g, 74 %). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 8.40 (t, J = 1.5 Hz, 1H, H$_6$), 8.28 (d, J = 1.5 Hz, 2H, H$_2$, H$_{10}$), 3.90 (s, 6H, H$_5$, H$_9$). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 164.14 (C4, C8), 135.84 (C2, C10), 132.24 (C6), 128.36 (C3, C7), 122.23 (C1), 52.83 (C5, C9).
DMF (12 mL) was placed into a 3-neck round bottom flask and was degassed by vigorously bubbling with nitrogen gas for 30 minutes. Dimethyl 5-bromoisophthalate (800.0 mg, 2.930 mmol), 4-formyl-phenylboronic acid (480.0 mg, 3.201 mmol), potassium carbonate (1.2400 g, 8.972 mmol), and tetrakis(triphenylphosphine)palladium (0) (105.2 mg, 0.091 mmol) were added to the round bottom flask. The solution was placed under a N₂ atmosphere and was heated to 100 °C with stirring for 18.5 hours. The product was then dissolved in water (30 mL) and then the product was extracted with a solution of diethyl ether (20 mL) and dichloromethane (50 mL) twice. The organic phases were combined and dried with sodium sulfate and filtered, the filtrate was taken, and the solvent was removed via rotary evaporation. The product was then obtained as a brown powder (1.6211 g, 186%). The product was then recrystallised with ethanol and collected via vacuum filtration. The product was then obtained as a grey-white powder (0.2534 g, 29%). ¹H NMR (400 MHz, DMSO-d₆) δ 10.09 (s, 1H, H₁), 8.48 (d, J = 1.6 Hz, 1H, H₁₁), 8.46 (d, J = 1.6 Hz, 2H, H₇, H₁₅), 8.04 (d, J = 8.3 Hz, 2H, H₄, H₁₆), 7.99 (d, J = 8.3 Hz, 2H, H₃, H₁₇), 3.93 (s, 6H, H₁₀, H₁₄). ¹³C NMR (101 MHz, DMSO-d₆) δ 192.79 (C₁), 165.13 (C₉, C₁₃), 143.42 (C₅), 140.09 (C₂), 135.79 (C₁₁), 131.77 (C₈, C₁₂), 131.16 (C₆), 130.30 (C₃, C₁₇), 129.22 (C₇, C₁₅), 127.78 (C₄, C₁₆), 52.64 (C₁₀, C₁₄). ESI-MS found (m/z): 299.09; calc (m/z): 299.09 [C₁₇H₁₅O₅]⁺.
Synthesis of Methylated Ligand 2 (methylated-L2) \(^{2,10,81}\)

1. 10-Phenanthroline-5, 6-dione (200.0 mg, 0.952 mmol) and ammonium acetate (2.000 g, 25.947 mmol) were dissolved in glacial acetic acid (10 mL). While stirring 4’-formylbiphenyl-3, 5-bismethoxycarbonyl (285.0 mg, 0.955 mmol) dissolved in acetic acid; (4 mL) was added to the solution. The solution was stirred for 4 hours at 95 °C and was quenched with water (100 mL); the solution was neutralized with a 30 % aqueous ammonium solution until the product precipitated. The precipitate was collected via vacuum filtration and washed with cold water and cold acetone, then oven-dried at 60 °C. The product was obtained as a light orange powder (192.4 mg, 41 %). \(^1\)H NMR (400 MHz, DMSO-d\(^6\)) δ 13.88 (s, 1H, N-H), 9.05 (s, 2H, H\(_2\), H\(_{28}\)), 8.96 (s, 2H, H\(_4\), H\(_{26}\)), 8.54 (s, 2H, H\(_{13}\), H\(_{21}\)), 8.47 (d, J = 17.7 Hz, 3H, H\(_{10}\), H\(_{17}\), H\(_{22}\)), 8.06 (s, 2H, H\(_9\), H\(_{23}\)), 7.85 (s, 2H, H\(_3\), H\(_{27}\)), 3.95 (s, 6H, H\(_{16}\), H\(_{20}\)). ES-MS found (m/z): 489.16; calc (m/z): 489.16 [C\(_{29}\)H\(_{20}\)N\(_4\)O\(_4\)H]\(^+\). IR: \(\nu_{CH}\) 2954 cm\(^{-1}\), \(\nu_{C=O}\) 1725 cm\(^{-1}\), \(\nu_{CH}\) 1434 cm\(^{-1}\), \(\nu_{CN}\) 1345 cm\(^{-1}\), \(\nu_{CO}\) 1248 cm\(^{-1}\), \(\nu_{Ben}\) 698 cm\(^{-1}\); elemental analysis found: C 62.92, H 4.08, N 10.50; calc for C\(_{29}\)H\(_{20}\)N\(_4\)O\(_4\)•4H\(_2\)O: C 62.14, H 5.03, N 9.99.
Attempted Synthesis of Ruthenium Metallo-Ligand 2 (Ru-L2) Complex

Tetrakis(dimethylsulfoxide)dichloro-ruthenium(II) (25.7 mg, 0.0530 mmol) and Methylated Ligand 2 (82.5 mg, 0.1689 mmol) were dissolved in a water/ethanol solution (1:1 4 mL). The solution was refluxed at 100 °C for 6 hours with stirring, then cooled to room temp, and then the solvent was removed via rotary evaporation. The product was obtained as a brown powder (60.7 mg, 63 %). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.98 (s, 3H), 8.89 (s, 3H), 8.42 (s, 15H), 8.21 (s, 6H), 7.95 (s, 6H), 7.81 (s, 6H), 3.96 – 3.81 (m, 18H). The product was dissolved in methanol (12.5 mL) then a saturated ammonium hexafluorophosphate aqueous solution (1.25 mL) was added dropwise until the product had precipitated. The product was filtered via vacuum filtration and washed with methanol. The product was obtained as a red-brown powder (69.8 mg, 73 %). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 9.03 (s, 3H), 8.83 (d, J = 32.1 Hz, 4H), 8.40 (d, J = 35.3 Hz, 15H), 8.15 (s, 5H), 7.96 (s, 6H), 7.82 (s, 6H), 3.87 (d, J = 13.4 Hz, 18H). The product was dissolved in ethanol (30 mL) then an aqueous sodium hydroxide solution (2 mol L$^{-1}$, 5 mL) was added to the solution. The solution was heated with stirring under reflux for 3 hours and then left to cool to room temp. The solvents were removed via rotary evaporation. The product was then dissolved in water (100 mL) and was acidified with a conc. hydrochloric acid solution (0.8 mL) until the product precipitated. The product was collected via vacuum filtration. The product was collected as a red-brown powder (36.3 mg, 40 %). The product was recrystallised in methanol and collected via vacuum filtration. The product was collected as a red-brown powder (0.8 mg, 1%). $^1$H NMR (400 MHz, DMSO-d$_6$) δ 8.54 (s), 5.74 (s), 2.08 (s), 1.91 (s), 1.23 (s).
Deprotection of Methylated-Ligand 2 (Methylated-L2) 

Methylated-Ligand 2 (263.0 mg, 0.538 mmol) was dissolved in ethanol (100 mL) then an aqueous sodium hydroxide solution (2 mol L\(^{-1}\), 33 mL) was added to the solution. The solution was heated with stirring under reflux for 3 hours and then left to cool to room temp. The solvents were removed via rotary evaporation. The product was then dissolved in water (300 mL) and was acidified with an aqueous hydrochloric acid solution (2 mol L\(^{-1}\), ~33 mL) until the product precipitated/the solution was neutralised. The precipitate was collected via vacuum filtration, washed with cold water and acetone, and left in a desiccator overnight. The product was collected as an orange-red powder (167.9 mg, 68 %). The product was recrystallised in ethanol. The product was collected as an orange-red powder (155.4 mg, 63 %). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\) 13.88 (s, 2H, H\(_{COOH}\)), 9.05 (d, \(J = 2.5\) Hz, 2H, H\(_2\), H\(_{26}\)), 8.96 (d, \(J = 8.2\) Hz, 2H, H\(_4\), H\(_{24}\)), 8.51 (d, \(J = 4.5\) Hz, 3H, H\(_{13}\), H\(_{16}\), H\(_{19}\)), 8.44 (d, \(J = 8.1\) Hz, 2H, H\(_{10}\), H\(_{20}\)), 8.04 (d, \(J = 8.1\) Hz, 2H, H\(_9\), H\(_{21}\)), 7.85 (s, 2H, H\(_3\), H\(_{25}\)). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 166.50 (C15, C18), 150.00 (C11, C12), 147.88 (C2, C26), 140.21 (C7, C8), 132.23 (C14, C17), 131.19 (C13, C16, C19), 129.76 (C4, C24), 127.52 (C9, C21), 126.98 (C10, C20). ES-MS found (m/z): 461.12; calc (m/z): 461.12 \([\text{C}_{27}\text{H}_{16}\text{N}_4\text{O}_4]^+\). IR: \(\nu_{\text{OH}}\) 3069 cm\(^{-1}\), \(\nu_{\text{NH}}\) 2917 cm\(^{-1}\), \(\nu_{\text{CH}}\) 1881 cm\(^{-1}\) (Aromatic), \(\nu_{\text{C=O}}\) 1694 cm\(^{-1}\), \(\nu_{\text{NH}}\) 1607 cm\(^{-1}\), \(\nu_{\text{CH}}\) 803 cm\(^{-1}\), \(\nu_{\text{CH}}\) 739 cm\(^{-1}\).
**Ligand 1 (L1) Crystal Jars**

Ligand 1 (8.4 mg, 0.020 mmol) was dissolved in a DMF/Formic Acid solution (50:1 1.5 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr and slowly cooled until colourless crystals formed.

**Methylated Ligand 2 (Methylated-L2) Crystal Jars**

Methylated Ligand 2 (9.8 mg, 0.020 mmol) was dissolved in Ethanol (2 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 90 °C for 24 hr and slowly cooled until white crystals formed.
Chapter 3: MOF Chemistry

3.1 Attempted Synthesis of L1 Ruthenium-Metal Photo-MOFs

Once a reasonable amount of Ru-L1 complex had been produced, efforts to produce photoactive bimetallic MOFs began. The initial experimental method was identical to the literature method of bimetallic Photo-MOF synthesis. The method involved ruthenium metallo-ligand and cobalt nitrate being dissolved in a solution of DMF with a small amount of trifluoroacetic acid (TFA) acting as the moderator. The solution was placed within a sealed unit and heated to 120 °C for 72 hours and was then left to cool. This reaction was a solvothermal reaction that occurred under autogenous pressure. The reaction occurring under autogenous pressure means that as the solution is heated, the solvents begin to boil, and the vapour produced causes the pressure of the sealed container to increase. This, in turn, increases the solvent’s boiling point, which allows an equilibrium to be reached where the reaction can take place at a temperature higher than the solvent’s boiling point. This is useful when facilitating a high activation energy reaction or if the reactants are insoluble except at high temperatures. The reason DMF is used is because, when heated, DMF can decompose into an amine which then deprotonates the ligand’s carboxylic acid groups, which allows the carboxylate groups to bind to the other metals. The purpose of the moderator is to help decompose the DMF or DEF into their amine forms. However, heating the solution without a moderator can also decompose the solvent at a slower rate, so while having an acid or other substance that can facilitate the decomposition of the solvent present as a moderator is helpful, it is not strictly necessary.

![Scheme 3.1: General reaction scheme for the synthesis of ruthenium-M (M = cobalt, copper, zinc, or cadmium) Photo-MOF](image-url)
This reaction was repeated several times. As the reactions were carried out, each component of the reaction was systematically varied to facilitate the production of the MOF (Scheme 3.1). Each component of the reaction was varied, starting with the reaction temperature which was decreased to as low as 80 °C at which the reaction did not take place, to up to 160 °C. From this method, the most effective temperature for crystal formation was approximately 140 °C. The solvents used were DMF or DEF, this was because only a solvent that decomposes into a base like an amine can be utilized for this reaction. However, it was ultimately found that DMF was the better solvent of the two. The moderators utilized were TFA, acetic acid, formic acid, and occasionally no moderator at all. Because DMF and DEF both decompose at high temperatures or when in the presence of acids, any of those moderators could be useful for MOF synthesis, including the system in which no moderator is added and only the heat is involved in the decomposition of the solvent. Eventually, it was determined that formic acid was the most effective moderator for this reaction. Lastly, the metals used in the MOF synthesis reaction were varied, including cobalt, copper, zinc, and cadmium. Unfortunately, none of these metals formed a viable crystal of a ruthenium-M (M = cobalt, copper, zinc, or cadmium) MOF. However, one of the reactions between cadmium nitrate and the metallo-ligand did produce a unique result.

While the other metals were used with various solvents and moderators, none of them produced viable crystals of a ruthenium-M Photo-MOF. On top of single crystal X-ray crystallography, an X-ray powder diffraction analysis was carried out on the ruthenium-cobalt product, and it was found the product was an amorphous powder. This is likely due to a combination of factors. Firstly, the ruthenium metallo-ligand was very insoluble, meaning that any fully formed ruthenium metallo-ligand present may not have been dissolved when the reaction was occurring and therefore would not have reacted with the metal ions. Secondly, the metallo-ligand used was an impure mixture that would greatly diminish the chance of a high-quality crystal being formed. Because of the inability to form MOFs with the ruthenium metallo-ligand and the unique result from one specific cadmium reaction, the research focus was moved from bimetallic ruthenium MOFs to single metal MOFs made with non-complexed L1.
3.2 Synthesis of Cadmium-L1 MOF

During an attempt to form a ruthenium-cadmium bimetallic MOF, a crystal was formed that, when analysed, showed that a MOF had been formed with only cadmium metal and L1 present. This may have happened due to one of two reasons, either the ruthenium complex decomposed, and the cadmium bound to the released L1 molecule and formed a MOF, or the ruthenium metallo-ligand complex had some residual un-complexed L1 still present which reacted with the cadmium to form a MOF on its own. The exact mechanism of how the MOF formed in that specific reaction is less relevant than the fact that it did at all. The formation of the cadmium MOF showed that the phenanthroline group in L1 was able to bind strongly to another metal. Even though the metal was not very nitrophilic, it still was able to bind to the two nitrogen atoms of the phenanthroline group. As such, a MOF could be formed by having a metal ion bond with the carboxylate group of the ligand and form a strong bidentate bond to the phenanthroline group of the ligand.

Scheme 3.2 General reaction scheme for the synthesis of a Cadmium-L1 MOF

The Cd(II) ion had two positive charges and cadmium atom’s coordination numbers are 4-8, but due to its large size it tends towards larger complexes with higher coordination.³ So the structure would likely be an octahedrally (6-coordinate) or even a dodecahedrally (8-coordinate) bound structure.

Unfortunately, other attempts to synthesise the same MOF structure by reacting pure L1 with cadmium nitrate did not produce viable crystals, so repeats of this structure were not obtained. Luckily the original crystal produced was of a high enough quality that the cadmium MOF was able to be characterised via single crystal X-ray crystallography with a high degree of accuracy.
3.3 Crystal structure of Cadmium- L1 MOF

All the figures in this section were produced in Mercury. They follow the colour code carbon: grey, nitrogen: blue, oxygen: red, hydrogen: white, cadmium: yellow.

**3D Cadmium-L1 MOF (Cd-MOF)**

![Diagram of Cadmium-L1 MOF](image)

**Figure 3.1: The asymmetric unit of Cadmium-L1 MOF.**

The cadmium-L1 MOF (Cd-MOF) was crystallised in DMF in the orthorhombic space group *Fd*dd. Cd-MOF formed a single-walled, six-fold interpenetrated framework with 1D diamond-shaped channels running the length of the *a* axis. The asymmetric unit consists of one deprotonated L1 and half a Cd$^{2+}$ cation. The Cd$^{2+}$ cation sits on a two-fold rotational symmetry axis. Within each molecule of L1 the phenanthroline group and first benzene ring are planar, and the second benzene ring has twisted $25.8^\circ$ with respect to the other rings.
Figure 3.2: The crystal structure of Cadmium-L1 MOF focused on a single fully satisfied Cd$^{2+}$ cation and its bound L1 molecules.

Each cadmium ion is eight-coordinate. The cadmium ion asymmetrically chelates to two carboxylate groups and also chelates to two phenanthroline groups. Due to the bidentate bonds between the cadmium ion and phenanthroline groups, the coordination geometry that the cadmium ion takes appears to be pseudo-tetrahedral. The standard asymmetric unit of Cd-MOF consists of half of a Cd$^{2+}$ ion and one deprotonated L1. This balances the charge, allowing this structure to be a neutral framework without additional charge balancing counter-anions. Interestingly the pseudo-tetrahedral appearance of the cadmium MOF could be considered to be an isoreticular analogue of a manganese MOF found in the literature.$^{10}$
Figure 3.3: View of Cd-MOF down the $a$ axis. Hydrogens were omitted for clarity.

The pseudo tetrahedral coordination geometry of the Cd$^{2+}$ ions lead to the framework having a diamondoid or adamantane type structure. Due to the shape of the framework, it also has regular diamondoid shaped pores running along the $a$ axis. Usually, for a framework with an adamantane structure, the pores would be open through multiple directions, making multidimensional pores. However, due to the extensive interpenetration of the Cd-MOF, the pores are only open along the $a$ axis. The edges of the phenanthroline groups did somewhat encroach on the channels, so the channels did not have a perfect diamond shape. The 1D channels were large with a distance of 1.88 nm between the carboxylate at the top and bottom of the pores. The distance between the edges of the phenanthroline groups on the same plane was only 0.84 nm. The relative volume of the MOF that the pores took up was 56.5 % of the unit cell or 18099 Å$^3$ (as calculated by Mercury, after PLATON SQUEEZE routine was run).

To refine the data and decrease the $R_1$ value, a PLATON SQUEEZE routine was run on the crystal. This resulted in a decrease of the $R_1$ value from 12.6 % to 8.9 %. In a total void volume of 18965 Å$^3$ (as calculated by PLATON), 3671 electrons were squeezed from the unit cell. This would be equivalent to 115 electrons removed in each asymmetric unit i.e., no. of electrons removed $\div Z = 3671 \div 32 = 115$. The removed electron density was likely attributed to three DMF molecules or two DMF molecules and three water molecules.
Figure 3.4: View of six-fold interpenetrated Cd-MOF down the $b$ axis. Individual networks were coloured separately, and hydrogens were omitted for clarity.

Cd-MOF formed a single-walled, six-fold interpenetrated framework with 1D diamond-shaped channels running the length of the $a$ axis. This means that the Cd-MOF has six identical networks, each interlaced within the pores of the other five structure (Figure 3.4).
3.4 Synthesis of Zinc-L1 MOF

Once it became clear that studying single metal MOFs would be more productive, zinc became one of the main metals investigated. Cadmium and zinc had similar coordination numbers and both could exist in 2+ oxidation states. As such, it was expected that the MOF produced by reacting zinc with L1 could be considered to be an isoreticular analogue of the Cd-MOF. Forming the zinc MOF involved a similar method as the various attempts made to synthesise the Cd-MOF with non-complexed L1. Zinc nitrate and L1 were dissolved in a solution of DMF and formic acid, then the solution was sealed in an airtight golden capped jar. The solution was heated in an oven to 140 °C for 72 hours and then left to cool slowly over a day or two (Scheme 3.3). This reaction also occurred under autogenous pressure allowing the solvents to remain liquid during the three-day heating period. The reaction needed to take place under autogenous pressure as the boiling point of formic acid is lower than 140 °C, and the acid needed to remain in the solution as a moderator.

Scheme 3.3: General reaction scheme for the synthesis of a Zinc-L1 MOF.

A crystal was formed from this reaction and was analysed via single crystal X-ray crystallography. However, the result was not the expected pseudo-tetrahedral structure. The zinc ions had bound to the formic acid moderator as well as the ligands, making a structure in which the zinc ions were bound to each other via formate bridges. This structure was identical to a zinc MOF published in late 2020 by Macreadie et al. The formation of this structure reveals that the moderator is important both in its ability to facilitate the MOF synthesis reaction but also that the moderator can directly bind to the metal ions in a MOF and become part of the framework.
3.5 Synthesis of Magnesium-L1 MOFs

While attempting to form crystals of L1 by heating them in a DMF/formic acid solution, one of the isolated crystals had an unexpected structure. Upon analysis, a small amount of magnesium was present due to an impurity, and that small amount of magnesium reacted with L1 to form a magnesium MOF. This led to multiple attempts to produce magnesium MOFs. The main method of Mg-MOF synthesis was the same synthetic reaction as the zinc and cadmium MOF synthesis reactions. Magnesium nitrate and L1 were dissolved in a solution of DMF and formic acid and sealed in an airtight glass jar. The solution was heated under autogenous pressure in an oven to 140 °C for 72 hours and then left to cool slowly over a day or two (Scheme 3.4).

![Scheme 3.4: General reaction scheme for the synthesis of a Magnesium-L1 MOF.](image)

From this reaction, a number of structures were obtained. Including the structure obtained from the impurity reaction there were four different products. The first structure found was a 1D double chain with only magnesium ions and L1 molecules present. This was noteworthy because instead of branching out, the ligand bent in on itself and formed a 1D chain instead of a 2D or 3D framework. The second structure obtained was a Mg-L1 MOF that also had formate groups binding the metal ions together to form a 2D sheet-like structure. The third structure found had a somewhat similar asymmetric unit to the second structure, with the magnesium ions being bound by formate groups as well as L1. Unlike the 2D sheet structure, the third MOF formed a 1D chain that did not pack to form a porous 3D structure. All three of these structures were subject to hydrogen bonding which formed them into large, ordered 3D frameworks with open pores. The fourth and final magnesium structure found did not involve L1, but instead involved the magnesium ions directly reacting with the formic acid to form a magnesium formate MOF. Unlike the other magnesium frameworks, this MOF was identical to a pre-existing structure. This particular structure proved to be quite frustrating as it tended to appear rather often and distract from more relevant crystal structures.\textsuperscript{11,85}
3.6 Crystal structures of Magnesium-L1 MOFs

All the figures in this section were produced in Mercury. They follow the colour code carbon: grey, nitrogen: blue, oxygen: red, hydrogen: white, magnesium: green.

**1D Magnesium-L1 MOF (Mg-MOF-1)**

![Diagram of 1D Magnesium-L1 MOF](image)

**Figure 3.5: The asymmetric unit of 1D chain Magnesium-L1 MOF plus H-bonded water molecule.**

The magnesium-L1 MOF (Mg-MOF-1) was crystallised in DMF in the monoclinic space group \(P2_1/c\). Mg-MOF-1 is a weakly zigzagging, double-walled, 1D chain structure running along the [1 0 1] diagonal axis. Multiple chains are held together via hydrogen bonding to form a framework with small 1D channels running the length of the \(a\) axis. The asymmetric unit consists of two complete deprotonated L1 ions, one \(\text{Mg}^{2+}\) cation, and one H-bonded water molecule. The water molecule is bound to the imidazole ring via hydrogen bonding with an \(\text{O}_{\text{H}_2\text{O}}\ldots\text{H-N}_\text{im}\) distance of 2.10 (N8-O5) Å corresponding to an \(\text{O}_{\text{H}_2\text{O}}\ldots\text{N}_\text{im}\) distance of 2.953(6) Å.
Figure 3.6 The crystal structure of 1D chain Mg-MOF-1 focused on a single fully satisfied Mg$^{2+}$ cation and its bound L1 ions, plus H-bonded water molecules.

The fully coordinated magnesium ion is octahedrally coordinated, with two bonds shared between two carboxylate groups of different L1 ions and four bonds shared between two phenanthroline groups of different L1 ions. The coordination of the magnesium ion could be considered pseudo-tetrahedral. As such, it would be expected that the framework formed would be a large 2D or 3D framework with large diamondoid pores, however, because of the binding capacity and small size of the magnesium ion this is not the case. Because L1 is slightly flexible when two parallel L1 ions bind to one magnesium ion, those same two L1 ions will bind to a symmetry related same magnesium ion at the other end producing a 1D chain motif.

Figure 3.7 An X-ray crystal structure of a 1D chain of Mg-MOF-1, plus H-bonded water molecules.

The binding between the magnesium ions and the L1 ions forms a 1D chain running along the [1 0 1] diagonal axis. The chain has a slight zig-zag motif but otherwise is relatively linear. As the chain progresses each ligand pair is rotated 90° from the previous pair. The chains are bound to each other via H-bonding between the ligands and the water solvent molecules.
The MOF crystal has formed as a double-walled zig-zagging 1D chain structure. This combined with the hydrogen bonding between the imidazole group to the water molecule to the carboxylate group, forms a double-walled, diamondoid shaped, layered 2D sheet framework. Due to the structure of the MOF, it has relatively small pores that form as 1D channels running along the $a$ axis. The 1D chains are being held together by the H-bonded water molecules. By measuring distances between the Mg$^{2+}$ ions and calculating a centroid between the overlapping carboxylate groups, it was found that the pores have a cross-section of $1.10 \times 1.89$ nm. The relative volume of the MOF that the pores took up was 15.1% of the unit cell or 685 Å$^3$ (as calculated by Mercury, after a PLATON SQUEEZE routine was run).

In an attempt to refine the data and decrease the $R_1$ value, a PLATON SQUEEZE routine was run. This however did not result in a decrease in the $R_1$ value, which remained at 6.6%. In a total void volume of 733 Å$^3$ (as calculated by PLATON), 252 electrons were squeezed from the unit cell. This would be equivalent to 126 electrons removed in each asymmetric unit i.e., no. of electrons removed $\div Z = 252 \div 4 = 63$. The removed electron density was attributed to one and a half DMF molecules.
2D Magnesium-L1 MOF with formate bridging (Mg-MOF-2)

Figure 3.9: The asymmetric unit of 2D sheet Magnesium-L1 MOF with formate bridging (Mg-MOF-2) plus H-bonded water molecules.

The magnesium-L1 MOF with formate bridging (Mg-MOF-2) was crystallised in DMF in the monoclinic space group \( P2_1/c \). Mg-MOF-2 formed a double-walled, 2D sheet framework with 1D channels running the length of the \( a \) axis. The asymmetric unit consists of two complete deprotonated L1 ions, one \( \text{Mg}^{2+} \) full cation and two halves of a \( \text{Mg}^{2+} \) cation, one coordinated formate ion, one coordinated hydroxide ion and three H-bonded water molecules. Mg1 and Mg2 are in special positions, so the framework is still neutral. The hydroxide ions and formate ions are both pointed into the channels. The water molecule is bound to the imidazole ring via hydrogen bonding with an \( \text{O}_{\text{H}_2\text{O}}...\text{H}-\text{N}_{\text{im}} \) distance of 1.88 (N3-O14) Å corresponding to an \( \text{O}_{\text{H}_2\text{O}}...\text{N}_{\text{im}} \) distance of 2.732(5) Å. As well as an \( \text{O}_{\text{H}_2\text{O}}...\text{H}-\text{N}_{\text{im}} \) distance of 2.02 (N7-O13) Å corresponding to an \( \text{O}_{\text{H}_2\text{O}}...\text{N}_{\text{im}} \) distance of 2.874(8) Å. The solvent water molecules O14 and O15 existed on special positions caused by symmetry, as shown above.
Figure 3.10: The crystal structure of the Mg-MOF-2 focused on the central four magnesium SBU and its bound L1 ions plus H-bonded water molecules.

Mg-MOF-2 forms a SBU with four magnesium ions as the metal node. There are three different magnesium bonding environments. Mg1 is octahedrally bound with two bonds split between two carboxylate groups and four bonds split between two phenanthroline groups. Because Mg1 has two monodentate bonds and two sets of bidentate bonds, it forms a pseudo tetrahedral geometry. Mg2 is octahedrally bound to six oxygen atoms, of which four belong to carboxylate groups of different L1 ions and two belong to formate groups. Mg3 is octahedrally bound with four bonds to four oxygen atoms and two bonds to two nitrogen atoms. The oxygen atoms that Mg3 are bound to are two carboxylate groups of different L1 ions, one formate group that is also bound to Mg2 and one hydroxide ion. The nitrogen atoms that Mg3 are bound to are a single phenanthroline group of another L1. Mg3 appears twice in the SBU since both Mg1 and Mg2 sit on a two-fold rotational symmetry axis.
Figure 3.11: View of Mg-MOF-2 down the a axis including H-bonded water molecules within the pores. Hydrogens were omitted for clarity.

The four magnesium SBU unit acting as the metal node of this MOF leads to it having a unique structure. The framework has a double-walled motif due to the coordination of the SBU and the L1 ions it is bound to shown in Figure 3.10. This is supplemented by weak π-π interactions between the various L1 ions which helps counteract the steric hindrance of having multiple large ligands so closely bound together. Due to the structure of the framework the pores within the MOF form as diamondoid 1D channels running the length of the a axis. Within the pores are some H bonded water molecules, and the hydroxide ion of the SBU does point into the MOF’s pores. By calculating the centroid of the Mg-SBU and measuring distances between them, it was found that the pores have a cross-section of $2.24 \times 1.61 \text{ nm}$. The calculated relative volume of the MOF that the pores took up was 28.3 % of the unit cell or $1682 \ \text{Å}^3$ (as calculated by Mercury, after the PLATON SQUEEZE routine was run).

To refine the data and decrease the $R_1$ value, a PLATON SQUEEZE routine was run. This resulted in a decrease of the $R_1$ value from 11.0% to 10.3 %. In a total void volume of $1919 \ \text{Å}^3$ (as calculated by PLATON), 503 electrons were squeezed from the unit cell. This would be equivalent to 126 electrons removed in each asymmetric unit i.e., no. of electrons removed $\div Z = 503 \div 4 = 126$. The removed electron density was attributed to three DMF molecules or two DMF molecules and five water molecules.
1D Magnesium-L1 MOF with formate bridging (Mg-MOF-3)

Figure 3.12: The asymmetric unit of 1D chain Magnesium-L1 MOF with formate bridging (Mg-MOF-3).

The magnesium-L1 MOF with formate bridging (Mg-MOF-3) was crystallised in DMF in the triclinic space group P-1. This structure formed a 1D chain running along the [1 0 1] diagonal axis. The asymmetric unit consists of two complete deprotonated L1 ions, two Mg$^{2+}$ cations, one coordinated formate ion, two coordinate DMF solvent molecules and one H-bonded water molecule. The water molecule is bound to the imidazole ring via hydrogen bonding with an O$_{H2O}$…N$_{im}$ distance of 1.88 (8) (N7-O11) Å.
Figure 3.13: The crystal structure a single chain-link of the 1D chain Magnesium-L1 MOF with formate bridging.

Mg-MOF-3 has two different magnesium bonding environments. Mg1 is octahedrally bound with one bond to a carboxylate group, two bonds to a single phenanthroline group, one bond to a coordinated DMF solvent molecule and two bonds to two separate, distinct formate ions. One of the formate groups acted as a bridging ligand between Mg1 and Mg2 while the other simply pointed outward perpendicular to the chain. Mg2 is octahedrally bound with one bond to each of two carboxylate groups, two bonds to a single phenanthroline group, one bond to a coordinated DMF solvent molecule and one bond to the bridging formate. The two carboxylate oxygen atoms (O3) that Mg2 are bound to are in special position due to them being symmetrically identical. As such each O3 atom is bound to two Mg2 ions forming a 2D diamond shaped, four-membered ring with an inversion symmetry centre in the middle of the ring.
Figure 3.14: The crystal structure a single chain-link of the 1D chain Magnesium-L1 MOF with formate bridging (side on view).

When looking down the [1 0 1] diagonal axis, it is shown that, the chain is made from repetitions of four ligands in a step-like structure. The chain’s centre is a double-walled core, held together by a four-membered ring containing two magnesium ions (Mg2) and two oxygen atoms (O3) as well as an inversion centre in the middle of the ring.

Figure 3.15: The crystal structure of the 1D chain Mg-L1 MOF with formate bridging.

This structure formed a 1D chain due to the binding properties and rigidity of L1, forming a Mg-L1-Mg chain. The chain containing Mg1 was bound to the chain containing Mg2 by a bridging formate group. That Mg2 chain was bound to a symmetrically identical chain containing Mg2, which was in turn bound to its own chain containing Mg1. Functionally, the 1D chain is four separate 1D chains bound together by formate bridging and a four-membered magnesium oxygen ring. The existence of partially coordinated formate groups on the edge of the chain indicates that this structure could have formed as a 2D sheet-like structure or even potentially a 3D network but was unable to.
Figure 3.16: View of packed Mg-MOF-3 down the \( a \) axis including H-bonded water molecules. Hydrogens were omitted for clarity.

Due to the shape of the chains and their ability to interlock with each other, the individual 1D chains pack together very tightly. The non-bridging formate ion bound to Mg1 has been shown to be H-bonded to both the imidazole group (N3) in the chain with Mg1 and the imidazole group (N8) in the chain with Mg2. Moreover, the imidazole group (N3) has even formed a H-bond to both oxygen atoms in the formate group (O7 and O8). The non-bridging formate ion is bound to the Mg1 chain imidazole ring via hydrogen bonding with an \( O_{\text{Formate}}...H-N_{\text{im}} \) distance of 2.18 (N3-O8) Å corresponding to an \( O_{\text{H2O}}...N_{\text{im}} \) distance of 2.999(8) Å. The same imidazole group is H-bonding to the other oxygen atom in the non-bridging formate with an \( O_{\text{Formate}}...H-N_{\text{im}} \) distance of 2.22 (N3-O7) Å corresponding to an \( O_{\text{H2O}}...N_{\text{im}} \) distance of 2.938(8) Å. The non-bridging formate ion is bound to the Mg2 chain imidazole ring \( O_{\text{Formate}}...H-N_{\text{im}} \) distance of 1.89 (N8-O8) Å corresponding to an \( O_{\text{Formate}}...N_{\text{im}} \) distance of 2.744(7) Å. Because of the way the structure packs and the multiple H-bonds between the various chains, the relative size of the pores in the crystal structure were shown to be effectively zero. Because of this, the relative solvent-accessible volume was also near or equal to zero, so no PLATON SQUEEZE program was run. Due to the lack of porosity this particular structure may not be considered a MOF.
3.6 Synthesis of Sodium Coordination-Polymers

As part of the ligands' characterisation, crystals of both L1 and L2 were needed for single crystal X-ray crystallographic analysis. Numerous attempts were made to produce L1 and L2 crystals via various methods. Attempts to synthesise L1 and L2 crystals using solvent diffusion or evaporation techniques did not work due to the low solubility of L1 and L2. Any attempt to form crystals at room temperature led to the ligand’s precipitating as an amorphous powder or not fully dissolving in the first place. Because of this, attempts were made to form L1 and L2 crystals in the same or similar conditions to those used to form the various MOFs reported above. This method allowed for two high quality crystals of L1 and one of the methylated-L2 to be produced. However, due to the strong binding capacities of both the phenanthroline group and the ligands' carboxylate groups, there were some unexpected side products. L1 and L2 can coordinate very well to metal ions; this means that any trace metal impurity in the solvent or cross-contamination could lead to unexpected metal-ligand complexes. As part of this structures were produced from reactions between L1 and L2 and various trace elements such as magnesium and sodium, forming the already mentioned magnesium MOFs as well as two new sodium-L1/L2 coordination polymers.

For the first crystal structure, in two sample vials, L1 was dissolved in ethanol and was heated to 90 °C for 24 hours under autogenous pressure. After a slow cooling process, neither sample vial possessed a crystal, as most of L1 precipitated as an amorphous powder. However, the solvents of the two vials were decanted and combined into a separate vial which was left uncapped for the solvent to evaporate slowly. A crystal did form in the third vial as the ethanol evaporated, but when analysed, the crystal was not of L1 but was of a 1D Na-L1 polymer chain.

For the second crystal structure, L2, in particular, was very difficult to dissolve even at high temperatures. As such a small amount of L2 was added to a solution of DMF and aqueous ammonium hydroxide in an attempt to deprotonate L2 and make it more soluble. This solution was heated to 140 °C for 72 hours under autogenous pressure. The structure produced from this process was a large, complex, 3D Na-L2 coordination polymer.
3.7 Crystal structure of Sodium Coordination-Polymers

All the figures in this section were produced in Mercury, they follow the colour code carbon: grey, nitrogen: blue, oxygen: red, hydrogen: white, sodium: purple.

**1D Sodium-L1 Coordination Polymer (Na-L1 Polymer)**

![Diagram of 1D Sodium-L1 Coordination Polymer](image)

Figure 3.17: The asymmetric unit of 1D chain Na-L1 Coordination Polymer (Na-L1-Polymer) plus H-bonded water molecule.

The sodium-L1 coordination polymer (Na-L1-Polymer) was crystallised in ethanol in the monoclinic space group C2/c. Na-L1-Polymer formed a strongly zig-zagging, double-walled, 1D chain running along the [1 0 1] diagonal axis. The asymmetric unit consists of one complete deprotonated L1 ion, one sodium cation, one coordinated ethanol solvent molecule, one coordinated disordered oxygen atom, and two H-bonded water molecules. The water molecule is bound to the imidazole ring via hydrogen bonding with an OH$_2$…H-N$_{im}$ distance of 1.96 (N3-O5) Å corresponding to an OH$_2$…N$_{im}$ distance of 2.811(9) Å. As well as a corresponding OH$_2$…N$_{im}$ distance of 2.806 (9) (N4-O6) Å
Figure 3.1: The crystal structure of 1D chain Na-L1-Polymer focused on two fully satisfied Na\(^+\) cations and their coordinated molecules, plus H-bonded water molecules.

A fully coordinated sodium ion in this structure is 5-coordinated. It has one bond to the carboxylate group of L1, two bonds to a single phenanthroline group of L1, one bond to the coordinated ethanol solvent molecule and one bond to a coordinated, disordered water molecule. The coordinated, disordered water molecule (O7) presents itself in two positions so the bond between the water molecule and the sodium ion presents as two bonds. A two-fold rotational symmetry axis passes through the space between the two positions of the disordered water molecule, indicating that the disorder is caused by symmetry. Because the sodium ion only binds to two L1 ions at opposite ends, it forms a 1D chain instead of a 2D or 3D structure. Additionally, each of the coordinated water molecules is bound to two sodium ions which causes the 1D chain to form as a double-walled structure.

Figure 3.19: An X-ray crystal structure of a 1D chain of Na-L1-Polymer, plus H-bonded water molecules.

The binding between the sodium ions and the L1 ions forms a 1D chain running along the [1 0 1] diagonal axis. The chain has a clear zig-zag motif. While the 1D chain does have a double-walled structure, it could also be described that two parallel 1D sodium-ligand chains are going in opposite directions. Unlike the Mg-MOF-1, which had two parallel sets of L1 ions bound to the same magnesium ion in the structure, the two Na-L1 chains are connected only by the disordered water molecule.
The crystal produced was packed in such a way that there was little room between each chain. These chains are held together by H-bonding between the water molecules. The N-H group of the imidazole ring H-bonds to the oxygen of the water molecule (O5) which then in turn H-bonds to the oxygen in the coordinated ethanol or the uncoordinated double-bonded oxygen in the carboxylate group. The water molecule is bound to the ethanol via hydrogen bonding with an $O_{\text{H}_{2}O}...O_{\text{EtOH}}$ distance of 2.786 (10) (O5-O3) Å. The water molecule is bound to the double bonded oxygen in the carboxylate group via H-bonding with an $O_{\text{H}_{2}O}...\text{COO}$ distance of 2.712 (10) (O5-O2) Å. Due to the way in which they are H-bonded to each other, the individual 1D chains stack very closely together. Because of this, there are not any large pores in the structure; in fact, the relative solvent-accessible volume of this structure was calculated to be less than one percent ($< 1\%$). Because of the lack of pores for disordered, uncoordinated solvent molecules to adsorb in a PLATON SQUEEZE routine was not required for this structure.
The Na-L2 coordination polymer (Na-L2-Polymer) was crystallised in DMF in the triclinic space group $P\bar{1}$. Na-L2-Polymer formed a two-fold interpenetrated 3D framework. The asymmetric unit consists of two complete deprotonated L2 ions, three sodium cations, one coordinated DMF solvent molecule, two coordinated water molecules, three uncoordinated water molecules and one ammonium cation to balance the overall charge. Within the asymmetric unit, there are four deprotonated carboxylate groups but only three bound sodium ions, leaving the structure with a single negative charge overall. Because of this an ammonium cation from the solvent is also present to counteract that and neutralize the crystal structure.
Figure 3.22: The crystal structure of Na-L2 Coordination Polymer focused on a single fully satisfied Na$^+$ ions. Uncoordinated solvent molecules removed for clarity.

Na-L2-Polymer has three different fully coordinated sodium environments. The fully satisfied Na1 ion is five-coordinate. It has two separate bonds to two carboxylate groups from two separate L2 ions, two bonds to a single phenanthroline group of a L2 ion and one bond to a coordinated water molecule. Fully satisfied Na2 has two separate bonds to two carboxylate groups of two different L2 ions, two bonds to a single phenanthroline group of L2 and one bond to a coordinated water molecule. Na1 and Na2 are coordinated to the same two oxygen atoms in the two carboxylate groups (O4 and O8). Fully satisfied Na3 has two bonds to both oxygen atoms of a single carboxylate group of L2 (O5 and O6), the third bond to an oxygen atom in a separate carboxylate group (O1), one bond to a coordinated DMF solvent molecule, and one bond to a coordinated water molecule. Due to a combination of the sodium ions five coordinate coordination geometry and the heavy twisting that the benzene rings of L2 undertake the crystal structure forms a very dense, complicated 3D structure.
Figure 3.23: View of Na-L2 Coordination Polymer down the $a$ axis. Hydrogens and uncoordinated solvent molecules were omitted for clarity.

Due to the five-coordinate nature of the sodium ions and the twisting of the carboxylate possessing benzene rings of the L2 ions, the overall structure of the Na-L2 coordination polymer is a complicated, two-fold interpenetrated, 3D framework. In the asymmetric unit, the second benzene ring of the first L2 molecule (C20-C25) has rotated 56.7° with respect to its phenanthroline group. Whereas the second benzene ring of the second L2 molecule (C47-C52) has rotated 49.7° with respect to its phenanthroline group. The crystal structure is two-fold interpenetrated with H-bonding between the imidazole groups and the carboxylate groups holding the two interpenetrated structures together. The COO…H-N$_{im}$ distance is 2.00 (N4-O3) Å corresponding to a COO…N$_{im}$ distance of 2.848(13) Å. Additionally, the COO…H-N$_{im}$ distance is 2.03 (N7-O7) Å corresponding to a COO…N$_{im}$ distance of 2.880(13) Å. Due to the framework structure, the individual pores within the MOF formed, but no channels formed. The pores are relatively small but do contain some uncoordinated water molecules and the uncoordinated ammonium cation solvent molecule. Without removing the uncoordinated solvent molecules, the calculated relative volume of the structure that the pores took up was 6.4 % of the unit cell or 181 Å$^3$. Since the uncoordinated ammonium ion was required to balance the structures charge, the measured crystal structure did not undergo a PLATON SQUEEZE routine.
Figure 3.24: View of two-fold interpenetrated Na-L2 Coordination Polymer down the \(b\) axis. Individual networks were coloured separately, and hydrogens were omitted for clarity.

Na-L2-Polymer formed a single-walled, two-fold interpenetrated framework. This means that the Na-L2-Polymer has two identical networks, each interlaced within the pores of the other structure (Figure 3.24).
3.8 Conclusion

In this chapter four new MOFs, two new coordination polymers and two already existing MOFs were reported. The first new MOF produced was a 3D six-fold interpenetrated cadmium MOF that was an isoreticular analogue of a literature manganese MOF. The second new MOF produced was a double-walled 1D chain magnesium MOF. It formed as a 1D chain structure instead of a 2D or 3D structure due to the small size of the magnesium ion and the flexibility that L1 possessed. The third new MOF produced was a double-walled 2D sheet structure of a magnesium MOF with formate bridging. The structure formed as multiple layered 2D sheets to form a 3D structure. The fourth and final new MOF structure was a 1D chain magnesium MOF with formate bridging and a double-walled core. This structure seems to be a version of MgMOF-2 with formate bridging that was unable to bind in one direction as it formed, because of DMF capping of binding sites, so ended up forming a 1D chain instead of a 2D sheet.

Comparing the four new MOFs, the cadmium structure is obviously the most different. Of the four, it is the only MOF that was 3D independent of H-bonding, the only one that was interpenetrated, and the only one that did not have a double-walled structure. Comparing the three magnesium MOF structures is more complicated. Mg-MOF-1 and Mg-MOF-3 are both 1D chains that run along the [1 0 1] diagonal axis, they both have double-walled structures and they both bind together via H-bonding to form a 3D network. The structure of Mg-MOF-1 is fairly simple with a single double-walled chain where the magnesium ions are bound to four L1 ions each and the L1 ions are bound to two magnesium ions each. The Mg-MOF-3 has four ligands stacked on top of each other with the outer two being perpendicular to the inner two’s double-walled core structure. The double-walled core of Mg-MOF-3 is also different from the other chain structure. Because each L1 ion in the core chain is bound to three magnesium ions, one from the phenanthroline and two from the same oxygen in the carboxylate group. The L1 ions on the outside of the chain are bound to two magnesium ions like the first structure but the magnesium ions are capped by DMF solvent molecules and non-bridging formate ions. The 3D structures of the two chains are different in that the zig-zag motif of Mg-MOF-1 produced moderately sized pores when packed together, whereas the chains of Mg-MOF-3 were so closely bound the pores were effectively non-existent.
Mg-MOF-2 is not too dissimilar to the structure that Mg-MOF-1 was expected to take. Considering the charge and coordination geometry of magnesium ions it would be expected that it would form an octahedral/pseudo-tetrahedral structure that would spread out and form a 2D or 3D framework. The formate bridging and binding between the carboxylate groups and multiple magnesium ions formed an SBU. This then allowed the L1 ions to spread out instead of bending back onto themselves and forming another 1D chain. Aside from that the biggest similarity between the two MOFs is that they are both double-walled. Thanks to the formate bridging SBU of Mg-MOF-2 the double-walled ligand chains are more spread out and consequently the pore sizes of the framework are larger than that of Mg-MOF-1. This is helped by the fact that it is a 2D structure and does not need to rely on H-bonding to hold the chains together, so it can have the ligands further apart while keeping the structure stable. As opposed to Mg-MOF-1, which is a series of 1D structures that need to be close enough together to H-bond, to keep the overall 3D structure intact.

Comparing Mg-MOF-2 to Mg-MOF-3 is interesting because, it seems that the chain structure was a partially formed structure that was unable to fully form as a 2D structure. The asymmetric unit of Mg-MOF-3 shows that, all the magnesium ions in Mg-MOF-3 are bound to a DMF solvent molecule and half of them are bound to a non-bridging formate ion. This likely formed a capping effect limiting the directions in which the structure could expand. In the 2D structure the magnesium ions bind to the same oxygen in the bridging formate ions. Whereas in the 1D structure the magnesium ions are bound to opposite ends of the bridging formate ions, making the magnesium ions further away from each other. Had the 1D structure been able to grow in more than one direction and become another 2D structure it likely would have had a different structure from Mg-MOF-2. It is difficult to determine why Mg-MOF-3 formed instead of Mg-MOF-2, especially considering that they both formed in the same crystal jar. However further research into the synthesis of Mg-MOFs with L1 have shown that when formic acid is present it is Mg-MOF-2 that forms usually. This seems to support the theory that Mg-MOF-3 was a by-product not the expected end-product.
The two new coordination polymers that were produced were both sodium containing molecules one that had bound to L1 and one that had bound to L2. The first coordination polymer was a double-walled 1D chain structure with a strong zig-zag motif. Because sodium has a five-coordinate binding geometry it binds to two L1 molecules at each end of the ligand, one ethanol solvent molecule and one water molecule. The water molecule is shared between two sodium ions which causes the structure to have its double-walled structure. The second coordination polymer is much more complicated. The asymmetric unit of the polymer has three Na⁺ ions, two L2²⁻ ions, coordinated and uncoordinated water molecules, an uncoordinated DMF solvent molecule, and a charge balancing uncoordinated NH₄⁺ ion. The five-coordinate nature of the sodium ions, combined with L2’s three functional groups which are in two different planes, and the coordinated water molecules, cause this structure to be very complicated. Generally speaking, the structure is a 3D, two-fold interpenetrated, network with relatively small pores. Comparing the two, Na-L1 is a relatively simple, non-interpenetrated, 1D, double-walled chain that can be H-Bonded to form a non-porous 3D structure. Whereas Na-L2 is a complex, two-fold interpenetrated, 3D, single walled network in which the two interpenetrated structures are bound together by H-bonding.

The two already existing MOFs that were produced were a zinc-L1 MOF with formate bridging and a magnesium formate MOF. The zinc MOF was a relatively new structure that was published in late 2020. The zinc MOF is a 3D structure with a 1D chain of zinc and formate ions acting as the core of the structure. Of the other MOFs produced the zinc MOF is most similar to the 2D magnesium MOF with formate bridging. But there are also some major differences, the ZN-MOF is 3D, interpenetrated and single walled, whereas the Mg-MOF-2 is 2D, not interpenetrated and has a double-walled structure. The magnesium formate MOF was a by-product of attempting to make other magnesium MOFs while using formic acid as a moderator. The magnesium formate MOF produced was a regular 3D structure that was not interpenetrated and had large pores down the b axis that were filled with DMF solvent molecules. Magnesium formate MOFs can form in a number of different topologies with very small variations depending on the coordination of the formate groups that form around the magnesium ions in the unit cell. Due to the small amounts of variations between literature examples of magnesium formate MOFs, the magnesium formate MOFs that were produced were nearly identical to a number of structures in the literature. The magnesium formate MOFs produced are not particularly similar to any of the other MOFs produced, not even the other Mg-MOFs that contained formate bridges.
Overall reported in this chapter were six new structures, five of which contain lightweight metal ions. This will likely lead into research on other structures using these ligands and other lightweight metals as well as these metal ions and other similar ligands. Expanded study into structures produced using L1 and L2 will likely lead to a wide variety of new structures due to how readily these ligands bind to the various metals that they come into contact with. That, combined with further study into the various other properties of the six already produced materials, will give a large amount of future work to be done in this field of research.
3.9 Experimental

General Information

Product Synthesis

All starting materials used were purchased from commercial suppliers and used as received with no further purification required. All solvents were also used as received and were of LR grade or better. For the product compounds which have been previously reported characterisation was used only to determine their successful synthesis.

X-ray Crystallography

Single crystals were mounted in paratone-N oil on a nylon loop. Single crystal X-ray data were collected on an Agilent Technologies Supernova system at 100 K at the University of Otago using mirror monochromated Mo Kα (λ = 0.71073 Å) radiation. The data were treated using CrysAlisPro software and Gaussian absorption corrections were applied. Intensities were corrected for Lorentz and polarization effects and a multi-scan absorption correction was applied. The structures were solved by direct methods SHELXT\textsuperscript{78} and refined on F2 using all data by full-matrix least-squares procedures SHELXT interfaced through the program WINGX.\textsuperscript{79} Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in ideal positions unless specified in special refinements. All calculations were performed using the WinGX interface.\textsuperscript{79} Detailed analyses of the extended structure were carried out using Mercury (Version 3.5.1).\textsuperscript{80} The CIF file generated from single crystal X-ray crystallography has been CIF checked and is of the standard required for publication.
Attempted Synthesis of Ligand 1 Ruthenium-Cobalt Photo-MOF (Ru-L1-Co Photo-MOF)

Ruthenium metallo-ligand and cobalt nitrate hexahydrate were placed in a small sample vial then dissolved in a solvent/acid solution via sonication at room temperature for 15 minutes. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The samples were left overnight before being place in the oven. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr. This method was repeated 6 times with variations on the acid/solvent combination solution as shown below. No viable crystals formed.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mass of Ruthenium Metallo-ligand</th>
<th>Mass of Cobalt Nitrate Hexahydrate</th>
<th>Solvent (volume)</th>
<th>Acid (volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>164-1</td>
<td>16.2 mg</td>
<td>29.2 mg</td>
<td>DMF (1.47 mL)</td>
<td>TFA (0.03 mL)</td>
</tr>
<tr>
<td>164-2</td>
<td>16.4 mg</td>
<td>31.9 mg</td>
<td>DEF (1.47 mL)</td>
<td>TFA (0.03 mL)</td>
</tr>
<tr>
<td>164-3</td>
<td>16.3 mg</td>
<td>32.1 mg</td>
<td>DMF (1.47 mL)</td>
<td>Formic acid (0.03 mL)</td>
</tr>
<tr>
<td>164-4</td>
<td>16.8 mg</td>
<td>30.6 mg</td>
<td>DEF (1.47 mL)</td>
<td>Formic acid (0.03 mL)</td>
</tr>
<tr>
<td>164-5</td>
<td>16.2 mg</td>
<td>32.3 mg</td>
<td>DMF (1.47 mL)</td>
<td>Acetic Acid (0.03 mL)</td>
</tr>
<tr>
<td>164-6</td>
<td>16.3 mg</td>
<td>33.2 mg</td>
<td>DEF (1.47 mL)</td>
<td>Acetic acid (0.03 mL)</td>
</tr>
</tbody>
</table>

Attempted Synthesis of Ligand 1 Ruthenium-Copper Photo-MOF (Ru-L1-Cu Photo-MOF)

Ruthenium metallo-ligand (16.4 mg, 0.010 mmol) was dissolved in a DMF/TFA solution (50:1 1.5 mL). Then copper nitrate trihydrate (24.2 mg, 0.100 mmol) was added and the solution was sonicated for 15 minutes at room temp. The solution was filtered to remove any undissolved solids and the resulting solution was poured into a small sample vial. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 120 °C for 72 hr. No viable crystals formed.
Attempted Synthesis of Ligand 1 Ruthenium-Zinc Photo-MOF (Ru-L1-Zn Photo-MOF)²

Ruthenium metallo-ligand (16.4 mg, 0.010 mmol) was dissolved in a DMF/TFA solution (50:1 1.5 mL) in a small sample vial. Then zinc nitrate hexahydrate (18.9 mg, 0.100 mmol) was added, and the solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 100 °C for 72 hr. No viable crystals formed.

Attempted Synthesis of Ligand 1 Ruthenium-Cadmium Photo-MOF (Ru-L1-Cd Photo-MOF)²

Ruthenium metallo-ligand and cadmium nitrate tetrahydrate were placed in a small sample vial then dissolved in a solvent/acid solution via sonication at room temperature for 15 minutes. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The samples were left overnight before being place in the oven. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr. This method was repeated 6 times with variations on the acid/solvent combination solution as shown below. No viable crystals formed.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mass of Ruthenium Metallo-ligand (mg)</th>
<th>Mass of Cadmium Nitrate Tetrahydrate (mg)</th>
<th>Solvent (volume)</th>
<th>Acid (volume)</th>
</tr>
</thead>
<tbody>
<tr>
<td>170-1</td>
<td>14.4 mg</td>
<td>33.6 mg</td>
<td>DMF (1.47 mL)</td>
<td>TFA (0.03 mL)</td>
</tr>
<tr>
<td>170-2</td>
<td>12.3 mg</td>
<td>32.3 mg</td>
<td>DEF (1.47 mL)</td>
<td>TFA (0.03 mL)</td>
</tr>
<tr>
<td>170-3</td>
<td>12.9 mg</td>
<td>34.8 mg</td>
<td>DMF (1.47 mL)</td>
<td>Formic acid (0.03 mL)</td>
</tr>
<tr>
<td>170-4</td>
<td>13.0 mg</td>
<td>31.4 mg</td>
<td>DEF (1.47 mL)</td>
<td>Formic acid (0.03 mL)</td>
</tr>
<tr>
<td>170-5</td>
<td>12.1 mg</td>
<td>32.0 mg</td>
<td>DMF (1.47 mL)</td>
<td>Acetic Acid (0.03 mL)</td>
</tr>
<tr>
<td>170-6</td>
<td>Approx. 10 mg</td>
<td>31.1 mg</td>
<td>DEF (1.47 mL)</td>
<td>Acetic acid (0.03 mL)</td>
</tr>
</tbody>
</table>
Attempted Synthesis of Ligand 1 Ruthenium-Zinc Photo-MOF (Ru-L1-Zn Photo-MOF)²

Ruthenium metallo-ligand (16.4 mg, 0.010 mmol) was dissolved in a DMF/TFA solution (50:1 1.5 mL) in a small sample vial. Then zinc nitrate hexahydrate (1.9 mg, 0.010 mmol) was added, and the solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 100 °C for 72 hr. No viable crystals formed.

Partially Successful Synthesis of Ligand 1 Ruthenium-Cadmium Photo-MOF (Ru-L1-Cd Photo-MOF)²,¹⁰

Ruthenium metallo-ligand (16.4 mg, 0.010 mmol) was dissolved in a DMF/Formic Acid solution (50:1 1.5 mL) in a small sample vial. Then cadmium nitrate tetrahydrate (30.8 mg, 0.100 mmol) was added and the solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr and cooled for approx. 24 hr until orange-red crystals formed.

Synthesis of Ligand 1 Zinc Photo-MOF (Zn-L1 Photo-MOF)¹⁰

Ligand 1 (8.3 mg, 0.020 mmol) and Zinc nitrate hexahydrate (3.0 mg, 0.010 mmol) were dissolved in a DMF/Formic Acid solution (50:1 1.5 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr and slowly cooled until colourless crystals formed. Method was repeated once.

Partially Successful Synthesis of Ligand 1 (L1) Crystals¹⁰

Ligand 1 (8.4 mg, 0.020 mmol) was dissolved in a DMF/Formic Acid solution (50:1 1.5 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr and slowly cooled until white crystals formed.
Synthesis of Ligand 1 Magnesium Photo-MOF (Mg-L1 Photo-MOF)\textsuperscript{10}

Ligand 1 (8.4 mg, 0.020 mmol) and magnesium nitrate hexahydrate (2.6 mg, 0.010 mmol) were dissolved in a DMF/Formic Acid solution (50:1, 2 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr and slowly cooled until orange-red crystals formed.

**Partially Successful Synthesis of Ligand 1 (L1) Crystals\textsuperscript{2,10}**

Ligand 1 (8.4 mg, 0.020 mmol) was dissolved in ethanol (2 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 90 °C for 24 hr and slowly cooled until white crystals formed. This method was repeated once more. After the solutions had cooled, the residual ethanol was decanted off and combined into another small sample vial and left in the cupboard without a lid to evaporate.

**Partially Successful Synthesis of Ligand 2 (L2) Crystals\textsuperscript{2,10}**

Ligand 2 (4.6 mg, 0.010 mmol) was dissolved in a DMF/Ammonium hydroxide (28%) solution (50:1, 2 mL) in a small sample vial. The solution was sonicated for 20 minutes at room temp. The open vial was placed inside a glass jar and sealed with a golden cap, which was placed into a sealed metal tube. The metal tube was placed upright in the oven and heated to 140 °C for 72 hr and slowly cooled until red crystals formed.
Chapter 4: Future Work

4.1 Restrictions in Research

Since this thesis is a one-year research only Master’s thesis, the limited time frame was the largest obstacle regarding this investigation. This was compounded by the approximately two-month long lockdown caused by the COVID-19 pandemic that began on March 23rd, less than one month into the start of this paper. Due to these factors, we have only just begun to research lightweight magnesium MOFs, L1 and L2, and their analogues.
4.2 Expanded Study of Lightweight Magnesium-L1 MOFs

Three different Mg-L1 MOFs have been synthesised and characterised via X-ray crystallography, as such, studies into the properties of those Mg-MOFs would be the next step. As the current method of synthesis of the Mg-MOF crystals results in a very small crystalline product, the first step would be determining a method of bulk synthesis of the Mg-MOFs. The planned method for this will involve dissolving L1 and magnesium nitrate in a more volatile solvent like methanol and adding a small amount of DMF. The solution is then sealed with a rubber cap with a needle pierced through the cap. The solution is heated around the volatile solvent's boiling point for a number of days until the volatile solvent has all or mostly evaporated. Depending on which Mg-MOF is desired, formic acid could also be added to produce a bulk amount of the Mg-MOFs with formate bridging (Scheme 4.1). This method would ideally produce either bulk crystals or bulk powder of the MOF, either of which will be useful for various types of analysis.

Scheme 4.1: Reaction scheme for the potential bulk synthesis of Mg-MOFs.

Once a reliable method of bulk synthesis of the various Mg-MOFs is determined, the study of the properties of the Mg-MOFs could begin. These studies would likely focus on the gas adsorption capacities and photophysical properties of the Mg-MOFs. Due to the lightweight nature and moderately sized pores of the Mg-MOF (Mg-MOF-1 and Mg-MOF-2), investigation into their ability to adsorb lightweight gasses such as H₂, N₂, or CO₂ could prove to be very fruitful. Regarding the photophysical properties of the Mg-MOFs, L1 and other similar phenanthroline containing organic molecules and metal-organic complex/frameworks have shown to be photoactive. As such the phenanthroline containing Mg-MOFs are therefore almost guaranteed to have some photoactive properties. As an extension of the gas adsorption studies of the Mg-MOFs isoreticular analogues of those MOFs (Mg-IRMOFs) will be synthesised (Scheme 4.2) and characterised, and their gas adsorption properties will be analysed. The ligand used for this will be 2-(4-carboxyphenyl)imidazo(4, 5-f)-1, 10-phenanthroline (HNCP), which is a shorter version of L1 with one less benzene ring.

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Scheme 4.2: Reaction scheme for the potential bulk synthesis of Isoreticular Magnesium Metal-Organic Frameworks (Mg-IRMOFs).

The gas adsorption and photophysical properties of the IRMOFs formed will be studied and compared to their respective isoreticular analogues. Further study into other lightweight non-transition metals and their capacity to form MOFs with L1 and HNCP will also be investigated compared to the Mg-MOFs formed.
4.3 Continued Study of L2, L3, and L4

Due to a lack of time and the difficulties of synthesising L2, additional study into L2 and the potential MOFs it could form, is also a worthwhile endeavour. Due to the more insoluble nature of L2, the bulk synthesis will likely be more difficult, but small-scale MOF synthesis with various metals will certainly be interesting. Firstly, more effective/reliable methods of synthesising L2 will be determined if possible. From there a complete characterisation of L2, including producing a crystal structure of unbound L2, will take place. From there a series of different metals, including transition metals and s-block metals, starting with magnesium, will be reacted with L2 to attempt to produce a series of MOFs. As well as L2 attempts will be made to produce L3 and L4 as well as any other similarly structured organic ligands. They, too, will be reacted with a series of metals starting with magnesium to produce various new MOF structures.
4.4 Ruthenium-Ligand Complexes and MOFs

Previous attempts made to produce a ruthenium-ligand complex using a modified literature method ended up producing impure mixed products that were not useful for the purposes of MOF synthesis. As such a method identical to the literature method will be used in the future to produce various bimetallic ruthenium-metal MOFs. This will also likely take place with various ligands aside from L1. The first ruthenium-metal MOF to be studied will likely be a ruthenium-copper MOF using L1 as the bridging ligand between the two metal ions.

Scheme 4.3: Synthesis of [Ru(phenanthroline-dione)₃]Cl₂ literature method.²

Scheme 4.4: Synthesis of [Ru(ligand)₃][PF₆]₂ literature method.²

Once a reliable method for the synthesis of bimetallic ruthenium-metal MOFs (Ru-M-MOFs) is found, characterisation of the products will take place. Then once a method to produce bulk quantities of the Ru-M-MOFs is determined, study of the gas adsorption and photophysical properties will also be undertaken.
References


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(65) Tokarev, S. D.; Fedorov, V. V.; Fedorova, O. A. Imidazo[4,5-f][1,10]phenanthroline complexes with Fe2+, Cd2+, Co2+ and Zn2+ ions. Mendeleev Commun. 2020, 30 (4), 445.


(73) Hamilton, A.; Cheng, Y.-C.; Yale University, USA . 2011.


(83) Borsari, M., 2014; p 1.


Appendix
Crystallographic tables

**Ligand Crystal Table**

<table>
<thead>
<tr>
<th>Structure</th>
<th>L1</th>
<th>Methylated-L2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{29}H_{23}N_{5}O_{3}</td>
<td>C_{31}H_{26}N_{4}O_{5}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>489.5</td>
<td>534.6</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>a/Å</td>
<td>13.4849(6)</td>
<td>18.307(2)</td>
</tr>
<tr>
<td>b/Å</td>
<td>17.7511(10)</td>
<td>19.497(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>9.7383(5)</td>
<td>14.2497(15)</td>
</tr>
<tr>
<td>α°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β°</td>
<td>96.602(4)</td>
<td>95.074(11)</td>
</tr>
<tr>
<td>γ°</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/Å³</td>
<td>2316(11)</td>
<td>5066 (51)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>T/K</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.094</td>
<td>0.097</td>
</tr>
<tr>
<td>Total reflections</td>
<td>18546</td>
<td>37591</td>
</tr>
<tr>
<td>Unique reflections (R_{int})</td>
<td>5147 (0.0351)</td>
<td>9361(0.2046)</td>
</tr>
<tr>
<td>R1 indices [I&gt;2σ(I)]</td>
<td>0.0618</td>
<td>0.1161</td>
</tr>
<tr>
<td>ωR2 (all data)</td>
<td>0.1690</td>
<td>0.2450</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>5147/0/337</td>
<td>9361/0/727</td>
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</table>

**MOF Crystal Tables**

<table>
<thead>
<tr>
<th>Structure</th>
<th>Cd-MOF</th>
<th>Mg-MOF-1</th>
<th>Mg-MOF-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{26}H_{18}N_{4}O_{2}Cd_{0.5}</td>
<td>C_{52}H_{32}N_{8}O_{3}Mg</td>
<td>C_{53}H_{31}N_{8}O_{3}Mg_{2}</td>
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<tr>
<td>Formula weight</td>
<td>471.6</td>
<td>873.2</td>
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<tr>
<td>Crystal system</td>
<td>Fddd</td>
<td>P2_1/c</td>
<td>P2_1/c</td>
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<tr>
<td>Space group</td>
<td>Orthorhombic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>17.5077(12)</td>
<td>16.9435(15)</td>
<td>16.4368(8)</td>
</tr>
<tr>
<td>b/Å</td>
<td>34.835(2)</td>
<td>15.3576(13)</td>
<td>22.443(2)</td>
</tr>
<tr>
<td>c/Å</td>
<td>52.499(4)</td>
<td>17.4249(15)</td>
<td>16.1269(14)</td>
</tr>
<tr>
<td>α°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β°</td>
<td>90</td>
<td>90.192(8)</td>
<td>93.519(6)</td>
</tr>
<tr>
<td>γ°</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V/Å³</td>
<td>32018(39)</td>
<td>4534(7)</td>
<td>5938(23)</td>
</tr>
<tr>
<td>Z</td>
<td>32</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>T/K</td>
<td>100(2)</td>
<td>127(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
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<td>0.097</td>
<td>0.095</td>
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<tr>
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<td>29422</td>
<td>19275</td>
<td>47518</td>
</tr>
<tr>
<td>Unique reflections (R_{int})</td>
<td>6716(0.1609)</td>
<td>9036(0.0661)</td>
<td>12987(0.1103)</td>
</tr>
<tr>
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<td>0.0903</td>
<td>0.1029</td>
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<tr>
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<td>0.2575</td>
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<td>Structure</td>
<td>Mg-MOF-3</td>
<td>Na-L1-Polymer</td>
<td>Na-L2 Polymer</td>
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</tr>
<tr>
<td>Formula</td>
<td>C_{60}H_{46}N_{10}O_{11}Mg_{2}</td>
<td>C_{28}H_{20}N_{4}O_{5}Na</td>
<td>C_{57}H_{35}N_{10}O_{14}Na_{3}</td>
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<tr>
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<td>Crystal system</td>
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<td>C2/c</td>
<td>P-1</td>
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<td>Monoclinic</td>
<td>Triclinic</td>
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<td>a/Å</td>
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<td>12.250(4)</td>
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<tr>
<td>b/Å</td>
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<tr>
<td>c/Å</td>
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<td>17.285(6)</td>
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<tr>
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<td>62.10(3)</td>
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<tr>
<td>β/°</td>
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<tr>
<td>γ/°</td>
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<td>69.56(3)</td>
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<tr>
<td>V/Å³</td>
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<td>2801(737)</td>
</tr>
<tr>
<td>Z</td>
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<td>8</td>
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</tr>
<tr>
<td>T/K</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<tr>
<td>μ/mm(^{-1})</td>
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<td>0.110</td>
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<tr>
<td>Total reflections</td>
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<td>43227</td>
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<td>Unique reflections (R_{int})</td>
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<td>5321(0.1443)</td>
<td>12307(0.3539)</td>
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