Leveraging Non-Covalent Interactions between Small Organic Molecules and Inorganic Scaffolds in the Design of Advanced Materials

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LEVERAGING NON-COVALENT INTERACTIONS BETWEEN SMALL ORGANIC MOLECULES AND INORGANIC SCAFFOLDS IN THE DESIGN OF ADVANCED MATERIALS

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LEVERAGING NON-COVALENT INTERACTIONS BETWEEN SMALL ORGANIC MOLECULES AND INORGANIC SCAFFOLDS IN THE DESIGN OF ADVANCED MATERIALS

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Leveraging Non-Covalent Interactions between Small Organic Molecules and Inorganic Scaffolds in the Design of Advanced Materials

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Powder diffraction is a powerful tool for studying crystal structures, especially as it relates to interactions of small organic molecules with inorganic compounds. The first part of this dissertation involves small organic ligands interacting with metal-organic framework, MOF-74. The first and simplest iteration involves the crystal structure solution of a neat, liquid loading of \( n \)-propylmercaptan to the open metal sites within the MOF-74 pores. Later studies investigate the leveraging of a similarly sized bitopic ligand in the solution loading of 1,2-ethanediithiol, which results in the amorphization of MOF-74. Having no crystallinity, amorphous or severely defected materials can be a challenge to study. Herein, our studies reveal that the defects occur via protonation of the native framework and dislocation of the metal cations. The result is a material with fluorescent properties and quenching specific to the exposure to aqueous silver(I). Additionally, defected MOF-74 remains porous upon loadings of up to 10%.
In the second portion of this dissertation, the family of cobalt(II) hydroxide materials was explored utilizing an interesting ligand candidate, sorbate. The neat packing observed in other sorbate compounds lends itself to the organizing of densely packed hybrid layers in cobalt(II) hydroxide sorbate [Co(OH)(sorb)]. Due to the cluster-forming habit of Co(OH)(sorb), the structure is solved by powder diffraction techniques. Additionally, a transformation of the material after exposure to high pressures is explored. The material is determined to be antiferromagnetic below 41.7 K with a large hysteretic effect indicative of canted antiferromagnetic ordering.

The final section of this dissertation will be pure structure solution of two important chemicals of the last century, zineb and potassium sorbate. Zineb is a fungicide which has found use since 1943, where it was marketed under the tradename Dithane Z-78. Despite such a long tenure of use, the crystal structure remained unsolved for decades. Using powder techniques, we can solve the crystal structure, which serves as a proxy to the other fungicides in this family. Additionally, the food preservative, potassium sorbate, crystallizes in a polycrystalline fashion, explaining the lack of crystal structures present in major crystallography databases. Potassium sorbate’s crystal structure is solved as a complement to the cobalt(II) hydroxide hybrid material research, but also to understand why potassium sorbate doesn’t undergo topochemical reactions. The crystal structure reveals misaligned π-orbitals, precluding any reactivity toward polymeric or [2+2] dimer products.
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LIST OF ABBREVIATIONS

Atomic displacement parameters\hspace{1em}\text{ADP}

Differential scanning calorimetry\hspace{1em}\text{DSC}

Dioxido-benzenedicarboxylate\hspace{1em}\text{dobdc}^{4+}

1,2-ethanedithiol\hspace{1em}\text{EDT}

Energy-dispersive X-ray spectroscopy\hspace{1em}\text{EDS}

Ethylene bis(dithiocarbamate)\hspace{1em}\text{EBDTC}

Excited-state intramolecular proton transfer\hspace{1em}\text{ESIPT}
<table>
<thead>
<tr>
<th>Term</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Field-cooled</td>
<td>FC</td>
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<tr>
<td>Fourier-transform infrared spectroscopy</td>
<td>FTIR</td>
</tr>
<tr>
<td>Metal(II) 2,5-dioxido-1,4-benzenedicarboxylate</td>
<td>MOF-74</td>
</tr>
<tr>
<td>Metal-organic framework</td>
<td>MOF</td>
</tr>
<tr>
<td>Methanol</td>
<td>MeOH</td>
</tr>
<tr>
<td>N,N-dimethylformamide</td>
<td>DMF</td>
</tr>
<tr>
<td>Nuclear Magnetic Resonance</td>
<td>NMR</td>
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<tr>
<td>n-propylmercaptan</td>
<td>nPM</td>
</tr>
<tr>
<td>Powder X-ray diffraction</td>
<td>PXRD</td>
</tr>
<tr>
<td>Powder neutron diffraction</td>
<td>PND</td>
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<tr>
<td>Simulated annealing</td>
<td>SA</td>
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<tr>
<td>Sorbate</td>
<td>sorb</td>
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<tr>
<td>Tetrahydrofuran</td>
<td>THF</td>
</tr>
<tr>
<td>Thermogravimetric analysis</td>
<td>TGA</td>
</tr>
</tbody>
</table>
Trimethylsilyl  TMS

Zero-field cooled  ZFC
ACKNOWLEDGMENTS

First and foremost, I would like to thank my research advisor, Tomče Runčevski, for giving me the opportunity to join his research group. The years spent performing the research presented within this dissertation were some of the most fulfilling of my life, full of excitement for chemistry and research. I look back and wonder what made him give me a chance, and I still almost can’t believe that he did. I hope that I’ve given back at least a fraction’s worth of the opportunities he has given to me, and I wish for his research to continue to grow and reach the highest levels.

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CHAPTER 1

INTRODUCTION

1.1 Brief history of X-ray diffraction

In the late 1800s, research was underway studying the diffraction of X-ray radiation by crystals.\(^1\) X-rays possess wavelengths of the same order as the distances observed on the atomic and molecular level, enabling their interaction. Even from the earliest days, it was realized that if one knew the exact location of molecules and atoms within a crystal, then the X-ray diffraction pattern could be predicted, and vice versa.\(^2\) X-ray crystallography is a discipline that has shaped chemistry for more than a century, beginning with the first NaCl-type crystal structures reported by Bragg in 1913.\(^3\) Research from Bragg formed the foundation of crystallography in recognizing that X-rays could interact with planes in crystals at specific angles that related the spacing of the planes to the wavelength of the incident X-ray.\(^4\) The result was in-phase scattering of electromagnetic radiation at specific angles, or a diffraction pattern. If the incident radiation approaches a crystallographic plane at angle \(\theta\), it will be scattered at the same angle \(\theta\). These diffraction peaks are observed where the photon distance traveled from plane to plane is equal to an integer multiple of the wavelength.
1.2  Structure and function of MOF-74 and post-synthetic modification

Metal-organic frameworks (MOFs) have become a huge field of research over the last three decades, producing materials that exhibit porosity, high surface area, as well as a high degree of tuneability.\textsuperscript{5} These materials are built from a combination of multitopic organic ligands, called linkers, and metal nodes, which can be metal oxide clusters or simple cations. Their highly crystalline nature allows for crystal structure determination from powder diffraction patterns, which can monitor how the structure changes under various physical changes and/or stimuli. While perfectly crystalline materials easily allow structure to function correlations, defects to the base MOF to generate new properties and applications are of growing interest. These defected MOFs are more difficult to study on account of their reduced crystallinity, but they have been found to improve properties like gas adsorption,\textsuperscript{6,7} catalytic activity,\textsuperscript{8,9} and proton conductivity.\textsuperscript{10} When the defects become so severe that crystallinity is destroyed, the framework is described as amorphous, or exhibiting no diffraction pattern. Such amorphous MOFs have been used to improve, or even elicit new applications for the material, in such areas as drug delivery,\textsuperscript{11} pollutant capture,\textsuperscript{12} and in the production of composite materials.\textsuperscript{13}

Specifically, MOF-74 is constructed from bivalent metal ions and 2,5-dioxido-1,4-benzenedicarboxylate (dobdc\textsuperscript{4-}) linkers, with the stoichiometry of M\textsubscript{2}(dobdc). Examples of M include Mg\textsuperscript{2+}, Zn\textsuperscript{2+}, Co\textsuperscript{2+}, Fe\textsuperscript{2+}, Ni\textsuperscript{2+}, etc (Figure 1-1). MOF-74’s structure contains hexagonal pores spanning 8.67 Å in diameter, with so-called “open metal sites” spaced 5.4 Å apart, where additional ligands can bind (Figure 1-1). Upon activation, or removal of the adsorbed solvent that is present after synthesis, the MOF pores become receptive to Lewis basic adsorbants at the open metal sites. Such adsorbants have been widely studied, and can range from small molecules up to ligands just small enough to fit inside the pores. In particular, the loading of thiols into MOF-74
is a neglected area of research, and we sought to explore the possibilities of thiol ligands for application or post-modification. Utilizing two thiol ligands, \( n \)-propylmercaptan (nPM) and 1,2-ethanedithiol (EDT), we probed the effect of mono- and ditopic ligand interaction when the length of the ligand is just shorter than optimal for interaction with adjacent sites.

**Figure 1-1.** Components of MOF-74 (left) and the crystal structure of methanol-solvated MOF-74 (right).

### 1.3 Applications of absorbate interaction with MOF-74

The open metal sites within the pores of MOF-74 suit it well for capturing small molecules, such as hydrogen,\(^{14}\) carbon dioxide,\(^{15,16}\) and water.\(^{17,18}\) In the case of carbon dioxide capture, the Long group’s research utilized a diamine bound at the open metal site to produce a carbamate upon exposure to carbon dioxide. The formed carbamate could then be removed and reloaded with fresh diamine to repeat the process.\(^{19}\) Because of these properties, MOF-74 has even been considered for oral drug delivery formulations, where active pharmaceutical ingredients can be captured within the MOF pores.\(^{20}\) Therefore, simple interactions with the open metal sites are generally found to be a reversible process, producing crystalline compounds easily studied by diffraction.
1.4 Structural changes of MOF-74 caused by adsorbates

The interactions of adsorbates within the MOF structure can cause structural disruptions, like the case of xylene separation in MOF-74, where a structural change resulted in major changes to the powder diffraction pattern intensities including new low angle peaks.$^{21}$ A p-xylene molecule binds to two open metal sites with weak van der Waals forces, resulting in a doubling of the unit cell to fit the additional low angle peaks. The unit cell doubling accommodates the distorted, irregular hexagonal pores. In the case of xylenes, the structural shift of the MOF-74 pores increases their capacity from 3 molecules per layer to 4, enabling greater xylene packing in the distorted framework.

1.5 Cobalt(II) hydroxide

Cobalt(II) hydroxide is a layered material in which sheets of octahedrally coordinated cobalt(II) stack regularly on top of one another (Figure 1-2).$^{22}$ In an arrangement known as a layered double hydroxide, each cobalt(II) cation is bound by 6 hydroxides; three from the top of the layer, and three from the bottom. Each hydroxide anion binds to three cobalt(II) ions from one side of the layer. Depending on the method that cobalt(II) hydroxide was produced, it may occur in the α- or β-phase, where the only difference is the separation of layers by anionic impurities present in the α-phase. The α-phase has a larger spacing, as well as more desirable electromagnetic properties. This inspires an alteration or “hybridization” of the base material, accomplished by using organic ligands to space the layers as a mimic of this structural difference present in the α-phase.
The brucite-type crystal structure of cobalt(II) hydroxide layers (A), interlayer spacing (B), and a representative octahedral cobalt center (C).

### 1.6 Interlayer separation of cobalt(II) hydroxide with organic ligands

The material hybridization of cobalt(II) hydroxide to an inorganic/organic composite material has gained popularity over the last two decades, resulting in materials with interesting electromagnetic properties through changes made to the coordination environment of the cobalt(II), as well as increasing the interlayer spacing to decrease magnetic interaction of the adjacent layers. Two examples of such materials are produced from cinnamate\textsuperscript{23} and terephthalate\textsuperscript{24} ligands, and result in an antiferromagnetic material with magnetic transition temperatures around 50 K, which is higher than the 12.3 K Néel temperature of Co(OH)\textsubscript{2}. Two ligand options exist: bitopic ligands that bridge adjacent layers together,\textsuperscript{25} or monotopic ligands that interact with ligands on adjacent layers, with end-on-end or interlocking structures being observed.\textsuperscript{26}
1.7 Sorbate as a ligand

Sorbic acid, \((2E, 4E)\)-hexa-2,4-dienoic acid, is an interesting ligand candidate as a small, linear molecule that can pack tightly together with the added stabilization of \(\pi\)-orbital stacking (Figure 1-3). As our choice modifying ligand to hybridize \(\text{Co(OH)}_2\), we can expect binding of the carboxylate functional groups to the cobalt(II) ions present in the layer, and a regular packing of the sorbate ligands between the layers to produce a material with a high degree of crystallinity and stability. Additionally, certain sorbate salts have been shown to undergo topochemical polymerization.\(^{27,28}\) However, as with all topochemical reactions, the \(\pi\)-orbital alignment and proximity of reactive double bonds are of key importance,\(^{29}\) so the crystal structure of the sorbate hybrid material should precede testing for such reactivity. Therefore, our interest in sorbate is two-fold, as we seek to test both the effect of increased spacing on the magnetic properties of cobalt(II) hydroxide, as well as the properties and reactivity of the ligand post-synthetically in a topochemical sense.
Figure 1-3. The published structure of sorbic acid looking down the $b$-axis, showcasing the tight packing of the small linear molecules.$^{30}$

1.8 Structure solution of unsolved crystals from powder diffraction

Zineb and potassium sorbate, as well as their derivatives, have found considerable use over the last century, with zineb as a fungicide for crops and potassium sorbate as a widely used food preservative. Both chemicals, despite such wide economic interest, have been left unsolved due to a crystal habit that makes it impossible via single crystal methods. Zineb forms very small, irregular polycrystallites, while potassium sorbate shows dendritic crystal growth, both a symptom of large anisotropic preference. After solving the crystal structure, the growth habit of the two samples can be rationalized with the interaction strengths of the various faces of the structure in mind.
1.9 References


CHAPTER 2

INTERACTION OF THIOLS WITH MOF-74: STRUCTURE AND PROPERTY CHARACTERIZATION

2.1 Introduction

MOF-74 is constructed from bivalent metal nodes (Mg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Zn$^{2+}$, Ni$^{2+}$) that are connected by linker, 2,5-dioxido-1,4-benzenedicarboxylate (dobdc$^{4-}$). This particular family of MOFs has been extremely well studied with hundreds of research articles being published to date. The resulting material exhibits hexagonal pores, formed from a network of interlocked metal(II) carboxylate chains. Each cation has square pyramidal molecular geometry, providing a site for an additional ligand (non-linker) to attach. These so called “open metal sites” (Scheme 2-1) allow binding of ligands for permanent or temporary modifications of the material, and have been the focus of many studies of post-modification. MOF-74 actually represents a larger family of hexagonally pored materials that maintains these open metal sites and hexagonal pores. Examples of some variants include extended linkers for larger pores, meta-substituted linkers, heteroatom substitutions in the core or terminal groups, and multivariate materials with mixed metals or linkers. These variations produce slight differences in structure but allow for similar absorption properties at the open metal sites. Therefore, MOF-74 can be considered the simplest representation for this family of materials.
Scheme 2-1. Structure of MOF-74, showing the open metal site geometry (magnified region)

In some cases, adsorption of molecules in the pores can slightly disrupt the shape of the pores. Even molecules that interact weakly with the open metal sites can distort the pores, as observed with the loading of $p$-xylene into Co-MOF-74.\textsuperscript{13} While the material is still crystalline in the distorted state, the unit cell volume is quadrupled, due to a doubling of two of the unit cell axes lengths. This doubling accommodates the distorted shape of the hexagonal pores. We sought to further probe this effect by using strongly adsorbing, bitopic ligands. While many adsorbates and ligands bound to MOF-74 have been shown in the literature, thiols remain a neglected area. Therefore, we sought to use thiols to probe the interaction of ligands with MOF-74 and observe the resulting changes to the structure and crystallinity.

The simplest thiol interaction with MOF-74 can be achieved by using 1-propanethiol, also called $n$-propylmercaptan (nPM). The aliphatic portion of the ligand is the perfect length to span from the open metal site to the center of the pore, or to another open metal site. In such a simple case, it would be expected to observe the aliphatic moieties interacting more preferentially with like aliphatic chains and extending into the center of the pores. Thus, the observed interaction between a thiol functional group and the open metal site of MOF-74 should be rather elementary.
However, if we want to cause distortion or even destroy the degree of crystallinity, an adsorbate with two strong interactions at each of two neighboring metal sites should be used. 1,2-Ethanedithiol (EDT), a bitopic ligand of similar length to nPM, has been selected for this job. EDT can strongly bind two metal sites within the MOF pore, while being shorter (4.6 Å) than the optimal length for the ideal connecting interaction (5.4 Å), as depicted in Scheme 2-2. Such an interaction will exert a pulling force on the metal centers, potentially leading to their dislocation from the native MOF sites. Additionally, interaction of a thiol group with a Lewis acid will increase the Brønsted acidity of the thiol proton. Combining these ideas of dislocating metal cations and increased acidity, the bitopic interaction should disrupt the symmetry of the pore, whether as distortion of the hexagons (unit cell doubling) or by framework destruction, or amorphization, via protonation of the linkers by the “activated” thiols.

Scheme 2-2. Depiction of a section of MOF-74, comparing the distance of adjacent open metal sites to the length of EDT
The resultant defected material, described in Scheme 2-3, shows protonation of the linker phenoxy group causing permanent, irreversible damage to the framework structure. Formation of phenol groups adjacent to carboxylate groups in the ortho-position results in a class of material known to undergo excited-state intramolecular proton-transfer (ESIPT) fluorescence. The resulting material from the EDT-loading experiments will be characterized via fluorescent spectroscopy to test for the presence of such phenols, as evidence of linker protonation.

Scheme 2-3. The Zn-MOF-74 scaffold with proposed defects caused by the bidentate ligand ethanedithiol.

2.2 Results and Discussion

2.2.1 Synthesis and activation of MOF-74

MOF-74 can be prepared by first dissolving a bivalent metal nitrate with the acidic form of the linker, 2,5-dihydroxyterephthalic acid (H₄dobdc), in DMF or mixed solvent. A solvothermal synthesis in a sealed bottle heated to 120 °C results in the formation of MOF-74 crystals. In this work, a separate method was used for Co-MOF-74 and Zn-MOF-74, both resulting in highly crystalline materials that can be activated before the neat loading experiments. Activation is the
process of heating a MOF sample in a scintillation vial to 160 °C under dynamic vacuum to remove solvent molecules from the pores. For methanolic solution loadings, the MOF was not activated first, as the final product of MOF synthesis is a methanol-solvated MOF and activation would have been purposeless.

2.2.2 Neat loading of \( n \)-propyl mercaptan @ Co-MOF-74

\( n \)-PM was loaded into Co-MOF-74 by introducing the activated MOF to liquid \( n \)-PM, in the inert atmosphere of a dry box. As expected, the crystal structure shows the thiol bound to the open metal site within the pores. Due to the large number of variables in the crystal structure solution, the Co-MOF-74 component was kept fixed, while the position of \( n \)-PM was allowed to freely optimize to a global minimum utilizing the real space global optimization simulated annealing (SA) technique (Figure 2-1). After convergence of the solution to a global minimum, the occupancy of the \( n \)-PM within the MOF was determined to be 90\%, indicating that the remaining open metal sites were occupied by residual solvent molecules from the MOF synthesis, or simply left open. Once a global minimum was reached, the structure was further optimized with Rietveld refinement, to obtain a structure with a predicted PXRD pattern in agreement with the experimental result. The atomic displacement parameters (ADPs) of the ligand carbon atoms were refined separately to allow for greater degrees of freedom on the aliphatic chain. The result, in Figure 2-1, shows the larger ellipsoids on the ligands indicative of more variability in the chain conformation.
Figure -2-1. The structure of nPM @ Co-MOF-74, as determined by simulated annealing of the neat loaded sample. The atoms are presented as ellipsoids of size relating to the atomic displacement parameters. Colors were: Co (blue), S (yellow), O (red), C (dark gray), H (light gray).

Since the nPM ligand has such high degrees of freedom, the solution was optimized with periodic density functional theory by Daniel Sethio in Elfi Kraka’s computation research group. The relaxation of atomic positions and unit cell parameters led to a structure in agreement with the result of the Rietveld refinement (Figure 2-2 and Table 2-1).
Figure 2-2. An overlay of the crystal structure obtained from simulated annealing (blue) and DFT optimization (red). Credit: Daniel Sethio

Table 2-1. Unit cell parameters for nPM @ Co-MOF-74

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<tr>
<th>Parameter</th>
<th>1-propanethiol-Co2(dobdc)</th>
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2.2.3 Solution loading of \( n \)-propyl mercaptan into Zn-MOF-74

In a methanolic solution loading of nPM, the crystal structure determined was very similar to the neatly loaded sample. Again, the thiol is bound to the open metal site, with the aliphatic portion facing the interior of the pore (Figure 2-3). However, the entire sample isn’t as perfect as the crystal structure suggests, as there were two small new peaks that are not accounted for. This discrepancy rectified with a two-phase Pawley fitting.

![Figure 2-3. The crystal structure of nPM@Co-MOF-74 produced from solution loading, looking down the c-axis. Atom colors were: Zn (blue), S (yellow), O (red), C (gray).](image)

2.2.4 Structure distortion observed for nPM

The sample, while crystalline, showed two additional peaks that could only be explained by doubling of the unit cell in the \( a \) - and \( b \)-axes caused by a distortion of the regular hexagons. The resulting doubled unit cell, confirmed with a two-phase Pawley fitting (Figure 2-4), is similar to the work by the Long group on xylenes.\(^ {14} \) Therefore, we can hypothesize that the thiol group is bound as usual for a majority of the sample, but in a small fraction of the sample, the methyl...
group interacts weakly with an adjacent metal site, causing a slight distortion. While this unit cell doubling only affected a small fraction of the sample, it did show that distortion of the sample can occur with a monotopic ligand that only binds one site strongly and the other weakly.

![Figure 2-4](image)

**Figure 2-4.** The Pawley fitting curve for the nPM @ Zn-MOF-74 considering one phase (top), showing that the small unit cell doesn’t completely fit the pattern, as there are two peaks that are completely neglected. The corrected Pawley (bottom) considered a doubled unit cell as a minor phase to account for the missed peaks.

2.2.5 **Solution loading of 1,2-ethanedithiol in MOF-74**

Solution loading of 100% EDT (referring to a 1:1 ratio between open metal sites and EDT) resulted in a nearly amorphous sample by PXRD, indicating that most of the native connectivity
and crystallinity was destroyed. Stepwise addition of EDT from 0-100%, in 10% increments, showed a gradual destruction of the framework, as seen in Figure 2-5.

![Figure 2-5](image.png)

**Figure 2-5.** Stepwise addition of EDT, as observed by PXRD patterns showing a gradual loss in the diffraction peaks at increased loading.

From the FTIR spectra, Figure 2-6, an sp³ C-H stretching at 2900 cm⁻¹, proved that EDT incorporates into the defected MOF. Further analysis of the FTIR spectra shows a broadening of the carbonyl stretching peak centered at 1620 cm⁻¹ with increased loading, as well as broadening bands for the aromatic stretching, symmetric carboxylate stretching, and antisymmetric carboxylate stretching modes in the region from 1400 – 1580 cm⁻¹. The broadening is symptomatic of the loss of regular structure, as presumably many variations of local environments exist within the defected material.
To confirm the existence of sulfur, as well as oxygen and zinc, within the defected material, electron dispersive X-ray spectroscopy (EDS) imaging was used. The EDS image, Figure 2-7, shows evenly dispersed Zn, S and O atoms, indicating that the defects are homogenously spread throughout the material. Also important to note from the backscattering image, the morphology of the defected material is borrowed from the original MOF shape, as the material still “looks” crystalline from the sharp edges and flat faces.
Figure 2-7. EDS imaging of the 100% EDT loaded sample showing, backscattering (top left), oxygen (red, top right), sulfur (green, bottom left), and zinc (blue, bottom right)

The porosity of the defected MOF as it relates to the amount of EDT added was measured, and showed an impressive maintenance of the porosity up to 10% of loading (Figure 2-8). Not surprisingly, the porosity disappeared at 100% loading, as at this point the pores are likely collapsed or full of EDT.
To test for the presence of protonated MOF linker, the sample was subjected to UV irradiation and showed a bright fluorescence, as compared to the non-fluorescent methanol-solvated and nPM-loaded MOF, Figure 2-9. This confirmed the transfer of protons from the EDT ligand to the MOF linker, partially explaining the amorphization due to the breaking of linker bonds to the zinc(II) cations. As nPM samples didn’t have fluorescent, it can be ascertained that the bitopic binding of EDT is partially responsible for the protonation, presumably from the dislocation of the cations.
Fluorescent spectra were observed to have an excitation maximum at 368 nm, and emission maximum at 510 nm, for a large Stokes shift indicative of an ESIPT mechanism (Figure 2-10). For dosed loading of EDT, the fluorescence increased proportionally to the destruction of the MOF up to a maximum intensity near 75% loading (Figure 2-11). If the interaction of EDT to the open metal sites were purely bidentate binding to single Zn-ions, we would expect a maximum occurring at 100%. Similarly, if every EDT interacted with exactly two open metal sites, we would expect the fluorescent maximum to occur at 50% loading. This value of ~75% infers a case where each EDT can interact with either one or two open metal sites.
Figure 2-10. Fluorescent excitation (left) and emission (right) for highly loaded (500%) samples of EDT (red), nPM (green) and MeOH (blue).

Figure 2-11. Fluorescent intensity as a function of loading %. Credit: Dr. Uroob Haris
2.2.6 Transition metal quenching observed selectivity

To test the sensing ability of the composite EDT-Zn-MOF-74 material, both the MeOH-solvated MOF and the defected EDT-MOF were soaked in solutions containing various transition metal ions (Figure 2-12). As expected, the MeOH-solvated MOF did not change from its normal state of very low fluorescence. However, for the EDT-Zn-MOF-74 samples, a significant reduction of fluorescent intensity was observed after the material was soaked in aqueous solutions of silver(I) and iron(III). The sample soaked in the silver(I) solution turned black, which may indicated a reduction to silver(0). For the Fe(III) sample, it is likely that the strong Lewis acidic nature of FeCl₃ destroyed the material, as a significant amount of EDT-Zn-MOF-74 was dissolved during this process.

While this selectivity may not find practical use, it shows that a MOF can be converted to a non-crystalline, highly fluorescent material that has some innate selectivity for a subset of transition metal cations. With a proper design, it is probable that a specific species could be targeted for a knock-down fluorescence sensor.
Figure 2-12. Images of the samples soaked in aqueous transition metal solutions under UV irradiation (top), and the fluorescence imaging intensities (Credit: Uroob Haris)
2.3 Conclusions

The difference between monotopic and bitopic ligands during solution loading was observed to result in two starkly contrasting materials. The solution loading of nPM resulted in a crystal structure very similar to that of the neatly loaded sample, while the solution loading of EDT contrastingly resulted in a loss of the crystallinity as observed by PXRD. The nPM-loaded sample was rather unchanged in terms of fluorescence, while the EDT-loaded samples became intensely fluorescent with a large Stokes shift. This result confirmed the protonation of the MOF linker was unique to the bitopic ligand, implying that a “pulling” effect of the bitopic ligand was in part responsible for the protonation and simultaneous structure destruction.

The large Stokes shift implies that an ESIPT mechanism is responsible for the fluorescent properties of the composite material, consistent with a protonated MOF-74 linker. In fact, computational studies showed that the MOF linker may not only become protonated but could potentially be replaced altogether by two EDT dianions, stitching together the gap formed. The overall resultant material is fluorescent due to protonation, reaching maximum intensity at ~75% loading and not increasing or decreasing upon higher loading dosages.

Experimental observation and computational studies infer that the material is a composite of zinc(II) ions, partially protonated linker, and EDT. Quenching of the fluorescence after exposure to aqueous solutions containing transition metals was likely dependent on the affinity for such ions for the composite material, in addition to their innate ability to quench the fluorescence of our system.
2.4 Experimental

2.4.1 Materials

nPM, Co(NO\textsubscript{3})\cdot6H\textsubscript{2}O and Zn(NO\textsubscript{3})\cdot6H\textsubscript{2}O were purchased from Alfa Aesar. DMF and MeOH were purchased from Fisher. EDT was purchased from TCI. 2,5-dihydroxyterephthalic acid was synthesized using a literature procedure\textsuperscript{17} from potassium carbonate (Fisher), formic acid (Alfa Aesar), and hydroquinone (Alfa Aesar). All chemicals were used as received without any additional purification or treatment.

2.4.2 Analyses

Powder X-ray diffraction (PXRD) data was collected on a laboratory Stoe Stadi-P powder diffractometer, operating in Debye–Scherrer geometry. The diffractometer was equipped with a molybdenum X-ray source and monochromatic Mo-K\textalpha\textsubscript{1} radiation (λ = 0.709 30 Å) obtained by a primary Ge(111) monochromator. The goniometer had 2 circles (140 mm and 80 mm). Two linear position sensitive silicon-strip (Mythen Dectris 1K, 50 μm step size) detectors were used to record the scattered X-ray intensity. The instrumental parameters for the diffractometer were refined against LnB6 NIST standard. Before data collection, each sample was dried under an inert atmosphere and densely packed in a borosilicate capillary (0.5 mm diameter). Diffraction data was collected at room temperature. The capillary was rotated for better particle statistics during the measurements. Diffraction data used for crystal structure solution and refinement was collected for 24 h utilizing the complete range of the two 1K detectors. Diffraction data for assessing the crystallinity and/or phase purity of the samples was collected for 1h.

Infrared spectra were collected with a Fourier transform infrared (FTIR) Thermo Fisher Nicolet iS50 spectrometer. The sample was ground, mixed with KBr powder, and pressed into a wafer.
The thermogravimetric analysis (TGA) was performed with Netzsch TG 209 F3 Tarsus instrument. The samples were placed in an alumina crucible and heated from 298 to 1273 K, at heating a rate of 10 K/min, under a constant flow of nitrogen.

The SEM images were obtained using a Leo 1450VPSE variable pressure electron microscope with a LaB6 tungsten filament electron source. Samples were measured without preparation, such as carbon coating. Images were obtained using a standard Everhart Thornley SE detector, a variable pressure SE detector, and a QBSD solid state backscatter detector.

Fluorescent emission/excitation spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer. For each measurement, 2.0 mg of sample was pressed between two glass slides and secured in a sample holder. Fluorescent imaging was captured using an EVOS-fl fluorescence microscope using a DAPI filter cube (λex = 357/44 nm, λem = 447/60 nm) with LED = 70% and integration time = 15 ms through a 40x objective. Three different fields of view were captured for each sample. The acquired images were processed using ImageJ software by converting to 8-bit, adjusting threshold using the “Huang” preset algorithm to create a selection, and then measuring the mean pixel intensity of the selection. Average values for each sample were obtained from three separate measurements, with standard deviation being used for error bars in the graph produced. The fluorescent imaging was performed by Uroob Haris from the Lippert group.
2.4.3 MOF synthesis and loading procedure

Preparation of Co-MOF-74

2,5-dihydroxyterephthalic acid (0.964 g, 4.86 mmol) and cobalt(II) nitrate hexahydrate (4.754 g, 16.34 mmol) were added to a 1 L pressure bottle, followed by 400 mL of a 1:1:1 solvent mixture of DMF–ethanol–water. The solvent mixture was sparged with nitrogen gas for 60 min immediately prior to use. Once the solids were dissolved, the bottle was placed in a 100 °C oven for 24 h before removing and cooling to room temperature. The mother liquor was decanted off and replaced with 200 mL of DMF, the bottle capped and placed into the oven for 24 h. The DMF soaking process was repeated two additional times, refreshing the DMF once per day. After decanting the DMF for the third time, the same procedure was repeated with methanol three times, with the oven set to 60 °C. Finally, the solid was filtered and dried in air overnight. The Co$_2$(dobdc) was activated by transferring a small amount to a scintillation vial and heating to 160 °C in an oil bath, under dynamic vacuum, for 18 h.

Preparation of Zn-MOF-74

The material Zn$_2$(dobdc) was synthesized following the literature; 2,5-dihydroxyterephthalic acid (2.00 g, 10.1 mmol) and zinc nitrate hexahydrate (8.00 g, 26.9 mmol) were transferred to a 1 L pressure bottle and dissolved in 400 mL of DMF, which had been degassed with nitrogen. The solids were dissolved, then 25 mL of degassed, deionized water was added, and the bottle placed into a 100 °C oven for 24 h. The red-orange supernatant was decanted, and the yellow-green crystals were soaked in approximately 200 mL of DMF for 8+ hours before decanting and replacing the solvent. After two more DMF soaks following the same procedure, methanol was added, and the bottle placed into a 60 °C oven for 8+ hours. After two more methanol soaks following the same procedure, the solid was filtered and dried on the benchtop. PXRD analysis
confirmed that the product is a single-phase, highly crystalline, MeOH-solvated Zn$_2$(dobdc). The vial was then transferred to a glovebox for storage.

**Loading of nPM into Co-MOF-74**

1-propanethiol–Co$_2$(dobdc) was prepared by soaking of the MOF in a neat excess of 1-propanethiol for 24 h. The powder was dried and packed into a 0.5 mm capillary under an inert atmosphere, before measuring the PXRD pattern.

**Solution loading EDT and nPM into Zn-MOF-74**

For the preparation of the EDT- and nPM-loaded samples, ~100 mg of MeOH-solvated Zn$_2$(dobdc) was transferred to 20 mL vials. The mmol of Zn$^{2+}$ in each vial was calculated using the methanol-solvated formula, Zn$_2$(dobdc)(MeOH)$_2$. Methanol solutions of both 0.1 M EDT and 0.1 M nPM were prepared. The convention for loading percent was based on the open zinc-sites. Using EDT as an example, 100 mol% of EDT per Zn$^{2+}$ correlates to 200 mol% of EDT per MOF. Each sample was prepared by first adding methanol, for dilution, followed by the corresponding amount of EDT or nPM solution. Methanol and the solution were added such that the total volume equaled 20 mL/mmol MOF, which meant a maximum concentration of 0.1 M nPM or EDT. For the 100% loading, the 0.1 M solution was added without dilution. The samples were soaked for 20 h, while being agitated several times. Finally, the samples were decanted and soaked in methanol for 30 minutes before collection by vacuum filtration. The samples were dried under air and characterized using PXRD to assess their crystallinity.
Sensing transition metals with EDT@Zn-MOF-74

To test the quenching selectivity of the fluorescent EDT@Zn-MOF-74 sample, we added a variety of 0.1 M transition metal solutions to ~100 mg samples of 100% EDT-Zn-MOF-74. After 24 h, the solids were collected by filtration and the fluorescent intensity was measured by Uroob Haris from Dr. Lippert’s research group using the procedure stated above.
2.5 References


2 McDonald, T.M. et al. Nature 2015, 519, 303-308


CHAPTER 3

COBALT(II) HYDROXIDE SORBATE: SYNTHESIS, STRUCTURE AND PROPERTIES

3.1 Introduction

Materials based on redox-active metal hydroxides, with metals such as Ni, Co, Fe, Ti, V, Mo, or Nb, are researched for the advancement of energy storage and renewable energy generation.\(^1\) The properties that lend them to such applications can be altered and sometimes enhanced by manipulating the solid-state structure with organic ligands.\(^4\) Such hybrid materials can be used in areas such as catalysis,\(^5\) gas sorption,\(^6\) pseudocapacitors,\(^7\) and supercapacitors.\(^8\) The resulting crystalline compounds can be studied with crystal structure solution, allowing for structure to function correlation.

Cobalt(II) hydroxide has many applications related to its electromagnetic properties, and is separated into two states, the α- and β-phases. The α-phase is very similar to the β-phase, and only differs in being an impure material, with anion intercalation causing a greater separation of the layers. Despite being impure, the α-phase finds applications as supercapacitors\(^9,10\) or pseudocapacitors.\(^11\) The β-phase is much more stable and has a large magnetocaloric effect, giving it potential in magnetic cooling applications.\(^12,13\) To enhance or alter these properties, hybrid organic/inorganic cobalt(II) hydroxides have been developed with a focus on changing the coordination of the Co\(^{2+}\) ions as well as changing the spacing of the hydroxide layers.\(^14,15,16,17\)
Of these layered types, the major difference is whether the spacer ligands bind to both of the layers as a bridge,\textsuperscript{18} or interact with just one hydroxide layer in a monotopic fashion.\textsuperscript{19}

The sorbate ligand has been well-known to the food industry as a great preservative;\textsuperscript{20} however, the highly unsaturated nature of sorbate makes it an interesting prospect for layered materials as well. The sorbate ligands tend to pack tightly together on account of their elongated, regular shape, as well as having stabilizing $\pi$-stacking interactions between ligands, as observed with lithium sorbate.\textsuperscript{21} These properties give sorbate a preference for layered solid states, just like brucite-type Co(OH)\textsubscript{2}, making them a great pairing for hybrid organic/inorganic material development. Additionally, as with previous studies for organic salts of sorbate,\textsuperscript{22,23} the potential exists for specific double bond alignment in the solid-state, to support topochemical polymerization. Polymerization of the interlayer ligands could add a possible route to post-synthetic modification of sorbate-based hybrid materials.

We synthesized cobalt(II) hydroxide sorbate as a polycrystalline material, characterized the crystal structure with powder diffraction techniques, and measured the magnetic properties. We also measured the neutron diffraction pattern in the antiferromagnetic state below 41.7 K in attempts to gain insight into the magnetic structure. However, the magnetic moments of the Co(II) cations were found to be small, precluding any magnetic contributions to the neutron diffraction data, and suggesting a canted antiferromagnetism.

High pressures were found to change the material’s crystal structure, utilizing a large volume press. Synchrotron X-ray measurements were taken before and after exposure to high pressure, showing an altered diffraction pattern. While magnetically, the properties didn’t change significantly, structurally we observed reduced/changed crystallinity, which may be an indication of polymerization\textsuperscript{24} or other topochemical reactions.
3.2 Results and Discussion

3.2.1 Solvothermal synthesis of cobalt(II) hydroxide sorbate

Solvothermal synthesis was performed in a pressure bottle with cobalt nitrate and potassium sorbate, utilizing an extra equivalent of sorbate as a weak base to generate low amounts of hydroxide to slow crystallization. Typically, these materials are made from the nearly insoluble base hydroxide, Co(OH)$_2$, in small quantities at high pressures, but utilizing our method we were able to synthesize the material at gram-scale under only moderate heating to 90 °C. Although samples were highly crystalline, as determined by PXRD, the microscopic imaging showed polycrystalline habit, precluding single crystal analysis. The powder pattern was single phase as determined by indexing and was ultimately solved using powder neutron patterns above and below the magnetic transition temperature.

3.2.2 Infrared spectrum of cobalt(II) hydroxide sorbate

The FTIR spectrum of cobalt(II) hydroxide sorbate, Figure 3-1, shows a Co-O stretching mode at 470 cm$^{-1}$, as well as a carbonyl stretching mode at 1680 cm$^{-1}$. The asymmetric and symmetric carboxylate stretching frequencies at 1605 and 1410 cm$^{-1}$, respectively, give a larger $\Delta_\nu$ indicative of either monodentate or possible non-symmetric bridging of two cobalt(II) ions by the carboxylate group. Also notable is the broad peak from 2400 – 3300 cm$^{-1}$, which may indicate that a small amount of sorbic acid, as a non-magnetic impurity, is present as an amorphous or adsorbed constituent of the overall material.
3.2.3 SEM imaging of cobalt(II) hydroxide sorbate

To better understand the crystal morphology of Co(OH)(sorb), scanning electron microscopy was used to gather images of the material (Figure 3.2). As seen in the images, the cobalt(II) hydroxide sorbate formed interwoven bunches of microscopic crystals, precluding single crystal analyses. Therefore, powder neutron diffraction was utilized to obtain high resolution data for the crystal structure solution from powder.
3.2.4 Crystal structure of cobalt(II) hydroxide sorbate

The crystal structure of cobalt(II) hydroxide sorbate (Figure 3-3), has a disrupted connectivity in comparison to the regular octahedra of cobalt(II) hydroxide (for the structure of CoOH₂, refer back to Chapter 1, Figure 1-2). The new molecular geometry is best described as distorted square pyramidal maintaining three bonds to hydroxide ions within the layers, albeit with a much flatter hydroxide layer (Figure 3-4). The three other hydroxide bonds have been replaced by a carboxylate bond from the top and bottom of each layer, which connects via μ₂-bridging to two adjacent Co(II) ions. The asymmetric nature of the bridging carboxylate group agrees with the findings from the FTIR spectrum. The double bonds of adjacent sorbate ligands are stacked a regular 3.8 – 4.2 Å apart, in a tightly packed non-polar layer. Adjacent layers of cobalt(II) hydroxide are held together by van der Waals forces between the terminal methyl groups.
**Figure 3-3.** Structure of Co(OH)(sorb) showing the increased interlayer spacing (A) as well as the distorted nature of the intralayer connectivity. Atoms are displayed as blue (Co), red (O), white (H), and gray (C). (Credit: Ryan A. Klein)

**Figure 3-4.** A snippet of the crystal structure of Co(OH)(sorb) determined from PND, focusing on the coordination of the cobalt(II)-ion. Atoms are displayed as blue (Co), red (O), white (H), and gray (C). (Credit: Ryan A. Klein)
3.2.5 Magnetic properties of cobalt(II) hydroxide sorbate

Cobalt(II) hydroxide sorbate exhibits paramagnetism above 41.7 K (Figure 3-5A), and antiferromagnetic long-range order below this temperature, which is indicated by the steep drop-off in the zero-field cooling (ZFC) measurement at temperatures below the Néel temperature. Spin canted antiferromagnetism is suspected as observed in previous materials, but our neutron diffraction patterns did not show any peak/intensity difference above and below this temperature to enable calculation of the canting angle. The magnetization curves below 41.7 K (Figure 3-5B), show a large hysteresis, which is also indicative of a spin canted antiferromagnetism. The saturation magnetization was calculated to be 0.13 $\mu_B$/Co from the magnetization curve, as compared to the effective magnetic moment, $\mu_{\text{eff}}$, of 3.79 $\mu_B$/Co, calculated from the inverse susceptibility plot (inset in Figure 3-5A) using the relationship, $C = \mu_0 \mu_{\text{eff}}^2 / 3k_B$. The low saturation magnetization is likely responsible for the lack of additional information from the PND data below the Néel temperature, and further suggests the hypothesized canted antiferromagnetism.
Figure 3-5. Temperature dependent magnetic susceptibility and inset, inverse susceptibility plot (A), using both zero-field cooling (ZFC) and field cooling (FC) techniques, and magnetization curves at variable temperature (B) for Co(OH)(sorb). (Credit: Dr. Wenhao Liu, UTD)

3.2.6 Thermal degradation profile of cobalt(II) hydroxide sorbate

In the TGA graph (Figure 3-6), an initial loss before 453 K could be potentially due to weakly adsorbed water or sorbic acid within the layers. The sample only seems disturbed within the layers’ spacing, with a slight increase in the d-spacing of the heated sample (Figure 3-7), and a reduced intensity/broadening at other reflections. The next small loss before 603 K is suspected to be the loss of water from the hydroxides of the layers, leading to the formation of cobalt oxide layers that are still separated by sorbate. After the largest mass loss before 823 K, corresponding
to a loss of sorbate, we observe a complete loss all of the Co(OH)(sorb) peaks in the PXRD pattern and instead see the formation of cobalt(II & III) oxides as confirmed by known crystal structures.\textsuperscript{22,23} Finally, after heating to 1273 K, the material has been reduced to \textit{fcc} metallic cobalt.\textsuperscript{24} It should be noted that heating of Co(OH)\textsubscript{2} resulted in the formation of CoO and not metallic cobalt. This difference could be due to the presence of Co\textsubscript{2}O\textsubscript{3} within the sample, which has a lower melting point than CoO, causing a liquid to form above 1168 K, which allowed the release of oxygen gas and the formation of the reduced metallic form of cobalt at such a low temperature.

\textbf{Figure 3-6.} Thermogravimetric analysis of Co(OH)(sorb) (blue), Co(OH)\textsubscript{2} (black), and sorbic acid (green).
3.2.7 SEM imaging of heated cobalt(II) hydroxide sorbate

Scanning electron microscopy (SEM) imaging was obtained for the Co(OH)(sorb) samples after different stages of heating under nitrogen atmosphere in the TGA (Figure 3-8). These images showed a preservation of the shape and size of the clusters, while converting overall to CoO/Co$_2$O$_3$ and eventually to metallic fcc-Co(0).

Figure 3-8. SEM images for the as prepared Co(OH)(sorb), as well as the thermally treated samples to 603 K and 1273 K.
3.2.8 Pressure and mechanochemical treatment of Co(OH)(sorb)

With the help of collaborators from DESY, Dr. Martin Etter and Dr.-Ing Shrikant Bhat, a Co(OH)(sorb) sample was subjected to 15 GPa of pressure in a high volume press. The PXRD pattern measured at DESY showed a change in the material, resulting in a changed powder pattern (Figure 3-9), although the number of peaks was too low for crystal structure solution. The resultant dark purple, dense, solid was sent back and we attempted to test it for the presence of polymer. To further investigate, the pressed product was digested in DCl/CD$_3$OD to dissolve, which was a slow process. After 18 h, the suspected polymer (Figure 3-10), had swelled in the solvent and the etched Co$^{2+}$ leached out. The solid only slowly dissolved after application of heat and agitation. The proposed polymer structure is shown in Scheme 3-1, highlighting the new allylic and aliphatic protons generated by the reaction.

![Figure 3-9. PXRD pattern before and after pressing Co(OH)(sorb) showing the loss of diffraction peak intensities. The sharp peaks in the diffraction pattern after pressing are due to the MgO casing used. Credit: Dr. Martin Etter and Dr.-Ing Shrikant Bhat from DESY.](image)
**Figure 3-10.** Image of the remaining, swelled solid in the NMR tube that slowly dissolved upon heating.

**Scheme 3-1.** Proposed product of pressed sample induced topochemical polymerization, highlighting new proton types formed.

The $^1$H NMR spectrum (Figure 3-11), shows a low concentration of sorbic acid present, which suggests that most of the sorbate ligands have reacted. Notably, two broad peaks around 0.97 and 1.67 ppm are observed, signifying the presence of $sp^3$ hybridized protons. The allylic region peak at 1.67 ppm the aliphatic peak at 0.97 ppm are consistent with what is expected on the proposed polymeric product. While the solubility was very low, the presence of these new, broad peaks may indicate that polymer has formed.
Figure 3-11. $^1$H NMR spectra overlay, showing the non-pressed sample in yellow and pressed sample in blue. The spectra are shown on relative scale, normalized to the sorbic acid peaks, to highlight the differences in the pressed sample. The pressed sample contains two notable broad peaks (highlighted by the red box) centered at 0.97 ppm and 1.67 ppm. Sorbic acid peaks are labelled with downward facing arrows.

To have better evidence for polymer formation, the pressed product was methylated with TMS-diazomethane in THF to prepare it for GPC analysis. After quenching the excess TMS-diazomethane with acetic acid, the crude mixture was subjected to GPC analysis, but no peaks confirming the presence of polymer were observed in the chromatogram.

In order to save the remaining 3 mg of pressed sample, a batch of untreated Co(OH)(sorb) was subjected to mechanochemical treatment in a high-impact ball mill at 30 Hz for 1 h. The resultant powder was dark purple, just as the pressed sample, and had a similar PXRD pattern to the XRD collected at DESY. After treating the ball milled product with TMS-diazomethane, the GPC analysis of the mechanochemically treated product showed the same result, indicating that there is either no significant polymer in the sample, or possibly that any polymer formed isn’t soluble in THF, which was used as the GPC eluent. The guard column of the GPC became
blocked after these measurements, indicating that perhaps the polymer was formed, but wasn’t soluble in THF as expected.

3.3 Conclusions

Cobalt(II) hydroxide sorbate is a unique material, owing to the increased interlayer spacing introduced by the sorbate ligand, as well as the close proximity and tight packing of sorbate ligands within the layer. The magnetic properties were like other CoOH$_2$-based materials with similar spacing, specifically antiferromagnetic behavior below 41.7 K, as well as the highly hysteric magnetization curve below this temperature. A spin canting mechanism was proposed based on the magnetic behavior, specifically the bifurcation of FC and ZFC temperature dependent magnetic susceptibility curves and large hysteresis observed. However, additional details like canting angle or magnetic structure could not be determined, likely due to the low overall magnetization per Co atom.

The resultant material showed some reactivity at high pressure transitioning to a phase with slightly different magnetic properties. Unfortunately, when trying to characterize this “polymer” product, we were unable to show any large molecules present due to solvent incompatibility with the GPC. The mechanochemical treatment seemed to produce similar results. As further research on cobalt(II) hydroxide sorbate is performed to better understand this transformation under pressure, it is possible that highly stable magnetic materials could be produced and tested for electromagnetic properties for such applications as magnetic cooling or battery cathode materials via post-synthetic, pressure-induced topochemical polymerization.
3.4 Experimental

3.4.1 Materials

Cobalt(II) nitrate hexahydrate (Acros Organics, 99% purity), cobalt(II) hydroxide (Strem, 97% purity), sorbic acid (TCI, >99% purity) and potassium sorbate (Alfa Aesar, 99% purity), were handled in air, and used as received.

3.4.2 Analyses

$^1$H NMR spectra were collected at room temperature in DCl/D$_2$O/CD$_3$CD (50 μL of 38% DCI in D$_2$O and 500 μL of methanol-d4) on a JEOL ECA 500 MHz spectrometer.

3.4.3 Synthetic and post-synthetic procedures

Solvothermal synthesis of Co(OH)(sorb)

Deionized water (400 mL) was sparged for 1 h prior to the addition of cobalt(II) nitrate hexahydrate (11.6 g, 40 mmol) and potassium sorbate (12.0 g, 80mmol). The sparge was removed, a pressure cap applied, and the bottle was transferred to a 90 °C oven for 16 h. The supernatant containing the pink solid was decanted, and the solid was soaked in deionized water at 90 °C for 24 h. After one additional round of decant/soaking, the pink solid was collected by vacuum filtration and dried on the bench for 24 h. Material was analyzed by $^1$H NMR, PXRD, PND, DSC and TGA.

Thermal degradation

Thermal treatment was performed in the TGA instrument to each of the variable temperatures at 10 °C/min, cooled and then the PXRD pattern was measured, and SEM images captured.
SEM imaging

The microscope images (Fig. 6) were collected on a JEOL Field Emission Scanning Electron Microscope (FE-SEM) IT500HR. Analytical Working Conditions: Vacuum in variable pressure (60-70Pa) 15kV high voltage, Beam Current ≈ 50 nA, 10 mm working distance.

Pressure treatment of Co(OH)(sorb)

For pressure treatment of the Co(OH)(sorb), a sample was sent to DESY for testing, under the supervision of Dr. Martin Etter and Dr.-Ing Shrikant Bhat, on a high volume press to 15 GPa in a casing of MgO.

Post-synthetic ball milling of Co(OH)(sorb)

Ball-milling experiments were performed for 1 h at 30 Hz. The intervals of milling were setup for 15 min of milling, followed by 5 min off, to limit heating of the sample and avoid overworking the high impact ball mill.

Acid digestion and NMR

The samples of synthesized, pressurized, and ball-milled product were digested in a DCl/D₂O/CD₃OD (25 μL 35% DCl in D₂O, 500 μL CD₃OD) solvent and the ¹H NMR spectrum was obtained on the JEOL instrument.

Methylation of potentially polymeric material

The pressed Co(OH)(sorb) was treated with TMS-diazomethane to methylate the polymer using a procedure from the literature.³⁰ Pressed Co(OH)(sorb) (2 mg, 0.01 mmol) was first digested/dissolved in a solution of 50 μL of 35% DCl in D₂O and 500 μL of CD₃OD. Once dissolved, the solution was transferred to a 20 mL scintillation vial where it was diluted with
2000 μL of THF and a magnetic stir bar was added. Then, excess TMS-diazomethane was added (500 μL) and allowed to stir for 24 h. Unfortunately, we were unable to confirm the existence of any polymer present, nor determine the size distribution with the subsequent GPC.
3.5 References


CHAPTER 4

STRUCTURE SOLUTION OF ZINEB AND POTASSIUM SORBATE WITH POWDER X-RAY DIFFRACTION

4.1 Introduction

The first structure determined from powder diffraction occurred just a few years after the solution of the first crystal structures from single crystals. In 1966, Rietveld published the first successful computational, full-matrix refinement of a crystal structure utilizing a least-squares algorithm.¹ In 1969, Rietveld published a method for the whole powder pattern fitting that enabled the refinement of many powder diffraction parameters in addition to R values that allowed the quality of fit to be scored.² Other advancements include refinement of unit cell parameters by Le Bail³ or Pawley⁴ fitting techniques, rigid body aided atomic positions,⁵ and the simulated annealing methods.⁶

Since the early days of crystallography, hundreds of thousands, or perhaps millions, of crystal structures have been solved, unlocking information about the materials, and helping explain their properties. Many crystalline compounds, however, have been left out due to their tendency to form crystals too small for effective single crystal analysis. A subset of these compounds form crystals large enough to give pristine powder diffraction patterns, which lend them perfectly to powder solution techniques.
4.1.1 Zineb history and molecular structure

Over the last 70 years, the earth’s population has grown from 2.5 to 8.0 billion people. Such growth has been supported, in part, by advancements in agriculture. One such advancement is the discovery of the fungicide zineb, or zinc ethane-1,2-diylbis(dithiocarbamate) (Scheme 4-1), which protects many staple crops like potato, cucurbits, apples, cereal grains, and peppers, among others.\textsuperscript{7,8} Despite the widespread use across the world, the crystal structure of zineb (see Scheme 4-1) was left unsolved, due to the tendency of zineb to form crystals of smaller size than is practical for typical single crystal diffraction techniques.

![Scheme 4-1. Molecular structure of Zineb, and the composition of related fungicides.](image)

4.1.2 Potassium sorbate uses and molecular structure

Potassium sorbate is a ubiquitous preservative found in many processed foods, see molecular structure in Scheme 4-2. It is a derivative of sorbic acid, which was originally isolated from berries of the Rowan tree. Surprisingly, although the use of this chemical is widespread in food, there is no reported crystal structure for potassium sorbate. Sorbic acid’s crystal structure is known (shown in Chapter 1, Figure 1-3),\textsuperscript{9} and showcases the efficient packing of the molecules, due in part to the linear shape, as well as stabilization of the two double bonds with π-π-interactions.
The only known crystal structure of an inorganic salt containing sorbate is that of lithium sorbate,\textsuperscript{10} which shows a layered material consisting of lithium carboxylate layers alternating with unsaturated organic layers. The sorbate ligands within the layers are aligned and spaced such that they undergo topochemical polymerization under X-ray irradiation or heating.\textsuperscript{10} Crystalline potassium sorbate is not known to undergo polymerization under any stimuli, and the crystal structure may lend some insight into why it isn’t known to be reactive. We sought to determine the crystal structure to explain the lack of reactivity observed.

4.2 Results and discussion

4.2.1 Unit cell determination of zineb

The powder diffraction data for zineb showed a highly crystalline sample. Indexing uncovered a triclinic, \textit{P}\textit{\textsubscript{i}} space group symmetry. Latter stages of structure solution confirmed this finding. Pawley fitting allowed for a precise determination of the unit cell parameters, which are shown in part of Table 4-1.


Table 4-1. Unit cell parameters and crystallographic details for Zineb

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4.2.2 Structure of zineb

Zineb’s crystal structure is built up of bidentate, thiocarbamate linkers, forming a coordination polymer. The asymmetric unit consists of one molecule of zineb, with two molecules within the unit cell, related by inversion symmetry. The chains of the coordination polymer are woven together by zinc-ions (Figure 4-1), which form Zn₂S₈ clusters (Figure 4-2). These zinc sulfide clusters are the basis of the layers within the structure, creating a 2D network. Additionally, a high degree of hydrogen bonding maintains connectivity between the 2D layers, stacking with an ABAB arrangement, where the layers are related by inversion symmetry.
Figure 4-1. Crystal structure of Zineb showing the connectivity of the zinc(II)-ions via EBDTC linkers (a), and the ABAB stacking observed for the hydrogen bonded layers.

The zinc-zinc distance measures 3.902(9) Å and each zinc-ion is coordinated by five sulfur atoms of the thiocarbamate groups. Four of the Zn-S bonds are between 2.325-2.426 Å, while one longer Zn-S contact is 2.925(8) Å, showing a similar coordination geometry to other metal thiocarbamate complexes.
The hydrogen bonding network (Figure 4-3) holds the layers together through four interlayer hydrogen bonds donated by the N-H groups and accepted by the sulfur atoms, with distances ranging from 3.332 to 3.749 Å. One additional hydrogen bond occurs within the layer between the N-H of one linker and a sulfur atom of another linker.
Each linker is centrosymmetric, resulting in two crystallographically unique linkers, with one half of each linker being present in the asymmetric unit and completed by the inversion symmetry element. This difference between the two linkers is underlined by the difference in hydrogen bonding, where one of the linkers only engages in interlayer hydrogen bonding interactions, while the other linker contains one potential intralayer hydrogen bond.

The Rietveld plot in Figure 4-4 shows a good agreement with the experimental diffraction data after the refinement of 63 variables, including background, peak shape, unit cell parameters and atomic/molecular positions and bond lengths. The unit cell parameters and data from the refinement can be viewed in Table 4-2.
4.2.3 Unit cell determination of potassium sorbate

Indexing determined potassium sorbate to crystallize in a $P2_1/c$ unit cell, containing four potassium sorbate molecules, related by symmetry an asymmetric unit of one potassium sorbate molecule. This unit cell (Table 4-2) was in good agreement with the peak positions was later confirmed after Rietveld refinement.
Table 4-2. Unit cell parameters and solution metrics for potassium sorbate

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<th>Value</th>
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4.2.4 Structure of potassium sorbate

Potassium sorbate crystallizes into layers stitched together by the interaction of the potassium-ions and carboxylate groups into a double layer. Much like the Co(OH)(sorb) crystal structure from previous work, the unsaturated, non-polar tails of sorbate stack neatly to separate these potassium carboxylate double layers (Figure 4-5). Unlike the Co(OH)(sorb) structure, the non-polar tails alternate their angle of connectivity to the layer for every other sorbate along the c-axis, while being somewhat aligned along the b-axis.
Figure 4-5. Crystal structure of potassium sorbate looking down the $b$-axis (A) and the $c$-axis (B), showing the potassium carboxylate 2-D layers propagating in the bc-plane.

Looking more closely at the coordination of the potassium ions in Figure 4-6, we can see that each potassium cation forms six contacts with sorbate’s carboxylate oxygen atoms, with four of these being monodentate contacts of between 2.70 and 2.87 Å in length, from the same side of the double-layer. Both remaining contacts originate from a single sorbate ligand in the form of a bidentate contact, via the opposite side of the double-layer, with K-O distances of 3.10(10) and 2.73(3).
Figure 4-6. A snippet of the crystal structure of potassium sorbate, showing one bidentate contact from the bottom layer, and 4 monodentate contacts from the same layer. Hydrogen atoms have been removed for clarity. Atom colors: K (purple), O (red), and C (gray).

With topochemical reactions in mind, clearly there is no relation between sorbate’s double bonds propagating down the $c$-axis, as their opposing angles preclude the alignment necessary for $\pi-\pi$ interaction. But to completely dispel the lack of topochemical reactivity, we must look at the most aligned sorbate ligands in the crystal structure, meaning those propagating in the direction of the $b$-axis (Figure 4-7). Topochemical polymerization is dependent on two main factors, distance and $\pi$-orbital alignment. In the case of potassium sorbate, the contact distance of 5.0(2) Å between the $\alpha$- and $\delta$-carbon atoms, coupled with the misalignment of the double bonds, explains the lack of reactivity observed with potassium sorbate towards polymeric products.
4.3 Conclusions

In this chapter, we have shown the ability to solve crystal structures from powder diffraction patterns. In particular, we have studied two compounds which don’t produce sufficiently large single crystals. We can hypothesize that this is due to the anisotropic disparity in the strength of interactions propagating along different axes of the crystal structure. For zineb, the layers are more weakly bound by hydrogen bonding as compared to the covalent bonding forming the interconnected zinc cluster layers. For potassium sorbate, a large difference can be seen between the layers held together by van der Waals forces, and the ionic binding that constructs the layers themselves. Both chemicals are important to modern society, zineb as a historic fungicide and a precursor to more modern fungicides, and potassium sorbate as a common preservative with well over 40 years of use in many types of food.
The crystal structure of zineb has been solved after nearly eight decades of use in agriculture. This highlights the usefulness of powder diffraction in giving us an eye into the previously unknown, solving a crystal structure that has been left alone for all these decades.

Potassium sorbate was studied due to being one of the most consumed preservatives in modern society, but also to investigate the lack of topochemical reactivity observed with this specific sorbate species. While potassium sorbate shares a similar packing with lithium sorbate, a key difference is the lack of π-orbital overlap, which precludes any sort of topochemical reaction.

4.4 Experimental

4.4.1 Materials

Potassium sorbate (Alfa Aesar, 99%) and zineb (Sigma Aldrich, analytical grade) were purchased and used as received.

4.4.2 Analyses

The PXRD patterns were collected on a Stoe Stadi-P powder diffractometer operating in transmission geometry, with the sample loaded into a 0.5 or 0.7 mm borosilicate capillary after lightly grinding the sample in a agate mortar and pestle. The capillary was rotated during the measurement to improve particle statistics. The molybdenum X-ray source was operated with a power of 50 kV/40 mA, and a Ge(111) monochromator to select for the Mo-K\textsubscript{α1} radiation of 0.7093 Å. Two linear position sensitive silicon-strip detectors (Mythen Decris 1K) were used to record scattered X-ray intensity, collecting from 1 – 74.6 ° two theta.

Powder diffraction data were analyzed using TOPAS-Academic V6 (Coelho Software, 2018) software. Indexing was performed using the singular value decomposition (LSI) function.
available in TOPAS. Indexing allowed for the unit cell symmetry and parameters to be determined, which was then optimized by way of structureless Pawley fitting,\textsuperscript{8} using the fundamental parameter (FP) approach.\textsuperscript{12} Once Pawley fitting confirmed a good fit for the unit cell to the experimental data, as well as determining other variables like the background coefficients (as a Chebyshev polynomial), and peak shape/instrumental contributions via simple axial model.

The crystal structure was solved with real-space global optimization of simulated annealing, using the Metropolis algorithm.\textsuperscript{10} Rigid bodies were necessary to reduce the degrees of freedom, and were constructed using Z-matrix notation.\textsuperscript{9} For Zineb, due to the symmetry of the linker itself, two halves were constructed as rigid bodies. For potassium sorbate, one full sorbate ligand was constructed. For both compounds, the cation was allowed to refine freely within the unit cell (cations were not included in rigid body). Simulated annealing was performed until a global minimum was reached, at which point the acquired model was subjected to whole-pattern Rietveld refinement.\textsuperscript{6}

For Rietveld refinement, the variables refined were as follows: unit cell parameters, peak shape/profile, background coefficients, structural parameters. Structural parameters for zineb included, the zinc ion, three degrees of freedom for each translation and rotation, bond lengths within the rigid bodies, ADPs (one for each atom type, hydrogen atoms were calculated as a multiplied factor of 1.5). For potassium sorbate, similar treatment was given, where a rigid body was constructed allowing free rotation of all single bonds in addition to the three translational and rotational degrees of freedom. Once the refinement converged, the figures of merit and difference curve were used to determine that the process was a success. The Rietveld plot of
zineb is shown above. The Rietveld plot of potassium sorbate, in Figure 4-8 below, shows that the experimental and predicted pattern are in good agreement.

*Figure 4-8.* Rietveld refinement plot of potassium sorbate, showing the experimental pattern as blue dots, the simulated pattern as a red line, the difference curve in gray, and the Bragg reflections in blue.
4.5 References


CHAPTER 5
CONCLUSIONS

Powder diffraction is a powerful technique for monitoring structural changes that occur within a crystalline material. The projects in this dissertation have used PXRD to show loss of crystallinity, as well as determine the crystal structures from those materials that were crystalline. The materials range from completely distorted or amorphous, to completely crystalline, and in each case the diffraction pattern yielded very important information. Crystal structures of MOF-74 with thiol ligands opened the door for more complex studies that utilized the same interaction to destroy the framework and illicit new fluorescent intensity. Also notable, the modification of the MOF-74 led to a material that could selectively interact with metal cations in aqueous environments.

A new material has been added to the library of hybrid cobalt(II) hydroxides, and the crystal structure and magnetic properties were described. While no concrete evidence of topochemical polymerization was obtained, we can confirm that a structural change had occurred to the material. Perhaps the material was simply compressed to a form with slower dissolution kinetics in the NMR solvent, or maybe a topochemical reaction only formed oligomers that had lower solubility in the DCI/CD$_3$OD solvent system.

Finally, two important chemicals without crystal structures in the literature were solved, yielding information that can help explain how they work, or in the case of potassium sorbate, why it doesn’t work in a topochemical sense as other sorbate salts do. The structure of zineb may
inform some of the properties like dissolution kinetics or toxicity. While zineb is mainly out of use, especially in the EU and US, these structure/property relationships may find use in explaining coordination polymers’ properties within agriculture or possibly in other fields.
Scheme 6-1. Enlarged regions of the MOF-74 crystal structure, showing the distance to the closest neighboring open metal sites.
Figure 6-1. Rietveld plot for MeOH @ Zn-MOF-74 showing the experimental pattern as blue dots, the simulated pattern as a red line, the difference curve in gray, and the Bragg reflections in blue.

Figure 6-2. Rietveld plot for nPM @ Zn-MOF-74 showing the experimental pattern as blue dots, the simulated pattern as a red line, the difference curve in gray, and the Bragg reflections in blue.
Figure 6-3. Comparison of PXRD patterns from excess loading of nPM (green) and EDT (red) compared to the MeOH-solvated (blue) MOF
Figure 6-4. TGA plot for methanol solvated Zn-MOF-74 (blue) and EDT-loaded Zn-MOF-74 (red).

Figure 6-5. SEM images of 0 (a & b) and 100 (c & d) mol% EDT/Zn loaded Zn2(dobdc)
Figure 6-6. SEM images of Zn-MOF-74 at each stage of the gradual loading, showing the maintenance of the crystal morphology despite losing crystallinity.

Figure 6-7. SEM images of nPM-loaded Zn-MOF-74 at 50 and 100% loading.
Figure 6-8. FTIR spectra of Co(OH)(sorb) (blue), sorbic acid (red), and Co(OH)$_2$ (black)

Figure 6-9. PXRD pattern for Co(OH)(sorb) compared to CoO and Co$_2$O$_3$ predicted patterns.
Figure 6-10. PXRD pattern for Co(OH)(sorb) compared to fcc-Co(0)
Figure 6-11. Rietveld plot for Co(OH)(sorb) at 100K and 6.71 K, showing that no extra peaks were observed below the magnetic transition temperature. Black circles are diffraction data, red line is the predicted pattern, and red ticks below the plot are the $hkl$ reflections of the solved crystal structure. Credit: Dr. Ryan Klein and Dr. Craig Brown for structure solution.
Table 6-1. The unit cell and structural differences between the 100 K and 6.71 K crystal structure determination of Co(OH)(sorb)

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<tbody>
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<td>100 K</td>
<td>6.5584(6)</td>
<td>6.3255(5)</td>
<td>16.837(1)</td>
<td>89.70(1)</td>
<td>698.5(1)</td>
</tr>
<tr>
<td>6.71 K</td>
<td>6.5566(5)</td>
<td>6.3124(4)</td>
<td>16.796(1)</td>
<td>89.532(8)</td>
<td>695.13(9)</td>
</tr>
</tbody>
</table>

Bond lengths at 6.71 K (Å)

| Co₁-OH  | 2.0(1), 2.3(1), 2.4(1) | Co₁-sorb | 1.8(1), 2.6(1) |
| Co₂-OH  | 1.9(1), 2.3(1), 2.3(1) | Co₂-sorb | 1.7(1), 2.6(1) |

Diamond plaquette

<table>
<thead>
<tr>
<th></th>
<th>Angle at 6.71 K (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101(4), 102(4)</td>
<td>Octagonal plaquette</td>
</tr>
</tbody>
</table>