THE STRUCTURE AND FUNCTION OF BORATE BASED METAL ORGANIC FRAMEWORKS

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THE STRUCTURE AND FUNCTION OF BORATE BASED METAL ORGANIC FRAMEWORKS

Barton H Hamilton

Dissertation

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ABSTRACT

This dissertation examines metal organic assemblies or coordination polymers synthesized from organic borate linkers. The coordinating anions BF(CN)$_3^-$, [B(C$_3$N$_2$H$_3$)$_4$]$^-$, (B(Im)$_4$)$^- \text{and} [B(C_4N$_2$H$_3$)$_4$]$^-$, (B(4-MeIm)$_4$)$^-$ react with metal ions to form coordination polymers. These coordination polymers have extended network structures.

The cyanide linking spacer, BF(CN)$_3^-$, forms isomorphous 1-D channeled network polymers with Cu(I) and Ag(I). The presence of the BF(CN)$_3^-$ anion stabilizes the +1 oxidation state of the metals.

Three alkaline earth metal network solids having the same formula, M[B(Im)$_4$]$_2$(H$_2$O)$_2$ (M = Mg, Ca, Sr), are presented and compared. The three compounds have different network structures with different degrees of hydrogen bonding. The Ca and Sr materials form 1-D linear chains and the Mg compound forms a 2-D network.

The coordination polymer Pb[B(Im)$_4$](NO$_3$)(xH$_2$O) is a layered material with the metal centers facing the interlayer spacing. This compound can undergo anion exchange and reversible intercalation of solvent water with retention of crystallinity. We observed changes in solvent intercalation by $^{207}$Pb solid state NMR (SSNMR) and thermogravimetric analysis (TGA). Exchange of $^{15}$N nitrate for nitrate and iodide for nitrate is monitored by $^{15}$N and $^{207}$Pb SSNMR, and single crystals of the facile iodide-exchanged material Pb[B(Im)$_4$I] were isolated. Benzoate can be placed in the interlayer
spacing for nitrate under self-assembly conditions and forms an alternating monolayer with the formula Pb[B(Im)₄](C₆H₅COO)(0.5H₂O).

To explore the influence of metal and counterion, the metal is replaced with isoelectronic Tl(I), affording Tl[B(Im)₄], and the borate is modified using 4-methylimidazole, resulting in Pb[B(4-MeIm)₄](NO₃) and Tl[B(4-MeIm)₄]. Like the parent Pb[B(Im)₄](NO₃)ₓ(H₂O), Tl[B(Im)₄] and Tl[B(4-MeIm)₄] are layered network structures but they lack counterions. Pb[B(4-MeIm)₄](NO₃) exhibits a 3-D network structure that lacks an open topology. This result is from the increased stereochemical activity (greater steric bulk toward other ligands) of the B(4-MeIm)₄⁻.

Metal–organic frameworks based on the Pb[B(Im)₄]⁺ can also be used as scaffolds to assemble radical TEMPO and PROXYL carboxylates. Pb[B(Im)₄](4-carboxy-TEMPO) and Pb[B(Im)₄](3-carboxy-PROXYL)(H₂O) are characterized by single crystal diffraction, IR, EA, SQUID magnetic susceptibility and EPR spectroscopy.

Crystals of Pb[B(Im)₄](NO₃)(nH₂O) can also undergo exchange of the nitrate for perrhenate, a model for pertechnetate, forming Pb[B(Im)₄](ReO₄). This exchange reaction is monitored by ²⁰⁷Pb solid-state NMR. The resultant structure is elucidated by single crystal X-ray diffraction. This system represents a new candidate for pertechnetate-sequestering materials.
DEDICATION

This dissertation is dedicated to my mother and father, Lois Jean and Bart Preston Hamilton, without whom I would not be who I am today. I also wish to dedicate this manuscript to my advisor, Christopher J. Ziegler, whom without his guidance and direction I would have never completed such a task. Without the support and encouragement of many, the result might have been different but definitively, the aforementioned have played major roles in my life and development. I wholeheartedly hope to accomplish all that I was inteneded to complete but little of which could have been done without my parents and advisor. I know your guidance and direction will always lead me in the correct direction.
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The time of graduate school contains both times of victory and defeat. Usually the failures represent the majority of the emotions experienced. The time spent working hard is not always directly correlated to the end result. I have experienced many victories and feel blessed. The realization of either emotion translates into a time in which opportunities are abundant or non-existent from the graduate students view. There are many ups and downs that people endure, both at school and at home. At the University of Akron, I have been fortunate enough to meet many people who have influenced my growth as a person and a researcher. Above all else, the many who have managed to tolerate me and still guide me along a direction that has been as fruitful as it has been.

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Many thanks to my family, other than my parents; brothers and sisters, aunts and uncles, grandparents and cousins all of whom believed in me more than I did. Friends of old and friends more recently acquired all need applauded. The dynamics of life involve
different people at different times and remove others when the time is necessary. Unable to name all those deserving, know that your efforts were appreciated.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xi</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>xviii</td>
</tr>
</tbody>
</table>

## CHAPTER

### I. INTRODUCTION TO SUPRAMOLECULAR CHEMISTRY

- Network Solid State Materials

### II. CYANO BORATES AS ORGANIC LINKERS

- Discussion
- Experimental

### III. TETRAKIS(IMIDAZOLYL)BORATES GROUP II NETWORK SOLIDS

- Discussion
- Experimental
IV. LEAD TETRAKIS(IMIDAZOLYL)BORATE SOLIDS: ANION EXCHANGE, SOLVENT INTERCALATION, AND SELF ASSEMBLY OF AN ORGANIC ANION.............................................................78

Discussion.............................................................................................................80

Experimental........................................................................................................97

V. LEAD AND THALLIUM TETRAKIS(IMIDAZOLYL)BORATES: MODIFYING STRUCTURE BY VARYING METAL AND ANION .................................................................101

Discussion.............................................................................................................103

Experimental........................................................................................................115

VI. THE ASSEMBLY OF ORGANIC RADICAL ANIONS BETWEEN METAL- BORATE SCAFFOLDS.................................................................119

Discussion.............................................................................................................121

Experimental........................................................................................................126

VII SEQUESTERING PERRHENATE WITH A BORATE-BASED COORDINATION POLYMER: A MODEL FOR PERTECHNETATE SEPARATION.........................................................130

Discussion.............................................................................................................131

Experimental........................................................................................................136

REFERENCES......................................................................................................139
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Table 2.1. Selected bond lengths (Å) and angles (°) for M(BF(CN)_3)-NCCH_3</td>
</tr>
<tr>
<td>2.2</td>
<td>Crystallographic data and structure refinement details for 1 and 2. Standard deviation parameters are given in parentheses</td>
</tr>
<tr>
<td>3.1</td>
<td>Angle deviations from the closed orientation for compounds 3 – 6</td>
</tr>
<tr>
<td>3.2</td>
<td>Selected bond distances (Å) and angles (°) about the metal centers</td>
</tr>
<tr>
<td>3.3</td>
<td>Crystal data and structural refinement parameters for 3-6</td>
</tr>
<tr>
<td>4.1</td>
<td>Selected bond lengths (Å) and angles (°) for compounds 7-9</td>
</tr>
<tr>
<td>4.2</td>
<td>Crystallographic data and structure parameters for compounds 7-9</td>
</tr>
<tr>
<td>5.1</td>
<td>Crystallographic data collection and structure parameters for compounds 10-12</td>
</tr>
<tr>
<td>5.2</td>
<td>Selected bond lengths and angles for compounds 7, 10, 11, and 12</td>
</tr>
<tr>
<td>6.1</td>
<td>Crystallographic data and structure refinement details for 14 and 15. Standard deviation parameters are given in parentheses</td>
</tr>
<tr>
<td>7.1</td>
<td>Crystallographic data and structure refinement details for Pb<a href="NO_3">B(Im)_4</a>(nH_2O) (7) (left) and Pb<a href="ReO_4">B(Im)_4</a> (16) (on the right). Standard deviation parameters are given in parentheses</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Supramolecular construction as demonstrated with the threading of one molecule through another. Taken from reference 5</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>This demonstrates the different levels of organization, above the molecular level using the calixarene bridged to another calixarene by the biphenol, forming helices. The helices wrap ending with the bundle of 7 helices emanating in one direction. Taken and modified from reference 4.</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>The starting molecular building blocks are shown above. The product exhibits a similar topology to natural tenorite but with expanded dimensions. Taken from reference 6.</td>
<td>7</td>
</tr>
<tr>
<td>1.4</td>
<td>The sum of the weaker molecular interactions bind the material into a robust supramolecular organic assembly. Taken and modified from reference 8.</td>
<td>9</td>
</tr>
<tr>
<td>1.5</td>
<td>Ball and stick representation of the packing of a glucose unit cell where the dashed lines are hydrogen bonding interactions linking the molecules to each other. Taken from reference 30.</td>
<td>13</td>
</tr>
<tr>
<td>1.6</td>
<td>Natural zeolite composition and conformation beginning with the tetrahedral Si/Al unit forming sodalite cages, ending with those cages forming rigid, porous minerals. Each line represents a [Si/Al-O-Si/Al] link. Taken from reference 31.</td>
<td>14</td>
</tr>
<tr>
<td>1.7</td>
<td>Representation of the zeolite ZSM-5 or the natural analog mutinate. Taken from reference 33.</td>
<td>15</td>
</tr>
<tr>
<td>1.8</td>
<td>Representation of a layered double hydroxide, smectite clay, like montmorillonite, where the spacing between layers can contract and expand depending on the hydration or guests but the structure of the layers remains. Taken from reference 34.</td>
<td>15</td>
</tr>
<tr>
<td>1.9</td>
<td>Rhomboids synthesized from triethylphosphine metal bistriﬂate and a bis(4-pyridyl)silane or diketone forming a discrete complex.</td>
<td>18</td>
</tr>
</tbody>
</table>
1.10 The bipyridine dicarboxylate reveals near orthogonal conformation of the pyridyl rings within the molecular chain once metal coordination has occurred.

1.11 Hydrogen atoms are omitted for clarity and the intrachain hydrogen bonds are denoted by the dashed lines. Taken from reference 44.

1.12 The interchain hydrogen bonding and packing as viewed down the c-axis. Hydrogen atoms are omitted for clarity. Taken from reference 44.

1.13 A diagram of the expanding layers of a two dimensional material upon incorporation of a guest molecule.

1.14 Efficiently packed 2-D sheets without any solvents or templates present. Taken from reference 46.

1.15 Corrugated layered structure of tetrahedral Zn[N(CN)₂]₂ close packing in the unit cell is evident with different Zn to Zn distances. Taken from reference 46.

1.16 Schematic diagram of Prussian blue analogs where M and M’ can be the same metal in different valence states or different metals. All linkers are nitrile bridged. Taken from reference 50.

1.17 A representation of interpenetration. Taken from references 35 and 50.

1.18 Demonstrating schematically the idea of pillaring and templating.

1.19 View of a single Ag₃(3-amino-1,2,4-triazole)₂ net along the c axis with the amino groups omitted for clarity. Taken from reference 62.

1.20 Crystal structure view of [Co(O₂CMe)₂(4,4’-tpccp)] exhibiting the 4 equatorial pyridyl chelation to the metal center and 2 axially coordinated monodentate acetates. Taken from references 63 and 64.

1.21 Linear linkers exhibiting different lengths: promoting chain formation, BDC (left), 4,4’-BPY (middle), and TPDC (right).

1.22 Trigonal planar linkers: promotes two-dimensional planar structures, BTC (right), and BTB (left).

1.23 Tetrahedral linkers: organic and metal based promoting three-dimensional networks.
1.24 A paddle-wheel SBU as reported by Yaghi and coworkers containing 2 zinc atoms bridged by 4 symmetric carboxylates with an apical water bound to each zinc center. Taken from reference 35………………………………… 35

1.25 Left is a representation of a 2-D H-bonded network comprised of a metal hexacyanide and three bis-amidinium dications chelated via hydrogen bonds. On the right is a X-ray structure of the network with solvent waters included in the void space, M = Fe or Co. Taken and modified from reference 12………………………………………………………………… 36

1.26 Molecular building blocks used in the construction of the ternary nets. a) 1,3,5-benzenetricarboxylate anion b) Zn₂(RCO₂)₄ c) Zn₂(RCO₂)₂(RCO₂)₂ d) Zn₂(RCO₂)₃(RCO₂). Taken from reference 39…………………………….... 37

1.27 Different (3,4)-connected nets a) Pt₃O₄ net, b) twisted boracite net, c) boracite net, and d) cubic C₃N₄ net. Taken from reference 39………………….... 38

1.28 A schematic representation demonstrating three isomers generated by reaction of the same building blocks a) 0-dimensional square, b) one-dimensional zigzag chain, c) one-dimensional helix. Taken from reference 24…………………………………………………………………………… 38

1.29 The structural geometry of the scorpionate resembles that of the scorpion. Taken from reference 87……………………………………………………... 42

1.30 Hydrotrispyrazolylborate [HB(pz)₃]⁻ Tp shown on the left, Hydrotris(3,5-dimethylpyrazolyl)borate [HB(3,5Me₂pz)₃]⁻ Tp* shown to the right………... 43

1.31 Drawing of the tetrahedral pzTp anion………………………………………… 44

1.32 Schematic representation of the tetrahedral tetrakiscyanoborate anion……… 45

1.33 Tetrahedral geometry depicted from different perspectives.³¹……………… 46

2.1 The structure of BF(CN)₃⁻………………………………………………………… 48

2.2 The local structure of the silver metal center with 50% thermal ellipsoids, copper exhibits the same geometry……………………………………………… 50

2.3 Extended structure viewed along the b axis. The copper metal center exhibits an essentially identical structure……………………………………………… 50
3.1 Asymmetric unit of B(Him)(Im)$_3$ protonation of one external nitrogen results in a neutral species…………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..
15N SSNMR spectra of (a) Pb[B(Im)4](NO3) after exposure to aqueous Na15NO3, (b) washed Pb[B(Im)4](15NO3) after exchange, (c) Na15NO3, and (d) Pb[B(Im)4]I. The spinning speed was 2.7 kHz.

207Pb SSNMR spectra of (a) Pb[B(Im)4](NO3)(0.25H2O), (b) Pb[B(Im)4](O2C7H5), and (c) Pb[B(Im)4]I. The spinning speed was 8kHz.

The asymmetric unit with 50% thermal ellipsoids of Pb[B(Im)4]I.

Extended structure of Pb[B(Im)4]I along the b axis shown on the right and the a axis on the left. Hydrogen atoms omitted for clarity.

The asymmetric unit with 50% thermal ellipsoids of Pb[B(Im)4](O2C7H5)(0.5H2O). The hydrogens on the water are not shown and only one of two orientations of the disordered benzoate is shown.

The layered structure of Pb[B(Im)4](O2C7H5)(0.5H2O) viewed down the b axis on the left and the a axis on the right. The solid lines from the metal center indicate short coordination bonds (<2.6 Å), and the dashed lines indicate longer coordination bonds (>2.7 Å). Hydrogen atoms and the solvent water have been omitted for clarity.

Structures of tetrakis(imidazolyl)borate (BX4−, left) and tetrakis(4-methylimidazolyl)borate (BY4−, right).

Asymmetric units with 50% thermal ellipsoids of compounds (7) (Pb[B(Im)4](NO3)(nH2O),(top left), (10) (Tl[BX4],(top right), and (12) (Tl[BY4](NO3), (bottom right). A view of the asymmetric unit of (11) (Pb[BY4](NO3)) can be seen on the bottom left, showing the full structure of the borate. In (11), the disordered nitrate has been omitted for clarity.

Extended structure of (7) along the c axis (left) and a axis (right). Hydrogen atoms have been deleted for clarity.
5.4 Line illustrations showing the two types of metal-borate connectivity observed in compounds 7, 10, 11, and 12, where Q is either imidazole (X) or 4-methylimidazole (Y). The left diagram shows the connectivity observed in compounds 7, 10, and 12, which exhibit asymmetric metal coordination environments bridged by pseudotetrahedral borates. The right diagram shows an axial view of the connectivity in compound 11, where the tetrahedral borates bridge the square planar metal sites to afford a 3D network structure. The nitrates in compound 7, and solvent water in 7) fit above and below the layers, while the disordered nitrates lie along the axial ordinate in 11…………………………………………………………………… 106

5.5 Extended structure of 10 along the b axis (left) and along the ac plane orthogonal to the b axis (right). The hydrogen atoms have been omitted for clarity. The right of the figure corresponds to the left view in figure 5.4…… 108

5.6 Extended structure of 11 along the c axis (left) and b axis (right). Hydrogen atoms and disordered nitrate have been omitted for clarity. The disordered nitrates lie along the c axis in the same lines as the Pb atoms. The left of the figure corresponds to the right view in figure 5.4……………………………… 112

5.7 Extended structure of 12 along the b axis (left) and a axis (right). The hydrogen atoms have been omitted for clarity. The solid lines about the metal ions indicate short coordination bonds (<2.6 Å), and the dashed lines indicate longer bonds (>2.7 Å). The right of the figure corresponds to the left view in figure 5.4………………………………………………………... 113

6.1 Organic radicals, nitoxides, self-assemble in the Pb[B(Im)₄]⁺ scaffold……… 120

6.2 Tetrakis(imidazolyl)borate (left) and the asymmetric unit (middle) and on the right, the network structure of Pb [B(Im)₄ ](NO₃) nH₂O………………… 121

6.3 The asymmetric units with 35% thermal ellipsoids of 14, TEMPO (left) and 15, PROXYL (right). Hydrogen atoms omitted for clarity………………… 122

6.4 Extended network structure of 14 along the b axis (left) and extended network structure of 15 along the ab plane (right). Hydrogen atoms have been omitted for clarity, and the radical guests are rendered in ball-and-stick format. The solid lines indicate coordination bonds less than 3 Å, while the dashed lines indicate bonds longer than 3 Å……………………………… 124

6.5 EPR spectra of 14(TEMPO) and 15(PROXYL), with the spectrum of 15 exhibiting hyperfine coupling where A_N = 6.3 G…………………………………… 125
7.1 Schematic representation of perrhenate exchange in Pb[B(Im)₄][NO₃](nH₂O), where stoichiometric quantities of perrhenate exchange for the interlayer nitrates........................................ 131

7.2 The $^{207}$Pb SSNMR spectrum of Pb[B(Im)₄][NO₃](1.5H₂O) (top) prior to exchange with 1.1 equivalents of NaReO₄ and after exchange (bottom)…… 132

7.3 The asymmetric unit (top) and the extended network structure (bottom) of Pb[B(Im)₄][ReO₄]. The material has the same network connectivity as in the parent Pb[B(Im)₄][NO₃](nH₂O), and the perrhenates occupy the interlayer spacing................................................................. 134
LIST OF ABBREVIATIONS

MAS – magic angle spinning
SSNMR – solid state nuclear magnetic resonance
EPR – electron paramagnetic resonance
TMS – tetramethylsilane
TGA – thermogravimetric analysis
TPA - tetrapropylammonium
B(Im)$_4$ – tetrakis imidazolyl borate anion
B(4-MeIm)$_4$ – tetrakis 4-methylimidazolyl borate anion
SQUID – superconducting quantum interference device
MOF – metal organic framework
SBU – secondary building unit
IR – infra-red spectroscopy
4-MeIm - 4-methylimidazole
EA – elemental analysis
BDC – benzene dicarboxylic acid
BTC – benzene tricarboxylic acid
bipy - bipyridine
TFA – trifluoroacetic acid
HMB - hexamethylbenzene

BTB - benzenetribenzoate

TPDC – tripheyldicarboxylic acid

tppcp – tetrakis(4-pyridyl)-1,2,9,10-diethano[2.2] paracyclophane

PPh$_3$ - triphenylphospnine
CHAPTER I

INTRODUCTION TO SUPRAMOLECULAR CHEMISTRY

Supramolecular chemistry involves the use of smaller, molecular based, well-defined units or building blocks to create larger assemblies.\textsuperscript{1-7} Often, the resultant assemblies exhibit properties similar to the components prior to introduction into the network structure. Specifically, the intentional introduction of a building block with a desired property into the supramolecular material often represents one of the design chemist’s fundamental goals.\textsuperscript{8} In addition, the properties of the final structure are more than the simple sum of the respective building blocks. Combination of these molecular building blocks can result in either the formation of discrete or infinite networks. In both discrete and infinite assemblies, the molecular building blocks are held together by reversible non-covalent and semi-labile bonding interactions that allow dynamic chemistry to proceed via self-assembly.\textsuperscript{4} This introduction will focus only on infinite assemblies.

An example of a supramolecular assembly, as reported by Stoddart and co-workers, can be seen in Figure 1.\textsuperscript{5} The primary structure consists of a dicarboxylic hydroquinone ring, 1, being threaded through a tetracationic cyclophane, 2, forming a pseudorotaxane. The synthesis of this assembly introduces two organic compounds in the solution phase where the inclusion complex can form. A new level of complexity is witnessed in the
construction and formation of the host lattice network. This assembly is stabilized by aryl-aryl, face-to-face, and face-to-edge π interactions. Molecule 1 possesses a π system that interacts with the deficient π system of molecule 2 forming the supermolecule. The next level of complexity involves hydrogen bonding of the external carboxyl groups of the hydroquinone that link together each pseudorotaxane forming the supramolecular array. The final product is a two-dimensional infinite network, macroscopic conglomerate, resulting from the extended π to π stacking contacts. This process is an example of a self-assembly and uses a bottom-up methodology.

Figure 1.1. Supramolecular construction as demonstrated with the threading of one molecule through another. Taken from reference 5.
The development of extended networks involves four levels of structural features; composition, constitution, configuration and conformation.\(^3\) Composition is defined as the number and types of units, atoms or molecules, present in the material. Constitution describes the connectivity of the basic building block units or synthons. Configuration describes the immediate orientation of neighboring moieties about a given synthon in 3-dimensional space. The molecular stereochemistry or other possible disposition of an immediate neighbor about a central atom or molecule is an equivalent means of defining configuration. Conformation describes the shape of the material in three-dimensions resulting from a particular assembly of configurations.

The self-assembly paradigm depends on weaker interactions, often starting with coordination bonds, to arrange molecular synthons in a spatially complex geometry and to afford the bulk material’s stability. As in proteins, a combination of weaker interactions sum to an energy total that is sufficient for the robustness of the compound.\(^9\) The use of these weaker interactions promotes reversibility so that correct orientation can result. The architectural objective is to construct a stable supramolecular complex exhibiting the function of the included molecule within the self-assembled supramolecular complex. The lability of the bonds in the overall system allows flexibility so that if an improper connection is made, the moiety may release, change orientation and recombine so that the final complex representing an energy minimum can be achieved. This allows dynamic chemical reactions to occur.\(^{10,11}\)

Molecular recognition pertaining to self-assembly processes, including directional interactions, and adaptation of the substrate, are some of the main goals of this
discipline. This designed flexibility, as bonding interactions decrease in strength and as structural complexity increases, allow the attainment of these objectives. Macroscopically, this molecular dynamics feature can also allow the material to complete its programmed function via these weaker, non-covalent interactions. Fundamentally, the ability to predict the structure at each level of complexity, a priori, is the aspiration of the crystal engineer.

An example of this as reported by Hosseini and coworkers, is shown below in Figure 1.2. This material demonstrates the self-assembly of the 1,3-alternate pyridyl substituted calix[4]arene backbone moiety with 4,4’-biphenol. The assembly is a chiral infinite single stranded 1-dimensional helical network that packs into a quintuplet through lateral association. Along with demonstrating self-assembly, this example also displays a bottom-up synthetic strategy, excluding the original synthesis of the calixarene.
Figure 1.2. This demonstrates the different levels of organization, above the molecular level using the calixarene bridged to another calixarene by the biphenol, forming helices. The helices wrap ending with the bundle of 7 helices emanating in one direction. Taken and modified from reference 14.
The bottom-up or engineering-up approach of synthesis takes advantage of nano-sized species to generate nanoentities through sequential processes that can be either commutative or not. The retrosynthetic ideology used by organic chemists is of a top-down approach and traditionally is instituted on the atomic to molecular level. The top-down approach starts from something large and builds the desired product from smaller components. Conversely, the bottom-up method begins with small units, like atoms or molecules, and assembles a network structure.

As an example of the bottom-up approach, Lu et al., reported the structure of \([(K_2)Zn(1,2,4,5-benzenetetracarboxylate)\cdot8H_2O]_n\) that exhibits the tenorite (CuO) network topology and can be seen in Figure 1.3 below. This synthesis involves metal carboxylate coordination to generate a tetrahedral geometry at the metal center. Successful completion of this metal centered node leads to generation of an analog of a naturally occurring mineral. The authors claim that this synthetic structure is the first exhibiting (CuO)-like network topology and attribute it to the challenges of generating a distorted tetrahedral geometry that leads to the desired tenorite topology. As seen in Figure 1.3 below, the metal geometry exhibits two angles different than the expected of 109.5° by less than 20° and the other two are more than 10° greater than the ideal 109.5°. The combination of square-planar organic linkers and tetrahedral zinc centers result in a (CuO)-like framework. The extended structure is a result of the selection of the individual building block (bottom-up) versus selection of a building block based on a desired final structure (top-down).
Figure 1.3. The starting molecular building blocks are shown above. The product exhibits a similar topology to natural tenorite but with expanded dimensions. Taken from reference 16.

Weak interactions are the essential ingredients for synthesis of these supramolecular systems. The energy associated with these noncovalent interactions must be an order of magnitude less than the previous level of complexity or possible rearrangement reactions may occur. Through multiple low energy interactions, the structural integrity of the materials is preserved. Stability of the product is contingent on the presence of these
numerous non-covalent, semi-labile structure supporting interactions. Removal of the forces that support the conformation of the final structure can ultimately lead to product degradation and decomposition, with framework collapse.

As an example of the effect of weaker non-covalent interactions on the robustness of the resultant material, a system from the Whitesides laboratory at Harvard will be discussed. A material was synthesized via hydrogen bonding, between the subunits cyanuric acid and melamine.\textsuperscript{18} As shown in figure 1.4, each building block can make nine hydrogen bonds via oxygen and nitrogen. The breaking of one of these hydrogen bonds involves \(\sim 7\) kcal of energy per mole, but nine of them results in a more substantial energy barrier. In addition, the influence of solvent, specifically chloroform, has been examined. The individual hydrogen bond enthalpies are decreased to about \(1 - 3\) kcal/mol with a total of 18 bonds per rosette. Breaking the rosette aggregate will require 18 times that value. As discussed in the review, and shown in Figure 4, two possible structural motifs can be seen in this lattice. The circular section is termed a cyclic rosette and, alternatively, the rectangular section is called a linear tape. Regardless of the motif observed, the sum of the hydrogen bond energies is enough to bind these two subunits into a fairly robust organic network.
Figure 1.4. The sum of the weaker molecular interactions bind the material into a robust supramolecular organic assembly. Taken and modified from reference 18.
Self-assembly is a dynamic process as one component associates with another where the orientation of the incoming unit must be correct.\textsuperscript{19,20} Improper orientation results in complex deformation minimally and, if not corrected, the energetic product minima is not observed. These weaker interactions are in equilibrium so that incoming units are capable of disengagement, reorientation for another interaction and finally correct approach. Covalent interactions at this level would require formal bond breaking and reforming. The final stable product does not result if an energy total for rearrangement is greater than the energy conserved through product complexation. The entropy forfeited by complexation must be on the order gained by complex stability.

The rational design of solid state materials is currently an active area of research.\textsuperscript{7,21,22} Molecular tectonics, crystal engineering or reticular synthesis are terms used to describe this field.\textsuperscript{13} Design is correlated with a degree of predictability and the \textit{a priori} knowledge of structure is the designers’ ultimate intent. The ability to design elaborate and sophisticated structures remains elusive but as the library of structures increases, specific target structure synthesis is progressing. There are different techniques being used to expedite this process.

Combinatorial synthetic methods generate massive assays of reactions by combining many materials with many different components.\textsuperscript{4} In traditional linear synthesis, one compound was synthesized, purified and analyzed. The combinatorial method generates many possible reactions containing many reagents. The use of robotics helps the individual chemist complete an array of reactions.\textsuperscript{23} In combinatorial synthesis, the number of different products can be immense. Observing change from the experiment,
then requires a variation in reaction conditions to investigate the preliminary result. Variation of reaction conditions can result in different products.\textsuperscript{24} Combinatorial syntheses have been used extensively in material design. 

Can the chemist learn anything from combinatorial synthesis? Multivariant systems can be difficult to analyze. When a direction is indicated by some observable change, experimental variations should be employed to clarify the results. A focused evaluation can be completed with a reduction in the number of variables involved. The obvious answer to the initial query would be that information could be gained but if the follow up to the initial observation does not occur the results would be general instead of precise and therefore, limited information is acquired. Combinatorial synthesis alone is not as informative as one might desire but with extended investigation it can lead to good results.
Network Solid State Materials

Network solids are defined as extended solid-state arrays formed from molecular complexes or clusters.\textsuperscript{25} Yaghi and O’Keeffe state that the idea of translating the molecular geometry and reactivity of a building block into the final bulk product is the main driving force for synthesis and investigation of these types of materials.\textsuperscript{7} Network solid types include metallic, ionic, covalent, and molecular. Metallic networks contain metal to metal bonds that can render these types of materials similar to the bulk elemental metal solid.\textsuperscript{26} Metal networks are often malleable resulting from the flexibility of the bonding interactions. Sodium chloride is a good example of an ionic network.\textsuperscript{27} Diamond is a classic example of a covalent network where the melting point is very high and the material is extremely hard.\textsuperscript{28,29} A molecular network is one where the components are held together through weaker forces than those binding the basic building block units together. Sugar is an example of this type of network.\textsuperscript{30} As shown in Figure 1.5, the stronger covalent interactions bind the glucose unit together while the weaker hydrogen bonds join all of the individual glucose molecules and pack them into the molecular network. Each type of network described above is an infinite assembly of smaller units. Network solids are found in nature but many analogs have been synthesized.\textsuperscript{31} The aforementioned solids are all of natural origin, but synthetic analogs presently outnumber the naturally occurring materials.
Currently, some of these synthetic species are used in industry. As shown in Figure 1.6 natural zeolites are built from smaller sodalite cages that are comprised, by the node-and-spacer definition, \textit{(vide infra)} of regular silicon based polygons. ZSM-5, a synthetic zeolite, has become one of the most widely used synthetic networks and can be seen in Figure 1.7. The petroleum industry has optimized the use of this synthetic 3-D tectoaluminosilicate, for cracking crude oil. Synthetic layered double hydroxides have been used as fillers and in separation processes and an example is shown in Figure 1.8.
Figure 1.6. Natural zeolite composition and conformation beginning with the tetrahedral Si/Al unit forming sodalite cages, ending with those cages forming rigid, porous minerals. Each line represents a [Si/Al-O-Si/Al] link. Taken from reference 31.
Figure 1.7 Representation of the zeolite ZSM-5 or the natural analog mutinate. Taken from reference 33.

Figure 1.8. Representation of a layered double hydroxide, like montmorillonite, where the spacing between layers can contract and expand depending on the hydration or guests but the structure of the layers remains. Taken from reference 34.
The main synthetic approach to molecular network solids involves the self-assembly of soluble molecular building blocks or synthons under optimal conditions. The terms reticular or modular are used to describe these syntheses. Synthons, as described by Desiraju, are structure directing recognition motifs involving non-covalent interactions that result with the formation of an extended network. Building networks up from the basic repeat unit has become an important approach used by materials chemists. Using the same synthon for construction represents one type of material but subtle variations in the reaction conditions can result in different network structures. To synthesize rationalized structures from first principles, one must consider the geometry, topology, and reactivity of the building block. One way to simplify the means by which we consider these materials is to use the concept of the node-and-spacer.

The concept of nets involving network structures was developed and described by Wells. The node-and-spacer approach, introduced later, reduces the description of a network to only points and lines. Each point is a vertex of some regular polygon and the spacer determines the length between points. Ideally, through judicious choice of node synthon and spacer synthon we can synthesize networks with specific structures. However, the node-and-spacer approach can often exhibit isomerism and multiple topologies can result. Factors such as temperature, solvent, stoichiometry, pH, and templates can all affect how a network assembles. The geometric simplification encountered with the node-and-spacer principle allows for improved construction of networks.
The best method of network characterization is by single crystal X-ray diffraction. Single crystal X-ray diffraction is a powerful technique for understanding the topology of a network. Therefore, isolation of large single domain crystals is an important synthetic goal in network solids synthesis. Solid-state materials, natural or synthetic can exist as either crystalline or amorphous substances. Although overlap of these two classes can occur, a material is generally described to be in one of these two divisions. Amorphous or microcrystalline species can still be characterized by other techniques. X-ray powder diffraction is the primary technique employed when materials are microcrystalline. Solid-state NMR techniques can also be used to characterize microcrystalline materials.

In crystalline networks, the arrangement of building blocks can result in topologies that lead to specific functions. Open framework materials can exhibit porosity and function in the role of catalysis, ion exchange or absorption.\textsuperscript{41} Commonly observed interpenetration of networks can preclude a material from functioning as a porous network. Porosity isotherms have been defined by IUPAC and represent the ability to quantifiably exchange nitrogen.\textsuperscript{42} Attempts to remove species from these ‘open channels’ often result in network collapse. Once a material has decomposed, it can rarely recombine back into the original network observed.

These crystalline complexes exist with different dimensionalities. If a connector closes in on itself to form a discrete polyhedra, a 0-dimensional assembly will result. The use of rigid multidentate chelators often result in discrete complexes of 0-dimensional assemblies seen by the dinuclear metallomacrocycles that have been synthesized and reported by Stang and coworkers, shown in Figure 1.9.\textsuperscript{43} These compounds demonstrate
the directional bonding approach utilizing platinum and palladium in a dative coordination bonding mode. The reaction of the triethyl phosphine metal bistri fluoride and a bis(4-pyridyl)silane or ketone, result in cages with large open cavities about 10.9Å x 8.0Å. As can be seen in Figure 1.9, the large open cavity is available for guests. The molecular building blocks described by the node and spacer description, are demonstrated with the metal triflate as the node linked by the bipyridyl spacer. From the functionality standpoint, guests can be incorporated if they possess the appropriate charge, size, and shape. These rhomboids are being investigated for ion exchange properties.

Figure 1.9 Rhomboids synthesized from triethylphosphine metal bistri fluoride and a bis(4-pyridyl)silane or diketone forming a discrete complex.\textsuperscript{43}
The simplest infinite networks are one-dimensional molecular chains. Weaker interactions combine these smaller units into three-dimensional assemblies in the crystal. An example that demonstrates a one-dimensional chain was reported by Chen et al. and is shown in Figure 1.11. Figure 1.10 is a schematic diagram of the ligand used by this group to synthesize the metal organic molecular chain. The silver atoms are monodentate bound by both carboxylate oxygen and pyridyl nitrogen as seen in Figure 1.11.

![Figure 1.10](image.png)

Figure 1.10. The bipyridine dicarboxylate reveals near orthogonal conformation of the pyridyl rings within the molecular chain once metal coordination has occurred.

The metal center shows oxygen chelation by both a carboxylate and water. The metal is also bound to two nitrogen pyridines. The pyridines are hydrogen bonded between chains to form a crystalline structure. The silver(I) ions are bridged by 2,2′-bipyridine-3,3′dicarboxylate forming infinite chains. The coordination sphere of the metal includes a distorted tetrahedral geometry coordinated by two nitrogen and two oxygen atoms. One of the oxygen atom interactions involves solvent water that is also hydrogen bound to an adjacent carboxylate. The intrachain hydrogen bonding is seen by
the dashed lines in Figure 1.11. A different perspective can be seen in Figure 1.12 showing the weak interactions between chains representing the less energetic bonding motif that bind these one-dimensional chains into a three-dimensional assembly.

Figure 1.11 Hydrogen atoms are omitted for clarity and the intrachain hydrogen bonds are denoted by the dashed lines. Taken from reference 44.
Figure 1.12. The interchain hydrogen bonding and packing as viewed down the c-axis. Hydrogen atoms are omitted for clarity. Taken from reference 44.

Two-dimensional networks contain stronger bonds between units in a layer while the interactions that bind the layers together are weaker. Intercalation and ion exchange are the major properties observed in these materials, and a diagram is shown in Figure 1.13. The dynamics of exchange between the layers can occur without network disruption. Physical parameters can change, but there is often no chemical change. Graphite, talc and clay are probably the best known and used of these naturally occurring two-dimensional networks. If a layer is charged, then there must be a local counterion present within the interlayer spacing to balance that charge. The ability to tune the chemical
properties of these materials can be accomplished through calcination, pH, guest molecules, or by changing the metal present within the networks layers. Physical and structural changes have been investigated including the idea of layer separation, termed exfoliation. The mechanism of exfoliation is a peeling process, much like the removal of the layers of an onion, where the layers can open up and guests are exchanged. A variety of synthetic layered networks have been synthesized.

Figure 1.13 A diagram of the expanding layers of a two dimensional material upon incorporation of a guest molecule.
An example of a synthetic two-dimensional solid was presented by Miller and co-workers, and can be seen in Figure 1.14.\textsuperscript{46} They reported the synthesis and structure of the zinc dicyanamide material, Zn[N(CN)\textsubscript{2}]\textsubscript{2}. The metal center exhibits a slightly distorted tetrahedral geometry with distinct layers, as shown in Figure 1.14. Each zinc center is bound to four dicyanamides. Unlike other reported metal structures that were complexed with this bridging ligand,\textsuperscript{47,48} an extended two dimensional network results instead of a one-dimensional ribbon. The layered network retains the basic $T_d$ symmetry at the metal ion. This material is unique and as shown in figure 1.15 demonstrates different distances between layers. Considering the distance from metal centers, the shortest spacing is 6.34 Å and the longest spacing is 7.62 Å. Solvents are not observed within the interlayer spacing and multiple layered interpenetration is not observed. The concept of interpenetration will be discussed later in this section.

![Figure 1.14 Efficiently packed 2-D sheets without any solvents or templates present.](image)

Taken from reference 46.
Figure 1.15 Corrugated layered structure of tetrahedral Zn\([\text{N(CN)}_2]\)\(_2\) close packing in the unit cell is evident with different Zn to Zn distances. Taken from reference 46.

Lastly, networks can have three-dimensional connectivity. As seen in Figure 1.6, zeolites are a family of naturally occurring, covalently connected three-dimensional minerals. Unlike the flexibility found with some two-dimensional materials, these networks are robust, silicate-based materials. Another example of a three-dimensional synthetic solid includes the Prussian blue materials, shown in figure 1.16.\(^{49-51}\) Originally, these species were used as dyes but presently their magnetic properties have become of interest.\(^{52}\) In contrast to zeolites, Prussian blue materials have octahedral metal centers linked by cyanides. The use of this bridging unit provides strong spin interactions between metal centers.\(^{53,54}\) The underlying goal of research into Prussian blue compounds is to synthesize materials that can magnetically order at temperatures at or
above room temperature instead of near absolute zero. Synthetic variants, both homo- and heterometallic have been investigated. The asymmetry of the cyanide moiety allows for preferential association at specified metal sites. As can be seen by comparing these two examples, three-dimensional solid-state networks can be either porous or condensed.

Figure 1.16 Schematic diagram of Prussian blue analogs where M and M’ can be the same metal in different valence states or different metals. All linkers are nitrile bridged.

Taken from reference 50.

The functionality of these materials is often contingent on their porosity. The ability of a solid-state network to demonstrate sorption properties involves the access of incoming guests to the open framework. Some of the nomenclature associated with the ability to exchange species include the terms sorption, adsorption and absorption. The
most general term is sorption designating the exchange of species in an electronically charged or neutral environment. Sorption can also describe ion exchange. All of these processes involve some degree of porosity so that the guest species can be incorporated. Absorption is when the guest enters into the material. Conversely, adsorption is when the association or interaction occurs on the exterior of the material.

Close packing and interpenetration can reduce the function of a solid-state material by limiting access to the interior spaces. Self-interpenetration, as shown in Figure 1.17, results in a reduction in open pore volume due to the close packing of the interpenetrated species. The resultant material is condensed. If any exchange is possible, only smaller guests can be exchanged due to the reduced volume available. There are materials where different species are interpenetrated. There are numerous reports of interpenetrated species of varying multiplicities. Varying degrees of close packing can lead to structures that exhibit different amounts of porosity.

Figure 1.17 A representation of interpenetration. Taken from references 35 and 50.
These networks can also adopt catenation, enclathration, and interdigitation structures.\textsuperscript{56} Catenation is when two species exhibit an interlocked molecular architecture. Rotoxanes are a family of molecules that demonstrate a specific type of catenation assembly.\textsuperscript{57} Enclathration is a containment without formal threading.\textsuperscript{58} These molecular cavities hold the guest in place through the use of weak interactions that can also permit exchange reactions to proceed. Interdigitation is when an appendage or protrusion from one species approaches an entanglement with another species.\textsuperscript{59} A lamellar or surfactant type structure best describes this situation. Fundamentally, the ability of a material to demonstrate sorption or hold another species within a limited region involves enclathration. These ideas are specific for open framework materials where molecules can enter into the structure or be surrounded by the host.

Templating and pillaring of porous open framework materials is an alternative approach to modification or tunability design resulting in controllable variations of the final product. Often, a guest molecule occupies a volume during a self-assembly process and becomes a templated material. Templating species are often alkali metals or soluble organics like quaternary amines or neutral alcohols. With zeolite synthesis, (TPA), tetrapropylammonium halides or hydroxide, have proved to be excellent templating agents.\textsuperscript{60} Generally the templating species is not removeable. The inability to remove a space filling species prohibits porous functionalities. Pillaring involves the introduction of a species that increases the open volume of a solid without destroying the overall connectivity. As shown in Figure 1.18, the first step in the process involves the pillaring of the exfoliated material, in this case $\gamma$-ZP. After the layers have been opened by the
pillaring step, the species to be exchanged can enter. Benefits to the pillaring of materials include: an increase in pore size leading to increased reactivity, a decrease in diffusion restraints allowing larger layered guests, and milder conditions compared to the synthesis of other modified zeolites.

\[ A = O_2P(OH)CH_2CH_2(OCH_2CH_2)_5OCH_2CH_2(OH)PO_2 \]

\[ B = H_2PO_2 \]

Figure 1.18 Demonstrating schematically the idea of pillaring and templating.\(^{12}\)
Metal Organic Frameworks

Metal organic frameworks or coordination polymers are a type of assembly where metals are bridged by organic linkers. An organic ligand serves as a Lewis base to a Lewis acidic metal center. The metals are the vertices of a regular polygon. The organic linkers are the spacers and represent the line segments that determine the perimeter of the regular polygon. This type of construction fits the node and spacer model. The introduction of site-specific binding moieties can result in novel and functional assemblies. This represents a common approach to the synthesis of these types of materials. Introduction of metals with a limited number of possible geometries helps in the prediction of the resultant architecture. Different metal geometries, along with directionality and lengths of the organic linkers are controllable variables that are available to the molecular architect.⁶¹

Crystals were at one time considered the graveyard of product synthesis. “Ein Kristall ist ein chemischer Friedhof” as stated by professor Leopold Ruzicka, and cited by J. D. Dunitz in *Trans. Am. Crystallogr. Assoc.* explicitly means a crystal is a chemical deadend. Technological advances now allow efficient, precise, and expedient elucidation of single crystalline materials. Now, elucidating the structure of a material via single crystal methods has become commonplace and essential. A few synthetic crystal growth methodologies include slow evaporation, solvent diffusion, gel diffusion, co-precipitation, condensation-addition polymerization and template switching. Methods using Lewis bases to deprotonate a species to initiate crystallization have also been used.
Each of the aforementioned methods often involves solvothermal techniques or slow evaporation.

An example of slow evaporation that yields 80% product in the form of needlelike crystals is shown in Figure 1.19. Chen and coworkers report the network \([\text{Ag}_6\text{Cl(3-amino-1,2,4-triazole)}_4]\text{OH·6H}_2\text{O}\) and demonstrate the crystal to crystal transformation induced by guest or temperature.\(^{62}\) Another example to illustrate a different technique of crystallization is template switching. This example uses 4-benzylrescorcinol in nitromethane resulting in an 88% yield after extraction with \(\text{CH}_2\text{Cl}_2\). Figure 1.20 shows the scheme and two-dimensional product \(\{[\text{Co(O}_2\text{CMe)}_2(4,4’\text{-tpccp})]\cdot2\text{MeOH·toluene}\}_n\) where 4,4’-tpccp is the ligand tetrakis(4-pyridyl)-1,2,9,10-diethano[2.2] paracyclopahne. The templated diolefin is photodimerized in the solid-state to generate the ligand. Addition of the ligand in a 1:1 methanolic solution of \(\text{Co(O}_2\text{CMe)}_2\cdot4\text{H}_2\text{O}\), followed by addition of toluene resulted in the product.\(^{63}\)

![Figure 1.19. View of a single \(\text{Ag}_3(3\text{-amino-1,2,4-triazole)}_2\) net along the \(c\) axis with the amino groups omitted for clarity. Taken from reference 62.](image)
Construction of metal organic frameworks with different sized cavities via the self-assembly process contradicts the premise of highest symmetry or nondefault nets which will be discussed later in this section. The objective of MacGillivray and coworkers was the intended synthesis of the octahedral Co(II) center, shown in Figure 1.20, leading to unequal channel dimensions. Rational design afforded the ligand as a template in the construction of a MOF with unequal diameter pores. An example supporting the
nondefault synthesis is seen through the use of different linear linkers and respective metal centers as reported by Yaghi and co-workers and seen in Figure 1.21.\textsuperscript{65,66} The ability to vary the size of the aperture and pore in the porous material with increased length of the organic linker, but retain the basic structural geometry demonstrates the nondefault principle. As shown in Figures 22 and 23, both two-dimensional and three-dimensional materials can be altered by use of geometrically similar spacers. All of the linking ligands shown, readily coordinate to metals. Generally coordination bonds are robust enough to bind the structures firmly while labile enough for interaction. The ability to tune a physical aspect of the material by altering the fundamental building block is a promising demonstration of topological control. The construction of low symmetry or nondefault nets implements a strategy proposed by Yaghi and O’Keeffe where an organic molecule directs synthesis of covalently fused nodes in the self-assembly process.\textsuperscript{32}

\begin{center}
\includegraphics[width=0.7\textwidth]{linkers.png}
\end{center}

**Figure 1.21.** Linear linkers exhibiting different lengths: promoting chain formation, BDC (left), 4,4’-BPY (middle), and TPDC (right).
Figure 1.22. Trigonal planar linkers: promotes two-dimensional planar structures, BTC (right), and BTB (left).

Figure 1.23. Tetrahedral linkers: organic and metal based promoting three-dimensional networks.

One method for construction of metal organic frameworks is through the use of a secondary building unit (SBU). The basic building units must be robust so that rearrangement does not occur during network formation. The idea of secondary building blocks, considering the node and spacer perspective, is to direct network dimensionality expansion from the SBU node. An example of creating metal centered nodes with cluster type construction can be seen in Figure 1.24. Yaghi and coworkers report the synthesis and structure of the paddle-wheel zinc carboxylate as a SBU node.\textsuperscript{25,35,67} Introduction of longer linkers, like those seen in Figure 1.21, should result in assemblies of greater
dimensions. An increased distance between nodes would be expected through the use of
the expanded form of the planar benzene tribenzoate linker, as shown in Figure 1.22. In
Figure 1.23, the organic tetracarboxylic adamantane and the germanium sulfide cluster
represent SBU units. In the paddle wheel example, Figure 1.24, the plane that subtends
all four of the carboxylate carbons forms a two-dimensional network, ignoring the axial
L. With the apical waters displaced, the exodentate planar linkers direct formation of a
three-dimensional network through the axial positions. Thermal removal of the water
and other solvent present within the open framework leads to the connections ultimately
forming the quasi three-dimensional network. The modification of organic linkers in a
SBU has also been accomplished. This has been observed and reported by Yaghi and
coworkers. The example by MacGillivray and coworkers demonstrates the synthesis of
the templating organic linker used in the network construction and different than most
SBU units, there is not a metal within the SBU unit. The use of the SBU principle can
include the introduction of existing moieties or the synthesis of novel SBU units to be
used as building blocks. As shown in Figure 1.22, BTC or trimesic acid is the smaller
triangular unit while the BTB should result in larger open spaces in the network.
Both primary and secondary coordination spheres are observed as a result of using more complex SBU units. In a network solid, the farther removed from the center of a given SBU the lower the energy of interaction. The weaker hydrogen bonds are associated with the outer secondary spheres and the stronger interactions with the primary level. Hosseini and coworkers report the development of a two-dimensional network achieved through the use of the secondary coordination sphere. Such a SBU generated network can be seen on the right in Figure 1.25. The initial metalhexacyano complex represents the primary coordination sphere involving iron, cobalt or chromium. The bis-amidinium dicationic ligand bridges adjacent cyano units via hydrogen bond association to the nitrogen of the cyano group which extends the network. Moreover, chirality was discussed regarding the presence of both enantiomers. Prediction agreements state that only a small number of high-symmetry structures will be the most common to form.
Figure 1.25. Left is a representation of a 2-D H-bonded network comprised of a metal hexacyanide and three bis-amidinium dications chelated via hydrogen bonds. On the right is a X-ray structure of the network with solvent waters included in the void space, M = Fe or Co. Taken and modified from reference 12.

There are only a few simple but important high-symmetry topologies in which the vast majority of novel assemblies will form. This is an idea presented by Yaghi and co-workers.\textsuperscript{32} For demonstrative purposes, the following discussion will only be concerned with three dimensional nets. Tetrahedral building blocks can result in over 100 different topologies. Less than half of those possible topologies have been reported and only a small fraction of those, contain the large majority of the reported networks.\textsuperscript{32}

The node-and-spacer approach falls short of complete network description as demonstrated by one of the most basic (3,4)-connected nets.\textsuperscript{37,38} The 3 and 4 denote
regular geometric shapes and minimal description of the connectivity. Different combinations result in different types of nets. Wells categorization would classify all of the different assemblies as (3,4) connected nets. An example from Zaworotkos’ lab shows three different network architectures from the same set of building blocks, and can be seen in Figure 1.26. BTC is the triangular unit when reacted with each of the other SBUs result in different topologies, seen in Figure 1.27. Predictable metal coordination sphere geometries and directional bifunctional ligand sets continue to produce networks that are not expected. In Figure 1.27, four different morphologies are observed with the same metal and linker. Figure 1.28 demonstrates how identical building blocks can result in diverse products. Predictability of resultant network structure is yet to become an absolute skill. As previously discussed, the node-and-spacer approach simplifies the rationalization of these assemblies, but has generated a need for an alternate approach. One new approach is termed vertex-linked polygons or polyhedra (VLPP), intended to help clarify any ambiguity.

![Figure 1.26. Molecular building blocks used in the construction of the ternary nets. a) 1,3,5-benzenetricarboxylate anion b) Zn$_2$(RCO$_2$)$_4$ c) Zn$_2$(RCO$_2$)$_2$(RCO$_2$)$_2$ d) Zn$_2$(RCO$_2$)$_3$(RCO$_2$). Taken from reference 39.](image-url)
Figure 1.27. Different (3,4)-connected nets a) Pt$_3$O$_4$ net, b) twisted boracite net, c) boracite net, and d) cubic C$_3$N$_4$ net. Taken from reference 39.

Figure 1.28. A schematic representation demonstrating three isomers generated by reaction of the same building blocks a) 0-dimensional square, b) one-dimensional zigzag chain, c) one-dimensional helix. Taken from reference 24.
Crucial to the synthesis and investigation of these open framework solids is the idea of functionality.\textsuperscript{68,69} The functions of these materials rely on the fact that the open cavities can allow passage of certain species to the active metal centers and exclude others. These processes include catalysis, ion exchange and guest absorption. The basic functions of these materials, whether two- or three-dimensional, are contingent on the topology of the material. Catalysis, the solid mediated increase in reaction rate of a chemical transformation, represents one of the most important functions of these types of materials. Ion exchange is when a solid-state material replaces one ion for another. Absorption is the process where a host material sorps a guest and contains it until another force is imposed.

Other possible functions include non-linear optical applications,\textsuperscript{70,71} magnetism,\textsuperscript{49,54} conductivity, luminescence, chirality,\textsuperscript{72} and spin-transition (spin-crossover). Long and coworkers are investigating the magnetic properties of Prussian blue analogs through the rational design of these heterometallic nitrile bridged materials.\textsuperscript{73-75} This group is also competing with Yaghi and coworkers for a material that will efficiently be used for hydrogen gas storage as an alternative fuel source.\textsuperscript{76} An example of luminescence is observed with the synthesis of a polymeric diphosphine Gold(I) complex that exhibits strong room temperature luminescence.\textsuperscript{77,78} Two thermally stable diamondoid based networks with distinct unsymmetrical bridging ligands, bis(isonicotinato)zinc and bis(4-pyridylacrylato)cadmium·H\textsubscript{2}O, have both been investigated for NLO behavior.\textsuperscript{79} Lin and coworkers approach the NLO research from the basis of the design and synthesis of noncentosymmetric chiral metal organic systems.\textsuperscript{80} The results indicate that the second

39
harmonic generation measurements are at least equivalent to the only reported NLO active diamondoid, KDP, potassium dideuterophosphate low temperature polymorph. Their zinc material exhibits values three times greater than the KDP polymorph. The ability to tune the function of these materials by alteration of the linkers affords generation of functional materials that exceeds previously seen materials.
Borate molecular building blocks

The first report on polyazolylborates was in 1966 by Trofimenko. The past four decades has witnessed an immense activity in this family of compounds. Applications of azolylborate compounds include the traditional variety of catalysis investigations to the active site modeling of enzymes. Metal deposition or extraction, C-H bond activation and transfer agents are also being used which add to the list of applications. In 2003 Trofimenko stated that he had synthesized about half of the 200 or so variants of tris(pyrazolyl) borates reported in the thousands of related articles. The initial emphasis in this area of chemistry involved the development and investigation of the tris(azolyl)borates and their single atom binding capacities. The tridentate chelation of the tris(pyrazolyl) species has been compared to the outline of a scorpion as seen in Figure 1.29.
The general formula of these anions is \([R_nB(pz)_{4-n}]^-,\) where \(n\) can be 0, 1, or 2, \(pz\) is a pyrazol-1-yl group and \(R\) is H, aryl or alkyl. Initially, three basic ligands hydrotrispyrazolylborate \([HB(pz)_3]^-\) (Tp), tetrakispyrazolylborate \([B(pz)_4]^-(pzTp)\), and hydrotris(3,5-dimethylpyrazolyl)borate \([HB(3,5Me_2pz)_3]^-\) (Tp\(^*\)) were synthesized. These represent the first generation of scorpionates.\(^{88}\) Each is anionic through tetrasubstituted boron. In addition to the boron-nitrogen bond of formation there is another basic nitrogen atom for further interaction. The Tp\(^*\) is sterically encumbered compared to the Tp ligand due to the two methyl groups at the three and five positions of each pyrazole ring. The three pyrazole rings bind in a tridentate fashion and typically restrict the metal center to a \(C_{3v}\) symmetry.\(^{89}\) Symmetric chelation is the usual mode of binding but
asymmetric association is also possible. As can be seen in Figure 1.30, the Tp\textsuperscript{*} borate is bulkier than the Tp borate.

![Diagram](image.png)

Figure 1.30. Hydrotrispyrazolylborate [HB(pz)$_3$]\textsuperscript{-} Tp shown on the left, Hydrotris(3,5-dimethylpyrazolyl)borate [HB(3,5Me$_2$pz)$_3$] Tp\textsuperscript{*} shown to the right.

The pzTp ligand can also bind in a tridentate manner.\textsuperscript{89} Unlike the tris(pyrazolyl)borates above, the tetrakis species pzTp has an additional pyrazole ring containing another external nitrogen, as shown in Figure 1.31. However, this fourth pyrazole ring does not bind to the same metal but directs the fourth binding site to interact with a different metal. Different from the tris chelating material forming monometallic species, the fourth pyrazole ring can interact in a bridging manner generating extended structural network assemblies. This represents a different ligand interaction than with the Tp and the Tp\textsuperscript{*} species. Infinite instead of discrete structures can be observed.

Examples of these tetrakis anions can be seen with the tetrakis(pyrazolyl)borates,\textsuperscript{82,86} shown in Figure 1.31, and tetrakis(cyano)borates,\textsuperscript{90} shown in Figure 1.32, below. Cyanoborates represent a ridgid, directional, condensed, and
electron rich spacer, as shown in Figure 1.32. The tetrahedral structure of this anion produces symmetric assemblies where the nitrogen atoms are bound to different metals.\textsuperscript{91} The ability of these nitrile linkers to release and bind in the appropriate conformation for crystal formation, but still retain a degree of robustness, make these ligands attractive species for network formation. The binding to metal centers with these $\pi$ electron rich ligands, can permit electronic communication between metal centers via this $\pi$ system. Networks have been reported involving, silver, lithium, and potassium.\textsuperscript{92-96}

![Figure 1.31. Drawing of the tetrahedral pzTp anion.](image)

The tetrakis(pyrazolyl)borate(pzTp) anion has not demonstrated an ability to generate network structures. Surprisingly, the Tp ligand alone has not resulted in any extended network structures. The Tp ligand and a few of its variants, with other supporting species, have generated infinite assemblies. Although the three-dimensional structures have not been reported, one- and two-dimensional materials have been published. Unlike the directionality of the tetracyanoborate, the pzTp species tends to generate discrete monomeric and dimeric products more readily. Many metals have been
chelated in both bi and tridentate fashion with other supporting ligands on the metal center for instance, carbonyl and phosphine. Larger metals like uranium require two tridentate pzTp anions and other supporting ligands to satisfy the cations coordination sphere. In the many reported examples of metal coordination, a variety of combinations have been investigated and there is not a true extended network structure involving a metal and only the tetrakis(pyrazolyl)borate anion. Changing the peripheral chelating group by modification of the pyrazole rings can lead to generation of extended structures but multiple searches on the basic ligand did not result in any network reports. The reason is probably in the fact that the ligands generate endodentate nitrogen atoms of the pzTp rings that create a cone angle that does not support this infinite network growth. In other words, the direction of the binding sites is oriented back toward the boron center. Also the possibility of ring rotation can alter the direction of the bonding interaction.

![Figure 1.32. Schematic representation of the tetrahedral tetrakis(cyanoborate) anion.](image)

Borates offer positive attributes to materials design for a plethora of reasons. Several factors make these boron materials promising for metal organic frameworks. These factors include their inherent tetrahedral geometry, anionic charge, inexpensive
starting materials, and ease of synthesis. Borates typically involve bonds to nitrogen, carbon and oxygen. The thermodynamic stability of these molecules results from the strength of these bonds.\textsuperscript{103} Kinetic stability of these organic borates is due to the small radius of the boron, which inhibits substitution reactions.\textsuperscript{104} In addition, the tetrahedral geometry of the central boron often leads to the generation of three dimensional network solids. As shown in Figure 1.33, the ideal tetrahedral geometry exhibiting 109.5° from any of the perspectives implicate the generation of three-dimensional architectures from the borate. The ease of borate synthesis, often one step in one-pot, from inexpensive starting materials is promising. All of these factors make borates attractive building blocks for metal organic framework investigations. The Tp ligands each have 9 external carbon atoms where substitutions can be made to generate electronically and sterically different species while still maintaining the same backbone. Likewise, the pzTp species contain 12 possible carbon atoms for modification. Synthesis of novel three-dimensional solid-state structures leading to improved function is the motivation of the research.

![Figure 1.33. Tetrahedral geometry depicted from different perspectives.\textsuperscript{31}](image-url)
CHAPTER II

CYANO BORATES AS ORGANIC LINKERS

The design of new molecular building blocks for the construction of coordination polymers continues to be an active area of research. Molecular components that lead to specific topologies, generate open sites at metal centers, or modulate electronic structure in the solid could enable the generation of functional materials with designed properties. In our recent work, we have begun to explore cyanoborates as anionic ligands for the synthesis of coordination polymers, and have found that they posses a number of desired attributes as materials components. In this chapter, we present the synthesis of materials based on the tricyanofluoroborate anion, BF(CN)$_3^-$, as seen in figure 2.1, using Cu(I) and Ag(I) metal centers. The resultant two compounds, both having the empirical formula M(BF(CN)$_3$)-NCCH$_3$, are isostructural, three-dimensional coordination polymers with solvent occupied sites at the metal centers. In both cases, the electron with-drawing nature of the bridging ligands results in stabilization of the +1 oxidation state for the metals and thus an air-stable Cu(I), (1), compound and light-stable Ag(I), (2), material.
Discussion

The synthesis of these compounds was uncovered while exploring reactions between the tetracyanoborate anion and Cu(I) and Ag(I). Two recent reports describe the preparation of the B(CN)$_4^-$ anion: one via a reaction using Me$_3$SiCN and a second involving boron halides and cyanide salts.$^{107,108}$ While working toward the preparation of Cu[B(CN)$_4^-$], we found that the tetracyanoborate anion is unstable in the presence of fluoride in aqueous solution, forming the tricyanofluoroborate species. We can observe this anion via $^{19}$F and $^{13}$C NMR, which show resonances appearing at -29.6 and 101.2 ppm, respectively. Electrospray MS also demonstrates the formation of this anion, affording a negative ion peak at m/z 108.2. The cyanoborate anion BF(CN)$_3^-$ can be synthesized directly by reacting three equivalents of Me$_3$SiCN with the tetrafluoroborate anion. It is interesting to note that this anion is similar to other coordinating nitrile compounds presented in the literature, including C(CN)$_3^-$ and 4,4',4''-tricyanotriphenylmethanol.$^{50,109}$

The diffusion of an acetonitrile solution (5 mL, 0.5 mmol), of B(CN)$_4^-$ into aqueous solutions of CuCl or AgNO$_3$ (5 mL, 0.5mmol) with an equivalent of NaF by layering,
results in formation of crystals over several days of the formula M(BF(CN)$_3$)-NCCH$_3$. Both reactions form yellow, needle-like crystals that are stable in light and air. The structures of both compounds were elucidated from single crystal X-ray diffraction experiments. The crystal system for both materials is orthorhombic, with a space group of $Pmn\alpha$. The coordination environment about the metal for the silver system is shown in Figure 2.2, with the extended network structure along the $b$ axis shown in Figure 2.3. The morphology of Cu(BF(CN)$_3$)-NCCH$_3$ is isostructural to that found in the silver compound. In each case, the metal centers are coordinated by three nitrile groups from different borate anions, with a fourth coordination site being occupied by a solvent acetonitrile. Selected bond distances and angles for the two compounds are shown in Table 1. Both the metals and the borates have nearly ideal tetrahedral geometries with angles close to 109.5°. In the silver compound, there is a greater deviation from the perfect tetrahedral geometry, exhibiting both larger (~115°) and smaller (~103°) angles. This divergence results from the increased radius of the Ag(I) cation relative to that of Cu(I). In addition, in both compounds the anions have virtually identical structures with the exception of minor bond length increases (B–C, C–N) in the silver compound due to increased backbonding from the metal relative to copper.
Figure 2.2. The local structure of the silver metal center with 50% thermal ellipsoids, copper exhibits the same geometry.

Figure 2.3. Extended structure viewed along the $b$ axis. The copper metal center exhibits an essentially identical structure.
Table 2.1. Selected bond lengths (Å) and angles (°) for M(BF(CN)$_3$)·NCCH$_3$.

<table>
<thead>
<tr>
<th></th>
<th>Cu (1)</th>
<th>Ag (2)</th>
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<tbody>
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<td>M-N(1)</td>
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<tr>
<td>M-N(3)</td>
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<td>C(2)-N(2)</td>
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<td>C(3)-N(3)</td>
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<td>B-C(3)</td>
<td>1.617(6)</td>
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<tr>
<td>B-F</td>
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<td>107.7(3)</td>
</tr>
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</table>
These two materials are network solids where the borates bridge the metal centers to form three-dimensional coordination polymers. As can be seen in Figure 2.3, this material is not as efficiently packed as an adamantine-type structure, and there are one-dimensional channels along the b axis. These channels are identical in the two materials with the exception of their diameters; the channels have dimensions of \(~6.3 \times 5.8\) Å in the copper compound and \(~7.7 \times 5.9\) Å in the silver material. In both cases, the coordinated acetonitrile solvent molecules interlace into the void spaces of these channels. The increase in channel diameter as one goes from Cu(I) to Ag(I) corresponds to the increase in bond distances observed in the asymmetric units of the two materials. As can be seen in Table 2.1, the metal–nitrogen bond distances lengthen approximately 0.25–0.3 Å in the silver compound relative to the copper material. We are currently investigating these materials to determine if the three-dimensional structure remains intact upon liberation of the acetonitrile solvent molecules. While both compounds show channel topologies, it is still unclear whether or not there is access to the metal-bound solvent molecules.

By using a bridging ligand with a non-coordinating moiety (fluorine), the resultant network polymers have potentially open sites at the metal centers. The presence of only three coordinating groups on the BF(CN)$_3^-$ species requires that either the metal adopt a lower coordination number structure or that solvent occupy the open sites at the metal in the extended solid. Both Cu(I) and Ag(I) metal centers frequently exhibit tetrahedral geometries in network solids, however lower coordination number complexes are occasionally observed.$^{35,42,105,110-112}$ In a network with a tetrahedral ligand, one would
expect the formation of a diamond-like adamantane structure with metals that form
tetrahedral complexes. This is observed in the structure of the salt LiB(CN)₄, since
lithium also frequently forms tetrahedral complexes. With only three cyano groups
present on the borate, the fourth coordination site on the metal is likely to be filled by a
solvent molecule, which is an acetonitrile in both cases. We are currently attempting to
grow crystals of these materials in non-coordinating solvents, in the hope that we can
isolate compounds with three-coordinate metals.

In addition to generating a porous network solid, the tricyanofluoroborate anion also
stabilizes the low oxidation states of the copper and silver metal sites in these solids.
Frequently, both Cu(I) and Ag(I) compounds are unstable to atmospheric dioxygen and
light, respectively, but the electron-withdrawing (p acceptor) character of the cyanide
groups bound to the metals significantly alter the potential of both metals to favor the
lower oxidation state.¹¹³,¹¹⁴ We can observe the backbonding in the weakened CN
stretching vibrations at 2241 cm⁻¹ for Cu(BF(CN)₃)·NCCH₃ and 2257 cm⁻¹ for
Ag(BF(CN)₃)·NCCH₃ relative to that found for B(CN)₂NCSiMe₃ at 2310 cm⁻¹ or for
B(CN)₄⁻ at 2271 cm⁻¹. The preference for the +1 oxidation state results in materials that
are air stable in the case of the copper material and light stable for the silver compound.
This apparent delocalization of electron density onto the ligand bodes well for the use of
the coordinating anion for use in magnetic materials, such as Prussian blue
analogues.¹¹⁵,¹¹⁶

The ability to tune the properties of the solid by changing the metal ion is also
encouraging for the design of other ordered solids. By altering the metal center, we can
obtain two isomorphous compounds that differ only in their unit cell dimensions and channel diameter. We are currently examining these materials to determine if changing the metal cation in these networks can also affect observed reactivity, such as loss of acetonitrile at high temperatures or affinity for soft ligand guests, such as thiols.

Experimental

All reagents and solvents were purchased from Aldrich and used as received. Water was purified by using a Milli-Q reagent water system. Mass spectra were obtained on a Micromass AutoSpec EBEhQ hybrid tandem mass spectrometer using FAB ionization. Solution NMR spectroscopy was performed on a Varian VXR 300 MHz NMR instrument.

Synthesis of LiB(CN)₄: The synthesis of LiB(CN)₄ was based on a report in the literature described by Williams and co-workers. In an argon flushed flask, Me₃SiCN (4.8 g, 0.048 mol) was added dropwise to a stirred mixture of LiBF₄ (1.0 g, 0.011 mol) in 50 ml of Bu₂O at -78° C. The solution was stirred at room temperature for 18 h. After reflux conditions for 4 h the solution was evaporated and then extracted with CH₃CN affording 1.14 g of offwhite product (89% yield). Due to hazardous conditions limited material prevented full characterization but $^{19}$F NMR -29.6 and $^{13}$C 101.2 ppm resonances were observed. $^{13}$C NMR was referenced using TMS (tetramethylsilane) and
\(^{19}\)F was referenced with TFA (trifluoroacetic acid). Electrospray MS revealed the negative ion peak at \(108.2 \, m/z\) corresponding to the anion BF(CN)\(_3^−\).

**Synthesis of M[BF(CN)\(_3\)]·NCCH\(_3\):** An acetonitrile solution of LiB(CN)\(_4\) (5 ml, 61 mg, 0.5 mmol) was carefully layered over an aqueous solution (5 ml, 0.5 mmol) of M(X) (CuCl or Ag\(\text{NO}_3\)) with an equivalent of NaF in a test tube. The tube was sealed and the layers were allowed to diffuse slowly at 60° C, after which single crystals were chosen and the remainder of the product was collected by filtration. IR (KBr) intense stretch Cu[BF(CN)\(_3\)]·NCCH\(_3\) 2241 cm\(^{-1}\) and Ag[BF(CN)\(_3\)]·NCCH\(_3\) at 2257 cm\(^{-1}\).

X-ray data were collected using Mo (0.71073 Å) radiation on a Syntex P(2)1 diffractometer. The crystals were coated in Paratone N-Exxon oil, mounted on a glass fiber, and placed under a cold stream of nitrogen at 159 K. Unit cell parameters were obtained by a least-squares analysis of 20 well-centered reflections with 20° < 2\(\theta\) < 30°. The structures were refined using the Bruker SHELXTL (version 6.1) software package and solved using direct methods until the final anisotropic full-matrix least-squares refinement on \(F^2\) converged.\(^{132}\) Selected experimental details are given in Table 2.1. Crystallographic data and structure refinement details for the two structures is provided in Table 2.2.
Table 2.2. Crystallographic data and structure refinement details for 1 and 2. Standard deviation parameters are given in parentheses.

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<td><strong>R_w(Fo^2)</strong></td>
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\[ a \quad R = \sum |F_o| - |F_c| \sum |F_o| \quad \text{b} \quad R_w = \left( \sum w(F_o^2) - |F_c^2| - |F_c^2| \right)^{1/2} \sum w(F_o^2)^{2/2}. \]
CHAPTER III

TETRAKIS(IMIDAZOLYL)BORATES GROUP II NETWORK SOLIDS

The construction of metal-organic frameworks is an area of continued interest that has developed into a mature field over the past decade.\textsuperscript{35,42,105,117,118} Much of the current study into coordination polymer based crystal design is focusing on two areas: the generation of solids with desired physical or chemical properties\textsuperscript{70} and the control of the topology of a particular solid or family of materials.\textsuperscript{119} With regard to the latter problem, molecular components based on pyridine (such as 4,4’-bipyridine) or carboxylic acids (such as 1,3,5-benzene tricarboxylate or 1,3,5,7-adamantane tetracarboxylate) have been and continue to be extensively examined.\textsuperscript{120-123} Researchers can explore the parameter spaces of design methodology and resultant structure through factors such as the ratio of components, the type of metal center, or the inclusion of templating reagents. Zaworotko and Yaghi both provide good descriptions of the recent developments in this rapidly evolving field.\textsuperscript{24,35,42,105,117,118}

In our work, we have chosen to examine tetrakis(imidazolyl)borate, B(Im)\textsuperscript{4−}, as an organic component of network solids. Tetrakis(azolyl)borates were first generated in 1967, but have not been previously investigated as a component of metal-organic
Tris(azolyl)-borates, including tris(imidazolyl)borates, have been examined as components for network systems, however.\textsuperscript{124,125} Using boron as a scaffold affords several advantages to the organic fragment in network solids.\textsuperscript{126} First, borate anions are inherently tetrahedral and thus can promote the formation of three-dimensional solids. In addition, the anionic character of this organic component can also, at least partially, balance the charge of the metals in the solid. This can eliminate the need for noncoordinating anions in the network matrix. Finally, tetrakis(imidazolyl)-borate is easy to synthesize from inexpensive and commercially available reagents, and functionalized variants can be readily generated. We have recently reported on this coordinating anion in the synthesis of a functional network solid, Pb[B(Im)\textsubscript{4}](NO\textsubscript{3})(1.35H\textsubscript{2}O).\textsuperscript{127} However, in addition to synthesizing functional solids, we also wish to understand how this anion forms extended network structures, such as with simple divalent metal cations.

In this chapter, we report the synthesis and structures of three group II metal cation networks incorporating B(Im)\textsubscript{4},(3). All three compounds have the empirical formula M[B(Im)\textsubscript{4}](H\textsubscript{2}O)\textsubscript{2} where M = Mg(4), Ca(5), and Sr(6). These three network solids have the same ligand set coordinated about the metal center, including four imidazole rings and two axial water molecules. However, by changing the metal cation, the morphology of the structure alters significantly between the three compounds. Altered factors include the geometry about the metal center, the conformation of the borate, and the extent of hydrogen bonding in the solid. In addition, we have investigated the structure of the protonated form of the borate anion, the neutral species B(HIm)(Im)\textsubscript{3}. We can use this
“anion-only” structure to examine conformational minima of tetrakis(imidazolyl)borate, and compare the preferred conformation to the borate conformations observed in the three metal network solids.

**Discussion**

In order to understand how tetrakis(imidazolyl)borate forms extended networks with metals, we decided to examine the structure and conformations of this organic anion more closely. As can be seen in Figure 3.1, the central boron atom has a tetrahedral geometry. The bond angles about the central atom are close to the ideal of 109.5°, as determined by inspection of the crystal structure of B(HIm)(Im)₃. The measured angles range between 106.1(3)° and 112.0(4)°. The directionality of the coordinating nitrogen, however, deviates from tetrahedral due to the asymmetry of the imidazole ring. In the protonated borate structure, the external nitrogen diverges from the ordinate of the B-N bond by an average of 18.8°, reducing the symmetry of the entire anion.

![Figure 3.1](image)

Figure 3.1. Asymmetric unit of B(HIm)(Im)₃ protonation of one external nitrogen results in a neutral species.
If the imidazole rings can rotate freely about the B-N bond, then it is clear that a variety of conformations can result. Predicting the low-energy geometries of this anion is a complex problem. Fortunately, the nature of the inquiry is similar to the work carried out by Mislow and co-workers in the 1970s on tetraphenylmethane and its derivatives.\textsuperscript{128,129} As in tetraphenylmethane, the various conformations of tetrakis(imidazolyl)borate can be considered as the imposition of four rotors around the central boron atom. Some of the simpler conformations of B(Im)\textsubscript{4} are shown below, in Figure 3.2.
Figure 3.2 Left are representations of the possible closed geometries with those on the right representing the open conformations for B(Im)$_4^-$.

The highest symmetry conformations of B(Im)$_4^-$, (3), can be designated as open or closed. A closed conformation will have an angle of 0°, and an open form will have an
ideal angle of 30°. With a symmetric cyclopentadiene (as shown at the top of the figure), both the open and closed forms would have D_{2d} symmetry. However, the reduced symmetry of the imidazole ring increases the number of open and closed conformations, resulting in a variety of high- and low-symmetry orientations. In addition, if one or more of the B-N bonds rotate from either of these open or closed geometries, a larger number of conformations result. As in tetraphenylmethane, rotation can be defined by an angle \( \phi \), the dihedral angle relative to the N-B-N plane. However, a ring can convert from an open to a closed orientation merely by rotating \( \pi/6 \) rad, or 30°. A variety of lower symmetry orientations can thus be imagined, including C_3, C_2, or C_1. We have examined the energy surface for the rotamers of this anion, including both the steric repulsion and bonding interactions that lead to preferred conformations. The steric interactions inhibit the molecule from adopting closed (coplanar) conformations, while the overlap of the \( \pi \) system is maximized by this orientation.

In our crystal structures, we can observe the orientations that the tetrakis(imidazole)borates adopt. Table 3.1 lists the deviations in degrees from closed orientations for all of the imidazole rings in the four structures presented in this chapter. The angles in Table 3.1 were measured by examining the dihedral angle between the plane of the imidazole ring and the closest B-N bond. As stated, a closed conformation will have an angle of 0°, and an open form will have an ideal angle of 30°. In the protonated form of the anion, all of the deviations are in the intermediate region between open and closed, ranging from about 10° to 20°. In the magnesium compound, the angles increase, with one in an open position with an angle measurement of 33.86°. The
measured angles can increase above 30° due to the slight deformation of the imidazole ring out of the plane of the B-N bond. In the strontium and calcium materials, all of the rings are in open positions, with angle measurements close to the ideal value of 30°.

Table 3.1. Angle deviations from the closed orientation for compounds 3 – 6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle deviations from closed (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(HIm)(Im)₃ (3)</td>
<td>20.78, 10.53, 16.32, 19.49</td>
</tr>
<tr>
<td>Mg[B(Im)₄]₂(H₂O)₂ (4)</td>
<td>20.73, 33.86, 16.33, 17.39</td>
</tr>
<tr>
<td>Ca[B(Im)₄]₂(H₂O)₂ (5)</td>
<td>30.07, 32.26, 28.65, 35.41</td>
</tr>
<tr>
<td>Sr[B(Im)₄]₂(H₂O)₂ (6)</td>
<td>26.75, 34.59, 34.99, 26.15</td>
</tr>
</tbody>
</table>

We can speculate that this change from intermediate to open angles arises from the increase in \( \pi \) donation from the imidazole ring to the metal centers as one goes down the group from Mg to Ca and Sr. The configuration of the protonated form represents an intermediate between the closed geometry, which maximizes \( \pi \) interactions between rings on the borate, and the open geometry, which minimizes steric repulsions. When the imidazole ring binds to a metal center, it can act as both a \( \sigma \) and \( \pi \) base, donating electron density into the metal center. Either \( \pi \) donation or acceptance will disrupt the boron-bridged imidazole-to-imidazole interaction, and decrease the tendency to maximize overlap by forming closed configurations. Without the driving force to form a closed configuration, the steric repulsions dominate the geometry and open positions result. While there are hydrogen-bonding differences between the Mg and Ca and Sr materials, it is important to note that the change from intermediate to open positions has no
relationship with the hydrogen bonding in the solid; in the Mg structure the hydrogen-bonded imidazole ring has an intermediate geometry (20.73°).

The multiplicity of conformations in tetrakis(imidazolyl)borate makes it difficult for predictions of how this anion will form extended network solids. However, in the three coordination polymers presented in this paper, the connectivity between the borate and the metal center is much simpler than might be expected. As can be seen in the formula for each of the three compounds, there are two borates and two waters per metal center. Since each metal has an octahedral coordination environment and since both water molecules are coordinating, only two of the imidazole rings per borate are bound to each metal site. Thus, there are only two angle measurements that we need to consider in order to examine the extended network structure of the three metal-organic frameworks presented in this chapter: the angle between equatorial positions about the metal (either 90° or 180°) and the metal-borate-metal angle (~90°).

Figure 3.3 Asymmetric units of M[B(Im)_4]_2·2H_2O, where M = Mg (a), Ca (b), and Sr (c).
Table 3.2. Selected bond distances (Å) and angles (°) about the metal centers.

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Lengths (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-O</td>
<td>2.075(3)</td>
<td>2.3190(16)</td>
<td>2.457(4)</td>
</tr>
<tr>
<td>M-N</td>
<td>2.188(3), 2.193(3)</td>
<td>2.4760(19), 2.4904(16)</td>
<td>2.631(4), 2.645(4)</td>
</tr>
<tr>
<td>Bond Angles (deg)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O-M-O</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
</tr>
<tr>
<td>N-M-O</td>
<td>90.11(14), 89.89(13), 90.62(13), 89.38(13)</td>
<td>92.95(7), 87.05(7), 83.23(6), 96.77(6)</td>
<td>85.29(14), 94.71(14), 99.56(13), 80.44(13)</td>
</tr>
<tr>
<td>N-M-N (cis)</td>
<td>89.41(13), 90.59(13)</td>
<td>90.78(5), 89.22(5)</td>
<td>90.95(12), 89.05(12)</td>
</tr>
<tr>
<td>N-M-N (trans)</td>
<td>180.0</td>
<td>180.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

In all three of the coordination networks with the divalent group II metal cations, the geometry about the metal center is identical (Figure 3.3). Table 3.2 lists selected bond distances and angles for the three metal compounds. Each metal center in the three solids is in an octahedral coordination environment, with four imidazole rings in the equatorial positions, and two solvent water molecules in the axial positions. As expected, the metal-ligand bond distances lengthen as one goes down the group. The metal-nitrogen bond distance increases from an average of 2.191(3) Å in Mg[B(Im)₄]₂(H₂O)₂ to 2.4752(18) Å in Ca[B(Im)₄]₂(H₂O)₂ and 2.638(4) Å in Sr[B(Im)₄]₂(H₂O)₂. Similarly, the metal-oxygen bond distances in the axial position expand from 2.075(3) to 2.3190(16) and 2.457(4) Å as one goes down the group. The bond lengths in the borates do not change significantly over the three compounds. Therefore, the increase in volume in the unit cell in the almost
identical Ca[B(Im)₄]₂(H₂O)₂ and Sr[B(Im)₄]₂(H₂O)₂ structures is directly attributable to
the increase in covalent radius of the metal ion.

Figure 3.4. Octahedral coordination environment about the metal in M[(B(Im)₄)₂(H₂O)],
where M = Mg (a), Ca (b), and Sr (c) with a diagram showing the M-N and M-O bonds.

Two of the structures Ca[B(Im)₄]₂(H₂O)₂ and Sr[B(Im)₄]₂(H₂O)₂ are nearly
isomorphous, belonging to a triclinic crystal system, and having the P-1 space group. However, the Mg[B(Im)₄]₂(H₂O)₂ unit cell is monoclinic and belongs to the P2₁/c space
group. The change in symmetry can be explained in part due to two variations in the
structure of the Mg compound from that of the Ca and Sr networks. First, the
orientations of the imidazole rings bound to the metal in Mg[B(Im)₄]₂(H₂O)₂ differ from
those found in the Ca or Sr analogues. In the Mg compound, two of the imidazole rings
are nearly parallel to the axial ordinate, while the remaining two are almost in the
equatorial plane and thus nearly orthogonal to the axial ordinate. In the Ca and Sr
compounds, two of the imidazole rings are in the plane of the axial ordinate, but the remaining two imidazole rings significantly deviate from the equatorial position observed in the Mg network solid. In Ca[$\text{B(Im)}_4\text{H}_2\text{O}_2$], these two imidazole rings are nearly orthogonal to the equatorial plane, but tilted $\sim$30° off of the B-N ordinate. In the Sr compound, this same tilt is also observed, but there is an additional $\sim$45° twist relative to the equatorial plane.

Figure 3.5. Hydrogen bonding interactions between imidazole and axially coordinated water in compound 4 (left) and compound 6 (right); 5 and 6 exhibit identical interactions.

Second, one of the most significant variations between the monoclinic and triclinic forms is the extent of hydrogen bonding in the solid, as shown in Figure 3.5. In each structure, there are two borates per metal ion for a total of eight imidazole rings. Only four of these imidazoles are coordinated to equatorial positions on the metal center, leaving four additional imidazole rings that are not involved in direct metal-ligand bonding. In the Ca and Sr structures, the noncoordinating rings are engaged in hydrogen
bonding to axially coordinated waters, forming two bonds per bound solvent molecule (Ca, 1.90, 1.87 Å; Sr, 1.98, 1.86 Å N-H bond distances). However, in Mg[B(Im)₄]₂(H₂O)₂, only one hydrogen bond is observed per water molecule and the noncoordinating imidazole rings (1.61 Å N-H bond distance). The remaining two imidazole rings do not exhibit any significant interactions to either the axial water molecules or the metal centers in Mg[B(Im)₄]₂(H₂O)₂. The observed differences in hydrogen bonding can be directly attributed to the nature of the metal-oxygen bond. The strength and polarity of the Mg-O bond reduces the ability of the bound solvent water molecules to engage in hydrogen bonding with nearby pendant imidazole rings. In the Ca and Sr compounds, this bond is weak enough that the axial water can donate both protons for hydrogen bonding to adjacent imidazole nitrogens.

Figure 3.6. Extended network structure of Mg[B(Im)₄]₂(H₂O) from two perspectives. The left view exhibits the interlaced brick pattern while on the right the discrete layering is apparent. Hydrogen atoms have been omitted for clarity.
In the extended network solid of the Mg compound, the metal-borate units form a layered structure (Figure 3.6). The pattern of these layers resembles an interlaced “brick wall” format. The imidazole-water hydrogen bonds occur within the same layer, and the remaining noncoordinating imidazole rings fill the space generated by the slight zigzag motion of the layer itself. In the Ca[B(Im)₄]₂(H₂O)₂ and Sr[B(Im)₄]₂(H₂O)₂ structures, the metal-borate units form one-dimensional chains in a linked diamond fashion, where two tetrakis(imidazolyl)borate units bridge metal sites (Figure 3.7). The remaining four imidazole rings of this bridge are engaged in hydrogen bonding to solvent waters on adjacent chains, one to each of the four chains surrounding every one-dimensional coordination assembly.

Figure 3.7. One-dimensional chains viewed along the $a$ axis for Ca[B(Im)₄]₂(H₂O)₂. The strontium structure is isomorphous. Hydrogen atoms omitted for clarity.
The formation of interlaced squares in Mg[B(Im)$_4$]$_2$(H$_2$O)$_2$ versus one-dimensional chains in the Ca[B(Im)$_4$]$_2$(H$_2$O)$_2$ and Sr[B(Im)$_4$]$_2$(H$_2$O)$_2$ structures results from how the borates can link together metals in either a one- or two-dimensional network. A diagram displaying how the molecular components of these solids fit together can be found in Figure 3.8. If a cis pair of borates on a metal is joined to the same adjacent metal center, then a one-dimensional chain of metal-imidazole squares results. This geometry is shown on the left in Figure 3.8 and is observed in the Ca and Sr compounds. However, if this same cis pair of borates goes to different metal centers, then alternative geometries could occur depending on whether the resulting network is two- or three-dimensional. In the planar case, this leads to the interlaced block pattern (right side of Figure 3.8) observed in the magnesium network solid. The metal-borates close in a figure-8 loop through cis linkages on the metals.

Figure 3.8. Illustrating the two types of solid morphologies observed for M[B(Im)$_4$]$_2$(H$_2$O)$_2$.  

70
In all of the structures presented in this chapter, the borates adopt a chiral conformation although tetrakis(imidazolyl)borate is not itself a chiral anion. In the protonated form, the enantiomers crystallize out separately into right- and left-handed crystal forms, while in the metal network solids there is an inversion center and thus both enantiomers are observed in the structures. The generation of a chiral solid by using enantiomerically pure conformers of tetrakis(imidazolyl)borate is unlikely. Although we are still in the process of calculating the energy barriers for isomerization of this anion, previous work on the energies of isomerization of tetraaryl-methanes show that rapid equilibration of all isomers occurs at room temperature. In the solution phase, the $^1$H NMR spectrum of B(HIm)(Im)$_3$ in CD$_3$OD does not change over the temperature range of 30 to -60 °C. In order to construct a chiral tetrakis(imidazolyl)borate metal-organic framework, either a substituted tetrakis(imidazolyl)borate that inhibits rotation or a chiral borate (with four different imidazole substitutents around the boron) should be employed.
Table 3.3. Crystal data and structural refinement parameters for 3-6.

<table>
<thead>
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</thead>
<tbody>
<tr>
<td>formula</td>
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<td>MgB$_2$C$_2$H$_8$N$_6$O$_2$</td>
<td>CaB$_2$C$_2$H$_8$N$_6$O$_2$</td>
<td>SrB$_2$C$_2$H$_8$N$_6$O$_2$</td>
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<td>9.6820(19)</td>
<td>9.809(2)</td>
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<td>$c$, Å</td>
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<td>1425.7(5)</td>
<td>766.2(3)</td>
<td>790.5(3)</td>
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<td>$\rho$(calc), Mg/m$^3$</td>
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<td>1.441</td>
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<td>1.432</td>
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<td>644</td>
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<td>348</td>
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<td>1.029</td>
<td>1.053</td>
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<td>$R$ [$I &gt; 2\sigma(I)$]</td>
<td>R1 = 0.0559, wR2 = 0.1502</td>
<td>R1 = 0.0685, wR2 = 0.1066</td>
<td>R1 = 0.0340, wR2 = 0.0655</td>
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<tr>
<td>$R$ (all data)</td>
<td>R1 = 0.0597, wR2 = 0.1522</td>
<td>R1 = 0.1558, R1 = 0.0473, wR2 = 0.1334</td>
<td>R1 = 0.0722, wR2 = 0.0702</td>
<td>R1 = 0.1111</td>
</tr>
</tbody>
</table>

Changing the metal ion in these solids not only changes the topology of the network but also affects the chemistry exhibited by the network. In the TGA measurements of the three metal-organic frameworks, the axial water molecules can be driven off with increasing temperature. The temperature at which these water molecules are removed decreases as one goes down the group, due to the decreasing strength of the metal-water
bond. Since the water molecules at the axial sites of the metals in these coordination polymers can be removed, they can be considered as open metal sites in these solids. We are currently investigating the substitution of coordinated water molecules through incubation of these crystals in other Lewis basic solvents, such as ammonia.

As can be seen in the three metal-organic networks presented in this chapter, the nature of the metal ion can be used to tune the structure of the solid. In the cases presented, a combination of the radius of the metal and its electronic character affect the topology of the resultant solid. Several parameters change as one goes down the group, including the closed/open conformation of the borate, the geometry of the imidazoles about the metal center, and the lengths of the metal-ligand bonds. These variations in geometries and hydrogen bonding result in differences between the magnesium structure, which adopts a brick wall layered pattern, and the calcium and strontium structures, which form one-dimensional square chains. We are continuing our work on these solids, including modifying the borate structure and examining the exchange of the axial water molecules.

**Experimental**

All reagents and solvents were purchased from Aldrich and used as received. Water was purified by using a Milli-Q reagent water system. Mass spectra were obtained on a Micromass AutoSpec EBEhQ hybrid tandem mass spectrometer using FAB ionization. Solution NMR spectroscopy was performed on a Varian VXR 300 MHz NMR
instrument. Elemental analysis was carried out at the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. Nitrogen analyses tend to be lower than calculated due to the formation of refractory boron nitrides. Thermogravimetric analysis was measured on a TA Instruments 2050 device. Solid-state NMR spectra were obtained on a Varian Unityplus-200 (4.7 T) spectrometer using Doty Scientific supersonic and standard MAS probes. Samples were packed into 7 mm silicon nitride rotors with Kel-F end caps and the spinning speed was 5kHz.

**Synthesis of Na[B(Im)₄]:** The synthesis of this material was based on a procedure developed by Trofimenko for sodium tetrakis(pyrazolyl)borate and is described by Chao and co-workers. In a nitrogen-flushed flask attached to an oil bubbler, sodium borohydride (3.78 g, 0.1 mol) and imidazole (54.5 g, 0.8 mol) were mixed and heated to 225 °C. The evolution of hydrogen gas from the reaction flask was monitored, and the reaction proceeded for 1.5 h, after which the evolution of gas ceased. The reaction flask was cooled to room temperature, and acetone (100 mL) was added to the reaction mixture. The acetone dissolves the unreacted imidazole and reaction byproducts, leaving the product Na[B(Im)₄] as an off-white solid. The crude product was then recrystallized from ethanol, affording 27.8 g of product (92% yield). $^1$H NMR (D₂O): 6.856 (H-5), 7.055 (H-4), 7.233 (H-2) ppm. $^{13}$C NMR: 122.28, 128.50, 140.92 ppm. $^{11}$B NMR (D₂O) 2.117 ppm. FAB MS (negative ion): 279 m/z (B(Im)₄⁻). IR (KBr): 3145, 3125, 3113, 3039, 2917, 2824, 2613, 2536, 2498, 2437, 1696, 1614, 1475, 1293, 1247, 1208, 1109, 1082, 1040, 923, 819, 776 cm⁻¹.
Synthesis of B(HIm)(Im)₃(3): Na[B(Im)₄] (250 mg, 0.8 mmol) was dissolved in 25 mL of H₂O at room temperature in a flask. To this solution was added 825 μL of 1.0 M HCl with stirring, and the pH of the resultant mixture approached neutrality. At this point, 100 μL aliquots of 1.0 M HCl were added to the solution until a while precipitate formed and the pH decreased to 6.9. The precipitate was collected by filtration and dried, affording 173 mg of product (69% yield). ¹H NMR (D₂O): 7.026 (H-5), 7.238 (H-4), 7.530 (H-2) ppm. ¹³C NMR: 122.03, 127.23, 139.43 ppm. ¹¹B NMR (D₂O) 2.327 ppm. FAB MS (negative ion): 279 m/z (B(Im)₄⁻). IR (KBr): 3449 3142, 3109, 3084, 3004, 2535, 2024, 1630, 1580, 1523, 1476, 1336, 1287, 1267, 1252, 1220, 1206, 1182, 1112, 1104, 1079, 935, 757, 669 cm⁻¹. CHN anal. Calcd for C₁₂H₁₃N₈B: C, 51.42; H, 4.64; N, 40.00. Found: C, 50.23; H, 4.57; N, 37.92.

Synthesis of M[B(Im)₄]₂(H₂O)₂ (M ) Mg (4), Ca (5), Sr (6)): A 1:1 water:ethanol solution (10 mL) of Na[B(Im)₄] (60 mg, 0.2 mmol) was carefully layered over an aqueous solution (10 mL) of M(X)₂·nH₂O (Mg(NO₃)₂, Ca(OAc)₂·H₂O, Sr(NO₃)₂, 0.1 mmol) in a narrow test tube. The tubes were then sealed and placed in an oven and the two layers allowed to diffuse slowly over 1 week at 60 °C, after which the product was collected by filtration.

Mg[B(Im)₄]₂(H₂O)₂(4): Yield: 57 mg (92%). Solid-state ¹³C MAS NMR: 122.4, 130.1, 132.0, 138.0, 141.2 ppm. IR (KBr): 3132, 3116, 3099, 2705, 2304, 1681, 1626, 1479,
1299, 1289, 1249, 1116, 1087, 934, 812, 759, 662 cm\(^{-1}\). CHN anal. Calcd for C\(_{24}\)H\(_{28}\)N\(_{16}\)B\(_2\)O\(_2\): C, 46.59; H, 4.57; N, 36.23. Found: C, 46.40; H, 4.88; N, 34.66.

**Ca[B(Im)\(_4\)]\(_2\)(H\(_2\)O)\(_2\)**: Yield: 49 mg (78%). Solid-state \(^{13}\)C MAS NMR: 119.9, 129.9, 140.3 ppm. IR (KBr): 3112, 3098, 2621, 2440, 1704, 1693, 1609, 1472, 1302, 1246, 1208, 1110, 1081, 932, 819, 753, 664 cm\(^{-1}\). CHN anal. Calcd for C\(_{24}\)H\(_{28}\)N\(_{16}\)B\(_2\)O\(_2\): C, 45.43; H, 4.45; N, 35.33. Found: C, 45.09; H, 4.67; N, 33.80.

**Sr[B(Im)\(_4\)]\(_2\)(H\(_2\)O)\(_2\)**: Yield: 54 mg (80%). Solid-state \(^{13}\)C MAS NMR: 120.5, 129.7, 140.5 ppm. IR (KBr): 3124, 3108, 3083, 2441, 1701, 1627, 1474, 1301, 1246, 1210, 1110, 1081, 929, 819, 757, 666 cm\(^{-1}\). CHN anal. Calcd for C\(_{24}\)H\(_{28}\)N\(_{16}\)B\(_2\)O\(_2\): C, 42.27; H, 4.14; N, 32.87. Found: C, 41.88; H, 3.96; N, 30.73.

**Thermogravimetric Analysis**: The TGA of compounds 4, 5, and 6 were carried out over a temperature range of 25-600 °C at a scan rate of 10 °C/min. Water loss (2 water molecules per formula unit) occurred between the temperatures of 172 and 209 °C for compound 4, 134 and 152 °C for compound 5, and 115 and 138 °C for compound 6. Decomposition of the three solids started at 287, 297, and 194 °C for 4, 5, and 6 respectively.

**X-ray Crystallography**: For 3, X-ray intensity data were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system.
equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 W power. A clear crystal was mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal. Analysis of the data showed negligible decay during data collection. The data were corrected for absorption with the SADABS program (ratio of minimum to maximum apparent transmission: 0.690050). Additional experimental details are provided in Table 3.3. The asymmetric unit for 3 is shown in Figure 3.1. The structure was refined using the Bruker SHELXTL (version 6.1) software package, in the space group $P\bar{2}_1$, with $Z = 2$ for the formula unit BC$_{12}$H$_{13}$N$_8$. The structure was solved using direct methods until the final anisotropic full-matrix least-squares refinement on $F^2$ converged.$^{132}$

For compounds 4, 5, and 6, X-ray data were collected using Mo (0.71073 Å) radiation on a Syntex P21 diffractometer. The crystals were coated in Paratone N-Exxon oil, mounted on a glass fiber, and placed under a cold stream of nitrogen at 159 K. Unit cell parameters were obtained by a least-squares analysis of 20 well-centered reflections with $20^\circ < \theta < 30^\circ$. The structures were refined using the Bruker SHELXTL (version 6.1) software package and solved using direct methods until the final anisotropic full-matrix least-squares refinement on $F^2$ converged.$^{132}$ Additional experimental details are given in Table 3.3. The asymmetric units for structures 4, 5, and 6 are shown in Figure 3.3.
CHAPTER IV

LEAD TETRAKIS(IMIDAZOLYL)BORATE SOLIDS: ANION EXCHANGE, SOLVENT INTERCALATION, AND SELF ASSEMBLY OF AN ORGANIC ANION

As the field of crystal design has grown over the past decade, synthetic efforts are being directed toward constructing functional solids. Coordination polymers are attractive targets for crystal design since one can design two aspects of the solid: the identity of the metal ion and the structure of the linking ligand unit. These two components of a coordination polymer can have a direct impact on its functionality; the metal ion can provide a site for reactivity within the solid, and the organic ligand can help control the topology of the network solid. In particular, network solids with Lewis acidic metals remain an area of focus in crystal engineering.

We have investigated the coordinating anion tetrakis(imidazolyl)borate (B(Im)$_4$-, Figure 4.1) as a component of coordination solids. This species is a robust, multidentate ligand that is readily synthesized from simple starting materials. The tetrahedral geometry about the boron in B(Im)$_4$- is structurally rigid and promotes the formation of three-dimensional structures in coordination solids. In addition, the anion can be readily modified to explore the effects of functionalization on network structure.
Finally, the anionic nature of tetrasubstituted boron can provide charge balance for the metals in coordination polymers.

Figure 4.1. Tetrakis(imidazolyl)borate.

In this chapter, we present a series of compounds that incorporate B(Im)$_4^-$ in a coordination polymer with Pb$^{2+}$. We have recently presented part of this work as a communication. These compounds have the generic formula Pb[B(Im)$_4$]X(nH$_2$O), where X is NO$_3^-$ in the parent structure, (7), and n ranges from 0 to 1.5. The parent material, grown by diffusing solutions of Pb(NO$_3$)$_2$ and Na[B(Im)$_4$], adopts a layered structure with noncoordinating nitrate found between the layers and the Pb ions facing the layer interface. This network solid, which resembles naturally occurring layered minerals, exhibits ion exchange behavior and water intercalation resulting from its tiered structure. Related materials of the formula Pb[B(Im)$_4$]X(nH$_2$O), where X = I$^-$ (8) or C$_6$H$_5$COO$^-$ (9), are generated by ion exchange of the nitrates or by self-assembly, respectively. In both of the nitrate-substituted structures, the Pb$^{2+}$ ion behaves as a Lewis acid, fulfilling an important criterion for functional coordination polymers. We have characterized these materials by X-ray structural elucidation, and their dynamic chemistry by using solid state NMR spectroscopy (SSNMR).
Discussion

The reaction of a H$_2$O/EtOH solution of Na[B(Im)$_4$] and aqueous Pb(NO$_3$)$_2$ produces a product with the formula Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), where $n = 0$-1.5. If the solutions are mixed together quickly, a microcrystalline product is produced, whereas slow diffusion of layered, equimolar solutions results in large, single, platelike crystals. The crystalline product is resilient to most organic solvents and water and desiccates rapidly upon exposure to dry air. The single crystals are suitable for X-ray structural elucidation. The repeating asymmetric unit of the crystal structure with 50% thermal ellipsoids is shown in Figure 4.2. One imidazole ring is linked to the metal center in this unit, and each of the remaining heterocycles are linked to different lead sites in adjacent asymmetric units. The nitrate anion, required for charge balance, and the water molecules occupy the void space in the unit.

Figure 4.2. The asymmetric unit of Pb[B(Im)$_4$](NO$_3$)(H$_2$O)$_{1.35}$. 
In the extended network, the Pb-borate units link together to form a layered solid, shown in Figure 4.3. Each metal is coordinated to four imidazole rings from different borates, although this is not obvious from the figure due to the overlapping perspective of the imidazole rings. The nitrates and solvent water molecules occupy the spacing between the Pb-borate tiers. The metal sites face the interlayer spacing, and the borates transverse the layer itself. The distance between Pb sites across the layer interface (based on the mean planes of the Pb centers) is ~3.4 Å, although the edges of the peripheral imidazole rings extend slightly further into the interlayer spacing. The borate-Pb layer is ~6.3 Å across using the same measurement convention.

Figure 4.3. Extended structure of Pb(B(Im)₄)(NO₃)(H₂O)₁.₃₅ (7), along the c axis(left) and a axis. Hydrogen atoms omitted for clarity.
Figure 4.4. Coordination environment of the metal center in Pb[B(Im)_4](NO_3)

exhibiting the VSEPR predicted disphenoidal geometry with a lone pair directed toward

the layer interface.

The environment around the metal sites in this solid is asymmetric and described as a
hemidirected Pb center. Figure 4.4 shows the coordination environment about each Pb
ion in the network solid, and Table 4.1 lists bond lengths and angles about the metal
center. The geometry at the Pb centers conforms to the VSEPR prediction of a
disphenoidal system with a stereochemically active lone pair in an equatorial position
directed toward the layer interface. There are no other bonding interactions in the
vicinity of the metal; the nitrates and the water molecules are not bound, and the closest
distance between metal centers is ~4.4 Å, which is much too long to be a bonding
contact. The Pb sites in this solid are coordinatively unsaturated since the large radius of
Pb can typically accommodate up to 8 ligands. The presence of a lone pair as well as a
low coordination number indicates that the metal sites in this solid could be amphoteric.
We have observed Lewis acidity of this solid upon replacement of the nitrate with a coordinating anion, which will be described below.

Table 4.1. Selected bond lengths (Å) and angles (°) for compounds 7-9.

<table>
<thead>
<tr>
<th></th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb-N (Å)</td>
<td>2.406(3)</td>
<td>2.381(7)</td>
<td></td>
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<tr>
<td></td>
<td>2.505(3)</td>
<td>2.531(6)</td>
<td>2.575(3)</td>
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<tr>
<td></td>
<td>2.523(4)</td>
<td>2.594(7)</td>
<td>2.717(3)</td>
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<td></td>
<td>2.643(3)</td>
<td>2.615(6)</td>
<td>2.776(3)</td>
</tr>
<tr>
<td>Pb-X (Å)</td>
<td></td>
<td>3.1507(7) (Pb-I)</td>
<td>2.478(3) (Pb-O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.542(3) (Pb-O)</td>
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<td>N-Pb-N (deg)</td>
<td>77.09(12)</td>
<td>76.4(2)</td>
<td>72.69(10)</td>
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<td></td>
<td>78.30(10)</td>
<td>76.6(2)</td>
<td>76.46(10)</td>
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<td>79.03(11)</td>
<td>79.0(2)</td>
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<td>80.66(12)</td>
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<td>79.08(10)</td>
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<td>83.86(11)</td>
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<td>149.58(11)</td>
<td>155.3(2)</td>
<td>146.87(10)</td>
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In addition, the layered structure of Pb[B(Im)₄](NO₃) suggests chemistry akin to that found in minerals with a similar topology. Layered minerals, such as clays and hydrotalcites, can intercalate neutral guests, exchange ions, and catalyze reactions in the
interlayer spacing. We investigated this topology-related chemistry in Pb[B(Im)$_4$](NO$_3$), focusing on intercalation chemistry and anion exchange. A number of coordination polymers exhibit both types of reactivity, which can be considered a measure of the potential usefulness of a network structure. For example, coordination solids that preferentially sequester certain anions could be used to treat wastewater contaminated with negatively charged toxic or radioactive species.$^{143-145}$

Table 4.2. Crystallographic data and structure parameters for compounds 7-9.

<table>
<thead>
<tr>
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<tr>
<td>mol formula</td>
<td>C$<em>{12}$H$</em>{14.70}$BN$<em>9$- O$</em>{4.35}$Pb</td>
<td>C$<em>{12}$H$</em>{12}$BI- N$_8$Pb</td>
<td>C$<em>{19}$H$</em>{18}$BN$<em>8$- O$</em>{2.50}$Pb</td>
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<tr>
<td>fw</td>
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<td>613.20</td>
<td>616.41</td>
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<td>P-1</td>
<td>P-1</td>
</tr>
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<td>b, Å</td>
<td>10.7463(9)</td>
<td>10.0336(19)</td>
<td>8.7774(10)</td>
</tr>
<tr>
<td>c, Å</td>
<td>11.2476(10)</td>
<td>10.965(2)</td>
<td>14.1567(16)</td>
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<tr>
<td>α,(deg)</td>
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<td>102.070(3)</td>
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</tr>
<tr>
<td>β, (deg)</td>
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<td>81.598(2)</td>
</tr>
<tr>
<td>γ,(deg)</td>
<td>67.0120(10)</td>
<td>103.875(3)</td>
<td>78.860(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>911.84(14)</td>
<td>847.2(3)</td>
<td>1036.7(2)</td>
</tr>
<tr>
<td>T (°C)</td>
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<td>-173</td>
<td>-173</td>
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<tr>
<td>λ(Å)</td>
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<td>0.71073</td>
<td>0.71073</td>
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<tr>
<td>abs coeff</td>
<td>μ$_{calc}$ (cm$^{-1}$)</td>
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<td>1.1789</td>
</tr>
<tr>
<td>δ$_{calc}$ (Mg/m$^3$)</td>
<td>2.084</td>
<td>2.404</td>
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</tr>
<tr>
<td>$R(F_o)$</td>
<td>0.0371</td>
<td>0.0511</td>
<td>0.0275</td>
</tr>
<tr>
<td>$R_w(F_o)^{2}$</td>
<td>0.0721</td>
<td>0.1000</td>
<td>0.0640</td>
</tr>
</tbody>
</table>

$^{a} R = \sum |F_o| - |F_i|/\sum |F_o|$. 
$^{b} R_w = [\sum w(F_o^2 - F_i^2)^2/\sum w(F_o^2)^2]^{1/2}$. 

84
The intercalation and ion-exchange chemistry of these layered materials is readily monitored by using solid state NMR (SSNMR). The effect of intercalation and/or exchange on the Pb environment was investigated by using $^{207}$Pb SSNMR, as this isotope is ideal for NMR studies: 23% natural abundance, $I = 1/2$, and a chemical shift range encompassing almost 8000 ppm that is very sensitive to changes in its local environment.$^{146,147}$ The $^{207}$Pb spectrum from the parent compound is shown in the top of Figure 4.5(a) where the isotropic chemical shift is -533 ppm, and the chemical shift anisotropy covers ~2500 ppm. As the spectrum was obtained by using a single excitation pulse (Bloch decay) with the RF frequency near the isotropic chemical shift, the intensities of the spinning sidebands nearer the edges of the spectrum are reduced in intensity from their actual values. However, this perturbation of the peak intensities does not affect the interpretation of the $^{207}$Pb NMR data. The coordination environment and network connectivity of Pb[B(Im)$_4$](NO$_3$) is similar to the litharge form of PbO,$^{148}$ however, the $^{207}$Pb chemical shift of litharge is +2000 ppm. The differences in the chemical shifts result in part from the substitution of nitrogen for oxygen in Pb[B(Im)$_4$](NO$_3$) as the coordinating atoms despite the similarities between the two solids.$^{149-151}$ The $^{207}$Pb spectrum (Figure 4.5(a)) consists of a single set of peaks indicating only one Pb environment in the material. Also, the relatively narrow line widths indicate a homogeneous local environment at each Pb site. These results are consistent with the single crystal XRD studies of the parent compound discussed above.
Figure 4.5. $^{207}$Pb SSNMR of Pb[(Im)$_4$](NO$_3$)(H$_2$O)$_x$ under 99% humidity (a) and 24% humidity (b). TGA measurements indicate that $x = 1.5$ and 0.25 for (a) and (b), respectively.

Crystals of Pb[(Im)$_4$](NO$_3$)(nH$_2$O) desiccate rapidly upon exposure to dry air, eventually resulting in Pb[(Im)$_4$](NO$_3$). The material can also be rehydrated without significant loss in crystallinity, indicative of the reversible intercalation of solvent water molecules. The extent of hydration and the effect of the presence of water at the Pb site was monitored by SSNMR. Two $^{207}$Pb SSNMR spectra from a slightly dry (equilibrated in 24% humidity at 25 °C) and a water saturated sample (equilibrated in 99% humidity at 25 °C) of Pb[(Im)$_4$](NO$_3$) are shown in Figure 4.5. The structures of both spectra are similar but shift by ~50 ppm downfield from the partially dry sample (0.25 water
molecules per unit) to the water saturated sample (1.5 solvent water molecules per unit). We confirmed the number of water molecules per asymmetric unit by TGA. The ~50 ppm shift is relatively small on the $^{207}$Pb chemical shift range and is indicative of a change in solvation only and not the coordination environment of the metal.

We began our investigation of anion exchange by replacing the nitrate in the solid Pb[B(Im)$_4$](NO$_3$) for labeled nitrate and monitoring by $^{15}$N SSNMR under magic angle spinning conditions. The initial $^{15}$N spectrum of Pb[B(Im)$_4$](NO$_3$) prior to exposure shows no signal (Figure 4.6d). We were able to replace some of the NO$_3^-$ in the solid with $^{15}$NO$_3^-$ by exposing crystals to an aqueous solution with a mole equivalent of Na$^{15}$NO$_3$. After collecting the crystals by filtration, the material was again characterized by $^{15}$N SSNMR. Prior to washing, the $^{15}$N NMR spectrum contains two peaks at 355.4 and 353.2 ppm as seen in figure 4.6a. This was reduced to a single peak at 353.2 ppm when the crystals were washed several additional times with water (Figure 4.6b). Comparison with the $^{15}$N NMR spectrum from solid Na$^{15}$NO$_3$ reveals that the peak at 355.4 ppm arises from adventitiously bound Na$^{15}$NO$_3$ (Figure 4.6c); thus, the peak at 353.2 ppm results from the intercalated labeled nitrate ions.
Figure 4.6. $^{15}$N SSNMR spectra of (a) Pb[Im]$_4$(NO$_3$) after exposure to aqueous Na$^{15}$NO$_3$, (b) washed Pb[Im]$_4$($^{15}$NO$_3$) after exchange, (c) Na$^{15}$NO$_3$, and (d) Pb[Im]$_4$I. The spinning speed was 2.7 kHZ.

We also expected that Pb[Im]$_4$(NO$_3$) should show a preference for soft anions due to the presence of the lead ions at the layer interface. We can monitor the replacement of nitrate for iodide by using the above $^{15}$NO$_3^-$ exchanged sample. The solid sample containing $^{15}$NO$_3^-$ was exposed to a mole equivalent solution of KI, collected, washed with water, and again examined by $^{15}$N SSNMR. The peak at 353.2 ppm is absent (Figure 4.6d), showing that iodide exchange has occurred replacing the nitrate anion in the layered material and returning the same spectra as before any labeled exchange had
taken place. Complete exchange takes place with iodide at stoichiometric concentrations. During both of the exchange interactions, the crystallinity of the material was not greatly affected; some loss of crystal size occurs depending on the vigor of stirring during the exchange process. Powder XRD patterns of Pb[B(Im)₄](NO₃) both before and after exchange with ¹⁵NO₃⁻ and I⁻ show no change in the degree of crystallinity, although the pattern does change upon exchange with I⁻, as expected. In addition, IR spectra of Pb[B(Im)₄](NO₃) before and after exchange with I⁻ show the same fingerprint except for the loss of a peak at 1385 cm⁻¹ that corresponds to a strongly absorbing nitrate vibration. Finally, CHN elemental analysis is in complete agreement with the complete exchange of iodide for nitrate.
The effect of the exchange of iodide for nitrate on the Pb site was also characterized by $^{207}$Pb SSNMR. The spectrum of the starting material prior to exchange, Pb[B(Im)$_4$](NO$_3$), is shown in Figure 4.7a. Upon substituting I$^-$ for NO$_3^-$, the $^{207}$Pb spectrum changes in both chemical shift and line width, as shown in Figure 4.7c. The $^{207}$Pb chemical shift moves downfield to 357 ppm, a result of perturbation of the electron distribution at the Pb. The magnitude of this shift (~900 ppm) is much larger than the
shift observed upon changing the water solvation of the Pb site (~50 ppm). However, the chemical shift change is also relatively small compared to the complete range of shifts observed for Pb (~8000 ppm). This change in chemical shift indicates that there is a direct interaction between the iodide and the metal, but the Pb[B(Im)$_4$] structure has not been significantly changed. The NMR results are in agreement with the aforementioned powder XRD and IR experiments that also indicated a small change in the Pb coordination.

![Figure 4.8. The asymmetric unit with 50% thermal ellipsoids of Pb[B(Im)$_4$]I.](image)

We were able to characterize the nature of this lead-iodide interaction by isolation of a single crystal from the exchange reaction. Figure 4.8 shows the structure of the asymmetric unit of Pb[B(Im)$_4$]I, and Figure 4.9 shows its extended network structure. As in the starting material, the borate-metal ratio remains the same, but the noncoordinating nitrate and water molecules have been replaced with the iodide. The metal center acts as a Lewis acid upon exchange with iodide, forming a Pb-I bond of 3.1507(7) Å. The mean distance for Pb(II)-I bonds for structures found in the Cambridge Structural Database
(CSD) has an average value of 3.22(16) Å, and the bond length found in Pb[B(Im)₄]I is in good agreement with this number. In the iodide exchanged material, the formation of this bond has the net effect of eliminating some of the void space in the asymmetric unit. The cell volume reduces from 911.84(14) Å³ in the nitrate compound to 847.2(3) Å³ in Pb[B(Im)₄]I. This bond also increases the coordination number from four to five, but the metal center still retains a hemidirected geometry.

Figure 4.9. Extended structure of Pb[B(Im)₄]I along the b axis shown on the right and the a axis on the left. Hydrogen atoms omitted for clarity.

In the extended network structure of Pb[B(Im)₄]I, the Pb-borate connectivity remains the same as that in the parent network Pb[B(Im)₄](NO₃), and the Pb ions still face the interlayer spacing. Upon examination of the extended structure, the change in asymmetric unit volume becomes more apparent. The Pb-I bond does not extend into the interlayer spacing, but the ordinate of the bond is directed roughly parallel to the layer itself. This effective elimination of the anion from the interlayer spacing allows the layers to pack more closely together than in the parent Pb[B(Im)₄](NO₃) structure. The
spacing decreases from ~3.4 Å between planes of the Pb atoms in the nitrate compound to a length of only ~3.0 Å in the iodide exchanged material.

The formation of a lead iodide bond in Pb[B(Im)$_4$I] upon exchange does not affect the metal-nitrogen bond lengths despite the modification of the geometry, as shown in Table 4.1. The average Pb-N bond lengths in Pb[B(Im)$_4$I] and Pb[B(Im)$_4$(NO$_3$)] both equal ~2.53 Å. In addition, the N-Pb-N angles do not significantly shift upon the binding of iodide to the metal, changing by only a few degrees. The similarity of the bond lengths and angles both before and after exchange explain in part how crystallinity is retained upon iodide exchange.

![Figure 4.10. The asymmetric unit with 50% thermal ellipsoids of Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5H$_2$O). The hydrogens on the water are not shown and only one of two orientations of the disordered benzoate is shown.](image)

We also explored exchange with the organic anion benzoate but found that we were unable to replace the nitrate using conditions similar to those for iodide. However, we did find that by growing crystals of Pb[B(Im)$_4$](NO$_3$) in the presence of a 3:1 mole
excess of an aqueous, buffered solution of benzoate, we were able to obtain 
Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5H$_2$O). In this case, unlike the iodide exchange, the material 
clearly forms by self-assembly. We characterized this material by X-ray crystallography, 
and the asymmetric unit is shown in Figure 4.10 with the extended network structure 
shown in Figure 4.11. As in the iodide exchanged structure, the stoichiometry and the 
connectivity of the lead-borate units are identical to that of the parent Pb[B(Im)$_4$](NO$_3$). 
The benzoate replaces the nitrate as the counterion and coordinates to the metal center in 
a symmetric bidentate fashion. While the coordination of iodide to the lead center 
decreases the volume of the asymmetric unit, the presence of the benzoate, a much larger 
anion, increases the cell volume significantly to 1036.7(2) Å$^3$.

Figure 4.11. The layered structure of Pb[B(Im)$_4$](O$_2$CC$_7$H$_5$)(0.5H$_2$O) viewed down 
the $b$ axis on the left and the $a$ axis on the right. The solid lines from the metal center 
indicate short coordination bonds (<2.6 Å), and the dashed lines indicate longer 
coordination bonds (>2.7 Å). Hydrogen atoms and the solvent water have been omitted 
for clarity.
The extended network structure of Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5H$_2$O) shows the same layered arrangement as observed in both Pb[B(Im)$_4$I] and Pb[B(Im)$_4$](NO$_3$). The benzoates occupy the interlayer spacing and arrange in an alternating monolayer. The presence of this monolayer significantly increases the spacing between the lead-borate tiers to a length of 5.99 Å between planes of the Pb atoms. Upon examination of the Pb-N bonds and the geometry around the metal center in Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5 H$_2$O), there are some changes relative to the parent Pb[B(Im)$_4$](NO$_3$) structure. The coordination of the benzoate has a larger effect on the Pb-N bond lengths, which increase to an average of ~2.62 Å. However, as in Pb[B(Im)$_4$I], the N-Pb-N bond angles do not change much upon substitution of the organic anion. The Pb-O bonds in Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5 H$_2$O) are similar to those observed for other structures with coordinated oxygens; we observe an average Pb-O bond length of ~2.51 Å compared to an average of 2.53(15) Å from the CSD.$^{142}$

The $^{207}$Pb SSNMR spectrum of Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5H$_2$O) shows a change in chemical shift relative to the parent compound. As can be seen in Figure 4.7b, the chemical shift of Pb[B(Im)$_4$](O$_2$CC$_6$H$_5$)(0.5H$_2$O) lies between those of the nitrate and iodide compounds, exhibiting the change to the Pb environment as one goes from the noncoordinating nitrate to the weak coordination of the carboxylate and then to the strong coordination of the iodide. Interestingly, the $^{207}$Pb SSNMR spectrum of the benzoate substituted material is close to that of the water-saturated nitrate material (Figure 4.5a). In the case of both the benzoate and water-saturated Pb[B(Im)$_4$](NO$_3$), there are oxygen
atoms close or bound to the metal center, which most likely governs the observed chemical shifts.

The difference (or lack thereof) in the lead coordination environment upon ligand binding may explain why iodide exchange can occur with retention of crystallinity. Since the bond lengths and angles do not significantly change upon substitution with iodide, the exchange of this anion could occur without disruption of the crystalline lattice. In addition, there is only a small change in the volume of the unit cell upon iodide exchange (~60 Å³, a 7% change). In contrast, replacing the nitrate with a benzoate imparts larger changes on the network structure. The bond lengths distort more than upon iodide exchange, and the volume of the unit cell increases by 13%. These differences may explain why Pb[B(Im)₄](O₂CC₆H₅)(0.5H₂O) only forms by self-assembly.

The ability to replace the nitrate in Pb[B(Im)₄](NO₃) with other anions bodes well for its potential use as a scaffold for advanced materials. We are currently investigating the incorporation of other organic and inorganic anions between the layers of Pb[B(Im)₄]⁺. In addition to examining the fundamental anion exchange chemistry of Pb[B(Im)₄]⁺ layered solids, we intend to incorporate guests with specific physical or chemical attributes. We anticipate that functional guest molecules will impart their properties onto the material.
Experimental

All reagents and solvents were purchased from Aldrich and used as received. Water was purified by using a Milli-Q reagent water system. Elemental analysis was performed at the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. Infrared spectroscopy was carried out on a Bomem MB-100 IR system. Sodium tetrakis(imidazolyl)borate was prepared as previously described.\textsuperscript{82,83,133}

Solid State Nuclear Magnetic Resonance: Solid-state NMR spectra were obtained on a Varian Unityplus-200 (4.7 T) spectrometer using Doty Scientific supersonic and standard magic-angle spinning (MAS) probes. Spectra were collected with MAS and sample spinning speeds of 2.7-8 kHz. Samples were packed into 7 mm silicon nitride rotors with Kel-F end caps. $^{15}\text{N}$ (20.5 MHz) Bloch decay spectra were acquired using a 200 s relaxation delay and a spinning speed of 2.7 kHz. $^{207}\text{Pb}$ (42.2 MHz) spectra were acquired using a Hahn-echo sequence with a 5 s relaxation delay and a spinning speed of 5-8 kHz. $^{15}\text{N}$ and $^{207}\text{Pb}$ chemical shifts were referenced to solid $^{15}\text{NH}_4^{15}\text{NO}_3$ ($\delta_{\text{NH}_4} = 0$ ppm) and 0.5 M Pb(NO$_3$)$_2$ ($\delta_{\text{Pb}} = -2941$ ppm) as external references, respectively. A 55 kHz decoupling field strength was used in all experiments. Isotropic chemical shifts in the $^{207}\text{Pb}$ spectra were determined by collecting the spectra at several sample spinning speeds.
Synthesis of \( \text{Pb[B(Im)}_4\text{]}(\text{NO}_3)(\text{nH}_2\text{O}) \) \((\text{n} = 0-1.5) \) (7): A solution of \( \text{Pb(NO}_3)_2 \) (331 mg, 1.0 mmol) in 10 mL deionized water was added to a 1:1 ethanol/water solution (10 mL) of sodium tetrakis(imidazolyl)borate (302 mg, 1.0 mmol). A white, microcrystalline precipitate of \( \text{Pb[B(Im)}_4\text{]}(\text{NO}_3)(\text{xH}_2\text{O}) \) formed immediately and was collected by filtration. Yield: 469 mg (82%). Large crystals of \( \text{Pb[B(Im)}_4\text{]}(\text{NO}_3)(\text{xH}_2\text{O}) \) were grown by slow diffusion of layers of the above two solutions at 60 °C. Anal. Calcd for \( \text{C}_{12}\text{H}_{12}\text{BN}_9\text{O}_3\text{Pb} \) (dried) (%): C, 26.2; H, 2.1; N, 22.3. Found: C, 26.33; H, 1.85; N, 22.84. IR (KBr): 3468, 3080, 1631, 1478, 1420, 1384, 1294, 1249, 1214, 1108, 1082, 1034, 1006, 940, 928, 816, 766, 663 cm\(^{-1}\). \( ^{13}\text{C SSNMR} \): 143, 131, 123 ppm.

Synthesis of \( \text{Pb[B(Im)}_4\text{]}\text{I} \) (8): Crystals of \( \text{Pb[B(Im)}_4\text{]}(\text{NO}_3)(\text{xH}_2\text{O}) \) (200 mg, 0.35 mmol) were suspended in a 10 mL aqueous solution of 1 equiv of NaI (51 mg, 0.35 mmol) and gently agitated for 24 h. Crystals of \( \text{Pb[B(Im)}_4\text{]}\text{I} \) were washed with water, collected by filtration, and air-dried. The yield was quantitative (110 mg). Anal. Calcd for \( \text{C}_{12}\text{H}_{12}\text{BN}_8\text{IPb} \) (%): C, 23.5; H, 1.9; N, 18.3. Found: C, 23.4; H, 1.80; N, 18.08. IR (KBr): 3467, 3080, 1484, 1475, 1299, 1247, 1212, 1106, 1081, 1037, 940, 928, 816, 762, 663 cm\(^{-1}\). \( ^{13}\text{C SSNMR} \): 148, 141, 131, 128, 124, 122 ppm.

Synthesis of \( \text{Pb[B(Im)}_4\text{]}(\text{C}_6\text{H}_5\text{COO})(0.5\text{H}_2\text{O}) \) (9): \( \text{Pb(NO}_3)_2 \) (218 mg, 0.67 mmol) was dissolved in 4 mL of deionized water and placed at the bottom of a narrow test tube. A solution was made of a 3-fold excess of sodium benzoate (290 mg, 2.0 mmol) and 1 equiv of sodium tetrakis(imidazolyl)borate (205 mg, 0.67 mmol) in 4 mL of deionized water.
water which was buffered with nitric acid to pH ~7.0. The benzoate/borate solution was carefully layered on top of the lead(II) solution, and the tube sealed and placed in an oven at 60 °C for 3 days. White, needlelike crystals of Pb[B(Im)₄](C₆H₅COO)(0.5H₂O) were collected by filtration. Yield: 302 mg (70%). Anal. Calcd for C₁₉H₁₈BN₈O₂.₅Pb (%): C, 37.0; H, 2.9; N, 18.1. Found: C, 36.61; H, 2.01; N, 17.58. IR (KBr): 3440, 3128, 1592, 1508, 1490, 1386, 1303, 1266, 1254, 1246, 1212, 1107, 1081, 1024, 936, 922, 851, 817, 754, 712, 683, 660 cm⁻¹. ¹³C SSNMR: 174, 143, 141, 139, 133, 130, 122 ppm.

**X-ray Crystallography:** The X-ray intensity data for compounds 7-9 were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å). The crystals were mounted on cryoloops using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystal. Frames were collected with a scan width of 0.3° in ω. The frames for each data set were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The data were corrected for absorption with the SADABS program. The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package until the final anisotropic full-matrix least-squares refinement on F² converged.¹² Experimental details for the three structures are shown in Table 4.2.

¹⁵NO₃⁻ **Anion Exchange Experiments:** A 300 mg sample of Pb[B(Im)₄](NO₃)(1.35 H₂O) was gently agitated in a 10 mL solution of one equivalent, 46.0 mg of Na¹⁵NO₃ for
24 h. The resultant exchanged crystals were then collected in quantitative yield. $^{15}\text{N}$ SSNMR spectra were taken of the sample prior to exchange, immediately after exchange, and after washing the exchanged sample with distilled H$_2$O.

**Thermogravometric Analysis:** Thermogravametric analysis was measured on a TA instruments 2050 device. The TGA measurements of compounds 7, 8, and 9 were carried out over a temperature range 25-600 °C at a scan rate of 10°/min.
The design of ordered solids, also known as crystal engineering, continues to be an important subfield of supramolecular chemistry.\textsuperscript{150} Over the past decade, a plethora of network systems have been synthesized, with many examples of coordination polymers\textsuperscript{153} and metal organic frameworks\textsuperscript{24,35} appearing in the literature. Although the fabrication of crystalline coordination polymers has become somewhat routine, two challenges remain in this field. With the maturation of crystal engineering, the development of functional solids is accelerating,\textsuperscript{35} with applications that range from the catalysis of organic transformations\textsuperscript{154-156} to magnetic materials\textsuperscript{115,157}. The second challenge concerns understanding the factors that control topology in network solids.\textsuperscript{158,159} While some advances have been made for certain ligand systems, there is still not a complete understanding of how network structures can be controlled through component selection, reaction stoichiometry, or crystal growth conditions.\textsuperscript{24,152} In
addition to theoretical studies, the generation of materials where small parameters have been changed can provide insight into the factors that affect network structure topology.

![Structures](image)

Figure 5.1. Structures of tetrakis(imidazolyl)borate (BX₄⁻, left) and tetrakis(4-methylimidazolyl)borate (BY₄⁻, right).

We have recently presented some of our initial work on network structures incorporating the coordinating anion tetrakis(imidazolyl)borate (Figure 5.1) and are currently exploring the structural parameter space of solids with this species. This synthon is negatively charged, structurally rigid, tetrahedral, and stable to temperatures in excess of 250 °C. Tetrakis(imidazolyl)borate can readily form network solids with metal cations and can afford solids with open or solvent-occupied metal sites. We have previously discussed how the conformations of tetrakis(imidazolyl)borate can contribute to structure in network solids. However, in addition to the rotamers of the borate, several other parameters could affect network connectivity, including the identity of the metal ion and the steric bulk of the organic fragment.
In this chapter, we are investigating how the identities of the components of a network solid affect its topology. In two earlier chapters, we described the layered network solid \( \text{Pb}[\text{B(Im)}_4](\text{NO}_3)(n\text{H}_2\text{O}) \) which can engage in mineral-like behavior and act as a scaffold for organic guests.\(^{141,160}\) In this section of the dissertation, we present three analogues of \( \text{Pb}[\text{B(Im)}_4](\text{NO}_3)n\text{H}_2\text{O} \) where either the metal and/or the borate have been slightly modified. Upon changing the metal from Pb to Tl and changing the borate to the more sterically hindered tetrakis(4-methylimidazolyl)borate, the structures of the metal-borate networks change significantly. Substitution of Tl for Pb both eliminates the need for the nitrate counterion as well as modifies the coordination at the metal center. The replacement of 4-methylimidazole for imidazole on the borate (Figure 5.1) increases the stereochemical activity of the ligand, which can change the coordination sphere around the metal center and significantly alter the extended network structure. By generating a series of related compounds, we observe that the symmetry about the metal center (holodirected versus hemidirected) in row 6 network solids controls the topology in these materials.

\section*{Discussion}

The reaction of a \( \text{Na}[\text{B(Im)}_4] \) and aqueous \( \text{Pb(NO}_3)_2 \) produces a product with the formula \( \text{Pb}[\text{B(Im)}_4](\text{NO}_3)n\text{H}_2\text{O} \) (7), where \( n = 0-1.5 \). This work has been published previously. Diffusion crystal growth from ethanol/water produces platelike crystals of this material, and the structure of the compound is readily elucidated by X-ray
crystallography. The repeating asymmetric unit of the crystal structure with 50% thermal ellipsoids is shown in Figure 5.2. In the crystal structure, there are 1.35 waters per asymmetric unit; however, the degree of hydration can vary in the bulk material depending on the extent of water intercalation. One imidazole ring is bound to the metal center in this unit, and the remaining heterocycles are coordinated to different lead sites in adjacent asymmetric units. The nitrate anion, required for charge balance, and the water molecules occupy the void space in the crystal.

Figure 5.2. Asymmetric units with 50% thermal ellipsoids of compounds (7) (Pb[B(Im)₄](NO₃)(nH₂O), (top left), (10) (Tl[BX₄], (top right), and (12) (Tl[BY₄](NO₃), (bottom right). A view of the asymmetric unit of (11) (Pb[BY₄](NO₃)) can be seen on the bottom left, showing the full structure of the borate. In (11), the disordered nitrate has been omitted for clarity.
Figure 5.3. Extended structure of (7) along the \(c\) axis (left) and \(a\) axis (right). Hydrogen atoms have been deleted for clarity.

In the case of \(\text{Pb[B(Im)\textsubscript{4}]}(\text{NO\textsubscript{3})}(\text{nH\textsubscript{2}O})\), the individual asymmetric units form an extended layered solid, as shown in Figure 5.3. The metal ions occupy sites at the layer interface, and the borates cross the layer itself. The nitrates and solvent water molecules reside in the void space between the \(\text{Pb}\)-borate tiers. There are no bonding contacts between the layers that have an approximate spacing of 3.4 Å. Each \(\text{Pb}\) ion is four coordinate and has a stereochemically active lone pair according to the VSEPR convention. \(\text{Pb(II)}\) is one of the lower main group elements that exhibits the “inert pair” effect, as demonstrated by the lack of participation of the \(6s^2\) electrons in covalent bond formation. If this pair of electrons exerts an effect on the structure at the metal site through nonspherical charge distribution, then an asymmetric geometry results, described as a hemidirected center. If the inert pair has no effect on metal geometry, then the VSEPR convention fails and a symmetric, holodirected geometry results.
Figure 5.4. Line illustrations showing the two types of metal-borate connectivity observed in compounds 7, 10, 11, and 12, where Q is either imidazole (X) or 4-methylimidazole (Y). The left diagram shows the connectivity observed in compounds 7, 10, and 12, which exhibit asymmetric metal coordination environments bridged by pseudotetrahedral borates. The right diagram shows an axial view of the connectivity in compound 11, where the tetrahedral borates bridge the square planar metal sites to afford a 3-D network structure. The nitrates in compound 7, (and solvent water in 7) fit above and below the layers, while the disordered nitrates lie along the axial ordinate in 11.

The formation of a layered geometry in 7 is not unexpected, considering the geometry of the metal center and the frequency of this morphology in Pb(II) solid-state structures. For example, the structure of the litharge form of PbO also adopts a layered topology with four-coordinate metal centers. The connectivity forms for two reasons: the asymmetric coordination geometry (square pyramidal) at the metal center; the volume ratios of the borate and Pb(II) cation. The radius ratio for the Pb(II) (1.19 Å) and the borate (boron to external nitrogen distance: ~5.06 Å) is 0.235, which is indicative of a lower coordination number ranging between 4 and 5 for the metal ion.
asymmetric geometry at the metal allows for the Pb-borate connectivity to close in on itself and form discrete layers. A line diagram displaying this layered metal-borate connectivity is shown in Figure 5.4. To test these observations on how geometry and radius ratio control structure in 7, we decided to generate several similar solids where the metal and/or the borate had been modified. With regard to the metal, we chose to make a thallium analogue of 7 to see if the metal radius does contribute to the formation of the layered topology. Mono-valent thallium is isoelectronic to Pb(II) and can exhibit the inert pair effect. The radius ratio of Tl(I) to tetrakis(imidazolyl)borate is 0.277, which is not much larger than in 7. Tl(I) can also exhibit asymmetric coordination environments similar to those of Pb(II). However, an analogous thallium borate would not require the presence of a nitrate counterion. In addition to changing the metal, we wanted to determine if the steric bulk of the borate anion could affect the geometry at the metal site.
Table 5.1. Crystallographic data collection and structure parameters for compounds 10-12.

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\[ a = R = \sum |F_0| - |F_c| \sum |F_c|, \quad R_w = [\sum w(F₀² - F_c²)²/w(F₀²)]^{1/2}. \]

The compounds Tl[B(Im)₄](10), Pb[B(4-MeIm)₄](NO₃)(11), and Tl[B(4-MeIm)₄](12) were synthesized using conditions identical with those for Pb[B(Im)₄](NO₃). All three procedures afforded crystalline products and large single crystals that could be investigated using X-ray diffraction methods. The parameters of the three data collections are presented in Table 5.1, and the structures of the repeating units of the three crystals are shown in Figure 5.2. Each compound shows an identical stoichiometry of metal to borate as seen in 7. Compounds 10 and 12 are both triclinic crystals with overall parameters similar to that found in 7; however, both materials lack a
nitrate counterion. Compound 11 is an orthorhombic crystal, and its asymmetric unit contains only one of the four imidazole rings on the borate. However, the stoichiometry of borate, lead, and nitrate in the empirical formula is identical with that of 7. In the solution of 11, the nitrate was disordered and was modeled as a diffuse contributor without specific atom positions.

We predicted that the structure of 10 would exhibit a network connectivity similar to that of 7 but without the presence of the nitrate counterion in the interlayer spacing. Inspection of the extended network structure of 10 (Figure 5.5) does indeed show that it closely resembles that of 7. The thallium borate units form two-dimensional layers, with the metal sites facing the interlayer spacing. Due to the charge balance between the borate and the Tl(I), there is no need for an additional counterion. As a result, the layers in the solid are closer together than in 7, and the volume of the asymmetric unit decreases significantly as one goes from 7 (911.84 Å) to 10 (708.20 Å). One important difference between the structures of 7 and 10 is the coordination at the metal; compound 10 has significantly longer metal-ligand bond distances than in 7. In particular, one imidazole-Tl bond is very long, 3.241(3) Å, which is more than 0.7 Å longer than the average Pb(II)-N bond distance of 2.52 Å in 7 and approaches the nonbonding limit. However, despite these long coordination bonds, the disphenoidal geometry results in a network structure very similar to that observed in 7 and shown on the left side of Figure 5.4.
Table 5.2. Selected bond lengths and angles for compounds 7, 10, 11, and 12.

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</table>

Figure 5.5. Extended structure of 10 along the b axis (left) and along the ac plane orthogonal to the b axis (right). The hydrogen atoms have been omitted for clarity. The right of the figure corresponds to the left view in Figure 5.4.
While switching from lead to thallium does not change the layered topology, modifying the borate can have a much more significant effect on the network structure. In compound 11, which contains tetrakis(4-methylimidazolyl)borate, the additional steric bulk affects the geometry around the metal. The environment changes from dispheniodal as in 7 and 10 to a square planar geometry of the imidazole rings in 11. The metal-ligand bond distance in 11 (2.653(5) Å) is only slightly longer than the average distance in 7, ~2.52 Å. Clearly, the steric bulk of the methyl group increases the stereochemical activity of the imidazole ring, widening the adjacent N-Pb-N bonds from an average angle of ~80° in 7 to ~90° in 11. As a result, the structure deviates from the VSEPR prediction, and there is no longer a clear stereochemically active lone pair contributing to the geometry. The axial sites in this structure are occupied by the disordered nitrate, which alternates between a symmetric bidentate and a monodentate coordination mode. The resultant structure is a symmetric, or holodirected, geometry about the metal center. The factors that control symmetric versus asymmetric geometries in Pb(II) compounds are still not understood fully; work continues in the fundamental coordination chemistry of lead.
Figure 5.6. Extended structure of 11 along the c axis (left) and b axis (right). Hydrogen atoms and disordered nitrate have been omitted for clarity. The disordered nitrates lie along the c axis in the same lines as the Pb atoms. The left of the figure corresponds to the right view in Figure 5.4.

The change from dispheniodal to square planar affects the network connectivity in compound 11 relative to that observed in 7 and 10. Figure 5.6 shows the network structure of compound 11, and the right side of Figure 5.4 displays an illustration of the connectivity observed from the axial direction. While the asymmetric geometries at the metal site in 7 and 10 result in the observed layer topologies, the highly symmetric coordination environment in 11 leads to three-dimensional connectivity. The metals line up along the c axis bridged by disordered nitrate counterions. The borates link the metal sites in a metal-borate square spiral pattern, exhibiting interlaced enantiomeric helices. Similar coordination modes have been observed in the group II metal imidazolylborates, but in those cases, the borates form closed loops with the metals and result in one-dimensional chains or two-dimensional layers. Due to the closed topology of 11, this
material does not reversibly intercalate water molecules nor does it exhibit ion exchange behavior with other anions, as observed in the layered compound 7.\textsuperscript{127,160}

Figure 5.7. Extended structure of 12 along the $b$ axis (left) and $a$ axis (right). The hydrogen atoms have been omitted for clarity. The solid lines about the metal ions indicate short coordination bonds (<2.6 Å), and the dashed lines indicate longer bonds (>2.7 Å). The right of the figure corresponds to the left view in Figure 5.4.

In compound 12, both the identity of the metal ion has been changed and the structure of the borate has been modified relative to that of species 7. While we expected that the charge balance in this material would eliminate any additional counterion in the solid, it was unclear what factors would dominate the network connectivity. Thallium prefers lower coordination numbers,\textsuperscript{151} which could allow for an asymmetric geometry and a layered topology, but the increased steric bulk of the 4-methyl imidazole ring could compete with the stereochemical activity of the lone pair. Elucidation of the structure of 12 (Figure 5.7) shows that long M-N bond distance preference for Tl(I) dominates the structure and that this allows for the formation of a layered topology similar to that in 7 and 10, as shown on the left side of Figure 5.4. As in 10, four imidazole rings are
coordinated to the metal center but exhibit much longer M-N bond distances than in 7 or 11. Interestingly, the average bond distance is shorter than in 10, which implies that crystal packing has a significant effect on the metal-ligand bond lengths in these compounds. The geometry is asymmetric and conforms to VSEPR prediction. Although the N-Tl-N bond angles are larger than those found in 10, the increased Tl-N bond lengths at the metal center translate into less crowding and a smaller effect of the increased steric bulk of the 4-methylimidazole.

In conclusion, we have begun to explore how the identity of metal ion and bulk of the borate affects a series of Pb[B(Im)₄](NO₃) analogues. Both Pb(II) and Tl(I) in these solids prefer asymmetric geometries, resulting in the observed 2D layered topologies. Increasing the steric bulk of the imidazole ring with a methyl group at the 4 position increases the nitrogen-metal-nitrogen bond angles of the solid. In 11, this results in a symmetric coordination environment around the metal and a closed 3D network structure. A similar bond angle widening is observed in 12, but due to the increased metal-ligand bond length, the geometry remains asymmetric and a layered structure results. We are continuing our investigation into the control of structure in Pb[B(Im)₄]X compounds and are expanding this work to different metals and borate structures as well as modifying the network through the identity of the interlayer counterion.
Experimental

All reagents and solvents were purchased from Aldrich and used as received. Water was purified by using a Milli-Q Reagent Water System. Elemental analysis was performed at the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois at Urbana-Champaign. Solution NMR spectroscopy was performed on a Varian VXR 300 MHz NMR instrument. Solid-state NMR spectra were obtained on a Varian Unityplus-200 (4.7 T) spectrometer using Doty Scientific supersonic and standard MAS probes. Samples were packed into 7 mm silicon nitride rotors with Kel-F end caps and the $^{13}$C samples collected at a spinning speed of 5kHz. Infrared spectroscopy was carried out on a Bomem MB-100 IR system. Mass spectra were obtained on a Micromass AutoSpec EBEhQ hybrid tandem mass spectrometer using FAB ionization. Sodium tetrakis(imidazolyl)borate was prepared as previously described.\textsuperscript{141}

**Synthesis of Na[B(4-MeIm)$_4$](13):** The synthesis of this material was based on a procedure developed by Trofimenko for sodium tetrakis(pyrazolyl)borate and is described by Chao and co-workers.\textsuperscript{82,133,165} Under neat conditions and in an inert nitrogen environment, 10.0 g (0.139 mol) of 4-methylimidazole was melted and stirred in the presence of 1.10 g (0.029 mol) of NaBH$_4$ in a round-bottom flask attached to an oil bubbler. As the heat was slowly increased to about 120 °C, the N$_2$ flow was stopped, and the H$_2$ gas evolution was monitored visually by observing the flow through the oil bubbler. Upon reaching 225 °C, H$_2$ gas generation ceased. The reaction mixture was
then cooled to 70 °C, and 200 mL of acetone was added with vigorous mixing. After isolation by vacuum filtration using a fine frit, the product was recrystallized from boiling ethanol and collected. A total of 1.23 g (12%) of the off-yellow product Na[B(4-MeIm)$_4$] was recovered. $^1$H NMR (D$_2$O): 2.098, 6.602, 7.218 ppm. $^{13}$C NMR: 11.98, 118.55, 137.82, 140.08 ppm. FAB MS (negative ion): m/z 335.4, (B(4-MeIm)$_4$). IR (KBr): 3444, 3145, 2918, 2867, 1655, 1568, 1490, 1449, 1383, 1326, 1264, 1233, 1139, 1053, 1007, 976, 940, 821, 765, 677 cm$^{-1}$.

**General Procedure for the Synthesis of Metal Borates:** The syntheses of the three variants were based on the synthesis of Pb[B(Im)$_4$](NO$_3$)$_2$·nH$_2$O (7).$^{127,160}$ A solution of the metal salt (1.0 mmol of metal ion) in 10 mL of deionized water was added to a 1:1 ethanol/water solution (10 mL) of sodium borate salt (1.0 mmol). White, microcrystalline precipitates typically formed immediately or upon minimization of the solution volume, which were then collected by filtration. Large crystals of each material could be grown by slow diffusion of layers of the above two solutions at 60° C.

**Tl[B(Im)$_4$] (10):** Compound 10 was generated using Tl$_2$SO$_4$ and NaB(Im)$_4$(7) with a yield of 83.2 mg (52%). IR (KBr): 3443, 3104, 1631, 1473, 1292, 1261, 1243, 1208, 1109, 1077, 918, 815, 768, 752, 664 cm$^{-1}$. Solid-State $^{13}$C MAS NMR: 123.09, 129.44, 144.44 ppm. Anal. Calcd for C$_{12}$H$_{12}$N$_8$BTl: C, 29.81; H, 2.48; N, 23.18. Found: C, 29.56; H, 2.40; N, 22.19.
Pb[B(4-MeIm)₄](NO₃) (11): Compound 11 was generated using Pb(NO₃)₂ and 13 with a yield of 17.2 mg (16%). IR (KBr): 3445, 3120, 2926, 1629, 1573, 1527, 1476, 1449, 1384, 1318, 1260, 1229, 1139, 1058, 1041, 1012, 976, 850, 824, 764, 672, 664, cm⁻¹. Solid-State ¹³C MAS NMR: 12.11, 121.36, 138.67 ppm. Anal. Calcd for C₁₆H₂₀N₉O₃BPb: C, 31.79; H, 3.31; N, 20.86. Found: C, 31.77; H, 3.37; N, 20.27.

Tl[B(4-MeIm)₄] (12): Compound 12 was generated using Tl₂SO₄ and 13 with a yield of 102 mg (56%). IR (KBr): 3445, 2919, 1633, 1478, 1445, 1383, 1330, 1263, 1232, 1140, 1008, 955, 849, 823, 767, 681, cm⁻¹. Solid-State ¹³C MAS NMR: 11.14, 14.61, 120.21, 138.10 ppm. Anal. Calcd for C₁₆H₂₀N₈BTl: C, 35.62; H, 3.71; N, 20.77. Found: C, 35.48; H, 3.65; N, 20.15.

**X-ray crystallography.** The X-ray intensity data for compounds 10-12 were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.710 73 Å). The crystals were mounted on cryoloops using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystal. Frames were collected with a scan width of 0.3° in θ. The frames for each data set were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The data were corrected for absorption with the SADABS program. The structure was solved and refined using the Bruker SHELXTL (version 6.1) software package until the final anisotropic full-matrix least-squares refinement on $F^2$. 

117
converged. Experimental details for the three structures are shown in Table 5.1, and selected bond lengths and angles are listed in Table 5.2.
CHAPTER VI

THE ASSEMBLY OF ORGANIC RADICAL ANIONS BETWEEN METAL-BORATE SCAFFOLDS

In supramolecular chemistry, discrete molecular building blocks are used to construct larger nanostructured assemblies.\textsuperscript{166,167} Crystal design, a subfield of this discipline, involves the assembly of molecular components into infinite three-dimensional networks.\textsuperscript{24,35,42,152} Often, regular arrays of molecules in crystalline network solids can exhibit unique physical properties, such as magnetism or non-linear optical behavior.\textsuperscript{50,70} Recently, we have found that we can use a lead borate metal organic scaffold to organize an anionic organic guest in a crystalline network.\textsuperscript{127,160} In this chapter, we present two network solids where the guest molecules are the carboxy-2,2,6,6-tetramethylpiperidinloxy free radical (4-carboxy-TEMPO) and carboxy-2,2,5,5-tetramethylpyrrolidinloxy free radical (3-carboxy-PROXYL), as shown in figure 6.1. These guest anions self-assemble into nanometer-spaced two-dimensional layers between tiers of lead tetrakis(imidazolyl) borate. Although both materials possess a layered architecture, the packing of the radical anions differs between the TEMPO and PROXYL materials. The inclusion of these radical guest molecules affords paramagnetic
coordination polymers, and bodes well for the future construction of layered magnetic materials. In assembled organic radicals, the magnetic properties of the materials depend on the organization and saturation of radicals; nitroxide radical layers have been shown to have spin interactions dominated by Heisenberg spin exchange.

Figure 6.1. Organic radicals, nitoxides, self-assemble in the Pb[B(Im)₄]⁺ scaffold.

We have presented several investigations into tetrakis(imidazolyl)borate (B(Im)₄⁻) (Figure. 6.3) network solids, and we recently uncovered a Pb-based material, Pb[B(Im)₄](NO₃)ₙH₂O, that exhibits a layered topology, with nitrates and solvent waters occupying the interlayer spacing. As in naturally occurring layered minerals, this compound can exchange the nitrate for other anions and can intercalate solvent molecules. In addition, when crystals are grown in the presence of a buffered excess of an organic anion in aqueous solution, the organic guests self assemble between the lead-borate layers of the solid. Previously, we have demonstrated that benzoates self assemble into monolayers between tiers of Pb[B(Im)₄]⁺ in the compound Pb[B(Im)₄](C₆H₅COO)₀.₅H₂O. This chemistry is similar to that observed in smectite clays, which have been
used to assemble a variety of guest molecules into ultra-thin monomolecular layers.$^{171-174}$

We have now turned our attention to organizing organic anions between the layers of Pb $[\text{B(Im)}_4]^+$ solids such that we can either carry out chemistry in the interlayer spacing, or impart a physical property onto the resultant solid. In this chapter, we have focused on the latter case, generating materials that possess the paramagnetism of the nitroxide radical guest. In addition, the electronic properties of the guest are affected by their packing in the interlayer spacing, as observed via EPR spectroscopy.

Figure 6.2. Tetrakis(imidazolyl)borate (left) and the asymmetric unit (middle) and on the right, the network structure of Pb $[\text{B(Im)}_4](\text{NO}_3)_n\text{H}_2\text{O}$.

Discussion

The growth of Pb$[\text{B(Im)}_4]^+$ solids in the presence of a buffered excess (2.5 equivalents in this case) of an anionic organic guest results in the insertion of this guest into the interlayer spacing of the resultant compounds. This procedure can be used to pack a variety of organic anions into lead-borate materials. In the present case, we can
insert the conjugate bases of 4-carboxy-TEMPO and 3-carboxy-PROXYL into the interlayer spacings of two new lead-borate materials, \( \text{Pb}\left[\text{B(Im)}_4\right]\)(4-carboxy-TEMPO)(14) and \( \text{Pb}\left[\text{B(Im)}_4\right]\)(3-carboxy-PROXYL)(\text{H}_2\text{O})(15). \) Slow diffusion of the reagent solutions results in the formation of crystalline products that are suitable for single-crystal X-ray diffraction.

The structures of both compounds were elucidated, and the asymmetric units of the two are shown in Figure 6.3. As in the parent material, \( \text{Pb}\left[\text{B(Im)}_4\right](\text{NO}_3) \), there is one borate per lead center and the organic radical anions provide charge balance. The coordination number increases in both compounds compared to the parent material. In 15, the carboxylate is bidentate (Pb--O bond distances 2.663(9) and 2.322(8) Å), with both oxygens coordinating to the metal in an asymmetric fashion. In 14, the asymmetric unit shows only one of the oxygens strongly coordinating to the lead (2.537(4) Å); the second oxygen coordinates to a Pb site in an adjacent asymmetric unit (2.540(4) Å). The second oxygen also weakly binds to the Pb in the asymmetric unit, with a very long bond length of 2.901(4) Å. This bidentate or bridging coordination mode exerts an effect on the number of imidazoles that coordinate to the metal center. In the parent \( \text{Pb}\left[\text{B(Im)}_4\right](\text{NO}_3) \) and in 15, each imidazole ring is coordinated to a lead center, and in compound 15 this results in a six-coordinate Pb(II). In 14, one imidazole per borate is non-coordinating in the Pb-borate layer, resulting in a five-coordinate metal center. In both compounds, the nitroxide oxygens of the TEMPO and PROXYL are only weakly interacting with adjacent metal centers, exhibiting Pb-O distances of 3.411(4) and 3.429(9) Å for 14 and 15, respectively.
The extended network structures of the two compounds show that the two organic radical anions pack very differently in the interlayer spacing, as shown in Figure 6.4. The lead borate units form two-dimensional layers in both compounds, with the lead metal sites facing the layer interface. Both the TEMPO and PROXYL anions bind to the Pb sites in this solid and occupy the interlayer spacing, however the shape of the anions and the mode of metal binding affect how the two guests arrange in their layers. In 14, the carboxylates bridge metal sites across the layer interface resulting in the TEMPO units splaying out in the interlayer spacing. In 15, however, the bidentate PROXYL units line up in an alternating monolayer with relative orthogonal orientations of the rings. In both cases, the nitroxides are orthogonal to the Pb-borate layers and approximately the same distances from the Pb centers. However, the nitroide ···nitroide separation differs between 14 and 15, with the spacing being shorter in the PROXYL material (6.250(13) and 6.455(13) Å) than in the TEMPO compound (7.210(5) Å).
Figure 6.4. Extended network structure of 14 along the b axis (left) and extended network structure of 15 along the ab plane (right). Hydrogen atoms have been omitted for clarity, and the radical guests are rendered in ball-and-stick format. The solid lines indicate coordination bonds less than 3 Å, while the dashed lines indicate bonds longer than 3 Å.

The EPR spectra of compounds 14 and 15 exhibit significant differences due to the environments of the nitroxide units (Figure 6.5). The spectra of both compounds have the same g value (2.007), but exhibit differing coupling constants. In nitroxide radicals, the nitrogen hyperfine coupling constant ($A_N$) is highly sensitive to the local environment, including hydrogen bonding and polarity.\textsuperscript{175-178} In compound 15, the EPR spectra exhibits observable hyperfine coupling ($A_N = 6.3$ G) due to the localization of the electron on the nitroxide nitrogen. This results from the microenvironment of the PROXYL in the interlayer spacing of 15, which orients the NO unit toward one of the oxygen atoms of a coordinated carboxylic acid (3.375(13) Å) and a solvent water molecule (3.130(13) Å). The latter interaction is short enough to qualify as a potential hydrogen bond. The spectrum of 14 shows a broad EPR transition which results from unresolved hyperfine coupling. This arises from the fact that the radical unit is in a local non-polar
environment in the interlayer spacing which does not induce charge separation on the nitrooxide. SQUID magnetic susceptibility measurements show that both 14 and 15 behave as simple paramagnets, as expected from the structures since the nitrosyl radicals are not close enough to interact to any significant extent. However, due to the differences in packing, a very small degree of antiferromagnetic coupling is observed in 15.

![EPR spectra](image)

Figure 6.5. EPR spectra of 14(TEMPO) and 15(PROXYL), with the spectrum of 15 exhibiting hyperfine coupling where $A_N = 6.3$ G.

In conclusion, we have used a layered Pb-borate network solid to organize organic guests into nanometer spaced monolayers. In the present case, the guest molecules are stable organic radicals. The two materials, a TEMPO and a PROXYL compound, exhibit different organizations of the guest radical molecules in the interlayer spacing, resulting in different electronic properties of the nitroxyl radicals between the two materials. We
are continuing our investigations into organizing magnetic guests on Pb-borate scaffolds, and are extending this work to other organic radicals as well as paramagnetic transition metal anions.

**Experimental**

**Synthesis of 14:** A 2 mL aqueous solution consisting of 0.050 g (0.17 mmol) of sodium tetrakis(imidazolyl)borate and 2.5 equivalents (0.078 g, 0.39 mmol) of 4-carboxy-TEMPO were buffered with one drop of 0.1 M NaOH to raise the pH to ~8. This resultant solution was layered on a 1 mL aqueous solution of one equivalent of lead nitrate (0.055 g, 0.17 mmol). The reaction vessel was sealed and incubated at 55 °C in an oven. Over three days, large single crystals grew that were suitable for single-crystal X-ray diffraction. 0.17 g of a red crystalline product was filtered off and collected with a 77% yield. IR(KBr): 3855, 3737, 3691, 3677, 3650, 3450, 3129, 2969, 2362, 2200, 1719, 1686, 1655, 1638, 1560, 1509, 1483, 1401, 1247, 1214, 1113, 1083, 943, 929, 820, 810, 754, 667 cm⁻¹. CHN anal. Calc. for PbBC₂₂O₃N₀H₂₈: C, 38.59; H, 4.09; N, 18.42. Found: C, 37.92; H, 4.06; N, 17.70%.

**Synthesis of 15:** An 8 mL aqueous solution of 0.10 g sodium tetrakis(imidazolyl)borate (0.33 mmol) and 2.5 equivalents of 3-carboxy-PROXYL (0.15 g, 0.78 mmol) was adjusted to pH 8 through the addition of 3 drops of 0.1 M NaOH. This solution was then layered atop a 4 mL aqueous solution of one equivalent of lead nitrate (0.11 g, 0.33
mmol). The test tube was sealed and incubated in an oven at 55 °C overnight. Large yellowish-green single crystals formed to yield 0.15 g of X-ray quality crystals in 68% yield. IR (KBr): 3905, 3855, 3840, 3448, 1735, 1719, 1701, 1686, 1655, 1638, 1618, 1578, 1560, 1542, 1509, 1499, 1490, 1476, 1459, 1384, 1294, 1248, 1213, 1108, 1081, 928, 816, 766, 668 cm⁻¹. CHN anal. Calc. for PbBC₂₁O₃₅N₉H₂₈: C, 37.06; H, 4.11; N, 18.53. Found: C, 36.98; H, 3.93; N, 17.39%.

**EPR Spectroscopy**

EPR experiments were carried out on a Bruker EMX X-band CW-EPR spectrometer consisting of an ER 041XG microwave bridge and an ER 4119HS cavity coupled with an ER 4131VT nitrogen-gas temperature controller (temperature stability of ±0.2 K). EPR spectra were acquired by taking a 42 s field-swept scan with the center field set to 3370 G, sweep width of either 150 G (PROXYL sample) or 600 G (TEMPO sample), microwave frequency of 9.434 GHz, microwave power of 0.2 mW, modulation frequency set to 100 kHz, and a modulation amplitude of 1.0 G. All spectra were acquired at room temperature. The solid samples were packed directly into 1-mm ID capillary tubes with the ends of the tubes capped with Critoseal (Fisher Scientific, Florence, KY), and placed into 4-mm fused quartz EPR tubes (Wilmad, Buena, NJ).

**X-Ray crystallography:** The X-ray intensity data for compounds 14 and 15 were measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-
ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ Å}$) operated at 2000 watts power. Crystals were mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystals. Frames were collected with a scan width of 0.3° in $\omega$.

Analyses of the data sets showed negligible decay during data collection. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of $F^2$ converged.$^{132}$ Experimental details for all of the structures are provided in Table 6.1.
Table 6.1. Crystallographic data and structure refinement details for 14 and 15.

Standard deviation parameters are given in parentheses.

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R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \quad R_w = \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w(F_o^2)^2}^{1/2}.
\]
CHAPTER VII

SEQUESTERING PERRHENATE WITH A BORATE-BASED COORDINATION POLYMER: A MODEL FOR PERTECHNETATE SEPARATION

The development of new crystalline materials using discrete molecular building blocks continues to grow rapidly, especially in the field of metal organic frameworks (MOFs). Often, these materials are designed with a specific function in mind, such as a particular chemical reactivity, like catalytic activity, or a physical property, like nonlinear optical behavior. In most cases, the topology governs the observed attribute; the specific arrangement of component molecules in the solid state affects the desired property. This is particularly true for network MOFs that exhibit an open topology. As in open framework minerals such as zeolites or clays, the porous or layered structure of a MOF determines the type of chemistry that is observed. Recently, we investigated a layered coordination polymer, Pb[B(Im)₄][NO₃](nH₂O), that exhibits chemistry similar to that observed in naturally occurring layered minerals, such as solvent intercalation and ion exchange. In this chapter, we present the perrhenate exchange chemistry of Pb[B(Im)₄][NO₃](nH₂O), resulting in complete replacement of the nitrates.
with perrhenate to form Pb[B(Im)$_4$](ReO$_4$) with retention of crystallinity in the network solid (Figure 7.1). Perrhenate is isoelectronic with the radioactive contaminant pertechnetate, TcO$_4^-$, and has been used to model pertechnetate separations by solid supports.\textsuperscript{183} To the best of our knowledge, this is the first investigation of a MOF as a candidate for pertechnetate radioactive waste remediation.

Figure 7.1. Schematic representation of perrhenate exchange in Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), where stoichiometric quantities of perrhenate exchange for the interlayer nitrates.

**Discussion**

In our previous work with Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), we demonstrated that the nitrates in the intralayer spacing of the solid could be exchanged for both $^{15}$N nitrate and for iodide, resulting in Pb[B(Im)$_4$]($^{15}$NO$_3$)(nH$_2$O) and Pb[B(Im)$_4$I], respectively. To evaluate the perrhenate sequestering ability of Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), we exposed crystals of this material to an aqueous solution containing a near stoichiometric (1.1
equiv) amount of NaReO₄ for 24 h. We used solid-state NMR (SSNMR) to monitor results from this exchange reaction. The $^{207}$Pb isotope is extremely useful for SSNMR studies, with a chemical-shift range encompassing almost 8000 ppm.¹⁴⁶,¹⁴⁷ Due to its large range, the chemical shift of the $^{207}$Pb nucleus is very sensitive to changes in its immediate metal environment.¹⁸⁴-¹⁹³

![Figure 7.2. The $^{207}$Pb SSNMR spectrum of Pb[B(Im)$_4$](NO₃)(1.5H₂O) (top) prior to exchange with 1.1 equivalents of NaReO₄ and after exchange (bottom).]
Figure 7.2 shows the $^{207}\text{Pb}$ SSNMR spectrum of the Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) crystals both before and after exposure to the perrhenate solution. The broad pattern of the $^{207}\text{Pb}$ spectrum (~2000 ppm) results from the large chemical shift anisotropy. Under magic-angle spinning (MAS) conditions, this pattern is broken up into a peak at the isotropic chemical shift, indicated with an asterisk, and a series of spinning sidebands. The changes in the overall shape of the pattern indicate that the substitution of ReO$_4^-$ for NO$_3^-$ does modify the electronic structure at the lead. In this chapter we have focused on the isotropic chemical shift of $^{207}\text{Pb}$, as our previous studies have shown that this parameter is sufficient to identify anion substitution.$^{127,160}$ The $^{207}\text{Pb}$ spectrum of Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) where n ~1.5 has an isotropic chemical shift of -533 ppm (reference, 0.5 M Pb(NO$_3$)$_2$ at -2941 ppm), determined by collecting the spectrum at several sample spinning speeds. After exposure, collection of the crystals, and washing, the material exhibits a change in isotropic chemical shift from -533 to -740 ppm. The lack of significant broadening of the peaks in the exposed spectrum is indicative of retention of crystallinity, and the chemical shift change is small and consistent with replacement of the noncoordinating nitrate with perrhenate. Similarly sized shifts are seen upon intercalation of water or exchange of other anions from between the layers of the parent Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) material.$^{127,160}$ For example, varying degrees of hydration induce chemical shifts between -533 and -460 ppm, while replacement of the nitrate for iodide, which forms a bond with the metal, changes the chemical shift to 357 ppm. We can also monitor exchange by using infrared spectroscopy and elemental analysis. The nitrate stretch in Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) appears at 1385 cm$^{-1}$. Upon
exchange, the band disappears and is replaced by a metal-oxygen stretching vibration at 908 cm\(^{-1}\).\(^{194}\) CHN elemental analysis also is consistent with complete exchange of nitrate for perrhenate.\(^{195,196}\)

Figure 7.3. The asymmetric unit (top) and the extended network structure (bottom) of Pb[B(Im)\(_4\)](ReO\(_4\)). The material has the same network connectivity as in the parent Pb[B(Im)\(_4\)](NO\(_3\))(nH\(_2\)O), and the perrhenates occupy the interlayer spacing.
We were able to isolate single crystals of the exchanged material Pb[B(Im)$_4$](ReO$_4$) by growing crystals of Pb[B(Im)$_4$](NO$_3$)(nH$_2$O) in the presence of a 5-fold excess of perrhenate. Single-crystal X-ray diffraction of crystals of this material resulted in elucidation of the structure of the exchanged material Pb[B(Im)$_4$](ReO$_4$). Figure 7.3 shows the asymmetric unit and layered network structure of Pb[B(Im)$_4$](ReO$_4$). The connectivity and stoichiometry of Pb(II) ions and tetrakis(imidazolyl)borate units are identical to that observed in Pb[B(Im)$_4$](NO$_3$)(nH$_2$O), except that in Pb[B(Im)$_4$](ReO$_4$) the nitrate has now been replaced by a noncoordinating perrhenate in the asymmetric unit void space. The extended network structure of the lead-borate layers is also identical to that seen in the parent material, and the perrhenates occupy the interlayer spacing between the lead-borate tiers. The volume of the asymmetric unit decreases slightly upon exchange of the perrhenate from 911.8 to 875.4 Å$^3$, and there are no crystallographically observed solvent water molecules in the exchanged structure. The $^{207}$Pb SSNMR spectrum of crystals of Pb[B(Im)$_4$](ReO$_4$) is identical to that of the exchanged material shown in Figure 7.2.

In conclusion, coordination polymers that exhibit ion-exchange properties have yet to be extensively investigated as potential waste-sequestering materials. In particular, due to their positively charged lattices, MOFs can be useful for separating anionic species from aqueous solution. We are continuing this work on anion separations with Pb[B(Im)$_4$]$^+$ based solids, and future work will evaluate this material for pertechnetate separations in both simulated and actual waste samples.
Experimental

**Synthesis of Pb[B(Im)$_4$](ReO$_4$):** In 4 mL of deionized water, 0.043 g (0.130 mmol) of Pb(NO$_3$)$_2$ was dissolved. Two mls of ethanol created the layer interface where 0.039 g (0.130 mmol) of Na[B(C$_3$N$_2$H$_3$)$_4$] and 0.179 g (0.650 mmol) of Na(ReO$_4$) in a 1:5 stoichiometric ratio in 8 mL of deionized water were carefully layered on the top of the metal solution in the test tube. The test tube was covered with parafilm and placed in the oven at 55°C. A few days later, large whitish transparent crystals formed such that x-ray diffraction elucidated the perrhenate anion between the layers. 0.0666 g (67%) of the crystalline product was washed with water and collected via filtration. IR (KBr): 3854, 3736, 3630, 3454, 3150, 3129, 2201, 1701, 1685, 1654, 1647, 1637, 1560, 1542, 1508, 1483, 1459, 1419, 1295, 1264, 1247, 1218, 1109, 1081, 1038, 926, 906, 876, 816, 755, 669, 658, 610, 497, 410 cm$^{-1}$. CHN anal. Calcd for C$_{12}$H$_{12}$N$_8$O$_4$B$_1$Re$_1$Pb: C, 19.50; H, 1.60; N, 15.20. Found: C, 18.67; H, 1.33; N, 14.08.

**Procedure for exchange of nitrate by perrhenate:** The exchange experiment was set up in a 500 mL beaker with 200 mL of deionized water and a stir bar. 0.584 g (1 mmol) of Pb[B(C$_3$N$_2$H$_3$)$_4$][NO$_3$]·(H$_2$O) were mixed with 0.310 g (1.1 mmol) of NaReO$_4$ for 24 hours. The sample was decanted and allowed to air dry. It was then placed in a humidity controlled environment where the hydration level reached 24% after a few days. This was accomplished through the presence of LiCl. It remained at that humidity level until the rotor was packed for the solid state NMR experiment to be completed about 2 months.
later. Solid-state NMR spectra were obtained on a Varian Unityplus-200 (4.7 T) spectrometer using Doty Scientific supersonic and standard magic-angle spinning (MAS) probes. The sample was packed into 7 mm silicon nitride rotors with Kel-F end caps. The $^{13}$C samples were collected at a spinning speed of 5 kHz.

**X-ray Crystallography**: The X-ray intensity data for the compound was measured at 100 K (Bruker KRYO-FLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2000 watts power. Crystals were mounted on a cryoloop using Paratone N-Exxon oil and placed under a stream of nitrogen. The detector was placed at a distance of 5.009 cm from the crystals. Frames were collected with a scan width of 0.3° in $\omega$. Analyses of the data sets showed negligible decay during data collection. The data were corrected for absorption with the SADABS program. The structures were refined using the Bruker SHELXTL Software Package (Version 6.1), and were solved using direct methods until the final anisotropic full-matrix, least squares refinement of $F^2$ converged.$^{132}$ Experimental details for all of the structures are provided in Table 7.1.
Table 7.1. Crystallographic data and structure refinement details for \( \text{Pb[B(Im)\textsubscript{4}](NO\textsubscript{3})(nH\textsubscript{2}O)} \) (7) (left) and \( \text{Pb[B(Im)\textsubscript{4}](ReO\textsubscript{4})} \) (16) (on the right). Standard deviation parameters are given in parentheses.

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\[ a \ R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}. \]

\[ b \ R_w = \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w(F_o^2)^2}]^{1/2}. \]
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141


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