SYNTHESIS AND CHARACTERIZATION OF COORDINATION POLYMERS AND STUDIES FOR
CO$_2$ CAPTURE

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Abstract

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The work in this dissertation is presented in two sections. Section 1 investigates the use of large metal cations in the construction of coordination polymers. Section 2 focuses on the synthesis of functionalized linkers for the construction of metal-organic frameworks (MOFs) for CO₂ uptake.

Chapters 2 and 3 describe work done on alkali metal aryloxide systems. Our group has previously shown alkali metal aryloxide aggregates are good candidates as secondary building units in the construction of coordination polymers. The majority of the previous work was done with lithium and sodium. The work described in Chapters 2 and 3 details the synthesis and structural characterization of potassium, rubidium and cesium phenoxide materials. A set of isostructural potassium, rubidium and cesium 4-ethylphenoxide species form 1-D inorganic rods, which are subsequently linked together to form 3-D hybrid organic-inorganic materials. Also, a series of three new cesium 2-iso-propylphenoxide materials has been characterized. Two of the three
species are hybrid organic-inorganic materials constructed of 1-D inorganic rods. Formation of 1-D inorganic rods is an emerging trend for large alkali metal phenoxide systems.

The final portion of Section 1 discusses work performed with various large metal cations including potassium, barium, lanthanum, cerium, neodymium and gadolinium. Prepared materials include 1-D chains, 2-D sheets, and 3-D networks. A homologous series of 2-D sheets is described in Chapter 4. The materials, 

\[[\text{LnX(C}_{10}\text{H}_{8}\text{N}_2\text{O}_2)_4(\text{CH}_3\text{OH})]^2\{\text{B(Ph)}_4\}^2\cdot(\text{CH}_3\text{OH})\} \text{ (Ln = La, X + Cl; Ln = Ce, X = Br; Ln = Gd, X = Cl)}\]

form 2-D square nets in which the lanthanide is bridged to four neighboring metal centers through 4,4'-dipyridyl-N,N'-dioxide linkers. Chapter 5 details the structural characterization of three interesting solids, a 1-D neodymium benzoate material, a 3-D potassium network and a 3-D barium material composed of a highly charged \([\text{Ba}_2(\text{C}_{10}\text{H}_{8}\text{N}_2\text{O}_2)_6]^{4+}\) network with a polymeric \([\text{Ba}_2(\text{NO}_3)_8]^{4-}\) anion in the channels.

Section 2 describes the synthesis, characterization and deprotonation studies on imidazolium based organic molecules and their use as linkers for the construction of MOFs for CO$_2$ uptake. Five imidazolium based organic linking molecules have been synthesized. These linkers were used in the construction of 1-D, 2-D, and 3-D MOFs. Two of the 2-D materials, \([\text{La}_3(\text{HL1Br})_2(\text{L1})(\text{OH})_3]\) and \([\text{Nd}(\text{HL1Br})_{1.5}(\text{H}_2\text{O})_{1.5}]\) are very similar and are constructed of 1-D lanthanide-carboxylate chains. A related 3-D material, \([\text{Nd}_2(\text{HL1Br})_3(\text{bipy})_{0.5}]\), is constructed of 2-D sheets nearly identical to those in \(7.4\) which are connected through 4,4'-bipyridine linkers.
For my parents, Jim & Sylvia, and my wife, Michelle, thank you.
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ABBREVIATIONS

1-D: One dimensional
2-D: Two dimensional
3-D: Three dimensional
bipy: 4,4’-bipyridine
bipy-O2: 4,4’-dipyridyl-N,N’-dioxide
CP: Coordination Polymer
H₂BDC: 1,4-benzenedicarboxylic acid
BuLi: n-butyl lithium
CSD: Cambridge Structural Database
diox: 1,4-dioxane
DMF: N,N-dimethylformamide
ESI-MS: Electrospray Ionization Mass Spectrometry
MOF: Metal-Organic Framework
PXRD: Powder X-ray Diffraction
SBU: Secondary Building Unit
THF: Tetrahydrofuran
NUMBERED COMPOUNDS

2.1 [{(4-Et-C₆H₄OLi)₄·(diox)₂·diox}]

2.2 [(4-Et-C₆H₄ONa)₆·(diox)₃]

2.3 [(4-Et-C₆H₄OK)₃·(diox)]

2.4 [(4-Et-C₆H₄ORb)₂·(diox)₀·₅]

2.5 [(4-Et-C₆H₄OCs)₂·(diox)₀·₅]

3.1 [(2-iPr-C₆H₄OCs)₂(H₂O)(diox)₀·₅]

3.2 [(2-iPr-C₆H₄OCs)₄(H₂O)₂·diox]ₑ·₅·₅

3.3 [(2-iPr-C₆H₄OCs)₃(H₂O)(diox)₂·₅]

4.1 [{LaCl(C₁₀H₈N₂O₂)₄(CH₃OH)]²⁺{B(C₆H₅)₄}₂(CH₃OH)]

4.2 [{CeBr(C₁₀H₈N₂O₂)₄(CH₃OH)]²⁺{B(C₆H₅)₄}₂(CH₃OH)₂]

4.3 [{GdCl(C₁₀H₈N₂O₂)₄(CH₃OH)]²⁺{B(C₆H₅)₄}₂(CH₃OH)₂]

5.1 [K₂(O₂C₆H₃N₂)₂(H₂O)₂·₂(H₂O)]

5.2 [{Ba₂(C₁₀H₈N₂O₂)₆}⁺⁺{Ba₂(NO₃)₈}⁺⁺]

5.3 [Nd₂Cl(C₆H₅COO)₅·(diox)]

7.1 [{CoCl(HL²)(CH₃COO)}⁻·{H₃L²}⁺]

7.2 [Cd(HL₁)₂·DMF]

7.3 [La₃(HL₁Br)₂(L₁)(OH)₃]
7.4 [Nd(HL1Br)_{1.5}(H_2O)_{1.5}]
7.5 [Nd_2(HL1Br)_3(bipy)_{0.5}]
7.6 [Cd_3K_2(HL5)_6·2H_2O]
SECTION 1: COORDINATION POLYMERS BUILT FROM LARGE METAL CATIONS

This section of the thesis focuses on our work to build coordination polymers using large metal cations (e.g. potassium, rubidium, cesium, barium and various lanthanides) to synthesize high-connectivity networks. Chapter 1 provides a general background on metal-organic frameworks (MOFs) and coordination polymers (CPs) as well as a brief discussion on network topology. Chapters 2 and 3 discuss alkali metal aryloxide materials prepared. Chapter 4 details an isoreticular series of lanthanide 2-D materials, and Chapter 5 contains fortuitous materials that were isolated.
CHAPTER 1:
INTRODUCTION

1.1 Overview

The synthesis and characterization of extended coordination networks is currently an area of both industrial and academic interest due to the many potential applications of these materials.\(^1-^4\) Rational and controlled design of these extended structures is still one of the primary challenges facing synthetic chemists.\(^5\) This chapter will provide background information on the design of coordination networks, previous work on alkali metals in CPs from our group including a brief introduction into network topology, and an overview of the work detailed in this section of the thesis.

1.2 The design of extended network materials

The node and linker approach to designing network materials, first described approximately 20 years ago,\(^6-^8\) uses metal ions as nodes and organic molecules as linkers. This approach builds off of classic coordination chemistry in which the metal ions have preferred coordination numbers and geometries. Extended polymeric materials may be produced when metal ions are paired with non-chelating ditopic organic ligands, Figure 1.1.
Figure 1. Illustration of the coordination of metals with a) convergent organic ligands to form molecular materials, and b) divergent organic linkers to form extended materials.

The type of interaction between the metal and the organic molecule determines what we call these materials. If the interaction is covalent the material is a metal-organic framework (MOF). Typically, MOFs contain organic linkers utilizing carboxylate groups or tetrazolate groups to coordinate to the metal, Figure 1.2a. If the interaction between the metal and linker is a Lewis acid/base interaction, the material is called a coordination polymer (CP). Common organic linkers in CPs use pyridyl groups, neutral oxygen donors or cyclic ethers to coordinate to the metal, Figure 1.2b. The choice of the metal greatly influences the resultant network because of its preferred coordination geometry. The geometries of the node and linker ultimately determine the type of network produced. For example, a tetrahedral node in combination with a linear divergent linker generally leads to a diamondoid network, Figure 1.3. \[
\{\text{Cu}_2(4,4'-\text{bipy})_4\cdot(D-\text{HCam})_2\cdot(4,4'-\text{bipy})_2\cdot12\text{H}_2\text{O}\}\text{ is a 3-D diamondoid material in which the Cu(II) ion adopts a tetrahedral coordination geometry. The Cu(II) metal center is the node and}
\]
4,4’-bipyridine acts as the linker, Figure 1.3. This is a porous material and it crystallizes with two mono-deprotonated D-camphorate anions, two 4,4’-bipyridine molecules and 12 solvent water molecules in the void space.\(^9\)

Figure 1.2. Some examples of common linkers used in a) MOFs and b) CPs.

![Diagram](image)

Figure 1.3. The complex \([\{\text{Cu}_2(4,4’-\text{bipy})_4(\text{D-HCam})_2(4,4’-\text{bipy})_2\cdot12\text{H}_2\text{O}\}\) forms a diamondoid net. The Cu ion is tetrahedrally coordinated by the 4,4’-bipy linkers. The Cu ion is the node and the 4,4’-bipyridine molecules are the linkers. All hydrogen atoms, counter ions and solvent molecules have been removed for clarity. Green – Cu, blue – N, black – C.

A similar strategy to designing network materials is the secondary building unit (SBU) approach. This strategy utilizes discrete metal aggregates as the nodes and organic molecules as the linkers, Figure 1.4. The discrete metal aggregates are called
secondary building units, hence the name the “SBU approach” to building networks.

Aside from the switch from a single metal center to SBU, this approach works similarly
to the node and linker strategy described above. The advantage to using this approach
is that more nodal geometries, and thus more networks, are accessible. For example, a
Y-shaped node with a single metal center would be difficult to achieve using a metal ion,
however, with SBUs it is more likely since that would require a tri-metallic aggregate
(Figure 1.4).

![Diagram showing the relationship between selected metal aggregates and their related nodal geometries.]

**Figure 1.4.** Relationship between selected metal aggregates and their related nodal geometries.
Metal aggregates with terminal ligands are common in classic coordination chemistry and so replacing those ligands with divergent linkers may lead to network materials, Figure 1.5. A molecular complex, [(Zn₄O)(C₆H₅COO)₆], consists of a [Zn₄O]⁶⁺ cluster in which the four Zn atoms sit at the corners of a tetrahedron that is centered by an oxo group. Each Zn-Zn edge of this tetrahedron is bridged by the carboxylate group of a benzoate, Figure 1.5a.¹⁰ In work by Yaghi’s group¹¹ the benzoic acid ligands surrounding the [Zn₄O]⁶⁺ cluster are replaced by the divergent linker 1,4-benzenedicarboxylic acid linkers, Figure 1.5b. This results in a 3-D material with primitive cubic topology where each [Zn₄O]⁶⁺ cluster is a node and the BDC molecules are linkers.

Figure 1.5. [Zn₄O]⁶⁺ aggregates in a) a molecular complex with benzoic acid, and b) the 3-D material, MOF-5, where benzoic acid has been replaced with benzene dicarboxylic acid. The [Zn₄O]⁶⁺ unit is the SBU for MOF-5.
1.3 Applications of MOFs and CPs

The interest in extended network solids comes from the numerous potential applications of these materials. These include a variety of fields such as catalysis, separation science, and small molecule storage to name a few. The broad applicability of these materials is typically due to their potential for high surface area, permanent porosity and the presence of tunable organic linkers. This section will highlight examples of the use of MOFs or CPs in each of these three areas. For a more complete review on the potential application of extended network solids a book on the subject was recently published.

The use of MOFs as heterogeneous catalyst has been an area of interest due to the tunability of the organic linkers. Wu and co-workers reported the synthesis of a homochiral cadmium MOF that could be used for asymmetric catalysis. The material, \([\text{Cd}_3\text{Cl}_6\text{L}_3\cdot4\text{DMF}\cdot6\text{MeOH}\cdot3\text{H}_2\text{O}]\) (\(L = (\text{R})\)-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthyl-4,4′-bipyridine), utilizes chiral organic linkers to build a porous MOF. The MOF can chemisorb titanium isopropoxide, which in turn catalyzes the highly enantioselective addition of ZnEt₂ to aromatic aldehydes. It was shown to rival homogeneous catalysts in enantiomeric excess and percent conversion for the transformation of 1-naphthaldehyde to \((\text{R})\)-1-(1-naphthyl)propanol. A variety of other aromatic aldehydes were tested with positive results.

Extended network solids have found a place in separation science due to their porous nature and the tunability of the pore size based on the choice of organic linker. The separation of alkane isomers is important in the petroleum industry to boost octane
ratings. Chen and co-workers reported the first example of a MOF that could be used for gaseous separation of alkane isomers.\textsuperscript{22} The 3-D network is flexible and expands and contracts upon guest uptake/removal. It is composed of \([\text{Zn}_2\text{(BDC)}_4]\) paddle-wheels, a classic dimeric unit in coordination chemistry, and the axial position of the paddle-wheel are occupied by 4,4'-bipy linkers, Figure 1.6. Upon guest removal, the paddle-wheel distorts and the 4,4'-bipy linkers bend, this accounts for the flexibility of the network. The 1-D channels are approximately 4.0 x 4.0 Å in cross-section, which is an ideal size to separate alkane isomers. A GC column packed with crystalline guest-free material was able to successfully separate mixtures of 2- methylbutane, n-pentane, 2,2-dimethylbutane, 2-methylpentane, and n-hexane.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_6.png}
\caption{a) The paddle-wheel structure of the SBU of \([\text{Zn(BDC)(bipy)}_{0.5}]\). b) A view of the 3-D \textbf{pcu} network showing the pores where alkane isomers can be separated.}
\end{figure}
The intense interest in network materials in recent years stems mostly from the potential of these solids in small molecule storage. Hydrogen storage in particular has been widely studied for use as a system for onboard storage of H\(_2\) in the automotive industry. Two of the best materials to date will be outlined here,\(^{27,28}\) for more information Yuan and Zhou have recently published a review on the state of the art in this area.\(^{29}\) The two materials being described here, [Zn\(_4\)O(bte)\(_{4/3}\)(bpdc)] (bte = 4,4′,4″-benzene-1,3,5-triyl-tris (ethyne-2,1-diyl)]tribenzoate ; and bpdc = biphenyl-4,4′-dicarboxylate) (MOF-210)\(^{28}\) and [Cu\(_3\)(ttei)] (ttei = 5,5′,5″–(((benzene-1,3,5-triyltris(ethyne-2,1-diyl))tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))triisophthalate) (NU-100),\(^{27}\) hold the record for highest surface area and largest H\(_2\) uptake for framework materials, respectively. For some perspective, the DOE has published targets for onboard hydrogen storage systems of 0.045 kg/kg by 2010 and 0.055 kg/kg by 2015.\(^{30}\) The units kg/kg = (mass of adsorbed H\(_2\))/(mass of absorbed H\(_2\) + mass of host). It is important to note that the mass of the host for an automotive application includes the weight of the container as well as other necessary components.

The current record holding material for highest surface area, [Zn\(_4\)O(bte)\(_{4/3}\)(bpdc)] (MOF-210), has a BET surface area of 6240 m\(^2\)g\(^{-1}\) and a Langmiur surface area of 10400 m\(^2\)g\(^{-1}\).\(^{28}\) MOF-210 also has a large H\(_2\) uptake at 0.0792 kg/kg at 77k and 50 bar. Evacuation of the pores was achieved with MOF-210 through the use of the supercritical CO\(_2\) method.\(^{31}\) Powder X-ray diffraction showed that the material retained its crystallinity, however, TGA showed that the material was not thermally stable.\(^{28}\) It is somewhat surprising that the MOF could be evacuated and retain crystallinity, often
times highly porous materials collapse once the guest solvent molecules are removed.
The current record holding material for largest H\(_2\) uptake, \([\text{Cu}_3(\text{ttei})]\) (NU-100), has an
uptake of 0.0905 kg/kg at 77K and 56 bar.\(^{27}\) Nu-100 also has a high BET surface area of
6143 m\(^2\)g\(^{-1}\). Activation of this material by removing all guest solvent molecules was also
achieved using supercritical CO\(_2\), and crystallinity was retained as confirmed by PXRD.
Surprisingly, TGA showed that this highly porous material was thermally stable to
325°C.\(^{27}\) While the uptake numbers above exceed both the 2010 and 2015 DOE targets,
there are two important things to consider. 1) The mass of the host is only the mass of
the framework itself. In a real world situation all of the necessary hardware would also
have to be considered, and this is a very significant amount of mass. 2) These
measurements were taken at a temperature of 77K, which is not a practical
temperature to maintain on an automobile.

1.4 Alkali metals in extended network materials

The vast majority of research on extended networks has been done with
transition metals, and specifically mid to late first row transition metals. Consequently,
very little work has been done in the area of s-block metals in extended networks.
There are a variety of reasons why these metals have been somewhat ignored; they
exhibit complex solution equilibria between aggregated complexes, the metal ligand
bonding is labile, the preference for fixed geometries and the spherical non-polarizable
nature of the cations all could lead to potential problems in network formation.\(^{32-34}\)
There are however a number of detailed studies on the factors determining the
molecular structure of alkali metal complexes, particularly lithium aryloxides in the solid state\textsuperscript{35–44} and solution\textsuperscript{45–52}. They tend to form well defined aggregates, most commonly tetrameric cubanes or ring dimers.\textsuperscript{35,37,39,41–44} The degree of aggregation for these complexes depends on several factors; the amount of steric bulk at the ortho positions, the nature of the donor solvent and electronic effects due to substitution of the aryl ring. This makes them ideal candidates to be used as SBU\textsuperscript{s} in the construction of network materials.

Our group decided to explore this area by rationally designing SBU\textsuperscript{s} through the judicious choice of aryloxide anion. The resultant SBU\textsuperscript{s} would then be linked into CPs through 1,4-dioxane, which is a divergent Lewis basic linker. Lithium aryloxide tetrameric cubanes are common aggregates in the solid state, and by introducing the divergent Lewis base dioxane a series of polymeric materials was synthesized\textsuperscript{53}. Interestingly, by varying only the aryloxide ligand, 1-D, 2-D and 3-D materials were all synthesized with [ArOLi]\textsubscript{4} SBU\textsuperscript{s}, Figure 1.7. The 1-D complex utilized simple phenoxide, and formed a tetrasolvated [(C\textsubscript{6}H\textsubscript{5}O)Li]\textsubscript{4} SBU, however only two of the four dioxane solvent molecules bridged. This led to a 1-D zig-zag chain structure, Figure 1.7a. Next 4-ethylphenoxide was used, and again a tetrasolvated [(4-Et-C\textsubscript{6}H\textsubscript{5}O)Li]\textsubscript{4} SBU formed. This time three of the four dioxanes bridged leading to a 2-D material, Figure 1.7b. A more complete discussion of this material is in Chapter 2. Finally, the 3-D material was synthesized with the much bulkier 1-naphthanol. All four solvent molecules of the tetrasolvated [(C\textsubscript{10}H\textsubscript{7}O)Li]\textsubscript{4} SBU bridge to neighboring SBU\textsuperscript{s} leading to a diamondoid net, Figure 1.7c.
The reason these similar aryloxide ligands lead to different extended structures is due to the efficiency with which they fill the void space in the structures. The smallest of the ligands, phenol, forms a 1-D chain because forming a 2-D or 3-D network would leave a large amount of void space which is unstable. A similar explanation can be used for the 2-D 4-ethylphenol material, a 3-D diamondoid network would have too much void space for the structure to support. The largest of the ligands, 1-naphthanol, is bulky enough to efficiently fill the void spaces in a diamondoid network, and thus a 3-D network is produced.
Figure 1.7. Sections of the polymeric structures of various Li-OAr materials built from tetrameric lithium SBUs. a) 1-D zig-zag chain; b) 2-D hexagonal sheet; c) 3-D diamondoid network.
Several other Li-OAr systems were explored resulting in additional CPs. After gaining experience building ArOLi networks, we sought to add a level of sophistication to the “design” of these materials. The use of 2,4,6-Me₃-C₆H₂O⁻ had previously been shown to produce tetrameric cubane SBUs which linked through dioxane to give a 3-D diamondoid net. The goal was to add stoichiometric amounts of N,N-dimethylaminoethanol, which would conceivably chelate forming five-membered Li-N-C-C-O rings. This would block the lithium site from solvation and effectively block polymer growth from that site in the SBU, Figure 1.8. The technique proved to be successful, and a series of compounds was characterized ranging from 3-D materials to 0-D molecular species. While this is far from an all encompassing method to control the product from a reaction, it added another level of sophistication to the “design” of extended structures which is still one of the greatest challenges facing synthetic CP chemists.

The encouraging results with lithium aryloxides led the group to explore the heavier alkali metals sodium, potassium and rubidium. Two isostructural sodium 3-D materials were synthesized via reaction of ArOH with sodium hydride in dioxane solution much like the lithium complexes described above. The sodium SBUs were hexameric aggregates in a triple-stack of dimers motif, which led to primitive cubic networks. Similar reactions with potassium and rubidium led to some very interesting and increasingly complicated results. It appears as though as the ionic radius of the metal increases, the predictability of the aggregation state of the SBU decreases. This resulted in a pentameric potassium aggregate, cage complexes encapsulating water
molecules$^{60}$ and 1-D inorganic rods.$^{59}$ Figure 1.9 shows an example of each of these SBU.$^{59}$ The extended structures also became more complicated. The materials that formed 1-D inorganic rods formed hybrid organic-inorganic materials using the rods as polymeric SBUs instead of the more common molecular SBUs.$^{59}$ The larger metals also led to the characterization of several high-connectivity networks, including the first uninodal 9-connected network.$^{58}$ There will be a brief discussion of network topology in the following section and more detailed description of these interesting materials in later chapters.

1.5 Network topology

An important topic when discussing extended structures, particularly 3-D materials, is the underlying topology. The topology of a material is simply the way in which a node in a network connects through the linkers to each of its neighboring
nodes. The classification and graphic representation of network topology often times does nothing to describe the nature of the chemical interactions constructing the framework; however it is an important way in which differing materials can be compared and described. An in depth discussion on network topology is beyond the scope of this work, but a basic understanding will be necessary as particular terms and symbols will be used throughout this thesis. A brief description of general topological trends, graphic network representation and the accompanying terminology and classification will be outlined below.

In recent years the number of extended structures reported in the literature has drastically increased. With this increase in the number of nets reported, a trend has emerged that a relatively few high symmetry topologies are dominant, as nature tends to favor symmetry when possible. Low-connectivity, high symmetry topologies dominate the landscape in uninodal MOF chemistry. Low-connectivity is considered any node with ≤6 connections. In particular the two most common nets are the 4-

Figure 1.9. Some interesting SBUs from potassium and rubidium materials. These highlight the increasing complexity of the materials as the cation size increases. a) The pentameric SBU of \([2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{OK})_5\cdot\text{(diox)}_5\] \(^{58}\) b) The hexameric SBU of \([\{(2\text{-}^1\text{BuC}_6\text{H}_4\text{OK})_6\supset\text{(H}_2\text{O})\cdot\text{(diox)}_4\}\] showing the encapsulated water molecule in green. \(^{60}\) c) The helical 1-D inorganic rod of \([\{(4\text{-}BrC}_6\text{H}_4\text{ORb})_5\cdot\text{(diox)}_5\}\] \(^{59}\)
connected diamondoid net (dia) and the 6-connected primitive cubic net (pcu).  
Conversely, high-connectivity (>6) networks are extremely rare. A large majority of high-connectivity nets adopt either the high symmetry 8-connected body-centered cubic (bcu) or 12-connected face-centered cubic net (fcu). There are a few explanations for this lack of high-connectivity networks: (1) for many materials it is sterically difficult to get greater than six linkers around a metal center or SBU and (2) there are no high symmetry geometries for 7-, 9-, 10- or 11-connected nodes.

Graphically representing networks is important for a number of reasons, the first of which is often times these networks are quite complicated to look at in the conventional chemical diagram form. Typically, topological representations are simplified down to ball and stick diagrams in which the node, no matter how complex, is represented as a single ball and the linker is shown as a stick. Even networks with simple topologies can be difficult to visualize unless they are simplified in this manner, Figure 1.10. Also, chemically networks can be very diverse even while having the same topology and these ball and stick representations can be used to easily compare very unique materials that are topologically identical. Materials that are topologically identical are said to be isoreticular, even if chemically they are unique.
Figure 1.10. Illustration of the simplification and graphical representation of a sodium aryloxide network. A view of a) a completely unsimplified portion of a pcu network and b) the same portion of the network with all aryloxide carbon atoms removed for clarity. c) The hexameric SBU bridging to six neighboring SBUs and its simplification to an octahedral node. d) The ball and stick representation of the underlying pcu topology of the network in a) the blue balls represent the Na$_6$O$_6$ hexameric aggregates and the gray sticks represent bridging dioxane. All hydrogen atoms have been removed for clarity. Yellow – sodium, red – oxygen, black – carbon.
Graphical representations are also very useful for describing complicated topologies by breaking them down into simpler subnets. Sometimes for uncommon and complicated topologies, even the ball and stick simplification can be somewhat difficult to view. However, usually a complicated 3-D network can be broken down into a series of simple 2-D subnets. Comparison of the component subnets and how they connect can be used to build relationships between seemingly unrelated network topologies, Figure 1.11.\textsuperscript{58}

Figure 1.11. Graphical representations of three 7-connected networks and the associated point symbols. The complicated 3-D nets can be described as a combination of simpler 2-D nets. The component 2-D nets are shown in either red or gray.\textsuperscript{58}

Along with visually representing network topologies, there are several ways in which networks are classified. The classification of network topologies has been greatly aided by the creation of several databases\textsuperscript{67–69} and a computer program for topological analysis\textsuperscript{70} in recent years. Each unique topology is assigned a three letter code which is always written in bold lower-case letters (diamondoid – \textit{dia}, primitive cubic – \textit{pcu}). This distinguishes these codes from those of zeolites which use three letter upper-case codes (e.g. FAU for faujasite).\textsuperscript{69}
Although the three letter codes do uniquely relate a network to its underlying topology, they do nothing to actually describe the topology. Commonly reported with the three letter codes will be a string of numbers in the form of \{A^aB^bC^c\} which is called the point symbol or Schlafli symbol. The point symbol is a description of the number and size of the shortest circuit at each angle of a vertex or node. Point symbols have the form \{A^aB^bC^c\} in which \(A < B < C\) and \(a + b + c = n(n-1)/2\) for an \(n\)-connected node. \(A, B\) and \(C\) represent the length of the shortest circuit for each angle and \(a, b\) and \(c\) represent the number of each circuit. For example, a primitive cubic network (pcu) has 6-connected nodes with 15 unique angles. Around each node there are twelve 4-membered rings and three 6-membered rings; so the point symbol for a pcu net is \(4^{12}6^3\) (see Figure 1.10d). Point symbols uniquely describe a network topology and are informative about the number and length of the shortest circuit for every angle at a node.

These symbols are useful when comparing complex topologies of networks with the same connectivity. For example, by comparing the point symbols for the 7-connected networks shown in Figure 1.12 it is readily apparent not only that these topologies are different, but the differences can be assessed. The network in Figure 1.11a has three 3-membered rings, twelve 4-membered rings, five 5-membered rings and one 6-membered ring while the network in Figure 1.11(b) has seventeen 4-membered rings and four 6-membered rings and Figure 1.11c has fifteen 4-membered rings and six 6-membered rings. The point symbols for the networks in Figure 1.11b and
c are particularly useful because it is not readily apparent from looking at the graphical representation that these two topologies only differ by the size of two circuits.\textsuperscript{58}

A combination of the graphical representations, three letter codes and point symbols will be used throughout this thesis. The basic information presented above is all the necessary background in network topology that will be required to understand the descriptions presented throughout. For more in depth discussion and analysis of network topology please refer to the literature on this topic.\textsuperscript{71–73}

1.6 Overview of this research

The goal of the research presented in this section of the thesis is to extend our work with the large alkali metals. By continuing to work with the large alkali metals (K, Rb, Cs) and expand to other large cations, such as barium and the lanthanides, the synthesis of more high-connectivity networks was sought. Unfortunately no high-connectivity networks were characterized, however many new and interesting materials were prepared.

Each chapter is a self-contained unit that details specific work done with large metal cations in the synthesis of CPs. Each chapter will include a brief introduction section that will give specific background pertinent to the information presented in that chapter. Chapter 2 contains details on a series of isoreticular alkali metal CPs, these materials also complete just the second complete homologous alkali metal aryloxide series reported to date. Chapter 3 will focus on a series of cesium coordination polymers built from both molecular and polymeric SBUs. Chapter 4 is our first work
with the lanthanide metals and describes another isoreticular series of materials.

Chapter 5 is a collection of fortuitous potassium, barium and neodymium materials that have been synthesized and characterized.

1.7 References


CHAPTER 2:

A STRUCTURAL STUDY ON THE EFFECTS OF ALKALI METAL CATION SIZE ON MOLECULAR AND EXTENDED STRUCTURES: THE HOMOLOGOUS SERIES \([(4\text{-ET-}C_6H_4OM)}\cdot(DIOX)n\), M = Li, Na, K, Rb, Cs

2.1 Introduction

2.1.1 Background

Our group has focused on the use of alkali metal aggregates as SBUs in constructing extended network materials. The well-known aggregation states of organo-alkali metal complexes\(^1-9\) lend themselves quite well to use as SBUs, Figure 2.1. Most of this chemistry has focused on the lighter alkali metals, Li and Na.\(^10-17\) While some work has been done with the heavier metals, K, Rb and Cs, their chemistry in this area is largely unexplored.\(^18-21\) In part, this is a consequence of the more advanced understanding of the coordination chemistry of organo-lithium and sodium complexes. In addition, the increased reactivity of the heavier alkali metals makes their preparation and handling more challenging. Nevertheless, the limited work completed on heavy alkali metal aryloxide complexes has produced some very interesting results. Two of the five reported 7-connected uninodal networks\(^22-24\) are built from K and Rb complexes,\(^19\) and the first of three reported 9-connected uninodal networks\(^25,26\) is a Rb framework.\(^19\)
Figure 2.2. In hopes of building on these interesting results and expanding on our understanding of alkali metal supramolecular chemistry, the alkali metal/4-Et-C₆H₄O⁻/1,4-dioxane system was studied in a systematic manner. The Li and Na analogues have previously been communicated and were found to form tetrameric and hexameric SBUs respectively.¹³,¹⁴ This increase in aggregation state led us to focus on the effect of increasing the ionic radius of the metal center on both the molecular and supramolecular structures.²⁷

Figure 2.1. Several classic organo-lithium aggregate complexes highlighting the influence of sterics and donor solvent molecules on aggregate size. a) [MeLi(THF)]₄,⁷ b) [PrLi]₆,⁸ c) [BuLi]₄,⁶ d) [¹BuLi(THF)]₄,⁹ e) [¹¹BuLi]₆.⁶ Red – oxygen, black – carbon, blue – lithium.
Figure 2.2. (Left) The SBUs and (right) the simplified network representations of the 7-connected networks a) \([\text{[(4-Cl-2,6-Me}_2\text{C}_6\text{H}_2\text{OM})_2\cdot(\text{diox})_{3.5}] (M = \text{K, Rb}), \text{b) } \text{[(2,4,6-Me}_3\text{C}_6\text{H}_2\text{OK})_5\cdot(\text{diox})_5]\text{; and the 9-connected network c) } \text{[(2-}^{\text{i}}\text{PrC}_6\text{H}_4\text{ORb})_6\cdot(\text{diox})_{4.5}]\text{. Pink – rubidium, purple – potassium, red – oxygen, black – carbon.}\]
This series of networks represents only the second homologous series of Group 1 non-nitro functionalized aryloxide compounds reported in the literature. The first homologous series is the solvent-free alkali metal phenoxide system, metal/C₆H₅O⁻. The solid state structures of these compounds were determined via Rietveld refinement of powder X-ray diffraction data. The crystallinity of the lithium compound was too poor to allow for structure solution, the other four homologues form 1-D inorganic rods, which will be discussed in section 2.2.2. There have also been several homologous nitro-functionalized aryloxide series reported. Non-aryloxide examples of homologous alkali metal complexes have been characterized, for example; the hexamethyldisilazide and tert-butoxide series.

For completeness the entire series of alkali metal/4-Et-C₆H₄O⁻/1,4-dioxane compounds will be discussed in this chapter, including the previously reported lithium and sodium materials.

2.1.2 [(4-Et-C₆H₄OLi)₄·(diox)₂₅·diox], (2.1)¹³

First, the molecular SBU structure will be described and then the extended structure. The molecular structure of 2.1 is composed of a tetrameric [(4-Et-C₆H₄O)Li]₄ cubane in which each metal center is solvated by 1,4-dioxane, Figure 2.3a. Aggregates are very common in organolithium chemistry in order to saturate the coordination sphere of the lithium atoms. The aggregation state typically depends on the steric bulk of the anion and any solvent present, as well as electronic factors. Tetrameric lithium cubanes are a well-known structural motif in which each lithium is coordinated
to three bridging anions and one solvating Lewis base.\textsuperscript{9,41} The Li – O\textsubscript{Ar} bond distances in 2.1 are typical of Li\textsubscript{4}O\textsubscript{4} cubanes ranging from 1.90 – 1.99 Å. Comparatively, the related simple phenoxide compound [(C\textsubscript{6}H\textsubscript{5}OLi)\textsubscript{4}(diox)\textsubscript{3}] has Li – O\textsubscript{Ar} distances ranging from 1.92 – 1.96 Å, while the sterically more bulky compounds [(C\textsubscript{10}H\textsubscript{7}OLi)\textsubscript{4}(diox)\textsubscript{3}(diox)]\textsuperscript{13} and [(2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2}OLi)\textsubscript{4}(diox)\textsubscript{2}(diox)]\textsuperscript{17} have Li – O\textsubscript{Ar} distances ranging from 1.94 – 1.95 Å and 1.98 – 2.00 Å respectively. Hence, these complexes all display a narrow range of cation–anion contact distances.

\textbf{Figure 2.3.} a) Thermal ellipsoid plot of the tetrameric SBU of 2.1. b) The SBU showing the three points of network extension (blue arrows) and the one terminally solvating 1,4-dioxane (red arrow). c) A portion of the extended 2-D structure, a 6\textsuperscript{3}-network, with two dioxane solvent molecules encapsulated in each pore. d) A side view of several 2-D sheets showing the interdigitation and close packing of the layers. Carbon atoms of the aryl groups and all hydrogens have been removed for clarity.
Next, the extended structure of 2.1 will be discussed. Tetra-solvated cubanes, such as in 2.1, are good candidates for use as SBUs in building MOFs. Potentially, the cubane could act as a tetrahedral node, thus most likely building a 3-D diamondoid network. This is the case for \([[(C_{10}H_{7}OLi)_{4}(diox)_{2}]\cdot3(diox)]\)^{13} which was the example shown in Figure 1.7c, and \([[(2,4,6-Me_{3}-C_{6}H_{2}OLi)_{4}(diox)_{2}]\cdot3(diox)]\)^{17}. However, only three of the solvating 1,4-dioxanes in 2.1 act as linear linkers, while the fourth terminally solvates a single metal center. Consequently, the extended structure is a 2-D 6\(^3\) network in which each SBU effectively acts as a trigonal node to form hexagonal sheets, as shown in Figure 2.3c. We have previously outlined that upon close examination of the extended structure that the 4-Et-C\(_6\)H\(_4\)O\(^-\) anions are not large enough to efficiently fill the large void volume that would be present in a 3-D diamondoid lattice.\(^{13}\) This leads to the formation of 2-D sheets that interdigitate to efficiently fill space, Figure 2.3d. Also, there are two 1,4-dioxane molecules encapsulated inside the hexagonal pore, which is capped on both the top and bottom by the aryl groups. The hexameric macrocycles adopt a chair conformation, with a cross-sectional diameter of \(\approx 17 – 19\ \text{Å}\).\(^{13}\) There is one other example, of a tetrameric lithium cubane acting as an SBU for a 2-D 6\(^3\) network, namely \([(Me_{2}NC_{2}H_{4}OLi)(2,4,6-Me_{3}-C_{6}H_{2}OLi)_{3}\cdot(diox)_{1.5}]\cdot\frac{1}{2}(C_{6}H_{14})]\)^{17}. This material was designed as a 2-D network by incorporating a chelating anion, N,N-dimethylethanolamine, into the cubane to occupy one of the four potential points of network extension. Thus, one lithium in the tetramer is chelated and cannot bridge to another SBU while the other three lithium metal centers are linked to neighboring SBUs.
via bridging 1,4-dioxane molecules. The resulting 2-D sheets align to form channels which are filled with disordered hexane.\(^\text{17}\)

### 2.1.3 [\((\text{4-Et-C}_6\text{H}_4\text{ONa})_6\cdot(\text{diox})_3\), (2.2)]\(^\text{14}\)

The molecular SBU will be described first and the extended structure will be discussed later. The molecular structure of 2.2 is composed of a hexameric [(4-Et-C\(_6\)H\(_4\)O)Na]\(_6\) unit that can be described as a triple-stack of dimers or two face sharing cubanes in which each metal center is solvated by a 1,4-dioxane molecule, Figure 2.4a. Hexameric sodium aggregates are also well known structural motifs.\(^\text{14,42}\) The aggregation is similar to lithium tetramers in that it aids in saturating the coordination sphere of the sodium atoms. However, since sodium has a larger ionic radius than lithium, the metals can accommodate a larger number of ligands; e.g. the five-coordinate metal centers in the center of the hexameric aggregates in 2.2. The Na – O\(_{Ar}\) distances in 2.2 are within the expected range. The bond distances range from 2.24 – 2.44 Å for the four coordinate metals, and 2.33 – 2.40 Å for the five coordinate metals. These are comparable to similar complexes, [(C\(_6\)H\(_5\)ONa)\(_6\)(THF)\(_6\)] and [{(4-F-C\(_6\)H\(_4\)ONa)\(_6\)(diox)}\(_3\)•(diox)], with distances ranging between 2.23 – 2.36 Å and 2.23 – 2.48 Å for four coordinate metals and 2.36 – 2.40 Å and 2.32 – 2.43 Å for five coordinate metals respectively.\(^\text{14,42}\)

Next the extended structure of 2.2 will be discussed. The sodium triple-stack of dimers motif has been reported several times in both extended and molecular species with anions ranging from hydrazides,\(^\text{43}\) oxides\(^\text{14,42,44,45}\) and thiolates.\(^\text{46}\) In 2.2, each metal
center is solvated by a 1,4-dioxane that bridges to another SBU. The extended structure is a 3-D network with a primitive cubic (pcu) topology, in which each SBU acts as an octahedral node, Figure 2.4b. Previously, \([(4-F-C_6H_4ONa)_6(diox)_3\cdot(diox))]\), was characterized containing sodium triple-stack of dimers acting as octahedral SBUs in building a pcu CP.\(^{14}\) Upon examination of the extended structure of 2.2, it becomes apparent that the cubic cavities are efficiently filled by the 4-Et-C_6H_4O^- groups, leaving essentially no solvent accessible void space.\(^{14}\) This stabilizes formation of the 3-D architecture, whereas in 2.1, the space would be insufficiently filled leading to the 2-D layered structure.\(^{13}\)

**Figure 2.4.** a) Thermal ellipsoid plot of the hexameric SBU of 2.2 showing all bridging 1,4-dioxanes. b) A portion of the extended structure of 2.2 showing the octahedral geometry of the SBUs. c) A simplified view of the extended structure of 2.2 showing its primitive cubic (pcu) topology (blue balls represent Na_6O_6 clusters and gray sticks represent bridging 1,4-dioxane).
2.2 Results and Discussion

2.2.1 Synthesis

The synthesis of 2.3-2.5 involved the reaction of 4-ethylphenol with the appropriate organometallic reagent in 1,4-dioxane solution, Scheme 2.1. X-ray quality crystals were obtained by slow cooling of saturated solutions in a hot water bath.

Compounds 2.3-2.5 are constructed of one dimensional inorganic rods, which are linked to form networks.\(^{27}\) An inorganic rod is a one dimensional polymer built exclusively from M-X (X = N, O, S, etc.) interactions. To differentiate inorganic rods from simple chain and ladder structures, we define rods to have some molecular 3-D character; whereas chains would have molecular 1-D character and ladders would have molecular 2-D character.

\[
\begin{align*}
3 \text{K[N(SiMe\textsubscript{3})\textsubscript{2}]} + 3 \text{4-Et-C\textsubscript{6}H\textsubscript{4}OH} & \xrightarrow{\text{1,4-diox}} [(\text{4-Et-C\textsubscript{6}H\textsubscript{4}OK})\textsubscript{3}(\text{diox})] \quad (2.3) \\
2 \text{Rb(O\textsubscript{t}Bu)\cdot HO\textsubscript{t}Bu} + 2 \text{4-Et-C\textsubscript{6}H\textsubscript{4}OH} & \xrightarrow{\text{1,4-diox}} [(\text{4-Et-C\textsubscript{6}H\textsubscript{4}ORb})\textsubscript{2}(\text{diox})\textsubscript{0.5}] \quad (2.4) \\
2 \text{Cs(O\textsubscript{t}Bu)\cdot HO\textsubscript{t}Bu} + 2 \text{4-Et-C\textsubscript{6}H\textsubscript{4}OH} & \xrightarrow{\text{1,4-diox}} [(\text{4-Et-C\textsubscript{6}H\textsubscript{4}OCs})\textsubscript{2}(\text{diox})\textsubscript{0.5}] \quad (2.5)
\end{align*}
\]

*Scheme 2.1. Preparation of 2.3-2.5.*

2.2.2 Inorganic rods

This section will focus on the inorganic rod SBUs of 2.3-2.5, while the extended structures will be discussed later. The materials 2.3-2.5 are isostructural and are constructed from 1-D inorganic rods built from M – O\textsubscript{Ar} interactions. The inorganic rods that build 2.3, 2.4 and 2.5 contain two unique metal environments, Figure 2.5. The first
is a metal center that is coordinated by six μ₄-O atoms of aryloxide ligands in a very
distorted octahedral geometry. The metal centers in this environment run down the
center of the rods. The second environment is a metal center coordinated to three μ₄-O
atoms of aryloxide ligands and one oxygen atom of a bridging 1,4-dioxane. The
geometry around this metal center is distorted trigonal pyramidal in which the base is
formed by the three O₀Ar ligands and the 1,4-dioxane is the apical ligand. The metal
centers in this environment run along the edges of the rods. The rods are isostructural
and as expected, the metrical parameters vary only due to the size of the metal cation.
A clear expansion of the rods can be observed as a measure of the M – O₀Ar bond
distances as the ionic radius of the metal increases from 2.3 to 2.4 to 2.5. This trend is
illustrated in Table 2.1 with a list of selected bond lengths for 2.3-2.5.

![Thermal ellipsoid plots of a portion of the inorganic rods in a) 2.3, b) 2.4, and c) 2.5. All carbon and hydrogen atoms have been removed for clarity.](image)

**Figure 2.5.** Thermal ellipsoid plots of a portion of the inorganic rods in a) 2.3, b) 2.4, and c) 2.5. All carbon and hydrogen atoms have been removed for clarity.
Given that the anions and solvent/linkers are identical in 2.1-2.5, the explanation as to why 2.3-2.5 form inorganic rods must be related to the cation size. Specifically, the steric bulk in close proximity to the metal center is the most important factor.

Going down Group 1, as the ionic radius increases, so does the maximum coordination number of the metal center. In 2.1, the lithium metal centers are all four coordinate. In 2.2, the two central sodium metals are five coordinate. When the ionic radius of the metal reaches beyond that of sodium, the metals can accommodate up to six ligands as

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is seen with the central metals in 2.3-2.5. It seems six is the maximum coordination number in this system.

The characterization of 2.3-2.5 opens the opportunity to review if any structural patterns are emerging for alkali metal rod architectures. Figure 2.6 shows a portion of each alkali metal inorganic rod, excluding simple chain and ladder structures, previously reported in the literature. Table 2.2 compares the average M-O_{Ar} distances of 2.3–2.5 with other alkali metal-aryloxide inorganic rods in the literature. The connectivity of the previously reported alkali metal aryloxide rods vary from simple face-sharing cubanes with just one edge missing, [(2-Me-C_6H_4OK)_2(THF)], (Figure 2.6f) to the quite complex helical rods in [(4-Br-C_6H_4ORb)_5·(diox)]_0.5 (Figure 2.6g).

Interestingly, the rods in (C_6H_5OM)_3 (M = K, Rb, Cs), [(4-Cl-C_6H_4OK)_3·(diox)] and [(4-Br-C_6H_4OK)_2·(diox)]_0.5 (Figure 2.6a-e) have virtually identical connectivity to compounds 2.3–2.5. The simple phenoxide rods are solvent-free and thus are not decorated with 1,4-dioxane molecules as in 2.3-2.5, [(4-Cl-C_6H_4OK)_3·(diox)] and [(4-Br-C_6H_4OK)_2·(diox)]_0.5. This similarity is most likely attributable to the similarity in local steric bulk at the metal centers. Since, varying the para-substituent on an aryloxide does not affect the coordination number of the metal, it does not influence the aggregation state. On the other hand, [(2-Me-C_6H_4OK)_2(THF)] is substituted at the ortho position and that likely is one reason that the inorganic rod formed is different from those of 2.3-2.5. The other rods in Figure 2.6i-k, are not built from aryloxide anions and so they should not be expected to form similar rods to 2.3-2.5. However, the (C_6H_5ONa) rod, (Figure 2.6h, is isostructural to the [M_2(p-C_6H_4O_2)] (M = Na, K) rods, Figure 2.6i,j.
The solvent-free phenoxide rods adopt a hexagonal packing array.\(^{28}\) The para-halide substituted aryloxide rods \(((4\text{-}Cl\text{-}C_6H_4OK)_3\cdot(diox))^{18}\) and \(((4\text{-}Br\text{-}C_6H_4OK)_2\cdot(diox))_{0.5}\) form pcu extended structures\(^{18}\) similar to compounds 2.3–2.5. Another para-halide substituted aryloxide rod, \(((4\text{-}Br\text{-}C_6H_4ORb)_3\cdot(diox))_3\), forms helical rods which do not connect together to form an extended network. The coordinating 1,4-dioxane molecules do not bridge, leaving the parallel rods to pack in a hexagonal packing array.\(^{18}\)
[(2-Me-C₆H₄OK)₂(THF)] is solvated by the monotopic Lewis base THF and thus cannot link with neighboring rods.⁴⁸

### TABLE 2.2

AVERAGE M – Oₐr DISTANCES IN ALKALI METAL-ARYL OXIDE INORGANIC RODS

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<td>(C₆H₅OK)₃</td>
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<td>[(4-Et-C₆H₄OK)₃·(diox)]</td>
<td>2.77</td>
<td>2.73</td>
<td>2.77</td>
<td></td>
<td></td>
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<tr>
<td>[(2-Me-C₆H₄OK)₂(THF)]</td>
<td>2.74</td>
<td>2.76</td>
<td></td>
<td></td>
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<td>48</td>
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<tr>
<td>[(4-Cl-C₆H₄OK)₃·(diox)]</td>
<td>2.73</td>
<td>2.74</td>
<td>2.75</td>
<td></td>
<td></td>
<td>18</td>
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<tr>
<td>[(4-Br-C₆H₄OK)₂·(diox)₀.₅]</td>
<td>2.75</td>
<td>2.75</td>
<td></td>
<td></td>
<td></td>
<td>18</td>
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<tr>
<td>(C₆H₅ORb)₃</td>
<td>2.97</td>
<td>2.87</td>
<td>2.89</td>
<td></td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>[(4-Et-C₆H₅ORb)₂·(diox)₀.₅]</td>
<td>2.86</td>
<td>2.89</td>
<td></td>
<td></td>
<td></td>
<td>27</td>
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<tr>
<td>[(4-Br-C₆H₄ORb)₅·(diox)₅]</td>
<td>2.87</td>
<td>2.93</td>
<td>2.89</td>
<td>2.88</td>
<td>2.90</td>
<td>18</td>
</tr>
<tr>
<td>(C₆H₅OCs)₃</td>
<td>3.09</td>
<td>3.04</td>
<td>3.09</td>
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<td></td>
<td>28</td>
</tr>
<tr>
<td>[(4-Et-C₆H₄OCs)₂·(diox)₀.₅]</td>
<td>3.04</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
<td>27</td>
</tr>
</tbody>
</table>
2.2.3 Extended structures

This section will detail the extended structures of 2.3-2.5. Each rod in 2.3-2.5 is connected to four other rods by bridging 1,4-dioxanes to form parallel layers with a 4\textsuperscript{4}-net topology. Thus the extended structure can be described as a pcu-type rod packing, Figure 2.7. The channels formed between the rods are occupied by the ethyl groups of the 4-Et-C\textsubscript{6}H\textsubscript{4}O\textsuperscript{−} ligands, which essentially completely fill the void space. This efficient filling of the void space along with the rigidity of the inorganic rods provides the stability for the 3-D architecture in 2.3-2.5.

While the extended structures of 3–5 are topologically the same, the coordination angle of the bridging 1,4-dioxane molecules are quite different. By measuring the angle, O\textsubscript{diox}' – O\textsubscript{diox} – M, it is clear that as the size of the metal cation

![Diagram](image)

**Figure 2.7.** A portion of 2.4 showing a) one channel; b) a wider view with all aryloxide carbon atoms removed and c) a side view of the structure showing the inorganic rods with all aryloxide carbon atoms removed for clarity. All hydrogen atoms are removed for clarity.
changes, the coordination angle of the 1,4-dioxane bridge is quite flexible. There are two crystallographically independent K/diox environments in 2.3 which have coordination angles of; O4’ – O4 – K1 = 157.0° and O5’ – O5 – K2 = 164.1°, and only one in each of 2.4 (O3’ – O3 – Rb1 = 155.2°) and 2.5 (O3’ – O3 – Cs1 = 121.7°). The difference between K2 and Cs1 is greater than 42°, as shown in Figure 2.8. It should also be noted that between all structures the metrical parameters within the 1,4-dioxane molecules remain very similar. Rather, it is the flexibility in the coordination environment of 1,4-dioxane to the metal centers that accounts for the large differences in bridging angles.

**Figure 2.8.** An overlay of bridging dioxanes in 2.3 (blue K1 and pink K2), 2.4 (red) and 2.5 (green) showing the difference in coordination angles. The oxygen atoms of the dioxanes are matched up and shown bridging two metal centers.
2.3 Summary

This work represents just the second complete homologous series of alkali metal aryloxides to be structurally characterized, and includes the first 3-D material built from cesium inorganic rods. Varying cation size, even in the presence of identical anions and solvents, can drastically affect the solid-state structures of the resulting coordination polymers. The Li and Na complexes 2.1 and 2.2 form discrete aggregates which act as SBU’s in the construction of 2-D and 3-D extended structures respectively. The heavier alkali metal analogues, 2.3–2.5, form isostructural 1-D inorganic rods which then connect to form hybrid organic-inorganic materials. The observation that the aggregation state increases as heavier alkali metals are used is due to the increased ionic radii of the cations. The larger ionic radii allow a greater coordination number which leads to larger aggregates in this series. In the case of K, Rb and Cs, the increase in coordination number leads to the formation of 1-D rods. This allows the larger alkali metals to fill their coordination sphere with the anionic O_ar as opposed to the neutral O_diox interactions. Even though the inorganic rod building units are isostructural the increasing cation size in 2.3–2.5 is reflected in varying coordination angles of the bridging 1,4-dioxane molecules.

The inorganic rods that build 2.3-2.5 are virtually identical to two potassium rods previously described in the literature and the heavier homologues of the alkali metal phenoxide system.\textsuperscript{18,28} Thus a pattern does seem to be emerging from this limited set that suggests the construction of these rods are inherently favorable. However, a larger sample size of characterized complexes is required before drawing conclusions.
2.4 Experimental

2.4.1 General procedures

All experimental manipulations were performed under a dry nitrogen atmosphere in flame-dried glassware using standard Schlenk techniques. 1,4-dioxane was distilled from sodium benzophenone and stored over 4 Å molecular sieves prior to use. Hexane was dried by passage through columns of copper-based catalyst and alumina (Innovative Technology). BuLi was purchased from Aldrich as a 1.6 M solution in hexane and was standardized by titration against salicylaldehyde phenylhydrazone directly before use. NaH was purchased from Aldrich and used as received. K[N(SiMe₃)₂] was purchased from Fluka and used without further purification. Rb and Cs metal were purchased from Strem. The 4-ethylphenol was purchased from Lancaster and dried by recrystallization from hexane prior to use. NMR spectra were obtained on a Varian Unity Plus 300 MHz instrument. Non-integral values for 1,4-dioxane is due to partial removal under vacuum upon isolation. ¹H and ¹³C spectra were referenced with respect to the residual solvent signal. FTIR spectra were obtained on a Nicolet Nexus 670 FT-IR under a stream of flowing nitrogen.

2.4.2 X-ray crystallography

Single-crystals were examined under Infineum V8512 oil. The datum crystal was affixed to a Mitegen mounting loop and transferred to the 100 K nitrogen stream of a Bruker APEX diffractometer equipped with an Oxford Cryosystems 700 series low-
temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 12 0.5° ϕ scans. The orientation matrix derived from this was transferred to COSMO to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Cell parameters were refined using reflections harvested from the data collection with $I > 10σ(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. The structures were solved and refined using SHELXTL. Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of full-matrix least-squares refinement on $F^2$. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2× the equivalent isotropic U of the parent atom.

2.4.3 Preparation and characterization

**Synthesis of [RbO'Bu·HO'Bu]**. Rubidium metal (5.0g, 58.8mmol) was added to a Schlenk flask. THF 60mL was added along with a stir bar. Excess tert-butanol (11.8mL, 126.4mmol) was added to the stirring reaction mixture and then heated to 70°C for 4 hours. After cooling to room temperature, the reaction mixture was filtered through a Celite pad. The solvent was removed from the filtrate under vacuum resulting in a white solid. The solid was heated at 50°C under vacuum overnight to yield a white powder. Yield: 12.31g (90%). **Caution: Rubidium metal is extremely reactive and reacts**
violently/explosively with air and water. \(^1\)H NMR (300 MHz, toluene-\textit{d}_8, 25°C) \(\delta = 1.15 \) (s, CH\textsubscript{3}).

**Synthesis of \([\text{CsO}^{\text{tBu}}\cdot \text{HO}^{\text{tBu}}]\).**\(^{40}\) Cesium metal (5.0g, 37.0mmol) was added to a Schlenk flask. THF 60mL was added along with a stir bar. Excess tert-butanol (6.2mL, 83.3mmol) was added to the stirring reaction mixture and then heated to 70°C for 4 hours. After cooling to room temperature, the reaction mixture was filtered through a Celite pad. The solvent was removed from the filtrate under vacuum resulting in a white solid. The solid was heated at 50°C under vacuum overnight to yield a white powder. Yield: 9.46g (91%). *Caution: Cesium metal is extremely reactive and reacts violently/explosively with air and water.* \(^1\)H NMR (300 MHz, toluene-\textit{d}_8, 25°C) \(\delta = 1.29 \) (s, CH\textsubscript{3}).

2.3 [\(\text{[4-Et-C}_6\text{H}_4\text{OK}]_3\cdot \text{(diox)}\)] - K[\(\text{N(SiMe}_3\text{)}_2\)] (3 mmol, 600 mg) was added to a stirred solution of 4-ethylphenol (3 mmol, 366 mg) in 1,4-dioxane (10 mL) to give a white precipitate. An additional 15 mL 1,4-dioxane was added and complete dissolution was achieved upon heating. X-ray quality crystals were obtained by slow cooling of the solution in a hot water bath. Crystalline yield 490 mg, 29%. Sample decomposed at 198 °C. \(^1\)H NMR (300 MHz, pyridine-\textit{d}_5, 25°C) \(\delta = 1.23 \) (3H, t, \(^3\)\(J_{HH} = 7.5 \) Hz, CH\textsubscript{3}, Et), 2.58 (2H, q, \(^3\)\(J_{HH} = 7.1 \) Hz, CH\textsubscript{2}, Et), 3.63 (4H, s, OCH\textsubscript{2}, dioxane), 6.87 (2H, d, \(^3\)\(J_{HH} = 7.3 \) Hz, o-H, Ph), 7.04 (2H, d, \(^3\)\(J_{HH} = 8.1 \) Hz, m-H, Ph). \(^{13}\)C\{\(^1\)H\} NMR (75 MHz, pyridine-\textit{d}_5, 25°C) \(\delta = 17.74 \) (CH\textsubscript{3}, Et), 29.07 (CH\textsubscript{2}, Et), 67.64 (OCH\textsubscript{2}, dioxane), 119.56 (o-C, Ph), 124.99 (m-C, Ph), 130.15 (\(p\)-C, Ph), 171.25 (i-C, PH). FTIR (nujol mull, cm\textsuperscript{-1}) 1600 (w), 1498 (m), 1322 (m), 1310 (m), 1165 (w). 1113 (w), 841 (w), 720 (w).
2.4 [(4-Et-C₆H₄ORb)₂(diox)₀.₅] - [Rb(OtBu)-HOTBu] (2 mmol, 465 mg) was added to a stirred solution of 4-ethylphenol (2 mmol, 244 mg) in 1,4-dioxane (10 mL) to give a white precipitate. An additional 10 mL 1,4-dioxane was added and the mixture was heated, N,N-dimethylformamide (1.5 mL) was added dropwise until complete dissolution was achieved. X-ray quality crystals were obtained by slow cooling of the solution in a hot water bath. Crystalline yield 281 mg, 31%. Sample decomposed at 198 °C. ¹H NMR (300 MHz, pyridine-d₅, 25°C) δ = 1.25 (3H, t, ³J_HH = 7.3 Hz, CH₃, Et), 2.59 (2H, q, ³J_HH = 7.5 Hz, CH₂, Et), 3.63 (2H, s, OCH₂, dioxane), 6.84 (2H, d, ³J_HH = 8.3 Hz, o-H, Ph), 7.06 (2H, d, ³J_HH = 8.3 Hz, m-H, Ph). ¹³C{¹H} NMR (75 MHz, pyridine-d₅, 25°C) δ = 17.63 (CH₃, Et), 29.06 (CH₂, Et), 67.64 (OCH₂, dioxane), 114.74 (o-C, Ph), 120.04 (m-C, Ph), 125.22 (m-C, Ph), 130.18 (p-C, Ph), 170.57 (i-C, Ph). FTIR (nujol mull, cm⁻¹) 1598 (w), 1498 (m), 1313 (m), 1164 (w), 1115 (w), 839 (w), 720 (w).

2.5 [(4-Et-C₆H₄OCs)₂(diox)₀.₅] - [Cs(OtBu)-HOTBu] (2 mmol, 560 mg) was added to a stirred solution of 4-ethylphenol (2 mmol, 244 mg) in 1,4-dioxane (10 mL) to give a white precipitate. Complete dissolution was achieved upon heating. X-ray quality crystals were obtained by slow cooling of the solution in a hot water bath. Crystalline yield 198 mg, 18%. Melting point 188 °C. ¹H NMR (300 MHz, pyridine-d₅, 25°C) δ = 1.25 (3H, t, ³J_HH = 7.5 Hz, CH₃, Et), 2.59 (2H, q, ³J_HH = 7.5 Hz, CH₂, Et), 3.63 (1.5H, s, OCH₂, dioxane), 6.84 (2H, d, ³J_HH = 8.3 Hz, o-H, Ph), 7.10 (2H, d, ³J_HH = 8.5 Hz, m-H, Ph). ¹³C{¹H} NMR (75 MHz, pyridine-d₅, 25°C) δ = 17.56 (CH₃, Et), 29.03 (CH₂, Et), 67.64 (OCH₂, dioxane), 114.74 (o-C, Ph), 120.04 (m-C, Ph), 130.31 (p-C, Ph), 170.01 (i-C, Ph). FTIR
(nujol mull, cm$^{-1}$) 1598 (m), 1496 (s), 1313 (m), 1164 (m), 1117 (w), 871 (w), 838 (m), 721 (w).

2.5 References


CHAPTER 3:
A STRUCTURAL STUDY OF MIXED WATER/1,4-DIOXANE SOLVATES OF CESIUM 2-ISO-PROPYLPHENOXIDE

3.1 Introduction

Coordination polymers (CPs) have received a great deal of attention recently due to their potential for high surface areas and permanent porosity.\textsuperscript{1-4} There are two common approaches to building CPs: the connection of single metal centers through multi-topic organic ligands or the use of well defined metal aggregates as secondary building units (SBUs) which are subsequently linked through multi-topic organic ligands.\textsuperscript{5-7} One less common approach to building CPs is to use 1-D inorganic rods as building blocks. An inorganic rod is a one dimensional polymer built exclusively from M-X (X = N, O, S, etc.) interactions. To differentiate inorganic rods from simple chain and ladder structures, we define rods to have some molecular 3-D character; whereas chains would have molecular 1-D character and ladders would have molecular 2-D character. Figure 3.1 shows an example of a 1-D chain, ladder and rod. Similarly to molecular SBUs, these inorganic rods can be connected through organic linkers to form hybrid organic-inorganic materials.\textsuperscript{8-12} There are a limited number of alkali metal inorganic rods reported\textsuperscript{11,13-18} and there are even fewer examples of CPs built using inorganic rods as SBUs.\textsuperscript{11,13,15,16,18} Building CPs around inorganic rods could have advantages over the
molecular SBU approach such as potentially providing increased thermal and chemical stabilities.

![Diagram](image)

**Figure 3.1.** An example of a a) chain from [2,6-\text{Pr}-\text{C}_6\text{H}_3\text{OK}],\textsuperscript{14} b) ladder from [2,6-\text{Ph}-\text{C}_6\text{H}_3\text{ORb}]\textsuperscript{24} and c) rod from [(2-\text{Me}-\text{C}_6\text{H}_4\text{OK})_2\text{(THF)}].\textsuperscript{14} The metals in a chain have a molecular 1-D structure, in a ladder a molecular 2-D structure and in a rod a molecular 3-D structure.

### 3.1.1 Alkali metal inorganic rods

There have been fourteen alkali metal inorganic rods reported to date, and Figure 3.2 shows a portion of each rod. Several anions have been used to build alkali metal inorganic rods, however, the majority are built from substituted aryloxides. Eight of the fourteen reported rods are isostructural, varying only in bond lengths and angles, Figure 3.2a-h. The simple phenoxide rods, [\text{C}_6\text{H}_5\text{OM}] (M = K, Rb, Cs), are solvent free.\textsuperscript{17}

The other isostructural rods: \[(4-\text{Cl}-\text{C}_6\text{H}_4\text{OK})_3\cdot\text{(diox)},\textsuperscript{11} [(4-\text{Br}-\text{C}_6\text{H}_4\text{OK})_2\cdot\text{(diox)}_{0.5}],\textsuperscript{11} [(4-\text{Et}-\text{C}_6\text{H}_4\text{OK})_3\cdot\text{(diox)}],\textsuperscript{13} [(4-\text{Et}-\text{C}_6\text{H}_4\text{ORb})_2\cdot\text{(diox)}_{0.5}]\textsuperscript{13} and [(4-\text{Et}-\text{C}_6\text{H}_4\text{Ocs})_2\cdot\text{(diox)}_{0.5}]\textsuperscript{13} are all built with \textit{para}-substituted aryloxides as the anion and are decorated with 1,4-dioxane molecules. On the other hand, [(2-\text{Me}-\text{C}_6\text{H}_4\text{OK})_2\text{(THF)}]\textsuperscript{14} is substituted at the \textit{ortho} position and that likely is one reason that the inorganic rod formed is different from those mentioned above. The rod can be described as a series of face-sharing cubanes.
with one edge missing, Figure 3.2i. The rods in [(4-Br-C₆H₄ORb)₅ · (diox)₅],¹¹ Figure 3.2j, are helical. Alternating rods have left- and right-handedness, so the material crystallizes in an achiral space group. The other rods in Figure 3.2l-n, are not built from aryloxide anions and so they should not be expected to form similar rods to those mentioned above. However, the (C₆H₅ONa) rod,¹⁷ Figure 3.2k, is isostructural to the [M₂{p-C₆H₄O₂}] (M = Na, K) rods.¹⁵,¹⁶

3.1.2 Alkali metal inorganic rods as SBUs

Eight of the fourteen rods described above are used as SBUs to build CPs. The para-halide substituted phenoxide complexes [(4-Cl-C₆H₄OK)₃ · (diox)] and [(4-Br-C₆H₄OK)₂ · (diox)₀.₅] form pcu extended structures similar to the three 4-Et-C₆H₄O⁻ compounds described in the previous chapter.¹¹ This similarity is most likely attributable to the similarity in local steric bulk at the metal centers. Since, varying the para-substituent on an aryloxide does not affect the coordination number of the metal, it does not influence the aggregation state. Two of the other rods that build CPs are [M₂{p-C₆H₄O₂}] where M = Na, K and 1,4-phenylenediolate acts as both the anion and the organic linker.¹⁵,¹⁶ The final alkali metal rod that builds a CP is [Na₂(C₅H₄NCO₂)$_₂$] in which the nicotinate acts as both the anion and the linker.¹⁸ These three materials also exhibit a pcu-type rod packing. This means all of the previous CPs built from inorganic rod SBUs form pcu-type rod packing 3-D materials.

Several of the rods which do not act as SBUs in extended structures simply do not contain any type of linking molecule. For example, [(2-Me-C₆H₄OK)$_₂$(THF)] is
solvated by monotopic THF molecules, which cannot possibly bridge between rods. Also, the simple phenoxide rods are solvent free and thus cannot link together. There is a possibility that if materials like these were synthesized in the presence of a divergent linker they too would become part of a 3-D hybrid material. The rubidium complex, \([(4-\text{Br-C}_6\text{H}_4\text{ORb})_5 \cdot (\text{diox})_5]\), however, is solvated by the divergent Lewis base 1,4-dioxane but the rods do not link together. The rods, decorated with terminal dioxane molecules, pack in a hexagonal packing array.

**Figure 3.2.** Sections of the inorganic rods of a) \((\text{C}_6\text{H}_5\text{OK})_3\), \(^{17}\) b) \([(4-\text{Cl-C}_6\text{H}_4\text{OK})_3 \cdot (\text{diox})]_3\), \(^{11}\) c) \([(4-\text{Br-C}_6\text{H}_4\text{OK})_2 \cdot (\text{diox})_0.5]_2\), \(^{11}\) d) \([(4-\text{Et-C}_6\text{H}_4\text{OK})_3 \cdot (\text{diox})]_3\), \(^{13}\) e) \((\text{C}_6\text{H}_5\text{ORb})_3\), \(^{17}\) f) \([(4-\text{Et-C}_6\text{H}_4\text{ORb})_2 \cdot (\text{diox})_0.5]_2\), \(^{13}\) g) \((\text{C}_6\text{H}_5\text{OCs})_3\), \(^{17}\) h) \([(4-\text{Et-C}_6\text{H}_4\text{OCs})_2 \cdot (\text{diox})_0.5]_2\), \(^{13}\) i) \([(2-\text{Me-C}_6\text{H}_4\text{OK})_2 \cdot (\text{THF})]_2\), \(^{14}\) j) \([(4-\text{Br-C}_6\text{H}_4\text{ORb})_5 \cdot (\text{diox})_5]\), \(^{11}\) k) \((\text{C}_6\text{H}_5\text{ONa})_2\), \(^{17}\) l) \(\text{Na}_2(\text{p-C}_6\text{H}_4\text{O}_2)\), \(^{15}\) and m) \(\text{K}_2(\text{p-C}_6\text{H}_4\text{O}_2)\), \(^{16}\) n) \(\text{Na}_2(\text{C}_5\text{H}_4\text{NCO}_2)_2\).\(^{18}\) Sodium, yellow; potassium, purple; rubidium, pink; cesium, blue; oxygen, red.
3.1.3 Heavy alkali metals CPs

In addition to the inorganic rods discussed above, the heavy alkali metals (K, Rb, Cs) have been shown to exhibit novel chemistry leading to a variety of unique materials. These metals are the largest in Group 1 and thus can accommodate a greater number of ligands. The potential for a larger number of ligands means there are a larger number of potential points for network extension. Earlier studies done in our group gave promising results. For example, three of the six reported 7-connected uninodal networks contain K and Rb and the first of three reported 9-connected uninodal networks is a Rb framework.\(^{19}\) Two of those 7-connected networks are isoreticular materials, \([(4-\text{Cl-2,6-Me}_2\text{C}_6\text{H}_2\text{OM})_2\cdot\text{diox}]_{3.5} (M = K, Rb)\), composed of metal-aryloxide dimers connected through dioxane bridges. The third 7-connected network, \([(2,4,6-\text{Me}_3\text{C}_6\text{H}_2\text{OK})_5\cdot\text{diox}]_5\), is built from potassium-aryloxide pentamers connected through dioxane bridges. Figure 3.3 shows the SBUs for the 7-connected materials.

The inspiration for the work described in this chapter derives from the results of the previously characterized potassium and rubidium \(^{2-1}\text{PrC}_6\text{H}_4\text{O}/\text{dioxane species. }\)\(^{19}\) \([(2-\text{PrC}_6\text{H}_4\text{ORb})_6\cdot\text{diox}]_{4.5}\) is the first reported 9-connected uninodal network.\(^{19}\) The nodes are rubidium-aryloxide hexametallic aggregates in a triple-stack-of-dimers motif and each metal is coordinated by at least one bridging dioxane molecule. Similarly, the potassium system forms a hexametallic triple-stack-of-dimers aggregate, however, it only links to six other aggregates forming a pcu network. The interesting property of this system is that one or two water molecules can be encapsulated in the potassium-aryloxide cage.\(^{20}\) Previously there were no examples of neutral water molecules
encapsulated in alkali metal cages. Encapsulation of one water molecule breaks the central K-O\textsubscript{Ar} bonds in the triple-stack-of-dimers aggregate, leaving instead a hexametallic drum aggregate. The extended structure is unaffected. Inclusion of a second water molecule again breaks open the aggregate leading to an open-drum type aggregate. In this case the extended structure is a 2-D 4\textsuperscript{4}-net bilayer. Figure 3.4 shows the SBUs and resulting frameworks for the potassium\textsuperscript{20} and rubidium\textsuperscript{19} materials. These intriguing and unexpected results with potassium and rubidium naturally led to the exploration of the 2-\textsuperscript{i}PrC\textsubscript{6}H\textsubscript{4}OH/dioxane system with the largest alkali metal, cesium.

}\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{33_3_4.jpg}
\caption{Figure 3.3. The a) dimeric SBU of [(4-Cl-2,6-Me\textsubscript{2}C\textsubscript{6}H\textsubscript{2}OM\textsubscript{2})(diox)\textsubscript{3.5}] (M = K, Rb); and b) pentameric SBU of [(2,4,6-Me\textsubscript{3}C\textsubscript{6}H\textsubscript{2}OK)\textsubscript{5}(diox)\textsubscript{3}]. Each SBU is a part of a 7-connected network. One of the nine dioxanes coordinated to the pentameric aggregate is terminal and two form a double-bridge, making it a 7-connected node. The aryloxide has been removed for clarity.}
\end{figure}
Figure 3.4. The molecular aggregates which act as SBUs and a portion of the resulting networks for a) [(2-1PrC₆H₄OK)₆•(diox)₅], b) [{{(2-1PrC₆H₄OK)₆•H₂O}•(diox)}₅•(diox)], c) [{{2-1PrC₆H₄OK)₆•(H₂O)₂}•(diox)₅•5.5}, and d) [(2-1PrC₆H₄ORb)₆•(diox)₄.5]. Purple: K; Red: O; Green: O\textsubscript{water}; Pink: Rb.
3.2 Results and Discussion

3.2.1 Synthesis

The equimolar reaction of 2-iso-propylphenol with cesium tert-butoxide in 1,4-dioxane solution yields \([\{(2\text{-}^\text{i}\text{Pr}-\text{C}_6\text{H}_4\text{OCs})_2(\text{H}_2\text{O})(\text{dioxane})_{0.5}\}\] (3.1); \([\{(2\text{-}^\text{i}\text{Pr}-\text{C}_6\text{H}_4\text{OCs})_4(\text{H}_2\text{O})_2(\text{dioxane})_{1.5}\}\] (3.2); and \([\{(2\text{-}^\text{i}\text{Pr}-\text{C}_6\text{H}_4\text{OCs})_3(\text{H}_2\text{O})_0.5(\text{dioxane})_{2.5}\}\] (3.3), Scheme 3.1. All three materials were crystallized upon cooling of a saturated 2:1 hexane:dioxane solution to room temperature. Materials 3.1 and 3.2 are hybrid organic-inorganic materials built from 1-D inorganic rods which are subsequently linked through dioxane molecules. Compound 3.3 is a 2-D sheet built from discrete SBUs which are linked through both dioxane bridges and Cs-C\(_\text{Ar}\) cation-π interactions.

\[
\begin{align*}
\text{[CsO'Bu·HO'Bu]} + \text{[diox / hex]} & \rightarrow \{(2\text{-}^\text{i}\text{Pr}-\text{C}_6\text{H}_4\text{OCs})_2(\text{H}_2\text{O})(\text{dioxane})_{0.5}\} \quad (3.1) \\
& \rightarrow \{(2\text{-}^\text{i}\text{Pr}-\text{C}_6\text{H}_4\text{OCs})_4(\text{H}_2\text{O})_2(\text{dioxane})_{1.5}\} \quad (3.2) \\
& \rightarrow \{(2\text{-}^\text{i}\text{Pr}-\text{C}_6\text{H}_4\text{OCs})_3(\text{H}_2\text{O})_0.5(\text{dioxane})_{2.5}\} \quad (3.3)
\end{align*}
\]

Scheme 3.1. Preparation of 3.1-3.3 which co-crystallize from the same reaction.

3.2.2 Characterization

This section will describe the unusual process of characterization of 3.1-3.3. Subsequent sections will discuss the presence and source of water in the structures, the molecular structures, and finally the extended structures. The isolation and characterization of 3.1-3.3 was not as straightforward as it is drawn in Scheme 3.1. All three materials have the same crystal morphology, so the characterization of 3.1-3.3...
was a stepwise process. Initially, the 3-D material 3.1 was structurally characterized by X-ray diffraction. Upon seeing this interesting highly porous structure, the remaining crystals were exposed to vacuum for several hours in order to try to evacuate the pores. After exposure to vacuum, nearly all of the crystals were destroyed. However, a small piece was left intact and was selected for single crystal X-ray diffraction. The resulting structure was that of the 2-D material 3.2. The initial conclusion was that evacuation of the pores in 3.1 had led to framework collapse resulting in 3.2. Naturally, attempts to reproduce 3.1 were conducted at which point a third species 3.3 was structurally characterized. This confusing result led us to believe it was possible multiple products were co-crystallizing from the same reaction. This is, in fact, what happens, which was shown by checking the unit cells of many crystals from the same reaction vessel. Out of the same reaction, 3.1, 3.2 and 3.3 co-crystallize.

The crystalline materials are extremely unstable when removed from the mother liquor. Examination under the microscope when searching for high quality single crystals had to be done quickly or the crystals would desolvate and disappear into the oil. This instability caused great difficulty in further characterization of the materials. After drying the crystals, a loss in crystallinity was proven by powder X-ray diffraction experiments, which showed only broad amorphous peaks. NMR analysis was also problematic for several reasons. The void spaces in the materials are filled with an unknown quantity of water and dioxane solvent molecules, so determining the actual ratio of those signals is unreliable. Also, upon isolation it is likely that much of this
solvent is lost in the desolvating decomposition of the crystalline material. For these reasons, $^1$H NMR analysis cannot reliably give the water:dioxane:phenoxide ratios. Despite the complex mixture resulting from the reaction, synthesis of the complexes is reproducible. Many reactions were run in order to test the reproducibility. Interestingly, only one of the materials, 3.1, could be selectively synthesized. This was carried out through the use of meticulously dried and degassed reagents, solvents and glassware. The reaction and crystallization proceeded exactly the same as before, however, only 3.1 was crystallized. This was confirmed by checking the unit cells of at least six crystals from the reaction each time it was carried out.

3.2.3 The presence of adventitious water

The source of the water in the structures of 3.1-3.3 cannot be easily explained. After initial characterization of the products, attempts were made to ensure everything was as dry as possible. The 1,4-dioxane was freshly distilled from sodium benzophenone onto 4 Å molecular sieves. Hexane was dried by passage through columns of copper-based catalyst and alumina and stored on 4 Å molecular sieves. The 2-iPr-phenol was also freshly distilled from calcium hydride onto 4 Å molecular sieves. The dioxane, hexane, 2-iPr-phenol and solid [CsO$^i$Bu·HO$^i$Bu] were individually checked by $^1$H NMR and no water was detected. However, the presence of water in the crystallized products could not be avoided. As was described above, 3.1 could be selectively prepared upon meticulous drying and degassing of the reagents, solvents and glassware. Compound 3.1, $[(2^{i}-$Pr-C$_6$H$_4$OCS)$_2$(H$_2$O)(dioxane)$_{0.5}]$, contains 0.5 H$_2$O per
cesium, which is not even the product with the least amount of water per cesium.

Compound 3.3, \([\text{[2-}^{1}\text{Pr-C}_6\text{H}_4\text{OCs}]_3\text{H}_2\text{O}0.5\text{(dioxane)2.5]}\), contains 0.17 H_2O per cesium, slightly less than 3.1. The structural importance of the water will be discussed in section 3.2.5.

There is some precedent in the literature for alkali metal aryloxide materials to incorporate adventitious water molecules. Previously, \[\text{[(2-}^{1}\text{Bu-C}_6\text{H}_4\text{OK})_6⊃(\text{H}_2\text{O})\text{-}(\text{diox})_4\]}\] was reported as a 2-D 4\(^4\)-net built from hexameric drum SBU\(\text{s}\),\(^{20}\) Figure 3.5. Encapsulated in the hexameric drum is a water molecule that cannot be removed. Attempts were made to synthesize this material without water, but were unsuccessful and resulted in a lower yield of the same product. Deliberate addition of excess water resulted in high yielding formation of the same product. The source of the water was never discovered. Similar reactions with 2-\(^{1}\text{Pr-C}_6\text{H}_4\text{OH}\) led to structures both with and without water encapsulation, Figure 3.4a-c. As is previously described in section 2.1.3, a series of \[\text{[2-}^{1}\text{Pr-C}_6\text{H}_4\text{OK}(\text{diox})_x(\text{H}_2\text{O})_y]\] was characterized in which the amount of encapsulated water could be varied based on experimental conditions.\(^{20}\)
3.2.4 Molecular and polymeric SBUs

This section will focus on the inorganic rod or molecular SBUs for 3.1-3.3, the extended structures of these materials will be discussed later. Compound 3.1 is a 3-D material composed of 1-D inorganic rods, Figure 3.6a. The 1-D inorganic rods are composed of Cs-O interactions. There are two unique cesium atoms in the structure, both are five coordinate. Cs1 is bonded to three $O_{Ar}$ atoms and two $O_{water}$ atoms. Cs2 is bonded to three $O_{Ar}$ atoms, one $O_{water}$ and one $O_{diox}$. The cesium $O_{Ar}/O_{water}$ interactions result in the formation of a corrugated 1-D rod decorated with bridging dioxane molecules.

Figure 3.5. The structure of $[\{(2-tBu-C_6H_4OK)_6(H_2O)\cdots(dioxane)\}_4]$ showing (a) the prismatic hexamer highlighting the two disordered water sites within the aggregate and the six coordinated dioxanes, and (b) the extended two-dimensional 4$^4$-net resulting from four bridging and two terminal dioxane molecules per hexameric aggregate.\textsuperscript{20}
Compound 3.2 is a 2-D material composed of 1-D inorganic rods, Figure 3.6b. The 1-D inorganic rods are once again composed of only Cs-O interactions. There are four unique cesium atoms in the structure; Cs1 and Cs4 are both six coordinate and are bonded to three O_{Ar} atoms and three O_{water} atoms. Cs2 and Cs3 are both five coordinate and are bonded to three O_{Ar} atoms, one O_{water} and one O_{diox}. The Cs-O_{Ar}/O_{water} interactions result in a corrugated 1-D rod isostructural to that of 3.1. The rod is decorated with dioxane molecules, however, only a portion of them bridge to other rods while the remaining dioxane molecules act as terminal donors.

Compound 3.3 is a 2-D network built from discrete inorganic SBUs, Figure 3.6c. The SBU can be described as a water-centered hexametallic aggregate in an open drum.
shape. It is a distorted hexagonal prism composed of Cs-O_{Ar} bonds in which one side of the prism is open. There are three unique cesium atoms in the structure. Cs1, which lies on the open edge of the drum, is coordinated by two O_{Ar} atoms and the aromatic ring of the 2-iso-propylphenoxide ligand across the open face of the drum. Cs2 is five coordinate in a distorted trigonal bipyramidal environment and is coordinated by three O_{Ar} atoms and two O_{diox} atoms. Cs3 is also five coordinate in a distorted trigonal bipyramidal environment and is coordinated by three O_{Ar} atoms, one O_{diox} and one O_{water}.

The inorganic rod in 3.1 is built from Cs-O_{Ar} and Cs-O_{water} interactions, selected bond lengths are presented in Table 3.1. The average Cs-O_{Ar} distances are 3.21 and 3.02 \text{Å} for Cs1 and Cs2 respectively. The average Cs-O_{water} distance for Cs1 is 3.18 \text{Å}. These distances fall within the range of Cs-O and Cs-O_{water} (average = 3.228 and 3.287 \text{Å} respectively) distances reported previously. The same can be said for 3.2 and 3.3 with the average Cs-O_{Ar} distances in 3.2 being 3.16, 3.01, 3.03 and 3.24 \text{ Å} for Cs1-Cs4 respectively and the average Cs-O_{water} distances being 3.34, 3.16, 3.07 and 3.40 \text{ Å}.

While in 3.3 the average Cs-O_{Ar} distances are 2.92, 3.00 and 3.00 \text{Å} for Cs1-Cs3 respectively and the Cs3-O_{water} distance is 3.16 \text{Å}. The Cs1-C_{Ar} cation-\pi interactions have average distances of 3.64 \text{Å} for the inter-SBU connection and 3.77 \text{Å} for the intra-SBU connection. These distances also fall within the range of Cs-C_{Ar} cation-\pi interaction distances that have been previously reported (3.202 – 4.747 \text{Å}, average = 3.605 \text{Å}).
There are no examples reported in the literature of Cs-based inorganic rods similar to 3.1 or 3.2. Only two cesium inorganic rods have been reported to date, \([\text{[Cs}_6\text{H}_5\text{OCS}}]_3^{17}\) and \([\text{[4-Et-C}_6\text{H}_4\text{OCS}}]_2\cdot\text{(diox)}_{0.5}]^{13}\) \([\text{[4-Et-C}_6\text{H}_4\text{OCS}}]_2\cdot\text{(diox)}_{0.5}]\) and \([\text{[Cs}_6\text{H}_5\text{OCs}}]_3\) are isostructural and were described in the previous chapter. The average Cs-O\(_{\text{Ar}}\) distances in \([\text{[4-Et-C}_6\text{H}_4\text{OCS}}]_2\cdot\text{(diox)}_{0.5}]\) are 3.04 and 3.05 Å for Cs1 and Cs2.
respectively, these distances are comparable to those in 3.1-3.3. The rods in 3.1 and 3.2 are isostructural and unlike any other alkali metal aryloxide inorganic rods in the literature.\textsuperscript{11,13,14,17}

3.2.5 Extended structures

This section will describe in detail the extended structures of 3.1-3.3. The extended 3-D structure of 3.1 is a \textit{kgm}-type rod packing which results in an interesting porous material, Figure 3.7. The 1-D channels run parallel to the inorganic rods along the c-axis and are filled with disordered solvent molecules. The channels are lined by the 2-\textit{iso}-propylphenoxide groups and are approximately 20 Å in diameter, leading to a material with ~34\% (10024.8 Å\textsuperscript{3}) solvent accessible void space.\textsuperscript{22} The extended 2-D structure of 3.2 is a layered structure of corrugated sheets, Figure 3.8. The sheets are offset from one another so that the rods of one sheet do not sit directly above or below the rods of another sheet. There is no void space between the sheets due to the offset nature in which they pack. The extended structure of 3.3 is composed of 1-D chains of SBUs which are linked through Cs2-diox-Cs2’ bridges. The chains are then linked together through double bridges of Cs1-C\texttextit{Ar} cation-\textit{π} interactions, Figure 3.9. There are two dioxane molecules which simply act as terminal donors. The sheets are well separated by these terminal dioxane molecules which project into the space between the layers, thus leaving no void space in the interlayer.
It is interesting to compare the composition of the inorganic building blocks for each structure obtained from this curious reaction which yields three unique crystalline products. The inorganic rods of 3.1 and 3.2 and the inorganic SBU of 3.3 contain slightly different amounts of water and dioxane per cesium, which likely accounts for the differences in extended structure.

The inorganic rod of 3.1 contains 0.5 H$_2$O and 0.25 dioxane per cesium, while the inorganic rod of 3.2 contains 0.5 H$_2$O and 0.375 dioxane per cesium. This slight
difference of 0.125 dioxane per cesium results in a decrease of dimensionality from 3-D in 3.1 to 2-D in 3.2. This result is not necessarily surprising, since increasing the linker-to-metal ratio in a CP increases the coordinative saturation around the metal centers thus resulting in fewer points for network extension. Similarly, when compared to 3.1, the amount of H$_2$O and dioxane per metal in 3.3 (Cs: H$_2$O: diox = 1: 0.17: 0.83) leads to a 2-D rather than 3-D network.

**Figure 3.8.** A portion of a) the inorganic rod of 3.2 showing solvating 1,4-dioxane molecules; b) the 2-D sheet of 3.2 showing the 1-D rods connected through bridging dioxane; and c) the packing of the 2-D nets. All hydrogen atoms have been removed for clarity. Blue: Cs; Red: O; Black: C.
The comparison of 3.2 to 3.3 is less straightforward. There is a decrease in the amount of H$_2$O per cesium, and a large increase in the amount of dioxane. This large increase in dioxane however does not result in the decrease of dimensionality of the extended structure. While the dimensionality does not change, the structure certainly does. The most obvious difference is that instead of a 1-D inorganic rod, 3.3 is built from discrete metal aggregates. This difference is likely tied to the decrease in the amount of H$_2$O since in all three structures the H$_2$O present is centered in either the rod or SBU. In

\textbf{Figure 3.9.} a) The molecular SBU of 3.3 showing the solvating 1,4-dioxane molecules. A portion of b) the 1-D polymer built from Cs-C$_{Ar}$ agostic interactions highlighting the inter- and intra-molecular interactions; and c) the 2-D extended structure of 3.3 showing the bridging dioxane molecules. All hydrogen atoms have been removed for clarity. Blue: Cs; Red: O; Black: C.
3.1 and 3.2 the water molecules facilitate the growth of the 1-D rod by bridging the metal centers from within the rod, providing structural support and allowing the rod to grow. In 3.3 there is less water present, and so the inorganic rod structure terminates into a discrete metal aggregate that acts as the SBU.

3.3 Summary

The reactions and resulting structures of the alkali metal/2-iso-propylphenoxide/dioxane system become more complicated with increasing cation size. As evidenced by the varying degrees of hydration for the potassium materials, the novel topology of the rubidium material, and the three unique materials that crystallize from the cesium reaction.

The characterization of two cesium aryloxide inorganic rods fits into the trend that has begun to emerge in which large cations tend to form 1-D rods instead of discrete molecular aggregates. Previous work from our group and others has shown that this is also the case with simple phenoxide, 2-methyl-phenoxide, 4-ethyl-phenoxide, 4-chloro-phenoxide, and 4-bromo-phenoxide. More aryloxide systems need to be explored with the larger alkali metals to further investigate this trend.

There are currently not enough alkali metal aryloxide inorganic rods structurally characterized for patterns to have emerged. However, the rods in 3.1 and 3.2 are isostructural, suggesting this could be an inherently stable configuration. Also, in the limited number of rods reported to date, eight of them are isostructural with just slight variations in the bond lengths and angles due to changes in cation size. As more rods
are characterized it will be interesting to see if structural patterns emerge both within the rods and for the hybrid materials they build.

3.4 Experimental Section

3.4.1 General Procedures

All experimental manipulations were performed under a dry nitrogen atmosphere in flame-dried glassware using standard Schlenk techniques. Dioxane was distilled from sodium benzophenone and stored over 4 Å molecular sieves prior to use. Hexane was dried by passage through columns of copper-based catalyst and alumina (Innovative Technology). Cesium metal was purchased from Strem. 2-iso-propylphenol was distilled from calcium hydride onto 4 Å molecular sieves prior to use.

3.4.2 X-ray Crystallography

Single-crystals were examined under Infineum V8512 oil. The datum crystal was affixed to a Mitegen mounting loop and transferred to the 100 K nitrogen stream of a Bruker APEX diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 12 0.5° φ scans. The orientation matrix derived from this was transferred to COSMO to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Cell parameters were refined using reflections harvested from the data collection with I > 10σ(I). All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. The structures were solved
and refined using SHELXTL. Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of full-matrix least-squares refinement on $F^2$. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2× the equivalent isotropic U of the parent atom.

3.4.3 Preparation

**Synthesis of [CsO$^t$Bu•HO$^t$Bu].**$^{23}$ Cesium metal (5.0g, 37.0mmol) was added to a Schlenk flask. THF 60mL was added along with a stir bar. Excess tert-butanol (6.2mL, 83.3mmol) was added to the stirring reaction mixture and then heated to 70°C for 4 hours. After cooling to room temperature, the reaction mixture was filtered through a Celite pad. The solvent was removed from the filtrate under vacuum resulting in a white solid. The solid was heated at 50°C under vacuum overnight to yield a white powder. Yield: 9.46g (91%). **Caution: Cesium metal is extremely reactive and reacts violently/explosively with air and water.** $^1$H NMR (300 MHz, toluene-d$_8$, 25°C ) $\delta$ = 1.29 (s, CH$_3$).

3.1 [(2-$^1$Pr-C$_6$H$_4$OCs)$_2$(H$_2$O)(dioxane)$_{0.5}$]; 3.2 [(2-$^1$Pr-C$_6$H$_4$OCs)$_4$(H$_2$O)$_2$(dioxane)$_{1.5}$]. and 3.3 [(2-$^1$Pr-C$_6$H$_4$OCs)$_3$(H$_2$O)$_{0.5}$(dioxane)$_{2.5}$]. 3.1-3.3 were synthesized concurrently in the same reaction vessel. 0.27mL (2.0mmol) of 2-iso-propylphenol was dissolved in 5mL 1,4-dioxane. 0.560g (2.0mmol) of [CsO$^t$Bu•HO$^t$Bu] was added to the stirring solution via solid addition tube. The resulting yellow solution was allowed to stir for 30 minutes.
The solvent was then removed by vacuum and the resulting orange oil was taken up in 10mL hexane. Hot dioxane (approximately 5mL) was added until everything dissolved and the solution was allowed to cool over the course of two days in a hot water bath. X-ray quality crystals of 3.1-3.3 were obtained upon slow cooling of the solution to room temperature. $^1$H NMR (300 MHz, THF-$d_8$, 25°C) $\delta$ = 1.14 (6H, d, $^2J_{HH} = 6.9$ Hz, CH$_3$, $^i$Pr), 3.32 (1H, m, CH, $^i$Pr), 3.56 (1.3H, s, CH$_2$, diox), 5.03 (1H, br s, H$_2$O), 6.06 (1H, t, $^3J_{HH} = 7.4$, m-H, Ph), 6.32 (1H, d, $^2J_{HH} = 8.1$ Hz, o-H, Ph), 6.70 (1H, t, $^3J_{HH} = 7.2$, p-H, Ph), 6.83 (1H, d, $^2J_{HH} = 7.2$ Hz, m-H, Ph).

Selective Synthesis of 3.1 \(\text{[(2-}^i\text{Pr-C}_6\text{H}_4\text{OCs})_2\text{(H}_2\text{O)(dioxane)}_{0.5}]\). Compound 3.1 can be selectively synthesized by taking extreme care to exclude oxygen and water prior to and during the reaction. The solvents and 2-isopropylphenol were dried immediately prior to use and all glassware was flame dried under vacuum three times over a two hour period prior to use. The purity of \([\text{CsO}^i\text{Bu\HO}^i\text{Bu}]\) was confirmed by $^1$H NMR. The procedure was the same as described above.

3.5 References


(21) The Cambridge Structural Database, version 5.33, updates February 2012.


CHAPTER 4:
A SERIES OF ISORETICULAR TWO DIMENSIONAL LANTHANIDE COORDINATION POLYMERS

4.1 Introduction

The solid-state structures of CPs can be very influential in determining the physical properties of the material, and often times the structures are quite complex. One way to simplify these complicated structures is to break the networks down to a series of nodes and linkers. This allows for the connectivity of the network, as well its underlying topology, to be more easily studied (see Chapter 1, section 1.4 for examples). Consequently, when this is done to the existing networks in the literature, a vast majority of the uninodal nets have a connectivity of six or less.¹ This means that each node connects to no more than six identical neighboring nodes. A relatively small number of networks have a connectivity of seven or greater, with the exception of 8-connected body-centered cubic²–⁶ and 12-connected face-centered cubic networks.⁷–¹⁰ These high connectivity networks seem to be rare for two reasons: First, sterically many nodes cannot support a large number of organic linkers. Attempts to circumvent this issue include using larger single metal centers such as lanthanides or metal aggregates as secondary building units (SBUs).¹¹,¹² Secondly, nature tends to favor structures that are symmetric. For low connectivity nets (≤6) there are some very common high
symmetry topologies such as 4-connected diamondoid and 6-connected primitive cubic.\textsuperscript{1} However, for high connectivity nets (>6) there are not common symmetric topologies (with the exceptions for 8- and 12-connected mentioned above), Figure 4.1.

\textbf{Figure 4.1.} Ball and stick network representations of the common network topologies a) 4-connected diamondoid, b) 6-connected primitive cubic, c) 8-connected body-centered cubic and d) 12-connected face-centered cubic.
There are limited examples of high connectivity nets including both single metal nodes and SBUs as nodes. Two 7-connected networks are reported with single lanthanide metal centers as nodes. The first is a lanthanum network using 4,4’-dipyridyl N,N’-dioxide (bipy-O$_2$) as the organic linker. In this case the lanthanum metal center is coordinated by eight linkers, which bridge to seven unique neighbors. The charge balancing anions (BPh$_4^-$ and ClO$_4^-$) occupy the void space within the structure. The other 7-connected material utilizing a single metal center is a praseodymium based 2-D structure. The metal center is coordinated by the oxygen atoms of three different 2,2’-diphenyldicarboxylic acid ligands and two nicotinic acid ligands as well as the nitrogen atom of one nicotinic acid ligand. This leads to a seven connected uninodal 2-D network, Figure 4.2. There are three additional 7-connected nets built from alkali metal aryloxide aggregates. These aggregates are connected through 1,4-dioxane linkers to make 3-D materials, these were discussed previously in sections 2.1 and 3.1.3. Finally, one cobalt 7-connected network is built from tetrameric SBUs connected through isonicotinate linkers.

Only four 9-connected networks have been characterized and all of them employ SBUs as nodes. The first reported 9-connected network is built from rubidium aryloxide pentamers linked through 1,4-dioxane bridges, this was discussed previously in sections 2.1 and 3.1.3. The other three are composed of first row transition metals, nickel and zinc. The first nickel material has a tri-nuclear mixed valent nickel core centered by a μ$_3$-OH, this SBU is linked through naphthalene-2,6-dicarboxylic acid and 4-(pyridine-4-yl)benzoate bridges. The second nickel material has a tetra-nuclear
Figure 4.2. The two 7-connected uninodal networks with single Ln metal centers as nodes. a) The coordination environment around La in [(La(C₁₀H₈N₂O₂)₄){B(C₆H₅)₄}(ClO₄)₂·2.75CH₃OH]; b) a view along the a-axis of the 3-D net; c) a view along the c-axis of the 3-D net. d) The coordination environment around Pr in [Pr(C₁₄H₈O₄)(C₆H₄NO₂)]; e) a view of the face of the 2-D sheet.

[Ni₄(μ₃-OH)₂] core surrounded by isonicotinate linkers and one propionate ligand. The zinc material has a tri-nuclear SBU in which the three metal atoms are connected through one 1-H-teterazole-5-acetate molecule. These SBUs are connected through other 1-H-teterazole-5-acetate bridges to nine unique neighbors. Figure 4.3 shows the SBUs for the four 9-connected networks.

We sought to combine these two approaches for building high connectivity nets by using lanthanide metals, which have large coordination spheres, within aggregates to
form SBUs. Champness and Schroder used La(ClO$_4$)$_3$ in order to completely charge separate their anions and thus give the most open coordination environment around the metal to allow for more linkers to coordinate. This approach did in fact lead to a high connectivity network, however there was no potential for SBU formation. In our work, the idea was to use lanthanide halides as a starting material, with the goal to retain one or two halide ions on the metal which have the potential to bridge between metals and form an aggregate that could be used as a SBU. SBUs built with large metals would give the most potential points for network extension.
Figure 4.3. The SBUs of the four reported 9-connected networks a) [(2-i-PrC₆H₄ORb)₆(diox)₄.₅];¹⁵ b) [Ni⁺²Ni⁺³(μ₃-OH)pba)₃(ndc)₁.₅];¹⁷ c) [Ni₄(ina)₅(μ₃-OH)₂(EtCOO)];¹⁶ d) [Zn₃(TAA)₃(H₂O)₃].¹⁸ All hydrogen atoms have been removed for clarity.
4.2 Results and discussion

4.2.1 Synthesis

The synthesis of 4.1-4.3 involved the reaction of sodium tetraphenyl borate and 4,4'-dipyridyl N,N'-dioxide with the appropriate lanthanide halide salt in methanol solution, Scheme 4.1. X-ray quality single crystals were grown from the reaction mixture upon sitting for several days.

\[
\text{LnX}_3 + 3 \text{Na[B(C}_6\text{H}_5\text{J}_4]} + 3.75 \text{O-N-N-O MeOH} \rightarrow \left[\text{LnX(C}_10\text{H}_8\text{N}_2\text{O}_2)_4(\text{CH}_3\text{OH})\right]^{x2}\left[\text{B(C}_6\text{H}_5\text{J}_4\text{J}_2(\text{CH}_3\text{OH})}_n\right]
\]

Scheme 4.1. Preparation of 4.1-4.3.

4.2.2 Molecular structure

This section will describe the molecular structure, the extended structure will be discussed in the following section. Since 4.1-4.3 are isostructural, only 4.1 will be described in detail. Compound 4.1 is composed of single lanthanum metal centers coordinated by bipy-O₂ linkers. Each lanthanum is eight coordinate, with the coordination sphere filled by six oxygen atoms from bipy-O₂ ligands, one methanol solvent molecule, and one chloride ion, Figure 4.4. Four of the six coordinated bipy-O₂ molecules bridge to neighboring metal centers. The La – O\text{bipy-O₂} bond distances range from 2.44 Å to 2.57 Å with an average of 2.49 Å. Table 4.1 contains selected bond lengths for 4.1-4.3. These numbers are well within the normal range for previously reported La – O\text{bipy-O₂} data (range: 2.419 – 2.655 Å, average: 2.503 Å).\(^{19}\) The La – O\text{MeOH} bond length is 2.52 Å which, again, is typical of La – O\text{MeOH} bond lengths (range: 2.413 –
2.696 Å, average: 2.575 Å). Finally, the La – Cl bond length is 2.89 Å and is a standard La – Cl bond distance (range: 2.564 – 3.272 Å, average: 2.882 Å). The bond distances for 4.2 and 4.3 are also typical for cerium and gadolinium complexes respectively.

![Figure 4.4](image)

**Figure 4.4.** A view of a) the coordination around the metal center in 4.1, and b) the orientation of the B(Ph)₄ anions with respect to the metal center in 4.1. All hydrogen atoms have been removed for clarity. Orange – boron; black – carbon; blue – nitrogen; red – oxygen; green – chloride; pink – lanthanum.
### Table 4.1

**Select Bond Distances (Å) for 4.1-4.3**

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<td>Ce(1)-O(7)</td>
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<tr>
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<td>2.519(6)</td>
<td>Ce(1)-O(9)</td>
<td>2.5309(12)</td>
</tr>
<tr>
<td>La(1)-Cl(1)</td>
<td>2.886(2)</td>
<td>Ce(1)-Br(1)</td>
<td>3.0569(3)</td>
</tr>
</tbody>
</table>

### 4.2.3 Extended Structure

Once again only 4.1 will be described in detail because 4.2 and 4.3 are isostructural to 4.1. The extended structure of 4.1 is a 2-D sheet which can be described as a $4^4$-net, or square net, Figure 4.5b. Four of the six bipy-O$_2$ linkers bridge to neighboring metal centers resulting in the distorted square net pattern in which the metals are at the corners of the squares and the linkers form the edges. The remaining two bipy-O$_2$ ligands do not bridge with the non-coordinating end projecting into the space between the 2-D layers. These two dangling ligands on each metal are located on the same side of the plane of the $4^4$-net. Moving along the b-axis of the unit cell, the dangling ligands on neighboring metals alternate between above and below the plane, while along the a-axis these ligands are all either “up” or “down”, Figure 4.5c. The chloride ion coordinated to the lanthanum always resides on the same side of the plane.
as the two dangling bipy-O₂ ligands. Contrastingly, the coordinated methanol molecule always resides on the opposite side of the plane as the dangling ligands. The two non-coordinating tetraphenyl borate ions per metal are located in between the 2-D layers. These ions keep the layers sufficiently separated so that they cannot be connected to form a 3-D network. There is also a solvent molecule in the interlayer.

Figure 4.5. Views of 4.1 showing a) the face of the 4⁴-net, b) the face of the 4⁴-net with all but linking bipy-O₂ ligands removed. A side view of c) the net showing the orientation of the pendant bipy-O₂ ligands, and d) the placement of the B(Ph)₄ anions with respect to the 2-D sheets. All hydrogens have been removed for clarity.

There is practically no solvent accessible void space (<6% for 4.1) in any of the materials 4.1-4.3 due to the efficient packing of the large anions in the interlayer and the dangling bipy-O₂ ligands which project over the square hole in the net. In the solid state, the layers are slightly offset from the layers directly above and below, which results in an ABAB layered crystalline solid.
4.2.4 Lanthanide/4,4’-dipyridyl N,N’-dioxide complexes in the literature

This section will describe Ln/bipy-O₂ complexes in the literature and compare them to 4.1-4.3. There are many examples of lanthanide/4,4’-dipyridyl N,N’-dioxide complexes in the literature, and quite a few are polymeric materials. Specifically for the metals in 4.1-4.3 (lanthanum, cerium, and gadolinium) there are 1-, 2-, and 3-D materials reported. These polymeric materials range from very simple extended structures to some quite complicated interesting solid state structures. The lanthanum complex [La(C₅H₄O₂F₃)₃(C₁₀H₈N₂O₂)] has a 1-D zig-zag chain structure in which the metal center is coordinated by three bidentate trifluoroacetylacetonato groups in a syn fashion and is linked to neighboring metal centers through bridging bipy-O₂ linkers.²⁰

[CeCl₂(C₁₀H₈N₂O₂)₂(H₂O)₃]Cl·H₂O] is a cerium material exhibiting a linear chain structure where the metal is coordinated by two bridging bipy-O₂ linkers and one terminal bipy-O₂ ligand as well as two chloride ions and three water molecules.²¹ Similarly,

[(Gd(C₁₀H₈N₂O₂)₄(H₂O)₃)(H₃O)(SiMo₁₂O₄₀)(C₁₀H₈N₂O₂)₀.₅(CH₃CN)₀.₅(H₂O)₃] is a gadolinium chain with two bridging and three terminal bipy-O₂ ligands.²² Another gadolinium 1-D material is a ladder structure, [Gd₂(NO₃)₆(C₁₀H₈N₂O₂)₃·2CH₂Cl₂], where the bipy-O₂ linkers make up both the “rungs” and “legs” of the ladder.²³

No cerium or gadolinium 2-D materials have been reported with bipy-O₂ as the linker, but several lanthanum 2-D structures have been characterized. All of these structures can be described by simple 4⁴-nets or variations of such networks. The simplest of these is a basic 4⁴-net similar to 4.1-4.3, [La(C₁₀H₈N₂O₂)₂(NO₃)₃] is composed of lanthanum metal centers chelated by three nitrate anions and bridged to four...
neighboring metals in plane to form a distorted square net.

\[\{\text{La}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{2.5}(\text{CH}_3\text{OH})_2(\text{C}_7\text{H}_{11}\text{CH}_2\text{CO}_2)\}\{\text{B}(\text{C}_6\text{H}_5)_{4}\cdot2.7\text{CH}_3\text{OH}\}\] is a bilayer structure where the lanthanum is bridged to four neighboring metals in plane by four bipy-O\_2 linkers forming a 4\_4-net which is cross-linked to a neighboring 4\_4-net by a fifth bipy-O\_2 linker. Coordinated methanol molecules and a chelating carboxylate group from 2-norbornane acetate fill out the coordination sphere of each metal center. A related structure is that of \{\text{La}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{4}(\text{ClO}_4)_{3}\cdot(\text{C}_6\text{H}_5\text{Cl})(\text{CH}_3\text{OH})\}, which is also a bilayer structure where the lanthanum is bridged to four neighboring metals in plane by six bipy-O\_2 linkers (two single and two double bridges) to form a 4\_4-net. Two additional bipy-O\_2 linkers cross-link the 4\_4-net with a neighboring net.\(^{24}\) Finally,

\[\{\text{La}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{7.3}(\text{CH}_3\text{OH})(\text{H}_2\text{O})_{0.4})(\text{CF}_3\text{SO}_3)_{6}\]\ is a bilayer structure in which the lanthanum is bridged to four neighboring metals in plane by four bipy-O\_2 linkers forming a 4\_4-net. This net is cross-linked with another 4\_4-net by four additional bipy-O\_2 linkers.\(^{25}\)

Figure 4.6 shows simplified representations of all of the 2-D networks discussed here as well as 4.1-4.3.
There have been several very interesting 3-D materials constructed from lanthanum with bipy-O$_2$ along with a few standard primitive cubic (pcu) and body-centered cubic (bcu) networks. [{La(C$_{10}$H$_8$N$_2$O$_2$)$_4$}$(NO_3)_3$]$^{24}$, b) [{La(C$_{10}$H$_8$N$_2$O$_2$)$_2$.5$(CH$_3$OH)$_2$}$(C_7H$_9$CH$_2$CO$_2$)]{B(C$_6$H$_5$)$_4$}·2.7CH$_3$OH$]^{24}$, c) [{La(C$_{10}$H$_8$N$_2$O$_2$)$_4$}][ClO$_4$]$_3$·(C$_6$H$_5$Cl)(CH$_3$OH)$]^{24}$, and d) [{La$_2$(C$_{10}$H$_8$N$_2$O$_2$)$_7$.3$(CH$_3$OH)(H$_2$O)$_{0.4}$}(CF$_3$SO$_3$)$_6$]$^{25}$ Red and blue layers are 4$^4$-nets, gray rods are cross-links between the nets.

Figure 4.6. Simplified representations of 2-D materials a) 4.1-4.3 and

[La(C$_{10}$H$_8$N$_2$O$_2$)$_2$(NO$_3$)$_3$]$^{24}$, b) 

[({La(C$_{10}$H$_8$N$_2$O$_2$)$_2$.5$(CH$_3$OH)$_2$}$(C_7H$_9$CH$_2$CO$_2$)]{B(C$_6$H$_5$)$_4$}·2.7CH$_3$OH]$^{24}$, c) 

[({La(C$_{10}$H$_8$N$_2$O$_2$)$_4$}][ClO$_4$]$_3$·(C$_6$H$_5$Cl)(CH$_3$OH)]$^{24}$, and d) 

[({La$_2$(C$_{10}$H$_8$N$_2$O$_2$)$_7$.3$(CH$_3$OH)(H$_2$O)$_{0.4}$}(CF$_3$SO$_3$)$_6$]$^{25}$ Red and blue layers are 4$^4$-nets, gray rods are cross-links between the nets.

There have been several very interesting 3-D materials constructed from lanthanum with bipy-O$_2$ along with a few standard primitive cubic (pcu) and body-centered cubic (bcu) networks. [{La(C$_{10}$H$_8$N$_2$O$_2$)$_4$}$(CF$_3$SO$_3$)$_3$·4.2CH$_3$OH] is an 8-connected bcu framework where each lanthanum is coordinated by eight bipy-O$_2$ linkers which bridge to eight neighboring metal centers.$^{13}$ In [{La(C$_{10}$H$_8$N$_2$O$_2$)$_4$}$(Co(C_7H$_{11}$B$_3$)$_2$)$_3$·CH$_3$OH] each metal center is also coordinated by eight bipy-O$_2$ ligands, however there are two double bridges so this material is a 6-connected pcu network.$^{13}$ These two topologies are quite common for 8- and 6-connected networks, respectively. However, 7-connected and non-bcu 8-connected nets are very rare.

[{La(C$_{10}$H$_8$N$_2$O$_2$)$_4$}B(C$_6$H$_5$)$_4$][ClO$_4$]$_2$·2.75CH$_3$OH] is a 7-connected network with the metal coordinated by eight bipy-O$_2$ linkers. There is one double bridge, so each lanthanum connects to seven neighboring metal centers, as described in section 4.1 and Figure 87.
4.2a–c. This was the first reported 7-connected uninodal net. One non-**bcu** 8-connected material is \([\text{La(C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{4}](\text{ClO}_4)_3\) which is built simply from lanthanum metal centers connected to eight neighboring metal centers through bipy-O\(_2\) bridges, Figure 4.7a. However, these neighboring metal centers have a different arrangement than the standard body-centered cubic packing. Two novel 5-connected networks of lanthanum and bipy-O\(_2\) have been reported. \([\text{La(La(C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{1.5}(\text{CH}_3\text{OH})_2\text{B(OCH}_3)_2\text{B}(\text{C}_6\text{H}_5)_{4}])_{2} \cdot 4.5\text{CH}_3\text{OH}\] is another 5-connected network with the lanthanum coordinated by five bipy-O\(_2\) linkers that bridge to five neighboring metal centers. The coordination sphere of each metal is filled by one methanol molecule and a chelating \(\{(\text{C}_6\text{H}_5)_{2}\text{B(OCH}_3)_2\}\) group, which is an intermediate in the methanolysis of \(\text{B}(\text{C}_6\text{H}_5)_{4}\), Figure 4.7d,e. Interestingly, these two 5-connected networks were crystallized from a nearly identical reaction to that which produced 4.1. The differences in the reactions are limited to the stoichiometric amounts of Na(BPh\(_4\)) and bipy-O\(_2\) used. Our experience in changing the stoichiometry of the reaction, as outlined below, resulted only in variation in the yield and not the product of the reaction. Recently, a heteroleptic material was constructed from lanthanum, bipy-O\(_2\), and benzoic acid. The lanthanum metal center is coordinated by four oxygen atoms from benzoate group, two bipy-O\(_2\) linkers, and two water molecules. The extended structure consists of La-benzoate 1-D chains which are linked together by bipy-O\(_2\)
molecules. This results in a **pcu** network, an isostructural gadolinium material is also reported.\textsuperscript{27}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.7}
\caption{a) The coordination environment around the 8-connected La node in \([\{\text{La}(\text{C}_{10}\text{H}_{8}\text{N}_{2}\text{O}_{2})_{4}\}\text{(ClO}_{4})_{3}\]. Views of the 5-connected network of \([\{\text{La}_{4}(\text{C}_{10}\text{H}_{8}\text{N}_{2}\text{O}_{2})_{10}(\text{CH}_{3}\text{OH})_{10}\text{Cl}_{3}\}\text{Cl}(\text{B}(\text{C}_{6}\text{H}_{5})_{4})_{8} \cdot 22\text{CH}_{3}\text{OH}]\) showing b) the 6\textsuperscript{3}-net and c) the crosslinking bipy-O\textsubscript{2} linkers. d) The coordination environment around the 5-connected La node in \([\{\text{La}(\text{C}_{10}\text{H}_{8}\text{N}_{2}\text{O}_{2})_{2.5}(\text{CH}_{3}\text{OH})_{1/2}(\text{C}_{6}\text{H}_{5})_{2}\text{B(OCH}_{3})_{2}\}\{\text{B}(\text{C}_{6}\text{H}_{5})_{4}\}_{2} \cdot 4.5\text{CH}_{3}\text{OH}]\) and e) a view of the network along the c-axis.}
\end{figure}
4.2.5 Effect of Reaction Stoichiometry on Product Formation

After observing products 4.1-4.3, attempts to alter the product of these reactions by changing the reaction stoichiometry were made. Specifically, variation of the number of halide ions that remained coordinated to the metal center was sought. Completely charge separating all of the anions would allow for an additional coordination site with potential for network extension by a bipy-O$_2$ linker. Retaining an additional halide ion per metal could lead to formation of lanthanide – halide clusters to act as SBUs for the formation of high-connectivity networks. Table 4.2 contains a representative sample of the reactions performed with various LaCl$_3$:Na(BPh$_4$):bipy-O$_2$ ratios for the synthesis of 4.1. In all cases varying the stoichiometry of the reaction either yielded no crystalline product that could be analyzed or 4.1. The only characterizable material produced from these reactions was 4.1, the stoichiometric variations only affected the yield of the reaction. This suggests there is an inherent stability to the structures of 4.1-4.3. Although, as is described above, there have been 3-D materials reported from a reaction of 1:3:2.5 LaCl$_3$:Na(BPh$_4$):bipy-O$_2$.$^{26}$
TABLE 4.2
THE EFFECT OF REACTION STOICHIOMETRY ON THE REACTION YIELD FOR THE
SYNTHESIS OF 4.1

<table>
<thead>
<tr>
<th>LaCl₃ (equiv.)</th>
<th>Na(BPh₄) (equiv.)</th>
<th>Bipy-O₂ (equiv.)</th>
<th>% Yield*</th>
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<tr>
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<tr>
<td>1</td>
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* Yield based on LaCl₃

4.3 Summary

The synthesis and characterization of various lanthanide coordination polymers resulted in a series of 2-D 4^4^-nets. These materials fit a pattern of lanthanide/4,4’-dipyridyl N,N’-dioxide 2-D materials in which a common structural feature is the 4^4^-net. In some cases, these 2-D sheets are cross-linked to provide 2-D bilayer materials. The 2-D sheets in 4.1-4.3 do not cross-link and thus are simple 4^4^-nets with pendant linkers on either side of the plane. The sheets are well separated by tetraphenyl borate ions, so as not to allow the pendant linkers to bridge between sheets. It appears the 4^4^-net is an inherently stable configuration within the class of lanthanide/4,4’-dipyridyl N,N’-dioxide materials; whether on its own or as a substructure of a more complex architecture. In the future this trend could allow chemists to systematically design desired materials a priori.
4.4 Experimental

4.4.1 General procedures

All lanthanide metal salts were purchased from Strem Chemical Company, Na(BPh₄) and 4,4’-dipyridyl N,N’-dioxide dihydrate were purchased from Aldrich and used without further purification. NMR spectra were obtained on a Varian Unity Plus 300 MHz instrument. Due to the paramagnetism of cerium and gadolinium $^{13}$C NMR spectra were not collected and integration of the $^1$H NMR spectra is not reported. $^1$H and $^{13}$C spectra were referenced with respect to the residual solvent signal.

4.4.2 X-ray crystallography

Single-crystals were examined under Infineum V8512 oil. The datum crystal was affixed to a Mitegen mounting loop and transferred to the 100 K nitrogen stream of a Bruker APEX diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 12 0.5° $\phi$ scans. The orientation matrix derived from this was transferred to COSMO to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Cell parameters were refined using reflections harvested from the data collection with $I > 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. The structures were solved and refined using SHELXTL. Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of
full-matrix least-squares refinement on $F^2$. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to $1.2 \times$ the equivalent isotropic $U$ of the parent atom.

4.4.3 Preparation and characterization

4.1 [{LaCl(C$_{10}$H$_8$N$_2$O$_2$)$_4$(CH$_3$OH)}]$^{2+}$[B(C$_6$H$_5$)$_4$]$^{2-}$ (CH$_3$OH)] - A solution of LaCl$_3$ (0.010g, 0.04mmol) and Na(BPh$_4$) (0.041g, 0.12mmol) in 10mL methanol was frozen in a liquid nitrogen bath. A solution of 4,4'-dipyridyl N,N'-dioxide dihydrate (0.033g, 0.15mmol) in 10mL methanol was layered on top of the frozen methanol layer. The vial was then loosely capped and allowed to warm to room temperature. Single crystals were collected after one day. Yield 0.051g, 78% based on LaCl$_3$. Sample decomposed at 205 °C. $^1$H NMR (300 MHz, dimethyl sulfoxide-$d_6$, 25°C) $\delta$ = 3.34 (4H, s, CH$_3$, CH$_3$OH), 6.78 (2H, t, $J_{HH}$ = 6.9 Hz, $p$-H, B(C$_6$H$_5$)$_4$), 6.92 (4H, t, $J_{HH}$ = 7.3 Hz, $m$-H, B(C$_6$H$_5$)$_4$), 7.17 (4H, br, $o$-H, B(C$_6$H$_5$)$_4$), 7.89 (4H, d, $J_{HH}$ = 7.5 Hz, $m$-H, C$_{10}$H$_8$N$_2$O$_2$), 8.30 (4H, d, $J_{HH}$ = 7.5 Hz, $o$-H, C$_{10}$H$_8$N$_2$O$_2$). $^{13}$C($^1$H) NMR (75 MHz, dimethyl sulfoxide-$d_5$, 25°C) $\delta$ = 121.56 ($m$-C, C$_{10}$H$_8$N$_2$O$_2$), 123.37 ($m$-C, B(C$_6$H$_5$)$_4$), 125.37 ($o$-C, B(C$_6$H$_5$)$_4$), 131.60 ($i$-C, B(C$_6$H$_5$)$_4$), 135.55 ($p$-C, C$_{10}$H$_8$N$_2$O$_2$), 139.18 ($o$-C, C$_{10}$H$_8$N$_2$O$_2$).

4.2 [{CeBr(C$_{10}$H$_8$N$_2$O$_2$)$_4$(CH$_3$OH)}]$^{2+}$[B(C$_6$H$_5$)$_4$]$^{2-}$ (CH$_3$OH)$_4$] - A solution of CeBr$_3$ (0.015g, 0.04mmol) and Na(BPh$_4$) (0.041g, 0.12mmol) in 10mL methanol was frozen in a liquid nitrogen bath. A solution of 4,4'-dipyridyl N,N'-dioxide dihydrate (0.033g, 0.15mmol) in 10mL methanol was layered on top of the frozen methanol layer. The vial
was then loosely capped and allowed to warm to room temperature. Single crystals were collected after five days. Yield 0.044g, 66% based on CeBr₃. Sample decomposed at 165 °C. ¹H NMR (300 MHz, dimethyl sulfoxide-d₆, 25°C ) δ= 3.34 ( s, CH₃, CH₃OH), 6.78 (br, p-H, B(C₆H₅)₄), 6.92 (br, m-H, B(C₆H₅)₄), 7.16 (br, o-H, B(C₆H₅)₄), 7.89 (d, J₉H = 7.5 Hz, m-H, C₁₀H₈N₂O₂), 8.30 (d, J₉H = 7.5 Hz, o-H, C₁₀H₈N₂O₂).

4.3 [(GdCl(C₁₀H₈N₂O₂)₂(CH₃OH))²⁺[B(C₆H₅)₄]⁻(CH₃OH)]⁻ - A solution of GdCl₃ (0.011g, 0.04mmol) and Na(BPh₄) (0.041g, 0.12mmol) in 10mL methanol was frozen in a liquid nitrogen bath. A solution of 4,4'-dipyridyl N,N'-dioxide dihydrate (0.033g, 0.15mmol) in 10mL methanol was layered on top of the frozen methanol layer. The vial was then loosely capped and allowed to warm to room temperature. Single crystals were collected after five days. Yield 0.026g, 39% based on GdCl₃. Sample decomposed at 180 °C. ¹H NMR (300 MHz, dimethyl sulfoxide-d₆, 25°C ) δ= 3.34 (br, CH₃, CH₃OH), 6.79 (br, p-H, B(C₆H₅)₄), 6.92 (br, m-H, B(C₆H₅)₄), 7.18 (br, o-H, B(C₆H₅)₄), 7.89 (br, m-H, C₁₀H₈N₂O₂), 8.31 (br, o-H, C₁₀H₈N₂O₂).

Caution: Upon warming to room temperature, the glass vials could shatter sending glass shards flying. We recommend placing the vials in an enclosed environment immediately upon removal from the liquid nitrogen bath.

4.5 References


(22) Wei, M.; He, C.; Sun, Q.; Meng, Q.; Duan, C. Inorg. Chem. 2007, 46, 5957-66.


CHAPTER 5:
FORTUITOUS STRUCTURES WITH LARGE CATIONS

5.1 Introduction

This chapter will discuss several materials that are not a part of a series, but were synthesized and characterized while attempting to use large metal cations to build high-connectivity networks. These materials are included as they are intrinsically interesting in their own right and for completeness. The first material to be discussed is a potassium species, which was crystallized as an intermediate in the synthesis of an organic linker. Next, a 3-D hybrid organic-inorganic barium network will be described, and finally a 1-D neodymium structure will be discussed.

5.2 [K$_2$(O$_2$C$_6$H$_3$N)$_2$(H$_2$O)$_2$]· 2(H$_2$O)

The 3-D material [K$_2$(O$_2$C$_6$H$_3$N)$_2$(H$_2$O)$_2$]· 2(H$_2$O), 5.1, was synthesized and crystallized during the synthesis of 2,2'-dipyridyl-5,5'-dicarboxylic acid, Scheme 5.1. 5.1 was initially isolated as a solid due to the low solubility of the final carboxylic acid product to be used in subsequent reactions as a linker. The 2,2'-dipyridyl-5,5'-dicarboxylate ligand has been used as a linear linker for a variety of MOFs.$^{1-4}$ It is a particularly interesting linker due to the fact that the pyridyl nitrogens have the ability to act as Lewis bases for binding metal centers.$^{3,4}$
Scheme 5.1. Preparation of 2,2’-dipyridyl-5,5’-dicarboxylic acid.

5.1 is the first homometallic alkali metal material constructed with this linker. Only one other material has been reported with an alkali metal, [PtRbCl$_2$(C$_{12}$H$_{7}$N$_2$O$_4$)(H$_2$O)], and this is a heterometallic Pt/Rb species. This bimetallic network consists of square planar platinum metal centers and seven coordinate rubidium metal centers. The coordination sphere of platinum is filled by chelating pyridyl nitrogen atoms and two bridging chloride ions. The rubidium is coordinated by two bridging chloride ions, four oxygen atoms from carboxylate groups and one water molecule. Figure 5.1b shows the coordination environment around each metal center.

5.2.1 Molecular Structure

This section describes the molecular structure of 5.1, the extended structure will be discussed below. The molecular structure of 5.1 consists of six-coordinate potassium metal centers in a distorted trigonal prismatic geometry. The metal centers are coordinated by four monodentate 2,2’-dipyridyl-5,5’-dicarboxylate linkers through carboxylate oxygen atoms and two oxygen atoms from water. Thus the coordination sphere of the metal center is filled by four 2,2’-dipyridyl-5,5’-dicarboxylate linkers and
two water molecules, Figure 5.1a. All of the oxygen atoms, including the water molecules, are μ₂-oxygens bridging to neighboring potassium atoms.⁵

Figure 5.1. a) The coordination environment around the potassium metal center of 5.1. The coordinated water molecules are shown in green, the hydrogen atoms were located in the difference map. b) The coordination environment of each metal center in the bimetallic network [PtRbCl₂(C₁₂H₁₇N₂O₄)(H₂O)].⁴ All calculated hydrogen atoms have been removed for clarity. Orange – platinum, light blue – rubidium, light green – chloride, purple – potassium, red – oxygen, green – oxygen (water), blue – nitrogen, black – carbon, pink – hydrogen.

5.2.2 Extended Structure

This section will detail the extended structure of 5.1. The extended structure of 5.1 is quite complex. Unlike all of the CPs previously described in this thesis, 5.1 is a binodal net. Each potassium is a six connected node and each 2,2’-dipyridyl-5,5’-dicarboxylate linker is an eight connected node, with each carboxylate group coordinated to four unique potassium atoms. Overall this arrangement generates a complex network with point symbol \( \{3^4,4^{12},5^{12}\}\{3^4,4^4,5^4,6^3\}_2 \).⁶ The extended structure is composed of 2-D sheets consisting of potassium-carboxylate and potassium-water
interactions, Figure 5.2a-b. The 3-D assembly is completed by connection of the sheets through the 2,2’-dipyridyl linkers, Figure 5.2c. Small channels run along the a-axis and contain the guest water molecules, Figure 5.2d. Both of the bridging water molecules participate as donors in hydrogen bonding interactions; one to guest water molecules (H-O 2.976(5) Å) and a second to an oxygen of a carboxylate (O-H 2.770(4) Å). A ball and stick representation of the network topology is shown in Figure 5.3.

5.3 \(\{\text{Ba}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{6}^{4+}\{\text{Ba}_2(\text{NO}_3)_{8}^{4-}\}}\)

The 3-D material \(\{\text{Ba}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{6}^{4+}\{\text{Ba}_2(\text{NO}_3)_{8}^{4-}\}}\), 5.2, was synthesized via reaction of barium nitrate with bipy-O_2 in DMF solution, Scheme 5.2. This material is highly charged in that the 3-D framework is formally 4+ and there are charge balancing ions in the pores of the network. However, the anion in 5.2 is quite unique and a search of the CSD yielded no instances of this anion being previously reported. This material was synthesized during a study similar to that which led to the synthesis and characterization of the materials in chapter 4. The goal was to completely charge separate the barium from the nitrate anions in order to get the maximum number of linkers around the metal center in the hopes of building a high-connectivity framework.

\[
2 \text{Ba(NO}_3)_2 + \text{O-N}_-\text{N}=\text{O} \xrightarrow{\text{DMF}} \{\text{Ba}_2(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{6}^{4+}\{\text{Ba}_2(\text{NO}_3)_{8}^{4-}\}} \]

\text{Scheme 5.2. Preparation of 5.2.}
Figure 5.2. A view of the 2-D sheets in 5.1 built from K-O\textsubscript{carbox}-O\textsubscript{water} interactions along the a) z-axis, and b) a-axis. c) Connection of those 2-D sheets through the 2,2’-dipryidyl-5,5’-dicarboxylate linkers. d) A portion of the 3-D network of 5.1 showing the small channel along the a-axis filled with guest water molecules. Purple – potassium, red – oxygen, green – oxygen (bridging water), blue – nitrogen, black – carbon, pink – hydrogen.
5.3.1 Molecular structure

This section will describe the molecular structure of 5.2, the extended structure will be discussed in the following section. The molecular structure of 5.2 consists of four unique barium metal centers, two in the framework and two as part of the counter anion. Ba1 and Ba2 are part of the cationic framework. Ba1 is coordinated to eight bipy-O₂ ligands in a square anti-prismatic geometry. Ba2 is in a nearly identical coordination environment of eight bipy-O₂ ligands in a square anti-prismatic geometry. The two unique barium centers are bridged through bipy-O₂ ligands to form a bimetallic unit, Figure 5.4. This bimetallic unit is part of a larger 1-D building block for the 3-D material which will be discussed in the next section. This portion of the structure, built from two Ba²⁺ cations and no anions, has a 4+ charge.
Ba3 and Ba4 are part of the anion in the structure. Ba3 is ten coordinate, ligated by five bidentate nitrate ions. Ba4 is also ten coordinate, ligated by four bidentate and two monodentate nitrate ions. These two bariums are bridged by nitrates to form a bimetallic unit, Figure 5.5. The bridging nitrates are the two monodentate ions coordinated to Ba4, but are bidentate coordinating to Ba3. The bimetallic unit is a part of a larger extended polymer which will be discussed in the following section. This portion of the structure, built from two Ba$^{2+}$ cations and eight nitrate anions, has a 4-charge. A search of the CSD reveals that this anion, [Ba$_2$(NO$_3$)$_8$]$^{4-}$, has never been reported in a structurally characterized material.$^7$
5.3.2 Extended Structure

This section will describe the extended structure of 5.2 including both the cationic and anionic portions. The extended structure of 5.2 consists of a 3-D cationic framework with a 1-D anionic chain running through the pores of the 3-D framework.

First, the 3-D network will be discussed. The 3-D network is composed of 1-D chains constructed of Ba-O_{bipy-O_2} interactions. The bimetallic units shown in Figure 5.4c connect to form the 1-D chains shown in Figure 5.6a. The 1-D chains are linked through the bipy-O_2 ligands in two dimensions to form a 3-D pcu-type rod packing, Figure 5.6b.

Figure 5.5. The coordination environment of a) Ba3 and b) Ba4 in the anionic portion of 5.2. c) The bimetallic unit of Ba3 and Ba4 showing the bridging nitrate ions.
This type of structure was described previously in Chapter 2 for the potassium, rubidium and cesium analogues in the 4-ethylphenoxide/dioxane system. Those structures contained 1-D inorganic rods whereas 5.2 contains 1-D inorganic chains.

Figure 5.6. a) The 1-D inorganic chain in the cationic portion of 5.2 showing the bimetallic unit extending into the chain. b) A portion of the 3-D network, viewed along the axis of the 1-D chains showing the pcu-type rod packing.
The anionic portion of the extended structure is quite strange, in that it is a 1-D polymer running through the channels of the 3-D architecture, Figure 5.7. To our knowledge, there have been no reports in the literature of polymeric anions in the pores of cationic frameworks. The 1-D chain is built from the bimetallic units shown in Figure 5.5c which link together through bridging nitrates. There is a single nitrate that bridges between the bimetallic units and it coordinates in a bidentate fashion to both Ba3 and Ba4.

Figure 5.7.  a) The 1-D inorganic chain in the anionic portion of 5.2, showing the bimetallic unit extending into the chain.  b) A view of the anionic polymers running through the pores of the 3-D cationic network.
5.4 $\text{[Nd}_2\text{Cl(C}_6\text{H}_5\text{COO})_3\text{(C}_4\text{H}_8\text{O}_2)]}$

The 1-D polymer $\text{[Nd}_2\text{Cl(C}_6\text{H}_5\text{COO})_3\text{(C}_4\text{H}_8\text{O}_2)]$, 5.3, was synthesized from the reaction of $\text{Nd(O}^\text{iPr})_3$ with three equivalents of benzoic acid in 1,4-dioxane solution, Scheme 5.3. The presence of chloride can be explained as carry-over from the synthesis of $\text{Nd(O}^\text{iPr})_3$ which is synthesized from $\text{NdCl}_3$ and $\text{NaO}^\text{iPr}$. 5.3 was synthesized while trying to build high-connectivity frameworks with SBUs containing large metal cations. However, instead of forming neodymium-benzoate SBUs which could be linked through 1,4-dioxane, a 1-D neodymium-benzoate polymer was crystallized. 5.3 is the first reported 1-D neodymium benzoate structure. The related compound $\text{[Nd}_2\text{(C}_6\text{H}_5\text{COO})_6\text{(CH}_3\text{OH})_4]$ was previously reported as a 2-D material based on PXRD data and there are several examples of other Ln-benzoate 1-D structures, however none with neodymium.

$$\text{Nd(O}^\text{iPr})_3 + 3 \text{HO-C} = \xrightarrow{\Delta \text{diox}} \text{[Nd}_2\text{Cl(C}_6\text{H}_5\text{COO})_3\text{(C}_4\text{H}_8\text{O}_2)]}$$

Scheme 5.3. Preparation of 5.3.

5.3 is also the only polymeric lanthanide/benzoate/halide structurally characterized material reported to date. Only two other lanthanide complexes have been structurally characterized with both a halide and benzoate ligand. These are the molecular complexes $[2\{\text{K}^+\text{Nd}_3\text{Cl}_6\text{(C}_6\text{H}_5\text{COO})_2\text{(Cp}^\text{*})_3\}^{2-}\text{(C}_7\text{H}_8)]^{17}$ and
[EuCl(C₆H₅COO)₂(C₆H₅COOH)₂(C₁₂H₈N₂)₂]¹⁸ The neodymium species is composed of a Nd₃Cl₅ core and each Nd is coordinated by a Cp* molecule. Two of the three metal centers are chelated by the carboxylate group of a benzoate anion while the third metal has a non-bridging chloride anion bound.¹⁷ The europium complex is composed of a 9-coordinate metal center coordinated by one chloride ion, two monodentate benzoate anions, two monodentate benzoic acid ligands and two chelating 1,10-phenanthroline ligands.¹⁸

5.4.1 Molecular structure

The molecular structure of 5.3 will be discussed in this section while the extended structure will be described later. The molecular structure of 5.3 consists of two unique Nd³⁺ metal centers. Nd1 is 9-coordinate in a very distorted mono-capped square anti-prismatic geometry. It is coordinated by two chelating carboxylate groups, three monodentate carboxylate groups, one chloride ion and one dioxane molecule. Nd2 is 8-coordinate in a distorted square anti-prismatic geometry. It is coordinated by one chelating carboxylate group, five monodentate carboxylate groups and one chloride ion, Figure 5.8.⁸ All of the bond distances are within the typical range for Nd-O and Nd-Cl interactions, respectively.⁷
Figure 5.8. The coordination environment around a) Nd1 and b) Nd2 in 5.3. c) A view of the bimetallic molecular structure of 5.3. Blue – neodymium, green – chloride, red – oxygen, black – carbon. All hydrogen atoms have been removed for clarity.
5.4.2 Extended structure

The extended structure of 5.3 will be described here. The extended structure of 5.3 is a 1-D polymeric chain composed of Nd/Cl/carboxylate interactions. The dioxane solvent molecule acts as a terminal donor and does not bridge. The 1-D chains extend along the crystallographic $b$-axis. Small channels also run along the crystallographic $b$-axis between the chains and are filled with disordered solvent molecules, Figure 5.9.\(^8\)

![Diagram of extended structure](image)

**Figure 5.9.** A portion of a) the 1-D chain of 5.3 and b) the 1-D chain extending along the $b$-axis within the unit cell, all aryl carbons have been removed for clarity. c) A view along the $b$-axis showing the small channels. All hydrogen atoms have been removed for clarity.
5.5 Experimental

5.5.1 General procedures

Complex 5.1 was prepared using a modification of the method of Seddon and Pilling\textsuperscript{19} for the preparation of 2,2'-dipyridyl-4,4'-dicarboxylic acid. 5,5'-dimethyl-2,2'-bipyridine, K[MnO\textsubscript{4}], 4,4'-dipyridyl N,N'-dioxide dihydrate and benzoic acid were purchased from Aldrich and used without further purification. Nd(O\textsuperscript{1}Pr\textsubscript{3}) was purchased from Strem and used without further purification. 1,4-dioxane was distilled onto molecular sieves from potassium benzophenone.

5.5.2 X-ray crystallography

Single-crystals were examined under Infineum V8512 oil. The datum crystal was affixed to a Mitegen mounting loop and transferred to the 100 K nitrogen stream of a Bruker APEX diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 12 0.5° φ scans. The orientation matrix derived from this was transferred to COSMO to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Cell parameters were refined using reflections harvested from the data collection with $I > 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. The structures were solved and refined using SHELXTL. Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of...
full-matrix least-squares refinement on $F^2$. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to 1.2× the equivalent isotropic U of the parent atom.

Sample 5.1 was submitted for synchrotron crystallographic analysis through the SCrALS (Service Crystallography at Advanced Light Source) program. Crystallographic data were collected at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The ALS is supported by the U.S. Department of Energy, Office of Energy Sciences, under contract DE-AC02–05CH11231.

5.5.3 Preparation

5.1 [K$_2$(O$_2$C$_6$H$_3$N)$_2$(H$_2$O)$_2$] · 2(H$_2$O) - K[MnO$_4$] (10 g, 63 mmol) was added to a solution of 5,5'-dimethyl-2,2'-bipyridine (1.6 g, 8.7 mmol) in 100 mL H$_2$O. The mixture was heated to reflux for 12 h. Upon cooling, the mixture was filtered and the black precipitate was washed with water (2 x 30 mL). The filtrate and the washings were combined and extracted with diethyl ether to remove unreacted starting material. The aqueous fraction was collected and the solvent was removed under vacuum, leaving a sticky white solid. The solid was heated under vacuum at 100°C overnight to give a fine white powder. Single crystals were grown from an aqueous solution upon slow evaporation of the solvent.

5.2 [{Ba$_2$(C$_{10}$H$_8$N$_2$O$_2$)$_6$}$_{4+}$ {Ba$_2$(NO$_3$)$_8$}$^{4-}$] – Ba(NO$_3$)$_2$ (0.105 g, 0.4 mmol) and 4,4’-dipyridyl-N,N’-dioxide dihydrate (0.045 g, 0.2 mmol) were dissolved in 10 mL warm
DMF. The solution was stirred and heated at 90°C overnight. The stirring was stopped and the solution was slowly cooled to room temperature in an oil bath, producing X-ray quality single crystals.

5.3 \([\text{Nd}_2 \text{Cl}(\text{C}_6\text{H}_5\text{COO})_3]\) - Benzoic acid (0.366 g, 3 mmol) was dissolved in 20 mL 1,4-dioxane. Solid Nd(O\text{iPr})_3 (0.321 g, 1 mmol) was added and the solution was refluxed overnight. The solution was allowed to cool to room temperature and then filtered. The filtrate was concentrated and single crystals were grown upon cooling of this saturated solution to room temperature in a hot water bath over the course of several days. Crystalline yield 0.069g (11.14%) calculated based on Nd.

5.6 References

(7) The Cambridge Structural Database, version 5.33, updates February 2012.


SECTION 2:

METAL-ORGANIC FRAMEWORKS FOR CARBON CAPTURE

This section of the thesis focuses on our work to synthesize metal-organic frameworks for carbon capture. The functional linkers used for this work are imidazolium salts, which are precursors to carbenes. Chapter 6 provides background on carbon capture and reactions of CO$_2$ with carbenes, and outlines the required characteristics of the linkers and materials synthesized for CO$_2$ uptake studies. Chapter 7 details the synthesis of the linkers, studies on the linkers in solution and structural descriptions of the materials synthesized.
6.1 Background on anthropogenic CO$_2$ and difficulties of carbon capture

One of the largest environmental issues facing the planet today is the excessive amount of CO$_2$ in our atmosphere. As a green house gas, anthropogenic CO$_2$ has become a major factor in global warming and is expected to be for the foreseeable future.\(^1\) The burning of fossil fuels is a huge source of anthropogenic CO$_2$; approximately 60% of the anthropogenic CO$_2$ produced in 2004 was attributed to large stationary sources such as power plants and other industrial processing applications.\(^2\) If materials can be designed which can selectively and reversibly adsorb CO$_2$ from the post combustion flue gas of these large sources, it would make a big impact on the amount of green house gases being released.

The focus is on post- rather than pre-combustion adsorption because existing power plants could be retro-fitted for post-combustion CO$_2$ capture, while entirely new facilities would have to be constructed for pre-combustion CO$_2$ capture. The conditions in post-combustion flue gas make it difficult to efficiently capture CO$_2$; typically CO$_2$ is approximately 7-16% of the gas mixed with things such as NO$_x$, SO$_x$, O$_2$, N$_2$ and water vapor.\(^3\) Post-combustion gas separation is predominately an issue of separating CO$_2$ and
N₂, since N₂ comprises approximately 70-75\% of post-combustion flue gas. Typically, the flue gas is at a temperature of 50-70 °C and a pressure of 1 bar. The low pressure of the flue gas also presents a potential problem with post-combustion CO₂ capture, because the partial pressure of CO₂ is quite low. This means the capture material must be able to selectively pull relatively small amounts of CO₂ out of dilute mixtures.

**6.2 Current technology**

The current state of the art, and most widely used and studied method, for post-combustion CO₂ uptake is aqueous amine systems.\(^5,6\) The reaction of CO₂ with an aqueous amine is a fairly simple straight forward reaction, Scheme 6.1. The reaction for primary and secondary amines is a 2:1 amine:CO₂ reaction to form a carbamate/ammonium ion pair, Scheme 6.1a. Upon heating the carbamate, CO₂ is released and two equivalents of the starting amine are regenerated as the ammonium reprotonates the amide. Hydrolysis of a fraction of the carbamate leads to the formation of a bicarbonate/ammonium ion pair and regeneration of one equivalent of the starting amine. This hydrolysis is one major pathway for degradation of the amine because of the formation of the ammonium bicarbonate salt. The reaction of CO₂ with tertiary aqueous amines is a 1:1 reaction leading to an ammonium bicarbonate salt, Scheme 6.1b. The reaction of primary and secondary amines with CO₂ is faster than that of the sterically hindered tertiary amines. However, the heat of formation for the carbamate is quite high, thus making regeneration of the amine more energy intensive.
The bicarbonate heat of formation for tertiary amines is lower, resulting in a lower energy cost to regenerate the amine.\textsuperscript{6}

\begin{equation}
\begin{array}{c}
\text{O} & \text{O} & \text{O} \\
\text{C} & \text{R}_1 & \text{N} - \text{R}_2 \\
\text{O} & \text{O} & \text{O} \\
\text{C} & \text{R}_1 & \text{N} - \text{R}_3 \\
\end{array}
\end{equation}

\textbf{Scheme 6.1.} The reaction of aqueous amines with CO$_2$. a) The reaction for primary and secondary amines. b) The reaction for tertiary amines.

\subsection*{6.2.1 Monoethanol amine}

The use of amine scrubbing for the removal of CO$_2$ has been employed since 1930.\textsuperscript{5} In particular, monoethanol amine (MEA) has been the most widely used. Here, the pros and cons of MEA, and amine scrubbers in general, will be discussed.

The use of MEA as a post-combustion CO$_2$ capture material has been widely used. Power plants throughout the world have implemented MEA scrubbing units, these typically use 20-30 wt% MEA.\textsuperscript{5} One very positive characteristic about this approach is that existing facilities can be retro-fitted for this process. This means it is one of the most readily accessible near-term solutions to carbon capture from large point sources. Also, the reaction between MEA and CO$_2$ has been extensively studied and is quite well understood.\textsuperscript{6} MEA and other simple amines are relatively inexpensive to produce, so their use on a large scale is financially feasible.
There are some very important drawbacks to MEA. The effectiveness of MEA, as well as other amine scrubbers, is largely dependent on how well the flue gas is purified of certain other species prior to exposure. Solvent evaporation and degradation are important issues with MEA and other aqueous amines. Contact with acid gases such as SO$_2$ and NO$_2$ result in heat stable insoluble salts. Therefore these gases must be removed from the flue gas prior to treatment with MEA. Excess oxygen also results in the formation of impurities in the system and also increases the likelihood of corrosion. These issues are minimized by pre-treatment of the flue gas before it enters the CO$_2$ scrubbing unit. Possibly the largest drawback comes from the efficiency of MEA. MEA and other primary and secondary amines are limited to a maximum of 50 mol% CO$_2$ loading. This is because it takes two moles of the amine to adsorb one mole of CO$_2$, Scheme 6.1a. In addition to this limitation on CO$_2$ loading, the carbamate formed is a fairly stable species, so it takes a significant amount of energy input to remove the CO$_2$ and regenerate the active amine species. For coal fired power plants, the energy penalty for a MEA system has been estimated at 25-40%. This huge energy penalty on the power plant is not only due to the heating of the saturated solution to regenerate the active amine, but also from having to pump the liquid around the scrubbing unit. As the MEA reacts with CO$_2$ and zwitterionic species form, the solution becomes more viscous due to electrostatic and hydrogen bonding interactions, Scheme 6.2.
Scheme 6.2. The reaction of MEA with CO$_2$ showing the resultant electrostatic and hydrogen bonding interactions between the ammonium and the carbamate.

6.2.2 Alternatives to MEA

There are several alternatives to MEA being studied and three of them will be briefly outlined in this section. The alternatives discussed in this section are: 1) the chilled ammonia process (CAP); 2) ionic liquids; and 3) aprotic heterocyclic anions (AHA).

In the CAP the flue gas is cooled and passed through a column of ammonium carbonate solution. This solution is chilled to 0-20°C and absorbs the CO$_2$ to produce ammonium bicarbonate. The ammonium bicarbonate solution is pressurized and heated to >100°C to release the CO$_2$. Ammonium carbonate is stable over a wide temperature range minimizing degradation during absorption and regeneration. Also, reaction by-products are less of a problem; it does not react with oxygen and by-products after reaction with NO$_2$ and SO$_2$ can be used as commercial fertilizers. There are several challenges associated with CAP, the low temperature causes a large energy penalty on the power plant and decreases the rate of absorption significantly. Also, there is a potential for unreacted ammonia to leak into the vent gas and be released at an unacceptable level into the environment.

Ionic liquids have been studied as an alternative to MEA, primarily due to their extremely low volatility. The relatively high volatility of MEA and other aqueous amines
is a problem because over time the amine evaporates from solution. Initially, various ionic liquids were studied and it was found that \( \text{CO}_2 \) is soluble in these ionic liquids.\(^{13-15} \) However, these ionic liquids were not designed for carbon capture. The rest of the ionic liquid discussion will focus on the first reported task-specific ionic liquid (TSIL).\(^ {16} \) This was specifically designed with \( \text{CO}_2 \) capture in mind. The cation of the TSIL is the functional portion and consists of an amine group tethered to an imidazolium core. This tethered amine acts similarly to the aqueous amines discussed above, Scheme 6.3. Two equivalents of TSIL are necessary per \( \text{CO}_2 \) in order for the ammonium/carbamate ion pair to form. Prolonged exposure of the TSIL to \( \text{CO}_2 \) results in the molar uptake approaching 0.5 mol \( \text{CO}_2 \)/ mol TSIL, which is the theoretical maximum for this system.

This and other ionic liquids overcome the issue of amine evaporation, however, the reaction is still a 2:1 TSIL:CO\(_2\) ratio. Also, ionic liquids are extremely viscous both pre- and post-complexation with \( \text{CO}_2 \).\(^ {16} \) The high viscosity would likely cause too large of an energy penalty on a power plant to make these systems economically feasible.

\[
\begin{align*}
2 \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N}
\end{array} \right) \text{BF}_4^- + \text{CO}_2 & \rightarrow \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N}
\end{array} \right) \text{BF}_4^+ \left( \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N}
\end{array} \right) \text{O} \\
\text{O} \\
\text{H}_2
\end{align*}
\]

**Scheme 6.3.** The reaction of \( \text{CO}_2 \) with two equivalents of TSIL to form an ammonium/carbamate ion pair.

The final alternative to MEA that will be discussed is the use of aprotic heterocyclic anions (AHAs). This is a new method of using ionic liquids that involves reaction at the anion instead of the cation. These are being studied in order to
overcome two major problems with the TSIL and MEA described above; 1) the 2:1 reaction stoichiometry and 2) the large increase in viscosity upon complexation with CO₂. The AHA being discussed here is 2-cyanopyrollide, Scheme 6.4 shows its reaction with CO₂. Uptake studies show that this reaction approaches a 1:1 reaction stoichiometry at the typical conditions found in post-combustion flue gas. In conjunction with the chemical absorption to form the carbamate, CO₂ is slightly soluble in this ionic liquid. At increased pressure of CO₂ a reaction stoichiometry of greater than one mole of CO₂ per AHA was observed due to this solubility. Additionally, samples of the ionic liquid spiked with H₂O showed no decrease in CO₂ uptake. Finally, by using an aprotic anion, the large increase in viscosity upon CO₂ complexation is avoided. In typical ionic liquids and aqueous amines, the extensive hydrogen bonding that occurs increases the viscosity of the liquid substantially. Here, there is no acidic proton to participate in hydrogen bonding interactions. It was shown that the viscosity of the pre- and post-complexation materials is nearly identical. The AHA approach seems to be a step in the right direction, however the intrinsic viscosity of ionic liquids is still an issue.

\[
\begin{align*}
\left[ \begin{array}{c}
\text{C}_{14}\text{H}_{29}^- \\
\text{P}^- \text{C}_{6}\text{H}_{13} \\
\text{C}_{6}\text{H}_{13} \\
\end{array} \right]^{\oplus} \cdot \text{CN} \quad + \quad \text{CO}_2 & \quad \iff \quad \left[ \begin{array}{c}
\text{C}_{14}\text{H}_{29}^- \\
\text{P}^- \text{C}_{6}\text{H}_{13} \\
\text{C}_{6}\text{H}_{13} \\
\end{array} \right]^{\oplus} \cdot \text{O} \quad \text{CO}_2
\end{align*}
\]

**Scheme 6.4.** The reaction of CO₂ with the AHA 2-cyanopyrollide.
6.3 CO₂ complexation with N-heterocyclic carbenes

Here, the complexation of CO₂ with N-heterocyclic carbenes (NHC) will be briefly discussed. Approximately ten years ago, several NHC carboxylate complexes were characterized.₁₈,₁₉ It was shown that the binding of CO₂ was reversible and that CO₂ could be removed upon heating. The NHC species reported consisted of both N-alkyl and N-aryl substituted heterocycles. A more in depth study of a large series of NHCs was published in 2009.²⁰ The species studied in this report include NHCs with symmetric N-alkyl substitution, asymmetric N-alkyl substitution, symmetric N-aryl substitution and hetero N-alkyl/N'-aryl substitution, Figure 6.1 shows the NHCs studied. These NHCs were carboxylated via reaction with CO₂ at room temperature. A trend was observed through TGA studies, it seems as the steric bulk of the N-substituents increases the decarboxylation happens more readily. Several of the NHCs studied contained methyl groups at the 4 and 5 positions of the heterocycle. The methylated species with small N-substituents decarboxylated at a higher temperature than their non-methylated homologues. This is due to the increased electron density on the carbene carbon, leading to a stronger C-CO₂ bond. However, the steric effects of large N-substituents overrides the methylation effect and very little change in the decarboxylation temperature is seen.
It should be pointed out that the NHCs are isoelectronic with the AHAs described in section 6.2.2, and they complex with CO$_2$ in a similar fashion. The reaction stoichiometry is 1:1 and the resulting product is a zwitterion, Scheme 6.5. Carbenes have potential in the area of CO$_2$ absorption because they are highly tunable molecules based on the variety of substituents that could be placed on the heterocycle. It has been shown that substitution on both the backbone and the nitrogen sites can affect the strength of the carbene-carboxylate bond.$^{20}$ This type of control could allow the molecule to be tuned to precisely the desired properties based on the intended use and conditions.

\[
R_1\cdots N\cdots N\cdots R_2 + CO_2 \rightleftharpoons R_1\cdots N\cdots R_2^+ \cdot CO_2^-
\]

**Scheme 6.5.** The reaction of a NHC with CO$_2$ to yield a zwitterionic imidazolium carboxylate.
6.4 Carbon capture potential in MOFs

MOFs have potential applications in many fields due to their potential to have permanent porosity, tunable organic linkers and high internal surface areas. Several of these potential applications were outlined in chapter 1.3. This section will specifically discuss CO$_2$ uptake in frameworks. Specifically, two strategies will be described: 1) the use of open metal sites in MOFs and 2) surface functionalization of MOFs. These two strategies focus on both increasing the CO$_2$ uptake capacity and selectivity of the material. Selectivity is an important and difficult issue because it is inefficient and unnecessary for a material to absorb all species present in the flue gas.

6.4.1 Open metal sites in MOFs

There have been a variety of studies on the effects of unsaturated metal sites within a MOF. The open metal sites interact with the quadrupole of the CO$_2$ preferentially to other gases such as N$_2$ or CH$_4$. This interaction not only aids in selectivity, but also allows for greater uptake capacity. For example, [Cu$_3$(btc)$_2$] (btc = 1,3,5-benzenetricarboxylate) is a framework composed of Cu$_2$(COO)$^-$ paddlewheel units that are linked through the btc ligands, Figure 6.2. The paddlewheel nodes of the framework have open metal sites at the apical positions, allowing interaction with guest CO$_2$ molecules. The highest CO$_2$ uptake for this material was reported to be 12.7 mmol g$^{-1}$ at 15 bar and 298 K. The mechanism of adsorption was found to be an end-on interaction of the CO$_2$ with the copper. Incredibly, in the presence of a small amount of water, this material has an enhanced CO$_2$ adsorption capacity and selectivity over N$_2$. 
and CH₄. When water is present, the quadrupole of the CO₂ interacts with the electric field produced by the water molecules coordinated to the metal centers.⁴⁰

A study was done on a series of isostructural 3-D materials [M₂(dobdc)(H₂O)₂] (dobdc = 2,5-dihydroxybenzenedicarboxylate) where M = Mg, Mn, Co, Ni, Zn in order to examine the effect of the identity of the open metal site. These materials form a 3-D honeycomb type structure with a large number of open metal sites upon removal of guest water molecules,⁴²,⁴³ Figure 6.3. It was found that the magnesium homologue has a CO₂ uptake more than double that of any other material in the series. Once again it was confirmed that an end-on interaction between the CO₂ and the magnesium was occurring.⁴³ The heat of adsorption for the magnesium species was found to be higher than the other metals and it took up more CO₂ molecules per unit cell.⁴² This study is important because it shows that the identity of the metal in the framework actually makes a difference in the resulting CO₂ uptake properties.

Figure 6.2. a) The paddlewheel SBU of [Cu₃(btc)₂] showing the open coordination sites. b) A portion of the extended structure showing the open coordination sites accessible to the pore.
6.4.2 Surface-functionalized materials

Two methods of functionalizing MOFs have been well studied and both will be briefly discussed here. The first method involves the use of MOFs with unsaturated metal sites. This approach takes MOFs with open metal sites, such as those described above, and grafts them with functional molecules.\textsuperscript{44–46} One example of this is the complex \([\text{Zn}_2(\text{bttb})(\text{py-CF}_3)_2]\) (where \text{bttb}^4 = 4,4',4'',4'''-benzene-1,2,4,5-tetrayltetрабenzoate) which incorporates 4-trifluoromethyl pyridine.\textsuperscript{44} The addition of this highly polar pyridine drastically increases the CO\textsubscript{2} selectivity over N\textsubscript{2} at low (0-2 bar) pressure compared to the non-functionalized MOF, \([\text{Zn}_2(\text{bttb})]\),\textsuperscript{46} Figure 6.4. The surface area of the functionalized material is significantly reduced (390 m\textsuperscript{2} g\textsuperscript{-1} vs. 1370 m\textsuperscript{2} g\textsuperscript{-1}) but the polar nature of the pyridine group selectively binds CO\textsubscript{2}.\textsuperscript{44} Another example capitalizes on the affinity of amines for CO\textsubscript{2}, by incorporating ethylenediamine into the
This material, \( \text{H}_3[\text{(Cu}_4\text{Cl)}^3\text{(BTTri)}_8](\text{H3BTTri} = 1,3,5\text{-tris(1H-1,2,3-triazol-5-yl)benzene}) \), has open coordination sites on the copper centers. The open coordination site are then complexed with ethylenediamine. At low pressure, the functionalized material has a greater CO\(_2\) adsorption owing to the higher affinity of the amine group for CO\(_2\). However, at higher pressures the non-functionalized material has a much greater uptake due to the larger pore volume.\(^{45}\) It is important to remember that typical post-combustion flue gas conditions are at low pressure (≤ 1 bar).

The second method to functionalize MOFs is to modify the organic linking molecule. Generally, this approach can be used to functionalize MOFs for a variety of application, but the focus here will be CO\(_2\) adsorption.\(^{47-51}\) One example of this is the material, \( [\text{H}_3\text{O}][\text{Zn}_7(\mu^3\text{-OH})_3\text{(bbs)}_6] \) (bbsH\(_2\) = 4,4’-bibenzoic acid-2,2’-sulfone).\(^{50}\) In this example, the common biphenyldicarboxylic acid linker was modified, Scheme 6.6. The polar 2,2’-sulfone functionality interacts selectively with the CO\(_2\) and was shown to

![Figure 6.4. The paddlewheel SBU of [Zn2(bttb)] showing the open coordination site where 4-trifluoromethypyridine coordinates.](image-url)
enhance the selectivity of the MOF over N₂, H₂ and CH₄. A more common approach is to functionalize the linker with an amino-group that will bind the CO₂.⁴⁷–⁴⁹ Benzenedicarboxylate (bdc) is one of the most studied linkers since its use by Yaghi to construct MOF-5.⁵² A variety of substituted bdc linkers have also been used,⁵³ including the 2-amino version. One example of this strategy is the study of MIL-53,⁵⁴[Al(OH)(bdc)], compared to the amino version amion-MIL-53,⁵⁵[Al(OH)(NH₂-bdc)], Figure 6.5. It was found that substituting amino-bdc into the framework the CO₂ selectivity over CH₄ increased. The amine groups not only interact well with the CO₂ molecules, but they reduce the number of non-polar sites in the network to further exclude CH₄ at low pressures.⁴⁹ A variety of avenues exist to tune the properties of MOFs, this makes them excellent candidates for CO₂ adsorption materials.

Scheme 6.6. Modification of 4,4’-biphenyldicarboxylic acid to 4,4’-bibenkoic acid-2,2-sulfone.

6.5 Overview of this research

The goal of the research presented in this section is to build on several of the ideas outlined above. The synthesis of surface-functionalized metal-organic frameworks for the purpose of CO₂ adsorption has been explored and is described in the following chapter. This includes the design and synthesis of novel organic linkers as well as
molecular studies of the linkers in solution. These linkers are based on an imidazolium core which acts as a precursor to a carbene.

Figure 6.5. A view of an Al₈ ring in a) MIL-53 and b) amino-MIL-53. c) A view of the extended structure of amino-MIL-53 along the a-axis.
6.6 References


CHAPTER 7:
SYNTHESIS OF IMIDAZOLIUM BASED ORGANIC LINKERS AND THEIR USE IN THE
CONSTRUCTION OF MOFS FOR CARBON CAPTURE

This chapter will describe the synthesis and characterization of a series of
organic linkers with an imidazolium core. The imidazolium core is the precursor to a N-
heterocyclic carbene which can be studied for CO$_2$ uptake. The purpose of these linkers
is to construct MOFs with increased CO$_2$ uptake and selectivity over conventional
systems.

7.1 Introduction

Over the past decade N-heterocyclic carbenes (NHCs) have been shown to bind
CO$_2$, Scheme 7.1.$^{1-3}$ The CO$_2$ can be removed through heating or exposure of the CO$_2$
complex to a vacuum. Studies have shown that the substituents on the N-heterocycle
play a role in the strength of the carbene-CO$_2$ interaction. Sterics play a role due to the
N-substituents; when they are large the carbene-CO$_2$ interaction is weaker. Substitution
on the heterocycle backbone also plays a role in that increased electron density in the
ring leads to a stronger carbene-CO$_2$ interaction and vice versa.$^1$ The tunable nature of
these molecules makes them good potential candidates for carbon capture. Carbene-
CO$_2$ interactions were previously discussed in section 6.3.
A discussion of strategies for carbon capture in MOFs can be found in section 6.4 of the previous chapter and an outline of several potential applications\textsuperscript{4–18} for MOFs can be found in section 1.3. The focus of previous work in this area has been directed towards the functionalization of MOFs for enhanced CO\textsubscript{2} selectivity and uptake. This strategy entails modifying the organic portion of a MOF to better interact with CO\textsubscript{2}. The modifications can lead to stronger van der Waals interactions\textsuperscript{19–21} with the quadrupole of CO\textsubscript{2} or interactions with more covalent character,\textsuperscript{20,22–26} such as those described above with carbenes.

### 7.1.1 MOFs containing carbenes and NHC precursors in the literature

There are no examples of “naked” carbenes incorporated in MOFs. However, there are several examples of NHC precursors\textsuperscript{27–34} and two organometallic carbene complexes\textsuperscript{32,34} in MOFs. In 2010, Yaghi reported a pair of MOFs containing a NHC precursor and an organometallic carbene complex respectively.\textsuperscript{32} IRMOF-76, [Zn\textsubscript{4}O(C\textsubscript{23}H\textsubscript{15}N\textsubscript{2}O\textsubscript{4})\textsubscript{3}(X)\textsubscript{3}] (X = BF\textsubscript{4}, PF\textsubscript{6}, OH), contains a linker with a NHC precursor, Figure 7.1a. This benzimidazolium based linker was incorporated in a 3-D \textit{pcu} porous MOF,
Figure 7.1b, with the imidazolium group accessible in the pores. Attempts to deprotonate the imidazolium to yield a carbene post-synthetically were unsuccessful. However, IRMOF-77, [Zn₄O(C₂₈H₂₁I₂N₂O₄Pd)₃], was synthesized using an organo-palladium version of the linker used in IRMOF-76, Figure 7.1c. The organometallic linker was synthesized and then used in the construction of IRMOF-77, Figure 7.1d, which is isoreticular with IRMOF-76. The palladium is accessible to the pores and thus is available for catalytic organic transformation purposes.³²

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**Figure 7.1.** a) The imidazolium based linker used in IRMOF-76 and b) a view of IRMOF-76 along the a-axis. c) The organo-palladium linker used in IRMOF-77 and d) a view of IRMOF-77. All hydrogen atoms have been removed for clarity.
While Yaghi et. al. could not post-synthetically deprotonate the NHC precursor, Wu reported in 2011 a system which was successfully modified. The linker is a bent molecule containing two imidazolium units and carboxylic acid linking groups, Figure 7.2. Reaction of this linker with copper salts leads to the crystallization of either a 2-D sheet or a 1-D zigzag chain, Figure 7.2. Treatment of either of these materials with a THF solution of Pd(OAc)$_2$ yields a catalytically active material. Unfortunately, no crystal structures of these materials are reported; however, various other analytical techniques confirmed that there was in fact palladium present and that it was not in the form of Pd$^0$ nano-particles.

7.1.2 Linker design

There are several factors to consider when designing new functional linkers, such as: size and shape, placement of the functional group and identity of the linking moiety. The size and shape of a linker is extremely important because it affects several properties of the resulting material. By selecting specific sizes and shapes, the properties of the resulting MOF can be tuned. This effect is similar to how the shape of a SBU affects the material, as described previously in section 1.2. In general relatively short linkers can lead to materials that have extremely small pores or completely non-porous materials. A short, bent linker can potentially chelate the metal center, Figure 7.3. Blocking a potential point of network extension, this can lead to a decrease in the dimensionality of the extended structure. On the other hand, extremely long linkers can lead to materials with very large pores. This sometimes

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results in compromising the structural integrity of the material once the pores are evacuated. The ideal linker for this project is a linker of intermediate length with the linking moieties approaching 180° apart, so as not to chelate the metals.

**Figure 7.2.** Reaction of the bent imidazolium containing linker with either Cu(NO$_3$)$_2$ or CuCl$_2$ results in either a 2-D or 1-D material. Treatment of these materials with Pd(OAc)$_2$ yields catalytically active materials.
The placement of the functional group ideally would be near the center of the linker. There are two main reasons for this: 1) accessibility to the pore and 2) to prevent chelation. With the functional moiety near the center of the organic linker, there is a greater chance that it will be easily accessible to potential pores within the material. For example, Yaghi’s work described above and shown in Figure 7.1 has the functional portion in the center of the linker and it is easily accessible to the pore. If it is too close to one end of the linker, it could be blocked from the pore by the metal node. Since our goal is to bind CO$_2$, the reactive portion of the linker must be able to come in contact with gas molecules passing through the pore system of the material. Also, with placement near the center of the linker, the risk of chelation is minimized. If the functional moiety is too close to the linking group, there is a chance the linker will chelate through the linking group and the functional portion of the molecule. This could

![Figure 7.3. Examples of chelation by short, bent potential linkers. a) A molecular complex of rhodium with 6-(carboxymethyl)-4-methyl-2-hydroxy-pyridine. b) The coordination environment of a cadmium in a 3-D network built from 5-carboxy-tetrazole.](image-url)
potentially make the functional portion inaccessible to the pore, or if the chelating atom is the carbene carbon completely block the reactive site.

The identity of the linking group can also influence the properties of the resulting MOF. The most common linking group in transition metal systems is the carboxylate group. This is due to the relatively strong interactions between the anionic COO$^-$ and the cationic $\text{M}^{n+}$. The strength of the interaction plays an important role in the overall stability of the MOF. A weak interaction leads to lability and decreases the thermal and chemical stability of the material. The identity of the linking group also comes into play when designing MOFs because of charge balance issues. A material constructed solely of neutral linkers typically has large anions filling the void space in order to balance the charge of the cationic metals, Figure 7.4. This is an issue when trying to evacuate the pores to activate the complex for an application such as gas uptake. Neutral linkers can be quite useful, however, in heteroleptic materials. Two-dimensional sheet structures can sometimes be transformed to 3-D materials through the addition of neutral linkers. These linkers act as pillars between the 2-D sheets leading to a 3-D porous material, Figure 7.5.
Taking the factors discussed above into account, this work focuses on a series of linkers, Figure 7.6. Four of the five linkers are very similar and differ only in the linking group. They are composed of an imidazolium core with the linking groups at the para position of the N-aryl substituents. By linking through the N-substituents, the linking groups are not the ideal 180° apart; they are approximately 160° apart. However, this angle is large enough and the linker is long enough to prevent chelation. Also, note that

Figure 7.4. a) A view of $[\{\text{La}_4\text{(C}_{10}\text{H}_8\text{N}_2\text{O}_2)_{10}\text{(CH}_3\text{OH})_{10}\text{Cl}_3\} \text{Cl}\{\text{B(C}_6\text{H}_5\text{)}_{4}\}_{8^*}\text{22CH}_3\text{OH}}]$ with the anions remove (left) and then including the anions (right).\textsuperscript{41} b) A view of $[\{\text{La}(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2)_4\}\{\text{B(C}_6\text{H}_5)_4\}(\text{ClO}_4)_2\cdot2.75\text{CH}_3\text{OH}}]$ with the anions removed (left) and then including the anions (right).\textsuperscript{42}
the functional portion, the imidazolium, is well separated from the linking groups by an aryl ring. Two of these four ligands have neutral linking groups, cyano and pyridyl, and two have anionic linking groups, carboxylate and aryloxide. This allows us to explore a variety of reaction conditions to build MOFs. The fifth linker in Figure 7.6 is identical to the linker used by Yaghi\textsuperscript{32} and shown in Figure 7.1a. This linker is being studied because it is already known to construct MOFs, but CO\textsubscript{2} uptake studies were not carried out. This linker is built around a benzimidazolium core with the N-substituents being methyl groups. The linking group is a benzoate moiety substituted on the 3 and 6 positions of the benzene ring of the core. This leads to a quite long, linear linker.

To identify each linker as well as provide information about the protonation state and counter ion, an abbreviated nomenclature will be introduced. Each linker will be given a symbol H\textsubscript{n}LNX, where H\textsubscript{n} equals the number of acid protons left on the molecule, N is simply an arbitrary unique label identifying the molecule and X is the

Figure 7.5. a) A paddlewheel [Zn\textsubscript{2}(bdc)\textsubscript{4}] SBU with bipy ligands in the axial positions. b) A view of the 3-D network showing the 2-D layers of Zn-bdc pillared by bipy.\textsuperscript{4}
counter ion. For example, the carboxylic acid functionalized linker,

\[ [\text{C}_3\text{H}_3\text{N}_2(\text{C}_6\text{H}_4\text{COOH})_2]^+\text{Br}^- \]

will be abbreviated \( \text{H}_3\text{L1Br} \). In this case, \( \text{L1} \) is the arbitrary label identifying the molecule, \( \text{H}_3 \) describes the number of acidic protons (one from the imidazolium and one from each of two carboxylic acids) and \( \text{Br} \) is the anion. The alcohol functionalized linker, \( [\text{C}_3\text{H}_3\text{N}_2(\text{C}_6\text{H}_4\text{OH})_2]^+\text{Cl}^- \), will be abbreviated \( \text{H}_3\text{L2Cl} \). The pyridyl linker, \( [\text{C}_3\text{H}_3\text{N}_2(\text{C}_6\text{H}_4\text{N})_2]^+\text{Cl}^- \), is \( \text{HL3Cl} \) and the cyano linker, \( [\text{C}_3\text{H}_3\text{N}_2(\text{C}_6\text{H}_4\text{CN})_2]^+\text{Cl}^- \), is \( \text{HL4Cl} \). The benzimidazolium based linker will be abbreviated \( \text{H}_3\text{L5(BF}_4^- \). All of the linkers and their identifiers can be seen in Figure 7.6.

![Figure 7.6](image)

**Figure 7.6.** The five imidazolium based linkers used in this work. The imidazolium proton is highlighted in red and any other acidic protons are highlighted in blue. Each linker is abbreviated as \( \text{H}_n\text{L1X-}\text{H}_n\text{L5X} \), this nomenclature identifies the linker as well as its protonation state and counter ion.
7.2 Linker synthesis

This section will give an overview of the synthesis of the linkers as well as the crystal structures of two of the five linkers. The carboxylic acid and cyano linkers, \( \text{H}_3\text{L}1\text{Br} \) and \( \text{HL}4\text{Cl} \), were previously reported by Sumby et al. and were synthesized via literature procedures, Scheme 7.2.\(^{31} \) The phenol and pyridyl linkers, \( \text{H}_3\text{L}2\text{Cl} \) and \( \text{HL}3\text{Cl} \), were synthesized by modifying the Sumby\(^{31} \) procedure, Scheme 7.3. A fine brown powder of \( \text{HL}4\text{Cl} \) is isolated upon removal of the toluene and trituration with acetonitrile. \( \text{H}_3\text{L}1\text{Br} \) is isolated as a fine brown powder via filtration and washed with ethylacetate. \( \text{H}_3\text{L}2\text{Cl} \) is isolated by the same method as \( \text{HL}4\text{Cl} \), trituration with acetonitrile, as a fine brown powder. A slight modification of the procedure, trituration with ethanol, yields the fine brown powder \( \text{HL}3\text{Cl} \).

\[ \text{\begin{align*}
&\text{H}_3\text{L}1\text{Br} \\
&\text{HL}4\text{Cl}
\end{align*}} \]

\( \text{Scheme 7.2.} \) The synthesis of \( \text{H}_3\text{L}1\text{Br} \) and \( \text{HL}4\text{Cl} \).

\[ \text{\begin{align*}
&\text{H}_3\text{L}2\text{Cl} \\
&\text{HL}3\text{Cl}
\end{align*}} \]

\( \text{Scheme 7.3.} \) The synthesis of \( \text{H}_3\text{L}2\text{Cl} \) (top) and \( \text{HL}3\text{Cl} \) (bottom).
Crystal structures of the linkers H₃L1(NO₃) and H₃L2Cl are shown in Figure 7.7. In both cases these molecular species were crystallized from reaction mixtures intended for the synthesis of MOFs. Attempts to intentionally crystallize the linkers consistently failed. H₃L1(NO₃) was crystallized from a reaction mixture containing Nd(NO₃)₃ and thus crystallized as the imidazolium nitrate salt and not the bromide salt, Figure 7.7a. H₃L2X was crystallized and characterized with a variety of anions, however only the imidazolium chloride salt is shown in Figure 7.7b. Each of the other crystal structures of H₃L2X are isostructural with the exception of the anion present.

Figure 7.7. Crystal structures of a) H₃L1(NO₃) and b) H₃L2Cl. All hydrogen atoms except the imidazolium hydrogen have been removed for clarity.

A model compound was also synthesized for the purposes of solution based studies. This molecule is identical to L1-L4 except it does not have any linking functionalities. The synthesis is very similar to that of HL4Cl, Scheme 7.4. This molecule, [C₃H₆N₂(C₆H₅)₂]⁺Cl⁻, (HL6Cl) is isolated as a fine brown powder by removing the solvent by vacuum and drying the solid at 70°C under vacuum.

The synthesis of H₃L5(BF₄), as described by Yaghi, is significantly more complicated than the previous linkers described, Scheme 7.5. For this reason,
collaborators in Prof. Ashfeld’s group synthesized this linker. It was provided as a gray powder in milligram quantities by Dr. Monika Vogt. \( H_3L5(BF_4) \) was not used in the molecular deprotonation studies described in the next section due to the small quantities obtained.

![Scheme 7.4. The synthesis of model compound HL6Cl.](image)

**Scheme 7.4.** The synthesis of model compound HL6Cl.

![Scheme 7.5. The synthesis of \( H_3L5(BF_4) \) as reported by Yaghi\(^{32}\) and performed by collaborator Dr. Monika Vogt.](image)

**Scheme 7.5.** The synthesis of \( H_3L5(BF_4) \) as reported by Yaghi\(^{32}\) and performed by collaborator Dr. Monika Vogt.
7.3 Molecular solution based deprotonation studies

This section will describe a series of solution based experiments on the molecular linker species. These were done in conjunction with MOF reactions in order to have 1:1 comparisons of CO$_2$ uptake of a linker in solution versus in a solid state species. Initially, a series of solubility tests were conducted in order to determine which solvent would be the best for deprotonation studies. A variety of solvents were tested, and in general, the imidazolium salts are quite insoluble in most solvents. The general conditions for the solubility test were 0.1 mmol of linker in 10.0 mL of solvent stirred at room temperature. A second set of solubility tests were conducted under basic conditions by the addition of an appropriate amount of NaH, Table 7.1 shows the results of the solubility tests. As stated above, due to the small quantities of H$_3$L5(BF$_4$) available and the difficulty in synthesizing it, this linker was not used in the solubility tests or deprotonation studies.

Overall, methanol was found to be the best solvent for room temperature procedures. All five of the linkers tested are soluble in basic methanol and three of the five are soluble in neat methanol, with the other two being slightly soluble. The linkers are also slightly soluble in DMSO and DMF with vigorous stirring over several minutes. The linkers HL4 and HL6 are slightly soluble in basic THF with prolonged stirring. The linkers are insoluble in the other six solvents tested, CH$_2$Cl$_2$, CHCl$_3$, CH$_3$CN, Et$_2$O, toluene and 1,4-dioxane.
TABLE 7.1
THE RESULTS OF SOLUBILITY TESTS FOR THE LINKERS $H_3L1Br$, $H_3L2Cl$, HL3Cl, HL4Cl
AND HL6Cl; THE VALUES IN PARENTHESES ARE FOR BASIC SOLUTIONS*

<table>
<thead>
<tr>
<th></th>
<th>$H_3L1Br$</th>
<th>$H_3L2Cl$</th>
<th>HL3Cl</th>
<th>HL4Cl</th>
<th>HL6Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>ss (s)</td>
<td>s (s)</td>
<td>ss (s)</td>
<td>s (s)</td>
<td>s (s)</td>
</tr>
<tr>
<td>THF</td>
<td>i (i)</td>
<td>i (i)</td>
<td>i (i)</td>
<td>i (ss)</td>
<td>i (ss)</td>
</tr>
<tr>
<td>DMF</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
</tr>
<tr>
<td>DMSO</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
<td>ss (ss)</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>i (i)</td>
<td>i (i)</td>
<td>i (i)</td>
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<tr>
<td>CHCl$_3$</td>
<td>i (i)</td>
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<tr>
<td>CH$_3$CN</td>
<td>i (i)</td>
<td>i (i)</td>
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<tr>
<td>Et$_2$O</td>
<td>i (i)</td>
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<tr>
<td>toluene</td>
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<tr>
<td>1,4-dioxane</td>
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</tr>
</tbody>
</table>

*s = soluble, ss = slightly soluble, i = insoluble

7.3.1 Deprotonation reactions

After performing the solubility tests, methanol was selected as the solvent to attempt deprotonation reactions. This section will outline the attempts to deprotonate the imidazolium salt and characterize the resultant carbene. A variety of bases were used in the deprotonation reactions; $^n$BuLi, NaH, KO$^t$Bu and KHMDS (HMDS = hexamethyldisilazide). The reactions with NaH, KO$^t$Bu and KHMDS were carried out in two ways: 1) addition of the solid base to a methanol solution of the linker and 2) addition of a methanol solution of base to a methanol solution of linker. The method of addition of the base did not make a difference in the reaction. It also appears as though the identity of the base used is not important to the reaction. The identity is not
important because in a methanol solution, the strong bases used deprotonate the solvent. The resulting CH$_3$OM species is actually the base that deprotonates the imidazolium. The pKa of imidazolium salts has been found to be approximately 20 – 25 in DMSO while the pKa of MeOH is 29 in DMSO. Attempts were made to crystallize the carbene for structural characterization by X-ray diffraction, however, all of these attempts failed. The crystallization methods tested were slow cooling of a hot saturated solution to room temperature, slow cooling of a saturated solution to -40 °C and slow diffusion of various organic solvents into a saturated methanol solution.

Characterization of the species in solution also proved to be difficult. Proton NMR analysis was the primary method of characterization for all of the species both before and after reaction with base. This method seemed to be reasonable as we hoped to observe the loss of the imidazolium proton. Ideally, the imidazolium proton could be identified in the $^1$H NMR spectrum and then after reaction with a base this signal in the spectrum would disappear. The first major issue with NMR analysis was the solubility. Due to the lack of solubility of the linkers in various solvents, it was difficult to get good quality spectra.

Proton NMR analysis was carried out in CD$_3$OD. The spectra of H$_3$L1Br, H$_3$L2Cl and HL4Cl all have clear resonances corresponding to the imidazolium proton. They also have clear resonances corresponding to the backbone CH=CH and aryl protons. The spectrum of H$_3$L2Cl shows small impurities in the aryl region, but otherwise is a clean spectrum. The spectrum of HL6Cl also shows a clear imidazolium resonance at 10.11 ppm, and a resonance for the CH=CH at 8.33. However, the aryl region of the spectrum
is complex. There are four sets of doublets within the 7.30 – 7.86 ppm range that could not be assigned. Unfortunately, this was a common result with this material and thus it is not the ideal model compound we had hoped it would be. The spectrum of HL3Cl does not contain a resonance corresponding to the imidazolium proton. An explanation for this might be the proton is quickly changing positions between the imidiazolium and the two pyridyl nitrogen atoms. There are two doublets in the aryl region corresponding to the pyridyl protons at 7.07 ppm and 8.22 ppm. There is also a singlet at 5.01 ppm that could not be assigned.

In situ deprotonation studies support the conclusion that there is carbene formation, however attempts to isolate pure carbene have been unsuccessful. Because pure carbene was not isolated, the proton NMR studies were done on solutions of imidazolium salt treated with NaH. In all cases where an imidazolium proton resonance was present in the initial spectrum, that signal disappeared after addition of the base. This shows that the deprotonation of the imidazolium proton has occurred, however the rest of the spectrum is not clear. In all cases there are multiple sets of signals that do not correspond to the parent imidazolium salt, but cannot be clearly assigned to one species. This suggests that upon deprotonation, the carbene interacts with other species in solution. The carbene could be interacting with NaX (X = Cl or Br), NaOMe (from reaction of NaH with HOMe), other carbenes or the solvent. All of these species would likely have slightly different resonances and this could be what gives rise to the assortment of signals in these spectra. The $^1$H NMR spectra can be seen in Appendix B.
ESI-MS was performed with methanolic solutions of each of the imidazolium salts. The results support the conclusion that imidazolium salts have indeed been synthesized. Multiple species characteristic of $\text{H}_3\text{L}1\text{Br}$ were detected: $[\text{M} – \text{Br} – 2\text{H}]^-$ at 307.07, in positive ion mode two sodium salts were detected at 331.07 and 353.05 for the $[\text{M} – \text{Br} – \text{H} + \text{Na}]^+$ and $[\text{M} – \text{Br} – 2\text{H} + 2\text{Na}]^+$ respectively. The other four imidazolium salts showed characteristic species as well. $\text{H}_3\text{L}2\text{Cl}$: 253.10 $[\text{M} – \text{Cl}]^+$; $\text{HL}3$: 257.06 $[\text{M} – \text{H}]$; $\text{HL}4\text{Cl}$: 271.11 $[\text{M} – \text{Cl}]^+$; and $\text{HL}6\text{Cl}$: 221.12 $[\text{M} – \text{Cl}]^+$. 

These solutions were then treated with $^7\text{BuLi}$ to deprotonate the imidazolium and again used for ESI-MS studies. These studies were inconclusive in determining carbene formation because the only characteristic species detected were the $[\text{M} – \text{H}]^-$ or $[\text{M} – \text{X}]^+$ ions. Both of these types of species were present prior to the addition of base as well, so no conclusion can be drawn from the ESI-MS studies on deprotonation. Two of these samples, $\text{H}_3\text{L}1\text{Br}$ and $\text{HL}4\text{Cl}$, were tested for CO$_2$ uptake by the addition of dry ice to the solution. The results again were inconclusive, since the mass spectra were unchanged from the initial base treated solutions.

Overall, these molecular deprotonation studies did not provide definitive characterization of the carbenes. They do however suggest that deprotonation of the imidazolium salt is occurring, but the complex mixture in solution makes characterization of the carbene difficult. Attempts were made to synthesize and isolate pure carbene, however the conventional literature methods were unsuccessful.$^{143}$ The method reported by Arduengo et. al. involves addition of KO$^\text{tBu}$ to a stirring suspension of imidazolium salt in THF. The solvent is then removed under vacuum and the resulting
residue is extracted into warm toluene and filtered through diatomaceous earth.\textsuperscript{43} When this method was attempted for the imidazolium salts discussed above, the lack of solubility in THF prevented the reaction from proceeding. Nothing was extracted into the warm toluene phase. The method reported by Louie \textit{et. al.} is an in situ deprotonation of the imidazolium with K(HMDS) in toluene followed by filtration of the soluble carbene away from potassium salts and finally reaction with CO\textsubscript{2} gas to produce a solid imidazolium carboxylate.\textsuperscript{1} This procedure was also tested and was unsuccessful. The lack of solubility in toluene prevents the deprotonation from occurring and the filtration step collects all of the unreacted imidazolium salt.

Both of the literature methods were also attempted in methanol to increase the initial solubility of the imidazolium salts. Once again these attempts were not successful and neither carbene nor imidazolium carboxylate could be isolated or characterized. Unfortunately, addition of CO\textsubscript{2} gas to the system after the addition of base does not yield an isolable solid as reported by Louie.\textsuperscript{1}

\section*{7.4 MOF synthesis}

This section will discuss the general strategy of MOF synthesis utilized with the linkers described above. Also, an outline of desired/required physical and chemical properties of ideal materials for CO\textsubscript{2} uptake with these linkers will be presented.

\subsection*{7.4.1 Synthetic strategy}

The strategy for synthesizing MOFs used for this project is quite different from the synthetic strategies used in chapters 2-5. The synthetic strategies described in those
earlier chapters generally relied on the soluble linkers and metal salts quickly reacting and then slowly crystallizing out of solution. The strategy here generally relies on linkers and metal salts which are only slightly soluble. These solids very slowly go into solution upon heating of the reaction mixture for several days. As the materials go into solution they react and then slowly crystallize from the hot reaction mixture. This high temperature technique is a common strategy for building MOFs. These reactions typically last from three to seven days at temperatures ranging from 50°C to 120°C, and are carried out by simply placing a scintillation vial of the reaction mixture undisturbed in an oil bath. Reactions requiring higher temperatures are typically carried out in specially designed thick-walled glass pressure tubes or stainless steel autoclaves. Temperatures for these reactions can be >200°C, however, no materials characterized for this project were synthesized under these conditions.

Solvothermal synthesis is probably the most widely used synthetic strategy for constructing MOFs, however, the chemist has very little control over the materials produced. Although this technique offers little in the way of predictability, there are several variables that can be used to try to tune a reaction. Changes in reaction temperature and time can impact the identity, and crystalline quality, of the product. Also, changing solvents or mixing solvents in varying ratios can drastically change the products of otherwise identical reactions. Sometimes, the identity of the starting materials can make a difference, such as using a NO₃⁻ salt versus a CH₃COO⁻ salt. The pH of a reaction mixture can also affect the reaction product. All of these variables lead to a vast experimental space to explore with each linker. The amount of variability is also
the root of the difficulties faced when trying to systematically and reproducibly build MOFs.

7.4.2 Required properties of MOFs for potential CO\textsubscript{2} uptake

There are some very specific and important properties that the MOFs need to have if they are to be potential materials for CO\textsubscript{2} uptake. These properties include the dimensionality and porosity of the material, the positioning of the imidazolium/carbene group within the MOF and the chemical and physical stability of the material. Ideally, the materials will be 3-D extended structures, this will most likely lead to a greater uptake than if the material was 1- or 2-D. In a 3-D material CO\textsubscript{2} could not only interact with the functionalized linkers but also fill the void space throughout the structure. A property that is essential is that the material must be porous. If CO\textsubscript{2} molecules cannot diffuse into the structure, then the only possible CO\textsubscript{2} uptake would be from surface interactions and all of the advantages MOFs offer are lost. Another required property of potential CO\textsubscript{2} uptake materials is that the functional moiety of the linkers must be accessible from the pores. In order for the functional linkers to enhance CO\textsubscript{2} uptake the CO\textsubscript{2} molecules must be able to interact with that portion of the linker. This also comes into play if the imidazolium is to be post-synthetically deprotonated. For the carbene–CO\textsubscript{2} interaction to occur, the imidazolium proton on the linker must be removed. This can potentially be done either in situ as the MOF is synthesized, or post-synthetically through the treatment of the imidazolium MOF with a base.
Chemical and physical stability of the material are important especially when discussing the potential of a material for practical, real-world applications. A material that will be used for flue gas separation needs to be chemically robust so that other species present in the flue gas (water, NO\textsubscript{x}, SO\textsubscript{x}) do not degrade the material. This is not an issue of selectivity of CO\textsubscript{2} over other species but of structural decomposition over time \textit{via} reaction with other species. Physically, the material has to be recyclable. This means the material would have to be stable enough to withstand many sorption/desorption cycles. Whether the desorption process requires heating or exposure to vacuum, the material cannot degrade significantly over time. These are lofty, yet necessary, goals for the synthesis of carbene functionalized MOFs for CO\textsubscript{2} uptake.

7.5 Structural description of the materials synthesized

This section will provide structural descriptions of the materials synthesized and characterized using the linkers and synthetic strategies described above. A variety of materials including 1-, 2- and 3-D extended structures were synthesized using alkali metals, transition metals and lanthanides. First, a 1-D cobalt structure will be discussed, next several 2-D materials are described and finally, two 3-D networks are discussed.

7.5.1 One-dimensional cobalt chain

The reaction of cobalt acetate with H\textsubscript{3}L2Cl in DMF solution at 80\textdegree{}C for 3 days yields dichroic (blue/pink) crystals of [CoCl(HL2)(CH\textsubscript{3}COO)][H\textsubscript{3}L2]\textsuperscript{+}, 7.1, Scheme 7.6. The molecular structure will be described first, followed by the extended structure.

The molecular structure of 7.1 is composed of a cobalt metal center coordinated by one chloride ion, two oxygen atoms from HL2 linkers and one oxygen from an acetate ion. The counter ion is a fully protonated H₃L₂ linker. Figure 7.8 shows the coordination environment around the cobalt as well as the counter cation. The coordinated chloride ion points directly toward the cation, the closest contact is the Cl···C contact (3.576 Å) highlighted by a red dashed line in Figure 7.8.

Figure 7.8. The molecular structure of 7.1 showing the coordination environment around cobalt. The red dashed line highlights the closest contact between the anion and cation. Light blue – cobalt, green – chloride, red – oxygen, blue – nitrogen, black – carbon, pink – hydrogen.

The extended structure of 7.1 is a simple 1-D chain polymer, Figure 7.9a. The chloride and acetate ions are terminal ligands while the HL2 molecules act as linear linkers between neighboring cobalt metal centers. The 1-D chain extends along the crystallographic b-axis. The cations occupy the space between neighboring chains, thus leaving no void space in the structure. Neighboring chains are offset from one another.
such that the terminal acetate ligand on cobalt points toward the C$_2$H$_2$ backbone of the bridging HL2 of the neighboring chain, Figure 7.9b.

Figure 7.9. a) A portion of the 1-D polymeric chain of 7.1 extending along the crystallographic b-axis. b) A portion of the extended structure of 7.1 showing the offset nature with which the 1-D chains pack in the structure.

This material is not suitable for CO$_2$ uptake studies as it does not meet several of the criteria outlined in section 7.4.2. The biggest problem with this material is that it is non-porous. This means that it is not possible for CO$_2$ to diffuse through into the material. Also, all of the imidazoliums are still protonated. In order to utilize the potential uptake ability of the functionalized linkers, the imidazolium proton must be removed. Since the structure is non-porous, it is also not possible to post-synthetically deprotonate the linkers.
7.5.2 Two-dimensional cadmium, lanthanum and neodymium materials

The three 2-D materials [Cd(HL1)₂·DMF] (7.2), [La₃(HL1Br)₂(L1)(OH)₃] (7.3), and [Nd(HL1Br)₁.₅(H₂O)₁.₅] (7.4) will be discussed separately. First 7.2 will be described, followed by 7.3 and finally 7.4. For each material, the molecular structure will be detailed followed by the extended structure.

The 2-D material [Cd(HL1)₂·DMF], 7.2 was crystallized from the reaction of cadmium nitrate with H3L1Br in DMF at 100°C for three days, Scheme 7.7. Prior to heating the reaction mixture, the pH was adjusted from 2.9 to 6.3 with several drops of triethylamine. This pH adjustment was done in order to facilitate the removal of all three acidic protons on the imidazolium linker in conjunction with network formation. This is one strategy to obtain materials with functional carbene moieties from the parent imidazolium.

![Scheme 7.7. Synthesis of the 2-D material 7.2.](image)

The molecular structure of 7.2 is composed of a cadmium metal center coordinated by three chelating carboxylate groups and one monodentate carboxylate group from the HL1 linkers, Figure 7.10a. There is also one unbound solvent DMF molecule. The four linkers surround the metal center in a distorted square planar arrangement. The extended structure of 7.2 is a 2-D 4⁴-net, Figure 7.10b. Each of the HL1 linkers bridges between two neighboring metal centers, this combined with the
approximately square planar arrangement leads to the construction of the square net. The DMF solvent molecules occupy the voids in the net. A structural search of cadmium coordinated by four carboxylate groups yielded no results in which the ligands were in an approximately square planar geometry similar to 7.2. The materials tended to be closer to tetrahedrally arranged, for example, \([\text{Cd(C}_{14}\text{H}_{8}\text{N}_{2}\text{O}_{4})_{2}\text{(H}_{2}\text{NMe}_{2})\cdot\text{(NH}_{3})]\), a cadmium 3,3'-azo-dibenzoate material forms a 3-D diamondoid network. Similarly, \([\{\text{Cd}_{5}(\text{BTC})_{4}\text{Cl}_{4}\text{·}4(\text{HNEt}_{3})\cdot2(\text{H}_{2}\text{O})]\), forms a complex 3-D architecture in which the cadmium metal center coordinated by four BTC linkers is in a tetrahedral environment.

![Figure 7.10. a) A view of the coordination environment around cadmium in 7.2. b) A portion of a 2-D sheet of 7.2 showing the DMF molecules in the holes of the square net.](image)

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The 2-D sheets pack together closely in the crystalline lattice, Figure 7.11a. The sheets, which are slightly corrugated, are offset from one another and interdigitate so that the metal of one sheet is next to the imidazolium ring of the neighboring sheet, Figure 7.11b. However, there are 1-D channels running through the structure along the crystallographic a-axis, Figure 7.11c. These 1-D channels lead to a porous material with 40.5% (1007.7 Å³/2490.9 Å³) solvent accessible void space. This material falls short of meeting all the criteria for a CO₂ uptake material. It does have solvent accessible void space and a pore system that appears to be lined by the potentially functional portion of the linker. However, the imidazolium is still protonated and the material is not 3-D.

The 2-D lanthanum material [La₃(HL1Br)₂(L1)(OH)₃], 7.3 was synthesized via reaction of lanthanum perchlorate with H₃L1Br in DMF at 100°C for three days, Scheme 7.8. The molecular structure of 7.3 is quite complex, Figure 7.12. One lanthanum metal center is coordinated by six monodentate carboxylate groups from the linkers, one bridging OH⁻ ligand and one terminal OH⁻ ligand. Four of the six linkers are HL1Br, meaning the imidazolium is still protonated and the Br⁻ ion is still present. The other two are L1, meaning they are completely deprotonated and the accompanying Br⁻ ion is not present. The carbene carbon of the L1 linkers has a close contact with a second lanthanum at 3.31 Å.
Scheme 7.8. Synthesis of the 2-D material 7.3.

Figure 7.11. a) A view of 7.2 along the crystallographic c-axis showing the close packing of the 2-D sheets. b) Two neighboring sheets highlighted in red and green respectively, showing the offset nature with which they pack. c) A portion of the extended structure of 7.2 along the crystallographic a-axis showing the 1-D channels.
The extended structure of 7.3 is a 2-D sheet built from 1-D La/COO⁻/OH⁻ chains linked by L1 and HL1Br bridges, Figure 7.13a. The corrugated 1-D chains extend along the crystallographic c-axis and are composed of lanthanum metal centers linked by carboxylate and hydroxide bridges. The bridging groups alternate between being four carboxylate groups or two carboxylate groups and one hydroxide, Figure 7.13b. The 2-D sheets stack together and are separated by bromide ions in the interlayer, Figure 7.13c. There is no void space within each 2-D sheet, however, there is space between the sheets giving the material 39.5% (2995.5 Å³/7587.7 Å³) solvent accessible void space.⁴⁷ Since the imidazoliums in the HL1Br linkers are still protonated and the carbenes in the L1 linkers appear to be coordinating to lanthanum, this material does not meet the criteria for CO₂ uptake. However, to date there have been no reports in the literature of an in situ generated carbene in an extended structure. The examples described in section 7.1.1 containing carbenes were done either pre-synthetically⁴² or post-
synthetically. While it is not a “naked” carbene, this is a novel preparation of a metal–carbene in an extended structure.

**Figure 7.13.** a) A portion of the 2-D sheet of 7.3. b) A portion of the 1-D chain of 7.3 showing the alternating bridging groups. c) A view showing the 2-D sheets stacking together with bromide ions in the interlayer.
The final 2-D material to be discussed is \([\text{Nd}(\text{HLBr})_{1.5}(\text{H}_2\text{O})_{1.5}]\), 7.4. 7.4 was synthesized via reaction of neodymium nitrate with \(\text{H}_3\text{LBr}\) in DMF solution at 100\(^\circ\)C for three days, Scheme 7.9. The molecular structure of 7.4 is composed of a neodymium metal center coordinated by six monodentate carboxylate groups from HL1Br linkers, one bridging water molecule and one terminal water molecule, Figure 7.14. All of the imidazolium groups on the HL1Br linkers are protonated and the accompanying bromide anions are also present.

Scheme 7.9. The synthesis of the 2-D material 7.4.

Figure 7.14. The molecular structure of 7.4, showing the coordination environment around neodymium. All hydrogen atoms except the imidazolium hydrogen have been removed. Orange – neodymium, brown – bromine, red – oxygen, blue – nitrogen, black – carbon, pink – hydrogen.
The extended structure of 7.4 is similar to that of 7.3 however, there are some differences. The biggest difference is that there are no carbene – neodymium interactions in 7.4 like the carbene – lanthanum interactions in 7.3. Topologically, these materials are the same. The 2-D structure of 7.4 is constructed of 1-D Nd/COO/H₂O chains linked by HL1Br bridges, Figure 7.15a. The corrugated chains extend along the crystallographic c-axis and are composed of neodymium metal centers bridged by carboxylate groups and water molecules. The bridging groups alternate between being four carboxylate groups or two carboxylate groups and one water, Figure 7.15b. The 2-D sheets stack together and are separated by bromide ions in the interlayer, Figure 7.15c. There is no void space within each 2-D sheet, however, there is space between the sheets giving the material 38.7% (2907.7 Å³/7507.2 Å³) solvent accessible void space. Much like 7.3, since all of the imidazolium groups are still protonated 7.4 does not seem like a good candidate for CO₂ uptake studies. Also, all of the void space for 7.3 and 7.4 is between the 2-D sheets; so it is possible that the reactive portion would not be accessible for interaction with CO₂ even if it was deprotonated.

The 1-D chains described for 7.3 and 7.4 are not uncommon in lanthanide carboxylate extended structures. These chains are not identical to those of 7.3 and 7.4, but they are 1-D Ln/COO⁻ chains; some of which are a part of higher dimensionality structures. There are three examples of these chains, [Ln₁₂(C₈H₄O₄)₁₈(H₂O)₂(DMF)₁₂·4H₂O] (Ln = La, Ce, Nd), containing bridging water molecules as well, similar to 7.4. The 2-D sheets of 7.3 and 7.4 do appear to be unique.
None of the materials including the 1-D chains are a part of 2-D structures similar to the ones described here.

Figure 7.15. a) A portion of the 2-D sheet of 7.4. b) A portion of the 1-D chain of 7.4 showing the alternating bridging groups. c) A view showing the 2-D sheets stacking together with bromide ions in the interlayer.
7.5.3 Three-dimensional cadmium and neodymium frameworks

The two 3-D materials, \([\text{Nd}_2(\text{HL1Br})_3(\text{bipy})_{0.5}] (7.5)\) and \([\text{Cd}_3\text{K}_2(\text{HL5})_62\text{H}_2\text{O}] (7.6)\), will be discussed separately. First, 7.5 will be described followed by 7.6. For each material the molecular structure will be described and then the extended structure will be discussed.

The 3-D network \([\text{Nd}_2(\text{HL1Br})_3(\text{bipy})_{0.5}]\), 7.5 was synthesized by the reaction of neodymium nitrate with H3L1Br and 4,4'-bipyridine (bipy) in DMF at 110°C for three days, Scheme 7.10. This reaction is very similar to the one that produced 7.4, the difference is the addition of bipy. This is not a coincidence, one strategy for building 3-D materials is to incorporate neutral pillaring linkers into previously characterized 2-D materials. In the case of 7.5 this strategy was successful and the coordinated water molecules in 7.4 are displaced in favor of the bipy ligand, the details of the structure will be discussed below.

\[
\text{Nd(NO}_3)_2\cdot6\text{H}_2\text{O} + \text{H}_3\text{L1Br} + 4,4'\text{-bipyridine} \rightarrow [\text{Nd}_2(\text{HL1Br})_3(\text{bipy})_{0.5}] \quad 7.5
\]

Scheme 7.10. The synthesis of the 3-D material 7.5.

The molecular structure of 7.5 contains two unique neodymium metal centers. The coordination environment of Nd1 consists of six oxygen atoms of monodentate carboxylate groups from the HL1Br linkers, Figure 7.16a. All of these carboxylate groups are bridging to neighboring neodymium atoms. The coordination environment of Nd2 also consists of six oxygen atoms of monodentate carboxylate groups from HL1Br linkers.
as well as a nitrogen from the bipy ligand, Figure 7.16b. Once again, all of the carboxylate groups bridge to neighboring neodymium atoms. Overall, the molecular structure is a bimetallic species in which the Nd1 is linked to Nd2 through bridging carboxylate groups of HL1Br linkers, Figure 7.16c.

**Figure 7.16.** A view of the coordination environment of a) Nd1 and b) Nd2 in 7.5. c) A view of the bimetallic molecular structure of 7.5. Orange – neodymium, brown – bromine, red – oxygen, blue – nitrogen, black – carbon.
The extended structure of 7.5 can be described by breaking it down into its component parts. The 3-D architecture is composed of 2-D sheets linked together, and the 2-D sheets are built from 1-D chains. First, the 1-D chains will be described followed by the 2-D sheets and finally the overall 3-D network. The 1-D chains in 7.5 are very similar to those previously described for 7.4. They are constructed from Nd/COO-interactions in which Nd1 links to Nd2 through alternating bridges of either four carboxylate groups of HL1Br or two carboxylate groups, Figure 7.17a. The difference between the chains of 7.5 and 7.4 (Figure 7.15b) is that there are no water molecules present in 7.5. These 1-D chains are linked together into a 2-D sheet through the HL1Br linkers. The 2-D sheets in 7.5 are identical to those in 7.4 (Figure 7.15a) with the exception of the water molecules discussed above in the 1-D chains, Figure 7.17b. Finally, the 3-D network is constructed from the 2-D sheets and pillaring bipy linkers, Figure 7.17c. The 4,4′-bipyridine coordinated to Nd2, shown in Figure 7.16, links the 2-D sheets by coordinating to another Nd2 in a neighboring sheet. Every Nd2 is linked to a neighboring Nd2 in a sheet either above or below through the bipy linkers, this leads to the 3-D architecture of 7.5.
Figure 7.17. a) A portion of a 1-D chain in 7.5. b) A portion of the 2-D sheet in 7.5 with bipy ligands removed for clarity. c) A portion of the 3-D network of 7.5 showing the bipy linkers pillaring between neighboring 2-D sheets.
The 3-D network of 7.5 is a uninodal, 7-connected framework with vco topology and point symbol \{3^6,4^6,5^8,6\}, Figure 7.18a. The SBU for the network is the bimetallic unit shown in Figure 7.16c which links to seven neighboring SBUs through the HL1Br and bipy linkers. There have only been five 3-D 7-connected uninodal networks reported in the literature, so this is an uncommon occurrence. It is interesting to note that out of the six 7-connected networks (including 7.5) they exhibit five novel topologies. The two networks that are isoreticular are isostructural potassium and rubidium homologues of [(4-Cl-2,6-Me₂C₆H₂OM)₂·(diox)₃]. The point symbol for these nets is \{3^3,4^{12},5^5,6\}, comparison of the point symbols for complex topologies is the easiest was to distinguish their differences. The related compound [(2,4,6-Me₃C₆H₂OK)₅·(diox)] is a 7-connected net with point symbol \{4^{15},6\}. There is one transition metal 7-connected net, [(Co₄(ina)(H₂O)(EtOH))·(NO₃)·2EtOH·4H₂O] (ina = iso-nicotinate), with point symbol \{3^3,4^{11},5^6,6\}. Finally, there is one lanthanide 7-connected net, [{La(bipy-O₂)₄}·{B(Ph)₄}{ClO₄}·2.75CH₃OH], with point symbol \{4^{17},6\}. By comparing the point symbols for these materials it is clear that the topologies are different. As more of the high connectivity networks are characterized it is interesting to see if topological patterns emerge, and as of yet there are no patterns emerging for 7-connected nets.

The network is porous, with 38.6% (6040.7 Å³/15655.0 Å³) solvent accessible void space. There are two types of pores in the network; a hexagonal channel with approximately 9.0 Å in diameter (Figure 7.18b) and a trapezoidal shaped channel with approximate dimensions of: short edge – 6.5 Å, long edge – 8.5 Å, height – 5.6 Å (Figure 7.18c). These pores in the material are filled with disordered solvent molecules. In the
crystal structure this electron density could not be reliably modeled, so the SQUEEZE routine from the program PLATON was applied. The details of the SQUEEZE results will be discussed in Appendix A with the specific structural details.

Figure 7.18. a) A picture of the reduced network topology \textbf{vco} where each pink ball is one SBU and is connected with seven neighboring SBUs. b) A space filling view along the \textit{b}-axis showing the hexagonal pores and a diagram of the pore. c) A space filling view along the \textit{a}-axis showing the trapezoidal pores and a diagram of the pore.
This material can be reliably reproduced, however never as a pure phase. Each reaction produces single crystalline 7.5 as well as other solid powder. Because of this phase impurity, it was not possible to attempt to activate the framework and potentially post-synthetically deprotonate the imidazoliums. Attempts to optimize the reaction for 7.5 were unsuccessful. A total of 70 combinations of reaction stoichiometry, solvent and temperature were studied and none of them resulted in a phase pure material, 7.5 or otherwise.

The final 3-D material, [Cd₃K₂(HL₅)₆·2H₂O], 7.6 was synthesized from the reaction of cadmium nitrate with H₃L₅(BF₄) and potassium hexafluorophosphate in DMF solution at 100°C for three days, Scheme 7.11. This reaction is a modified version of that reported by Yaghi et al.³² in which they synthesized a zinc MOF with the H₃L₅(BF₄) molecule, as described above in section 7.1.1. Based on the reaction from the literature, K(PF₆) was added to the reaction mixture. In the previously reported material, no potassium is present in the final product and no explanation is given as to why this was added. However, it is an essential part of the structure of 7.6, and identical reactions performed in the absence of K(PF₆) yield no crystalline product.

Scheme 7.11. The synthesis of the 3-D material 7.6.
The molecular structure of 7.6 is composed of a pentanuclear aggregate of three cadmium atoms and two potassium atoms. The metal centers are held together by bridging carboxylate groups from the HL5 linkers. Each of the cadmium metal centers are eight coordinate, binding to four chelating carboxylate groups of HL5 linkers. The two potassium atoms are six coordinate with a coordination environment of six oxygen atoms from six carboxylate groups, Figure 7.19. There are also two unbound water molecules per pentanuclear aggregate in the structure.

![Diagram](image)

**Figure 7.19.** The molecular structure of 7.6 showing the pentanuclear cluster a) showing all HL5 linkers and b) showing only the carboxylates of the HL5 linkers. All hydrogens and solvent water molecules have been removed for clarity. Green – cadmium, purple – potassium, red – oxygen, blue – nitrogen, black – carbon.

The 3-D extended structure of 7.6 is an eight-connected network. The cluster shown in Figure 7.19b is the SBU and it is linked through the twelve surrounding HL5 linkers to eight neighboring SBU. There are a total of four single bridges and four double bridges; this accounts for all twelve linkers bridging to only eight neighboring SBUs. This is an interpenetrated 3-D network, which means one identical network of 7.6 has grown.
inside another network of 7.6. Figure 7.20a,b shows simplified network representations of one of these networks and of the interpenetrated material. Even with the interpenetration, there is a large amount of void space in the material: 39.0% (27946.2 Å³/71721.0 Å³). It should be noted that even though the percentage of void space in the unit cell is similar to those previously stated for 7.2 – 7.5, due to the great size of the unit cell of 7.6 the actual void volume is significantly larger. The pores run along the a-axis of the crystalline material and are lined by the imidazolium groups, Figure 7.20c,d shows a view of the single network and the interpenetrated networks.

The topology of the eight-connected network is similar to that of body-centered cubic (bcu) networks. The point symbol for 7.6 is \{4^{20},6^{8}\} and the point symbol for bcu is \{4^{24},6^{4}\}, by looking at the point symbols for 7.6 and bcu it is simple to observe the difference between the two. The network of 7.6 has twenty 4-membered cycles and eight 6-membered cycles while bcu has twenty-four 4-membered cycles and four 6-membered cycles. Figure 7.20e,f shows simplified network representations of each type of net for easy comparison.
Figure 7.20. A view along the a-axis of 7.6 of the simplified network representation of a) a single net and b) the interpenetrated material with individual nets in different colors. A view along the a-axis of 7.6 showing the pores in c) a single net and d) the interpenetrated material. e) A view of the simplified network representation of 7.6. f) A view of the simplified network representation of bcu.
Similarly to 7.5, the pores in the 7.6 are filled with disordered molecules. In the crystal structure this electron density could not be reliably modeled, so the SQUEEZE routine from the program PLATON was applied. The details of the SQUEEZE results will be discussed in Appendix A with the specific structural details. However, in 7.6 not all of the disordered molecules were solvent molecules. There are two anions unaccounted for in the crystal structure. By adding up the charges from the empirical formula of 7.6, [Cd$_3$K$_2$(HL5)$_6$·2H$_2$O], an overall 2+ charge is left. The identity of these anions is not known, however it is most likely to be NO$_3^-$, BF$_4^-$, PF$_6^-$ or a combination of these since those are the anions initially present in the reaction. The large amount of unknown solvent present in the highly porous material would interfere with other analytical techniques to identify the anions.

7.6 is a unique interesting material for reasons unrelated to its potential carbon capture abilities. First, the linker has only been used in two materials reported to date. The two materials are those reported by Yaghi et. al. and described in section 7.1.1. Also, the Cd$_3$K$_2$ aggregate that acts as the SBU in 7.6 is unique. In fact there are no reported examples of any M$_3$A$_2$ (M = transition metal, A = alkali metal) aggregate similar to 7.6. There are a large amount of polymeric chains containing transition metals and alkali metals, but no discrete aggregates that are quite like the Cd$_3$K$_2$ species.

This material would be interesting to study for CO$_2$ uptake and post-synthetic deprotonation, however, a phase pure material could not be synthesized. Multiple reactions with various conditions were tested, but 7.6 could not be synthesized as a phase pure material. Attempts to characterize the mixture of products by PXRD were
unsuccessful. Upon drying the solid, the crystallinity of the material was lost and only an amorphous signal was obtained. This speaks to the lack of stability of 7.6 upon solvent removal and suggests that network activation would have been problematic if a phase pure material could have been obtained.

7.6 Experimental

7.6.1 General procedures

All anilines, paraformaldehyde and aqueous glyoxal were purchased from Aldrich and used without further purification. Toluene was dried by passage through columns of copper-based catalyst and alumina (Innovative Technology) and stored on 4Å molecular sieves. NMR spectra were obtained on a Varian Unity Plus 300 MHz instrument and referenced to residual solvent signals. Mass spectra were recorded on a Bruker microTOF-Q II mass spectrometer.

7.6.2 X-ray Crystallography

Single-crystals were examined under Infineum V8512 oil. The datum crystal was affixed to a Mitegen mounting loop and transferred to the 100 K nitrogen stream of a Bruker APEX diffractometer equipped with an Oxford Cryosystems 700 series low-temperature apparatus. Cell parameters were determined using reflections harvested from three sets of 12 0.5° φ scans. The orientation matrix derived from this was transferred to COSMO to determine the optimum data collection strategy requiring a minimum of 4-fold redundancy. Cell parameters were refined using reflections
harvested from the data collection with $I \geq 10\sigma(I)$. All data were corrected for Lorentz and polarization effects, and runs were scaled using SADABS. The structures were solved and refined using SHELXTL. Structure solution was by direct methods. Non-hydrogen atoms not present in the direct methods solution were located by successive cycles of full-matrix least-squares refinement on $F^2$. All non-hydrogen atoms were refined with parameters for anisotropic thermal motion. Hydrogen atoms were placed at calculated geometries and allowed to ride on the position of the parent atom. Hydrogen thermal parameters were set to $1.2 \times$ the equivalent isotropic $U$ of the parent atom.

7.6.3 Preparation

**Synthesis of [C$_{17}$H$_{13}$BrN$_2$O$_4$], H$_3$L$_1$Br.$^{31}$** To a stirred solution of paraformaldehyde (0.98g, 33 mmol) in toluene (40mL) was added 4-cyanoaniline (7.72g, 65.2 mmol) and aqueous glyoxal (40% (v/v), 4.74g, 32.6 mmol). Concentrated HCl (3.72mL, 32.6 mmol) was added dropwise. The reaction mixture was refluxed for several hours, collecting water in a Dean-Stark trap. The solution was allowed to cool to room temperature and the solvent was removed by vacuum. HBr (90mL) was added to the solid and refluxed overnight. The resulting brown solid was filtered, washed with ethyl acetate and dried by pulling air through. Yield 7.76g (61%). $^1$H NMR (300 MHz, CD$_3$OD, 25°C) $\delta$ = 7.98 (4H, d, $^2$J$_{HH}$ = 8.6 Hz, $m$-CH,Ph), 8.33 (4H, d, $^2$J$_{HH}$ = 8.6 Hz, $o$-CH, Ph), 8.46 (2H, s, CH=CH, C$_3$H$_3$N$_2$), 10.33 (1H, s, CH, C$_3$H$_3$N$_2$). MS (ESI): $m/z$ Calculated for C$_{17}$H$_{11}$Na$_2$N$_2$O$_4$ [M − 2H − Br + 2Na]$^+$: 353.05, found 353.05; C$_{17}$H$_{12}$Na$_2$N$_2$O$_4$ [M − H − Br + Na]$^+$: 331.07, found
331.07; C_{17}H_{12}N_{2}O_{4} [M – 2H – Br]: 307.07, found 307.07; C_{17}H_{10}N_{2}O_{4} [M – 3H – Br]^{2-}: 153.03, found 153.03.

**Synthesis of [C_{13}H_{13}ClN_{2}O_{2}], H_{3}L_{2}Cl.** To a stirred solution of paraformaldehyde (0.98g, 33 mmol) in toluene (40mL) was added 4-hydroxyaniline (7.11g, 65.2 mmol) and aqueous glyoxal (40% (v/v), 4.74g, 32.6 mmol). Concentrated HCl (3.72mL, 32.6 mmol) was added dropwise. The reaction mixture was refluxed for several hours, collecting water in a Dean-Stark trap. The solution was allowed to cool to room temperature and the solvent was removed by vacuum. The resulting solid was triturated with acetonitrile to produce a fine brown powder. Yield 9.07g (96%). \(^1\)H NMR (300 MHz, CD_{3}OD, 25°C) \(\delta= 6.89\ (1.4H, d, ^2J_{HH} = 9.1\ Hz),\ 7.02\ (4H, d, ^2J_{HH} = 9.1\ Hz, m-CH, Ph),\ 7.19\ (1.2H, d, ^2J_{HH} = 9.1\ Hz),\ 7.61\ (4H, d, ^2J_{HH} = 9.1\ Hz, o-CH, Ph),\ 8.12\ (2H, s, CH=CH, C_{3}H_{3}N_{2}),\ 9.78\ (1H, s, CH, C_{3}H_{3}N_{2}).\) MS (ESI): m/z Calculated for C_{15}H_{13}N_{2}O_{2} [M – Cl]^{+}: 253.10, found 253.10.

**Synthesis of [C_{13}H_{11}ClN_{4}], HL_{3}Cl.** To a stirred solution of paraformaldehyde (1.5g, 50 mmol) in toluene (75mL) was added 4-aminopyridine (9.4g, 100.0 mmol) and aqueous glyoxal (40% (v/v), 7.25g, 50 mmol). Concentrated HCl (5.70mL, 50 mmol) was added dropwise. The reaction mixture was refluxed for several hours, collecting water in a Dean-Stark trap. The solution was allowed to cool to room temperature and the solvent was removed by vacuum. The resulting solid was triturated with acetonitrile to produce a fine brown powder. Yield 7.44g (57%). \(^1\)H NMR (300 MHz, CD_{3}OD, 25°C) \(\delta= 4.03\ (0.15H, s),\ 5.01\ (3.1H, s),\ 7.07\ (4H, d, ^2J_{HH} = 7.2\ Hz, m-CH, Py),\ 8.22\ (4H, d, ^2J_{HH} = 7.5\ Hz, o-CH, Py).\) MS (ESI): m/z Calculated for C_{13}H_{10}ClN_{4} [M – H]^{-}: 257.06, found 257.06.
Synthesis of [C$_{17}$H$_{11}$ClN$_4$], HL4Cl. To a stirred solution of paraformaldehyde (0.98g, 33 mmol) in toluene (40mL) was added 4-cyanoaniline (7.72g, 65.2 mmol) and aqueous glyoxal (40% (v/v), 4.74g, 32.6 mmol). Concentrated HCl (3.72mL, 32.6 mmol) was added dropwise. The reaction mixture was refluxed for several hours, collecting water in a Dean-Stark trap. The solution was allowed to cool to room temperature and the solvent was removed by vacuum. The resulting solid was triturated with acetonitrile to produce a brown powder. Yield 5.44g (54%). $^1$H NMR (300 MHz, CD$_3$OD, 25°C ) $\delta$= 8.09 (8H, d, $^2$$J_{HH}$ = 5.8 Hz, CH, Ph), 8.49 (2H, s, CH=CH, C$_3$H$_3$N$_2$), 10.40 (1H, s, CH, C$_3$H$_3$N$_2$). MS (ESI): m/z Calculated for C$_{17}$H$_{11}$N$_4$ [M – Cl]$^+$: 271.10, found 271.11.

Synthesis of [C$_{15}$H$_{13}$ClN$_2$], HL6Cl. To a stirred solution of paraformaldehyde (0.98g, 33 mmol) in toluene (40mL) was added aniline (6.07g, 65.2 mmol) and aqueous glyoxal (40% (v/v), 4.74g, 32.6 mmol). Concentrated HCl (3.72mL, 32.6 mmol) was added dropwise. The reaction mixture was refluxed for several hours, collecting water in a Dean-Stark trap. The solution was allowed to cool to room temperature and the solvent was removed by vacuum producing a brown powder. Yield 6.89g (83%). $^1$H NMR (300 MHz, CD$_3$OD, 25°C ) $\delta$ = 7.31 (7.2H, d, $^2$$J_{HH}$ = 8.8 Hz), 7.41 (7.1H, d, $^2$$J_{HH}$ = 8.3 Hz), 7.70 (4.1H, d, $^2$$J_{HH}$ = 8.3 Hz), 7.85 (4.3H, d, $^2$$J_{HH}$ = 8.6 Hz), 8.33 (2H, s, CH=CH, C$_3$H$_3$N$_2$), 10.11 (1H, s, CH, C$_3$H$_3$N$_2$). MS (ESI): m/z Calculated for C$_{15}$H$_{13}$N$_2$ [M – Cl]$^+$: 221.11, found 221.12.

7.1 [CoCl(HL2)(CH$_3$COO)][H$_3$L2]$^+$. Cobalt acetate tetrahydrate (0.075g, 0.3 mmol), H$_3$L2Cl (0.087g, 0.3 mmol) and DMF (8mL) were added to a 20mL scintillation vial. The vial was capped and placed in an oil bath at 80°C for 3 days. After 3 days the
vial was removed from the oil bath and allowed to cool to room temperature. A mixture of dichroic crystals of 7.1 and amorphous powder was obtained.

7.2 [Cd(HL1)2·DMF]. Cadmium nitrate tetrahydrate (0.093g, 0.3 mmol), H3L1Br (0.117g, 0.3 mmol) and DMF (10mL) were added to a 20mL scintillation vial. A stir bar was added and six drops of triethylamine were added as the pH was monitored by a pH meter. The pH was adjusted from 2.9 to 6.3. The stir bar was removed and the vial was capped and placed in an oil bath at 100°C for 3 days. After 3 days the vial was removed from the oil bath and allowed to cool to room temperature. A mixture of colorless crystals of 7.2 and amorphous powder was obtained.

7.3 [La3(HL1Br)2(L1)(OH)3]. Lanthanum perchlorate hexahydrate (0.109g, 0.2 mmol), H3L1Br (0.117g, 0.3 mmol) and DMF (8mL) were added to a 20mL scintillation vial. The vial was capped and placed in an oil bath at 100°C for 3 days. After 3 days the vial was removed from the oil bath and allowed to cool to room temperature. A mixture of colorless crystals of 7.3 and amorphous powder was obtained.

7.4 [Nd(HL1Br)1.5(H2O)1.5]. Neodymium nitrate hexahydrate (0.131g, 0.3 mmol), H3L1Br (0.117g, 0.3 mmol) and DMF (8mL) were added to a 20mL scintillation vial. The vial was capped and placed in an oil bath at 100°C for 3 days. After 3 days the vial was removed from the oil bath and allowed to cool to room temperature. A mixture of pale blue crystals of 7.4 and amorphous powder was obtained.

7.5 [Nd2(HL1Br)3(bipy)0.5]. Neodymium nitrate hexahydrate (0.131g, 0.3 mmol), H3L1Br (0.117g, 0.3 mmol), 4,4'-bipyridine (0.047g, 0.3 mmol) and DMF (8mL) were added to a 20mL scintillation vial. The vial was capped and placed in an oil bath at
110°C for 3 days. After 3 days the vial was removed from the oil bath and allowed to cool to room temperature. A mixture of pale blue crystals of 7.5 and amorphous powder was obtained.

7.6 [Cd₃K₂(HL5)₆·2H₂O]. Cadmium nitrate tetrahydrate (0.093g, 0.3 mmol), H₃L5(BF₄) (0.047g, 0.1 mmol), potassium hexafluorophosphate (0.186g, 1.0 mmol) and DMF (15mL) were added to a 30mL scintillation vial. The vial was capped and placed in an oil bath at 100°C for 3 days. After 3 days the vial was removed from the oil bath and the hot DMF was decanted and replaced with 15mL fresh DMF. A mixture of colorless crystals of 7.6 and amorphous powder was obtained.

7.7 References


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(44) The Cambridge Structural Database, version 5.33, updates February 2012.


APPENDIX A:
CRYSTALLOGRAPHIC INFORMATION

A.1 Specific Structural Details

2.3 [(4-Et-C₆H₄OK)₃·(diox)]

The asymmetric unit contains three potassium centers and three 4-Et-C₆H₄O⁻ ligands. Two of the phenoxide ligands act as $\mu^2$ bridges and one acts as a $\mu^3$ bridge between the potassium centers. K1 and K2 are each solvated by half of a dioxane molecule. The ethyl group on one of the phenoxide ligands is disordered over two positions. Alternate positions were modeled for C7 and C8 and site occupancies were refined to 0.5. Symmetry expansion generates a 3-D hybrid organic-inorganic material constructed from inorganic rods, which are linked through dioxane bridges.
2.4 [(4-Et-C₆H₄ORb)₂·(diox)₀.₅]

The asymmetric unit contains two rubidium centers and two 4-Et-C₆H₄O⁻ ligands. Each of the phenoxide ligands act as a μ² bridge between rubidium centers. Rb1 is solvated by half of a dioxane molecule. Symmetry expansion generates a 3-D hybrid organic-inorganic material constructed from inorganic rods, which are linked through dioxane bridges. No disorder was modeled for the structure.
2.5 [(4-Et-C₆H₄OCs)₂(diox)₀.₅]

The asymmetric unit contains two cesium centers and two 4-Et-C₆H₄O⁻ ligands. Each of the phenoxide ligands act as a μ² bridge between rubidium centers. Cs1 is solvated by half of a dioxane molecule. Symmetry expansion generates a 3-D hybrid organic-inorganic material constructed from inorganic rods, which are linked through dioxane bridges. No disorder was modeled for the structure.

3.1 [(2-iPr-C₆H₄OCs)₂(H₂O)(diox)₀.₅]

The asymmetric unit contains two cesium centers, two 2-iPr-C₆H₄O⁻ ligands and one water molecule. The water molecule and one of the phenoxide ligands act as μ² bridges between the cesium centers. Cs1 is coordinated by a non-bridging phenoxide ligand. Cs2 is solvated by half of a dioxane molecule. There is positional disorder in the dioxane molecule. An alternate position was modeled for C20 and the site occupancy was refined to 0.5. Symmetry expansion generates a 3-D hybrid organic-inorganic material constructed of inorganic rods, which are linked through dioxane bridges.
3.2 [(2-\textsuperscript{1}Pr-C\textsubscript{6}H\textsubscript{4}OCs)\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2}(diox)\textsubscript{1.5}]

The asymmetric unit contains four cesium centers, four 2-\textsuperscript{1}Pr-C\textsubscript{6}H\textsubscript{4}O\textsuperscript{−} ligands and two water molecules. Two of the phenoxide ligands act as $\mu^2$ bridges between cesium centers and two act as $\mu^3$ bridges. Both water molecules act as $\mu^2$ bridges between cesium centers. Cs2 is solvated by one dioxane molecule. Cs3 is solvated by half of a dioxane molecule. Symmetry expansion generates a 2-D hybrid organic-inorganic material constructed of inorganic rods, which are linked through dioxane bridges. No disorder was modeled for the structure.
3.3 [(2-^1^Pr-C^6_H^4)OCs]_{3}(H^2O)(diox)_{2.5}]

The asymmetric unit contains three cesium centers, three 2^-^1^Pr-C^6_H^4^0^- ligands and one water molecule. One of the phenoxide ligands acts as a $\mu^3$ bridge between cesium centers and two act as $\mu^2$ bridges. Cs2 is solvated by one and a half dioxane molecules. Cs3 is solvated by one dioxane molecule and one water molecule. Symmetry expansion generates a 2-D extended structure, constructed from hexametallic aggregates. These aggregates are linked into 1-D chains through dioxane bridges. The 1-D chains are connected through Cs···C^Ar agostic interactions into a 2-D sheet. No disorder was modeled for the structure.
The asymmetric unit contains one lanthanum center coordinated by one chloride ion, four bipy-O₂ molecules and one methanol molecule. There are two tetraphenyl borate counter anions and one methanol solvent molecule as well. Symmetry expansion generates a 2-D extended structure constructed from lanthanum centers linked through bipy-O₂ molecules. Two of the four bipy-O₂ molecules bridge to neighboring lanthanum centers while the other two are terminal donors. The tetraphenyl borate counter anions and the methanol solvent molecule occupy the space between the 2-D sheets. No disorder was modeled for the structure.
4.2 \([\text{CeBr(bipy-O}_2\text{)}_4(\text{CH}_3\text{OH})]^{2+}[\text{B(C}_6\text{H}_5\text{)}_4]^{-}\cdot(\text{CH}_3\text{OH})\]

The asymmetric unit contains one cerium center coordinated by one bromide ion, four bipy-O\(_2\) molecules and one methanol molecule. There are two tetraphenyl borate counter anions and one methanol solvent molecule as well. Symmetry expansion generates a 2-D extended structure constructed from cerium centers linked through bipy-O\(_2\) molecules. Two of the four bipy-O\(_2\) molecules bridge to neighboring cerium centers while the other two are terminal donors. The tetraphenyl borate counter anions and the methanol solvent molecule occupy the space between the 2-D sheets. No disorder was modeled for the structure.
4.3 \([(\text{GdCl(bipy-O}_2\text{-})_4(\text{CH}_3\text{OH})])^{2+}(\text{B(C}_6\text{H}_5)_4)_2\cdot2(\text{CH}_3\text{OH})\]

The asymmetric unit contains one gadolinium center coordinated by one chloride ion, four bipy-O$_2$ molecules and one methanol molecule. There are two tetraphenyl borate counter anions and two methanol solvent molecules as well. Symmetry expansion generates a 2-D extended structure constructed from gadolinium centers linked through bipy-O$_2$ molecules. Two of the four bipy-O$_2$ molecules bridge to neighboring gadolinium centers while the other two are terminal donors. The tetraphenyl borate counter anions and the methanol solvent molecules occupy the space between the 2-D sheets. No disorder was modeled for the structure.
The asymmetric unit contains one potassium center coordinated by half of one 2,2’-dipyridyl-5,5’-dicarboxylate ligand and one water molecule. There is one solvent water molecule. Symmetry expansion generates a 3-D extended structure composed of 2-D sheets consisting of potassium-carboxylate and potassium-water interactions. The 2-D sheets are connected through the 2,2’-dipyridyl linkers. There are small channels through the 3-D structure that contain the guest water molecules. No disorder was modeled for the structure.
5.2 $\left\{\text{Ba}_2(\text{bipy-O}_2)_6\right\}^{4+}\left\{\text{Ba}_2(\text{NO}_3)_8\right\}^{4-}$

The asymmetric unit contains four barium centers. Ba1 and Ba2 are part of a bimetallic barium tetra-cationic molecule in which the barium centers are bridged through two $\mu^2$ bipy-O$_2$ ligands. Ba1 is also coordinated by three non-bridging bipy-O$_2$ ligands and Ba2 is coordinated by one non-bridging bipy-O$_2$ ligand. Ba3 and Ba4 are part of a bimetallic barium tetra-anionic molecule in which the barium centers are bridged through two nitrate ions. Ba3 and Ba4 are also coordinated by three non-bridging nitrate anions.

Symmetry expansion of the cationic unit generates a 3-D extended structure constructed from 1-D inorganic chains of Ba – O$_\text{bipy}$ interactions. These 1-D chains are connected into a 3-D architecture through the bipy-O$_2$ molecules. There are 1-D channels running through the 3-D structure. Symmetry expansion of the anionic unit generates a 1-D Ba – NO$_3$ polymer contained in the channel of the 3-D structure. No disorder was modeled for the structure.
5.3 [Nd₂Cl(C₆H₅COO)₅(diox)]

The asymmetric unit contains a bimetallic neodymium molecule. The neodymium centers are bridged through one $\mu^2$ chloride ion and two $\mu^2$ benzoate ions. Nd1 is also coordinated by one non-bridging benzoate ion and one dioxane solvent molecule. Nd2 is also coordinated by two non-bridging benzoate ions. There is positional disorder in two of the benzoate molecules. An alternate position was modeled for each affected carbon atom and the site occupancy was refined to 0.5. Symmetry expansion generates a 1-D extended structure. The polymer is a chain constructed from the bimetallic units linked through benzoate bridges. The dioxane molecule acts as a terminal donor. Small channels between the chains are filled with disordered solvent molecules. The solvent could not be reliably modeled and was omitted through use of the SQUEEZE routine within PLATON. The void space analysis yielded a volume of 540 Å³ with an electron count of 224, located at a center of symmetry. This corresponds well to five molecules of dioxane per unit cell.
The asymmetric unit contains one cobalt center coordinated by one chloride ion, one acetate ion and half of one HL2 ligand in the anionic unit. The cationic unit is half of a H$_3$L$_2$ ion. Symmetry expansion of the anionic unit generates a 1-D chain constructed of cobalt centers connected through HL2 bridges. Symmetry expansion of the cationic unit generates a full H$_3$L$_2$ cation. There is one cation per cobalt in the extended structure. No disorder was modeled in the structure.
7.2 [Cd(HL1)$_2$-DMF]

The asymmetric unit contains one cadmium center coordinated by one monodentate HL1 ligand and one bidentate HL1 ligand. There is one DMF solvent molecule present. Symmetry expansion generates a 2-D extended structure constructed from cadmium centers connected through HL1 bridges. The DMF molecule is located within square holes in the 2-D sheet structure. No disorder was modeled for the structure.
7.3 [La₃(HL1Br)₂(L1)(OH)₃]

The asymmetric unit contains one lanthanum center coordinated by monodentate carboxylate groups of two half HL1Br ligands and one half L1 ligand and one and a half hydroxide ions. La2 is in close contact with the carbene carbon of L1 at 3.31 Å. Symmetry expansion generates a 2-D extended structure constructed of 1-D chains of La1/COO’/OH-. The 1-D chains are connected through the HL1Br and L1 molecules. The La2 atoms lay within the 2-D corrugated layers in close contact with the carbene. The bromide ions are located between the 2-D sheets. There is 39.5% (2995.5 Å³/7587.7 Å³) solvent accessible void space between the sheets, but none within the layers. The void space is full of disordered solvent molecules, which could not be reliably modeled and was omitted through use of the SQUEEZE routine within PLATON. The void space analysis yielded an electron count of 1429 electrons. No disorder was modeled for the structure.
7.4 [Nd(HL1Br)$_{1.5}$(H$_2$O)$_{1.5}$] 

The asymmetric unit contains one neodymium center coordinated by monodentate carboxylate groups of three half HL1Br ligands and one and a half water molecules. Symmetry expansion generates a 2-D extended structure constructed of 1-D chains of Nd1/COO$^-$/H$_2$O. The 1-D chains are connected through the HL1Br molecules. The bromide ions are located between the 2-D sheets. There is 38.7% (2907.7 Å$^3$/7507.2 Å$^3$) solvent accessible void space between the sheets, but none within the layers. The void space is full of disordered solvent molecules, which could not be reliably modeled and was omitted through use of the SQUEEZE routine within PLATON. The void space analysis yielded an electron count of 975 electrons. No disorder was modeled for the structure.

7.5 [Nd$_2$(HL1Br)$_3$(bipy)$_{0.5}$] 

The asymmetric unit contains two neodymium centers bridged by two carboxylate groups of HL1Br ligands. Nd1 is also coordinated by a monodentate carboxylate group of a non-bridging HL1Br ligand. Nd2 is coordinated by half of one 4,4$'$-bipyridine molecule. Br3 and Br4 are each half occupancy sites. Symmetry expansion generates a 3-D extended structure constructed of 1-D chains of Nd1/COO$.^-$ The 1-D chains are
connected through the HL1Br molecules to form 2-D sheets. The 2-D sheets are linked together by the bipy molecules to complete the 3-D architecture. There is 38.6% (6040.7 Å³/15655.0 Å³) solvent accessible void space in the porous structure. The void space is full of disordered solvent molecules, which could not be reliably modeled and was omitted through use of the SQUEEZE routine within PLATON. The void space analysis yielded 2343 electrons. No disorder was modeled for the structure.

### 7.6 [Cd₃K₂(HL₅)₆·2H₂O]

The asymmetric unit contains two cadmium centers and one potassium center. These three metal centers are connected through bridging carboxylate groups from three HL₅ ligands. There is one solvent water molecule in the asymmetric unit. Symmetry expansion generates a 3-D extended structure constructed from a [Cd₃K₂(COO⁻)₁₂] aggregate that acts as an SBU. The aggregate is connected to eight neighboring aggregates through the HL₅ molecules. This is an interpenetrated network. The solvent water molecules are encapsulated within the pores of the 3-D material. There is 39.0%
(27946.2 Å³/71721.0 Å³) solvent accessible void space, containing disordered solvent molecules and anions. This electron density could not be reliably modeled, so the SQUEEZE routine from the program PLATON was applied. The void space analysis yielded 11341 electrons. No disorder was modeled for the structure.
### A.2 Tables of Crystallographic Data

#### TABLE A.1

**CRYSTALLOGRAPHIC DATA FOR 2.3 – 2.5**

| Compound | Formula | FW | Wavelength/ Å | Crystal system | Space group | \(a\)/ Å | \(b\)/ Å | \(c\)/ Å | \(α/°\) | \(β/°\) | \(γ/°\) | \(V/Å^3\) | \(Z\) | \(d_{\text{calc}}/ \text{g cm}^{-3}\) | Size/mm | \(\mu(\lambda)/ \text{mm}^{-1}\) | Max./min. transmission | Reflections collected | Ind. refln | Parameters refined | R(int) | R1, wR2 [I>2σ(I)] | R1, wR2 (all data) | Goodness-of-fit on F^2 | Largest peak, hole/ e Å^{-3} |
|----------|---------|----|--------------|----------------|-------------|-----------|---------|---------|---------|---------|---------|--------|--------|--------|---------------------|----------------------|------------------------|------------------------|------------------------|-----------------------|------------------------|---------------------|
| 2.3      | C\(_{28}\)H\(_{35}\)K\(_3\)O\(_5\) | 568.86 | 1.54178 | Monoclinic | P2(1)/c | 19.2016(12) | 20.4584(12) | 7.2704(5) | 90.113(4) | 4       | 1.323   | 2856.1(3) | 4       | 4       | 4.518 | 0.8056/0.3921 | 24003 | 5193 | 328 | 0.0758 | 0.0659, 0.1238 | 0.0956, 0.1380 | 1.053 | 0.541, -0.635 |
| 2.4      | C\(_{29}\)H\(_{36}\)O\(_3\)Rb\(_3\) | 714.94 | 1.54178 | Orthorhombic | Pnma | 7.4579(3) | 19.2403(6) | 21.0434(6) |               |          | 1.573   | 3019.56(18) | 4       | 4       | 6.431 | 0.5381/0.2661 | 13355 | 2721 | 182 | 0.0342 | 0.0590, 0.2025 | 0.0642, 0.2065 | 1.656 | 1.131, -2.016 |
| 2.5      | C\(_{28}\)H\(_{30}\)Cs\(_3\)O\(_5\) | 845.25 | 1.54178 | Orthorhombic | Pnma | 7.8905(3) | 19.0010(7) | 21.1957(9) |               |          | 1.767   | 3177.8(2) | 4       | 4       | 26.944 | 0.2218/0.0438 | 15495 | 3010 | 185 | 0.0689 | 0.0442, 0.1171 | 0.0603, 0.1298 | 0.906 | 1.999, -0.903 |
## TABLE A.2

**CRYSTALLOGRAPHIC DATA FOR 3.1 – 3.3**

<table>
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<tr>
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<th>3.2</th>
<th>3.3</th>
</tr>
</thead>
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<td><strong>Formula</strong></td>
<td>C_{20}H_{26}Cs_{2}O_{4}</td>
<td>C_{42}H_{56}Cs_{4}O_{9}</td>
<td>C_{37}H_{50}Cs_{3}O_{8.50}</td>
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<td><strong>FW</strong></td>
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<td>1029.50</td>
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<td><strong>Wavelength/ Å</strong></td>
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<td>1.54178</td>
<td>1.54178</td>
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<td><strong>Crystal system</strong></td>
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<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>R-3c</td>
<td>P-1</td>
<td>P2/n</td>
</tr>
<tr>
<td><strong>a/ Å</strong></td>
<td>52.8193(13)</td>
<td>12.0756(13)</td>
<td>14.2208(3)</td>
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<tr>
<td><strong>b/ Å</strong></td>
<td>52.8193(13)</td>
<td>13.7149(15)</td>
<td>15.1796(3)</td>
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<tr>
<td><strong>c/ Å</strong></td>
<td>12.1691(3)</td>
<td>15.8561(16)</td>
<td>19.7511(4)</td>
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<tr>
<td><strong>α/°</strong></td>
<td>69.089(5)</td>
<td>81.234(5)</td>
<td>85.516(6)</td>
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<td><strong>β/°</strong></td>
<td>81.234(5)</td>
<td>1.54178</td>
<td>1.54178</td>
</tr>
<tr>
<td><strong>γ/°</strong></td>
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<td>101.2210(10)</td>
<td>101.2210(10)</td>
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<td><strong>V/Å³</strong></td>
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<td>2423.6(4)</td>
<td>4182.09(15)</td>
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<td><strong>Z</strong></td>
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<td>4</td>
</tr>
<tr>
<td><strong>d_{calc}/ g cm⁻³</strong></td>
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<td>1.694</td>
<td>1.635</td>
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<td><strong>Size/mm</strong></td>
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<td>0.26 × 0.18 × 0.11</td>
<td>0.26 × 0.17 × 0.11</td>
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<tr>
<td><strong>μ(λ)/ mm⁻¹</strong></td>
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<td>23.647</td>
<td>20.654</td>
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<tr>
<td><strong>Max./min. transmission</strong></td>
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<td>0.7532/0.2809</td>
<td>0.2097/0.0751</td>
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<tr>
<td><strong>Reflections collected</strong></td>
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<td>23254</td>
<td>39147</td>
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<td><strong>Ind. refin</strong></td>
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<td>6214</td>
<td>7782</td>
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<td><strong>Parameters refined</strong></td>
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<td>443</td>
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<td><strong>R(int)</strong></td>
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<td>0.0542</td>
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<td><strong>R1, wR2 [I&gt;2σ(I)]</strong></td>
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<td><strong>R1, wR2 (all data)</strong></td>
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<td><strong>Goodness-of-fit on F²</strong></td>
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<td>1.051</td>
<td>1.039</td>
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<td><strong>Largest peak, hole/ e Å⁻³</strong></td>
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<td>2.167, -1.265</td>
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<td>4.2</td>
<td>4.3</td>
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<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
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<td>Formula</td>
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<td>Orthorhombic</td>
<td>Orthorhombic</td>
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<td>Space group</td>
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<td>P2(1)2(1)2(1)</td>
<td>P2(1)2(1)2(1)</td>
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<td>13.4296(6)</td>
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<tr>
<td>$b$/ Å</td>
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<td>23.9961(16)</td>
<td>24.0424(14)</td>
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<tr>
<td>$c$/ Å</td>
<td>24.720(5)</td>
<td>24.9582(16)</td>
<td>24.8784(15)</td>
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<td>$\alpha$/°</td>
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</tr>
<tr>
<td>$\beta$/°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\gamma$/°</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V$/Å³</td>
<td>8002(3)</td>
<td>8071.4(9)</td>
<td>8032.7(8)</td>
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<tr>
<td>$Z$</td>
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<td>4</td>
<td>4</td>
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<td>$d_{calc}$/ g cm⁻³</td>
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<td>1.413</td>
<td>1.389</td>
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<td>$\mu$(Å)/ mm⁻¹</td>
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<td>Max./min. transmission</td>
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<td>0.8934/0.6793</td>
<td>0.6672/0.4828</td>
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<td>190496</td>
<td>75206</td>
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<td>21342</td>
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<td>Parameters refined</td>
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<td>1032</td>
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<td>R(int)</td>
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<td>R1, wR2 [I&gt;2σ(I)]</td>
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<td>0.0261, 0.0.562</td>
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<td>Goodness-of-fit on $F^2$</td>
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<td>2.960, -1.314</td>
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### TABLE A.4

**CRYSTALLOGRAPHIC DATA FOR 5.1 – 5.3**

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<th>5.3</th>
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</thead>
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<td>$C_6H_7KNO_4$</td>
<td>$C_{60}H_{48}Ba_4N_{20}O_{36}$</td>
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<td>Triclinic</td>
<td>Triclinic</td>
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<tr>
<td>Space group</td>
<td>P2(1)/c</td>
<td>P-1</td>
<td>P-1</td>
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<td>$a$/ Å</td>
<td>3.6769</td>
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<td>8.2042(14)</td>
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<td>14.2614(7)</td>
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<td>102.785(3)</td>
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<td>96.783(2)</td>
<td>96.943(3)</td>
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<td>$\gamma$/°</td>
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<td>97.803(2)</td>
<td>104.316(3)</td>
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<td>0.685/0.606</td>
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<td>0.0448, 0.1195</td>
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<td>0.0517, 0.1072</td>
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<td>R1, wR2 (all data)</td>
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## TABLE A.5

CRystallographic Data for 7.1 – 7.3

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<td>C₃₇H₂₉CdN₅O₉</td>
<td>C₅₁H₃₂Br₂La₃N₆O₁₅</td>
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<td>Wavelength/ Å</td>
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<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>Crystal system</td>
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<td>Triclinic</td>
<td>Orthorhombic</td>
</tr>
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<td>Space group</td>
<td>Cm</td>
<td>P-1</td>
<td>Pnma</td>
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<td>b/ Å</td>
<td>16.087(8)</td>
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<td>13.3260(13)</td>
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<td>c/ Å</td>
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<td>86.383(2)</td>
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<td>β/°</td>
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<td>86.285(2)</td>
<td>86.383(2)</td>
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<td>γ/°</td>
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<td>86.383(2)</td>
<td>86.383(2)</td>
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<td>V/Å³</td>
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<td>2490.9(2)</td>
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<td>1.067</td>
<td>1.353</td>
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<td>μ(λ)/ mm⁻¹</td>
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**TABLE A.6**

CRYSTALLOGRAPHIC DATA FOR 7.4 – 7.6

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<th>Crystal system</th>
<th>Space group</th>
<th>a/ Å</th>
<th>b/ Å</th>
<th>c/ Å</th>
<th>α/°</th>
<th>β/°</th>
<th>γ/°</th>
<th>V/Å³</th>
<th>Z</th>
<th>d calc/ g cm⁻³</th>
<th>Size/mm</th>
<th>μ(λ)/ mm⁻¹</th>
<th>Max./min. transmission</th>
<th>Reflections collected</th>
<th>Ind. refln</th>
<th>Parameters refined</th>
<th>R(int)</th>
<th>R1, wR2 [I&gt;2σ(I)]</th>
<th>R1, wR2 (all data)</th>
<th>Goodness-of-fit on F²</th>
<th>Largest peak, hole/ e Å⁻³</th>
</tr>
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<td>Pmna</td>
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<td>344</td>
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<td>1.262, -0.732</td>
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<td>0.71073</td>
<td>Orthorhombic</td>
<td>Pbcn</td>
<td>13.2102(5)</td>
<td>34.245(7)</td>
<td>50.543(2)</td>
<td>15655(6)</td>
<td>8</td>
<td>1.297</td>
<td>0.15 × 0.13 × 0.05</td>
<td>2.892</td>
<td>0.7447/0.6260</td>
<td>186820</td>
<td>8198</td>
<td>335</td>
<td>0.1317</td>
<td>0.1047, 0.2776</td>
<td>0.1504, 0.3105</td>
<td>1.064</td>
<td>5.207, -1.805</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₁₃₈H₁₀₂Cd₃K₂N₁₂O₂₆</td>
<td>2759.72</td>
<td>0.71073</td>
<td>Orthorhombic</td>
<td>Fddd</td>
<td>16.4917(6)</td>
<td>27.349(6)</td>
<td>54.646(2)</td>
<td>71721(5)</td>
<td>16</td>
<td>1.022</td>
<td>0.23 × 0.19 × 0.16</td>
<td>0.454</td>
<td>0.7451/0.6366</td>
<td>698731</td>
<td>15470</td>
<td>822</td>
<td>0.0821</td>
<td>0.0658, 0.1864</td>
<td>0.0910, 0.1973</td>
<td>1.528</td>
<td>1.005, -0.824</td>
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</tbody>
</table>
APPENDIX B:

$^1$H NMR SPECTRA OF THE H$_{NLX}$ IMIDAZOLIUM SALTS

B.1 Imidazolium Salts in CD$_3$OD
B.2 Imidazolium Salts + NaH in CD$_3$OD