SOLVENT-FREE SYNTHESIS AND DESIGN OF METAL-ORGANIC MATERIALS AND MOLECULAR SOLIDS IN THE SOLID STATE

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ABSTRACT

Framework materials, including porous coordination polymers and molecular solids, have great potential for use in a range of industrial applications. Although the design of novel framework materials has become a focal point of materials chemistry, the rising environmental strain imposed by chemical processes has highlighted the increased need to develop more sustainable methods for their synthesis. Molecular framework solids, on the other hand, still require a robust, reliable method for their design which will enable their development as a functional material. As an alternative to conventional solution-based methods, solid-state chemistry has rapidly evolved as the primary choice for efficient, environmentally-friendly synthesis of coordination polymers and molecular solids. Herein described is the introduction and design of accelerated aging, a novel methodology which enables the mild, environmentally-friendly synthesis of microporous metal-organic materials directly from metal oxides with minimal energy input. The synthesis of a series of model ZIFs composed of varying metal centres and ligands has been demonstrated, while salt additives were utilised in catalytic amounts to effect the templated formation of either microporous or non-porous frameworks. In addition, the accelerated aging technique has been adapted as a tool to monitor and observe the solid-state stability of ZIFs under dynamic variations in temperature, atmosphere, and mildly acidic conditions. This study led to the discovery that ZIFs are unstable in moist carbon dioxide, which bears significance to the potential industrial applications of these materials. It also highlights the lack of understanding of the factors governing solid-state reactivity under accelerated aging conditions. In that context, multinuclear solid-state NMR was selected to monitor the formation and transformation of ZIFs in the solid state. In particular, $^{111}$Cd NMR was exploited to track the coordination environment of Cd$^{2+}$ during accelerated aging reactions.

The materials studied in this work have been developed using design principles which take advantage of the binding geometries of metal ions and organic ligands, namely the node-and-linker approach. Conversely, attempts to achieve the design of molecular framework solids has been met with less success due to the weaker nature of non-covalent interactions. The node-and-linker approach has been thus adapted, for the first time, towards the predicted self-assembly of hydrogen-bonded molecular solids. A new family of two- and three-dimensional hydrogen-bonded materials called supramolecular imidazolium frameworks (SIFs) has been designed using sulfate, selenate, dichromate, and squarate anions as four-connected nodes and imidazolate
cations as ditopic linkers. Described herein is the development of new methodologies for the solvent-free synthesis of metal-organic materials and the design of molecular framework solids, in addition to new approaches towards elucidating the factors governing their self-assembly and solid-state properties.
RÉSUMÉ

Les matériaux dotés d’une structure tridimensionnel, dont les polymères de coordination et les solides moléculaires, sont particulièrement prometteurs dans de nombreux domaines incluant la séparation sélective, l’entreposage de gaz, et la catalyse. Bien que la recherche concernant l’optimisation de nouveaux solides microporeux est importante, les effets secondaires négatifs environnementaux de l’industrie chimique mettent en évidence la nécessité de développer des méthodes plus durables pour synthétiser des matériaux fonctionnels. Par le fait même, l’avancement des architectures supramoléculaires, une classe relativement nouvelle de matériaux bi et tridimensionnels, nécessite un style de conception robuste qui permettrait leur reconception. La chimie du solide a récemment été connue comme méthode afin d’augmenter l’efficacité de la production des matériaux. Cette thèse présente la synthèse douce et verte de matières avec une structure d’imidazolate zéolitique (ZIFs), nommée accelerated aging. Cette méthode permet la synthèse des ZIFs à partir des oxydes métalliques, sans avoir besoin de solvants ni de températures élevées. La production d’une série de ZIFs composée de différents métaux et liants a été élaborée à part d’accelerated aging, en utilisant une famille d’ajouts ioniques qui servent à diriger l’assemblage de structures qui sont microporeuses ou non-poreuses. À part de servir comme méthode pour la production quantitative des matériaux microporeux, accelerated aging sert à découvrir les variables importantes gouvernant la stabilité et l’auto-assemblage des structures organométalliques de type zéolitique. Accelerated aging a été adapté comme méthode pour surveiller les changements chimiques et structurels des ZIFs en présence de dioxyde de carbone et de vapeur d’eau. En conséquence, l’instabilité surprenant des ZIFs en atmosphère humide de dioxyde de carbone a été découverte. Notre carence de connaissance sur les variables gouvernant la synthèse et stabilité des ZIFs en forme solide met l’accent sur la nécessité de développer des méthodes pour leur analyse. Dans ce but, la spectroscopie résonance magnétique nucléaire (RMN) multinucléaire des solides a été utilisé pour surveiller la synthèse et les transformations des ZIFs. Particulièrement, la RMN de $^{111}$Cd a été choisie comme méthode d’observation des changements dans l’environnement de coordination de Cd$^{2+}$ durant l’accelerated aging. De surcroît, les styles de conception pour l’assemblage des structures d’imidazolate zéolitique sont utilisés comme approche robuste pour l’auto-assemblage fiable des structures ouvertes fondées sur la liaison hydrogène intermoléculaire.
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Firstly, I would like to express my sincere gratitude to my PhD supervisor, Prof. Tomislav Friščić, who was always ready to provide boundless support, guidance, knowledge, and encouragement throughout my PhD study and in the completion of my thesis, and whose sheer enthusiasm for all things chemistry was truly motivating and inspiring.

I would like to thank the members of my PhD Advisory Committee, Prof. Audrey H. Moores, Prof. D. Scott Bohle, and Prof. Amy S. Blum, for their valuable and insightful feedback regarding my research over the past four years and during my yearly Review presentations.

My sincere thanks also goes to Prof. Amy S. Blum and Prof. Gonzalo Cosa from McGill University, Prof. Robert Schurko from the University of Windsor, Prof. Kenneth D. M. Harris from Cardiff University, Dr. Krunoslav Užarević and Dr. Ivan Halasz from Ruđer Bošković Institute, and Prof. Bill Jones from Cambridge University for the collaborations, some still ongoing, which have greatly enriched my graduate school learning experience. Prof. D. Scott Bohle and Prof. Xavier Ottenwaelder from Concordia University are acknowledged for invaluable help in collecting single crystal X-ray diffraction data. Thank you to Dr. Robin S. Stein at McGill University for her expertise with running solid-state NMR spectra, and for giving me valuable advice regarding the research discussed in Chapter 5.

To my colleagues, lab mates, and friends in the Friščić group and in the Department of Chemistry, many of which I have had the absolute fortune to work with, thank you for making my graduate school experience an amazing one. A special thanks goes to Louis Do, Davin Tan, Ghada Ayoub, Yuneng Lu, Joanne Yu, Abdul Khalil, Ross Koby, Dr. Josê-Gregorio Hernández, Karen Ardila Fierro, Dr. Athanassios D. Katsenis, and Athena Fidelli, for always being there to help me out in lab, discuss chemistry, and for being great friends.

Last, but not least, thank you to my family, especially my mom, Donatina Zampino, my dad, Giovanni Mottillo, and my brother, Dr. Salvatore Mottillo, for always being there for me, for encouraging me throughout my studies, and for their constant love and support, which has brought me to where I am today.
PREFACE AND CONTRIBUTION OF AUTHORS

This Dissertation entitled, “Solvent-free synthesis and design of metal-organic materials and molecular solids in the solid state”, describes research conducted and published by myself, Cristina Mottillo, from September 2011 to September 2015.

Prof. Tomislav Friščić provided guidance in all aspects of this Dissertation and the research described herein, in addition to editing and revision of all manuscripts included here.

Chapter 1 consists of a literature review covering previous work in the areas of green chemistry, the design of metal-organic framework materials, and the solid-state formation of coordination bonds as applied to the synthesis of coordination polymers, subjects which are relevant to all chapters in this Dissertation. Section 1.3 of Chapter 1 consists of the text of a Perspective article entitled “Advances in the solid-state transformations of coordination bonds: from the ball mill to the aging chamber” written by Cristina Mottillo and edited by Prof. Tomislav Friščić, to be submitted shortly to the journal *Dalton Transactions*. This article, which has been formatted and modified for inclusion in this Thesis, describes the recent advancements made in the areas of mechanochemical and solid-state synthesis of coordination polymers.

The research presented in Chapter 2 has been published in the journal *Chemical Science* as an Edge article entitled, “Accelerated aging: a low energy, solvent-free alternative to solvothermal and mechanochemical synthesis of metal–organic materials”. This article has been co-authored by Dr. Matthew J. Cliffe, Cristina Mottillo, Dr. Robin S. Stein, and Dr. Dejan-Krešimir Bučar, and written by Prof. Tomislav Friščić. Cristina Mottillo provided a significant contribution towards the modification of the manuscript for publication and drafting of the Supplementary Information. Preliminary findings led by Dr. Matthew J. Cliffe and Prof. Tomislav Friščić at the University of Cambridge, including proof-of-principle reactions and powder X-ray diffraction experiments, comprised only a small fraction of the results published in the paper, and served as the starting point for the work conducted by Cristina Mottillo. Initial findings by Dr. Matthew J. Cliffe and Prof. Tomislav Friščić have been reproduced, validated, and substantially expanded upon at McGill University by Cristina Mottillo, who conducted all of the described experiments and solid-state analysis, including PXRD, Fourier-transform infrared attenuated total reflection spectroscopy (FTIR-ATR), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A small number of select FTIR-ATR, PXRD, and solid-
state nuclear magnetic resonance (ssNMR) experiments were conducted at the University of Cambridge by Dr. Dejan-Krešimir Bučar and Dr. Robin S. Stein, respectively.

Chapter 3 describes results published as a full paper entitled, “Mineral neogenesis as an inspiration for mild, solvent-free synthesis of bulk microporous metal-organic frameworks from metal (Zn, Co) oxides” in the journal *Green Chemistry*, and co-authored by Cristina Mottillo, Yuneng Lu, Minh-Hao Pham, Dr. Matthew J. Cliffe, and Prof. Trong-On Do and written by Prof. Tomislav Friščić. Although the paper was drafted by Prof. Tomislav Friščić, Cristina Mottillo provided a significant contribution towards the modification of the manuscript for publication and wrote the Supplementary Information. The contribution of Yuneng Lu, an undergraduate summer student, consisted of running select reactions and recrystallization experiments, and conducting PXRD, FTIR-ATR, and TGA analyses under the direct guidance and supervision of Cristina Mottillo. Minh-Hao Pham and Prof. Trong-On Do from Université Laval provided sorption measurements. Preliminary aging reactions were conducted by Dr. Matthew J. Cliffe at the University of Cambridge, and reproduced by Cristina Mottillo at McGill University. All other reactions were conducted by Cristina Mottillo in addition to the collection and interpretation of all PXRD, FTIR-ATR, ssNMR, and TGA data.

Chapter 4 consists of a manuscript entitled, “Carbon dioxide sensitivity of zeolitic imidazolate frameworks”, published in *Angew. Chem. Int. Ed*, which was written by Cristina Mottillo and edited by Prof. Tomislav Friščić. Section 4.2 consists of the manuscript, slightly modified and formatted for inclusion in this Thesis. All results, including those not explicitly described in the manuscript or its Supplementary Information have been obtained by Cristina Mottillo. An ongoing collaboration extending the work presented the paper is currently underway with Professor Kenneth D. M. Harris of Cardiff University, who conducted the *ab initio* structure solutions presented in Chapter 4.

Chapter 5 describes the solid-state accelerated aging synthesis of cadmium imidazolate frameworks by accelerated aging, and the use of *ex situ* PXRD and solid-state NMR to monitor these reactions. All reactions and PXRD analyses were conducted by Cristina Mottillo. Multinuclear solid-state NMR data on pre-made samples was collected by Christopher O’Keefe, a PhD student under the supervision of Prof. Robert Schurko at the University of Windsor. *Ex situ* reaction monitoring ssNMR data were collected in the laboratory of Prof. Robert Schurko at the University of Windsor.
the University of Windsor by Christopher O’Keefe and Cristina Mottillo, during a one-week research exchange. This work will be submitted for publication shortly.

Chapter 6 is based on a manuscript entitled, “Supramolecular imidazolium frameworks: direct analogues of metal azolate frameworks with charge-inverted node-and-linker structure” published in *Chemical Communications* as a back cover article, which was written by Cristina Mottillo and edited by Prof. Tomislav Friščić. All experimental results described in Chapter 6 were obtained by Cristina Mottillo.

Chapter 7 extends on the research published in Chapter 6, presented in part as a manuscript entitled, “Reliable design and self-assembly of squarate-based supramolecular imidazolium frameworks” which is to be submitted for publication soon, and was written by Cristina Mottillo, edited by Prof. Tomislav Friščić, and co-authored by Joanne Yu, a summer student from the Department of Chemistry and Biochemistry of the University of Windsor. The contribution of Joanne Yu consisted of synthesis and solid-state analysis of squarate-based SIFs, which included PXRD, TGA, FTIR-ATR spectroscopy under the direct supervision of Cristina Mottillo. Single crystals for XRD analysis were obtained by Joanne Yu, and analyzed by single crystal X-ray diffraction for structure elucidation by Cristina Mottillo.
LIST OF ABBREVIATIONS

4mpy: 4-methylpyridine
AFM: Atomic force microscopy
BET: Brunauer-Emmett-Teller
bpy: 4,4-bipyridine
bpe: trans-1,2-bis(4-pyridyl)ethylene
CdIF: Cadmium imidazolate framework
CNacacH: 3-cyano-pentane-2,4-dione
cnge: cyanoguanidine
COD: Crystallography Open Database
CP-MAS: Cross-polarization magic-angle spinning
CSD: Cambridge Structural Database
dabco: 1,4-diazabicyclo[2.2.2]octane
dace: diaminocyclohexane
DMF: N, N’-dimethylformamide
DMSO: dimethyl sulfoxide
DP-MAS: Direct-polarization magic-angle spinning
dpp: 1,3-di-(4-pyridyl)propane
DSC: Differential scanning calorimetry
EtOH: Ethanol
etu: ethylenediamine
FTIR-ATR: Fourier transform infrared total attenuated reflection
H2fum: fumaric acid
H2nap: naproxen
H3btc: 1,3,5-benzenetricarboxylic acid
HAlldIm: imidazole-2-carboxaldehyde
HBIm: Benzimidazole
HCaf: Caffeine
HEtBlm: 2-ethylbenzimidazole
HEtlm: 2-ethylimidazole
HIm: Imidazole
Hi-PrIm: 2-isopropylimidazole
HMeBIm: 2-methylbenzimidazole
HMeIm: 2-methylimidazole
HPhBIm: 2-phenylbenzimidazole
HPhIm: 2-phenylimidazole
H_{2}sq: Squaric acid
ILAG: Ion- and liquid-assisted grinding
LAG: Liquid-assisted grinding
MAF: Metal azolate framework
MeOH: Methanol
MOF: Metal-organic framework
n-BuOH: n-butanol
NMR: Nuclear magnetic resonance
py: pyridine
pyz: pyrazine
PXRD: Powder X-ray diffraction
RH: Relative humidity
SIF: Supramolecular imidazolate framework
ssNMR: Solid-state NMR
TGA: Thermogravimetric analysis
tpt: tris(4-pyridyl)triazine
VAG: Vapour-assisted aging
XRD: X-ray diffraction
ZIF: Zeolitic imidazolate framework
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INTRODUCTION

This Dissertation will introduce how solid-state chemistry and related synthetic methods have been identified as invaluable methodologies for the more sustainable formation of metal-organic complexes, including metal-organic frameworks and coordination polymers. It will subsequently, in Chapters 2 and 3, present “accelerated aging”, a technique for the solvent-free, quantitative synthesis of ZIFs from metal oxides. The proposed diffusion-limited mechanisms underlying accelerated aging reactions will be discussed, as well as its development into a reliable tool for the self-assembly of highly porous metal-organic materials, some of them which are difficult to obtain on bulk scale in solution. Furthermore, Chapter 4 will discuss the use of accelerated aging as a method for discerning the behaviour of ZIFs under different conditions of atmosphere and temperature, and the surprising instability of ZIFs under moist CO₂, an effect which has major implications on their use as carbon dioxide sequestration materials. Chapter 5 will highlight how, with the goal of determining the mechanisms governing accelerated aging reactivity, ¹¹¹Cd NMR is a useful tool for elucidating and monitoring the coordination environment of the metal. While the importance of coordination polymers has been established, molecular solids are an emerging class of framework materials that have found limited application in catalysis and gas storage. Unlike coordination polymers, the design of organic framework solids has been hindered by the inherent weakness of non-covalent interactions. Chapters 6 and 7 will outline a novel and strategic design of two-dimensional molecular solids using the approach commonly used for ZIFs. The node-and-linker approach has been adapted, for the first time, to the robust self-assembly of a new class of hydrogen-bonded framework solids called supramolecular imidazolium frameworks.
CHAPTER 1

LITERATURE REVIEW

1.1 Green Chemistry

The increased awareness of the negative environmental impact of chemical processes among academic and industrial researchers has inspired the development of a global initiative to design cleaner, more sustainable approaches to chemical and materials synthesis.\(^1\) In the early 1990s, a global call to action by various government agencies, including the United States Environmental Protection Agency, resulted in the conception of the field of Green Chemistry.\(^2\) Green Chemistry is defined as the efficient production or use of chemical products using raw materials preferably generated from renewable sources, while eliminating waste and minimizing hazardous reagents and/or solvents.\(^3\) In that context, Anastas and Warner devised a series of guidelines for chemists to utilise in the evaluation and design of new, greener chemical synthetic procedures. These 12 Principles of Green Chemistry\(^4\) (Figure 1.1), later conveniently summarized with the acronym PRODUCTIVELY,\(^5\) were aimed at increasing the efficiency of chemical transformations, while mitigating hazards posed towards humans, wildlife, and the environment in general. These guidelines were also recently expanded with 12 additional Principles which assess the sustainable scalability of a chemical process.\(^6\)

Ultimately, the value of green chemistry lies in the ability to apply its concepts in larger, industrial-scale settings. In such a profit-oriented manufacturing environment, the application of the 12 Principles of Chemistry is often evaluated at the same time with perceived profitability or increase in market potential.\(^7\) This is likely to be true for new process being implemented for the first time, as well as for processes that are designed to replace an incumbent procedure. The cost of choosing the more sustainable process or replacing an already established one must be either minimal or mitigated by the cost reduction due to the new process. There exist nonetheless cases in the pharmaceutical and fine chemicals industries demonstrating the successful replacement of a wasteful or a hazardous synthetic procedure with a more sustainable one. Such examples include the replacement of the traditional synthesis of the commercial drug Lyrica\(^®\) (pregabalin), which included a resolution step, whereby 70% of the racemic product mixture was discarded. The classical resolution step was replaced with a biocatalytic resolution which was conducted early in the synthetic pathway, and allowed for recycling of the unused enantiomer.\(^8\) In addition,
the traditional procedure for the synthesis of disodium aminodiacetate, the active ingredient in the herbicide Roundup™, which required the use of hydrogen cyanide, was replaced with a safer, milder process by means of a reusable solid catalyst.⁹

**Figure 1.1** The 12 Principles of Green Chemistry.

### 1.1.1 Green chemistry metrics

As demonstrated above, the practical application of the 12 Principles of Green Chemistry often involves comparing two processes and selecting the candidate which is safer and more efficient. However, quantitatively evaluating the relative sustainability of one chemical process vs. its incumbent can be a challenge without normalized guidelines or formulas to abide by. It is with that in mind that a series of metrics have been developed (and continue to be developed) which serve to quantify the level of waste production, energy usage, atom efficiency, process sustainability and environmental safety of a chemical process. Among them are simple formulas or guidelines which can be applied to measure the renewability, carbon efficiency, effective mass yield, or toxicity in a synthetic procedure.¹⁰ Broader metrics, such as Life Cycle Assessment (LCA),¹¹ process scalability,¹² and operational efficiency,¹⁰ which keep track of a range of process parameters, have been devised and are more geared towards industrial processes. For the purposes of this introduction, a few selected green chemistry metrics used in the evaluation of laboratory-scale transformations will be described further.
1.1.1.1 The E-factor

In 1992, Sheldon proposed the Environmental-factor or the E-factor, that is defined as the mass ratio of waste to product (Equation 1.1). The E-factor, which quantifies the amount of waste that is produced during the course of a chemical process,\(^{13}\) puts emphasis on the important notion of waste management in chemistry. Another Green Chemistry metric, the Environmental Quotient, can be calculated by multiplying the E-factor by an integer Q.\(^{14}\) The factor Q represents the level of unfriendliness of the waste product and can range from 1, for the friendliest compound, to 1000, for the compound which poses the most hazard to the environment. The E-factor has also been modified and adapted to quantify other aspects of chemical synthesis, particularly in the pharmaceutical industry. For example, the Mass Intensity index, defined as the mass ratio of all materials used in a process to the amount of product obtained, defines how much material is really needed to produce one kilogram of product instead of how much waste is produced.\(^{15}\)

\[
\text{Equation 1.1 } \text{E-factor} = \frac{\text{Total waste (kg)}}{\text{Product (kg)}}
\]

1.1.1.2 Atom economy

The term atom economy,\(^{16}\) originally coined by Trost in 1991 at the same time that a similar concept, atom utilisation, was proposed by Sheldon,\(^{17}\) quantifies the conversion efficiency of a chemical synthesis. To obtain the atom economy for a reaction, the molar mass of the product is divided by the sum of the molar mass of all the reactants multiplied by the corresponding stoichiometric coefficients (Equation 1.2). The resulting formula, however, does not take into account the yield of the reaction, leading to the development of the reaction mass efficiency equation (Equation 1.3).\(^{15}\) The mass efficiency is calculated by dividing the mass of the product by the mass of all reactants, thereby taking yield into account and making it more robust and realistic than the atom economy. In both cases, specific guidelines on what to include as reactants make it possible to obtain these two values in the most accurate manner possible.

\[
\text{Equation 1.2 } \text{Atom Economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants}} \times 100\%
\]

\[
\text{Equation 1.3 } \text{Reaction Mass Efficiency} = \frac{\text{Mass of product}}{\text{Mass of all reactants}} \times 100\%
\]
1.1.1.3 Eco-Scale

The metrics described above are limited only to certain aspects of a reaction and make select assumptions which delimit their general applicability and accuracy. The Eco-Scale is a more recently developed evaluation system which attempts to be inclusive by taking into account most or all aspects of a chemical process, ranging from cost, solvent use, reaction temperature and yield, to the number and choice of purification steps.\(^\text{18}\) In this system, each chemical synthesis is given a rating of 100 points, and penalty points are deducted based on criteria defined as more or less detrimental to the environment. There is no lower limit to the Eco-Scale rating, and the lower the rating of a particular process the less sustainable it is according to this evaluation system.

1.1.2 Solid-state chemistry as a green alternative

It is considered that solvents generally account for approximately 90% of the weight in processes generating pharmaceuticals or fine chemicals.\(^\text{19}\) It is therefore no surprise that a majority of waste coming from the chemical industry consists of solvents, which are often highly toxic and difficult to recycle. Methods of mitigating the hazards posed by organic solvents include replacing them with greener alternatives such as water, non-halogenated counterparts,\(^\text{12}\) supercritical fluids,\(^\text{20}\) and ionic liquids.\(^\text{21}\)

However, avoiding solution chemistry altogether would probably be the ideal method to answering the problem of solvent waste and its potential toxicity. Therefore, conducting chemistry in the solid state is generally a more sustainable alternative to conventional solution-based methods, due to the avoidance of solvent use. Although solid-state methods for making new materials, such as mechanical alloying, have been used in the metallurgical industry for several decades,\(^\text{22}\) only recently has solid-state chemistry been demonstrated as a versatile and generally applicable alternative to conventional solution-based synthesis. Mechanochemistry,\(^\text{23}\) melt reactions,\(^\text{24}\) and diffusion-limited vapour-assisted methods, including vapour digestion,\(^\text{25}\) accelerated aging,\(^\text{26}\) and vapour-assisted aging\(^\text{27}\) are methodologies which have been applied with great success to organic, supramolecular, inorganic, and organometallic transformations while requiring little to no solvent.

Among the currently available methodologies for solid-state synthesis, mechanochemistry appears to be the most widely investigated one. As such, in addition to proof-
of-principle studies demonstrating that mechanochemistry can be adapted to a particular synthetic problem, the greener aspect of mechanochemistry has been evaluated and reported. For example, the Hamilton group has recently reported the mechanochemical synthesis of meso-tetrasubstituted porphyrins by ball milling. The established solution-based procedures for making meso-tetrasubstituted porphyrins are reputed for their poor yields, large solvent volumes, and need for extensive purification steps. The evaluation of the E-factor and EcoScale metrics for both the standard solution-based synthesis and the new mechanochemical alternatives revealed the latter are greatly superior in terms of waste production and general sustainability (Table 1.1).

<table>
<thead>
<tr>
<th></th>
<th>Lindsey synthesis</th>
<th>Mechanochemical condensation step</th>
<th>Two-step mechanochemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>E factor</td>
<td>2784</td>
<td>1682</td>
<td>19.7</td>
</tr>
<tr>
<td>EcoScale</td>
<td>-46</td>
<td>-33.5</td>
<td>6.64</td>
</tr>
</tbody>
</table>

**Table 1.1** Comparison between the E-factor and EcoScale metrics for the Lindsey synthesis of porphyrins and the two-step mechanochemical alternative. Adapted with permission from Reference [28].

Another example where mechanochemistry was shown to be a more efficient alternative to the conventional solution-based synthesis was reported by Konnert and coworkers. They demonstrated that the preparation of N-protected amino acids could be achieved by ball milling using significantly less solvent than is normally required in the conventional methods. A comparison between the E-factors for both the solution-based and mechanochemical procedures revealed that the latter yields less waste produced per kilogram of product, and is therefore more environmentally-friendly. In yet another example, the Mack group conducted the solution-based Wittig synthesis of stilbene in tandem with the mechanochemical procedure previously reported by Shearouse et al. The EcoScale rating for the solution synthesis was calculated and found to be 35, whereas the solid-state procedure obtained a rating of 77 out of 100. It is thus evident that solid-state chemistry, and mechanochemistry in particular, can be more sustainable alternatives to conventional solution-based methods for chemical synthesis.
1.2 Zeolitic imidazolate frameworks (ZIFs)

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are a class of coordination polymers composed of metal ions and organic linkers, characterized by the presence of accessible voids. Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs and belong to the family of metal azolate framework (MAF) materials. Generally speaking, ZIFs are composed of tetrahedrally-coordinated divalent metal ions and imidazolate ligands. The metal ions, which are most commonly Zn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$, combine with imidazolate ligands to form two- or three-dimensional framework structures. Although the synthesis of metal imidazolates had already been described in the literature, ZIF structures were formally described first by the Chen group and introduced as functional materials by the Yaghi group in 2006. Since then, up to thousands of ZIF structures have been reported. ZIFs differ from some of their MOF counterparts in that they are generally more stable towards evacuation, varying chemical environments, and moisture. This property, combined with their relatively high microporosities and amenability to post-synthetic modification (PSM), have made ZIFs viable and popular candidates for a wide variety of industrial applications. This has been exemplified by the recent commercialization of the highly studied prototypical ZIF, sodalite (SOD)-topology Zn(Melm)$_2$ (ZIF-8) (Melm = 2-methylimidazole), sold as Basolite Z1200® and MTA2®. Some of the most cited applications for ZIFs include carbon dioxide storage and sequestration, catalysis, and molecular separation. The ability to tune ZIF materials pre- and post-synthetically has been explored to make light- and pH-sensitive sensors, in addition to enhancing the properties of known ZIFs.

1.2.1 Design

1.2.1.1 Node-and-linker approach applied to ZIFs

The node-and-linker approach is a design concept, first developed by Robson, which enables the assembly of nodes of predicted binding geometries and linkers into two-dimensional or three-dimensional structures (Figure 1.2). In the case of ZIFs, Zn$^{2+}$ ions are found in a tetrahedral coordination environment connected to imidazolate linkers. This geometric and stoichiometric relationship between nodes and linkers in ZIFs is markedly similar to the relationship between tetrahedral Si$^{4+}$ centers and O$^{2-}$ bridges in zeolites. Importantly, the angle
between the Si-O bonds in zeolites is expected to be similar or identical to the angle between the Zn-N bonds in ZIFs. This similarity has enabled the prediction that combining metal ions with imidazolate ligands could result in the synthesis of open structures similar to zeolites, and in fact, many ZIFs adopt the same network topologies as zeolites.

**Figure 1.2** The node-and-linker approach as applied to metal-organic frameworks.

### 1.2.1.2 Topologies

The combination of metal nodes and organic linkers can yield a virtually infinite number of arrangements in three-dimensional space and, consequently, there is a very large number of possible MOF structures. The concept of network topologies is therefore used to describe and differentiate between these arrangements. Interestingly, however, MOFs have been observed to adopt only a small fraction of these possible topologies. Ockwig et al. analyzed the structures of over 1000 reported MOFs and concluded that, depending on the coordination geometry of the building blocks, only two or three topologies were predominant. These results, partially summarized in Table 1.1, revealed that MOFs prefer to crystallize in a manner which maximizes the symmetry at the vertices, or nodes, depending on the shape of the building blocks.
<table>
<thead>
<tr>
<th>Coordination geometry</th>
<th>Topology</th>
<th>Frequency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trigonal</td>
<td>SrSi₂ (srs)</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>ThSi₂ (ths)</td>
<td>24</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>diamondoid (dia)</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>SrAl₂ (sra)</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>sodalite (SOD)</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>quartz (qtz)</td>
<td>3</td>
</tr>
<tr>
<td>Square planar</td>
<td>NbO (nbo)</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>CdSO₄ (cds)</td>
<td>38</td>
</tr>
<tr>
<td>Trigonal bipyramidal</td>
<td>BN (bnn)</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>square pyramid net (sqp)</td>
<td>30</td>
</tr>
<tr>
<td>Octahedral</td>
<td>primitive cubic (pcu)</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>NiAs (nia)</td>
<td>4</td>
</tr>
</tbody>
</table>

**Table 1.2** List of the most frequently observed MOF topologies by coordination geometry of the secondary building unit.

In the case of ZIFs, the imidazolate anion forms a bridge which connects tetrahedral metal nodes at an angle of 145°, which is very similar to the angle between Si-O bonds in zeolites (Figure 1.3). As a result, many ZIF frameworks adopt zeolitic topologies, such as sodalite (SOD), chabazite (CHA), and zeolite rho (RHO). Typically, the topology of a particular ZIF structure is designated by a three-letter code, facilitating the differentiation of various polymorphs of a ZIF. Two such examples are the Zn(EtIm)₂ (EtIm = 2-ethylimidazole) framework, which can adopt zeolite topologies RHO, ANA, and Cd(MelIm)₂ structure which can adopt both the SOD and merlinoite (MER) topologies. Aside from three-letter codes, other types of descriptors exist to define a certain topology, including the point symbol notation, the vertex symbol notation, and the coordination sequence.

![Zeolitic Imidazolate Frameworks](image1.png)

**Figure 1.3** Similarity in the Si-O-Si and M-Im-M bond angles in zeolites and ZIFs.
1.2.2 Synthesis

Solution-based methods including solvothermal and hydrothermal syntheses have been the conventional choice for the synthesis of ZIFs.\textsuperscript{35,38b,53} Solvents such as N, N'-dimethylformamide (DMF) or methanol (MeOH) are typically used, with nitrate or chloride salts selected as the metal source and imidazole derivatives as ligands. The reactions are conducted in an autoclave at temperatures usually at or above the boiling point of the solvent for several hours to days. Recently, however, a paradigm shift towards milder methodologies for the synthesis of metal-organic materials has led the search for more sustainable routes to ZIF materials. To that end, methods to decrease reaction times as well as to avoid the need for high temperatures have been studied. In that context, using microwave radiation as an alternative to conventional heating has been shown to greatly reduce the reaction times needed for ZIF synthesis. For example, Bao \textit{et al.} reported the aqueous microwave synthesis of the prototypical ZIF-8 in 30 minutes.\textsuperscript{54} The conventional solvothermal method used to synthesize ZIF-8 requires heating to \textasciitilde 145°C for as long as 24 hours.\textsuperscript{38b} The ability to produce ZIF materials in room temperature solution has also been investigated with the goal of further reducing the energy input required. Room temperature layering of a methanolic solution of HMeIm or HEtIm with a solution of Zn(OH)\(_2\) in aqueous ammonia resulted in slow formation of single crystals of SOD- and ANA-topology ZIFs, including ZIF-8.\textsuperscript{38a} Furthermore, room-temperature solution synthesis has been demonstrated as a rapid route to microcrystalline or nanocrystalline ZIFs. The reaction of metal (zinc or cobalt(II)) salts with imidazole derivatives in the presence of a strong base, such as trimethylamine or ammonium hydroxide, results in crystallization of the materials ZIF-8 or ZIF-67 within ten minutes.\textsuperscript{55} The particle size of the resulting ZIF material was found to be dependent on the amount of base added.\textsuperscript{55a} Several groups have also demonstrated the base-less room temperature synthesis of bulk or nanocrystalline ZIFs in either water or MeOH.\textsuperscript{56} The projected use of ZIFs on an industrial scale has highlighted the need for evaluating the scalability of every new synthetic process. In that context, the Ahn group reported the sonochemical synthesis of ZIF-8 at room temperature with the addition of NaOH and trimethylamine bases, and demonstrated that it could successfully be applied to the one-liter scale.\textsuperscript{57} In order to further reduce waste produced during the production of ZIF materials, there have been recent efforts to eliminate the need for solvent altogether. Such a case is the solid-state steam-assisted synthesis of ZIF-8 and its cobalt(II) analogue ZIF-67, devised by Shi \textit{et al.}\textsuperscript{58} Additionally, several groups,
including ours, have pioneered the synthesis of ZIFs in the solid state, through melt reactions, mechanochemistry, and accelerated aging. This will be discussed in further detail in Section 1.3.

1.2.2.1 Synthetic design

Synthetic design is an important factor in the search for new ZIF materials, with differing structures, topologies, and chemical functionality leading to vastly different topologies and porosity levels. High-throughput solvothermal synthesis has been an efficient methodology for rapidly screening reaction conditions to lead to the discovery of new ZIFs.\textsuperscript{59} Additionally, adding templating agents,\textsuperscript{60} changing reaction solvent,\textsuperscript{61} or varying the chemical structure of the imidazolate linker\textsuperscript{62} can direct the formation of novel ZIF materials. In other cases, simply changing the metal salt precursor has resulted in varying product morphology, presumably due to the templating effect of ions in the solution.\textsuperscript{63} The concept of using ZIF structures as molecules on which to conduct chemistry has vastly expanded the possibilities in functionalizing ZIFs to convey a specific property into the material or to obtain structures which otherwise are not attainable. Post-synthetic modification of the ZIF material, either in the form of covalent functionalization of the linkers\textsuperscript{64} or through solvent-assisted linker exchange, also known as postsynthetic ligand exchange,\textsuperscript{65} are valuable techniques in that context.

![Figure 1.4 Crystal structures of cobalt(II)-based ZIFs obtained solvothermally by solvent-templating (ethanol (EtOH) vs. toluene),\textsuperscript{61} or the addition of a templating additive (piperazine or pyridine (py)).\textsuperscript{60}](image_url)
1.3 Advances in the solid-state transformations of coordination bonds: from the ball mill to the aging chamber

The following Section 3 contains a Perspective Article entitled, “Advances in the solid-state transformations of coordination bonds: from the ball mill to the aging chamber” discussing the recent discoveries in the field of solid-state formation of coordination complexes and coordination polymers, written by C. Mottillo with guidance and editing contributions from Prof. T. Friščić, which will be submitted for publication shortly. The text has been formatted for inclusion in this Dissertation.

1.3.1 Introduction

This Perspective provides a brief overview of recent advances in solvent-free synthesis and transformations of molecules and materials based on metal-ligand coordination bonds. The focus of the article is on metal-organic structures and it builds on previous reviews provided a decade ago by the James group and the Braga group. Considering that coordination chemistry in the solid state is a rapidly advancing area, as well as that a number of recent reviews have already addressed solid-state and mechanochemical transformations of inorganic, organic and organometallic compounds, this Perspective is not intended to be comprehensive. Instead, it provides an overview of the current research landscape, and takes the opportunity to highlight basic aspects of the techniques and underlying mechanisms. In doing so, we focus largely on mechanochemistry, but also address other emergent solid-state techniques, such as vapour-assisted reactivity, and thermally and microwave-induced transformations.

1.3.2 The role of solvent-free synthesis in coordination chemistry

The development of solvent-free synthesis has been driven largely by the need for synthetic procedures that are cleaner and more energy- and materials-efficient than existing solvent-based ones. This rationale is obvious in the context of organic synthesis, especially of pharmaceutically relevant molecules and materials. Until recently, a lack of established, commercially relevant targets has meant that a similar impetus for the development of solvent-free synthesis has largely been absent in the chemistry of coordination compounds. As a result, the development of solvent-free, solid-state strategies for transformations of coordination bonds has been mostly driven by academic curiosity. However, recent commercialisation of
coordination polymers with open framework structures, also known as metal-organic frameworks (MOFs)\(^{66}\) or porous coordination polymers (PCPs),\(^{33b,67}\) now creates a need for coordination chemistry with low environmental impact, high atom and energy efficiency, as well as potential for efficient, high-throughput materials screening.

As a rapidly expanding family of 2- or 3-dimensional (2-D or 3-D, respectively) coordination polymers with open or even microporous architectures, MOFs have been at the forefront of materials chemistry for over two decades. Mostly based on designs involving metal centres as nodes and designer organic molecules as linkers,\(^{47a,68}\) MOFs can access remarkable porosity and surface areas,\(^{69}\) exhibit high stability to temperature and diverse environments,\(^{70}\) and can be chemically modified,\(^{71}\) making them ideal contenders for advanced applications.\(^{72-74}\)

The judicious combination of metal nodes and rigid organic linkers, central to the node-and-linker approach and the associated isoreticular synthetic strategy,\(^{47a,75}\) has enabled the discovery and formation of hundreds, if not thousands, of MOFs. Of these, several have already entered commercialisation, including the highly studied ZIF-8 (also known as MAF-4, sold as Basolite Z1200\(^{®}\) and MTA2\(^{®}\)),\(^{38b}\) HKUST-1,\(^{76}\) MIL-53\(^{77}\), MOF-5,\(^{32b}\) and UiO-66\(^{78}\) (Figure 1.5).

Commercialisation and unabated growth of interest in new and advanced applications of MOFs (e.g. conductivity, photovoltaic behaviour, catalysis)\(^{72,79,80}\) have brought into the limelight the inefficiencies of conventional, solution-based coordination polymer syntheses. These are normally solvothermal, \(i.e.\) involving high-boiling solvents (an example is N,N-dimethylformamide, DMF), excess reagents, and produces products in limited yields (70%) and phase purity.\(^{32c,59,81}\)
Such limitations are strong driving forces to search for more energy-, materials-, cost-, and time-efficient processes.\textsuperscript{1a,81} The assessment that solvent accounts for up to 90\% of weight used in all pharmaceutical or fine chemical batch processes\textsuperscript{19} makes solvent-free or solvent-reduced synthesis, such as mechanochemistry,\textsuperscript{23a,82} accelerated aging\textsuperscript{83} and thermally-assisted\textsuperscript{84} reactions central in developing alternative synthetic techniques. The aim of this Perspective review is to highlight the most recent advances in the formation of coordination bonds in the solid state. More comprehensive overviews of techniques used for coordination polymer synthesis can be found in recent reviews.\textsuperscript{85,86}

Although the ability to induce chemical reactions in the solid state has been known for millennia, only recently has it been validated as a versatile method to conduct organic,\textsuperscript{87} inorganic,\textsuperscript{88} and organometallic\textsuperscript{89} transformations leading to diverse high-value materials, including pharmaceuticals,\textsuperscript{90} nanoparticles,\textsuperscript{91} and microporous materials.\textsuperscript{92} Formation of coordination bonds appears particularly amenable to solid-state chemistry, with a large array of literature examples demonstrating the synthesis of small molecule complexes,\textsuperscript{93} clusters and cages,\textsuperscript{94} and coordination polymers.\textsuperscript{95} Inspired by such work, several pioneering reports have demonstrated that not only is the solid-state synthesis of MOFs feasible, but that it can be faster and higher yielding than many alternatives.\textsuperscript{96} Moreover, solid-state synthesis in the form of mechanochemistry is also readily scalable and adaptable to continuous manufacture.\textsuperscript{97}
Importantly, concepts fundamental to MOF synthesis in solution (i.e., the node-and-linker design, structure templating ubiquitous for the synthesis of zeolite\textsuperscript{98} or other types of open frameworks\textsuperscript{99}) not only remain applicable in the solid state, but are also expanded by it, leading to the discovery of new structures and polymorphs.

Of all solid-state techniques, mechanochemistry is the focal point of efforts to design solid-state syntheses of coordination polymers and MOFs. Often found to lead to shorter reaction times and higher yields than its solution counterparts, mechanochemistry also enables the use of otherwise inert, poorly soluble but industrially highly desirable feedstocks, such as metal oxides or carbonates. The efficiency and synthetic scope of mechanochemistry are increased through modified techniques of liquid-assisted grinding (LAG, also known as solvent-drop grinding or kneading)\textsuperscript{100-102} and ion- and liquid-assisted grinding (ILAG),\textsuperscript{103} each involving the use of a catalytic liquid additive, or a combination of a liquid and a salt additive, respectively, as a means to induce, enhance or direct reactivity of solid reactants. The success of mechanochemistry in coordination polymer synthesis has also inspired the emergence of other synthetic approaches that dismiss the use of bulk solvents, based on vapour-assisted reactions,\textsuperscript{83} reactions in the melt,\textsuperscript{84} as well as microwave-assisted solid-state synthesis.\textsuperscript{104} With efficiency, including high yields and low cost, of solid-state MOF synthesis becoming increasingly attractive, it is also becoming essential to determine factors, reaction kinetics, and mechanisms controlling the assembly and stability of materials under such conditions. This led to exciting advances in reaction monitoring, either \textit{ex situ} (i.e., in a stepwise manner) or \textit{in situ}, via real-time X-ray diffraction or spectroscopy, which will also be covered in this perspective.\textsuperscript{105} For a more detailed overview of mechanistic studies pertinent to mechanochemical transformations, we recommend a recent review.\textsuperscript{106}

\textbf{1.3.3 Solid-state synthesis of coordination polymers}

\textbf{1.3.3.1 Mechanochemistry, history, scope and benefits}

There is a number of methods through which mechanical force can achieve or facilitate molecular-level transformations, such as bond cleavage or formation, amorphisation and triboelectric or charge separation effects,\textsuperscript{107} including ultrasonic irradiation,\textsuperscript{108} individual molecule stretching using an atomic force microscope (AFM),\textsuperscript{109} rubbing, shearing, grinding or milling. The focus of this Perspective is on reactions by milling or grinding, which is the form of
mechanochemistry most commonly applied to bulk synthesis. According to Takács,\textsuperscript{110} written records on using mechanical force to induce chemical reactions date at least as far back as 4\textsuperscript{th} century B.C., when Theophrastus of Eresos described the formation of elemental mercury by manual grinding of HgS in a copper (or bronze) mortar. The small amount of vinegar used to “lubricate” this reaction brings about an uncanny resemblance to modern techniques of LAG and ILAG.\textsuperscript{103} More recent examples include the formation of silver amalgam by trituration of AgCl with HgCl\textsubscript{2},\textsuperscript{111} and numerous examples of large-scale processing of insoluble inorganic minerals.\textsuperscript{112} Mechanochemistry and milling are used in the synthesis of a wide range of inorganic materials, as in oxide, sulfide, carbide, nitride or boride formation,\textsuperscript{113-117} and are central to mechanical alloying.\textsuperscript{118}

Milling and grinding appear to have been adopted as synthetic techniques first by organic chemists, including Wöhler in the 19\textsuperscript{th} century\textsuperscript{119} and a number of solid-state organic chemistry research groups in the 20\textsuperscript{th} century, notably Paul and Curtin,\textsuperscript{120} and Etter.\textsuperscript{121,122} However, it is only in the past 30 years that mechanochemistry has been recognised as a reliable synthetic tool, largely by synthetic chemists interested in “soft materials”, such as crystalline and amorphous organic solids,\textsuperscript{123} including polymorphs, pharmaceutical cocrystals,\textsuperscript{124} salts\textsuperscript{125} and coordination polymers.\textsuperscript{126-130} More recently, mechanochemistry has also become of interest to researchers in metal-catalysed and organocatalytic covalent bond formation,\textsuperscript{131,132} including C-H activation, as well as organometallic chemists.\textsuperscript{133} The modern interest in mechanochemistry has, to a large extent, been inspired by pioneering reports of the Toda group,\textsuperscript{134} who demonstrated that organic reactions and host-guest inclusion can not only take place mechanochemically without solvent, but also that they can be highly specific and yield products inaccessible by conventional (\textit{i.e.} in solution) means.\textsuperscript{135}

The benefits of mechanochemistry in synthetic chemistry are two-fold: \textit{i}) on one hand, mechanochemistry can make chemical processes more environmentally-friendly by virtually eliminating solvent use, enabling reactivity at ambient conditions of temperature and pressure, shortening reaction times, increasing yields, and \textit{ii}) there is a growing body of evidence that mechanochemical synthesis can enable the formation of products not attainable traditionally, for example by making accessible new materials or new synthetic routes which may be hindered or impossible in solution by solvent-based interferences, such as solvation effects, solubility limitations or solvolysis.\textsuperscript{136,137} Historically, the simplest method to conduct grinding chemistry is
with a mortar and pestle. It is our opinion, however, that the simplicity of this technique is often more than offset by inherent drawbacks: the impracticality for employing long reaction times, poor reproducibility caused by poor reporting of experimental variables (which does not include only the choice of experimenter, but also temperature, humidity, pressure, material and radius of curvature of the mortar, \textit{etc.}) and difficulty of scaling-up.

These drawbacks are readily eliminated by using electronically controlled ball mills, leading to greater reproducibility, improved control over and definition of reaction parameters (\textit{e.g.} time, frequency of shaking or rotation, ratio of weight of milling media to that of sample, ratio of volume of added liquid to solid being ground, \textit{etc.}), making the screening of reactivity more effective and systematic. Varying designs of milling apparatus, such as shaker mills, planetary mills,\textsuperscript{138} and twin screw extrusion (TSE) equipment (\textbf{Figure 1.6}),\textsuperscript{139,140} can provide an array of grinding force types and scaling-up opportunities. Selection of the number and material of milling media, varying in size, number, hardness and density provides an effective and powerful way to modulate mechanochemical reaction conditions. Usually employed milling media are made of stainless steel (density \(~7.7\ \text{g cm}^{-3}\)) or zirconia (density 4.5 g cm\(^{-3}\)), although alumina (density 3.95 g cm\(^{-3}\)), agate (density 2.6 g cm\(^{-3}\)) and tungsten carbide (density 15.63 g cm\(^{-3}\)) are also often employed. In addition to well-established milling technologies involving shaker (or mixer) mills (\textbf{Figure 1.6}), planetary mills or attritors, alternative setups permitting control over photochemical or thermochemical behaviour have been recently reported, such as vortex\textsuperscript{141} and lysis mills,\textsuperscript{142} respectively.
The formation of coordination bonds is a recently introduced and rapidly advancing area of mechanochemistry. One of the first examples of complex metal-organic structures formed mechanochemically was given by the Otera group, who reported the coordination-driven self-assembly of platinum(II)- and palladium(II)-based molecular squares by manually grinding the respective ethylenediamine nitrate salts with bridging ligands 4,4-bipyridine (bipy) or tris(4-pyridyl)triazine (tpt).\textsuperscript{143} The previously reported solution synthesis of the same molecular squares and cages at 100 °C required several weeks for near completion, while mechanochemical synthesis afforded these supramolecular structures within 10 minutes, in quantitative yield. Indeed, quantitative formation of products in a short time (e.g. 30-60 min) is often encountered and, in our experience, may be a hallmark of mechanochemical formation of coordination bonds, making this non-conventional synthetic approach much simpler compared to its solution counterparts, as it avoids the need for purification or filtration procedures.

One recently recognised emergent benefit of mechanochemical reactivity is the excellent stoichiometric control of product formation. Using mechanochemical synthesis of metal complexes with cyanoguanidine (enge) as a model reaction, Štrukil and co-workers demonstrated that the stoichiometry and, therefore, topological properties of the reaction product

\textbf{Figure 1.6} Apparatus for conducting and analyzing mechanochemical reactions: a) agate mortar and pestle used for manual grinding; b) automated laboratory shaker mill; c) setup for \textit{in situ} monitoring of mechanochemical reactions by synchrotron X-ray diffraction (Adapted with permission from Reference [196b]); d) large-scale twin screw extrusion (TSE) reactor setup (Adapted with permission from Reference [97]).
can be predetermined by the ratio of reactants (Figure 1.7a).

Specifically, milling of equimolar amounts of ZnCl₂ and cnge afforded the one-dimensional (1-D) polymer Zn(cnge)Cl₂, whereas milling of a mixture of the two reactants in the respective 1:2 stoichiometric ratio yielded the discrete (0-D) complex Zn(cnge)₂Cl₂. Attempts to synthesize each complex in solution, from different solvents, afforded mixtures of the two complexes, most likely due to differences in solubility of Zn(cnge)Cl₂ and Zn(cnge)₂Cl₂. Excellent stoichiometric control was also observed for the reaction of CdCl₂ with cnge, as well as for mechanochemical cocrystallization and thiourea click coupling reactions. Besides stoichiometric control, another highly exciting aspect of using mechanochemistry to synthesize coordination compounds is the discovery of materials that may be difficult or even impossible to attain from solution. The Bowmaker group, for example, reports that milling of AgCl and ethylenethiourea (etu) in a respective 1:1.5 stoichiometric ratio resulted in the complex AgCl(etu)₁.₅, also obtainable from solution. However, mechanochemistry also permitted the synthesis of the previously not known AgCl(etu)₃, by milling of AgCl(etu)₁.₅ with 1.5 more equivalents of etu (Figure 1.7b). In contrast, attempts to form the hypothetical AgCl(etu)₂ mechanochemically gave only mixtures of AgCl(etu)₃ and AgCl(etu)₁.₅, thereby illustrating how mechanochemistry can be used to screen for coordination compounds or potentially refute their existence.
Mechanosynthesis by neat grinding encompasses both manual grinding of reactants, only in a mortar with a pestle, or their milling in some type of automated milling apparatus. Early on, Thabet et al. pioneered the synthesis of metal complexes by neat grinding, by reporting the solventless mechanochemical reaction of neutral ligands with metal halides. Such ligand addition is a useful route to form complex coordination polymers. The Nassimbeni group reported the mechanochemical addition of pyrazine (pyz) to ZnBr$_2$, resulting in a square-grid (sql) topology coordination polymer ZnBr$_2$(pyz)$_2$. Preformed ZnBr$_2$(pyz)$_2$ was then milled with additional pyz to induce the formation of yet another polymer ZnBr$_2$(pyz)$_2$ of 2-D sql topology. Extensive investigations of mechanochemical formation of coordination complexes and

**Figure 1.7**

a) Control of product stoichiometry in the mechanochemical synthesis of zinc complexes with cnge can be achieved by selecting the ratio of starting materials; b) Mechanochemical synthesis of silver(I) complexes of ethylenethiourea (etu) to obtain products not formed in solution.

1.3.3.2 *Mechanochemical synthesis by neat grinding*

Mechanosynthesis by neat grinding encompasses both manual grinding of reactants, only in a mortar with a pestle, or their milling in some type of automated milling apparatus. Early on, Thabet et al. pioneered the synthesis of metal complexes by neat grinding, by reporting the solventless mechanochemical reaction of neutral ligands with metal halides. Such ligand addition is a useful route to form complex coordination polymers. The Nassimbeni group reported the mechanochemical addition of pyrazine (pyz) to ZnBr$_2$, resulting in a square-grid (sql) topology coordination polymer ZnBr$_2$(pyz)$_2$. Preformed ZnBr$_2$(pyz)$_2$ was then milled with additional pyz to induce the formation of yet another polymer ZnBr$_2$(pyz)$_2$ of 2-D sql topology. Extensive investigations of mechanochemical formation of coordination complexes and
polymers by neat grinding, as well as kneading, were reported by the Braga group. One example is the grinding reaction of silver(I) acetate (AgOAc) with trans-1,4-diaminocyclohexane (dace) under ambient conditions, the product of which was recrystallized in different conditions to form a series of hydrated isomeric coordination polymers.\(^{151}\) Ligand or metal exchange by neat grinding is also an effective route to coordination polymers. This was demonstrated for the first time by the Steed group, who reported the synthesis of a 1-D coordination polymer of copper(II) acetate and 1,3-di-(4-pyridyl)propane (dpp), by grinding copper(II) acetate monohydrate and dpp in a mortar and pestle, thereby inducing the exchange of the labile water molecules coordinated onto the copper(II) paddlewheel unit for bidentate dpp.\(^ {152}\) Importantly, this transformation demonstrated the retention of the copper(II) acetate paddlewheel motif, as mechanochemical grinding effectively resulted only in the exchange of axial water ligands with bridging dpp. This possibility to utilize pre-formed metal-organic clusters as reactants in the formation of complex metal-organic structures was subsequently utilised in mechanochemical synthesis of the popular material MOF-5.\(^ {153}\) In a report by Jobágyy et al., cyanoaurate(I)-based coordination polymers were synthesized via metal exchange by neat milling of potassium cyanoaurates(I) with metal halides.\(^ {154}\) The method provided a more reliable pathway to the medicinally-relevant cyanoaurate(I) complexes, whose solution synthesis can result in several coexisting species which are difficult to separate.

The inherent basicity of some metal salts enables the mechanochemical synthesis of coordination polymers by acid-base reaction with proton-donating ligands. For example, Yoshida et al. reported the synthesis of Co(II), Fe(II), Cu(II) and Ni(II)-based coordination polymers by milling the corresponding metal(II) acetates with the acidic 3-cyano-pentane-2,4-dione ligand (CNacacH).\(^ {95}\) This work was followed by the mechanochemical synthesis of related Cd(CNacac)\(_2\) coordination polymers, whereby selectivity for 2-D or 3-D structures was achieved by controlling the metal-to-ligand ratio.\(^ {156}\) In a step towards developing a simpler and cleaner synthesis of coordination polymers via mechanochemistry by limiting the formation of solid or liquid by-products, the Orpen group inaugurated the use of basic metal carbonates to synthesize coordination polymers based on pyrazolate ligands.\(^ {157}\) While the carbonate ion present in the reactant provided an internal base for deprotonation of the ligand, the same materials could also be obtained from diverse metal chlorides, by performing the mechanochemical procedure in the presence of KOH as a stoichiometric external base additive (Figure 1.8).
1.3.3.3 Liquid-assisted grinding (LAG)

The above mentioned reactions mostly involve hydrated salts which are likely to release water upon grinding, or those which release other liquid by-products, such as acetic acid. It has been proposed that, in such cases, the nominally neat grinding reactions are actually enhanced by in situ generated liquid phases which aid reactivity through yet unclear mechanisms, possibly including an increase in surface mobility of reactants, their partial dissolution, or even eutectic formation. A systematic screen for the reactivity of different metal salts in mechanochemical synthesis of coordination compounds, conducted by the James group, established a clear correlation between mechanochemical reaction speed and efficiency and the use of hydrated reactants and/or the formation of liquid byproducts. Such enhancement of reactivity can also be achieved deliberately, through the addition of small (catalytic) amounts of an external liquid additive. Specifically, the failure of neat grinding to induce reactivity in some systems can be circumvented by the addition of accelerating agents, such as a small amount of liquid. Such LAG methodology relies on a small amount of liquid to induce, facilitate, or accelerate reactivity.

So far, there have been only a few systematic investigations on how and why the liquid additive in LAG affects the course of mechanosynthesis. The so far only systematic investigation of how mechanochemical reactivity is affected by the solubility of reactants in the liquid additive.
has focused on the formation of model pharmaceutical cocrystals involving either caffeine (caf) or theophylline with tartaric or malic acids as cocrystal formers.\textsuperscript{160} This study introduced the parameter $\eta$, corresponding to the ratio of added liquid (in microliters) to the weight of solid reactants (in milligrams), as a way to quantitatively describe the mechanochemical LAG environment and compare it to other types of solution- or solvent-assisted reactivity (Figure 1.9). This provides a convenient and quantitative way to describe LAG reactions, instead of discussing reactions with “a drop” or “a small amount” of added liquid. In such a scenario, neat grinding is defined by $\eta=0 \ \mu\text{L mg}^{-1}$. The exploration of different $\eta$ values for the same model reaction enabled LAG to be defined as an $\eta$ range in which the mechanochemical reactions were not affected by differences in solubility of reactants (Table 1.2). This was empirically established to be between 0-2 $\mu\text{L mg}^{-1}$. For higher values of $\eta$, specifically 2-12 $\mu\text{L mg}^{-1}$, the system behaved as a slurry whose reactivity was largely affected by differences in reactant solubility in the added liquid. For $\eta>12 \ \mu\text{L mg}^{-1}$ the system was a solution with reactivity controlled by thermodynamic solubilities of reactants and products.\textsuperscript{160}

**Figure 1.9** Yield of the mechanochemical synthesis of the cocrystal between caffeine and L-tartaric acid as a function of the value $\eta$. Adapted with permission from reference [160].
<table>
<thead>
<tr>
<th>liquid additive</th>
<th>Solubility</th>
<th>product</th>
</tr>
</thead>
<tbody>
<tr>
<td>none (neat grinding)</td>
<td>—</td>
<td>no reaction</td>
</tr>
<tr>
<td>water</td>
<td>15</td>
<td>400 caf hydrate</td>
</tr>
<tr>
<td>MeOH</td>
<td>10</td>
<td>170 cocrystal</td>
</tr>
<tr>
<td>EtOH</td>
<td>6</td>
<td>72 cocrystal</td>
</tr>
<tr>
<td>i-propanol</td>
<td>3</td>
<td>27 cocrystal</td>
</tr>
<tr>
<td>n-butanol</td>
<td>3</td>
<td>16 cocrystal</td>
</tr>
<tr>
<td>2,2,2-trifluoroethanol</td>
<td>450</td>
<td>2 cocrystal + caf</td>
</tr>
<tr>
<td>benzene</td>
<td>&lt;2</td>
<td>&lt;2 cocrystal + caf</td>
</tr>
<tr>
<td>fluorobenzene</td>
<td>15</td>
<td>&lt;2 cocrystal + caf</td>
</tr>
<tr>
<td>acetonitrile</td>
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<td>13 cocrystal</td>
</tr>
<tr>
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<td>45</td>
<td>&lt;2 cocrystal</td>
</tr>
<tr>
<td>chloroform</td>
<td>135</td>
<td>&lt;2 cocrystal</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>7</td>
<td>9 cocrystal</td>
</tr>
<tr>
<td>di-i-propyl ether</td>
<td>&lt;2</td>
<td>&lt;2 cocrystal</td>
</tr>
<tr>
<td>ethylmethyl ketone</td>
<td>8</td>
<td>15 cocrystal</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>&lt;2</td>
<td>&lt;2 no reaction</td>
</tr>
</tbody>
</table>

Table 1.3 Independence of cocrystal formation between caffeine and L-tartaric acid on the solubilities of the reagents in selected LAG solvents.160

Liquid-assisted grinding can provide access to synthetic pathways which are not available through neat grinding, or activate inert, insoluble starting materials such as metal carbonates. For example, the attempted synthesis of the coordination polymer [CoCl₂(bipy)]ₙ by grinding anhydrous CoCl₂ with bipy gave no reaction.161 However, adding a small amount of ethanol (EtOH) to the reaction mixture resulted in rapid, full conversion into [CoCl₂(bipy)]ₙ by manual grinding (kneading). In a similar manner, the solid-state reaction between Ag(etu)₁.₅ and 1.5 equivalents of etu was accelerated with the addition of a small amount of water.148 Whereas the neat reaction did not result in full conversion after several minutes, LAG afforded quantitative yields within one minute.

In addition to accelerating mechanochemical transformations, LAG has been shown to enable the solid-state and reversible self-assembly of otherwise inaccessible host-guest complexes. This was clearly demonstrated by Braga and co-workers, who investigated the effect
of the liquid additive on the formation of inclusion compounds of the 1-D coordination polymer of $[\text{CuCl}_2(\text{dace})]_\infty$.\textsuperscript{162} Whereas milling of CuCl$_2$ and dace in the presence of water as a LAG additive gave a hydrated material $[\text{CuCl}_2(\text{dace})]_\infty\cdot n\text{H}_2\text{O}$, doing so in the presence of a series of organic liquids such as dimethyl sulfoxide (DMSO), 2-propanol, or acetone resulted in reversible inclusion of the solvent guests into the host structure of the coordination polymer.\textsuperscript{102} Interestingly, the uptake of larger guest molecules, including 2-propanol or acetone, could not be achieved by the suspension of $[\text{CuCl}_2(\text{dace})]_\infty$ in these solvents. However, pre-kneading $[\text{CuCl}_2(\text{dace})]_\infty$ with a small amount of the liquid enabled formation of inclusion compounds after suspension in a series of solvents.

The lower melting points and higher solubilities of metal halides, nitrates, and acetates, make them amenable for use as reagents in solid-state synthesis.\textsuperscript{159} However, in many respects, metal oxides, hydroxides and carbonates are ideal as precursors in coordination polymer synthesis, as they are less costly, less toxic, and give off water and CO$_2$ as the only by-product. Nonetheless, the high melting points of metal oxides and generally inert nature have, until recently, prevented their use in most solution-based or solvent-free syntheses of metal-organic compounds. Among the first to recognize the reactivity of metal oxides towards organic ligands upon grinding was the group of Fernandez-Bertran,\textsuperscript{163} who established the partial or complete formation of metal imidazolates $\text{M(Im)}_n$ (where $\text{M}=\text{Zn, Hg, Ag, Cd}$, $n=1,2$) by manual grinding of ZnO, HgO, Ag$_2$O, and CdO with solid imidazole (HIm). Notably, oxides of Al, Mg, Ca, and Ba were not reactive under these conditions, suggesting that the determining step in the mechanochemical reaction was the complexation of the metal cation by the ligand, rather than deprotonation of HIm. Although reaction products were not characterized by any other method except infrared spectroscopy, it is very likely that the reaction involving ZnO is the first example of a mechanochemically prepared zeolitic imidazolate framework (ZIF).

The mechanochemical reactivity of metal oxides can be greatly enhanced by the use of LAG and ILAG methodologies, as demonstrated by several reports from the Friščić group.\textsuperscript{164} For example, whereas brief (30-60 minutes) milling of ZnO with fumaric acid (H$_2$fum) does not lead to the formation of a new material, milling in the presence of different liquid additives enables the rapid and quantitative assembly of structurally and chemically diverse coordination polymers. Milling of ZnO and H$_2$fum in a 1:1 stoichiometric ratio in the presence of 3 or 4 equivalents of water selectively and quantitatively yields the previously known and structurally
characterized one-dimensional coordination polymers Zn(fum)·4H₂O and Zn(fum)·5H₂O, respectively. Selective formation of these two coordination polymers provides another example of excellent atom efficiency and control over reaction stoichiometry achievable under milling conditions, as all components of the reaction, including the liquid additive and water by-product of the neutralization reaction, become included in the final product.

Milling in the presence of catalytic amounts of methanol (MeOH) or EtOH, however, leads to the quantitative synthesis of previously unknown phases, established to be the anhydrous 3-D polymer Zn(fum) and a hydrated 2-D coordination polymer Zn(fum)·2H₂O. The formation of different metal-organic phases by milling with different liquid additives could be readily associated to the amount and the activity of water in the liquid additive. Liquid phases of high hydrogen bonding propensity, such as MeOH or EtOH, significantly reduce the thermodynamic activity of water and facilitate the formation of anhydrous phases or materials with low level of hydration. Liquids that are not particularly efficient in reducing water activity, such as 2-propanol or acetonitrile, lead to the formation of highly hydrated materials. This reactivity was readily expanded to the synthesis of 3-D open pillared MOFs by conducting the milling in the presence of a pillaring ligand, such as bipy or trans-1,2-bis(4-pyridyl)ethylene (bpe).

1.3.4 Mechanochemical screening for metal-based derivatives of active pharmaceutical ingredients (APIs)

Mechanochemical and other types of solid-state transformations of coordination bonds (e.g. accelerated aging) are gaining popularity for the synthesis of new, metal-based derivatives of active pharmaceutical ingredients (APIs). This development comes on top of the now well-established application of liquid-assisted mechanochemistry (e.g. LAG, kneading) in screening for new API forms (polymorphs, cocrystals, solvates, salts).

Although solid-state reactivity of APIs with metal-containing excipients (e.g. MgO) has been known in pharmaceutical materials science for a long time, the first targeted synthesis of metal complexes by grinding of metal salts with APIs was probably reported by the Braga group, who synthesized complexes of the neuroleptic drug gabapentin by kneading of this API with zinc chloride and silver nitrate. Subsequent work, mostly by the research groups of Duarte and of Braga, has demonstrated facile synthesis of a wide diversity of metal API complexes, including discrete complexes as well as coordination networks. Exploration of gabapentin
complexation with lanthanide (La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$, Er$^{3+}$) chlorides led to complexes exhibiting two modes of gabapentin coordination, in contrast to those obtained from solution. In a related study, the mechanochemical synthesis of the silver complex with 4-aminosalicylic acid led to an anhydrous product, in contrast to synthesis from solution that persistently yielded a hydrate.

It can be envisaged that metal oxides, hydroxides and carbonates are highly desirable reactants for synthesis of pharmaceutical materials, not only because of their accessibility, low cost and inherently lower toxicity compared to soluble metal chlorides and nitrates, but also because their reactivity is expected to generate only water, or mixtures of water and CO$_2$, as the byproduct. This was the guiding idea for developing a mechanochemical synthesis of the metallodrug bismuth(III) subsalicylate, the active component of the well-known anti-ulcer drug Pepto-Bismol®

Mechanochemical LAG reaction of MgO with either R- or RS-ibuprofen leads to the formation of a hydrated magnesium complex. The complex exhibits a higher solubility in aqueous environment compared to the API itself, providing a potential explanation for higher activity of ibuprofen formulations involving MgO as the excipient. In a similar fashion, LAG of MgO with salicylic acid, either alone or in the presence of additional complexation agents, led to the formation of magnesium salicylate complexes. Derivatization of APIs by complexation with magnesium ions is particularly advantageous for pharmaceutical applications because, in contrast to most other metals, magnesium is not considered to have any notable toxic effects. With that in mind, LAG with MgO was used as a means to generate new solid forms of the API naproxen (H$_2$nap). In particular, the systematic variation of the amount and activity of water in
the milling liquid led to the formation of structurally different hydrated phases. High activity and concentration of water led to a strongly hydrated material Mg(nap)₂·8H₂O that could not be structurally characterised, but is most likely based on Mg(H₂O)₆²⁺ ions and nap⁻ counterions. In contrast, a less hydrated coordination polymer Mg(nap)₂·H₂O was obtained by LAG at lower water activity. At intermediate water activity levels an intermediate hydrate Mg(nap)₂·xH₂O (x=3.5-3.7) was obtained, with Mg²⁺ ions octahedrally coordinated by H₂O and nap⁻ ligands (Figure 1.10b).¹⁷³

Figure 1.10 a) Liquid-assisted grinding synthesis of the API bismuth subsalicylate, active ingredient in Pepto-Bismol¹⁷⁰, b) Increasing water content in the LAG solvent of the reaction between MgO and naproxen shows increasingly hydrated product as results of mechanochemical reaction.¹⁷³

1.3.5 Synthesis of MOFs by neat grinding

The first entry of mechanochemistry into the synthesis of a microporous metal-organic framework was the neat milling synthesis of copper(II) isonicotinate, reported by the James group. The MOF was prepared in quantitative yield by brief (10 minutes) milling of solid copper(II) acetate monohydrate (Cu(OAc)₂·H₂O) with isonicotinic acid using a shaker mill. The product was obtained in the form of a solvate, with water and/or acetic acid by-products included in the framework pores. The porous framework was obtained by evacuating the
mechanochemical product at 200 °C. This work was subsequently expanded to the synthesis of one of the archetypal MOFs, HKUST-1, by milling Cu(OAc)$_2$·H$_2$O with 1,3,5-benzenetricarboxylic acid (H$_3$btc, trimesic acid) (Figure 1.11a). The mechanochemically prepared MOFs have been shown to have identical or even superior properties compared to those made from solution. Neat grinding was also successful in preparing MOFs based on diverse other metals and linkers. A recent example is the synthesis of a porous cadmium-based MOF from cadmium acetate, 4,4’-oxybis(benzoic acid), and bipy, reported by the Junk and Morsali groups (Figure 1.11b). Zhang et al. demonstrated the synthesis of soluble coordination polymers starting from phenol ligands and zinc acetate. A so far unique example of using a metal hydride as a precursor in the mechanosynthesis of a MOF is the formation of an yttrium-based framework by neat milling of YH$_3$ with H$_3$btc (Figure 1.11c).

Although solution-based (including solvothermal) synthesis of MOFs is highly dependent on using soluble metal salts, in particular chlorides, nitrates or acetates, such approaches have recently been criticised by manufacturing industries due to unavoidable safety risks and environmental challenges, due to inherent toxicity and corrosive nature of such salts, as well as the formation of waste mineral acids that must be neutralized through stoichiometric base, generating waste salts. It is, therefore, not surprising that industrial researchers have recognized a need to develop alternative approaches to MOF synthesis, that would avoid solvothermal treatment and utilize safer, less corrosive but also significantly less soluble reagents, such as sulfates, oxides, hydroxides or carbonates. Several groups have been pursuing mechanochemistry for the efficient synthesis of MOFs from metal oxides and metal carbonates. Whereas most of this work was achieved through the application of LAG and ILAG techniques, there are examples of 3-D open MOFs obtained by neat grinding. One of the earliest reported examples is the synthesis of open MOFs from lanthanide(III) carbonates and H$_3$btc. The mechanochemical reactions readily yielded 3-D frameworks and, by using mixtures of carbonates of different lanthanide metals, it was also possible to obtain MOFs with different metal nodes.
The neat grinding synthesis of MOFs from metal carbonates is also adaptable for large-scale continuous manufacture of commercially-relevant MOFs, as demonstrated by the James group who described the synthesis of aluminium-based MOF Al(fumarate)(OH) from fumaric acid and aluminium sulfate hydrate by twin screw extrusion.\textsuperscript{97}

Neat milling is not an efficient approach for the synthesis of ZIFs from a metal oxide, as reported by Beldon \textit{et al.} who reported incomplete conversion of ZnO into the commercially relevant framework ZIF-8 by ball milling with 2-methylimidazole (HMeIm). This result was subsequently corroborated by real time reaction monitoring using \textit{in situ} synchrotron X-ray powder diffraction.\textsuperscript{184} Although the reaction did not reach completion within 90 min, \textit{in situ} collected X-ray diffractograms clearly indicated the formation of the sodalite-topology (SOD) ZIF-8. More information on the mechanism of this and potentially other neat grinding transformations was provided by the Tanaka group, who used high-resolution scanning electron microscopy to establish the formation of core-shell nanostructures consisting of ZnO encapsulated by the product ZIF-8.\textsuperscript{185}

**Figure 1.11** Mechanochemical synthesis of various MOFs by neat grinding or LAG: a) Synthesis of HKUST-1 from copper salts and trimesic acid\textsuperscript{175}; b) Synthesis of pillared MOF TMU-09 from cadmium acetate\textsuperscript{176}; c) Solid-state synthesis of yttrium-based MOF MIL-78.\textsuperscript{178}
The addition of a small amount of liquid has been shown to dramatically enhance or accelerate the synthesis of coordination polymers from oxides or carbonates. An early demonstration of such reactivity was provided by Adams and co-workers, who demonstrated the assembly of coordination polymers by LAG or neat milling reaction of transition metal carbonates with protonated hydrochloride salts of organic linkers, such as bipy.\(^{186}\)

Variation of the liquid additive in LAG offers a means to direct the formation of metal-organic structures, as demonstrated by Yuan et al., who explored the mechanochemical reactions of basic zinc carbonate and terephthalic acid in the presence of different liquid additives.\(^{182}\) Milling with water led to the formation of a 1-D coordination polymer zinc terephthalate dihydrate, whereas milling in the presence of MeOH yielded the 3-D close-packed monohydrate framework. In contrast to these close-packed materials, milling with DMF yielded an open structure with square-grid topology, consisting of two-dimensional sheets based on zinc carboxylate paddlewheel secondary building units (SBUs) interconnected by terephthalate linkers. These mechanochemically obtained products readily interconverted by LAG with an appropriate liquid. In contrast, attempts to achieve similar structural interconversions by stirring of the materials in the appropriate solvent were largely unsuccessful, indicating enhanced structural flexibility of metal-organic materials under milling conditions.

In the first example of mechanochemical synthesis of open MOFs from a metal oxide, Fábián and coworkers synthesized pillared MOFs by ball milling of ZnO, H\(_2\)fum and either bipy or bpe as the pillaring ligand. While neat grinding did not result in any significant conversion, LAG with DMF resulted in quantitative formation of the targeted 3-D pillared MOFs.\(^{164a}\) Importantly, the authors established that the reaction progress was limited by the amount of liquid present. The minimum amount of liquid required for the complete conversion of the reaction mixture was calculated from the published structures of the corresponding MOF with solvent included in the pores. If the liquid content was insufficient to completely fill the voids of the nascent MOF, the reaction would not lead to completion, highlighting a dual role of the liquid additive in MOF synthesis: as a means to accelerate the reaction, and as a space filling or even structure-templating agent. Importantly, the LAG synthesis of these pillared MOFs was readily conducted using either MeOH, EtOH or \(i\)-PrOH as the liquid additive, providing a means to completely avoid the use of teratogenic DMF in pillared MOF synthesis.
mechanochemically synthesized MOFs were readily desolvated by heating, as evidenced by structural characterisation of the MOF based on bpe pillars from PXRD data collected on the desolvated material. Similarly, the structure of the guest-free pillared MOF based on fumarate and bpy ligands was determined by Fujii and coworkers from PXRD data collected on thermally desolvated materials prepared by LAG from ZnO.164b

The use of LAG was also central in developing a mechanochemical synthesis of the archetypal MOF-5 (also known as IRMOF-1) material by the Lewinski group. The synthesis of MOF-5 was achieved by mechanochemical reaction of terephthalic acid with zinc-oxo carboxylate or amidate clusters containing the pre-assembled Zn_4O^{6+} unit (Figure 1.12).153 Whereas the neat reaction using the benzoate-based cluster proceeded poorly in the absence of LAG additive, adding a small amount of N,N-diethylformamide resulted in the full conversion of reactants to MOF-5 which, after evacuation, exhibited a high surface area of 1831 m^2/g.

An interesting example of mechanochemical MOF synthesis was provided by the Matoga group,187 who demonstrated the mechanochemical transformation of a neutral manganese isonicotinate MOF (JUK-1) into a charged, proton-conducting MOF by neat grinding or LAG with NH_4SCN. The mechanochemical reaction involves the attachment of isothiocyanate ligands onto and rearrangement of manganese-based MOF nodes, resulting in an anionic 2-D framework material containing NH_4^+ cations suitable for proton conduction. An early approach to mechanochemical ZIF synthesis was by grinding of imidazolium halometallate salts with an external base, such as KOH, reported by the Orpen group.188

![Figure 1.12](image.png)

Figure 1.12 Solid-state mechanochemical synthesis of the archetypal MOF-5 framework from pre-formed oxo-zinc precursors. Adapted with permission from Reference [153].
Whereas the available literature indicates that carbonates and hydroxides are readily applied as precursors for LAG synthesis of MOFs, the use of metal oxides is often more challenging, as demonstrated by attempted syntheses of ZIFs from ZnO that did not reach complete conversion either by neat grinding or by LAG. Reactivity of metal oxides can, however, be facilitated by ILAG, *i.e.* by conducting LAG in the presence of a catalytic amount of a simple salt. The first report of the ILAG technique addressed the formation of the popular pillared MOF based on open square grid sheets of zinc terephthalate separated by 1,4-diazabicyclo[2.2.2]octane (dabco) as the pillaring ligand.\(^{181}\) Regardless of the choice of milling liquid, the pillared MOF could not be synthesized by simple LAG of ZnO, terephthalic acid and dabco, giving instead mixtures of dabco terephthalate and ZnO. This is in clear contrast to analogous pillared MOFs based on fumaric acid, which were readily obtainable by LAG. However, LAG in the presence of a catalytic amount (ca. 5 mol% with respect to Zn) of nitrate ions, in the form of an ammonium or alkaline metal nitrate, rapidly (within 30 minutes) yielded the expected MOF. Replacement of nitrates with sulfates yielded a different pillared MOF based on hexagonal, Kagome-topology zinc terephthalate sheets, demonstrating the active role of the salt additive in controlling the topology of the MOF product. Besides leading to a topologically different product, sulfates were also significantly more active as ILAG additives, enabling MOF synthesis at amounts as low as 300 ppm with respect to zinc.

The use of ILAG also enabled quantitative, room-temperature formation of close-packed as well as microporous ZIFs by milling, using only stoichiometric amounts of reagents.\(^{184}\) In particular, catalytic amounts of ionic additives, such as NH\(_4\)NO\(_3\), ammonium methanesulfonate (NH\(_4\)CH\(_3\)SO\(_3\)) or (NH\(_4\))\(_2\)SO\(_4\) enabled the complete conversion of ZnO into ZIFs based on HIm, HMeIm and 2-ethylimidazole (HMeIm). Both the liquid and the salt additives in ILAG were found to actively direct the topology of the ZIF products, which were all obtained within 30 minutes, at room temperature. Importantly, the ILAG approach enabled the synthesis of ZIF-8, whose typical solution-based syntheses require large amounts of solvent (e.g. DMF, concentrated aqueous ammonia), reaction times in hours or days, and afford moderate yields.\(^{189}\) The chemical and physical properties, including the surface area, of mechanochemically made ZIF-8 were identical to the conventionally prepared material.
1.3.7 Recent mechanistic studies

1.3.7.1 Ex situ (stepwise) monitoring of mechanochemical reactions

Due to the recent rapid growth of synthetic applications of mechanochemical milling and grinding, the understanding of underlying mechanisms is becoming a highly active area of research. Until very recently, the analysis of the course of mechanochemical reactions has been possible only through stepwise, *ex situ* monitoring techniques, based on periodically interrupting the grinding or milling process and analysing the reaction mixture through available solid-state analytical techniques. For this purpose, a wide range of techniques have been applied, most notably PXRD, Raman or attenuated total reflectance (ATR) infrared spectroscopy, Mössbauer spectroscopy, surface area analysis, solid-state nuclear magnetic resonance (ssNMR) spectroscopy, and thermal analysis (*e.g.* thermogravimetric analysis and/or differential scanning calorimetry). In many cases, structural characterization of mechanochemical products is achieved by comparing the experimental X-ray diffractogram of the powdered reaction mixture to one simulated from crystallographic data available in the Cambridge Structural database (CSD). In certain cases, structural characterisation of previously not known materials is also possible through PXRD structure solution techniques. Alternatively, single crystal X-ray diffraction is also applicable in case that mechanochemically prepared phases can be recrystallized in the form of sufficiently good quality single crystals.190

Although mechanistic studies of mechanochemical reactions involving coordination compounds are rare, they appear to suggest general trends in reaction mechanisms. In particular, different *ex situ* studies of the formation of coordination polymers and MOFs by LAG and ILAG reveal stepwise mechanisms in which an initially formed low-density or highly solvated product is transformed, directly or *via* intermediate phases, into a denser, less solvated final product.

This is well illustrated by stepwise monitoring of the reaction between ZnO and H₂fum in the presence of 3 equivalents of water.165 Although the final product of the reaction is the tetrahydrate coordination polymer Zn(H₂O)₄(fum), whose composition is dictated by the stoichiometric composition of the reaction mixture, interrupting the milling after five minutes reveals the intermediate formation of the more solvated pentahydrate Zn(H₂O)₄(fum)·H₂O. Appearance of Zn(H₂O)₄(fum)·H₂O intermediate was explained by a mass action effect, as the relative amount of water to the nascent zinc fumarate polymer is large in early stages of the
reaction. The described stepwise mechanism was subsequently confirmed in an independent study by the Boldyreva group.

A stepwise reaction sequence was also observed in the ball milling synthesis of copper(II) acetate monohydrate from CuO: milling of CuO with a stoichiometric amount of acetic acid, in the presence of a catalytic amount of H₂O, initially yields an acetic acid solvate of the copper(II) acetate paddlewheel dimer. The final product of the reaction is the anticipated copper(II) acetate paddlewheel dimer. Again, the intermediate formation of a solvate was explained by the initially large amount of acetic acid reactant with respect to the nascent copper(II) acetate complex.

An *ex situ* mechanistic investigation of the mechanochemical ZIF synthesis was reported by Beldon *et al.*, who established and analysed the ILAG reaction of ZnO and $\text{HEtIm}$. Whereas the final reaction product was the close-packed quartz ($\text{qtz}$) topology $\text{Zn(ETIm)}_2$, as established by structure determination from PXRD data, interrupting the reaction at different time intervals revealed the initial formation of the open, low-density zeolite $\rho$ (RHO) topology framework, RHO-$\text{Zn(ETIm)}_2$, which is subsequently replaced by the more dense analcime (ANA) topology framework ANA-$\text{Zn(ETIm)}_2$. Upon further milling, ANA-$\text{Zn(ETIm)}_2$ transforms into the final product, $\text{qtz-Zn(ETIm)}_2$ (Figure 1.13a).

Stepwise formation of $\text{qtz-Zn(ETIm)}_2$ can again be explained by a mass action effect, as the relative amount of the liquid additive with respect to the nascent $\text{Zn(ETIm)}_2$ coordination polymer is certainly larger in the initial moments of the reaction. However, the RHO$\rightarrow$ANA$\rightarrow$qtz sequence is also consistent with the Ostwald’s rule of stages, as it corresponds to the transformation of a framework with a low tetrahedral density (number of tetrahedral centres per 1000 Å³,) and, therefore, low thermodynamic stability, into structures of increasing tetrahedral density and, therefore, stability.
The first investigation of kinetics of the mechanochemical synthesis of an open MOF was reported by the James group, by using Raman spectroscopy to monitor the LAG synthesis of an open Zn(Im)$_2$ framework in the presence of DMF. The difference in characteristic Raman scattering signals of free and coordinated imidazole species enabled time-resolved observation of the ZIF formation. A plot of the time-dependent variation in the fraction of unreacted HIm was consistent with a 2$^{nd}$-order reaction kinetics law (Figure 1.13b). The unexpected similarity of the mechanochemical LAG reaction kinetics to a kinetic rate law that is normally observed in dilute solutions has been explained through a pseudo-fluid model of reaction kinetics, wherein reaction progress depends on the number of collisions between the ZnO and HIm particles. This suggestion was buttressed by the high dependence of the reaction rate on the milling frequency which, presumably, should directly affect the frequency of contacts between reactant particles. In contrast, the reaction rate, for a set milling frequency, was not unaffected by changes in temperature.
One persistent problem of stepwise reaction monitoring is in ensuring a sufficiently small time interval between measurements. Highly impressive work in that context has been presented by the Emmerling group, who demonstrated the rapid stepwise analysis of the ball milling synthesis of a novel bismuth coordination polymer (\(H_2\text{Im}\)(Bi(bdc)\(_2\)) (bdc=benzene-1,4-dicarboxylate). Reaction monitoring by PXRD analysis at time intervals as short as 10 seconds revealed that the reaction proceeds through an intermediate Bi\(_6\text{O}_5\text{(OH)}_3\text{(NO}_3\text{)}_5\text{(H}_2\text{O)}_3\) phase, which appears a 10 seconds into milling and disappears after one minute.

1.3.7.2 In situ and real-time monitoring of MOF synthesis

Techniques for \textit{ex situ} reaction monitoring are instrumentally simple, readily accessible in most laboratories and, as described in the previous section, can provide valuable information on the course of mechanochemical reactions. However, \textit{ex situ} studies are also subject to significant limitations. Specifically, mechanochemical reactions may proceed too quickly for reliable \textit{ex situ} analysis, as reaction intermediates, including crystalline and amorphous phases, can appear and disappear on the time scale of seconds. Moreover, physicochemical transformations induced by milling are very likely to continue even after mechanical agitation has ceased, limiting the quantitative reliability of \textit{ex situ} studies. Examples of such transformations include continuation of the reaction, relaxation of activated phases, or reaction of mechanically activated material with air during sample preparation.

These obstacles can be circumvented by recently introduced techniques for \textit{in situ} reaction monitoring, first developed using high energy synchrotron X-ray diffraction, and followed by the development of a more readily accessible Raman spectroscopy technique. Most recently, a combined synchrotron X-ray diffraction and Raman monitoring system was presented by the Emmerling group. The first \textit{in situ} X-ray diffraction study of a mechanochemical reaction addressed the reactions of ZnO with different imidazole derivatives under neat grinding, LAG and ILAG conditions. This study confirmed the appearance of low-density frameworks as intermediates in the formation of close packed ZIFs, not only for the ILAG reaction of ZnO and H\textit{EtIm} but also, for example, for the reaction of ZnO with H\textit{Im} in the presence of a limited amount of DMF: \textit{in situ} monitoring revealed the initial formation of the open Zn(Im)\(_2\) framework with \textit{cag} topology, which subsequently transformed into the close-packed \textit{zni-Zn(Im)}\(_2\). For the reactions involving H\textit{MeIm}, the time-dependent change in the
intensity of diffraction lines of the ZIF-8 product revealed complete conversion within eight minutes for the ILAG reaction, whereas LAG led to maximum, incomplete conversion within 30 minutes. In both cases, product revealed sigmoidal behaviour, suggesting ZIF-8 formation from an initially amorphous product via an Avrami-type nucleation and growth mechanism.

Quantitative evaluation of the reaction kinetics was achieved by Halasz and co-workers by conducting LAG and ILAG reactions in the presence of an internal diffraction standard, revealing that the loss of ZnO diffraction lines over time resembles a 1st order reaction rate law. This result is consistent with solution-type reaction rate laws observed by the James group using Raman spectroscopy, corroborating the pseudo-fluid model of a rapidly mixed mechanochemical reaction. Importantly, quantitative in situ studies enabled the evaluation of the amorphous content throughout the reaction. Rietveld analysis of in situ collected data indicated that the amorphous content during LAG and ILAG reactions achieves a steady state of ca. 30% by weight (Figure 1.14). Quantitative analysis of the reaction mixture ex situ, however, revealed no more than 7% by weight of amorphous material, indicating the rapid relaxation of amorphous materials during sample extraction and analysis.

Figure 1.14 Quantitative in situ monitoring of the mechanochemical synthesis of the close-packed structure zni-Zn(Im): a) the reaction scheme, b) Reitveld-extracted weight values of reactant, product, and amorphous phases in LAG reaction changing over time; c) Reactant, product, and amorphous phase concentrations for ILAG reaction changing over time. Adapted with permission from Reference [11a].
Reaction monitoring \textit{in situ} led to unexpected discovery of a metastable polymorph of ZIF-8, exhibiting a previously not reported tetrahedral network topology named katsenite (three letter abbreviation \textit{kat}). Specifically, attempts to conduct a greener synthesis of ZIF-8 by milling of ZnO and HMeIm with water as the milling liquid and acetic acid (AcOH) as the acid catalyst revealed the amorphisation of initially formed ZIF-8. Upon further milling, however, the amorphous material underwent crystallisation, first into the higher density \textit{kat}-Zn(Melm)$_2$ and subsequently into the final, close-packed product \textit{dia}-Zn(Melm)$_2$. The SOD$\rightarrow$kat$\rightarrow$dia sequence again follows the Ostwald rule of stages (Figure 1.15).$^{196a}$ This was confirmed also by density functional theory (DFT) evaluation of framework stability. For a more comprehensive overview of \textit{in situ} techniques for mechanochemical reaction monitoring, as applied to coordination compounds and cocrystals, we recommend a recent review.$^{105}$

\textbf{Figure 1.15} Scheme summarizing the sequence SOD$\rightarrow$kat$\rightarrow$dia in the mechanochemical reaction between ZnO and HMeIm with dilute AcOH. \textit{In situ} monitoring by X-ray diffraction led to discovery of the new ZIF \textit{kat}-Zn(Melm)$_2$, which forms upon recrystallization of amorphous Zn(Melm)$_2$ before converting to the denser \textit{dia}-Zn(Melm)$_2$ framework.$^{196a}$

1.3.8 Synthesis assisted by solvent vapour: vapour digestion, accelerated aging and vapour-assisted grinding

While mechanochemistry offers attractive advantages for the synthesis of coordination compounds, including almost complete elimination of solvents and ability to conduct reactions quickly and at room temperature, there is evidence that transformations involving acid-base reactions and exchange of coordination bonds can also take place, albeit slower, even without significant input of mechanical energy. Such reasoning has recently given birth to attractive, solvent-free and low-energy synthetic approaches wherein the transformations of well mixed reactant solids are facilitated by exposure to suitable environmental conditions. Despite a number of different names for such techniques, including vapour digestion, accelerated aging or vapour-
assisted grinding (VAG), their common facet is the use or an organic or inorganic (e.g. water, ammonia) vapours to enhance transformations of solid-state reactants, effectively exploiting molecular mobility at the gas-solid interface to achieve clean and low-energy synthesis of molecules and materials. Some of the early systematic studies of such reactivity has been reported in the pioneering quantitative studies of Byrn et al. on spontaneous reactivity in mixtures of carboxylic acid-based APIs (e.g. flufenamic acid) and the excipient MgO upon exposure to humid air. While oriented primarily towards understanding of the stability of pharmaceutical formulations, this work clearly demonstrated how vapour-assisted reactivity permits room-temperature transformation of high-melting substances, such as the well-known refractory MgO (melting point 2400 °C).

1.3.8.1 Vapour digestion

The use of organic vapours as a catalyst to induce reactivity in mixtures of solids was first proposed as a solvent-free technique for the synthesis of organometallic materials by the Braga group, who exposed mixtures of a pyridine-substituted ferrocene and suberic acid to vapours of different organic liquids. Besides demonstrating a simple means to induce solid-state reactivity, this work also demonstrated a structure-directing effect of the organic vapours, as non-polar liquids led to the assembly of hydrogen-bonded cocrystals, and polar liquids led to a proton-transfer reaction to form a salt. Vapour digestion has since been extensively used in the synthesis of pharmaceutically relevant cocrystals, as well as in the assembly of metal-organic fluorescent and phosphorescent materials based on copper iodide clusters.

1.3.8.2 Accelerated aging: synthesis of MOFs inspired by mineral neogenesis

In 2013, Qi and co-workers demonstrated that exposure of static (i.e. not stirred) solid-state mixtures of oxalic acid and diverse main group and transition metal oxides to elevated humidity can enable the quantitative synthesis of metal oxalate coordination polymers. For example, no reaction was observed upon aging of a 1:1 stoichiometric mixture of zinc oxide and oxalic acid at room temperature and relative humidity (RH). However, exposure to high humidity (98% RH) at 45 °C led to quantitative formation of the 1-D chain polymer zinc oxalate hydrate.
Although the use of high humidity at mild conditions represents a novel direction in the synthesis of metal-organic materials, including MOFs, the transformations themselves are highly reminiscent of geological processes of mineral neogenesis (or mineral weathering) that take place upon exposure of simple binary minerals (e.g. metal oxides, sulphides, etc.) to small organic molecules of biological origin, such as oxalic acid that is excreted by lichens and is also abundant in guano, in the form of ammonium oxalate. Indeed, the formation of metal oxalate deposits through action of lichens of guano is a well-known geological phenomenon, leading to minerals such as Mooloite, Lindbergite, etc.

Importantly, the accelerated aging transformations could be readily directed towards the formation of open anionic MOF structures by addition of suitable organoammonium templating species in the static reaction mixtures (Figure 1.16b). Specifically, the addition of 1,3-propanediammonium oxalate induced the formation of 2-D metal oxalate MOFs with hcb (“chickenwire”) topology, whereas the addition of n-propylammonium oxalate induced the formation of open 3-D anionic MOFs. These results are consistent with structure-templating studies in solution described by Cheetham and Rao. In this way, accelerated aging enabled the synthesis of previously reported zinc MOFs directly from the oxide, as well as the synthesis of previously not known isostructural MOFs based on Ni(II) and Co(II) ions.
This study also established that different metal oxides exhibit different rates of conversion upon accelerated aging with oxalic acid. In most cases, the reaction rates could be enhanced by brief milling of the solid-state mixture. In case of MnO, such mechanical activation also affected the
nature of the final product, as enhanced reactivity led to the formation of less stable (kinetic) polymorph of manganese(II) oxalate dihydrate coordination polymer.

The difference in reactivity of different metal oxides was exploited for kinetic separation of solid-state mixtures. For example, exposing a 1:1:1 stoichiometric mixture of ZnO, CuO and oxalic acid to 98% RH and 45 °C led to selective transformation of ZnO into zinc oxalate. The resulting mixture of zinc oxalate and CuO could be readily resolved by flotation with a dense liquid, such as CH$_2$I$_2$, enabling a completely solvent-free separation of zinc and copper in their oxide form. Similar kinetic resolution of binary metal oxide mixtures was also demonstrated for systems comprising PbO and CuO, as well as ZnO and PbO, providing an attractive, clean methodology for resolution of mineral concentrates of base metals (Figure 1.16d).

Accelerated aging was also readily applicable to materials that are not found in geological context, such as ZIFs. So far, accelerated aging has enabled the spontaneous self-assembly of a range of ZIFs from metal oxides (CoO, ZnO) and 2-substituted imidazoles HIm, HMeIm and HEtIm. Although exposing solid-state mixtures of an oxide with an imidazole to high humidity (98%-100% RH) and mild temperature (45 °C) led to poor conversion or none at all, addition of catalytic amounts of protic salts was found to enable quantitative or nearly quantitative formation of ZIFs, without any bulk solvent. For example, a mixture of ZnO with Him underwent partial conversion to form the non-porous \( zni-Zn(Im)^2 \) framework. However, the addition of ca. 5 mol% (with respect to zinc) of NH$_4$NO$_3$ afforded complete conversion to the zni-topology framework product upon exposure to 100% RH and 45 °C. Similarly, reactions with HMeIm and HEtIm in the presence of a catalytic salt afforded non-porous diamondoid topology (dia) \( Zn(MeIm)^2 \) and quartz topology (qtz) \( Zn(EtIm)^2 \) MOFs.

Reaction enhancement by protic salts was explained by an imidazolium-based proton transfer cycle. The aging reaction of (NH$_4$)$_2$SO$_4$ and HIm revealed the formation of an imidazolium sulfate salt, \((H_2Im)_2SO_4 \cdot H_2O\), suggesting that accelerated aging reactions involve an imidazolium species that is sufficiently acidic to react with a metal oxide and is also regenerated throughout the reaction. In such a scenario, the reaction proceeds through the formation of a metal imidazole complex on the metal oxide surface, which is subsequently deprotonated by the remaining imidazole reagent to regenerate the active imidazolium species.
This proposed mechanism enabled the targeted development of imidazolium and xanthine salt catalysts, resulting in a library of potential catalysts that can be used to screen for and optimise accelerated aging syntheses of MOFs. Such systematic investigation revealed caffeinium sulfate as a particularly successful catalyst for the synthesis of ZIF-8, which was obtained in gram amounts within a day. The prepared ZIF-8 exhibited a surface area on par to solvothermally-prepared material as well as commercially available Basolite Z1200® (Figure 1.16a). With HEtIm, the accelerated aging reaction was optimised to enable the first bulk synthesis of microporous RHO-Zn(EtIm)₂. Importantly, a bulk solution-based synthesis of this ZIF was reported only later. Similarly, accelerated aging of CoO with HIm, HMelIm and HEtIm led to the quantitative formation of ZIFs with zni-, SOD-, and qtz-topologies, demonstrating the ability to obtain a diversity of open and close-packed metal-organic architectures from dense, normally inert starting materials in the solid state, without any solvent and under mild conditions.

A two-step synthetic procedure, that combines activation by milling, followed by aging, was developed by the Yuan group to achieve the conversion of CuO into the popular, commercially relevant framework HKUST-1. The procedure consists of ILAG of CuO and trimesic acid in the presence of DMF and NH₄Cl salt additive. Exposure of the resulting solid to water vapour led to the assembly of the HKUST-1 framework within 6 hours. Key to the aging formation of HKUST-1 appears to be the intermediate active species Cu(NH₃)₂Cl₂ formed in the pre-milling step. The two-step procedure can also be performed if initial milling is conducted in the absence of a liquid phase, i.e. by milling in the presence of 5 mol% NH₄Cl. However, in this case the quantitative assembly of HKUST-1 requires significantly more time, 6 days.
Vapour-assisted solid-state reactivity was applied to the synthesis of a MOF based on biologically relevant molecule (a Bio-MOF) by exposing equimolar mixtures of copper(II) acetate monohydrate and adenine (H\textit{ade}) to humidity or acetic acid vapour (Figure 1.16c). The aging reaction, which yields the open framework Cu(\textit{ade})(OAc) in the form of a solvate with water and acetic acid, was accelerated if initial mixing of the reagents was conducted by brief ball milling, rather than by manual grinding. Most importantly, the use of acetic acid vapour was key to achieving rapid conversion of the reaction mixture. Exposure to humidity led to complete conversion after 12 hours at room temperature, whereas AcOH vapours induced the quantitative assembly of the Bio-MOF in 30 minutes. In contrast, attempts to use MeOH vapours led to incomplete reaction that no longer advanced after 6 hours.202

An interesting demonstration of the potential of vapour-assisted reactivity in activating metal oxides involved exposure of mixtures of lanthanide metal oxides and trimesic acid to vapours of water or organic solvents (EtOH, DMF). After three days exposure to water vapour, oxides of lanthanum, neodymium, samarium and europium yielded a 1-D coordination polymer of composition M(btc)(H2O)6 (M=La, Nd, Sm, Eu).27 Similar reactivity was observed upon exposure to EtOH vapour, but with neodymium exhibiting only partial conversion. With DMF, the same product was obtained, but this time only in the case of lanthanum and europium. These results represent the first observation of solvent-free transformation of highly stable oxides of three-valent metals into metal-organic materials. The vapour-assisted aging reactivity of lanthanide metal carbonates led to the same product except, surprisingly, Tb2(CO3)2, which yielded the open framework Tb(btc)(H2O), exhibiting 6 Å-wide pores.

1.3.8.3 From accelerated aging to materials testing procedure

Accelerated aging syntheses of open ZIFs reveal unexpected dynamics of the nascent metal-organic structures. For example, attempts to assemble an open MOF by aging of ZnO and H\textit{MeIm} in the presence of simple ammonium salts revealed that the initially formed ZIF-8 structure readily collapses into the dense, thermodynamically more stable \textit{dia}-Zn(\textit{MeIm})2. Similarly, the initially obtained \textit{RHO}-Zn(EtIm)2 rearranges into the non-porous \textit{qtz}-Zn(EtIm)2 in the absence of a suitable space-filling agent.200 Whereas these synthetic obstacles were resolved by using more advanced protic catalysts, they also suggest that aging in high humidity as a simple stability testing procedure. Indeed, accelerated aging bears resemblance to standard
procedures for testing the environmental stability of pharmaceutical solids, and exposure to high humidity was explored as a means to evaluate MOF stability by the Kaskel group\textsuperscript{203} and, very recently, the Zaworotko group.\textsuperscript{204}

Accelerated aging was used as a means to evaluate ZIF stability in complex atmospheres by Mottillo \textit{et al.}, who exposed open and close-packed ZIFs of Zn, Co(II) and Cd to gaseous Ar, N\textsubscript{2} or CO\textsubscript{2} in the presence of water vapour.\textsuperscript{205} All ZIFs were largely stable in humid Ar and N\textsubscript{2}. Humid CO\textsubscript{2}, however, induced unexpected and rapid transformation of almost all ZIFs, with the exception of \textit{zni}-Zn(Im)\textsubscript{2}, into complex metal carbonates. Whereas the structures of these products remain unknown, the presence of imidazole and carbonate species was confirmed by ssNMR and ATR infrared analysis. For cadmium-based ZIFs, PXRD analysis revealed the formation of CdCO\textsubscript{3} along with a complex carbonate based on Cd(HIm)\textsubscript{6}\textsuperscript{2+} cations. The sensitivity of ZIFs to moist CO\textsubscript{2} contrasts their known stability in dry CO\textsubscript{2} and resistance to steam or boiling water,\textsuperscript{206,207} highlighting the importance of using complex atmospheres to evaluate the stability of MOFs and their suitability for particular applications.\textsuperscript{208}

\textbf{Figure 1.18} Degradation of the diamondoid-topology framework Cd(Im)\textsubscript{2} by aging in humid carbon dioxide to the complex carbonate Cd(HIm)\textsubscript{6}CO\textsubscript{3}·3H\textsubscript{2}O.\textsuperscript{205} Adapted with permission from Reference [205].

\subsection*{1.3.9 Thermal solid-state synthesis}

The use of liquid additives or templating auxiliaries, although advantageous for previously discussed synthetic methods, can cause problematic in the context of certain synthetic environments. For example, the production of lanthanide MOFs is often limited to oxygen coordination environments, due to the preference for binding oxygen. In addition, this behaviour can be inhibitory for the synthesis of lanthanide MOFs due to the tendency for the metal to
preferentially bind coordinating solvents such as DMF. In that context, avoiding the use of solvents altogether, *i.e.* synthesis in the solid state, can be advantageous. To that end, the Müller-Buschbaum group devised the completely solvent-free synthesis of a europium(II)-based MOF comprising the ligand 1H-1,2,3-triazole (Htz). Europium metal and Htz were sealed in inert atmosphere and allowed to react in the melt to afford the close-packed structure Eu₃(tz)₆(Htz)₂. The structure consisted of octahedrally-coordinated Eu²⁺ ions surrounded by solely nitrogen-atom donating ligands. Following their work with lanthanides, the same group adapted the thermally-assisted solvent-free methodology towards the synthesis of transition metal-based ZIFs in the melt, namely incorporating cobalt(II) ions. The synthesis of the close-packed ZIF of zni topology, Co(im)₂, was achieved *via* a stepwise and temperature-sensitive process. The reaction of cobalt metal and HIm under vacuum at the different temperatures, 150 °C, 210 °C, or 300 °C resulted in the synthesis of three chemically and structurally distinct cobalt(II) imidazolates of decreasing HIm:cobalt ratio, Co₃(Im)₆(HIm)₂, Co₄(Im)₈(HIm), and zni-Co(im)₂. Interestingly, heating already formed Co₃(Im)₆(HIm)₂ to 210 °C resulted in the loss of HIm to form Co₄(Im)₈(HIm), and heating the compound further to 225 °C yielded the homoleptic zni-Co(im)₂. Interestingly, the stepwise formation of coordination polymers of high ligand content at the start of the reaction when there is a large amount of ligand available for reaction is consistent with the mass action effect, as was seen in the LAG synthesis of zinc fumarate coordination polymers.

Early contributions to the thermal synthesis of coordination polymers revealed the synthesis of iron imidazolates in the melt. The Trotter group demonstrated that the reaction of ferrocene and HIm at 150 °C in a sealed tube under inert atmosphere yields the polymeric compound Fe₃(Im)₆(HIm)₂. The methodology was also extended to the HMeIm ligand, from which combined with Fe(II) to form the close-packed qtz-Fe(II)(MeIm)₂ as well as an open framework incorporating ferrocene as a guest (Figure 1.19). While the work of Trotter and Müller-Bauschbaum exemplified the fairly high reactivity between transition metals or lanthanides and imidazole ligands, Lin *et al.* demonstrated that the solid-state thermal synthesis could also be achieved from a simple metal oxide. Namely, the synthesis of MAF-4, also known as ZIF-8, was achieved by heating a solid mixture of ZnO and HMeIm for several hours. Using higher temperatures resulted in greater crystallinity of MAF-4 material which was free of unreacted ligand and could be used for sorption experiments without subsequent activation by
washing or evacuation. While such studied show that metal oxides are viable starting materials for the thermally-mediated synthesis of coordination polymers, the composition and topology of the products obtained were relatively uncontrollable. To circumvent this problem, the Román group presented one of the first examples of the structure-directed formation of MOFs in a solvent-free reaction. The synthesis of a series of zinc- and cobalt(II)-based imidazolate MOFs was achieved by means of the thermal reaction between metal oxides or hydroxides and azole ligands with or without the presence of templating agents. Templating agents 1-butanol, py, and 4-methylpyridine (4mpy) enabled the formation of a series of topologically distinct structures incorporating the ligands HIm and HMeIm, including the novel frameworks neb-topology Zn(Im)2·(py)0.5 and nog-topology Co(Im)2·H2O)2.5·(4mpy)0.2. The Luque group expanded the scope of thermally-assisted synthesis of open coordination polymers from metal oxides and hydroxides by establishing the possibility to synthesize a series of zinc- and nickel(II)-based bioMOFs based on adenine and carboxylic acid ligands.

1.3.11 Conclusions

As metal-organic frameworks are established as useful industrial materials, the synthetic routes leading to their production must be optimized. Currently, the most common method of
synthesizing MOFs is not in line with the requirements for green, environmentally-friendly processes, due to high solvent volumes and high temperatures often needed in contrast to low-to-moderate yields. Thus, solid-state synthesis has been identified as a promising route to the quantitative, efficient, and greener formation of MOFs. In particular, mechanochemistry has been well-investigated and established as a viable, scalable MOF synthesis. Although recent advancements in monitoring mechanochemical reactions has revealed factors which govern the assembly of MOFs in the solid-state, there are many questions remaining about the mechanisms driving mechanochemistry. The questions must be answered for the design of new framework synthesis, the discovery of new reaction routes, and the adoption of mechanosynthesis on an industrial scale.

1.4 Using green chemistry metrics to compare solution-based and solid-state chemistry

The above sections point out the many advantages of using solid-state chemistry for the synthesis of discrete coordination complexes and coordination polymers, including MOFs. In addition to stoichiometric control, the enabled use of simpler reagents, and allowing the discovery of new polymorphic forms of previously known materials, solid-state methods serve as more environmentally-friendly alternatives to conventional solution-based methods. This was exemplified by the work of both Hamilton and Konnert, who calculated and compared the green metrics for the solution-based and mechanochemical synthesis of porphyrins and amino acids, respectively. In both cases, the mechanosynthesis yielded improved green metrics compared to the conventional solution syntheses.

While it is clear that mechanochemistry is a more environmentally-friendly alternative to conventional methods, several groups have focused on developing increasingly energy-efficient synthetic methods by virtually eliminating the need for prolonged mechanical agitation. The accelerated aging technique developed by our group for the synthesis of ZIF-8 exemplifies this concept. The grinding step in the mechanosynthesis of ZIF-8 was replaced by slow static aging in high humidity at mild temperatures. In order to further quantify the advantages of accelerated aging versus mechanochemistry, the values of six green chemistry metrics for the 10 gram mechanochemical (ILAG),\textsuperscript{184} accelerated aging,\textsuperscript{26} and solvothermal synthesis of ZIF-8\textsuperscript{38b} were tabulated and compared (Table 1.4).
It is fairly simple to justify the observed improvement in green metrics for the solid-state synthesis of ZIF-8 versus the solvothermal procedure. The solvothermal synthesis of ZIF-8 affords sub-quantitative yields and requires heating toxic and corrosive Zn(NO₃)₂ at high temperatures for several hours in large amounts of DMF. On the other hand, the mechanochemical ILAG synthesis of ZIF-8 gives quantitative yields in 30 minutes from ZnO, with virtually no solvent required. Interestingly however, a comparison between the green metrics of the mechanochemical process and accelerated aging revealed only a marginal improvement in E-factor, mass intensity, and reaction mass efficiency, while all other metrics remained the same. It appears that although the green metrics investigated take account of the amount and type of reagents used, the yield of the process, in addition to the generation of waste in the form of solvent or reaction by-products, they do not take into account energy consumption, scalability, and overall process complexity, which may be significant for comparing the greenness of solid-state methods. In the case of accelerated aging, the decreased reliance on costly and energy-consumptive milling apparatus is advantageous. For example, the power consumption of a 29 cu. ft. incubator oven heated to 45 °C, which can theoretically yield up to 5 Kg of ZIF-8 per day, was measured to be 300 W. This is significantly lower than the 3 kW power consumption of a laboratory-scale Retsch PM400 planetary mill, which would have to be

<table>
<thead>
<tr>
<th>Green metric (ideal value)</th>
<th>Solvothermal synthesis³⁸b</th>
<th>Mechanochemistry¹⁸⁴</th>
<th>Accelerated aging²⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom economy (100)</td>
<td>53.46%</td>
<td>92.65%</td>
<td>92.65%</td>
</tr>
<tr>
<td>Effective mass yield (100)</td>
<td>0.066%</td>
<td>92.76%</td>
<td>92.76%</td>
</tr>
<tr>
<td>E-factor (↓)</td>
<td>2126.58</td>
<td>8.22</td>
<td>7.92</td>
</tr>
<tr>
<td>Mass intensity (↓)</td>
<td>2133.4</td>
<td>9.34</td>
<td>9.04</td>
</tr>
<tr>
<td>Reaction mass efficiency (100)</td>
<td>11.85%</td>
<td>89.44%</td>
<td>92.11%</td>
</tr>
<tr>
<td>EcoScale (100)</td>
<td>16.5</td>
<td>77</td>
<td>77</td>
</tr>
</tbody>
</table>

Table 1.4 Calculated green chemistry metrics for the solvothermal,³⁸b mechanochemical,¹⁸⁴ and accelerated aging²⁶ synthesis of pure ZIF-8.
running nonstop for 12 hours to yield 5 Kg of ZIF-8. The increased time required for accelerated aging is thus offset by the energy saved. Other factors not taken into account by the green metrics relate to the relative simplicity of accelerated aging as compared to mechanochemistry. The scaleup of accelerated aging should in theory only require larger aging chambers and temperatures akin to some areas of the globe, while the adaptation of mechanochemistry on the large scale requires increasingly specialized and energy-intensive milling apparatus. Additionally, the simplicity of aging can reduce the energy and costs associated with cleaning and maintenance of complex equipment. The points above highlight the potential drawbacks of green chemistry metrics when applied to the comparison of solid-state chemistry, and call for the development of modified metrics adapted for solid-state methods as they become increasingly valuable as environmentally-friendly alternatives for materials synthesis.

1.5 References


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CHAPTER 2

ACCELERATED AGING: A LOW-ENERGY, SOLVENT-FREE ALTERNATIVE TO SOLVOTHERMAL AND MECHANOCHEMICAL SYNTHESIS OF METAL-ORGANIC MATERIALS

The work presented in this chapter is based on a published Edge Article entitled “Accelerated aging: a low-energy, solvent-free alternative to solvothermal and mechanochemical synthesis of metal-organic materials”, co-authored by Dr. M. J. Cliffe, C. Mottillo, Dr. R. S. Stein, Dr. D.-K. Bučar and written by Prof. T. Friščić (Chem. Sci., 2012, 3, 2495). Preliminary results were obtained by Dr. M. J. Cliffe and Prof. T. Friščić at the University of Cambridge. The contribution of Dr. R. S. Stein and Dr. D.-K. Bučar consisted of the collection of selected solid-state infrared spectroscopy, solid-state nuclear magnetic resonance spectroscopy, and powder X-ray diffraction data at the University of Cambridge. These results were repeated and substantially expanded upon by C. Mottillo at McGill University under the supervision of Prof. T. Friščić. The contribution of C. Mottillo consisted of modification of the manuscript for publication and compiling the Supplementary Information section. The work has been re-written for inclusion in this chapter. The results have been expanded upon with additional data, including that from the Supplementary Information of the paper, for the purpose of being incorporated in this Thesis.

2.1 Introduction and connecting text

The increasing environmental impact incurred by industrial chemical processes has driven the search for more sustainable alternatives to synthesize functional materials. In that context, limiting solvent use, as well as increasing atom economy and energy efficiency, are imperatives for the design of “greener” synthetic routes. Recently, solid-state methodologies such as mechanochemistry have been devised as environmentally-friendly alternatives to conventional approaches in the synthesis of coordination compounds and metal-organic frameworks (MOFs), as well as in organic synthesis. Further reducing energy input by avoiding mechanical agitation and relying entirely on the diffusion of solid reactants is an attractive, but challenging goal that has been addressed in recent literature. Vapour digestion, a technique developed by Braga and coworkers, involves exposure of solid mixtures of reagents to organic vapours over the course of hours to days. The selection of protic vs non-protic vapours was found to have structure-directing role in the solid-state formation of salts and co-crystals from solid reagents. Demonstrating that such solvent-free, diffusion-based reactivity can also be used
to form metal complexes, Byrn et al. reported the activation of poorly soluble metal oxides under high relative humidity (RH) and mild temperatures. Specifically, magnesium-based active pharmaceutical ingredients (APIs) were obtained by reacting mixtures of solid MgO and a carboxylic acid in a humid atmosphere. Such a process is reminiscent of the naturally-occurring transformations of inorganic minerals, called mineral neogenesis or weathering. In such cases, the slow transformation of inorganic binary minerals, such as oxides or sulfides, occurs due to the biologically-generated of organic ligands and complexation agents such as oxalic and norstictic acids. The work of Byrn et al. inspired the herein described development of a solvent- and energy-reduced technique for the synthesis of metal-organic materials, by suggesting that metal oxide activation can be readily achieved under such mild conditions.

In particular, this chapter describes the self-assembly of 3-dimensional zeolitic imidazolate frameworks (ZIFs), a class of MOFs composed of metal nodes and imidazolate-type linkers, through a process called “accelerated aging”. ZIFs are a promising class of MOFs, owing to their high chemical and thermal stability, mechanical properties, amenability to post-synthetic modification, as well as high CO2 sorption capacity. Mechanochemical synthesis has been previously described as an alternative methodology for the synthesis of ZIFs from poorly soluble metal oxides on short (less than one hour) timescales. The reactions were both accelerated and templated by the addition of catalytic amounts of salt additives, in a process called ion- and liquid-assisted grinding. In contrast to such mechanically-activated synthesis of ZIFs, the herein presented accelerated aging technique involves the purely diffusion-based solid-state activation of metal oxides, and their reaction with imidazole derivatives under mild (45 ºC) temperatures and high relative humidity (98% RH). This Chapter will outline the synthesis of ZIFs of imidazole (HIm), 2-methylimidazole (HMeIm), 2-ethylimidazole (HEtIm), and benzimidazole (HBlm) by a salt-catalyzed accelerated aging process (Figure 2.1).
2.2 Synthesis of close-packed ZIFs by accelerated aging

Initial experiments exploring the accelerated aging synthesis of ZIFs consisted of manually grinding a 1:2 stoichiometric mixture of ZnO and the ligand precursor (HIm, HMeIm, HEtIm, or HBIm) in an agate mortar and pestle for 5 minutes. The gentle mixing of starting materials was conducted to minimize inducing any mechanochemical activation. Analysis of powder X-ray diffraction (PXRD) patterns of the solid mixtures collected immediately after grinding confirmed that manual mixing did not cause any appreciable reactivity (Figure 2.2). No new crystalline phases were observed in the patterns of the starting mixtures, as determined by comparison of the PXRD patterns of the reagent mixtures and those of the individual starting materials.

Ambient laboratory conditions (20 °C to 23 °C and 60-70% RH) were selected as the first set of conditions for aging experiments. Product formation was ascertained by comparing the PXRD pattern of the aged mixtures to the PXRD patterns of the reagent mixtures immediately after manual grinding, as well as to those of the individual starting materials. A reduction in the relative intensities of peaks corresponding to ZnO and an increase in the intensity of new reflections was indicative of conversion to new crystalline phases. The identity of newly formed
phases was determined by comparing the experimental PXRD data with simulated powder patterns calculated from crystal structures of previously known ZIFs or Zn-imidazolate complexes, which are found in the Cambridge Structural Database (CSD). After 3 days aging at room temperature and humidity, the reaction between ZnO and HIm resulted in formation of the oligomeric complex Zn\(_4(\text{Im})_8(\text{HIm})\) (CSD code KUMXEW),\(^{15}\) as seen from PXRD analysis (Figure 2.2). Allowing the reaction to continue for six days in total did not reveal any noticeable increase in ZnO conversion, as evaluated by qualitative visual comparison between the PXRD patterns after 3 and 6 days. Reactions with HMeIm resulted in no apparent product formation after 6 days aging. X-ray powder diffraction analysis of the reaction with HEtIm after 4 days revealed low-intensity diffraction peaks corresponding to the open framework RHO-Zn(EtIm)\(_2\) (CSD code MECWOH) (Figure 2.2).\(^{16}\)

![Selected PXRD patterns of samples aged at room temperature and humidity: a) ZnO; b) HIm; c) simulated pattern for Zn\(_4(\text{Im})_8(\text{HIm})\) (CSD code KUMXEW); 1:2 mixture of ZnO and HIm: d) immediately after grinding; e) 3 days aging; f) 6 days aging; g) HMeIm; 1:2 mixture of ZnO and HMeIm: h) immediately after grinding; i) after 6 days aging; j) HEtIm; k) simulated pattern for RHO-Zn(EtIm)\(_2\) (CSD code MECWOH); 1:2 mixture of ZnO and HEtIm: l) immediately after grinding; m) after 4 days aging.](image)

The poor conversion at ambient, room temperature conditions led us to explore the effect of the amount of water vapour on reaction speed.\(^{17}\) For this purpose, selected accelerated aging
experiments were repeated with HIm, HMeIm, and HEtIm, at an elevated humidity level of 98% RH. After several days aging at 98% RH and room temperature, a PXRD analysis of all experiments demonstrated similar results as those under ambient conditions. This strongly suggested that the poor reactivity of the metal oxide was contributing to the poor conversion observed in aging synthesis. Previous reports of activating metal oxides in solid-state mechanochemical reactions using catalytic salt additives suggested that the same approach, *i.e.* addition of catalytic amounts of (NH₄)₂SO₄, could accelerate the aging synthesis of ZIFs.¹⁴ The addition of 4 mol% (NH₄)₂SO₄ with respect to ZnO was investigated in addition to conditions explored in the previous set of experiments (both ambient conditions and 98% RH at room temperature). Any improvement in reactivity due to the addition of a salt catalyst was ascertained by comparing the PXRD patterns of the products from salt-catalyzed aging reactions and the PXRD data from reactions in the absence of salt catalyst. An observed decrease in the relative intensity of peaks corresponding to ZnO at the end of the reaction was considered sufficient evidence to suggest an increase in conversion had occurred. Under ambient conditions the addition of (NH₄)₂SO₄ led to higher conversions in all cases. X-ray powder diffraction analysis of the reaction product of ZnO and HIm revealed greater conversion to Zn₄(Im)₈(HIm) (CSD code KUMXEW),¹⁵ although the reaction was still incomplete after 6 days (Figure 2.3). Greater product formation in the form of a mixture of RHO-Zn(EtIm)₂ (CSD code MECWOH) and analcime-topology (ANA) Zn(EtIm)₂ (CSD code MECWIB) was observed for the reaction using HEtIm.¹⁶ Only in the case of HMeIm did the addition of (NH₄)₂SO₄ not result in any improved reactivity, as determined by PXRD analysis (Figure 2.3).
Combining the addition of salt catalyst with high humidity (98% RH), however, resulted in higher conversion for all explored reaction systems, which was especially notable in the case of that involving HMeIm. Weak reflections corresponding to the sodalite (SOD) topology ZIF-8.
(CSD code VELVOY)\(^{18}\) and its close-packed polymorph \textit{dia}-Zn(\textit{MeIm})\(_2\) (CSD code OFERUN01)\(^{19}\) were evident by PXRD analysis after 6 days (Figure 2.3). The reaction with \(\text{HIm}\) yielded the close-packed \textit{zni}-Zn(Im)\(_2\) (CSD code IMIDZB03) in addition to its high-pressure \(\beta\)-polymorph (CSD code IMIDZB07), which was reported by Spencer \textit{et al.}\(^{20}\). Incomplete conversion to a mixture of the two products RHO-Zn(\textit{EtIm})\(_2\) and ANA-Zn(\textit{EtIm})\(_2\) was observed by PXRD analysis of the system containing \(\text{HEtIm}\).

Conceptually, these demonstrate the ability to achieve the room temperature synthesis of three-dimensional ZIF structures by accelerated aging, albeit in incomplete conversion. With the goal of improving the accelerated aging methodology such that it can enable the quantitative solid-state synthesis of ZIFs, a mild temperature increase was investigated as a means to drive the reactions to completion. At 98% RH and 45 °C, the oligomeric structure Zn\(_4\)(Im)\(_8\)(\text{HIm})\) (CSD code KUMXEW) formed from the reaction of ZnO and \text{HIm} in the absence of a salt catalyst, although reflections of ZnO were still apparent by PXRD analysis after 10 days (Figure 2.4). Increasing the temperature improved the reactivity of ZnO with \(\text{HMelm}\), and weak reflections matching those of the simulated PXRD pattern of ZIF-8 (CSD code VELVOY) were evident in the X-ray diffractogram of the reactant mixture after 15 days. The reaction of ZnO and \(\text{HEtIm}\) at 45 °C and 98% RH exhibited similar behavior as that at room temperature, showing the slow conversion to RHO-Zn(\textit{EtIm})\(_2\). After 15 days, PXRD analysis of the reaction mixture revealed that it consisted of a mixture of products RHO-Zn(\textit{EtIm})\(_2\), \textit{qtz}-Zn(\textit{EtIm})\(_2\) (CSD code EHERTE),\(^{14a}\) as well as unreacted ZnO. The \textit{qtz}-Zn(\textit{EtIm})\(_2\) structure is the close-packed, non-porous polymorph of RHO-Zn(\textit{EtIm})\(_2\).
Conducting the reactions at 45 ºC and 98% RH in the presence of salt additives resulted in the disappearance of reflections corresponding to ZnO for all explored systems. In the case of HIm, complete conversion of ZnO was observed by PXRD analysis within several days although, instead of Zn₄(Im)₈(HIm) (CSD code KUMXEW), the reaction yielded the close-packed zni-Zn(Im)₂ (CSD code IMIDZB03) structure as a single phase (Figure 2.5). Powder X-ray diffraction analysis of the aging reaction between ZnO and HMeIm in the presence of (NH₄)₂SO₄ after 3 days showed nearly complete conversion to ZIF-8. However, weak reflections of another phase were also apparent (Figure 2.5). After aging for 6 days, the reflections corresponding to ZIF-8 nearly completely disappeared, while those of the second phase became more prominent. Comparison of these new reflections with known Zn-methylimidazolates enabled the second phase to be identified as the close-packed polymorph of ZIF-8, dia-Zn(MeIm)₂ (CSD code OFERUN01), first reported by Shi et al. Addition of salt additive to the reaction between ZnO and HEtIm led to rapid formation of the close-packed qtz-Zn(EtIm)₂ framework.

**Figure 2.4** Selected PXRD patterns of reaction mixtures aged at 45 ºC and 98% RH: a) ZnO; b) simulated pattern for Zn₄(Im)₈(HIm) (CSD code KUMXEW); c) 1:2.25 mixture of ZnO and HIm after 10 days d) HMeIm; e) simulated pattern for SOD-Zn(MeIm)₂ (CSD code VELVOY); f) 1:2 mixture of ZnO and HMeIm after 6 days; g) simulated pattern for RHO-Zn(EtIm)₂ (CSD code MECWOH; h) simulated pattern for qtz-Zn(EtIm)₂ (CSD code ZNETIM2); i) 1:2 mixture of ZnO and HEtIm after 6 days.
In addition to phase analysis by PXRD, the products of accelerated aging were analyzed by solid-state Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy. The FTIR-ATR spectrum of the product formed from the salt-catalyzed reaction between ZnO and HIm at 45 °C and 98% RH showed the disappearance of N-H absorption bands centered around 3100 cm⁻¹, as well as the appearance of a broad O-H band around 3300 cm⁻¹, most likely corresponding to adsorbed moisture in the sample (Figure 2.6).

**Figure 2.5** Selected PXRD patterns of reaction mixtures aged in the presence of 4 mol% (NH₄)₂SO₄ at 45 °C and 98% RH: a) ZnO; b) simulated pattern for zni-Zn(Im)₂ (CSD code IMIDZB03); c) 1:2 mixture of ZnO and HIm after 4 days d) simulated pattern for SOD-Zn(Melm)₂ (CSD code VELVOY); e) simulated pattern for dia-Zn(Melm)₂ (CSD code OFERUN01) f) 1:2 mixture of ZnO and HMelm after 3 days; g) 1:2 mixture of ZnO and HMelm after 6 days; h) simulated pattern for qtz-Zn(EtIm)₂ (CSD code ZNETIM2); i) simulated pattern for qtz-Zn(EtIm)₂ (CSD code ZNETIM2); 1:2 mixture of ZnO and HEtIm after 3 days.
2.3 Scale-up of the synthesis of dia-Zn(\text{MeIm})_2 and qtz-Zn(\text{EtIm})_2

The development of accelerated aging as a reliable alternative for the greener synthesis of ZIFs is reliant on the scalability of the technique. In that context, the syntheses of dia-Zn(\text{MeIm})_2 and qtz-Zn(\text{EtIm})_2 frameworks were conducted on a ten-gram scale to ascertain the scalability of the accelerated aging methodology. Reactants ZnO and solid H\text{MeIm} or H\text{EtIm} were ground in a mortar and pestle, and placed in a glass Petri dish of 10 cm diameter in order to maximize the available surface area of the powder sample (Figure 2.7). Powder X-ray diffraction analysis of product sampled from different areas of the reaction volume showed full conversion of ZnO at 35 days (Figure 2.8). It is worth noting that the 20-fold increase in scale required only a 4-fold increase in reaction time.

**Figure 2.6** Selected FTIR-ATR spectra for the reaction between ZnO and H\text{Im} in the presence of (NH_4)_2SO_4 under 45 ºC and 98% RH: a) immediately after grinding; b) after 4 days aging.
Figure 2.7 Example of 10 gram synthesis of \textit{dia}-Zn(\textit{MeIm})\textsubscript{2}. Canadian ten cent coin (a dime) shown for size comparison.

Figure 2.8 Selected PXRD patterns of the reaction mixtures to form \textit{dia}-Zn(\textit{MeIm})\textsubscript{2} and \textit{qtz}-Zn(\textit{EtIm})\textsubscript{2} on the 10 gram scale: a) ZnO; b) simulated pattern for \textit{dia}-Zn(\textit{MeIm})\textsubscript{2} (CSD code OFERUN01); c) 1:2 mixture of ZnO and H\textit{MeIm} after 35 days d) simulated pattern for \textit{qtz}-Zn(\textit{EtIm})\textsubscript{2} (CSD code ZNETIM2); e) 1:2 mixture of ZnO and H\textit{EtIm} after 35 days.
Analysis of the FTIR-ATR spectra of the \textit{dia-Zn(Melm)}_2 and \textit{qtz-Zn(EtIm)}_2 products from accelerated aging synthesis on a ten-gram scale revealed no N-H absorption bands in the range of 3250 cm\(^{-1}\) to 2250 cm\(^{-1}\), suggesting the replacement of N-H bonds with N-Zn bonds. Prominent but broad N-H absorption bands centered at 2800 cm\(^{-1}\) in the spectra of initial mixtures were nonexistent in the product samples. In addition, the intense absorption band for ZnO at 500 cm\(^{-1}\) was no longer found in the product mixtures, consistent with conversion of ZnO to the ZIFs (Figure 2.9).

![Selected FTIR-ATR spectra for the large-scale synthesis of \textit{dia-Zn(Melm)}_2 and \textit{qtz-Zn(EtIm)}_2 at 45 °C and 98% RH: a) immediately after grinding; b) after 35 days aging; c) immediately after grinding; d) after 35 days aging.]

2.4 Analysis and conversion between close-packed and open polymorphs of ZIFs

The rapid conversion of ZIF-8 to its non-porous \textit{dia}-polymorph under mild conditions of accelerated aging is surprising, due to the reported high stability of ZIFs under relatively harsh thermal and chemical conditions.\(^{10,18}\) The \textit{dia}-framework was previously described only once, in a synthesis of ZIF-8 using a very large excess of H\textit{Melm} under steam-assisted conditions.\(^{19}\)

Further characterization of the \textit{dia-Zn(Melm)}_2 framework from a ten-gram synthesis was conducted using thermogravimetric analysis (TGA) and \textsuperscript{13}C solid-state magic-angle spinning
nuclear magnetic resonance spectroscopy (CP-MAS ssNMR). TGA of the unwashed sample in dynamic atmosphere of N₂ revealed a broad decomposition step after 200 °C followed by decomposition of the framework at 600 °C (Figure 2.10a). Since zinc-based imidazolates are usually expected not to decompose prior to 400 °C, it was presumed that the first weight loss step represents the loss of unreacted HMeIm or salt catalyst remaining in the sample. Indeed, the thermogram of the sample washed with water and dried in vacuo overnight showed no weight loss prior to 400 °C suggesting any remaining water-soluble ligand or salt catalyst had been removed (Figure 2.10b).

**Figure 2.10** a) TGA thermogram of the dia-Zn(MeIm)₂ synthesized on the 10 gram scale; b) thermogram of sample from a), washed in H₂O and dried in vacuo overnight. The green trace is the TGA signal. The blue trace is the derivative of the TGA signal.
The $^{13}$C CP-MAS ssNMR spectrum of the $\text{dia-Zn(Melm)}_2$ product revealed signals at chemical shifts consistent with each of three chemically distinct carbon species found in the $\text{Melm}^-$ ion. Each peak exhibited a multiplicity of four, which is expected due to the presence of four crystallographically-inequivalent $\text{Melm}^-$ ligands in the asymmetric unit ($Z' = 4$) of $\text{dia-Zn(Melm)}_2$ (Figure 2.11).

The results presented in this Section indicate that, thus far, accelerated aging favors the formation of close-packed ZIFs. In certain cases, the exposure of solid molecular materials to a gas phase has been demonstrated to induce conversion to open structures.\textsuperscript{22} With the intention of demonstrating a method which would render the solid-state synthesis of porous frameworks also possible, a sample of $\text{dia-Zn(Melm)}_2$ synthesized by aging was exposed to methanol vapors at 45 °C. After several days, near full conversion of $\text{dia-Zn(Melm)}_2$ to ZIF-8 was seen by PXRD analysis, with small reflections of the $\text{dia}$ framework still apparent in the diffractogram (Figure 2.12).
13C CP-MAS ssNMR analysis of dia-Zn(MeIm)$_2$ exposed to MeOH vapours revealed reduction of the multiplicity of the signals from four to one. This was consistent with an increase in symmetry from $Z'=4$ in dia-Zn(MeIm)$_2$ to $Z'=1$ in ZIF-8 (Figure 2.13).
To confirm the synthesis of a porous framework, nitrogen gas sorption measurements were conducted by Minh-Hao Pham from the laboratory of Prof. Trong-On Do at Université Laval, on a sample of ZIF-8 which was synthesized by MeOH-induced expansion of dia-Zn(MeIm)₂. Sorption analysis revealed a Brunauer-Emmett-Teller (BET) surface area of 1293 m²g⁻¹, which is in the range of previously published values for this type of material.¹⁸,²¹ This is remarkable considering a portion of the sample still consisted of the non-porous dia-Zn(MeIm)₂ (Figure 2.12). While similar guest-induced flexibility of frameworks has been reported previously in the case of molecular materials and carboxylate MOFs,²³ this is, to our knowledge, the first time such solvent vapour-induced transformation from non-porous to porous structure has been reported in a ZIF.

The apparent propensity for accelerated aging to yield close-packed ZIF structures led us to explore a second class of imidazole derivatives, based on benzimidazole (HBlm). Although the SOD topology Zn(BIm)₂,¹⁸,²⁴ which is isostructural to ZIF-8, has been reported, we did not observe its formation in the aging reaction of ZnO with HBlm. After allowing a 1:2 stoichiometric mixture of ZnO and HBlm to react for 33 days at 45 °C and 98% RH, no new reflections were observed by PXRD analysis (Figure 2.14). ZnO conversion was slightly enhanced by the addition of 4 mol% (NH₄)₂SO₄ with respect to ZnO, as seen by a reduction in relative intensities of the X-ray reflections of the latter. Low-intensity X-ray reflections corresponding to the two-dimensional non-porous square-grid (sql)-topology Zn(BIm)₂ (CSD code KOLYAM) were also observed by PXRD analysis.²⁵
2.5 Role of catalytic salt additives

Due to their inherently high stability and low solubility, metal oxides have usually not been amenable to use in solution-based synthesis, as well as in the solid state. The discussed activation of metal oxides by the addition of a very small amount of a mildly acidic salt in accelerated aging prompted a more detailed investigation of the role of (NH$_4$)$_2$SO$_4$ as a catalyst in such reactions. As a first experiment in such a study, a mixture of (NH$_4$)$_2$SO$_4$ and ZnO was left to react at 45 ºC and 98% RH. Within days, the reaction mixture began to deliquesce, leading to a white slurry composed predominantly of ZnO. Powder X-ray diffraction of the resultant paste after 7 days and a search of the literature regarding ammonium- or sulfate-based salts of zinc permitted identification of the product as Zn(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O, also known as Tutton’s salt (Figure 2.15). The sample was not ground prior to collection of PXRD data. Therefore, the difference in the relative peak intensities between the experimental and simulated PXRD patterns of Zn(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O can be explained by the presence of large crystallites in the sample analyzed by PXRD, which most likely led to preferred orientation effects. Thermogravimetric analysis and FTIR-ATR spectroscopy further confirmed the identity of the product.
ATR spectrum of the product after 7 days aging revealed a strong absorption band centered at 3024 cm\(^{-1}\) corresponding to the O-H stretch (Figure 2.16). In addition, an absorption band at 1063 cm\(^{-1}\) representing the S-O stretch of the sulfate anion was now present in the spectrum. The thermogram of Tutton’s salt made by such an aging reaction showed a significant weight loss at \(ca.\) 100 °C, amounting to 25% of the total weight. This is in agreement with the loss of six H\(_2\)O molecules from the salt structure, which would account for 26.9% of the total calculated molar mass of Zn(NH\(_4\))\(_2\)(SO\(_4\))\(_2\)-6H\(_2\)O. The final residue from calcining the salt in dynamic atmosphere of air amounted to \(ca.\) 40% of the total weight of the sample, which corresponds well to a residue consisting of anhydrous ZnSO\(_4\) (Figure 2.17).

**Figure 2.15** PXRD patterns of the aging reaction between ZnO and (NH\(_4\))\(_2\)SO\(_4\) at 45 °C and 98% RH: a) ZnO; b) (NH\(_4\))\(_2\)SO\(_4\); c) simulated pattern for Zn(NH\(_4\))\(_2\)(SO\(_4\))\(_2\)-6H\(_2\)O (Crystallography Open Database (COD) ID 2310635); d) product of ZnO and (NH\(_4\))\(_2\)SO\(_4\) after 7 days aging.
Figure 2.16 Selected FTIR-ATR spectra for the aging reaction between ZnO and (NH₄)₂SO₄ at 45 ºC and 98% RH: a) ZnO; b) (NH₄)₂SO₄; c) reaction mixture after 7 days aging.

Figure 2.17 Thermogram of Tutton’s salt, Zn(NH₄)₂(SO₄)₂·6H₂O, synthesized by accelerated aging, recorded in dynamic atmosphere of air. The first weight loss step of 25.0% is in agreement with the expected weight loss for the removal of six water molecules from Zn(NH₄)₂(SO₄)₂·6H₂O.
Differential scanning calorimetry (DSC) analysis conducted on Zn(NH₄)₂(SO₄)₂·6H₂O made by accelerated aging showed an endotherm with an onset at 100 °C (Figure 2.18). This endotherm was assigned to the loss of water of crystallization, as it was consistent with the significant weight loss observed at 100 °C by TGA analysis, as well as with the boiling point of water.

Although the formation of Tutton’s salt from the aging reaction of ZnO and (NH₄)₂SO₄ would supply a reason for the apparent activation of ZnO by transforming it to a more soluble sulfate salt, it does not explain the catalytic role of the salt additive. In order to elucidate any possible effect, the salt catalyst was having on the imidazole reactant, a homogeneous 1:2 stoichiometric mixture of (NH₄)₂SO₄ and HIm was exposed to 98% RH at 45 °C. The mixture rapidly deliquesced to form a liquid. After aging for two weeks, the formation of a crystalline crust was observed. Single crystals were extracted from the vial and their structure determined by single crystal X-ray diffraction. The structure consisted of imidazolium sulfate dihydrate (H₂Im)₂SO₄·2H₂O, which crystallizes in non-centrosymmetric tetragonal space group P4₁2₁2 (Figure 2.19), with unit cell parameters \( a = 7.9553(6) \) Å and \( c = 18.7605(13) \) Å (See Appendix for detailed crystallographic information). Figure 2.19 shows a general view of the crystal.
packing in \((\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}\), showing helical chains of \(\text{SO}_4^{2-}\) ions surrounded by four water molecules and hydrogen bonding to two imidazolium cations.

**Figure 2.19** Crystal packing of \((\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}\), showing helical chains of \(\text{SO}_4^{2-}\) ions and water molecules along the \(c\)-axis, surrounded by \(\text{H}_2\text{Im}^+\) ions.

In the structure, the \(\text{SO}_4^{2-}\) ions are related by symmetry along the \(4_1\) screw axis, to form helical chains linked by hydrogen-bonded water molecules. The \(\text{SO}_4^{2-}\) ions are connected to water molecules by O-H--O hydrogen bonds (\(\sim2.78\ \text{Å}, \sim170^\circ\)). The \(\text{H}_2\text{Im}^+\) ions link to the \(\text{SO}_4^{2-}\) ions via N-H--O hydrogen bonds (\(\sim2.7\ \text{Å}, \sim170^\circ\)). **Figure 2.20** highlights the symmetry-related sulfate anions surrounding the \(4_1\) axis, which runs parallel to the \(c\)-axis of the unit cell.
The sulfate salt of HIm could also be synthesized by reacting H$_2$SO$_4$ with HIm in acetonitrile solution. Experimental PXRD patterns of the single crystals obtained by aging and the bulk sample from solution matched the simulated pattern from single crystal X-ray data (Figure 2.21). Some neutral imidazole was apparent in the aging sample, indicating that the reaction was not complete despite there being an appropriate stoichiometric ratio (2:1 HIm: (NH$_4$)$_2$SO$_4$) of starting materials.

**Figure 2.20** View of crystal packing of (H$_2$Im)$_2$SO$_4$·2H$_2$O as seen down a 41 screw axis, highlighting the four symmetrically-equivalent sulfate anions.
The FTIR-ATR spectra of the aged and solution-made samples of \((\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}\) confirmed the formation of a hydrate sulfate salt of imidazole. The spectra of the aged and solution-made samples were almost identical, and an O-H stretching frequency was observed at 3306 cm\(^{-1}\). In addition to this, the N-H stretch absorption bands from 3100 cm\(^{-1}\) to 3500 cm\(^{-1}\) were still present, and an absorption band corresponding to the S-O stretch of \(\text{SO}_4^{2-}\) ions was found at 1050 cm\(^{-1}\) (Figure 2.22). Thermogravimetric analysis of the bulk sample from solution revealed a 13% weight loss with an onset at 30 °C and maximum loss rate at 55 °C, correlating well to the loss of two water molecules (the calculated weight percent of water in \((\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}\) is 13.3%) (Figure 2.23). The relatively low temperature of the loss of water suggested that the water molecules are poorly bound within the crystal structure of \((\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}\).
**Figure 2.22** Selected FTIR-ATR spectra of synthesized samples of (H₂Im)₂SO₄·2H₂O: a) HIm; b) (NH₄)₂SO₄; c) 2:1 mixture of HIm and (NH₄)₂SO₄ after 7 days aging at 45 °C and 98% RH; d) (H₂Im)₂SO₄·2H₂O synthesized from solution.

**Figure 2.23** Thermogram of (H₂Im)₂SO₄·2H₂O made from solution, showing a 13% weight loss, consistent with the removal of two water molecules (the weight percent of water in (H₂Im)₂SO₄·2H₂O is 13.3%). The green line represents the TGA signal and the blue line is the first derivative of the TGA signal.
2.5.1 Mechanism of catalytic activity of (H₂Im)₂SO₄·2H₂O

The formation of H₂Im⁺ provides a possible explanation for the catalytic activity of (NH₄)₂SO₄ in the synthesis of ZIFs by accelerated aging. The reaction of HIm with ammonium sulfate is proposed in **Equation 2.1**. The basic HIm is protonated by the mildly acidic NH₄⁺ cation. However, this process should be disfavored by the fact that the pKa of NH₄⁺ is 9.25, while that of the conjugate acid of HIm is 7.05. The driving force in this reaction must therefore be the release of NH₃ gas, which drives the equilibrium towards the formation of (H₂Im)₂SO₄·2H₂O.

![Equation 2.1](image)

**Equation 2.1** Proposed equilibrium reaction between HIm and NH₄⁺ to form H₂Im⁺, resulting in the release of NH₃ gas.

The catalytic effect of ammonium salt can therefore be tentatively explained through the formation of an imidazolium cation intermediate. This cation is of high acidity, so it can attack the surface of ZnO by protonating the oxide species, while the imidazole binds to the Zn²⁺ cation. The still positively-charged imidazole moiety binding to the surface of ZnO could subsequently be deprotonated by another neutral HIm molecule, which then becomes the new catalytic species. The cycle repeats itself, with the newly reacted ZnO surface available for binding to another HIm ligand, as depicted in **Figure 2.24**.
The catalytic mechanism described above implies that the salt (H$_2$Im)$_2$SO$_4$·2H$_2$O should be able to catalyze the reaction between ZnO and HIm in a similar manner to (NH$_4$)$_2$SO$_4$. To confirm this, ZnO and HIm were manually ground in a 1:2 stoichiometric ratio in the presence of 4 mol% (H$_2$Im)$_2$SO$_4$·2H$_2$O for 5 minutes, which resulted in the immediate formation of Zn$_4$(Im)$_8$(HIm) observable by PXRD analysis, with a small amount of ZnO still apparent in the PXRD pattern. Aging the sample at 45 ºC and 98% RH for 7 days resulted in complete consumption of remaining ZnO, indicated by complete disappearance of ZnO reflections from the PXRD pattern of the reaction mixture (Figure 2.25).

**Figure 2.24** Proposed catalytic cycle explaining the role of (H$_2$Im)$_2$SO$_4$·2H$_2$O in inducing the activation of ZnO and subsequent reaction to form Zn(Im)$_2$.²⁹
2.6 Conclusion

The increasingly negative environmental impact of chemical synthesis is highlighting the need for new synthetic routes to functional materials which require less solvent, minimal energy use, yet display higher efficiency. Inspired by the work of Braga and Byrn, it was herein demonstrated that the efficient, diffusion-based synthesis of 3-D ZIFs can be achieved from reagent mixtures entirely in the solid state, accelerated by exposure to high humidity, mild temperatures, and in the presence of catalytic amounts of salt additives. The synthesis of five separate ZIFs from HIm, HMeIm, HEtIm, and HBIm was achieved directly from ZnO, without the need for prior derivatization of the oxide. Metal oxide activation was enabled by the addition of small amounts of (NH₄)₂SO₄, which probably acts as an initiator to a proposed catalytic cycle involving an imidazolium cation intermediate. In addition to four close-packed structures, the porous and highly studied ZIF-8 was also synthesized by exposing its non-porous polymorph \textit{dia}-Zn(\textit{MeIm})₂ to methanol vapours. This not only demonstrated that the synthesis of porous
metal-organic frameworks could be achieved, indirectly, from dense metal oxides in a mild manner, but also serves as the first example of guest vapour-induced expansion of a close-packed ZIF. Accelerated aging or vapour-induced chemistry is thus not only a viable method for the “green” synthesis of functional organic\textsuperscript{30a} and metal-organic\textsuperscript{30b} materials, but also a means to study their solid-state properties (\textit{e.g.} stability) and structural dynamics under complex conditions of atmosphere and temperature (See Section 4). Accelerated aging represents a direct application of the mineral weathering concept from nature, to the more sustainable synthesis of metal-organic materials. The investigation of accelerated aging as a synthetic method, materials testing tool, and a means to screen for other imidazolium cation-based salt catalysts, will be discussed in subsequent chapters.

2.7 References


CHAPTER 3
MINERAL NEOGENESIS AS AN INSPIRATION FOR MILD, SOLVENT-FREE
SYNTHESES OF BULK MICROPOROUS METAL-ORGANIC FRAMEWORKS FROM
METAL (Zn, Co) OXIDES

3.1 Introduction and connecting text

The results reported in this chapter have been published in the journal Green Chemistry as a full paper entitled “Mineral neogenesis as an inspiration for mild, solvent-free synthesis of bulk microporous metal-organic frameworks from metal (Zn, Co) oxides”,¹ co-authored by C. Mottillo, Y. Lu, M.-H. Pham, Dr. M. J. Cliffe, Prof. T.-O. Do, and Prof. T. Friščić. A considerable part of that manuscript was written by Prof. T. Friščić and has thus been re-written by C. Mottillo for inclusion into this Thesis. C. Mottillo’s contribution to the drafting of the manuscript was in the form of significant editing, scientific discussions about content, and writing the Supplementary Information. C. Mottillo contributed to the majority of reactions, recrystallization experiments, and solid-state analysis described herein, as well as all crystal structure determinations. The contribution of Y. Lu, a 2013 summer undergraduate student, consisted of conducting select accelerated aging reactions, recrystallization experiments, and solid-state analyses of products and starting materials during her four-month summer internship under the direct supervision of C. Mottillo. Sorption measurements were provided by M.-H. Pham and Prof. T.-O. Do at Université Laval. Dr. M. J. Cliffe provided preliminary accelerated aging reaction data, collected at University of Cambridge and later also reproduced by C. Mottillo for inclusion into the paper.

Microporous metal-organic frameworks (MOFs)² have been extensively investigated for their potential industrial applications in the fields of gas storage and separation,³ catalysis,⁴ and sensing.⁴ A vast range of MOF classes, such as carboxylate-based MOFs and those built from zirconia clusters, have particularly advantageous properties including high porosity and chemical robustness.⁵ Zeolitic imidazolate frameworks (ZIFs), on the other hand, are attractive due to their appreciably high porosities, chemical and thermal stability, as well as relative ease of synthesis. Nonetheless, most current synthetic methods for the bulk synthesis of ZIFs remain highly energy- and solvent-intensive. The current impetus to conduct chemistry in an increasingly environmentally-friendly manner, especially in the context of the synthesis of functional materials, has driven the development of greener methodologies aimed at the formation of ZIFs.⁶
Apart from the design of aqueous and room-temperature syntheses\textsuperscript{7,8} of the commercially-available ZIF-8,\textsuperscript{9} also known as MAF-4\textsuperscript{10} and sold as Basolite Z1200® or MTA2®, the synthesis of such materials has also been recently demonstrated in the solid state. Such methodologies include steam-assisted syntheses of ZIFs including ZIF-8, its non-porous polymorph \textit{dia-Zn(Melm)}\textsubscript{2}, as well as cobalt-based ZIFs.\textsuperscript{11} In addition, several groups have developed the quantitative mechanochemical synthesis of MOFs and ZIFs, virtually eliminating the need for bulk solvents or high reaction temperatures.\textsuperscript{12} The conventional solution-based methods require the use of corrosive nitrate, chloride, or sulfate salts as metal sources, which makes targeting mild metal oxides and carbonates\textsuperscript{12c} an industrially-attractive alternative.\textsuperscript{13} Until recently, the use of metal oxides as starting points for the solution-based synthesis of metal-organic materials has been limited by their poor solubility and high lattice energies, which can range between 2-12 MJ/mol.\textsuperscript{14} This is why solid-state methodologies, such as mechanochemistry, which have a diminished reliance on reactant solubility, are an ideal alternative towards the use of metal oxide starting materials. Our group thus developed the room-temperature mechanochemical synthesis of ZIFs\textsuperscript{15ab} and metal-organic pharmaceutical derivatives\textsuperscript{15c} directly from metal oxides. Further to this, our group also published the mild, solvent-free self-assembly of ZIFs from metal oxides called accelerated aging, which has been described in the previous chapter.\textsuperscript{16} Accelerated aging mimics mineral neogenesis, the naturally-occurring transformation of inorganic minerals in the presence of biological molecules released by bio-organisms, in a process that enables the synthesis of metal-organic materials directly from metal oxides. It was demonstrated that accelerated aging enables the formation of non-porous ZIFs from imidazole (H\textit{Im}), 2-methylimidazole (HMelm), and 2-ethylimidazole (H\textit{EtIm}), including \textit{zni-Zn(Im)}\textsubscript{2},\textsuperscript{17} \textit{dia-Zn(Melm)}\textsubscript{2},\textsuperscript{11} and \textit{qtz-Zn(EtIm)}\textsubscript{2}.\textsuperscript{15} Due to the importance of generating metal-organic materials from high-melting, insoluble metal oxides, these results were an inspiration to expand the scope of this methodology towards the synthesis of microporous materials.

This Chapter describes the development of accelerated aging into a method for generating microporous ZIFs, including the highly studied ZIF-8, from metal oxides in quantitative yields (\textbf{Scheme 3.1}). The application of this method to the bulk synthesis of cobalt-based ZIFs, as well as ZIFs formed from alternative ligands, including H\textit{EtIm}, is also demonstrated. In this Chapter, a screen of several salt catalysts revealed that the reaction could be selectively driven to provide a single product with a framework topology dependent on the choice of the salt additive. Also
reported here is the unexpected sensitivity of ZIFs to mildly acidic salt additives under conditions of high humidity and mild temperature increase from room temperature.

3.2 Selection and analysis of salt additives

As discussed in Chapter 2, (NH₄)₂SO₄ can serve as catalyst in the accelerated aging synthesis of non-porous ZIFs from ZnO and imidazole derivatives, by presumably initiating a catalytic cycle involving the formation of an imidazolium cation intermediate. Indeed, it was determined that the product of reacting (NH₄)₂SO₄ and HIm, the salt (H₂Im)₂SO₄·2H₂O, effected full conversion of ZnO and HIm into the oligomeric structure Zn₄(Im)₈(HIm) (CSD code KUMXEW).¹⁸ Faced with a successful proof-of-principle concept which indicated that the formation of 3-D, but non-porous ZIFs could be catalyzed by imidazolium salts, it was postulated that screening a selection of substituted imidazolium salts may enable the directed synthesis of open frameworks. The synthesis of a series of imidazolium-based sulfate salts was therefore conducted, and their use as catalysts for the accelerated aging synthesis of ZIFs was investigated. The initial salt screen involved the imidazole derivatives HIm, HMeIm, HEtIm, and (HBiIm), which could possibly be incorporated into the framework, therefore reducing the necessity to wash out remaining salt catalyst post-synthetically. In addition, the sulfate salt of caffeine (Caf), which bears similar properties to imidazole, but could not act as a framework linker due to methylation on the 7-position nitrogen atom was also tested. Control experiments were conducted using KHSO₄ as a salt additive, to verify the possibility of synthesizing ZIFs by accelerated aging with the use of an ammonia-free, inorganic acidic salt catalyst.

Typical salt synthesis was conducted in solution, whereby the reaction of the imidazole with H₂SO₄ in acetonitrile led to precipitation of the corresponding slightly soluble sulfate salt.
With the goal of eliminating possible side-reactions and synthetic difficulties, this screen focused on salts which were simple to isolate, could be readily characterized, and were also air and moisture stable. The initial screen therefore eliminated (H₂MeIm)₂SO₄ and (H₂EtIm)₂SO₄ which were very hygroscopic and rapidly deliquesced in air. Overall, four potential salt catalysts were prepared: (H₂Im)₂SO₄·2H₂O, (HCAF)(HSO₄), (HCAF)(HSO₄)·H₂O, and (H₂BIm)₂SO₄ (Figure 3.2) which were all characterized by powder X-ray diffraction (PXRD), single crystal X-ray diffraction (XRD), thermogravimetric analysis (TGA), solid-state cross-polarization magic-angle spinning nuclear magnetic resonance (CP-MAS ssNMR) spectroscopy, and Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy. Full characterization of the HIm and HBlm-based salt catalysts have been described in detail in Chapters 2 and 6, respectively.

![Figure 3.2 Salt catalysts screened for the accelerated aging synthesis of porous ZIFs.](image)

The attempted synthesis of (HCAF)(HSO₄) resulted in a crystalline powder which by PXRD analysis could not be identified as any known polymorphic forms of caffeine, or its hydrate (Figure 3.3). Recrystallization of the product from methanol (MeOH) resulted in translucent prism-shaped crystals, which were analyzed by single crystal XRD. Indexing and unit cell determination revealed that the crystals consisted of (HCAF)(HSO₄)·H₂O (Cambridge Structural Database (CSD) code AYUBEC), the structure of which was previously reported by Jerin and coworkers.¹⁹b The simulated PXRD pattern of the monohydrate did not match the experimental pattern of the initially obtained product (Figure 3.3), and it was therefore concluded that the synthesized product and the crystals sampled from the recrystallization experiment were distinct crystalline phases. The salt (HCAF)(HSO₄)·H₂O crystallizes in monoclinic space group P2₁/c, with one HCAF⁺ ion, HSO₄⁻ ion, and one water molecule comprising the asymmetric unit. The HSO₄⁻ anions and water molecules connect via charge-assisted O-H---O hydrogen bonds (2.479(3) Å, 171(3)°) to form corrugated tapes which are surrounded by HCAF⁺ ions. The caffeinium ions connect to HSO₄⁻ ions via N⁺--H---O hydrogen bonds (2.709(2) Å, 174(2)°) (Figure 3.4).
Figure 3.3 Selected PXRD patterns for caffeinium-based sulfate salts: a) commercial caffeine reagent; b) simulated pattern for (H\text{Caf})(\text{HSO}_4)\cdot\text{H}_2\text{O} (CSD code AYUBEC); c) (H\text{Caf})(\text{HSO}_4) synthesized from solution; d) simulated pattern for (H\text{Caf})(\text{HSO}_4).

Figure 3.4 Crystal packing of (H\text{Caf})(\text{HSO}_4)\cdot\text{H}_2\text{O} (CSD code AYUBEC), showing two-dimensional tapes of hydrogen-bonded \text{HSO}_4^- anions and water molecules, surrounded by H\text{Caf}^+ ions connected to the \text{HSO}_4^- anions via N^+-H--O hydrogen bonds.
Recrystallization of the product obtained from solution synthesis was subsequently conducted in a closed vial using a mixture of nitromethane with MeOH, a solvent which may strongly hydrogen bond to water and therefore hinder the formation of a hydrate. Indeed, crystallization upon cooling resulted in the formation of translucent crystals which were analyzed by single crystal XRD. The obtained compound (HCAF)(HSO4) was found to crystallize in the monoclinic $P2_1\overline{1}2_1$ space group, with one HCAF$^+$ and one HSO$_4^-$ ion in the asymmetric unit, corresponding to $Z=4$. The HSO$_4^-$ ions form a 2-D chain bound by O-H--O$^-$ hydrogen bonds (2.590(7) Å, 163.3°), surrounded bilaterally by HCAF$^+$ ions which connect to HSO$_4^-$ ions via charge-assisted N$^+$-H--O hydrogen bonds (2.804(7) Å, 150.6°) ([Figure 3.5]).

![Figure 3.5](image.png)

**Figure 3.5** Fragment of the crystal structure of (HCAF)(HSO4), showing linear chains of HSO$_4^-$ ions connected to HCAF$^+$ ions by N$^+$-H--O hydrogen bonds.
The result is a structure which looks very similar to that of \( \text{(H} \text{Caf})(\text{HSO}_4) \cdot \text{H}_2\text{O} \), in the absence of water molecules embedded in the \( \text{HSO}_4^- \) chains. Comparison of the simulated PXRD pattern of \( \text{(H} \text{Caf})(\text{HSO}_4) \) and the experimental pattern of the freshly prepared product revealed they were identical phases (Figure 3.3). Thermogravimetric analysis of \( \text{(H} \text{Caf})(\text{HSO}_4) \) in dynamic atmosphere of air showed one decomposition step with an onset of 200 °C and complete degradation by 350 °C (Figure 3.6b). Analysis of the FTIR-ATR spectrum of \( \text{(H} \text{Caf})(\text{HSO}_4) \) revealed strong, broad absorption bands corresponding to the N-H stretch in the region 3250 cm\(^{-1}\) to 2250 cm\(^{-1}\). In addition, a strong band at 1150 cm\(^{-1}\) was evident, corresponding to the S-O stretch of \( \text{HSO}_4^- \) (Figure 3.7). Since these bands were not present in the FTIR-ATR spectrum of caffeine, this indicated that protonation of the 9-position nitrogen atom occurred and was consistent with formation of a salt.

Analysis of the solid-state natural abundance \(^{15}\text{N} \) CP-MAS ssNMR spectrum of \( \text{(H} \text{Caf})(\text{HSO}_4) \) revealed only three signals at -213.7 ppm, -225.9 ppm, and -267.49 ppm.
Conversely, the spectrum of neutral caffeine revealed four signals corresponding to the chemical shifts of all four chemically distinct nitrogen atoms of caffeine. The peak at -151.79 ppm, which corresponded to the relatively deshielded 9-position nitrogen atom, was found in the spectrum of Caf and was not present in that of (HCAF)(HSO₄), consistent with protonation of Caf and formation of a salt.²⁰

The unexpected formation of (HCAF)(HSO₄)·H₂O was presumably due to the presence of water in solution during the recrystallization process. The formation of the hydrate serendipitously provided a new catalytic protic salt, which is why it was interesting to isolate (HCAF)(HSO₄)·H₂O as a bulk powder for further characterization and exploration as a salt catalyst in accelerated aging. The salt (HCAF)(HSO₄) was subjected to humid atmosphere (98% RH) at 45 °C for two days. The resulting change in experimental PXRD pattern revealed a crystalline phase identical to that of (HCAF)(HSO₄)·H₂O. Thermogravimetric analysis of (HCAF)(HSO₄)·H₂O indicated the loss of one water molecule at 100 °C (Figure 3.6a). Analysis of the FTIR-ATR spectrum of (HCAF)(HSO₄)·H₂O revealed an O-H stretching frequency at 3342 cm⁻¹, consistent with a hydrate, as well as a band at 1133 cm⁻¹ corresponding to the S-O stretch of the HSO₄⁻ ion. Once prepared, (HCAF)(HSO₄) used in accelerated aging reactions was thus

Figure 3.7 FTIR-ATR spectra of the hydrogensulfate salts of caffeine: a) commercial caffeine; b) (HCAF)HSO₄ synthesized from solution; c) (HCAF)HSO₄·H₂O obtained by high humidity treatment of (HCAF)HSO₄ at 45 °C.
was kept in a desiccator to prevent conversion to (H\text{Caf})(\text{HSO}_4)\cdot\text{H}_2\text{O} under ambient humidity conditions.

Figure 3.8 Solid-state CP-MAS $^{15}$N NMR spectrum demonstrating protonation of the 9-position nitrogen atom of the purine ring of caffeine: a) caffeine reagent; b) (H\text{Caf})(\text{HSO}_4) made from acetonitrile solution.

3.3 Accelerated aging synthesis of ZIF-8

ZIF-8 was selected as the first target in the screen of catalytic and templating properties of imidazolium and xanthine salts, due to its status as a thoroughly investigated, prototypical ZIF. The synthesis of ZIF-8 was typically attempted by reacting 2 mmol of ZnO with 4 mmol of solid HMeIm, in the presence of 4 mol\% (with respect to ZnO) of a salt additive (KHSO$_4$, (H$_2$Im)$_2$SO$_4$·2H$_2$O,\textsuperscript{25a} (H\text{Caf})(\text{HSO}_4), (H\text{Caf})(\text{HSO}_4)\cdot\text{H}_2\text{O}, or (H$_2$BIm)$_2$SO$_4$). The mixtures were mechanically milled for five minutes in a Retsch MM400 shaker mill prior to aging, to create fine solid mixtures while avoiding mechanical activation. The PXRD patterns collected for each reaction mixture immediately after milling were compared to the experimental PXRD patterns of the starting materials. Comparison of the X-ray diffraction patterns of the milled mixtures with those of ZnO, HMeIm, and the salt selected as catalyst for that particular experiment, revealed that no new crystalline phases had formed, suggesting that no reaction had occurred in any of the systems. The system involving (H$_2$Im)$_2$SO$_4$·2H$_2$O was the exception to this observation. In this case, low intensity reflections of ZIF-8 product were apparent in the PXRD pattern of the reaction mixture immediately after milling (Figure 3.9).
After pre-milling, the samples were aged at 45 ºC and 98% relative humidity (RH), conditions that have been established as most favourable for the aging synthesis of ZIFs in Chapter 2. The reactions were monitored by PXRD, and the extent of conversion was ascertained by qualitative assessment of the decrease in intensity of reflections corresponding to ZnO, as well as the appearance of reflections corresponding to new crystalline phases. The identity of any new phases was determined by comparing the experimental PXRD patterns with simulated patterns for previously described zinc-methylimidazolates. After several days, PXRD analysis of the reaction mixture with (H2Im)2SO4·2H2O revealed the majority of ZnO had converted to ZIF-8. However, complete disappearance of ZnO was never achieved (Figure 3.10). In addition, small amounts of another, poorly soluble phase were apparent in the PXRD pattern. This material was later identified as the product of ZIF-8 degradation in the presence of moist CO2, an effect which is described in more detail in Chapter 4. After removing the reaction mixture from the controlled conditions, it was stirred overnight in MeOH, and subsequently evacuated at 80 ºC to remove.
any traces of unreacted imidazole or remaining salt catalyst. Thermogravimetric analysis of the product synthesized in the presence of $(\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}$ in dynamic atmosphere of air revealed decomposition of the framework at 450 °C, with ZnO remaining after calcination (Figure 3.11).

**Figure 3.10** Selected PXRD data for the accelerated aging synthesis of ZIF-8 conducted at 45 °C and 98% RH in the presence of varying salt additives: a) ZnO; b) $\text{HMeIm}$; c) simulated pattern for ZIF-8 (CSD code VELVOY); d) simulated pattern for $\text{dia-Zn(Melm)}_2$ (CSD code OFERUN01); mixture of ZnO and $\text{HMeIm}$ in the presence of: e) KHSO$_4$ after 7 days; f) $(\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}$ after 8 days; g) $(\text{HCAF})(\text{HSO}_4)$ after 11 days; h) $(\text{HCAF})(\text{HSO}_4)\cdot\text{H}_2\text{O}$ after 8 days; and i) $(\text{H}_2\text{BIm})_2\text{SO}_4$ after 61 days.
The percent weight of ZnO residue from the thermogram was used to calculate the percent conversion using the formula which is discussed in Chapter 8, Section 8.7.5. The salt \((\text{H}_2\text{Im})_2\text{SO}_4\) exhibited similar catalytic activity to \((\text{H}_2\text{Im})_2\text{SO}_4\cdot2\text{H}_2\text{O}\), although the reaction was incomplete even after 61 days, judged by the presence of clearly observable diffraction signals corresponding to ZnO in the PXRD pattern of the reaction mixture. On the other hand, PXRD analysis of the reaction catalyzed by \((\text{H}_\text{Caf})(\text{HSO}_4)\) revealed complete disappearance of ZnO after 11 days and indicated that pure ZIF-8 was the product (Figure 3.10). TGA analysis of the sample activated by washing in MeOH and evacuating at 80 °C overnight revealed a ZnO residue of 36.3%, corresponding to 99% conversion (the theoretical value for percent ZnO residue of a pure sample of ZIF-8 is 35.8%). TGA-based conversions for select samples described in this section are given in Table 3.1. Interestingly, the hydrate of \((\text{H}_\text{Caf})(\text{HSO}_4)\) was not as effective at catalyzing the reaction. Significant amounts of ZnO were still present in the PXRD pattern after 8 days aging at 98% RH and 45 °C. The high efficiency of \((\text{H}_\text{Caf})(\text{HSO}_4)\) at catalyzing the accelerated aging synthesis of ZIF-8 could be explained by the high pKa of the \text{H}_\text{Caf}^+ ion. Whereas the calculated pKa values of \text{HSO}_4^-, \text{H}_2\text{Im}^+, and \text{H}_2\text{BIm}^+ are 1.90, 6.97, and 5.79 respectively.
respectively, that of H$\text{Caf}^+$ is -0.92. This does not, however, explain the poor catalytic activity of (H$\text{Caf}$)(HSO$_4$)$\cdot$H$_2$O. Solid-state structure and composition, in addition to pKa, may be a contributing factor in the efficiency of acidic salt as catalysts for accelerated aging reactions.

<table>
<thead>
<tr>
<th>Product</th>
<th>Additive</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>(H$\text{Caf}$)(HSO$_4$)</td>
<td>99</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>(H$_2$Im)$_2$(SO$_4$)$\cdot$2H$_2$O</td>
<td>87</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>KHSO$_4^a$</td>
<td>96</td>
</tr>
</tbody>
</table>

*Table 3.1* Selected percent conversion of ZnO for accelerated aging reactions producing ZIF-8 as the product, calculated from the ZnO residue remaining after thermal analysis.

*a) Using 20% excess HMeIm.*

Remarkably, the synthesis of open 3-D frameworks has been demonstrated in the solid state from dense, inert metal oxides. In order to demonstrate that the synthesis of microporous metal-organic materials can be achieved without the use of solvents or organic additives in the most atom-economic manner possible, it was necessary to determine the surface areas of ZIF-8 samples synthesized by accelerated aging in two cases: 1) first, ZIF-8 synthesized in the presence of a protic, ammonia-free inorganic salt as a catalyst, and 2) ZIF-8 made by accelerated aging with organic salt catalysts without post-synthetic washing. In the first case, Brunauer-Emmett-Teller (BET) N$_2$ sorption analysis on a ZIF-8 sample made with KHSO$_4$, after washing in MeOH and evacuation, revealed a surface area of 1413 m$^2$g$^{-1}$. Samples of ZIF-8 which had been synthesized in the presence of (H$\text{Caf}$)(HSO$_4$) and (H$_2$Im)$_2$SO$_4$$\cdot$2H$_2$O salts, which have only been evacuated overnight but not washed in MeOH, revealed surface areas of 822 m$^2$g$^{-1}$ and 930 m$^2$g$^{-1}$ respectively. The first scenario demonstrated that the transition from densely packed, poorly reactive, solid metal oxides, to microporous ZIF-8 can be achieved without the addition of any organic salt catalysts. The second case confirmed that accelerated aging enables synthesis of microporous ZIF-8 in an entirely solvent-free manner. *Table 3.2* lists the BET surface area and pore volume values for the samples of ZIF-8 synthesized in the presence of (H$\text{Caf}$)(HSO$_4$), (H$_2$Im)$_2$(SO$_4$)$\cdot$2H$_2$O, and KHSO$_4$.  

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In the initial report on accelerated aging, it was determined that the reaction of ZnO with HMeIm in the presence of (NH₄)₂SO₄ led to the formation of ZIF-8 as an unstable intermediate, which quickly collapsed to its close-packed polymorph dia-Zn(MeIm)₂ (CSD code OFERUN01). This behaviour is somewhat surprising, since ZIF-8 has been frequently cited for its high resistance to temperature, moisture, solvothermal treatment, and mechanical processing. To observe the formation and rapid collapse of this framework under such mild conditions is unexpected. It was therefore interesting to verify whether such instability is inherent to products of accelerated aging systems, and whether it can be induced by exposing a pure sample of ZIF-8 to a small amount of an acidic salt. The solid-state behaviour of two ZIF-8 samples was tested in the presence of 4 mol% (NH₄)₂SO₄ (with respect to Zn): i) a washed and evacuated sample of ZIF-8 synthesized by accelerated aging and ii) a sample of commercially available ZIF-8, sold as Basolite Z1200®. Samples were mechanically ball milled with (NH₄)₂SO₄ for five minutes to ensure intimate mixture. Qualitative PXRD analysis of the samples directly after milling confirmed that the process did not induce any noticeable phase change or amorphization of ZIF-8. PXRD analysis of the in-house made ZIF-8 sample revealed the partial formation to dia-Zn(MeIm)₂ after eight days aging at 98% RH and 45 °C (Figure 3.12). The sample of Basolite Z1200® also collapsed to the non-porous framework after nine days, albeit to a lesser extent. This not only demonstrated that the collapse of the ZIF-8 structure is independent of the method of synthesis, but also that accelerated aging samples behave similar to solution-made and commercially sold counterparts.

### Table 3.2

<table>
<thead>
<tr>
<th>Product</th>
<th>Additive</th>
<th>BET area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>(HCaf)(HSO₄)</td>
<td>822ᵃ, 1137ᵇ</td>
<td>0.40ᵃ, 0.58ᵇ</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>(H₂Im)₂(SO₄)·2H₂O</td>
<td>930ᵃ</td>
<td>0.44ᵃ</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>KHSO₄ᶜ</td>
<td>1413ᵇ</td>
<td>0.69ᵇ</td>
</tr>
</tbody>
</table>

ᵃ) Before washing. ᵇ) After washing. ᶜ) Using 20% excess HMeIm.

3.4 Structural instability of ZIF-8

In the initial report on accelerated aging, it was determined that the reaction of ZnO with HMeIm in the presence of (NH₄)₂SO₄ led to the formation of ZIF-8 as an unstable intermediate, which quickly collapsed to its close-packed polymorph dia-Zn(MeIm)₂ (CSD code OFERUN01). This behaviour is somewhat surprising, since ZIF-8 has been frequently cited for its high resistance to temperature, moisture, solvothermal treatment, and mechanical processing. To observe the formation and rapid collapse of this framework under such mild conditions is unexpected. It was therefore interesting to verify whether such instability is inherent to products of accelerated aging systems, and whether it can be induced by exposing a pure sample of ZIF-8 to a small amount of an acidic salt. The solid-state behaviour of two ZIF-8 samples was tested in the presence of 4 mol% (NH₄)₂SO₄ (with respect to Zn): i) a washed and evacuated sample of ZIF-8 synthesized by accelerated aging and ii) a sample of commercially available ZIF-8, sold as Basolite Z1200®. Samples were mechanically ball milled with (NH₄)₂SO₄ for five minutes to ensure intimate mixture. Qualitative PXRD analysis of the samples directly after milling confirmed that the process did not induce any noticeable phase change or amorphization of ZIF-8. PXRD analysis of the in-house made ZIF-8 sample revealed the partial formation to dia-Zn(MeIm)₂ after eight days aging at 98% RH and 45 °C (Figure 3.12). The sample of Basolite Z1200® also collapsed to the non-porous framework after nine days, albeit to a lesser extent. This not only demonstrated that the collapse of the ZIF-8 structure is independent of the method of synthesis, but also that accelerated aging samples behave similar to solution-made and commercially sold counterparts.
3.5 Accelerated aging synthesis of ZIFs based on 2-ethylimidazole

The screen of imidazolium salt additives as catalysts in the synthesis of porous ZIFs was expanded to systems based on H\text{EtIm}. Whereas the synthesis of the close-packed \textit{qtz}-Zn(\text{EtIm})\textsubscript{2} was achieved with the use of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} as a salt catalyst was described in Chapter 2, two other microporous polymorphs of this material exist, RHO-Zn(\text{EtIm})\textsubscript{2} and ANA-Zn(\text{EtIm})\textsubscript{2}. For this study, the salts (H\text{Caf})(HSO\textsubscript{4}), (H\text{Caf})(HSO\textsubscript{4})\textsubscript{·}H\textsubscript{2}O, and KHSO\textsubscript{4} were selected as the best candidates for protic catalysis from previous experiments with H\text{MeIm}. Solid H\text{EtIm} was premilled with ZnO in a 2:1 stoichiometric ratio in the presence of 4 mol\% of the salt additive using the same methodology as described in Section 3.3. In all cases, the rapid formation of RHO-Zn(\text{EtIm})\textsubscript{2} was evident by PXRD analysis after one day of aging. Unlike with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, the...
rapid collapse of RHO-Zn(EtIm)$_2$ to the $qtz$-Zn(EtIm)$_2$ did not occur in the presence of (HCAf)(HSO$_4$) after aging for 6 days at 45 °C and 98% RH. Only after aging for approximately two months were reflections consistent with $qtz$-Zn(EtIm)$_2$ apparent in the PXRD pattern of the reaction mixture (Figure 3.13). Even after this lengthy reaction time, the complete disappearance of ZnO was never observed by PXRD analysis and, therefore, isolation of the porous framework as a pure phase was not possible. In an attempt to increase conversion, the reaction was conducted in the presence of large excess amounts (20 mol%, 50 mol%, 100 mol%) of HEtIm. While a gradual increase in excess ligand resulted in increasingly higher conversions estimated by qualitative analysis of the PXRD patterns after aging, a 150 mol% excess was required to obtain full disappearance of X-ray reflections corresponding to ZnO (Figure 3.13). The explanation of this observation will be discussed in detail in the next Section.

Figure 3.13 Selected PXRD patterns for the synthesis of RHO-Zn(EtIm)$_2$ by accelerated aging: a) commercial ZnO; b) commercial HEtIm; c) simulated pattern for RHO-Zn(EtIm)$_2$ (CSD code MECWOH); d) simulated pattern for $qtz$-Zn(EtIm)$_2$ (CSD code EHER); mixture of ZnO and HEtIm aged at 45 °C and 98% RH in the presence of 4 mol% (HCAf)(HSO$_4$) for: e) 0 days; f) 2 days; g) 6 days; h) 56 days; and i) 2 days with a 150 mol% excess of HEtIm.
3.6 Ligand deactivation based on framework inclusion

As outlined in Section 3.3, from five salt catalysts used for the synthesis of ZIF-8, only (HCAF)(HSO₄) resulted in complete conversion of ZnO. While this may be due to increased pKa of HCAF⁺, it does not explain why there were no reflections pertaining to HMeIm in the X-ray powder diffraction patterns of all incomplete reactions, while reflections of ZnO remained clearly observable. Due to the reaction mixtures being open to air for several days or weeks at a time, it was considered that sublimation of HMeIm from the system could be a cause for the apparently incomplete reactions. To test this possibility, isothermal TGA analysis was conducted on a pure sample of solid HMeIm under dynamic atmosphere of air at 45 ºC. Examination of the TGA thermogram revealed a 3% weight loss which had occurred after 14 hours (Figure 3.14).

![Figure 3.14 TGA thermogram of commercial HMeIm in dynamic atmosphere of air, at 45 ºC overnight. A weight loss of ~3% was observed, tentatively resulting from the slow sublimation of HMeIm.](image)

While the sublimation of HMeIm was observed by TGA, it is unlikely that it was the cause of sub-quantitative conversion seen in accelerated aging reactions. A second potential source of poor conversion could be the incorporation of HMeIm into the nascent ZIF framework, as a guest. Such entrapment would hinder HMeIm from reacting with remaining ZnO. To verify this hypothesis, the synthesis of ZIF-8 was conducted in the presence of 20 mol% excess HMeIm, so that the excess ligand could compensate for any HMeIm trapped inside the ZIF-8 framework being formed. The salt KHSO₄ was selected as the catalyst in this case, because it would not be large enough to occlude the pores of ZIF-8. PXRD analysis of the reaction mixture after aging at 45 ºC and 98% RH revealed that using excess HMeIm resulted in improved conversion,
determined by a reduction in intensity of reflections corresponding to ZnO. Nonetheless, TGA analysis in air revealed that full conversion was not achieved. Whereas the expected ZnO residue from calcining a pure sample of ZIF-8 in air is 35.8%, the residue from the sample with 20% excess HMeIm was 37.3%, corresponding to 96% conversion. This led to the assumption that inclusion, and therefore, deactivation of free HMeIm into the nascent framework was to blame for incomplete reaction of ZnO. This was verified by $^{13}$C CP-MAS ssNMR, conducted on the pristine sample of ZIF-8 obtained using KH$_2$SO$_4$ as the catalyst and containing 20 mol% excess HMeIm. The cross-polarization spectrum did not show any significant signals other than those expected for ZIF-8 (Figure 3.15). However, when the sample was analyzed by $^{13}$C direct-polarization (DP) ssNMR, strong signals corresponding to free HMeIm became apparent. The solid-state $^{13}$C NMR spectrum of HMeIm, whose four carbons are symmetrically inequivalent, showed four separate signals, positioned at chemical shifts of 12.10 ppm, 115.92 ppm, 123.75 ppm, 142.66 ppm, consistent with carbon atoms of the methyl group and the 4, 5, and 2-positions of the imidazole ring, respectively. All these signals were apparent in the $^{13}$C DP-MAS ssNMR spectrum of the sample containing 20 mol% excess HMeIm, implying that loosely-bound, disordered HMeIm was trapped in the pores of ZIF-8. The signal at 110.50 ppm, which corresponds to the 4- and 5-position carbon atoms, represented an average of the two signals expected at 115.92 ppm and 123.75 ppm for crystalline HMeIm, consistent with the liquid-like state of the ligand trapped in ZIF-8 pores.
The poor conversion of stoichiometric amounts of ZnO and H\textsubscript{EtIm} to RHO-Zn(EtIm)\textsubscript{2}, described in Section 3.5, was believed to also be due to inclusion of H\textsubscript{EtIm} into the pores of the nascent framework. It is possible that H\textsubscript{EtIm}, acting as a templating or a space-filling agent, was being incorporated and bound into the large pores of RHO-Zn(EtIm)\textsubscript{2}, thereby becoming unavailable for further reaction. Comparing the solid-state \textsuperscript{13}C CP- and DP-MAS NMR spectra of the pristine sample of the reaction mixture containing (H\textsubscript{Caf})(HSO\textsubscript{4}) catalyst was again indicative of the incorporation of free H\textsubscript{EtIm} in the pores of RHO-Zn(EtIm)\textsubscript{2} (Figure 3.16). The CP-MAS ssNMR spectrum only revealed signals at 149.95 ppm, 125.15 ppm, 114.98 ppm, 21.14 ppm, and 10.79 ppm, corresponding to the five chemically inequivalent carbon atoms of the EtIm\textsuperscript{-} ligands constituting the ZIF framework. Meanwhile, analysis of the DP-MAS ssNMR spectrum revealed four new signals, which were consistent with the five signals of the carbon atoms of HEtIm.

**Figure 3.15** Solid-state \textsuperscript{13}C NMR spectra demonstrating the space-filling effect of HMeIm ligand during the formation of ZIF-8 during accelerated aging reactions: a) CP-MAS spectrum of commercial HMeIm; b) CP-MAS spectrum of an unwashed sample of ZIF-8 made with a 20 mol% excess HMeIm in the presence of KHSO\textsubscript{4} at 45 °C and 98% RH; c) the DP-MAS spectrum of the same sample as in b).
3.7 Accelerated aging synthesis of cobalt-based ZIF-67

Apart from Zn\(^{2+}\), another frequently used metal ion in ZIF design is Co\(^{2+}\). The accelerated aging synthesis of ZIF-67, the cobalt analogue of ZIF-8, from CoO was therefore identified as a valid challenge to address. Attempts to synthesize ZIF-67 from CoO mechanochemically using the ball milling methodology previously reported for mechanochemical ZIF-8 synthesis was unsuccessful. The milling reaction of CoO with HMeIm in the presence of sub-stoichiometric amounts of NH\(_4\)NO\(_3\) by ion- and liquid-assisted grinding (ILAG) resulted in the formation of no new phases, as seen by PXRD analysis. Whereas usual ILAG conditions result in the quantitative synthesis of ZIF-8 in 30 minutes, no reaction was observed with CoO even after 90 minutes milling.

The attempted accelerated aging synthesis of ZIF-67 from a 1:2 stoichiometric mixture of CoO and HMeIm was conducted without salt catalyst. After aging for over one week at 45 °C and 98% RH the formation of ZIF-67 was observable by PXRD, although X-ray reflections for

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**Figure 3.16** Solid-state \(^{13}\)C NMR spectra demonstrating the space-filling effect of HEtIm ligand during the formation of RHO-Zn(EtIm)\(_2\) during accelerated aging reactions: a) CP-MAS spectrum of commercial HEtIm; b) CP-MAS spectrum of an unwashed sample of RHO-Zn(EtIm)\(_2\) made with a 150 mol% excess HEtIm in the presence of (HCAF)(HSO\(_4\)) at 45 °C and 98% RH; c) the DP-MAS spectrum of the same sample as in b).
CoO were still apparent after several days. The conversion from CoO to ZIF-67 was accompanied with the mixture showing a stark colour change from black to deep purple. Aging the reactants in the presence of (HCAF)(HSO₄) or (NH₄)₂SO₄ in 4 mol% amount with respect to CoO led to the near-complete disappearance of CoO as ascertained by PXRD analysis (Figure 3.17). The synthesis of ZIF-67 in the presence of KHSO₄, however, led to the apparent complete disappearance of X-ray reflections corresponding to CoO. Analysis of the PXRD patterns of samples containing (HCAF)(HSO₄) or KHSO₄ revealed that the formation of ZIF-67 was accompanied by the appearance of an unidentified crystalline phase, having an X-ray reflection at 14.0º 2θ. This species was found to be soluble in MeOH, and could be washed off.

Figure 3.17 Selected PXRD patterns showing the synthesis of Co-ZIF-67 from CoO by accelerated aging at 45ºC and 98% RH: a) commercial CoO; b) commercial HMeIm; c) simulated pattern for SOD-Co(MeIm)₂, ZIF-67 (CSD code GITTOT); mixture of CoO and HMeIm aged in the presence of: d) (NH₄)₂SO₄ for 7 days; e) (HCAF)(HSO₄) for 7 days; f) KHSO₄ for 7 days and; f) KHSO₄ for 27 days, after washing in MeOH (WD) overnight and evacuating at 80 ºC overnight.

Powder X-ray diffraction is not a reliable method for determining the extent of reaction due to the fluorescence emission of Co²⁺ under Cu-Kα radiation, resulting in a high background signal that would render any weak X-ray reflections of residual CoO undetectable. Thus, thermogravimetric analysis was conducted in air on the washed and evacuated samples of ZIF-
67, and the percent conversions calculated based on the amount of Co₃O₄ remaining after calcination, using the equation shown in Chapter 8, Section 8.7.5. Reactions using (HCAF)(HSO₄) and KHSO₄ salt catalysts resulted in 72% and 61% conversion, respectively (Table 3.3).

<table>
<thead>
<tr>
<th>Product</th>
<th>Additive</th>
<th>Conversion (%)</th>
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<tr>
<td>ZIF-67</td>
<td>(HCAF)(HSO₄)</td>
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</tr>
<tr>
<td>ZIF-67</td>
<td>KHSO₄</td>
<td>61</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>(NH₄)₂SO₄</td>
<td>71</td>
</tr>
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</table>

**Table 3.3** Selected CoO conversions for the synthesis of ZIF-67 in the presence of ionic additives (HCAF)(HSO₄), KHSO₄, and (NH₄)₂SO₄.

Brunauer-Emmett-Teller surface area analysis of the pristine sample made with (HCAF)(HSO₄) revealed a surface area of 943 m²g⁻¹. After washing the sample with MeOH and evacuating, the porosity was increased to 1115 m²g⁻¹ (Table 3.4). While full conversion was not achieved, it is remarkable that the surface areas of ZIF-67 samples were higher than those for ZIF-8, despite the fact that 30% by weight of the mixture consisted of non-porous CoO. Interestingly, the reaction between CoO and HMelm with (NH₄)₂SO₄, unlike in the case with ZnO, never resulted in the non-porous material dia-Co(Melm)₂. Using (NH₄)₂SO₄ in the reaction resulted in ZIF-67 formation at a conversion of 71%.

<table>
<thead>
<tr>
<th>Product</th>
<th>Additive</th>
<th>BET area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
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<tr>
<td>ZIF-67</td>
<td>(HCAF)(HSO₄)</td>
<td>943ᵃ, 1115ᵇ</td>
<td>0.45ᵃ, 0.56ᵇ</td>
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<tr>
<td>ZIF-67</td>
<td>KHSO₄</td>
<td>1058ᵇ</td>
<td>0.53ᵇ</td>
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<tr>
<td>ZIF-67</td>
<td>(NH₄)₂SO₄</td>
<td>1227ᵇ</td>
<td>0.60ᵇ</td>
</tr>
</tbody>
</table>

**Table 3.4** Selected BET surface area and pore volume values for ZIF-67 samples synthesized by accelerated aging. ᵃ) Before washing, after evacuation. ᵇ) After washing and evacuation.
3.8 Increasing reactivity with 100% relative humidity

The synthesis of porous ZIFs in quantitative yields by the salt-mediated activation and solid-state reaction of metal oxides has been clearly demonstrated. Despite this, reacting solid materials over the course of days to weeks may be unreasonable in the context of efficient materials synthesis. Thus, an increase in relative humidity from 98% to 100% was investigated as a way of making accelerated aging more time-efficient. Conducting the reactions in an environment saturated with water vapour was believed to maximize moisture transfer to the reactants and offset time taken to re-equilibrate the system after periodic opening of the reaction chamber for analysis. After two days, reacting a 1:2 stoichiometric mixture of ZnO and HMeIm in a humidity chamber equilibrated at 100% RH with pure water as the humidity source resulted in full conversion with the salt catalysts (H$_2$Im)$_2$SO$_4$·2H$_2$O and (HCAF)(HSO$_4$), as determined by PXRD analysis and TGA. An excess of 20 mol% HMeIm was required to achieve full conversion when KHSO$_4$ was selected as the catalytic additive. The catalytic additive (H$_2$BIm)$_2$SO$_4$, which at 98% RH was incomplete after 61 days aging, led to 93% conversion to ZIF-8 after reacting for four days at 100% RH. In contrast to (HCAF)(HSO$_4$), the reaction catalyzed by (HCAF)(HSO$_4$)·H$_2$O was still incomplete after 8 days, as revealed by analysis of PXRD patterns (Figure 3.18). The increase in relative humidity also led to an increase in the conversion of ZIF-67 formed from CoO. The reaction of CoO and HMeIm reached 77% conversion in 3 days under these conditions using (HCAF)(HSO$_4$) as the salt catalyst.
In addition to enabling faster reactivity, applying a 100% RH environment allowed the quantitative synthesis of ZIF-8 on a five gram scale within 4 days (Figure 3.20), i.e. on a time-scale which was previously only achievable for at most a 0.5 gram synthesis at 98% RH. It is notable that the timescales of accelerated aging reactions may exceed the 30 minutes needed for the mechanochemical synthesis of ZIF-8, rendering accelerated aging a slower synthetic route for ZIF synthesis. Nonetheless, the one to two days required for full conversion by aging are within the range of conventional solution methods reported for MOFs and ZIFs, which can often require several hours to several days reaction time.

Figure 3.18 Selected PXRD patterns showing an increase in ZnO conversion and reaction speed during the accelerated aging synthesis of ZIF-8 at 100% RH and 45 ºC: a) commercial ZnO; b) commercial HMeIm; c) simulated pattern for SOD-Zn(Melm)2, (CSD code VELVOY); d) simulated pattern for dia-Zn(Melm)2, (CSD code OFERUN01); mixture of ZnO and HMeIm aged in the presence of: e) KHSO4 for 2 days; f) KHSO4 and 20 mol% excess HMeIm for 2 days; g) (HIm)2SO4·2H2O for 2 days; h) (Hcaf)(HSO4) for 1 day; i) (Hcaf)(HSO4)·H2O for 4 days; and j) .
3.9 Conclusion

Accelerated aging has been established as a mild, environmentally-friendly methodology for the spontaneous self-assembly of microporous ZIFs in the solid state. By enabling the activation of relatively inert, poorly soluble metal oxides, accelerated aging avoids the use of toxic and hazardous chloride or nitrate salts as starting materials, and virtually eliminates the need for solvent. The directed synthesis of a series of microporous ZIFs based on both Zn$^{2+}$ and Co$^{2+}$, as well as both HMeIm and HEtIm ligands has been achieved, due to a screen of protic salt additives based on imidazole and xanthine derivatives. These salts, only required in catalytic amounts, can also act as space-filling templates able to drive accelerated aging reactions towards the synthesis of open metal-organic frameworks. In addition to providing a new synthetic route to ZIF materials, accelerated aging has also enabled the surprising discovery that ZIF-8, both when in-house made and when obtained from commercial sources, is susceptible to collapse under mild conditions of temperature and humidity. Accelerated aging is thus not only a scalable (up to ten grams), versatile and “green” synthetic tool for the synthesis of metal-organic materials, but a valuable asset in the search for factors governing the solid-state stability of ZIFs. The exploration of accelerated aging as a way to strategically evaluate how varying conditions affect the solid-state behaviour of ZIFs will be discussed in the next Chapter.
3.10 References
21. pKₐ calculations were done using Marvin, ChemAxon online calculator (http://www.chemaxon.com/marvin/sketch/index.jsp).
CHAPTER 4
CARBON DIOXIDE SENSITIVITY OF ZEOLITIC IMIDAZOLATE FRAMEWORKS

The work discussed in this chapter is based on a paper entitled “Carbon dioxide sensitivity of zeolitic imidazolate frameworks”, co-authored by C. Mottillo and Prof. T. Friščič (Angew. Chem. Int. Ed., 2014, 53, 7471). Section 4.1 contains the manuscript with minor modifications, which was written by C. Mottillo, edited by Prof. Tomislav Friščič, and has been formatted and edited for inclusion into this Thesis. The subsequent sections consist of a detailed analysis of the results described in the paper and the Supplementary Information associated with it. All results described in Section 4.1 and other sections of this chapter were obtained by C. Mottillo. These include additional results obtained after publication of the manuscript, some of which have been obtained in collaboration with Prof. Kenneth D. M. Harris from Cardiff University.

4.1 Introduction and connecting text

As discussed in the preceding chapters, zeolitic imidazolate frameworks (ZIFs) are a promising subfamily of metal-azolate frameworks (MAFs) due to their advanced properties which are relevant for industrial applications. ZIFs, especially the commercially-relevant ZIF-8, have been fervently studied in the context of carbon dioxide gas storage and separation, due to their high CO$_2$ sorption capacity and reported high stability. However, the successful commercialization of ZIFs requires a deeper and more thorough understanding of their solid-state properties, particularly their stability under complex conditions relevant to their industrial applications. The stability of ZIFs has been assessed both in the context of the synthesis and the design of novel materials as well as in specialized proceedings of research that explicitly evaluate stability under a specific set of conditions. In most cases, retention of structural integrity and gas sorption performance have been used as metrics for the level of resistance ZIFs have to hydrolysis, solvolysis, or chemical environments similar to those in flue gas. The results of such evaluations have led to the conclusion that ZIFs are among the more stable among the differing classes of MOFs. However, it can be argued that the idealized environments and short-term nature of experiments in such studies do not account for effects occurring over longer time frames under more complex and varying physical and chemical conditions. In several cases, the fact that the commercially-available ZIF-8 has been found to be structurally altered in certain aqueous environments, and until now, the resulting material has not been examined further,
indicates that more studies are required to establish the solid-state stability of ZIFs under more complex atmospheres. In the preceding chapters, the potential use of accelerated aging for elucidating the solid-state stability of ZIFs has been hinted at.\textsuperscript{17} In particular, the study of accelerated aging synthesis led to the discovery that ZIF-8, either synthesized in-house or purchased as Basolite Z1200\textsuperscript{®}, which prior to now has been generally considered to be of high thermal and chemical stability, is unstable to high humidity in the presence of small amounts of mildly acidic salts.\textsuperscript{18} The results described in this chapter focus on expanding the study of ZIF stability in humid conditions to include varying conditions of atmosphere and temperature, and establishing the effect of these parameters on the physical and chemical properties of ZIFs in the solid state. In particular, this chapter provides a study of the stability of seven model ZIF materials differing in choice of metal, node, imidazolate ligand, and level of porosity (Figure 4.1). The results reveal the surprisingly high sensitivity of all but one of these ZIFs to carbon dioxide gas in humid conditions. The products of these degradation processes are, in some cases, members of a series of isostructural complex carbonate salts which rapidly form upon exposing the ZIFs to carbon dioxide in the presence of either water or water vapour. These results provide a rationale to further expand the use of accelerated aging to diverse other types of MOFs and develop it into a general methodology for establishing the stability of functional, metal-organic materials in different atmospheres. Indeed, similar work has recently been initiated by other groups.\textsuperscript{19}
Zeolitic imidazolate frameworks (ZIFs) have been identified as excellent candidates for applications in catalysis and gas storage and separation. The use of ZIFs for the sequestration, capture, and separation of CO$_2$ from other gases is of particular interest. The porous framework ZIF-8, based on zinc and 2-methylimidazole (HMeIm), has been studied extensively for its water stability, high storage capacity, and selectivity for CO$_2$ sorption, and it is now commercially manufactured as Basolite Z1200® and MTA2®. While these properties of ZIF-8 have been validated in idealized laboratory settings, implementation of ZIFs for CO$_2$ capture on an industrial scale requires a thorough understanding of stability in complex compositions of flue gas and in complex conditions of temperature, pressure, and atmosphere. Research into the stability of ZIFs to individual environmental factors determined they are stable to high temperatures, pressure, and pH. The
CO\textsubscript{2} sorption capacity of ZIF-8 remains unchanged after exposure to humidity for a few days\textsuperscript{11}. Although the applications of ZIFs in carbon capture require a clear understanding\textsuperscript{12,13} of their chemical and structural resistance to water, CO\textsubscript{2}, and other components of flue gas, different evaluations of stability of ZIF-8 towards water have recently led to conflicting results. Whereas ZIF-8 was reported to be resistant to steam for hours\textsuperscript{14} and stable in boiling in water for at least a week,\textsuperscript{2} recent reports noted the appearance of unidentified reflections in powder X-ray diffraction (PXRD) patterns of ZIF-8 after storage in room temperature water for >24 h.\textsuperscript{15,16} Such apparently incongruent results highlight the need to develop reliable approaches to evaluate the long-term structural and chemical (in)stability of ZIFs. Recently, we reported the accelerated aging technique for conducting environmentally friendly synthesis of ZIFs,\textsuperscript{17} achieved by exposing solid reagents to high relative humidity (RH) and mild temperature (up to 45 °C) over several days, sometimes in the presence of catalytic protic salts. Besides offering a new route to make ZIF-8, accelerated aging also revealed its slow rearrangement into a non-porous polymorph with a diamondoid (\textit{dia}) topology, \textit{dia-}\textit{Zn(Melm)}\textsubscript{2}.\textsuperscript{18}

We now demonstrate accelerated aging as a method to evaluate the long-term stability of ZIFs under different conditions of atmosphere, mild acidity, and water vapor. Importantly, we report the unexpected chemical degradation of Basolite Z1200® by humid CO\textsubscript{2} (Figure 4.2), leading to a previously not described complex carbonate (1). We expand this stability analysis, with similar results, to four other ZIFs based on zinc, cobalt, and cadmium involving either H\textit{MeIm} or imidazole (H\textit{Im}): the porous sodalite (SOD) topology Co(\textit{MeIm})\textsubscript{2} (ZIF-67),\textsuperscript{4,7} the non-porous \textit{dia-}\textit{Zn(Melm)}\textsubscript{2},\textsuperscript{20} the non-porous interpenetrated \textit{dia-Cd(Im)}\textsubscript{2},\textsuperscript{21} and the non-porous \textit{zni-Zn(Im)}\textsubscript{2}.\textsuperscript{22}
Samples of Basolite Z1200® were aged at 100 % RH and 45 °C under air, CO₂, or Ar. After 3 days in CO₂, PXRD revealed X-ray reflections of a new crystalline phase (1) that could not be correlated to any reported zinc 2-methylimidazolates (Figure 4.3). After 12 days, PXRD indicated that the sample was a mixture of starting material and 1. Aging of Basolite Z1200 in air and Ar did not result in any significant changes in the PXRD pattern after 20 days (Figure 4.3).

We next explored how protic salts affect the transformation ZIF-8→1. Basolite Z1200® was mixed with 4 % mol NH₄NO₃ by 5 min milling prior to aging. After 6 days, aging in moist air and Ar led to partial rearrangement of ZIF-8 into dia-Zn(Melm)₂ (Figure 4.3), while humid CO₂ gave 1. Comparison of PXRD patterns revealed that the transformation ZIF-8→1 advanced more in the presence of NH₄NO₃. To verify if this might have been caused by pre-milling, pure Basolite Z1200 was milled for 5 min prior to aging in humid CO₂. In this case the reaction was slower than with NH₄NO₃ salt, confirming that a protic additive accelerates the reaction.
Compound 1 has, to our knowledge, not yet been explicitly described in the literature. However, inspection of the supporting information from a 2010 publication by Shi et al. reveals

![Figure 4.3](image)

**Figure 4.3** a) Selected PXRD patterns of aging ZIF-8 in CO₂, air, and Ar. ZIF-8 reacts with CO₂ in the presence of water and water vapor. A characteristic reflection of 1 is marked by *. b) Selected $^{13}$C CP-MAS ssNMR spectra for the reaction of ZIF-8 to form 1. Signals of carbonate anions are marked with *.

Compound 1 has, to our knowledge, not yet been explicitly described in the literature. However, inspection of the supporting information from a 2010 publication by Shi et al. reveals
a material with a PXRD pattern consistent with \( \mathbf{1} \) forming in a reaction of zinc acetate dihydrate and HMeIm under steam-assisted conditions in a Teflon® autoclave at 120 °C.\(^{20}\) We also recognized the formation of \( \mathbf{1} \) in the recently published PXRD data for ZIF-8 that was extensively washed or suspended in water, indicating the active participation of dissolved CO\(_2\) in what was initially considered a hydrolytic degradation.\(^{15,16}\) Next, we sought a means to synthesize pure \( \mathbf{1} \). Whereas a solution reaction of Zn(NO\(_3\))\(_6\)-6H\(_2\)O, Na\(_2\)CO\(_3\), and HMeIm in water yielded a mixture of ZIF-8 and \( \mathbf{1} \), we found that \( \mathbf{1} \) is readily obtained by simply exposing an aqueous slurry of Basolite Z1200® to CO\(_2\) at room temperature for 2 hours. The product was analyzed by thermogravimetric analysis (TGA), Fourier transform infrared attenuated total reflection (FTIR-ATR), and cross-polarization magic angle spinning (CP-MAS) solid-state \(^{13}\)C NMR (ssNMR) spectroscopy. TGA in air revealed that the content of zinc in \( \mathbf{1} \) is higher than in ZIF-8, indicating a loss of organic ligand in the transformation \( \text{ZIF-8} \rightarrow \mathbf{1} \). The FTIR-ATR spectrum of \( \mathbf{1} \) revealed a new band at 1330 cm\(^{-1}\), which is consistent with a carbonate. Carbonate formation was confirmed by ssNMR, which revealed two new signals at 163.7 ppm and 165.7 ppm, consistent with two non-equivalent carbonate species (Figure 4.3). Analysis by ssNMR also revealed the presence of at least three non-equivalent methyl groups and resolved at least two sets of signals consistent with carbon atoms of the methylimidazole ring. Analysis by ssNMR of a ZIF-8 sample aged in humid CO\(_2\) also revealed free HMeIm, consistent with the observed higher content of zinc in \( \mathbf{1} \) than in ZIF-8. The addition of 0.1 M aqueous HNO\(_3\) to \( \mathbf{1} \) led to effervescence, consistent with a carbonate. Elemental analysis revealed the contents of carbon, hydrogen, and nitrogen in \( \mathbf{1} \) as 33.01%, 3.15%, and 16.98 %, respectively. These values, combined with TGA, suggest a composition \( \text{Zn(Melm)}_2\text{ZnCO}_3\cdot0.66\text{HMeIm} \). We conclude that \( \mathbf{1} \) is a complex carbonate involving carbonate and methylimidazolate species.

To verify if degradation of ZIF-8 in humid CO\(_2\) may be associated with its porosity or topology, we explored the cobalt analogue of ZIF-8, SOD-Co(Melm)\(_2\) (ZIF-67), and the non-porous \( \text{dia-Zn(Melm)}_2, \text{zni-Zn(Im)}_2 \) and \( \text{dia-Cd(Im)}_2 \), all readily obtained as pure bulk phases. After 9 days aging in CO\(_2\) and 100 % RH, PXRD revealed ZIF-67 formed a material (2) isostructural to \( \mathbf{1} \). PXRD analysis of \( \text{dia-Zn(Melm)}_2 \) after one day in CO\(_2\) at 100 %RH revealed the formation of \( \mathbf{1} \), indicating that ZIF-8 degradation is not caused by its porosity or topology. Remarkably, \( \text{zni-Zn(Im)}_2 \) did not exhibit any sign of degradation under any of the explored conditions.
For \textit{dia-Cd(Im)$_2$},\textsuperscript{21} PXRD analysis after two days in humid CO$_2$ revealed complete disappearance of the ZIF (Figure 4.4). Specifically, the diffractogram exhibited new X-ray reflections consistent with a mixture of cadmium carbonate (CdCO$_3$, crystallography open database code 1011341) and a complex hydrated carbonate Cd(HIm)$_6$CO$_3$·3 H$_2$O (3, CSD code IMCDCP01), involving octahedrally coordinated Cd(HIm)$_6^{2+}$ cations. Stirring of the product mixture in dilute (0.1 M) aqueous acetic acid dissolved 3, allowing CdCO$_3$ to be separated and its identity fully confirmed by PXRD, TGA, and FTIR-ATR. Formation of 3 and CdCO$_3$ most likely results from the 1:2 ratio of Cd$^{2+}$ and HIm$^-$ in the starting \textit{dia-Cd(Im)$_2$} material. Indeed, aging of a mixture of \textit{dia-Cd(Im)$_2$} and four equivalents of HIm (corresponding to a Cd:HIm ratio of 1:6, as in 3) gave 3 as the only product. Exposure of \textit{dia-Cd(Im)$_2$} to humid air or Ar for 20 days caused no change observable by PXRD or ssNMR. Aging of \textit{dia-Cd(Im)$_2$} in the presence of 4 mol \% NH$_4$NO$_3$ gave similar results. In humid Ar, no change was observed. While aging in humid air demonstrated no change after 13 days, the sample converted into a mixture of the starting material, 3, and CdCO$_3$ after 64 days. Thus, even atmospheric CO$_2$ can cause the decomposition of certain ZIFs.
In summary, long-term exposure of ZIFs to carbon dioxide in the presence of moisture induces their chemical degradation into complex carbonates. This discovery is highly important for the development of ZIFs for carbon sequestration and, being in stark contrast to well-established stability of ZIFs in pure CO₂, highlights the need to consider complex environments when assessing the stability of metal–organic frameworks. We have identified the complex...
carbonate 1 as the product of previously reported hydrolytic degradation of ZIF-8, indicating that the inconsistencies in evaluating ZIF-8 stability towards water might be caused by the overlooked effects of dissolved CO$_2$. As the solubility of CO$_2$ in water drops with increasing temperature, it is possible that ZIF-8 is stable to boiling water, but slowly degrades to form 1 in room temperature water that is richer in CO$_2$. In support of this view, we find that the long-term exposure of different ZIFs to moisture in Ar does not lead to any noticeable changes while, in some cases, even atmospheric CO$_2$ in moist air caused degradation. The range of materials tested herein, including the commercial Basolite Z1200®, shows that sensitivity to moist CO$_2$ is encountered across different framework compositions and topologies. Our study also revealed that zni-Zn(Im)$_2$ did not undergo any degradation, indicating that certain parameters of ZIF structure and composition can hinder their decomposition. We believe that further evaluation of long-term stability of ZIFs in multi-component environments, in combination with theoretical assessment of their stability and CO$_2$ binding affinity, will be central for elucidating these parameters and facilitate the development of materials for CO$_2$ sequestration, catalytic polycarbonate synthesis, or CO$_2$ splitting.

4.3 Structural analysis of 1 by ab initio structure solution from powder X-ray diffraction data

The inability to obtain single crystals of 1 for single crystal X-ray diffraction analysis limits the ability to obtain structural data. However, detailed solid-state analysis of the degradation product of ZIF-8 allowed us to obtain information regarding its composition. As indicated earlier, $^{13}$C ssNMR spectroscopy revealed the presence of two crystallographically-independent carbonate species, and possibly two crystallographically-inequivalent 2-methylimidazole (either neutral or anionic, MeIm$^-$) species in the structure. Elemental analysis, combined with TGA, suggested a Zn:MeIm ratio of less than 1:2, indicating the loss of some of the organic ligand upon decomposition in moist CO$_2$. Calculations taking into consideration the relative weight percent of C, N, and H atoms from elemental analysis data, as well as the fact that thermal degradation of 1 in air resulted in 39.0% ZnO residue, suggested a composition of Zn$_2$(MeIm)$_2$CO$_3$·0.66 HMeIm (Figure 4.5). The sample used for TGA appeared pure by way of PXRD analysis, and was thoroughly washed in water to remove any possible traces of unbound HMeIm. The lack of any ligand impurity was confirmed by comparing the TGA of the pure material which revealed a single decomposition step at 450 °C, with that of an unwashed sample, which clearly showed the removal of excess HMeIm beginning at 150 °C (Figure 4.6).
Figure 4.5  TGA thermogram of 1, washed in water, filtered, and dried in vacuo overnight. Calcining in air revealed only a single decomposition step was observed at 450 °C, with a ZnO residue of 39.0%. This value is consistent with the composition of the initial product being Zn2(MeIm)2CO3·0.66 HMeIm.

Figure 4.6  TGA thermogram of 1, synthesized from aqueous slurry and not washed. In order to obtain a powder for analysis, the slurry was exposed to air at room temperature to allow the water to evaporate. The weight loss at 190 °C is consistent with the loss of unbound HMeIm which resulted from the transformation of ZIF-8 to 1 in moist CO2.
The FTIR-ATR spectrum of pure 1 confirmed the presence of carbonate by the appearance of an absorption band at 1330 cm\(^{-1}\), corresponding to the C-O stretch (Figure 4.7). Very low intensity absorption bands in the region of 3200 cm\(^{-1}\) to 2900 cm\(^{-1}\) also suggested the presence of neutral H\text{Melm} which, if correct, would support the suggestion from elemental and thermal analysis data that 1 contains additional neutral ligand.

**Figure 4.7** Selected FTIR-ATR spectra for Basolite Z1200\(^\circledR\) in aqueous slurry exposed to CO\(_2\): a) commercial Basolite Z1200\(^\circledR\); b) Basolite Z1200\(^\circledR\) suspended in H\(_2\)O and CO\(_2\) for 2 hours.

The absence of single crystals of 1 meant that conducting \textit{ab initio} structure solution from X-ray powder diffraction data (PXRD) had to be considered as a method to determine the crystal structure of 1. Subsequent to the publication of this work, Basnayake \textit{et al.} synthesized a compound similar to 1, of composition Zn\(_2\)(\text{Melm})\(_2\)CO\(_3\) (CSD code HOYQAP), and determined its structure from single crystal diffraction data.\(^{26}\) Although comparison of the simulated pattern from Zn\(_2\)(\text{Melm})\(_2\)CO\(_3\) and experimental data for 1 revealed they are very similar complexes, minor differences in diffraction line positions and intensities encouraged the further investigation of 1. The inherent difficulty in structure determination from PXRD data for such mixed complexes of unknown formula encouraged us to collaborate with Prof. Kenneth D. M. Harris of Cardiff University, Wales, who conducted the \textit{ab initio} structure determination from high-quality X-ray powder diffraction data. Structure solution and refinement from a PXRD pattern of pure 1
revealed that the compound crystallizes in orthorhombic space group *Pba*2 with formula Zn₂(MeIm)₂CO₃ and unit cell parameters *a* = 10.53 Å, *b* = 12.05 Å, *c* = 4.69 Å. The structure consists of chains of tetrahedral carbonate-bound Zn²⁺ atoms connected by MeIm⁻ anions to form a 3-D network with small 4.5 Å channels (*Figure 4.8*). The asymmetric unit consists of one crystallographically unique MeIm⁻, one carbonate, and one Zn²⁺ ion, effectively questioning the accuracy of the formula Zn₂(MeIm)₂CO₃·0.66 HMeIm that was obtained based on ssNMR, TGA, and elemental analysis data.

*Figure 4.8.* Fragment of the crystal structure of 1, viewed down the *c*-axis, as determined by *ab initio* structure solution from powder X-ray diffraction data.

The experimental and simulated PXRD patterns for 1 are nearly identical (*Figure 4.9*). The source of the discrepancy between *ab initio* structure solution and solid-state data for 1 has yet to be elucidated.
4.4 Role of aqueous CO$_3^{2-}$ in ZIF degradation

The results in the present paper clearly indicate that ZIF-8, in addition to other ZIFs, is unstable under conditions which combine carbon dioxide and water in its liquid or vapor form. The conversion of the pre-formed ZIFs to complex carbonates occurs within minutes to days when exposed to carbon dioxide in humidity or aqueous suspensions. The sensitivity of ZIFs to moist CO$_2$ or carbonic acid affects not only the stability and applicability of these materials but also can affect the course of their synthesis. To that effect, Basnayake and coworkers recently confirmed that high concentrations of CO$_2$ during the solvothermal synthesis of ZIF-8 leads to the formation of 1. They reported the reaction between Zn(NO$_3$)$_2$·6H$_2$O and HMeIm yielded a phase similar to 1 both when CO$_2$ was added to the reaction vessel, as well as when carbonate impurities were introduced in situ into the reaction mixture as a result of hydrolysis of DMF at 140 °C. To further investigate the role of carbon dioxide or carbonate ions on ZIF-8 synthesis in solution, the course of ZIF-8 synthesis was explored in the presence of added carbonate anions. A rapid synthesis of ZIF-8 was published by Pan et al. in 2010, whereby combining...
Zn(NO$_3$)$_2$·6H$_2$O and HMeIm in water at room temperature led to the formation of nanocrystalline ZIF-8.$^{27}$ Following this method, an aqueous solution of Zn(NO$_3$)$_2$·6H$_2$O was added to a saturated mixture of Na$_2$CO$_3$ and HMeIm, after which a precipitate formed. Powder X-ray diffraction analysis of the precipitate revealed that the powder consisted of a mixture of ZIF-8 and 1 (Figure 4.10), thus demonstrating that simply having CO$_3^{2-}$ present in the solution is sufficient to induce the formation of 1 instead of ZIF-8.

![Figure 4.10 PXRD patterns for the solution synthesis of Zn$_2$(Melm)$_2$CO$_3$ (1): a) Zn(NO$_3$)$_2$·H$_2$O; b) Na$_2$CO$_3$; c) HMeIm; d) simulated pattern for SOD-Zn(Melm)$_2$ (CSD code VELVOY); e) dia-Zn(Melm)$_2$ (CSD code OFERUN01); f) Zn$_2$(Melm)$_2$CO$_3$ (1) from aqueous slurry; g) product from reaction of Zn(NO$_3$)$_2$·H$_2$O, HMeIm, and Na$_2$CO$_3$ in aqueous suspension.](image)

The formation of 1 from solutions containing Na$_2$CO$_3$ suggests that CO$_3^{2-}$ can compete with HMeIm for coordination to Zn$^{2+}$. A different case was the degradation of CdIFs in moist CO$_2$, where the complex carbonate degradation product contained a Cd:HMeIm ratio larger than that found in the initial MOF. The transformation of dia-Cd(Im)$_2$ to the complex Cd(Im)$_6$CO$_3$·3H$_2$O consisted of such a case. A pure sample of dia-Cd(Im)$_2$ was synthesized
using a method based on the previously reported solution synthesis of zinc and cadmium-imidazolates.\textsuperscript{21,28} When such a sample of \textit{dia-Cd(Im)}\textsubscript{2} was exposed to humid CO\textsubscript{2} without additional H\textit{Im}, a fraction of Cd\textsuperscript{2+} was converted to CdCO\textsubscript{3}, such that the final product was a mixture of Cd(H\textit{Im})\textsubscript{6}CO\textsubscript{3}·3H\textsubscript{2}O and CdCO\textsubscript{3} (\textbf{Figure 4.11}). The CdCO\textsubscript{3} byproduct was isolated by digesting the mixture with dilute acetic acid which dissolved and removed only Cd(H\textit{Im})\textsubscript{6}CO\textsubscript{3}·3H\textsubscript{2}O.

\textbf{Figure 4.11} Selected PXRD patterns confirming the formation of CdCO\textsubscript{3} by-product from the transformation of \textit{dia-Cd(Im)}\textsubscript{2} in humid CO\textsubscript{2} gas: a) simulated pattern for \textit{dia-Cd(Im)}\textsubscript{2} (CSD code BAYQAU); b) \textit{dia-Cd(Im)}\textsubscript{2} synthesized from solution; c) simulated pattern for CdCO\textsubscript{3} (COD ID 1011341); d) simulated pattern for Cd(H\textit{Im})\textsubscript{6}CO\textsubscript{3}·3H\textsubscript{2}O (CSD code IMDCDP01); e) \textit{dia-Cd(Im)}\textsubscript{2} aged in CO\textsubscript{2} at 45 °C and 100% RH for 3 days; f) \textit{dia-Cd(Im)}\textsubscript{2} degradation product digested in 0.1M acetic acid.

The remaining CdCO\textsubscript{3} was isolated and analyzed by TGA and FTIR-ATR spectroscopy. The experimental residue of CdO from calcining CdCO\textsubscript{3} in air was 75.5%, which was fully consistent with the theoretical expectation (\textbf{Figure 4.12}).
Analyzing the sample of Cd(HIm)$_6$CO$_3$·3H$_2$O obtained from the degradation of \textit{dia}-Cd(HIm)$_2$ in humid CO$_2$ in the absence of HIm by FTIR-ATR spectroscopy revealed new absorption bands relating to the N-H stretch of HIm and O-H stretch of H$_2$O at 2790 cm$^{-1}$ and 3365 cm$^{-1}$ respectively (Figure 4.13). The presence of CdCO$_3$ in the mixture was also confirmed by the appearance of the carbonate C-O stretching frequency at 1364 cm$^{-1}$. FTIR-ATR analysis of the mixture digested in acetic acid revealed only three absorption bands consistent with CdCO$_3$, one of which corresponded to the C-O stretching frequency of the carbonate ion at 1361 cm$^{-1}$.

Figure 4.12 TGA thermogram of CdCO$_3$ isolated by digesting the product of CO$_2$-induced degradation of \textit{dia}-Cd(HIm)$_2$ in 0.1 M acetic acid. The experimental CdO residue obtained from calcination in dynamic atmosphere of air consisted of 74.5%, which matched the expected value of 75.5%.
The ability of CO$_2$ to directly form a simple carbonate in the case of cadmium-based ZIFs is explained by the discrepancy in metal-ligand ratio between $\text{dia-Cd(Im)}_2$ and Cd(HIm)$_6$CO$_3$·3H$_2$O, although it also implies that CO$_2$ can act as a potential side reactant in accelerated aging synthesis of metal-organic materials. Evidence to this effect was provided by allowing commercial CdO to age in humid (98% RH) air for 12 days. PXRD analysis of the aged CdO sample revealed partial conversion to CdCO$_3$, as seen by comparing the experimental PXRD pattern with the simulated pattern of CdCO$_3$ (Crystallography Open Database (COD) code 1011341) (Figure 4.14).

**Figure 4.13** Selected FTIR-ATR spectra of samples of $\text{dia-Cd(Im)}_2$ in humid CO$_2$: a) $\text{dia-Cd(Im)}_2$; b) Cd(HIm)$_6$CO$_3$·3H$_2$O; c) mixture of $\text{dia-Cd(Im)}_2$ and NH$_4$NO$_3$ in moist CO$_2$ after 9 days; d) mixture of $\text{dia-Cd(Im)}_2$ and NH$_4$NO$_3$ in moist CO$_2$ after 9 days, digested in 0.1M AcOH.
The conversion of CdO to a carbonate under CO2 concentrations found in air highlights the importance atmosphere can have in driving accelerated aging reactions towards undesirable side products.

4.5 Carbon dioxide sensitivity of a family of ZIFs

4.5.1 Carbon dioxide sensitivity of SOD-Co(MeIm)2 (ZIF-67)

The stability studies outlined in this chapter have a particular significance to ZIF-8, in the context of CO2 separation and sequestration. However, using aging for the study of CO2 stability in ZIFs has provided a platform for establishing the effect of porosity, metal center, and ligand type on their stability under long term exposure to different atmospheres, humidity levels, and temperatures. While it may not be surprising that dia-Cd(Im)2 was equally, if not more, susceptible to CO2-induced degradation, due to the lower expected stability of the Cd-N bond compared to that of the Zn-N bond, it was tentatively predicted that ZIF-67, the Co analogue of ZIF-8, should be more resistant to degradation in humid CO2 gas. Namely, in the previous study, it was shown that ZIF-8 quickly collapsed to its non-porous dia-Zn(MeIm)2 polymorph in the presence of (NH4)2SO4 at 98% RH and 45 ºC. Conversely, its cobalt(II) analogue ZIF-67

Figure 4.14. Selected PXRD patterns revealing the conversion of CdO to CdCO3 at 45 ºC and 100% RH: a) CdO; b) simulated pattern for CdCO3 (COD ID 1011341); c) CdO aged for 12 days.
remained stable for several weeks. However, as shown in **Figure 4.15**, exposure of ZIF-67 (sample courtesy of MOF-Technologies, Ltd.) to moist carbon dioxide led to the rapid conversion to a product isostructural to 1.

![Figure 4.15](image)

**Figure 4.15.** Selected PXRD patterns of ZIF-67 subjected to CO₂ gas at 45 °C and 100% RH: a) simulated pattern for SOD-Co(MeIm)₂ (CSD code GITTOT); b) ZIF-67 sample; c) Zn₂(MeIm)₂CO₃ (1); d) ZIF-67 in CO₂ at 100%RH for 9 days.

The formation of the carbonate was further confirmed by FTIR-ATR spectroscopy, whereby the characteristic absorption band at 1330 cm⁻¹ appeared, consistent with the C-O stretch of the carbonate anion (**Figure 4.16**).
4.5.2 Carbon dioxide sensitivity of dia-Zn(MeIm)$_2$

In addition to the type of metal cation in the ZIF, the level of void space in MOFs and ZIFs can also affect the relative stability of the material, with open structures being more prone to structural changes upon solvent removal or chemical modification. For example, attempts to synthesize ZIF-8 by accelerated aging in the presence of ammonium salts results in its rapid conversion to the close-packed dia-Zn(MeIm)$_2$. Likewise, attempts to synthesize the highly porous RHO-Zn(EtIm)$_2$ by accelerated aging requires the addition of 150 mol% excess of HETIm to prevent the MOF from collapsing into the non-porous qtz-Zn(EtIm)$_2$. In that context, it was expected that denser, non-porous ZIFs may be less susceptible to degradation at room temperature than their lower density, porous polymorphs. The density of ZIF structures can be expressed as the number of tetrahedral centers (T) per unit cell volume (V) in nm$^3$, or T/V.

**Figure 4.16.** Selected FTIR-ATR spectra of SOD-Co(MeIm)$_2$ in CO$_2$ gas and 100% RH or in an aqueous slurry: a) ZIF-67; b) ZIF-67 subjected to CO$_2$ at 45ºC and 100% RH for 9 days; c) ZIF-67 in aqueous slurry and CO$_2$ atmosphere.
Keeping in mind that the density of $\text{dia-Zn(MeIm)}_2$ is 4.2 nm$^{-3}$ and that of ZIF-8 is 2.8 nm$^{-3}$, it was postulated that $\text{dia-Zn(MeIm)}_2$ could possibly be less sensitive to degradation in moist CO$_2$.\cite{30} To test this, a sample of $\text{dia-Zn(MeIm)}_2$ made by accelerated aging was exposed to CO$_2$ gas at 100% RH. After one day, the appearance of X-ray reflections consistent with 1 was observed by X-ray powder diffraction (Figure 4.17).

![Figure 4.17](image)

**Figure 4.17.** Selected PXRD patterns showing the instability of $\text{dia-Zn(MeIm)}_2$ in humid CO$_2$: a) simulated pattern for $\text{dia-Zn(MeIm)}_2$ (CSD code OFERUN01); b) Zn$_2$(MeIm)$_2$CO$_3$ (1); c) $\text{dia-Zn(MeIm)}_2$ synthesized by accelerated aging; d) $\text{dia-Zn(MeIm)}_2$ aged in CO$_2$ at 45 °C and 100% RH for 1 day.

Solid-state $^{13}$C CP-MAS NMR spectroscopy of 1 obtained by exposing $\text{dia-Zn(MeIm)}_2$ to moist CO$_2$ gas confirmed conclusions made by X-ray powder diffraction analysis. In Figure 4.18, the $^{13}$C CP-MAS ssNMR spectrum of the reaction mixture revealed the appearance of two signals at 162.75 and 165.71 ppm, corresponding to the two inequivalent carbonate species found in 1, and indicative of the conversion of $\text{dia-Zn(MeIm)}_2$ to a phase isostructural to 1. Strong signals at chemical shifts corresponding to the four chemically inequivalent carbon atoms of MeIm$^-$ were however still apparent in the NMR spectrum, which was in agreement with PXRD data that indicated only partial transformation of $\text{dia-Zn(MeIm)}_2$ to 1. There are four
crystallographically-distinct \textit{MeIm} ions in the asymmetric unit of the \textit{dia-Zn(MeIm)}	extsubscript{2} structure, leading to the four-fold splitting of these signals observed in the ssNMR spectrum of \textit{dia-Zn(MeIm)}	extsubscript{2}.

Figure 4.18. Solid-state \textsuperscript{13}C NMR spectra of \textit{dia-Zn(MeIm)}	extsubscript{2} exposed to humid CO\textsubscript{2}: a) Zn\textsubscript{2}(MeIm)\textsubscript{2}CO\textsubscript{3} (1); b) \textit{dia-Zn(MeIm)}	extsubscript{2}; c) \textit{dia-Zn(MeIm)}	extsubscript{2} aged in CO\textsubscript{2} at 45 °C and 100% RH for 1 day.

Analysis of \textit{dia-Zn(MeIm)}	extsubscript{2} aged in moist CO\textsubscript{2} by FTIR-ATR spectroscopy revealed absorption bands similar to those found in 1 made by ZIF-8 degradation, particularly a C-O stretch at 1338 cm\textsuperscript{-1} (Figure 4.19).
4.5.3 Carbon dioxide sensitivity of RHO-Zn(EtIm)$_2$

Upon exposure to moist CO$_2$, the porous RHO-Zn(EtIm)$_2$ (CSD code MECWOH) readily transformed to a new, previously unknown carbonate phase (2) similar to 1. **Figure 4.20** shows the powder X-ray diffraction data of RHO-Zn(EtIm)$_2$ which has been suspended in an aqueous slurry and exposed to CO$_2$ gas. After two hours of exposure, PXRD analysis revealed the appearance of a crystalline phase resembling that of 1.

**Figure 4.19.** Selected FTIR-ATR spectra of dia-Zn(MeIm)$_2$ aged in moist CO$_2$: a) dia-Zn(MeIm)$_2$; b) dia-Zn(MeIm)$_2$ aged under CO$_2$ atmosphere at 100% RH for 1 day.
Solid-state CP-MAS $^{13}$C NMR of the degradation product of RHO-Zn(EtIm)$_2$ is shown in Figure 4.21. There are two chemical shifts for each ethyl carbon at 13.83 ppm and 22.32 ppm, as well as additional peaks for the aromatic carbons at 125.44 ppm and 158.02 ppm suggesting, as in the case of 1, that there are two crystallographically-distinct 2-ethylimidazole species. Two signals corresponding to carbon atoms of carbonate ions were also found at 163.54 ppm and 166.34 ppm.

Figure 4.20 Selected PXRD patterns revealing the conversion of RHO-Zn(EtIm)$_2$ to a carbonate phase similar to 1 in an aqueous slurry under CO$_2$ gas: a) simulated pattern for RHO-Zn(EtIm)$_2$ (CSD code MECWOH); b) Zn$_2$(Melm)$_2$CO$_3$ (1); c) RHO-Zn(EtIm)$_2$ synthesized by aging; d) RHO-Zn(EtIm)$_2$ in aqueous slurry and CO$_2$ for 2 hours (2).
Thermal analysis of the degradation product of RHO-Zn(EtIm)$_2$ in dynamic atmosphere of air revealed a ZnO residue of 38.7%, which would suggest that the composition of 2 is Zn$_2$(EtIm)$_2$CO$_3$$\cdot$0.66H$_2$EtIm, similar to that of 1. Nonetheless, *ab initio* structure solution conducted at Cardiff University revealed a structure of composition Zn$_2$(EtIm)$_2$CO$_3$. As seen in Figure 4.22, 2 crystallizes in the orthorhombic space group *Pba2* with unit cell parameters $a = 10.35$ Å, $b = 13.20$ Å, $c = 4.74$ Å. The structure of Zn$_2$(EtIm)$_2$CO$_3$ appears very similar to that of Zn$_2$(MeIm)$_2$CO$_3$. Carbonate ions form chains connected by EtIm$^-$ ligands, forming channels parallel to the $c$-axis. The channels are occluded by ethyl moieties of the EtIm$^-$ ligands.

**Figure 4.21** Solid-state $^{13}$C NMR spectra of RHO-Zn(EtIm)$_2$ exposed to humid CO$_2$: a) Zn$_2$(Melm)$_2$CO$_3$ (1); b) RHO-Zn(EtIm)$_2$; c) RHO-Zn(EtIm)$_2$ in aqueous slurry and CO$_2$ (2).
Despite the discrepancy in composition suggested from thermal analysis and that indicated by structure solution, the simulated and experimental PXRD patterns were found to be very similar (Figure 4.23).

Figure 4.22 Fragment of the crystal structure of Zn$_2$(EtIm)$_2$CO$_3$, viewed down the c-axis.

Figure 4.23 Selected PXRD data comparing: a) the experimental pattern of 2 and b) simulated pattern of Zn$_2$(EtIm)$_2$CO$_3$. 
4.5.4 Carbon dioxide sensitivity of SOD-Zn(AldIm)$_2$

Due to the presence of the electron-withdrawing carbonyl group, it was possible that a ZIF composed of the ligand imidazole-2-carboxaldehyde (H$_{2}$AldIm) may be more stable in humid CO$_2$ than the ZIFs comprising alkylated imidazole derivatives. In combination with Zn$^{2+}$ ions, AldIm$^-$ anions form a sodalite topology ZIF isostructural to ZIF-8, known as ZIF-90. To further investigate the effect of ligand functionalization on the stability of the framework, SOD-Zn(AldIm)$_2$ (CSD code WOJGEI) was tested under exposure to water and CO$_2$ gas. When exposed to CO$_2$ gas in an aqueous slurry, mechanochemically$^{31}$ prepared ZIF-90 readily degraded to form another mixed carbonate (3) similar to 1, as demonstrated by PXRD data (Figure 4.24).

![Figure 4.24 PXRD patterns showing the degradation of ZIF-90 in moist CO$_2$: a) ZIF-90; b) Zn$_2$(MelIm)$_2$CO$_3$ (1); c) ZIF-90 synthesized mechanochemically; d) ZIF-90 exposed to CO$_2$ in aqueous slurry.](image-url)
Analysis of the solid-state $^{13}$C CP-MAS ssNMR spectrum of 3, shown in Figure 4.25, revealed expected signals at chemical shifts characteristic of carbons belonging to imidazole-2-carboxaldehyde, in addition to the appearance of a new signal at 163.47 ppm consistent with the presence of one crystallographically-independent carbonate species.

![Solid-state $^{13}$C NMR spectra demonstrating the effect of exposing SOD-Zn(AldIm)$_2$ to CO$_2$ in an aqueous slurry: a) Zn$_2$(MelIm)$_2$CO$_3$ (1); b) SOD-Zn(AldIm)$_2$ in aqueous slurry under atmosphere of CO$_2$.](image)

**Figure 4.25.** Solid-state $^{13}$C NMR spectra demonstrating the effect of exposing SOD-Zn(AldIm)$_2$ to CO$_2$ in an aqueous slurry: a) Zn$_2$(MelIm)$_2$CO$_3$ (1); b) SOD-Zn(AldIm)$_2$ in aqueous slurry under atmosphere of CO$_2$.

*Ab initio* crystal structure determination for 3 from PXRD data revealed a material isostructural to and having a formula similar to that of 1. Specifically, Zn$_2$(AldIm)$_2$CO$_3$ crystallizes in space group *Pba2* (Figure 4.26), with unit cell parameters $a = 10.94$ Å, $b = 11.58$ Å, $c = 4.62$ Å. The experimental PXRD pattern of the CO$_2$ degradation product of ZIF-90 was consistent with the simulated pattern from crystal structure data (Figure 4.27).
Figure 4.26 Fragment of the crystal structure of Zn$_2$(AldIm)$_2$CO$_3$, viewed down the $c$-axis.

Figure 4.27 PXRD patterns of ZIF-90 in an aqueous slurry and after exposure to CO$_2$: a) Zn$_2$(Melm)$_2$CO$_3$ (1); b) SOD-Zn(AldIm)$_2$ in aqueous slurry and CO$_2$ (3); c) simulated pattern for Zn$_2$(AldIm)$_2$CO$_3$ (3).
4.5.5 Stability of \textit{zni-Zn(Im)}\textsubscript{2} in the presence of moist CO\textsubscript{2}

Lastly, \textit{zni-Zn(Im)}\textsubscript{2}\textsuperscript{22} was tested for degradation upon exposure to moist CO\textsubscript{2} gas. This ZIF is characterized by very low porosity and the presence of a simple, unsubstituted imidazolate linker, thus making it fundamental for establishing the effect of porosity and/or linker nature on stability. Powder X-ray diffraction patterns of the material after exposure to humid CO\textsubscript{2} for 5 days as well as in a slurry under CO\textsubscript{2} atmosphere did not reveal any new crystalline phases (Figure 4.28). Seifert and coworkers previously investigated the theoretical stability of this \textit{zni}-topology material, and concluded that it should be the most stable topology among those adopted by three-dimensional ZIFs based on unsubstituted imidazolate ligands\textsuperscript{32}. This highly dense structure can be postulated as the reason for the resistance of \textit{zni-Zn(Im)}\textsubscript{2} to carbon dioxide degradation.

Comparison of the FTIR-ATR spectra of \textit{zni-Zn(Im)}\textsubscript{2} before and after exposure to moist CO\textsubscript{2} gas revealed no new absorption bands that could be associated with to a carbonate species, thereby further confirming that \textit{zni-Zn(Im)}\textsubscript{2} did not transform into a carbonate (Figure 4.29). In addition, all signals in the \textsuperscript{13}C CP-MAS ssNMR spectrum of \textit{zni-Zn(Im)}\textsubscript{2} after exposure to humid CO\textsubscript{2}
could be associated to the three chemically-inequivalent carbon atoms of the imidazolate ligand bound in the framework (Figure 4.30).

Figure 4.29 FTIR-ATR spectra of \(\text{zni}-\text{Zn(Im)}_2\) aged in moist CO\(_2\): a) \(\text{zni}-\text{Zn(Im)}_2\); b) \(\text{zni}-\text{Zn(Im)}_2\) aged under CO\(_2\) atmosphere at 100% RH for 5 days.

Figure 4.30 Solid-state \(^{13}\)C CP-MAS NMR spectra of \(\text{zni}-\text{Zn(Im)}_2\) exposed to humid CO\(_2\): a) \(\text{zni}-\text{Zn(Im)}_2\) synthesized by acelerated aging; b) \(\text{zni}-\text{Zn(Im)}_2\) aged in CO\(_2\) atmosphere and 100% RH for 5 days.
4.6 Conclusion

Sensitivity to carbon dioxide and moisture has been demonstrated for a series of ZIF model materials. When exposed to 100% RH or suspended in an aqueous slurry in the presence of CO₂ gas at 45 ºC, six out of seven model ZIFs converted to complex carbonates, irrespective of their initial porosity (or framework density), metal choice (Zn, Cd, Co), or ligand (Im⁻, MeIm⁻, EtIm⁻, and AldIm⁻). While the CO₂ degradation product of dia-Cd(Im)₂ consisted of the known Cd(HIm)₆CO₃·3H₂O and CdCO₃, all other ZIFs converted to a set of isostructural complex carbonates of so far uncertain compositions. The product of ZIF-8 degradation (1) in particular has been observed in previous literature, however its structure and solid-state properties have been analyzed herein for the first time. The structure of 1 was elucidated by ab initio structure solution from powder X-ray diffraction data, and consists of a 3-dimensional framework composed of ZnCO₃ chains connected by MeIm⁻ ligands. Likewise, structures of the degradation products of RHO-Zn(EtIm)₂ and ZIF-90 in moist CO₂ were elucidated by ab initio methods and established to be similar to the product of ZIF-8 degradation. Despite the similarity between the simulated and experimental powder X-ray diffraction patterns of 1, 2, and 3, the apparent discrepancy between the stoichiometry implied in the crystal structures and that determined from elemental and thermal analyses warrants further detailed studies of these materials. Accelerated aging, i.e. the exposure of solid reagents or materials to controlled conditions of humidity, temperature, and atmosphere, is a valuable methodology for the determination of the solid-state stability of metal-organic materials.

4.7 References


31. ZIF-90 was synthesized mechanochemically using an unpublished method devised by Matt J. Cliffe, at the University of Cambridge.

CHAPTER 5
SYNTHESIS AND DISCOVERY OF CADMIUM-IMIDAZOLATE FRAMEWORKS BY ACCELERATED AGING AND MULTINUCLEAR ($^{111}$Cd, $^{13}$C, $^1$H) SOLID-STATE NMR

5.1 Introduction and connecting text

The following chapter describes results which are soon to be submitted for publication and which were obtained in collaboration with the group of Prof. R. Schurko at the University of Windsor. Unless specified otherwise, all experiments discussed in this chapter, in particular aging experiments monitored by powder X-ray diffraction analysis, were conducted by C. Mottillo at McGill University. The data discussed in Section 5.6 was collected by C. O’Keefe, a PhD student under the supervision of Prof. Robert Schurko, on samples synthesized by C. Mottillo at McGill University. The results described in Section 5.7 were obtained during a one-week collaborative research exchange at the University of Windsor jointly by C. Mottillo and C. O’Keefe.

In the herein described work, only popular, widely-investigated ZIFs have been selected for investigating how solid-state chemistry can be adapted for the synthesis of metal-organic materials. The mechanochemical synthesis of ZIFs, for example, has focused on zinc-based structures of simple imidazoles including $\text{HIm}$, $\text{HMeIm}$, and $\text{HETIm}$.$^1$ The relatively reactive nature of ZnO and simplicity of the ZIF targets have made zinc an ideal starting point for such investigations. The popularity of ZIF-8 has also made this class of ZIFs a valuable, commercially-interesting choice for solid-state studies.$^2$ Like with mechanochemical synthesis, the study of the self-assembly of ZIFs using accelerated aging began with the more commonly described zinc- and cobalt(II)-based materials.$^3$ Despite this, the derivatization of other, less reactive oxides or those incorporating metal centres with multiple accessible oxidation states, such as MgO, PbO, CuO, and NiO, to form complexes and 3-D coordination polymers has also been described.$^4$

Cadmium-based metal-organic frameworks (MOFs) are a quickly expanding class of coordination polymers,$^5$ but remain less studied compared to those employing zinc and cobalt(II) metal centers as nodes.$^3$ In part, this is due to the inherent toxicity of $\text{Cd}^{2+}$, which limits their perceived potential for applications in industrial settings, where the risk of environmental or health-related contamination can be great. The Morsali and Junk groups reported the mechanochemical synthesis of a cadmium-based MOF which can be used to selectively extract...
There exist other examples where cadmium-based MOFs have been synthesized and used in proof-of-principle studies as luminescence-based sensors. Nonetheless, there now exists a series of ca. 15 cadmium-based ZIFs, called cadmium imidazolate frameworks (CdIFs). These were first reported by Tian et al. and consist of a series of materials based on a range of 2-substituted imidazole linkers. Furthermore, Karagiardidi et al. reported the solvent-assisted linker exchange of single crystals of CdIFs formed in solution. The interest in CdIFs lies in the inherent flexibility of the Cd-N bond, which is longer and weaker than that of its divalent zinc and cobalt(II) counterparts. This means that in addition to the nascent ZIF being templated by external solvent guest molecules, and functionalization in the 2-position, the weaker coordination bonds may a further opportunity to form undiscovered, or otherwise unusual framework topologies.

Aside from the observation that ZIFs can be less stable than previously thought, which was noted by looking at them under aging conditions, it is also apparent that the often kinetically-driven solution processes can yield different ZIF products compared to accelerated aging synthesis. Namely, it appears that unless structure templating is encouraged by specific salt catalysts, accelerated aging results almost exclusively in the formation of the more thermodynamically stable polymorphs of ZIFs. Moreover, in accelerated aging synthesis, the formation of the final product is often mediated by low-density, thermodynamically less stable intermediate frameworks. Therefore, a system which exploits this behaviour while aiding the discovery of accelerated aging mechanisms by identifying new phases will be of interesting the context of fundamental mechanistic studies, as well as the discovery of new materials. The notable differences in topologies between CdIFs and zinc-based ZIFs involving the same ligands, combined with the fact that solid-state synthesis of CdIFs has remained largely unexplored, make CdIFs attractive and intriguing targets for detailed mechanistic studies of accelerated aging reactions. The perceived flexibility of CdIFs may allow for the exploration of different factors controlling to their solid-state synthesis, and elucidate their effect on the result of accelerated aging reactions.

The progression of solid-state reactions should ideally be monitored by non-invasive techniques, including X-ray diffraction, solid-state NMR, or FTIR-ATR and Raman spectroscopy, in order to enable observation of the reaction without causing unwanted chemical changes in the system. Non-invasive methods based on in situ monitoring, including powder
synchrotron X-ray diffraction and Raman spectroscopy in particular, have proven pivotal in
determining the kinetics and mechanisms of mechanochemical ZIF synthesis.\textsuperscript{11,12} In situ studies have also served for the identification of a new, transient polymorph of the ZIF-8 structure, which would not have been discovered otherwise.\textsuperscript{13} The longer reaction times of accelerated aging, however, make such in situ rapid detection methods unrealistic, and, indeed, not necessary, due to the cost of synchrotron time and large volume of data needed to monitor the reaction from start to finish. But, longer reaction times associated with accelerated aging provided an opportunity to study transformations using methods currently unavailable to studying mechanochemistry, specifically, solid-state NMR spectroscopy. In that context, this section reports the monitoring of accelerated aging synthesis of CdIFs by solid-state NMR in conjunction with ex situ powder X-ray diffraction (PXRD). While PXRD can enable the identification of crystalline phases formed, it cannot give insight into the transient complexes formed in amounts below the experimental detection limit, often estimated to be 0.05-5\% w/w.\textsuperscript{14} Therefore, in this work, PXRD analysis was combined with solid-state NMR as a dual and complementary approach to elucidate the identity of product formed, simultaneously with changes in the local coordination environment of the metal ion as the reaction progresses. Cadmium-based frameworks provide a system uniquely amenable to this approach, as both \textsuperscript{113}Cd and \textsuperscript{111}Cd are abundant NMR-active spin $\frac{1}{2}$ nuclei of \textsuperscript{112}Cd, facilitating the observation of reaction progress. The NMR-active metals have previously been exploited to identify and monitor changes of the coordination environments in small-molecule complexes,\textsuperscript{15a-b} MOFs,\textsuperscript{15c-f} as well as proteins.\textsuperscript{15g-h} Presented here is the use of solid-state \textsuperscript{111}Cd NMR for the time-resolved monitoring of the synthesis of CdIFs in the solid state.

5.2 Accelerated aging synthesis of CdIFs

The solid-state synthesis of ZIFs from ZnO or CoO and imidazole derivatives by means of the accelerated aging methodology has been described in Chapters 2 and 3. Using CdO and solid imidazole derivatives as reagents was, therefore, anticipated to provide a logical approach for the aging synthesis of CdIFs. The previously established reaction parameters (45 °C and 100\% relative humidity, RH) were selected as the preferred conditions for the accelerated aging formation of CdIFs. Likewise, as in the case of Zn- and Co-based ZIFs, a selection of various imidazole derivatives was studied as ligands: imidazole (H\textsubscript{Im}), 2-methylimidazole (H\textsubscript{MeIm}), and 2-ethylimidazole (H\textsubscript{EtIm}). In addition to conducting these reactions in the absence of a
catalyst, a screen of the salts NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, and (HCAF)HSO$_4$, added in 4 mol% with respect to CdO was performed to establish whether they exhibit any structure-directing effects in CdIF synthesis (Figure 5.1).

![Figure 5.1 Schematic summary of the results of this study, exploring the synthesis of CdIFs based on HIm, HMelm, HETlm, by accelerated aging in the presence or absence of a salt catalyst.]

5.2.1 Accelerated aging synthesis of Cd(Im)$_2$

The preliminary investigation of the accelerated aging synthesis of CdIFs consisted of milling the solid reagents for five minutes in order to achieve intimate mixing, and analyzing the mixture by powder X-ray diffraction (PXRD) immediately afterwards. Any potential conversion was generally ascertained by qualitative observation of the intensity of reflections corresponding to CdO, and the identity of any crystalline products was judged by comparing the experimental PXRD patterns with those simulated from crystal structures of known CdIFs or ZIFs. Mechanical milling of a 1:2 stoichiometric mixture of CdO and HIm immediately resulted in the partial formation of an unknown crystalline phase, as determined by PXRD analysis (Figure...
A previous report by Fernández-Bertrán and coworkers described the solid-state synthesis of a Cd(\textit{Im})\textsubscript{2} by manual grinding of CdO and H\textit{Im}, the structure of which had not been determined\textsuperscript{17}. A qualitative comparison between their published PXRD pattern and the pattern collected after five minutes mechanical milling revealed that the two may be similar, or even identical phases. Any definitive conclusion regarding the identity of both phases could not be made because both PXRD patterns were collected on an impure and poorly crystalline samples. The Cambridge Structural Database (CSD) was searched for known metal(II) imidazolates, with the intention of identifying this phase. A comparison of the simulated PXRD pattern of the \textit{crb}-topology Zn(\textit{Im})\textsubscript{2} (CSD code GITTEJ)\textsuperscript{10a} and the experimental PXRD pattern of the unknown product suggested they may be similar (Figure 5.2). The inability to obtain the product as a pure phase, however, meant that its identity could not be confirmed with certainty. After a total of seven days aging at 100% RH and 45 °C, the unknown phase disappeared and the formation of \textit{dia}-Cd(\textit{Im})\textsubscript{2} (CSD code BAYQAU)\textsuperscript{7f} which was previously described by Maschiocchi \textit{et al}, was observed. Small reflections corresponding to the complex carbonate Cd(H\textit{Im})\textsubscript{6}CO\textsubscript{3}·3H\textsubscript{2}O (CSD code IMCDCP01)\textsuperscript{18} were also apparent in the PXRD pattern recorded after aging. After these seven days, the reaction was incomplete, as evidenced by the observation of reflections belonging to CdO. Our previous study regarding the accelerated aging synthesis of ZIFs revealed that adding small amounts of protic salt catalysts in some cases augmented the conversion of the metal oxide\textsuperscript{3}. In addition, the selection of ammonium \textit{vs}. ammonium-free salt catalysts was shown to direct the reaction towards the formation of non-porous or porous materials, respectively. Therefore, the salts (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, NH\textsubscript{4}NO\textsubscript{3}, and (H\textit{Caf})HSO\textsubscript{4}, were selected as potential catalysts for the synthesis of CdIFs by accelerated aging. This enabled the comparison between the catalytic and structure-templating effects of inorganic, ammonium-based salts and the organic caffeinium-based hydrogensulfate salt, previously shown to be a very efficient catalyst for the synthesis of microporous ZIF-8\textsuperscript{3b}.

Analysis by PXRD revealed again that milling of CdO and H\textit{Im}, this time in the presence of 4 mol\% NH\textsubscript{4}NO\textsubscript{3} with respect to CdO, yields a small amount of the tentatively identified \textit{crb}-Cd(\textit{Im})\textsubscript{2} (Figure 5.2). In addition to this tentatively identified phase, weak X-ray reflections corresponding to the previously described \textit{dia}-Cd(\textit{Im})\textsubscript{2} were also evident by PXRD analysis. This was ascertained by a qualitative comparison of the experimental pattern with the pattern simulated from the crystal structure data of \textit{dia}-Cd(\textit{Im})\textsubscript{2} (CSD code BAYQAU). After six days
aging at 100% RH and 45 °C, PXRD analysis of the reaction mixture revealed that full conversion of CdO had been achieved, as shown by the absence of X-ray reflections corresponding to CdO. However, as in the case of the neat reaction, weak reflections corresponding to Cd(HIm)_6CO_3·3H_2O were noticeable in the PXRD pattern in addition to those corresponding to $\text{dia-Cd(Im)}_2$ (Figure 5.2). Using (NH_4)_2SO_4 salt instead of NH_4NO_3 as the additive resulted in a similar reaction sequence. Namely, PXRD analysis showed that a mixture of the tentatively identified $\text{crb-Cd(Im)}_2$ and $\text{dia-Cd(Im)}_2$ had formed upon pre-milling. In this case, however, qualitative comparison between the reflections corresponding to both phases suggested that the fraction of $\text{dia-Cd(Im)}_2$ was considerably higher than that of tentative $\text{crb-Cd(Im)}_2$. After six days aging, the presence of CdO was nearly undetectable by PXRD, suggesting that complete or near-complete conversion had been achieved. The salt catalyst $\text{(HCAf)HSO}_4$, which exhibited excellent catalytic properties in the aging synthesis of ZIF-8 and related ZIFs, also induced the rapid conversion of CdO to $\text{dia-Cd(Im)}_2$. Analysis by PXRD immediately after pre-milling revealed that mixture with $\text{(HCAf)HSO}_4$ contained a large amount of unreacted CdO and a small amount of tentatively identified $\text{crb-Cd(Im)}_2$. After six days, complete conversion of CdO was observed, and the presence of any impurities, including Cd(HIm)_6CO_3·3H_2O was undetectable. The accelerating effect of protic salts as catalysts in the accelerated aging synthesis of CdIFs has thus been clearly demonstrated. The formation of a small amount of Cd(HIm)_6CO_3·3H_2O occurred in some cases, presumably as a result of the high HIm:CdO ratio at the onset of the reaction, in combination with carbon dioxide gas present in the atmosphere.
Figure 5.2 PXRD patterns corresponding to the accelerated aging synthesis of HIm-based CdIFs at 100% RH and 45 °C: a) CdO; b) HIm; c) simulated pattern for dia-Cd(HIm)$_2$ (CSD code BAYQAU); d) simulated pattern for Cd(HIm)$_6$CO$_3$·3H$_2$O (CSD code IMCDCP01); e) simulated pattern for crb-Zn(HIm)$_2$ (CSD code GITTEJ); f) mixture of CdO and HIm after aging for: f) 0 days; g) 7 days; mixture of CdO and HIm in the presence of 4 mol% NH$_4$NO$_3$ after aging for: h) 0 days; i) 6 days; mixture of CdO and HIm in the presence of 4 mol% (NH$_4$)$_2$SO$_4$ after aging for: j) 0 days; k) 6 days; mixture of CdO and HIm in the presence of 4 mol% (H$_2$Caf)(HSO$_4$) after aging for: l) 0 days; m) 6 days.
5.2.2 Accelerated aging synthesis of Cd(EtIm)$_2$

Several cadmium-imidazolates involving HEtIm have been previously reported in the literature, some of them adopting the same topology as ZIF structures based on Zn$^{2+}$ (e.g. RHO-Zn(EtIm)$_2$ and qtz-Zn(EtIm)$_2$). As in the case of Cd(Im)$_2$ synthesis, the aging reaction between HEtIm and CdO was first explored without salt catalyst and, subsequently, also in the presence of 4 mol% of each of the salts (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, and (HCaf)HSO$_4$. In general, HEtIm appeared to be more reactive than HIm under accelerated aging conditions. After premilling for five minutes in a ball mill, PXRD analysis of all four reaction mixtures revealed the disappearance of reflections belonging to HEtIm, suggesting it became amorphous. Neither the appearance of new crystalline phases nor the attenuation of the diffraction peaks belonging to CdO were observed by qualitative PXRD analysis (Figure 5.3). In reactions containing no catalyst, as well as those catalyzed by (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$, PXRD analysis revealed the formation of a small amount of the previously described porous framework RHO-Cd(EtIm)$_2$ (CSD code GUPCEA) after reacting at 45 ºC and 100% RH for two days. The complete conversion of CdO was observed in all three reactions after aging for five additional days, with the non-porous qtz-Cd(EtIm)$_2$ (CSD code GUPCOK01) being the final and only product. In the case of the reaction catalyzed by (HCaf)HSO$_4$, complete disappearance of reflections corresponding to CdO was observed after two days aging (Figure 5.3).
Figure 5.3 PXRD patterns corresponding to the accelerated aging synthesis of HEtIm-based CdIFs at 100% RH and 45 °C: a) CdO; b) HEtIm; c) simulated pattern for RHO-Cd(EtIm)$_2$ (CSD code GUPCEA); d) simulated pattern for qtz-Cd(EtIm)$_2$ (CSD code GUPCOK01); mixture of CdO and HEtIm after aging for: e) 0 days; f) 2 days; g) 7 days; mixture of CdO and HEtIm in the presence of 4 mol% NH$_4$NO$_3$ after aging for: h) 0 days; i) 2 days; j) 7 days; mixture of CdO and HEtIm in the presence of 4 mol% (NH$_4$)$_2$SO$_4$ after aging for: k) 0 days; l) 3 days; m) 7 days; mixture of CdO and HEtIm in the presence of 4 mol% (HCAF)(HSO$_4$) after aging for: n) 0 days; o) 2 days.
5.2.3 Accelerated aging synthesis of Cd(MeIm)$_2$

Exploring the structure-directing effect of catalytic salt additives on the accelerated aging synthesis of CdIFs was of particular interest for the system involving HMeIm. In combination with Cd$^{2+}$, HMeIm forms a sodalite (SOD)-topology CdIF which is analogous to SOD-Zn(MeIm)$_2$ (ZIF-8). In the reaction between ZnO and HMeIm, the choice of salt catalyst resulted in either the formation of microporous ZIF-8 from ZnO, or its non-porous dia-topology polymorph. However, unlike that system, aging of a 1:2 stoichiometric mixture of CdO and HMeIm at 100% RH and 45 ºC for 12 days did not result in the formation of SOD-Cd(MeIm)$_2$, but gave a product of unknown structure (I), as determined by PXRD analysis (Figure 5.4). A search of the CSD for metal imidazolates with simulated PXRD patterns matching that of the unknown product was unsuccessful. In addition to X-ray reflections corresponding to a new phase, the PXRD pattern of the neat reaction mixture contained low-intensity reflections corresponding to CdO and CdCO$_3$. The two possible reasons for this were: i) the reaction required the presence of a catalyst to reach complete conversion of CdO, or ii) the ligand-to-metal ratio in the structure is higher than 2:1, leaving unreacted CdO. In both cases, the unreacted CdO was converting to CdCO$_3$, an effect which has been discussed in Chapter 4. Reacting CdO and HMeIm in the presence of 4 mol% NH$_4$NO$_3$ resulted again in the formation of I after 7 days, although low-intensity X-ray reflections for CdO were still apparent in the PXRD pattern. Using (NH$_4$)$_2$SO$_4$ as the salt additive resulted in incomplete conversion of CdO to I. However, allowing the reaction to proceed for five more days and analyzing the mixture by PXRD, interestingly, revealed the disappearance of X-ray reflections corresponding to I and full conversion of CdO to the previously described yqt1-Cd(MeIm)$_2$. The same behaviour was observed in the reaction catalyzed by (H Caf)$\text{-HSO}_4$, which revealed the intermediate formation of I after two days and its subsequent conversion to yqt1-Cd(MeIm)$_2$ after seven days.
Figure 5.4 Comparison of PXRD patterns corresponding to the accelerated aging synthesis of HMeIm-based CdIFs at 100% RH and 45 °C: a) commercial CdO; b) commercial HMeIm; c) CdCO₃, commercial sample; d) simulated pattern for yqt1-Cd(Melm)_2 (CSD code GUPBOJ); mixture of CdO and HMeIm after aging for: e) 0 days; f) 12 days; mixture of CdO and HMeIm in the presence of 4 mol% NH₄NO₃ after aging for: g) 0 days; h) 7 days; mixture of CdO and HMeIm in the presence of 4 mol% (NH₄)₂SO₄ after aging for: i) 0 days; j) 2 days; k) 7 days; mixture of CdO and HMeIm in the presence of 4 mol% (HCAF)(HSO₄) after aging for: l) 0 days; m) 2 days; n) 7 days.

The presence of weak X-ray reflections corresponding to CdO even in the PXRD pattern of the reaction catalyzed by NH₄NO₃ implied that there was insufficient HMeIm to react with CdO.
when a 2:1 ratio of reagents was used. To verify this, CdO was reacted with a very large excess (1:6 stoichiometric ratio) of HMeIm. The reaction mixture was analyzed by PXRD after 6 days aging at 100% RH and 45 °C. The PXRD pattern revealed the complete conversion of CdO into 1 by the absence of reflections corresponding to CdO. Strong X-ray diffraction peaks corresponding to HMeIm were nonetheless evident in the PXRD pattern. This sample was stirred in MeOH for one hour to remove excess HMeIm reagent, and dried under vacuum for thorough solid-state analysis by Fourier-transform infrared attenuated total reflection spectroscopy (FTIR-ATR), thermogravimetric analysis (TGA), and solid-state $^{13}$C, $^1$H, and $^{111}$Cd NMR.

5.3 Solid-state analysis of 1 by FTIR-ATR and TGA

The solid-state FTIR-ATR spectrum of 1 was compared to the spectra for neutral, solid HMeIm and a pristine sample of yqt1-Cd(MeIm)$_2$, made by accelerated aging. Analysis of the FTIR-ATR spectrum of HMeIm revealed a broad set of absorption bands spanning from 3250 cm$^{-1}$ to 2250 cm$^{-1}$, corresponding to the N-H stretching (Figure 5.5). These vibrational bands were not found in the spectrum of yqt1-Cd(MeIm)$_2$, consistent with the absence of N-H bonds and full coordination of all MeIm$^-$ ligands to Cd$^{2+}$ ions. In addition, the C-H bending frequencies, which are normally represented by absorption bands at 1114 cm$^{-1}$ and 914 cm$^{-1}$ in the spectrum of HMeIm, are shifted to 1146 cm$^{-1}$ and 987 cm$^{-1}$ in the spectrum of yqt1-Cd(MeIm)$_2$. Broad absorption bands in the range of 3250 cm$^{-1}$ to 2400 cm$^{-1}$ were observed in the FTIR-ATR spectrum of 1, contrasting the spectrum of yqt1-Cd(MeIm)$_2$ and consistent with the presence of neutral HMeIm in the structure. This was further confirmed by the appearance of two sets of absorption bands for the C-H bending at both 1110 cm$^{-1}$ and 893 cm$^{-1}$ in addition to 1142 cm$^{-1}$ and 990 cm$^{-1}$, suggesting that the framework of 1 contains both neutral and anionic 2-methylimidazole species.
Thermogravimetric analysis of the washed and dried sample of 1 in dynamic atmosphere of N₂ demonstrated a weight loss step of 19.8% with an onset at 145 °C. This temperature is consistent with the melting point of HMeIm, which suggested that this step corresponded to the loss of neutral HMeIm from the structure (Figure 5.6). Calculating the potential molar mass of the entire framework while presuming that the first step corresponded to the loss of one neutral HMeIm molecule, suggested a Cd²⁺:HMeIm ratio of 1:3. Considering this ratio, the removal of one HMeIm molecule corresponds to ca. 23% of the entire structure, which is fairly consistent with TGA data. The structure of 1 must therefore contain one neutral HMeIm molecule for every one unit of Cd(MeIm)₂, leading to the proposed formula Cd(MeIm)₂·(HMeIm).

Figure 5.5 Comparison of FTIR-ATR spectra for the known CdIF yqt1-Cd(MeIm)₂ with a pure sample of 1: a) commercial HMeIm; b) pristine yqt1-Cd(MeIm)₂ made by accelerated aging in the presence of (HCAF)(HSO₄); c) sample of 1, synthesized by accelerated aging with a 1:6 stoichiometric ratio of CdO:HMeIm, washed in MeOH and dried by vacuum filtration.
It is evident from the preceding section that the accelerated aging syntheses of CdIFs involving HIm, HMeIm, and HEtIm tend to proceed via the formation of less dense, and possibly less stable structures, before yielding denser polymorphs as the final products. This is not unlike the processes observed during the accelerated aging and mechanochemical syntheses of zinc-based ZIFs,\(^1\) and is in line with Ostwald’s rule of stages.\(^{20}\) However, as seen in the reaction of CdO and HMeIm or HIm, the accelerated aging of CdIFs led to the formation of unidentified materials as intermediate phases. In the case of HMeIm, the ability to selectively direct the reaction to yield the intermediate 1 in pure form by controlling stoichiometric composition of the reaction mixture and switching the catalytic salt additive provided the opportunity to determine the structure of a new, unidentified CdIF so far only accessible by solid-state synthesis. In addition, this system provided an interesting opportunity to investigate the structure-directing role of NH\(_4\)NO\(_3\) and, at the same time, elucidate the driving factors behind accelerated aging reactivity.

Attempts to recrystallize 1 or obtain single crystals suitable for crystal structure determination directly from solution were unsuccessful, due to the poorly soluble nature of 1 and the tendency to form other polymorphs of Cd(Mel)m\(_2\). Having obtained FTIR-ATR and TGA

**Figure 5.6** TGA thermogram of a sample of 1 synthesized by accelerated aging with a 1:6 stoichiometric ratio of CdO and HMeIm, using 4 mol% NH\(_4\)NO\(_3\) salt catalyst after washing in MeOH. The onset temperature of 145 °C for the first weight loss step is consistent with the melting point of HMeIm. Assuming this step corresponds to the loss of neutral HMeIm from the structure, the weight loss of 19.8% is consistent with a Cd:HMeIm ratio of 1:3.
data on 1, solid-state multinuclear \(^{111}\text{Cd}, \, ^{13}\text{C}, \, \text{and} \, ^{1}\text{H}\) NMR (ssNMR) was identified as a potential method to further understand the type and symmetry of the \(\text{Cd}^{2+}\)-environment found in the structure. The data obtained in this analysis also serves as the basis for monitoring the progression of \(\text{Cd}^{2+}\) environments from the onset of the accelerated aging reaction, to the formation of the final product, the results of which will be discussed in the next section.

In order to make accurate conclusions regarding the \(^{111}\text{Cd}, \, ^{13}\text{C}, \, \text{and} \, ^{1}\text{H}\) environments in 1, ssNMR data was collected on a series of Cd-imidazolates with known structures. The CdIFs \(yqt1\)-Cd(MeIm)_2 (CSD code GUPBOJ),\(^{7a}\) and \(dia\)-Cd(Im)_2 (CSD code BAYQAU),\(^{7f}\) and the complex Cd(HIm)_6CO_3·3H_2O (CSD code IMCDCP01)\(^{18}\) were selected for this purpose, due to their expected isotropic chemical shifts to be similar to 1. The selection of both CdIF structures and the discrete complex Cd(HIm)_6CO_3·3H_2O provided data required to distinguish the NMR signals of Cd\(^{2+}\) in tetrahedral or octahedral environments, as well as identify the possible presence of neutral or anionic 2-methylimidazole ligands. Figure 5.7 depicts fragments of the crystal structures of model compounds \(yqt1\)-Cd(MeIm)_2, \(dia\)-Cd(Im)_2, and Cd(HIm)_6CO_3·3H_2O. The asymmetric unit of \(yqt1\)-Cd(MeIm)_2 contains two crystallographically distinct Cd\(^{2+}\) ions tetrahedrally coordinated to four MeIm\(^-\) ligands. One of the MeIm\(^-\) ligands is disordered about a center of inversion. There is only one crystallographically independent and tetrahedrally coordinated Cd\(^{2+}\) ion in the asymmetric unit of the \(dia\)-Cd(Im)_2 structure. Lastly, the Cd\(^{2+}\) ions in Cd(HIm)_6CO_3·3H_2O are in an octahedral environment and surrounded by six neutral HIm ligands.
Samples of pure $yqt1\text{-Cd(MeIm)}_2$, $\text{dia-Cd(Im)}_2$, $\text{Cd(HIm)}_6\text{CO}_3\cdot3\text{H}_2\text{O}$, and 1 were synthesized by C. Mottillo and solid-state $^1\text{H}$-$^{111}\text{Cd}$ CP, $^1\text{H}$, and $^1\text{H}$-$^{13}\text{C}$ CP NMR spectra were collected for these samples by C. O’Keefe at the University of Windsor. The NMR-active nucleus $^{111}\text{Cd}$ was selected instead of $^{113}\text{Cd}$, due to radio waves in the vicinity of the Chemistry and Biochemistry Department whose frequency is coincident with the resonance frequency of $^{113}\text{Cd}$. Analysis of the $^1\text{H}$-$^{111}\text{Cd}$ CP-MAS ssNMR spectrum of $yqt1\text{-Cd(MeIm)}_2$ revealed two signals with isotropic chemical shifts at 436.8 ppm and 416.9 ppm (Figure 5.8). The chemical shifts are consistent for Cd$^{2+}$ in a tetrahedral environment surrounded by four nitrogen-donor atoms.\textsuperscript{21} The presence of two signals is consistent with the existence of two symmetrically inequivalent Cd$^{2+}$ species in the asymmetric unit of the reported crystal structure. The signal found at 436.8 ppm shows $J$-coupling of the $^{111}\text{Cd}$ to the four $^{14}\text{N}$ nuclei, with a multiplicity of nine. This number is consistent with having four equivalent spin 1 nuclei surrounding the Cd$^{2+}$ ion. The $^1\text{H}$-$^{111}\text{Cd}$ CP-MAS ssNMR spectrum of $\text{dia-Cd(Im)}_2$ revealed one signal with a chemical shift of 436.3 ppm, which resembles that of $yqt1\text{-Cd(MeIm)}_2$ and is again consistent with one tetrahedrally-coordinated $^{111}\text{Cd}$ species. The signal again exhibited clear $J$-coupling, with a multiplicity of nine. The $^1\text{H}$-$^{111}\text{Cd}$ CP-MAS ssNMR spectrum of $\text{Cd(HIm)}_6\text{CO}_3\cdot3\text{H}_2\text{O}$ contained a signal at a markedly different chemical shift than the previously discussed CdIFs. An isotropic shift at 251.5 ppm was observed, which is consistent with Cd$^{2+}$ being in an octahedral environment composed of six nitrogen-donor atom ligands.\textsuperscript{22} Comparison of the $^1\text{H}$-$^{111}\text{Cd}$ CP-

\textbf{Figure 5.7} Fragments of the crystal structures of known cadmium-based imidazolates, showing the coordination geometry around Cd$^{2+}$ ions: a) $yqt1\text{-Cd(MeIm)}_2$ (CSD code GUPBOJ)\textsuperscript{7a} showing the two crystallographically-distinct Cd$^{2+}$ ions that are found in the asymmetric unit and the disorder exhibited by one of the MeIm$^-$ ligands; b) $\text{dia-Cd(Im)}_2$ (CSD code BAYQAU)\textsuperscript{7f} showing the tetrahedral environment of Cd$^{2+}$; c) $\text{Cd(HIm)}_6\text{CO}_3\cdot3\text{H}_2\text{O}$ (CSD code IMCDCP01),\textsuperscript{18} showing the neutral HIm ligands arranged octahedrally about Cd$^{2+}$.\n
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MAS ssNMR spectrum of 1 with those of the above described samples indicated $^{111}$Cd nuclei are most likely in a tetrahedral environment formed by $\text{MeIm}^-$ ligands. The isotropic chemical shift of the signal found in the spectrum of 1, 441.7 ppm, was similar to that of $\text{yqt1-Cd(MeIm)}_2$ and $\text{dia-Cd(Im)}_2$ (Figure 5.8).

![SSNMR spectra](image)

**Figure 5.8** Comparison of solid-state $^1$H-$^{111}$Cd CP-MAS NMR spectra for known Cd-imidazolate structures and 1: a) $\text{yqt1-Cd(MeIm)}_2$; b) $\text{dia-Cd(Im)}_2$; c) Cd($\text{HIm})_6\text{CO}_3\cdot3\text{H}_2\text{O}$; d) Cd($\text{MeIm})_2\cdot(\text{HMeIm})$ (1). Spinning side bands are denoted by *. Data collected by Chris O’Keefe.

A comparison of the $^1$H MAS ssNMR spectra of all four compounds suggested that 1 also contains neutral $\text{HMeIm}$ incorporated in its structure. Firstly, analysis of the $^1$H MAS spectrum of $\text{yqt1-Cd(MeIm)}_2$ revealed two broad, unresolved signals at 4.28 ppm and 0.52 ppm, consistent with the protons found on the imidazole ring and on the methyl substituent, respectively (Figure 5.9). Conversely, the $^1$H MAS ssNMR spectrum of $\text{dia-Cd(Im)}_2$ revealed only one signal at a chemical shift of 5.04 ppm, as would be expected for the three protons found on the imidazole
ring. Altogether three signals were observed in the $^1$H MAS ssNMR spectrum of Cd(HIm)$_6$CO$_3$·3H$_2$O, two at 3.48 ppm and 4.95 ppm, consistent with the expected chemical shifts for the protons on the three water molecules in the structure and the protons on the imidazole ring, respectively. The third signal, observed at 12.39 ppm, was assigned to the N-H protons on the imidazole ligands. Lastly, the $^1$H MAS ssNMR spectrum of 1 also revealed three signals. The first two signals at 0.49 ppm and 3.87 ppm were consistent with protons found on the methyl substituent and imidazole ring, respectively. However, the third signal at 13.19 ppm was consistent with the signal corresponding to the N-H proton in the spectrum of Cd(HIm)$_6$CO$_3$·3H$_2$O (Figure 5.9). This supports the FTIR-ATR and thermogravimetric analyses suggesting that the structure of 1 also potentially contains neutral HMeIm as an included guest.
5.5 Monitoring the accelerated aging synthesis of CdIFs by $^{111}$Cd ssNMR

The previous section described the $^{111}$Cd and $^1$H NMR analysis of 1, and provided a set of expected chemical shifts for both tetrahedrally- and octahedrally-coordinated Cd$^{2+}$ ions bound to nitrogen-donor atom ligands. With these expected chemical shifts in mind, the accelerated aging reactions of CdO described in Section 5.3 were repeated and stepwise monitored by $^1$H-
$^{111}$Cd CP-MAS ssNMR spectroscopy. The accelerated aging reactions between CdO and HMeIm were conducted at 100% RH and 45 °C in the absence of catalyst, as well as with NH$_4$NO$_3$ and (HCAF)(HSO$_4$) salts as catalytic additives, at the University of Windsor. The reagents were milled in a mechanical shaker mill, and the $^1$H-$^{111}$Cd CP-MAS ssNMR spectra collected immediately. CdO was not expected to contribute a signal in the CP-MAS spectra. In the case of the neat reaction, the spectrum of the reaction mixture revealed one signal at 436.32 ppm, which was consistent with Cd$^{2+}$ being in a tetrahedral environment, and suggested the formation of a small amount of 1 (Figure 5.10). This is surprising since PXRD analysis of the reaction mixture showed no traces of 1 after pre-milling CdO and HMeIm for five minutes. After aging for 12 hours, the spectrum remained similar, with the exception of an increase in signal intensity, suggesting more of the product had formed.

Immediately after milling, a mixture of CdO and HMeIm in the presence of 4 mol% NH$_4$NO$_3$ already contained small amounts of 1, as determined by $^1$H-$^{111}$Cd CP-MAS ssNMR analysis. However, unlike the neat reaction, one signal with an isotropic chemical shift of 156.38 ppm was observed in the spectrum of the mixture immediately after pre-milling. This chemical shift was consistent with Cd$^{2+}$ ions in an octahedral environment, and matched the expected signal for Cd(OH)$_2$. After aging for two hours, the signals of 1 and octahedral Cd$^{2+}$ remained unchanged and a third signal appeared at 173.74 ppm (Figure 5.11). This signal was also consistent with a tetrahedral Cd$^{2+}$ complex. The reason for the appearance of these signals
remains unknown but could possibly be explained by the formation of cadmium-ammino or -nitrato complexes, due to the presence of ammonia and NO$_3^-$ ions in the reaction system. While the signals were not consistent with the chemical shifts of known nitrate complexes of cadmium,$^{24}$ it is possible that Cd(NH$_3)_2$(NO$_3$)$_2$ could be forming from CdO and NH$_4$NO$_3$, as has been observed in other studies.$^{25}$ The complex Cd(NH$_3)_2$(NO$_3$)$_2$ was found to form from a melt mixture of CdO and NH$_4$NO$_3$, although, to the best of our knowledge, its detailed solid-state analysis has not been reported. Finally, the lack of change in intensities of the two signals at 156.39 ppm and 176.74 ppm implied that these belonged to a by-product of the reaction, and not an intermediate on the path towards the formation of 1.

![Figure 5.11 Ex-situ time-resolved $^1$H-$^{111}$Cd CP-MAS NMR spectra for the accelerated aging reaction between CdO and HMelm in the presence of 4 mol% NH$_4$NO$_3$ at 100% RH and 45ºC.](image)

The $^1$H-$^{111}$Cd CP-MAS NMR analysis of a mixture of CdO and HMelm which had been mechanically milled for five minutes in the presence of 4 mol% (HCAF)(HSO$_4$) revealed only a low intensity signal at 157.76 ppm (Figure 5.12). This signal was also observed in the spectrum of the reaction mixture containing NH$_4$NO$_3$ and can possibly be associated with the formation of a small amount of Cd(OH)$_2$. Incidentally, the previously proposed catalytic cycle leading to the activation of metal oxides in accelerated aging synthesis, described in Chapter 2, involves
protonation of the oxide surface to form a transient hydroxide species. This may provide an explanation for the appearance of the signal at 157.76 ppm very early in the reaction. Until 23 hours of reaction time, the only signal in the $^1H-^{111}Cd$ CP-MAS NMR spectrum of the reaction mixture containing (HCAF)(HSO$_4$) was that of 1 (Figure 5.12) and was found at -473.90 ppm. However, the appearance of two signals corresponding to the Cd$^{2+}$ environments of yqtl-Cd(MeIm)$_2$ was observed after 48 hours, which is also very consistent with PXRD data.

![Figure 5.12 Ex-situ time-resolved $^1H-^{111}Cd$ CP-MAS NMR spectra for the accelerated aging reaction between CdO and HMeIm in the presence of 4 mol% (HCAF)(HSO$_4$) at 100% RH and 45ºC. Spinning side bands are denoted by *.](image)

Further analysis of the source of the signal at 173.74 ppm in the reaction catalyzed by NH$_4$NO$_3$ was conducted, with the goal of understanding the structure-directing effect of NH$_4$NO$_3$ at forming 1. Since this signal was only observed in the reaction containing NH$_4$NO$_3$, it was assumed that it was caused by a cadmium species containing ammino or nitrato ligands in octahedral geometry. Indeed, the 1:1 reaction between CdO and NH$_4$NO$_3$ at 100% RH and 45 ºC for 18 hours resulted in the formation of a beige solid, which showed a signal at 173.55 ppm
upon $^{1}H-^{111}Cd$ CP-MAS NMR analysis (Figure 5.13). The static $^{1}H-^{111}Cd$ CP NMR analysis of the product exhibited a broad span of $\sim$350 ppm, suggesting the presence of a distorted octahedral geometry around the $^{111}Cd$ nucleus, or deviation from perfect octahedral symmetry. The qualitative observation of asymmetry in the static $^{111}Cd$-NMR spectrum was also consistent with several different cadmium environments.

![Figure 5.13](image)

**Figure 5.13** Solid state $^{1}H-^{111}Cd$ CP NMR spectra of the reaction mixture, aged for 18 hours at 100% RH and 45 °C, involving a 1:1 stoichiometric ratio of CdO and NH$_4$NO$_3$: a) CP-MAS spectrum; b) CP-static spectrum. Spinning side bands are denoted by *.

Information regarding the composition, symmetry, and coordination geometry of 1 extrapolated from the FTIR-ATR, TGA, and multinuclear solid-state NMR analyses described in this chapter rendered the elucidation of its crystal structure possible from powder X-ray diffraction. The preliminary structure, shown in **Figure 5.14**, was solved by Prof. Laszlo Fábián from the University of East Anglia, and determined to be an open framework of composition Cd(Melm)$_2$(HMeIm). The Cd$^{2+}$ ions are coordinated tetrahedrally to four Melm$^-$ cations, to assemble into a three-dimensional diamondoid (dia) framework (topological analysis provided by Dr. Athanassios D. Katsenis, McGill University). The structure crystallizes in orthorhombic space group $Pna2_1$, with unit cell parameters, $a = 10.10245(55)$ Å, $b = 16.7887(11)$ Å, and $c = 9.45324(47)$ Å. The structure exhibits channels aligned parallel with the crystallographic $c$-axis, and occupied by chains of hydrogen-bonded neutral HMeIm molecules. The PXRD pattern
simulated from the crystal data is identical to the experimental pattern of bulk \textit{dia-Cd(MeIm)}\textsubscript{2}\-(HMeIm) (Figure 5.15).

**Figure 5.14** Fragment of the preliminary crystal structure of \textit{dia-Cd(MeIm)}\textsubscript{2}\-(HMeIm), viewed down the crystallographic \textit{c}-axis, parallel to channels occupied by neutral HMeIm.

**Figure 5.15** Comparison between: a) the experimental powder X-ray diffraction pattern of \textit{dia-Cd(MeIm)}\textsubscript{2}\-(HMeIm) synthesized by accelerated aging and b) the simulated PXRD pattern calculated from crystal structure data obtained by structure solution from PXRD data.
5.6 Conclusion

The results described in this Chapter are an extension of the work presented in Chapters 2 and 3 outlining the accelerated aging synthesis of ZIFs. However, while the ability to synthesize a class of three-dimensional (3-D) cadmium-based ZIFs, has been successfully demonstrated, accelerated aging has also been established as a technique for the discovery of new, open, 3-D frameworks which are so far not accessible from solution. Selecting NH₄NO₃ as the salt catalyst in the reaction between CdO and HMelm instead of (HCAF)(HSO₄) resulted in the templated synthesis of the new and open framework $\text{dia-Cd(Melm)}_2\cdot(\text{HMeIm})$ instead of the known close-packed $\text{yqt1-Cd(Melm)}_2$. The observation that Cd($\text{Melm}$)$_2\cdot(\text{HMeIm})$ consisted of not only a novel framework but is also an intermediate towards the formation of $\text{yqt1-Cd(Melm)}_2$ inspired the search for determining the factors governing the reactivity and structure-directing effects in accelerated aging. Solid-state $^{111}$Cd NMR was demonstrated to be a valuable technique to monitor the coordination environment of Cd$^{2+}$ and observe the formation of intermediates not detectable by conventional PXRD analysis. Using the system involving HMelm as a model ligand, the accelerated aging synthesis of $\text{yqt1-Cd(Melm)}_2$ and Cd($\text{Melm}$)$_2\cdot(\text{HMeIm})$ was monitored \textit{ex situ} by PXRD and ssNMR. Indeed, $^1$H-$^{111}$Cd CP-MAS ssNMR revealed the formation of the intermediate Cd($\text{Melm}$)$_2\cdot(\text{HMeIm})$ immediately after superficial mixing of the solid reagents. The appearance of signals corresponding to unidentified Cd species in a possibly octahedral environment emphasizes the need for a deeper understanding of the mechanisms of accelerated aging reactions and solid-state chemistry in general. Moreover, solid-state NMR is a valuable alternative to conventional reaction monitoring techniques such as PXRD, due to the enhanced ability to observe small concentrations of non-crystalline transient species forming and reacting in real time. Such studies can potentially shed new and much needed light on concepts of mechanochemical activation and templating, which are known to be important driving factors in the synthesis of materials in the solid state.

5.7 References


6.1 Introduction and connecting text

The work presented in this chapter includes results published in the article entitled “Supramolecular imidazolium frameworks: direct analogues of metal azolate frameworks with charge-inverted node-and-linker structure”, co-authored by C. Mottillo and Prof. T. Friščić (Chem. Commun., 2015, 51, 8924). All synthetic experiments and solid-state analyses were conducted by C. Mottillo. The manuscript was written by C. Mottillo with guidance regarding content and editing provided by Prof. T. Friščić. Section 6.2 consists of the manuscript text, formatted and slightly modified for inclusion into this Thesis. Subsequently, Section 6.3 cites additional data found in the Supplementary Information of the paper and includes a more detailed solid-state analysis of the structures presented in Section 6.2. Section 6.4 describes the design of a new dichromate-based supramolecular imidazolium framework, results which will soon be included in a manuscript to be submitted for publication.

Framework solids have emerged as a very important class of materials for a variety of applications such as molecular separation, catalysis, and sensing. This has been particularly true for metal-organic frameworks (MOFs), which have been highlighted as promising materials due to their tunable structures, high porosity, and in some cases, chemical and thermal stability. As the commercialization of MOFs and their potential use in industrial applications have become increasingly realistic, there has been a mounting imperative to devise more environmentally-friendly routes for their synthesis. In addition to improving synthetic methodologies for MOFs and zeolitic imidazolate frameworks (ZIFs), with the development of greener techniques such as mechanochemical synthesis, accelerated aging, and aqueous solution synthesis, the development of novel types of framework materials is also of importance. The design of new MOFs has been successfully achieved in this regard, with the node-and-linker approach and the concept of modular chemistry being used to design new MOFs with enhanced porosity, stability, and functionality. The node-and-linker approach has been a valuable tool for the design of MOFs. The inspiration for the design of ZIFs, a subfamily of metal azolate frameworks (MAFs), has originated, at least in part, from the
structures of zeolites. Zeolites are composed predominantly of tetravalent silicon species tetrahedrally surrounded by bridging oxide moieties. The angle between the Si-O-Si bonds in zeolites is 145°, which is identical to the angle between the metal-imidazolate-metal bonds found in ZIFs. As a result, many ZIFs form 3-dimensional (3-D) networks which adopt topologies similar or identical to those found in zeolites.

On the other hand, the rational design of alternate classes of framework materials, such as hydrogen-bonded frameworks\textsuperscript{18} and covalent organic frameworks (COFs),\textsuperscript{19} has proven to be more challenging. The advantages of these frameworks include lower densities, greater solution processability, and, for COFs, greater stability due to strong covalent bonds. However, relying on relatively weak non-covalent interactions for framework formation, as well as the relatively arduous synthetic pathways needed for the assembly of covalent-organic frameworks have posed limitations towards the design of such materials.\textsuperscript{20} Drawing inspiration from the relationship between ZIFs and zeolites, this chapter outlines the development of a surprisingly reliable design strategy for the design of molecular framework solids. Using the node-and-linker approach, combining tetrahedral nodes with ditopic imidazolium linkers results in direct analogues of MAFs, but with inverted polarity of nodes and linkers. Called supramolecular imidazolium frameworks (SIFs), these structures represent the first instances of using the node-and-linker approach towards the reliable design of hydrogen-bonded framework materials analogous to a known family of MOFs.\textsuperscript{1} The following section consists of the published manuscript text, with minor modifications. The extension of the herein presented approach towards the design of a new SIF with the 3-D diamondoid (\textit{dia}) topology is also discussed in Section 6.4 of this chapter.

6.2 Design of supramolecular imidazolium frameworks

The development of designs for the synthesis of network solids is a central area of solid-state chemistry and materials science.\textsuperscript{21,22} Traditionally dominated by inorganic solids\textsuperscript{23} (silicates and zeolites), this area is now expanded by coordination polymers\textsuperscript{24} (including metal–organic frameworks),\textsuperscript{5} and covalent organic frameworks.\textsuperscript{19} Such a development is attributable to the systematic application of geometrical analysis to framework synthesis, specifically the node-and-linker approach,\textsuperscript{24,14} which predicts framework formation based on the judicious choice of building blocks with suitable geometry and connectivity. This approach has had less success\textsuperscript{20} for molecular solids due to the flexibility of underlying supramolecular interactions (\textit{e.g.} hydrogen and halogen bonds), which makes the crystal structures of molecular solids highly
sensitive to variations in constituent building blocks. Instead, the design of open frameworks in molecular solids relies mostly on the self-assembly of shape-designed molecules or molecular clusters, or the use of strong charge-assisted hydrogen bonds centred on a particular type of organoammonium cation.

We now report a reliable node-and-linker design for open, hydrogen-bonded (4,4)-nets. The design uses tetrahedral sulfate or selenate anions as nodes and substituted imidazolium cations as linkers, providing the first examples of reliable framework synthesis involving negatively charged nodes and positive linkers. The resulting self-assembled imidazolium frameworks are direct analogues of square grid metal azolate frameworks (MAFs) but with inverted polarity of nodes and linkers.

Benzimidazolium sulfate was synthesized from benzimidazole (H\textsubscript{2}BIm) and H\textsubscript{2}SO\textsubscript{4} in acetonitrile. X-ray diffraction on single crystals grown from methanol (MeOH) revealed hydrogen-bonded sheets involving SO\textsubscript{4}\textsuperscript{2−} anions as four-connected nodes and H\textsubscript{2}BIm\textsuperscript{+} cations as 1,3-connected linkers. The result is an open, non-interpenetrated net of (4,4)-topology (also: square grid, \textit{sql}-topology) in which each node is shared between four 4-rings (Figure 6.1). Linker protonation was confirmed by solid-state \textsuperscript{15}N CP-MAS NMR (ssNMR), and powder X-ray diffraction (PXRD) was used to confirm that bulk material was identical to the single crystals. The net in (H\textsubscript{2}BIm)\textsubscript{2}SO\textsubscript{4} resembles that found in \textit{sql}-zinc benzimidazolate (Zn(BIm)\textsubscript{2}, CSD KOLYAM) and nickel(II)imidazolate (CSD ALIDUU). The direct analogy between Zn(BIm)\textsubscript{2} and (H\textsubscript{2}BIm)\textsubscript{2}SO\textsubscript{4} structures is summarised by factors of geometry and stoichiometry: (i) structural similarity of SO\textsubscript{4}\textsuperscript{2−} to the tetrahedrally coordinated Zn\textsuperscript{2+}; (ii) geometrical similarity of imidazolate anions and imidazolium cations as linkers and (iii) 1:2 stoichiometry of nodes and linkers. In this analogy, the Zn--N bonds of Zn(BIm)\textsubscript{2} are replaced by N--H--O− hydrogen bonds in (H\textsubscript{2}BIm)\textsubscript{2}SO\textsubscript{4}, resulting in a grid spacing of \(~0.1\) nm (hydrogen bond parameters for all structures can be found in Appendix A). Each 4-ring creates a \textit{ca.} 20 Å\textsuperscript{3} void, too small to accommodate guests, as confirmed by thermogravimetric analysis (TGA) and nitrogen sorption measurements.
The description of (H₂BIm)₂SO₄ as a (4,4)-net of anionic nodes and cationic linkers led us to explore the robustness of this framework to linker modifications. Attempts to use 2-H or 2-methylimidazole as linkers gave hydrates or crystals too deliquescent for handling. However, 2-ethylimidazole (H₂EtIm, Figure 6.2a) gave crystals that, although deliquescent, were suitable for structural determination by X-ray diffraction. The structure of (H₂EtIm)₂SO₄ consists of layers with distorted square grid topology, confirming the ability of imidazolium cations to assemble with SO₄²⁻ into a (4,4)-net (Figure 6.2b). Distortion of the square grid can be quantified by φ, the acute angle formed by three nearest-neighbor anions in a sheet. While an ideal square grid would have φ = 90°, in (H₂EtIm)₂SO₄ this value is 62° (Figure 6.2b). The sheets of (H₂EtIm)₂SO₄ exhibit voids of ca. 6 Å diameter, occupied by ethyl residues from neighboring sheets. Tolerance of the benzimidazolium sulfate (4,4)-net to substitution was explored by using 2-phenylbenzimidazole (HPhBIm) and 2-methylbenzimidazole (HMeBIm) as linkers (Figure 6.2a). Crystallisation of (H₂PhBIm)₂SO₄ from either MeOH or ethanol (EtOH) gave
isostructural solvates in which cations and anions assembled into a (4,4)-net, with solvent attached to each sheet by O–H⋯O− bonds (Figure 6.2c and d). These solvates show that the assembly of square grid imidazolium frameworks tolerates hydrogen bonding to protic solvents. Only with (H₂MeBIm)₂SO₄ the synthesis of the (4,4)-net was unsuccessful: all crystallisation attempts gave the SiS₂-type structure in which cations and anions retain the respective bridging and tetrahedral geometries, but form chains of 2-rings with shared nodes (Figure 6.2e).³²,³³

![Figure 6.2](image)  

Figure 6.2 a) Molecular structures of H₂EtIm, H₂PhBIm and H₂MeBIm; b) a hydrogen-bonded sheet in (H₂EtIm)₂SO₄; c) a hydrogen-bonded sheet of (H₂PhBIm)₂SO₄ in the corresponding MeOH solvate, with solvent molecules and phenyl substituents omitted; d) two hydrogen-bonded sheets of (H₂PhBIm)₂SO₄ (blue) with MeOH molecules shown (red); e) a SiS₂-type chain in (H₂MeBIm)₂SO₄.
Next, we explored the selenate ions as larger framework nodes with an intramolecular O⋯O distance of 2.70 Å, compared to 2.40 Å in SO$_4^{2−}$. The salts were prepared by reacting benzimidazoles with a solution of concentrated aqueous H$_2$SeO$_4$ in acetonitrile. Structural analysis of (H$_2$BIm)$_2$SeO$_4$ revealed square grid sheets similar to those in (H$_2$BIm)$_2$SO$_4$ (Figure 6.3a). Both HPhBIm and HMeBIm selenate salts also afforded (4,4)-nets. Unlike the corresponding sulfate, (H$_2$PhBIm)$_2$SeO$_4$ could be crystallized in a non-solvated form by using $N,N$-dimethylformamide as a solvent, yielding a structure based on corrugated sheets of alternating 4-rings with $\varphi = 45°$ and $\varphi = 88°$ (Figure 6.3b). Crystallisation of (H$_2$PhBIm)$_2$SeO$_4$ from MeOH gave a solvate isostructural to that of (H$_2$PhBIm)$_2$SO$_4$, with square grid sheets lined by MeOH molecules.

![Figure 6.3](image)

Figure 6.3 a) The (4,4)-topology sheet in (H$_2$BIm)$_2$SeO$_4$; b) corrugated sheet of (4,4)-topology in non-solvated (H$_2$PhBIm)$_2$SeO$_4$; c) (4,4)-net in the MeOH and water solvate of (H$_2$MeBIm)$_2$SeO$_4$ with phenyl substituents omitted for clarity; d) sheets of (H$_2$MeBIm)$_2$SeO$_4$ intercalated by layers of MeOH and water (space-filling).

Crystallisation of (H$_2$MeBIm)$_2$SeO$_4$ from a MeOH–acetone solvent mixture produced square grid layers of H$_2$MeBIm$^+$ and SeO$_4^{2−}$, separated by alternating layers of water and MeOH.
molecules (Figure 6.3c and d). The herein described solvates of (H$_2$PhBIm)$_2$SO$_4$, (H$_2$PhBIm)$_2$SeO$_4$ and (H$_2$MeBIm)$_2$SeO$_4$ highlight the robustness of the (4,4)-net to changes in the anion size and hydrogen bonding with protic solvents.

In conclusion, we demonstrated the first reliable design for open square-grid frameworks using a charge-inverted node-and-linker design. The structures of the presented salts demonstrate the unique versatility of imidazoles to generate geometrically similar anionic and cationic framework linkers: the assembly of tetrahedral sulfate or selenate anions with imidazolium linkers yields structures that are direct analogues of MAFs, based on stoichiometry and geometry of nodes and linkers. Although the obtained (4,4)-nets are not microporous, we believe that imidazolium frameworks illustrate an attractive new design for open supramolecular frameworks. The generality of this design is reflected in its robustness to variations in node and linker components, as well as to competitive hydrogen bonding with protic solvents. While (H$_2$MeBIm)$_2$SO$_4$ did not form a (4,4)-net, the cations and anions retained their binding geometries to form a SiS$_2$-type structure, suggesting that further exploration might reveal other charge-inverted analogues of MAFs or silica-like materials. With that in mind, we are now exploring imidazolium salts of other anions.

6.3 Solid-state analysis and properties of SIFs

In supplement to Section 6.2, which described the node-and-linker design and structural characteristics of SIFs, this section will now provide a deeper analysis of the stability and thermal properties of these materials. Although single crystal X-ray diffraction analysis demonstrated that the crystals used for structural analysis consisted of salts forming 2-D frameworks composed of sulfate or selenate nodes and imidazolium linkers, this only represented a small fraction of the population of crystals obtained in each crystallization experiment. Supporting the claim that the node-and-linker approach has been reproducibly applied to molecular solids in our work therefore requires evidence that 2-D frameworks were formed in bulk, and not just in isolated cases. In order to confirm that SIFs had been synthesized in bulk, two sets of analyses were conducted: i) the experimental PXRD patterns of the initially synthesized products were compared to the simulated patterns calculated from the crystal structures obtained from single crystal X-ray diffraction data, and ii) if the initially synthesized bulk products were not identical in crystalline phase to the single crystals used for X-ray diffraction, analysis was conducted on the entire crystal populations obtained from
recrystallization experiments to ensure that they all belonged to the same crystalline phase. In the case of \((\text{H}_2\text{BIm})_2\text{SO}_4\), the experimental PXRD pattern of the powder obtained from solution synthesis was identical to the PXRD pattern simulated from crystal structure data. Likewise, the experimental PXRD pattern for \((\text{H}_2\text{BIm})_2\text{SeO}_4\) synthesized in solution indicated that the bulk product consisted of the phase represented by single crystal structure data (Figure 6.4).

![Figure 6.4](image)

**Figure 6.4** Comparison of the experimental PXRD patterns for HBlm-based SIFs with the simulated PXRD patterns calculated from the crystal structures of \((\text{H}_2\text{BIm})_2\text{SO}_4\) and \((\text{H}_2\text{BIm})_2\text{SeO}_4\): a) simulated pattern for \((\text{H}_2\text{BIm})_2\text{SO}_4\); b) \((\text{H}_2\text{BIm})_2\text{SO}_4\) synthesized in solution; c) simulated pattern for \((\text{H}_2\text{BIm})_2\text{SeO}_4\); d) \((\text{H}_2\text{BIm})_2\text{SeO}_4\) synthesized in solution.

In all other cases, however, the simulated PXRD patterns did not match those of the initially synthesized product, indicating the crystallization resulted in structurally distinct SIFs. Therefore, it was necessary to obtain powder X-ray diffraction data of all the crystals obtained in a single crystallization experiment, whenever possible. In the first of such cases, crystals of \((\text{H}_2\text{MeBIm})_2\text{SO}_4\) were removed from the mother liquor, dried in air, ground in a mortar and pestle, and analyzed by PXRD (Figure 6.5). The experimental PXRD pattern collected for all the crystals matched the simulated pattern calculated from crystal structure data, demonstrating that the reported framework was obtained reproducibly for all crystals from the same crystallization experiment.
experiment. In the case of all other structures, however, removal of the crystals from their mother liquors resulted in loss of crystallinity or phase changes, due to desolvation or conversion to a hydrate. Thus, powder X-ray diffraction patterns were obtained while the crystals still remained soaked in their respective mother liquors. These results, shown in Figure 6.5, demonstrate by comparing the experimental and simulated patterns that all crystals obtained for \((\text{H}_2\text{MeBIm})_2\text{SeO}_4\cdot\text{MeOH}\cdot0.5\text{H}_2\text{O}\), \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\), and \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\), consist of the same phase that was characterized by single crystal X-ray diffraction. Powder X-ray diffraction analysis was not possible in the case of \((\text{H}_2\text{EtIm})_2\text{SO}_4\) due to rapid deliquescence of the salt and in the cases of \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{EtOH}\) and \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{MeOH}\), due to rapid solvent loss from the structure.

**Figure 6.5** Comparison of the experimental and simulated PXRD patterns for SIFs based on HMeBIm and HPhBIm, demonstrating that all crystals from recrystallization experiments were the same phase as the single crystal used for structural analysis: a) simulated pattern for \((\text{H}_2\text{MeBIm})_2\text{SO}_4\); b) single crystals of \((\text{H}_2\text{MeBIm})_2\text{SO}_4\), dried and manually ground in air; c) simulated pattern for \((\text{H}_2\text{MeBIm})_2\text{SeO}_4\cdot\text{MeOH}\cdot0.5\text{H}_2\text{O}\); d) single crystals of \((\text{H}_2\text{MeBIm})_2\text{SeO}_4\cdot\text{MeOH}\cdot0.5\text{H}_2\text{O}\), immersed in mother liquor consisting of a 1:1 mixture of acetone and MeOH; e) simulated pattern for \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\); f) single crystals of \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\), immersed in mother liquor of DMSO; g) simulated pattern for \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\); h) single crystals of \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\), immersed in mother liquor of MeOH.
As mentioned in Section 6.2, in addition to forming the non-solvated SIF \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\), \(\text{H}_2\text{PhBIm}^+\) cations assembled with \(\text{SO}_4^{2-}\) and \(\text{SeO}_4^{2-}\) anions to form a set of three isostructural, but chemically distinct solvates. Remarkably, when recrystallized from MeOH or ethanol (EtOH), \((\text{H}_2\text{PhBIm})_2\text{SO}_4\) formed both a MeOH and EtOH solvate, respectively. Analysis of the unit cell dimensions and simulated PXRD patterns obtained from single crystal XRD data revealed that the two are isostructural (Figure 6.6). Upon recrystallization from MeOH, \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\) also formed a MeOH solvate, \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\), which also is isostructural to \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{MeOH}\) and \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{EtOH}\) (Figure 6.6).

Figure 6.6 Simulated PXRD patterns calculated from the structures of HPhBIm-based SIFs: a) \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{MeOH}\); b) \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{EtOH}\); c) \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\).

The analysis of these three structures emphasizes the resistance of the inverted node-and-linker motif towards the interference of competing hydrogen bond donors. It also further confirms the reliability of the inverted node-and-linker approach at enabling the design of 2-D frameworks. Namely, not only did the salts \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{MeOH}\), \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{EtOH}\), and \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\) consist of 2-D SIFs, but assembled to form three isostructural frameworks with different nodes (\(\text{SO}_4^{2-}\) and \(\text{SeO}_4^{2-}\)) and distinct solvents of crystallization (MeOH and EtOH). Shown in Figure 6.7 are analogous fragments of the crystal structures of \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{MeOH}\), \((\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{EtOH}\), and \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}\), showing
layers of $\text{H}_2\text{PhBIm}^+$ cations and $\text{SO}_4^{2-}$ and $\text{SeO}_4^{2-}$ nodes intercalated by included MeOH or EtOH solvent molecules.

Figure 6.7 Identical views down the crystallographic $b$-axis of isostructural sulfate- and selenate-based SIFs formed from $\text{HPhBIm}$, showing the 2-D layers consisting of $\text{SO}_4^{2-}$ or $\text{SeO}_4^{2-}$ anions and $\text{H}_2\text{PhBIm}^+$ cations separated by layers of MeOH or EtOH solvent molecules: a) $(\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{MeOH}$; b) $(\text{H}_2\text{PhBIm})_2\text{SO}_4\cdot2\text{EtOH}$, and c) $(\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH}$.

Formation of 4-fold nets of the kind found in two-dimensional MAFs based on imidazolium cations and sulfate or selenate anions requires a 1:2 respective stoichiometry of nodes and linkers. Therefore, it is necessary that the sulfate and selenate anions be fully deprotonated, which they are in all the crystal structures described in this chapter. Namely, X-ray diffraction data shows that in each sulfate structure all four sulfate S-O$^-$ bonds are approximately 1.46 Å in length and the Se-O$^-$ bond distances are all around 1.64 Å in selenate-based salts. These values are consistent with bond lengths expected for fully deprotonated sulfate and selenate anions.
further confirm that the anionic nodes are fully deprotonated, \((\text{H}_2\text{BIm})_2\text{SO}_4\) and \((\text{H}_2\text{BIm})_2\text{SeO}_4\) were used as model compounds for solid-state natural abundance \(^{15}\text{N}\) cross-polarization magic-angle spinning (CP-MAS) NMR (ssNMR) studies. The spectrum of neutral benzimidazole, shown in Figure 6.8, shows two signals, one at -144.69 ppm and another at -222.82 ppm corresponding to the non-protonated and protonated nitrogen atoms, respectively. As seen in Figure 6.8b and 6.8c, the \(^{15}\text{N}\) CP-MAS ssNMR spectra for \((\text{H}_2\text{BIm})_2\text{SO}_4\) and \((\text{H}_2\text{BIm})_2\text{SeO}_4\) show one signal each, with a chemical shift of -216.80 ppm and -216.95 ppm, respectively. This ssNMR data indicates that the nitrogen atoms in \((\text{H}_2\text{BIm})_2\text{SO}_4\) and \((\text{H}_2\text{BIm})_2\text{SeO}_4\) are in only one type of chemical environment, which is consistent with having both nitrogen atoms of each benzimidazole unit protonated.

**Figure 6.8** Solid-state \(^{15}\text{N}\) CP-MAS NMR spectra for \text{HBIm}-based SIFs, demonstrating full protonation of benzimidazole units: a) \text{HBIm}; b) \((\text{H}_2\text{BIm})_2\text{SO}_4\) synthesized from solution; c) \((\text{H}_2\text{BIm})_2\text{SeO}_4\) synthesized from solution.
To further characterize the herein described SIFs, all samples which were sufficiently stable in air were analyzed by FTIR-ATR spectroscopy. Figure 6.9 shows the FTIR-ATR spectrum of \((\text{H}_2\text{BIm})_2\text{SO}_4\), revealing a strong absorption band corresponding to the S-O stretch of the sulfate anion at 1045 cm\(^{-1}\). The FTIR-ATR spectrum of \((\text{H}_2\text{BIm})_2\text{SeO}_4\) is seen in Figure 6.9, and also shows the characteristic Se-O stretch for the selenate ion at 857 cm\(^{-1}\). The single crystals of \((\text{H}_2\text{MeBIm})_2\text{SO}_4\) were manually ground in a mortar and pestle, and analysis of the FTIR-ATR spectrum also revealed the characteristic sulfate S-O stretch at 1081 cm\(^{-1}\).

![FTIR-ATR spectra](image)

**Figure 6.9** FTIR-ATR spectra relevant for HBlm- and HMeBlm-based SIFs: a) HBlm; b) \((\text{H}_2\text{BIm})_2\text{SO}_4\) synthesized from solution; c) \((\text{H}_2\text{BIm})_2\text{SeO}_4\) synthesized in solution; d) HMeBlm, and e) \((\text{H}_2\text{MeBIm})_2\text{SO}_4\) synthesized from solution.

Although extensive analysis was not possible for most of the SIFs described herein, either due to desolvation or due to deliquescence which would occur during handling and sample preparation, \((\text{H}_2\text{BIm})_2\text{SO}_4\), \((\text{H}_2\text{MeBIm})_2\text{SO}_4\), \((\text{H}_2\text{BIm})_2\text{SeO}_4\) were sufficiently stable to be analyzed by thermogravimetric analysis (TGA). For example, **Figure 6.10** shows the thermal
decomposition of \((\text{H}_2\text{BIm})_2\text{SO}_4\) in air, revealing a weight loss of 36.3\% at 250 °C, which might fit well to the loss of one \text{HBIIm} molecule. When analyzed by TGA under a dynamic atmosphere of air, single crystals of \((\text{H}_2\text{MeBIm})_2\text{SO}_4\) which had been crushed in air prior to analysis, displayed similar thermal behaviour, with a weight loss of 38.4\%, consistent with the loss of one \text{HMeBIm} unit (Figure 6.11). The TGA thermogram for the aerobic decomposition of \((\text{H}_2\text{BIm})_2\text{SeO}_4\) is shown in Figure 6.12. In this case, the primary decomposition step could not be associated with any particular component of the salt. This is most likely due to the instability and oxidizing properties of the selenate anion, leading to a more complex breakdown profile.

![TGA thermogram of (H2BIm)2SO4 under dynamic atmosphere of air.](image)

**Figure 6.10** TGA thermogram of \((\text{H}_2\text{BIm})_2\text{SO}_4\) under dynamic atmosphere of air. The first step of 36.3\% is consistent with one \text{HBIIm} molecule which would account for an expected percent loss of 35.3\%.

![TGA thermogram of single crystals of (H2MeBIm)2SO4, dried and crushed in air.](image)

**Figure 6.11** TGA thermogram of single crystals of \((\text{H}_2\text{MeBIm})_2\text{SO}_4\), dried and crushed in air. The first weight loss of 38.4\% is consistent with the removal of approximately one \text{HMeIm} molecule (expected weight loss for one \text{HMeIm} molecule is 36.5\%).
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As a logical step towards expanding the inverted node-and-linker concept for designing SIFs, the use of alternative oxyanions as nodes for assembly with imidazolium cations was explored. Oxyanions were evaluated as possible nodes according to the following criteria: i) anions with a charge of 2-, ii) anions bearing at least four hydrogen-bond acceptor sites, iii) anions stable under standard laboratory conditions and, in the case of oxometallates, iv) possible control over conversion to polyoxometallates. The chromate (CrO$_4^{2-}$) dianion was found to satisfy these criteria very well, and therefore the synthesis of chromate salts of imidazole derivatives was attempted. Due to the relatively small amount of literature describing imidazolium chromate(VI) or dichromate(VI) salts, the next section will be devoted to a brief overview of previous work in this area.
6.4.1 The chromate(VI) anion

Due to the highly corrosive and oxidizing properties of chromic(VI) acid, it was not favourable to obtain chromate salts by reaction with the acid as was done to obtain sulfates and selenates of imidazole derivatives. Instead, chromate salts were investigated as milder reagents for the synthesis of chromate-based SIFs. The chromate anion, with formula CrO$_4^{2-}$, exists in a pH-dependent equilibrium with its dianionic counterpart dichromate, Cr$_2$O$_7^{2-}$, according to Equation 6.1.$^{34}$ In basic conditions, yellow CrO$_4^{2-}$ is the predominant form, while orange Cr$_2$O$_7^{2-}$ is predominant in acidic conditions. This was taken into account during the attempted synthesis of imidazolium chromates.

$$2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+ (\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$$

**Equation 6.1** pH-dependent equilibrium of the chromate and dichromate anions in aqueous solution.

Organic chromate and dichromate salts have generally been used for chrome plating or selective oxidation in organic synthesis.$^{35}$ Compared to the highly studied pyridinium dichromate, imidazole-based chromate(VI) salts are a relatively new class of oxidants whose use for alcohol and aldehyde oxidation has been exemplified in several studies.$^{36}$ To the best of our knowledge, the structures of only one ammonium dichromate(IV) salt based on imidazole and four dichromate(VI) salts based on benzimidazole and its derivatives have been described in the literature (Figure 6.13).$^{37}$
In all cases, the respective salts were obtained by reacting the imidazole derivative with CrO$_3$ in a neutral or acidic aqueous solution. Structural analyses have been reported for the four dichromate(VI) salts based on benzimidazole (H$_2$BIm), 2-methylbenzimidazole (HMeBIm), 2-ethylbenzimidazole (HEtBIm), and 2-$n$-propylbenzimidazole (H$n$-PrBIm). The structure of benzimidazolium dichromate, (H$_2$BIm)$_2$Cr$_2$O$_7$ (CSD code HAFJEE),$^{37b}$ did not exhibit a 2-D or 3-D framework topology. Instead, dichromate(VI) anions assembled to form linear chains connected by hydrogen-bonded H$_2$BIm$^+$ ions. On the other hand, the reported structures of the dichromate(VI) salts of HMeBIm and HPrBIm consisted of 2-D $sq$-topology nets, which bore marked resemblance to 2-D sulfate and selenate SIFs (Figure 6.14). In the case of (H$_2$PrBIm)$_2$Cr$_2$O$_7$ (CSD code HAFJII),$^{37b}$ dichromate(VI) anions serve as 4-connected nodes linking to four ditopic H$_2$PrBIm$^+$ cationic linkers via N$^\equiv$H--O hydrogen bonds (Figure 6.14b), in the same manner that tetrahedral SeO$_4^{2-}$ nodes link to four H$_2$MeBIm$^+$ cations in the structure of (H$_2$MeBIm)$_2$SeO$_4$·MeOH·0.5H$_2$O (Figure 6.14a and b). The 2-dimensional framework of (H$_2$MeBIm)$_2$Cr$_2$O$_7$ (CSD code HAFJOO)$^{37b}$ is also composed of dichromate(VI) nodes hydrogen-bonding to four H$_2$MeBIm$^+$ ions to form a $sq$-topology net (Figure 6.14c).

**Figure 6.13** a) Imidazole and benzimidazole derivatives used in the reported structures of imidazolium-based dichromate salts$^{37}$; b) analogous connectivity between nodes and linkers in SIFs (left) and between dichromate anions and imidazolium cations (right); c) capped-stick diagram comparing the node and linker relationship between anions and cations in the structures of (H$_2$MeBIm)$_2$SO$_4$ and the previously reported (H$_2$MeBIm)$_2$Cr$_2$O$_7$. 

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The structure of \((\text{H}_2\text{MeBIm})_2\text{Cr}_2\text{O}_7\) (CSD code HAFJAA)\(^{37b}\) did not consist of a two-dimensional framework. Remarkably, \((\text{H}_2\text{MeBIm})_2\text{Cr}_2\text{O}_7\) assembled to form a structure resembling that of the 1-D chains found in SiS\(_2\) (Figure 6.15). This behaviour is reminiscent of the way the SIF \((\text{H}_2\text{MeBIm})_2\text{SO}_4\) adopts the SiS\(_2\)-type structure, as described previously in Section 6.2.

Figure 6.14 a) Fragment of the 2-D net formed by the hydrogen-bonded assembly of SeO\(_4^{2-}\) nodes and H\(_2\text{MeBIm}^+\) cation linkers in the salt \((\text{H}_2\text{MeBIm})_2\text{SeO}_4\cdot\text{MeOH} \cdot 0.5\text{H}_2\text{O}\); square-grid framework formed by: b) the assembly of H\(_2\text{PhBIm}\) cations and Cr\(_2\text{O}_7^{2-}\) anions in \((\text{H}_2\text{PrBIm})_2\text{Cr}_2\text{O}_7\);\(^{37b}\) and c) H\(_2\text{MeBIm}\) cations and Cr\(_2\text{O}_7^{2-}\) anions in \((\text{H}_2\text{MeBIm})_2\text{Cr}_2\text{O}_7\).\(^{37b}\)

Figure 6.15 SiS\(_2\)-type structures of sulfate and dichromate-based imidazolium salts: a) fragment of the structure of \((\text{H}_2\text{MeBIm})_2\text{SO}_4\) and b) fragment of the SiS\(_2\)-type structure of \((\text{H}_2\text{EtBIm})_2\text{Cr}_2\text{O}_7\).\(^{37b}\)
6.4.2 Synthesis of benzimidazolium dichromate

Our previous experience in designing SIFs with simple imidazolium derivatives such as HIm and HMeIm, resulted in compounds which were too sensitive to handle under standard laboratory conditions. Sulfate and selenate SIFs of HBlm on the other hand, were generally facile to analyze and did not tend to form highly deliquescent salts. Benzimidazole was therefore selected as the first ligand to explore SIF formation with chromate anions. In Chapter 2, the synthesis of an imidazolium sulfate salt by reacting (NH₄)₂SO₄ with imidazole under high humidity and 45 °C was described. Thus instead of using CrO₃ as the anion source, the reaction of (NH₄)₂CrO₄ with HBlm was attempted with the intention of forming (H₂Blm)₂CrO₄ according to Scheme 6.1.

**Scheme 6.1** Herein proposed assembly of chromate anions and H₂Blm⁺ cations into a SIF.

Benzimidazole and (NH₄)₂CrO₄ were milled in a 2:1 ratio in the presence of 100 µL water for 30 minutes. The resulting yellow paste with an ammonia-like odor was subsequently placed in 100 mL H₂O, where the appearance of bubbles in the slurry suggested the release of gas. The distinct smell of ammonia coming from the slurry suggested that NH₃ was being formed. The slurry was stirred until the bubbling was no longer apparent. The water was then removed using rotary evaporation at 70 °C, and the yellow solid collected for powder X-ray diffraction analysis. Upon recrystallization by evaporation, however, orange translucent crystals were obtained and removed from the mother liquor. Single crystal X-ray diffraction analysis did not reveal the expected compound (H₂Blm)₂CrO₄, but instead the monoclinic structure of composition [H₃(Blm)₂]₂Cr₂O₇. The asymmetric unit of the structure consists of half a dichromate anion, and one neutral and one cationic benzimidazole unit. The overall structure is composed of Cr₂O₇²⁻ anions, each connecting in a pseudo-tetrahedral geometry to self-assembled hydrogen-bonded linkers of composition H₃(Blm)₂⁺. Each of these linkers can be viewed as a hydrogen-bonded complex of a neutral HBlm molecule with a protonated H₂Blm⁺ cation (Figure 6.16), connected
via an N⁺-H---N hydrogen bond of 1.849 Å in length (Figure 6.17). The self-assembled linker H₃(BIm)₂⁺ is situated on a center of inversion, making the two HBlm-based moieties equivalent.

![Diagram of molecular structure](image)

**Figure 6.16** Neutral HBlm and cationic H₂BIm⁺ form extended hydrogen-bonded linkers connected to Cr₂O₇²⁻ nodes in the SIF [H₃(BIm)₂]₂Cr₂O₇. The arrow and the red dots denote the centre of inversion relating the neutral and cationic molecules. The proton between is disordered over both molecules, in 50% occupancy imposed by inversion symmetry.

Each of the hydrogen-bonded linkers thus has a single positive charge and possesses two free N-H hydrogen bond donor sites, enabling connectivity to two Cr₂O₇²⁻ nodes via two N-H--O hydrogen bonds (2.128 Å, 156.1° and 2.170 Å, 146.5°). The effective stoichiometric ratio of
linkers and nodes remains 2:1, consistent with sulfate and selenate-based SIFs. The increased linker length resulting from the hydrogen-bonded dimerization of $\text{HBIH}$ and $\text{H}_2\text{BIm}^+$ caused an increase in the distances between adjacent nodes as compared to those found known structures of square-grid benzimidazolium dichromates. For example, the distance between adjacent nodes in $[\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7$ is ca. 14.7 Å, whereas the internodal distance found in the structure of $(\text{H}_2\text{MeBIm})_2\text{Cr}_2\text{O}_7$ (CSD code HAFJOO) is ca. 9.9 Å (Figure 6.18).

![Figure 6.18 Increased node-to-node distance due to an extended cationic linker in $[\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7$. Left: distance of 9.9 Å between dichromate nodes in the previously reported $(\text{H}_2\text{MeBIm})_2\text{Cr}_2\text{O}_7$.37b Right: distance of 14.7 Å between dichromate nodes in the SIF $[\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7$.](image)

Tetrahedrally-connected $\text{Cr}_2\text{O}_7^{2-}$ nodes and extended $\text{H}_3(\text{BIm})_2^+$ linkers assemble to form the apparently first example of a 3-dimensional SIF with diamondoid (dia) topology. Seven independent nets are translated along the $b$-axis to form a 7-fold interpenetrated diamondoid framework (Figure 6.19). The interpenetration observed in the structure eliminates any potential voids, thereby excluding any ability for guest inclusion.

![Figure 6.19 The seven independent diamondoid nets formed by $[\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7$, and their interpenetrated topology. Phenyl rings have been omitted for clarity.38](image)
The structure of \([\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7\) is in stark contrast to that of the previously published \((\text{H}_2\text{BIm})_2\text{Cr}_2\text{O}_7\),\(^{37b}\) which consisted of linear chains of dichromate anions surrounded by hydrogen-bonded \(\text{H}_2\text{BIm}^+\) cations.

![Figure 6.20 PXRD patterns for the reaction between \((\text{NH}_4)\text{CrO}_4\) and \(\text{HBIm}\): a) \((\text{NH}_4)\text{CrO}_4\); b) \(\text{HBIm}\); c) simulated pattern for \((\text{H}_2\text{BIm})_2\text{Cr}_2\text{O}_7\) (CSD code HAFJEE); d) LAG reaction between \(\text{HBIm}\) and \((\text{NH}_4)\text{CrO}_4\), 50 μL H₂O, 30 min, 30 Hz; e) simulated pattern for \([\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7\).](Image)

Analysis of the bulk reaction product between \(\text{HBIm}\) and \((\text{NH}_4)\text{CrO}_4\) by powder X-ray diffraction demonstrated the formation of a new crystalline phase that did not match any of the starting materials. Comparison of the PXRD pattern of the reaction mixture with that simulated from the structural data for \([\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7\) revealed that the product consisted of \([\text{H}_3(\text{BIm})_2]\text{Cr}_2\text{O}_7\) and one or more additional crystalline phases. It is notable that the final product contained a dichromate, even though \((\text{NH}_4)\text{CrO}_4\) was used as the starting material. Since \(\text{Cr}_2\text{O}_7^{2-}\) is the predominant species even at neutral pH, it is likely that using H₂O as the LAG liquid resulted in the conversion of \(\text{CrO}_4^{2-}\) to \(\text{Cr}_2\text{O}_7^{2-}\) and subsequent formation of the dichromate salt.
6.5 Conclusion

The node-and-linker approach has been applied to the design of hydrogen-bonded supramolecular imidazolium frameworks. Combining tetrahedral sulfate or selenate nodes with imidazolium cation linkers resulted in the reliable and generally applicable formation of charge-inverted analogues of 2-D metal-azolate frameworks. The formation of 4-fold nets was demonstrated irrespective of the choice of node (SO$_4^{2-}$ and SeO$_4^{2-}$), organic substituents on the linker (HMeIm, HEtIm, HBlm, and HPhBIm), and revealed a remarkable resistance to competing hydrogen-bond interactions. Specifically, crystal structures of SIFs of HMeIm and HPhBIm included water and solvent molecules which did not disrupt the node-and-linker relationship between imidazolium cations and tetrahedral anions.

In not yet published work, the chromate anion was also investigated as an alternative node for the formation of SIFs, resulting in the discovery of a new 7-fold interpenetrated SIF with diamondoid topology, based on dichromate nodes and extended linkers consisting of H$_3$BIm$^2+$ hydrogen-bonded dimers. The structure, which is the first example of a 3-D SIF achieved using the inverted node-and-linker approach, combines dichromate anions with unusual extended linkers formed of hydrogen-bonded neutral and cationic BIm groups. As observed in this case, linker extension through non-covalent interactions, in addition to linker modification, can result in new topologies and extend the range of application of this inverted node-and-linker design. The presented synthesis of SIFs from sulfate, selenate and dichromate nodes not only encourages the discovery of new structures, but is demonstrated as a reliable design strategy for molecular materials. Future research in this area will be directed towards exploring strategies for preventing and controlling network inter-penetration, initially established in the context of MOF synthesis.

6.6 References


32. Formation of the SiS$_2$-structure might be driven by short C–H$_3$⋯π contacts (3.5 Å) between neighbouring cations.


38. Topological analysis and image rendering was provided by Dr. Athanassios D. Katsenis, of McGill University.
Showcasing the work from Dr Tomislav Friščič’s Group, Department of Chemistry, McGill University, Canada

Supramolecular imidazolium frameworks: direct analogues of metal azolate frameworks with charge-inverted node-and-linker structure

Supramolecular imidazolium frameworks mirror the structures of square-grid metal azolates, but are based on a novel node-and-linker design of inverted polarity, consisting of cationic imidazolium linkers and anionic sulfate or selenate nodes.

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CHAPTER 7

RELIABLE DESIGN AND SELF-ASSEMBLY OF SQUARATE-BASED
SUPRAMOLECULAR IMIDAZOLIUM FRAMEWORKS

7.1 Introduction and connecting text

The results presented in this chapter are based on the manuscript of a paper to be submitted shortly for publication, entitled “Reliable design and self-assembly of squarate-based supramolecular imidazolium frameworks”, and co-authored by C. Mottillo, J. Yu, and Prof. T. Friščić. Sections 7.1 and 7.2 consist of a draft of the paper to be submitted, which has been written by C. Mottillo, edited by Prof. T. Friščić, and formatted for inclusion into this Thesis. The subsequent sections outline the detailed solid-state analysis of the materials described in this chapter, and include data which will be incorporated into the Supplementary Information of the manuscript. The synthesis and solid-state analysis described herein has been conducted by summer undergraduate student J. Yu under the direct guidance and supervision of C. Mottillo. The collection of single crystal X-ray diffraction data and all crystal structure determination was conducted by C. Mottillo.

Framework solids are highly investigated for applications in molecular separation,\(^1\) sensing,\(^2\) and catalysis.\(^3\) Enhancing the chemical, physical, and structural properties of framework materials necessitates design strategies which permit the reliable prediction of framework topology and structural features. In that context, the node-and-linker approach design strategy has enabled major advances in the synthesis of metal-organic and organic porous materials,\(^4\) by exploiting the expected binding geometries of metal ions or clusters, organic building blocks, and linkers to predict the assembly of 2-D or 3-D networks. On the other hand, the reliable self-assembly of molecular framework solids has proven more challenging due to the relatively labile nature of non-covalent interactions.\(^5\) Attempts to predict the structure of molecular solids have relied on the inherent complementarity of framework components, as in the case of supramolecular synthons,\(^6\) molecular tectonics,\(^7\) or more recently, the concept of topological enforcement.\(^8\) Alternatively, the formation of 3-D networks has been aided by charge-assisted hydrogen bonds,\(^9\) thereby strengthening connecting sites and rendering them less susceptible to competing non-covalent interactions and component functionalization.

Inspired by a need for the more design based development of molecular framework solids, my work has demonstrated, for the first time, that the node-and-linker approach can be
used to predict the reliable assembly of a new class of hydrogen-bonded network solids, called supramolecular imidazolium frameworks (SIFs).\textsuperscript{10} Combining tetrahedral sulfate or selenate nodes with linear imidazolium cation linkers \textit{via} charge-assisted hydrogen bonds resulted in their consistent assembly to form open two-dimensional (2-D) frameworks of square-lattice (sql) topology, which in some cases, were analogous to 2-D metal azolate frameworks. We now present the design of a new class of SIFs using our inverted node-and-linker approach, employing squarate (sq\textsuperscript{2-}) nodes and imidazolium cation linkers to effect the predicted assembly of open square-grid frameworks. The squarate anion, which has been widely investigated for its ability to participate in the formation of both metal-organic and supramolecular framework architectures,\textsuperscript{11} but never in this context, herein serves as a planar 4-connected node linked by ditopic imidazolium linkers. In moving from a tetrahedral to a planar node, we demonstrate the reliable synthesis of two-dimensional networks, across a surprisingly broad range of chemically and structurally distinct imidazolium linkers (Figure 7.1). The synthesis of mixed-linker SIFs has also been demonstrated, where the square-grid framework motif is maintained despite the insertion of chemically-distinct linkers into the structure.
7.2 Results and discussion

7.2.1 Squarate-based SIFs based on imidazole derivatives

Initial experiments to form squarate-based SIFs consisted of reacting imidazole (HIm) with squaric acid (Hsq) in a 2:1 stoichiometric ratio, in a mixture of acetonitrile and water. X-ray powder diffraction (PXRD) analysis of the resulting precipitate revealed a phase distinct from the starting materials. X-ray diffraction (XRD) analysis of single crystals grown from pyridine revealed a salt of composition (HIm)_{2}sq. In the salt, divalent squarate anions act as nodes and imidazolium cations act as linear linkers to form a 2-D network of square lattice (sql).
topology (Figure 7.2a). Each squarate anion is connected to four surrounding imidazolium cations through N$^\text{+}$-H--O charge-assisted hydrogen bonds, such that the sq$^{2-}$ to H$_2$Im ratio is 1:2.§ While the structure is composed of open sheets, the void space within the four-rings is partially occluded by the 4- and 5-position carbon atoms of the imidazole linkers. With an idealized square grid structure requiring that all nodes be equidistant and the angle $\phi$ set at 90º, the 2-D sheets are at a near-perfect arrangement, displaying node-to-node distances of ca. 9.8 Å and 9.9 Å with $\phi$= 89.7º (Figure 7.2). Comparison of the experimental powder X-ray diffraction (PXRD) pattern and the one simulated based on crystal structure data demonstrated that the crystals were isostructural to the bulk product. Solid-state $^{15}$N cross-polarization magic-angle spinning nuclear magnetic resonance (CP-MAS ssNMR) spectroscopy of the powder (H$_2$Im)sq revealed only one nitrogen species, suggesting full protonation of imidazole. The comparison with the $^{15}$N CP-MAS ssNMR spectrum of neutral solid imidazole could not be achieved due to too long acquisition times.

Next, we sought to investigate the effect of linker modification at the 2-position on the formation of squarate-based SIF structures. We began with the next simplest candidate, 2-methylimidazole (HMeIm), the squarate salt of which was synthesized in the same manner as (H$_2$Im)sq. Recrystallization from methanol (MeOH) upon slow evaporation in air resulted in single crystals which, by single crystal XRD, consisted of a hydrogen-bonded framework with composition (H$_2$MeIm)sq. Consistent with the (H$_2$Im)sq structure, squarate nodes and H$_2$MeIm$^+$ linkers again combine to form 2-D square grid sheets held together by charge-assisted hydrogen bonds. Introducing a methyl group on the 2-position caused the grid spacing to increase to ca. 10.4 Å, potentially due to steric bulk caused by two methyl groups pointing into the void space within each four-ring. The 2-D sheets of (H$_2$MeIm)sq are again near-perfect square grid frameworks, this time showing equilateral edges and $\phi$=88.5º. Comparison of the experimental PXRD pattern of the initial product with the simulated pattern from crystal data showed the two were identical. Natural abundance $^{15}$N CP-MAS ssNMR spectroscopy of the salt in powdered form revealed only one equivalent nitrogen species, as was the case with (H$_2$Im)sq. In comparison with the $^{15}$N CP-MAS ssNMR spectrum of neutral solid HMeIm, which exhibits

§ The distances and angles of N$^\text{+}$-H--O hydrogen bonds were found to be approximately 2.7 Å and 170º for all other structures described in this chapter. Detailed tables of hydrogen bond parameters for all squarate-based SIF structures described herein can be found in Appendix B.
two separate resonance signals for one protonated and one deprotonated nitrogen atom, this indicates that HMeIm groups are fully protonated in (H₂MeIm)₂sq. We next investigated the effect of increasing the steric bulk in the 2-position of the imidazolium ion linker on the formation of 2-D SIFs based on squarate nodes. For this purpose, we selected 2-ethylimidazole (HEtIm), 2-isopropylimidazole (Hi-PrIm), and 2-phenylimidazole (HPhIm) as analogous imidazoles with increasingly bulky substitutions on the 2-position. Remarkably, all these cases revealed the persistent assembly of 2-D hydrogen-bonded square grids from planar squarate anions surrounded by four imidazolium linkers (Figure 7.2).

![Figure 7.2](image-url)

**Figure 7.2** Fragments of the crystal structures of: a) (H₂Im)₂sq; b) (H₂MeIm)₂sq; c) (H₂EtIm)₂sq and d) (H₂i-PrIm)₂sq, showing four-rings formed by four sq²⁻ nodes and four imidazolium linkers.

Like in the case of (H₂MeIm)₂sq, crystals of (H₂EtIm)₂sq obtained from ethanol (EtOH) upon evaporation in air demonstrated a near-perfect square grid structure with equilateral four-ring edges measuring *ca.* 10.6 Å and φ = 91.2°. The slight increase in φ and in the distance between nodes as compared to those found in the structure of (H₂Im)₂sq is presumably due to the strain placed on the framework by opposing ethyl groups, leading to the expansion of the grid. This effect is further exacerbated in the case of (H₂i-PrIm)₂sq, whereby increased steric bulk leads to an increase in the four-ring dimensions to 10.7 Å, and brings the φ-angle to 92.1°. Remarkably,
whether the linker consists of a smaller, unsubstituted imidazole, or an imidazole with a larger, 
sterically-demanding isopropyl substituent, the structures observed remain square grid networks 
with near-ideal sq1-topology. The change in framework dimensions due to the increasing 
bulkiness of the 2-position moiety was also accompanied by an increase in the angle between the 
N+-H and O-C bonds involving the carbonyl carbons of the squarate anion and the imidazolium 
group. Whereas the largest angle in (H2Im)2sq is 115.8°, those in (H2MeIm)2sq, (H2EtIm)2sq, 
and (H2i-PrIm)2sq are found to be 117.2°, 119.4°, and 122.7° respectively.

The linker 2-phenylimidazole (HPhIm) represents a notable example of how the node- 
and-linker relationship in SIFs is resistant to both chemical modification and competing 
hydrogen bonding, as it is the linker in the herein explored series of imidazoles with the bulkiest 
functionality on the 2-position. The reaction of squaric acid with HPhIm and crystallization from 
DMF led to the formation of (H2PhIm)2sq·H2O, as evidenced by PXRD, thermogravimetric 
analysis (TGA), and Fourier-transform infrared attenuated total reflection spectroscopy (FTIR- 
ATR). Despite the presence of a water molecule connected to sq2- through O-H--O hydrogen 
 bonding (See Appendix B for hydrogen-bonding parameters), (H2PhIm)2sq·H2O assembles into 
distorted square grid sheets of squarate nodes surrounded by HPhIm linkers. The 2-D sheets are 
pillared by interstitial water molecules connecting sq2- ions in adjacent layers (Figure 7.3). The 
space within each four-ring is too small to accommodate a large phenyl ring, leading to 
corrugation of the network which allows the eclipsing of phenyl rings and retention of the square 
grid topology (Figure 7.4). Despite the described corrugation to allow for eclipsing of the 2-
position phenyl substituents, the spacing of the nodes maintains a nearly perfect square lattice 
arrangement, characterized by d = 10.1 Å and φ = 81.9°.

Figure 7.3 Fragment of the crystal structure of (H2PhIm)2sq·H2O, viewed down the c-axis. 
Layers of (H2PhIm)2sq are intercalated by water molecules connected to sq2- nodes by O-H--O hydrogen bonds.
7.2.2 SIFs based on benzimidazole derivatives

In order to elucidate the effect of more sterically demanding linkers on SIF structures, bulkier benzimidazole (H\textsubscript{2}BIm\textsuperscript{+}) and its derivatives were next used as linkers in squarate-based SIFs. In the structures of the herein described benzimidazolium squarates, the surprisingly reliable assembly of sql-topology grids was again observed. In the first case, H\textsubscript{2}BIm\textsuperscript{+} was reacted with H\textsubscript{2}sq in a mixture of acetonitrile and water, upon which the formation of a white precipitate was observed. X-ray diffraction analysis of single crystals obtained from recrystallizing the powder in hot MeOH upon cooling, revealed a 2-D square-grid hydrogen-bonded framework consisting of benzimidazolium squarate, (H\textsubscript{2}BIm\textsuperscript{+})\textsubscript{2}sq. Due to the steric demands of the benzimidazolium linkers, (H\textsubscript{2}BIm\textsuperscript{+})\textsubscript{2}sq exhibits a distortion from a perfect square-grid, manifested by the contraction of four-ring edges from $d = 10.1$ Å seen in (H\textsubscript{2}PhIm\textsuperscript{+})\textsubscript{2}sq·H\textsubscript{2}O to $d = 7.5$ Å, which is most likely resulting from favourable $\pi$-interactions between two opposing H\textsubscript{2}BIm\textsuperscript{+} linkers. The distortion of the square grid of (H\textsubscript{2}BIm\textsuperscript{+})\textsubscript{2}sq is also manifested as a reduction in the angle $\phi$ from 81.9º to 78.4º and the corrugation of the 2-D sheets. The cumulative result of these distortions was the arrangement of H\textsubscript{2}BIm\textsuperscript{+} linkers and sq\textsuperscript{2-} nodes to resemble a “dogbone” motif, whereby H\textsubscript{2}BIm\textsuperscript{+} linkers stack over one another, leaving virtually no void space within the grids (Figure 7.5).

**Figure 7.4** A fragment of the crystal structure of (H\textsubscript{2}PhIm\textsuperscript{+})\textsubscript{2}sq highlighting eclipsing of phenyl rings when viewed parallel to the crystallographic $a$-axis, and framework distortion from an ideal square-grid with $\phi = 90.0^\circ$ to a grid with $\phi = 81.9^\circ$. 

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Investigation of the effect of 2-position functionalization on the formation of SIFs from benzimidazole derivatives was initiated by replacing \( \text{HBI} \) with 2-methylbenzimidazole (\( \text{HMeBI} \)). A solution of \( \text{HMeBI} \) in acetonitrile was mixed with an aqueous solution of \( \text{H}_2\text{sq} \) to form a precipitate. Single crystal X-ray diffraction analysis of single crystals obtained from EtOH upon slow evaporation in air revealed a slightly distorted 2-D \( \text{sql} \)-topology framework consisting of \( \text{H}_2\text{MeBI}_2\text{sq} \). The structure of \( \text{H}_2\text{MeBI}_2\text{sq} \) is the first SIF described herein which does not have equilateral four-ring edges. The two distances between \( \text{sq}^2 \) nodes are \( d_1 = 10.8 \text{ Å} \) and \( d_2 = 10.9 \text{ Å} \), and the distortion from an ideal square-grid framework is further exacerbated with a \( \phi \) value of 81.6°. Similar to the series of imidazole-based squarate structures, the methyl groups of \( \text{H}_2\text{MeBI}_2\text{sq} \) occlude the voids which would normally be found within the four-rings (Figure 7.6a). Rotation of the \( \text{H}_2\text{MeBI}^+ \) linkers outside the plane of the 2-D framework, which was possibly caused by favorable C-H--π interactions between the 2-position methyl groups and the phenyl ring, resulted in corrugation of the sheets as seen in Figure 7.6b.

Figure 7.5 Fragment of the distorted 2-D square-grid framework of \( \text{H}_2\text{BIm}_2\text{sq} \), viewed down the \( a \)-axis. The top-right four-ring is outlined to highlight its resemblance to the shape of a dog bone. Four rings fit together in alternating orientations to form what is described as a “dogbone” motif in the structure of \( \text{H}_2\text{BIm}_2\text{sq} \).
The bulky 2-phenylbenzimidazole (HPhBIm) was selected as the last benzimidazole derivative to screen in the design of squarate-based SIFs. Solid HPhBIm and H2sq were reacted in a mixture of acetonitrile and water, upon which a precipitate formed. Structural analysis of single crystals of the powder, obtained using either DMF or MeOH as solvents, revealed the formation of a hydrate and a MeOH solvate of formula (H2PhBIm)2sq·2H2O and (H2PhBIm)2sq·2MeOH respectively. The presence of the hydrate and MeOH solvate was confirmed by TGA and FTIR-ATR analyses. Structural analysis of both salts revealed that formation of a square grid framework was hindered in each case by competitive hydrogen bonding to water and MeOH. The composition of the initial product obtained from solution synthesis was determined to be also (H2PhBIm)2sq·2H2O by comparing the experimental and simulated powder patterns. Thermogravimetric analysis of (H2PhBIm)2sq·2H2O made from solution showed a weight loss of 4.1% with an onset at 90 °C, which is consistent with the loss of two water molecules and the composition suggested from crystal structure data. Thermal desolvation of the hydrate at 150 °C under vacuum led to a structurally distinct crystalline phase, as observed by powder X-ray diffraction analysis. Thermogravimetric analysis of the resulting

Figure 7.6 a) Fragment of the crystal structure of (H2MeBIm)2sq, showing one four-ring composed of each four H2MeBIm+ linkers and sq2- nodes; b) View of the crystal structure of (H2MeBIm)2sq down the crystallographic c-axis, highlighting stacked corrugated sheets.
powder concluded that the new phase was not a solvate, and, therefore did not contain any competing hydrogen bond donors. Further analysis of this new phase by solid state $^{15}$N CP-MAS NMR revealed only one signal corresponding to the chemical shift of the protonated N atom in HPhBlm, suggesting full protonation of both nitrogen atoms, and the formation of a salt of composition (H$_2$PhBlm)$_2$sq (Polymorph 1). Attempts to obtain single crystals of this unknown phase by screening a series of recrystallization solvents were unsuccessful, and either yielded the aforementioned dihydrate or MeOH solvate.

7.2.3 Mechanochemical synthesis of SIFs

The existence of solvated and non-solvated forms of (H$_2$PhBlm)$_2$sq suggested that the additional steric bulk imposed by the phenyl substituents of HPhBlm was inducing increased structural flexibility or “frustration” in SIFs incorporating this linker. This effect was also seen in previous work, where sulfate- and selenate-based SIFs based on HPhBlm exhibited the highest susceptibility to solvent inclusion (Chapter 6). We were thus encouraged to investigate the synthesis of distinct forms of this SIF mechanochemically. Mechanochemistry was chosen as a well-established method for the screening of new forms of molecular solids, even those considered not obtainable from solution. Milling solid HPhBlm and H$_2$sq in a 2:1 stoichiometric ratio for 30 minutes did not result in the appearance of new crystalline phases, as judged by PXRD analysis. The reaction was thus aided with the addition of a catalytic amount of liquid additives, in a process called liquid-assisted grinding (LAG). The solid reagents were milled for 30 minutes in the presence of 50 μL MeOH and the reaction mixture analyzed by PXRD. Comparison of the experimental PXRD pattern with the pattern of (H$_2$PhBlm)$_2$sq·2MeOH simulated from structural data revealed that the product consisted of a mixture of (H$_2$PhBlm)$_2$sq·2MeOH and another unknown crystalline phase which corresponded neither to the previously encountered hydrate, nor the anhydrate obtained from thermal treatment of (H$_2$PhBlm)$_2$sq·2H$_2$O. The 30 minute LAG reaction of HPhBlm and H$_2$sq in the presence of 50 μL of either EtOH or $n$-butanol ($n$-BuOH) led to the formation of this new phase as the only crystalline product, as determined by qualitative analysis of the PXRD patterns of the product after milling. Thermogravimetric analysis revealed this material did not contain crystallized water or solvent. Subsequent recrystallization of the unknown phase obtained by LAG with $n$-BuOH, using $n$-BuOH also as the recrystallization solvent yielded diffraction-quality single crystals which when analyzed by single crystal XRD were found to consist of a second
polymorph of anhydrous (H$_2$PhIm)$_2$sq (Polymorph 2). Structural analysis revealed a distorted 2-D framework of squarate nodes and 2-phenylenzimidazolium linkers featuring equilateral edges and $\varphi = 81.6^\circ$ (Figure 7.7). In this structure, the steric bulk imposed by the phenyl substituents leads to pivoting of the ligands outside the plane of the 2-D sheet. As a result, the voids within the cavities are not occluded by the phenyl group substituents. However, there is no free space, as this also gave way to penetration of the phenyl groups from adjacent sheets to enter the void of neighboring sheet.

**Figure 7.7** a) Fragment of the crystal structure of (H$_2$PhBIm)$_2$sq, showing the four-ring formed by H$_2$PhBIm$^+$ cations and squarate nodes; b) view of (H$_2$PhBIm)$_2$sq highlighting interdigitating 2-D sheets. Wireframe: single sheet of (H$_2$PhIm)$_2$sq with squarate nodes highlighted in red and H$_2$PhIm$^+$ linkers highlighted in blue. Spacefill: H$_2$PhIm$^+$ linkers from adjacent sheets interdigitating the voids of the middle sheet.
7.2.4 Mixed-linker SIFs

One of the advantages of coordination polymers, in particular zeolitic imidazolate frameworks, has been the observation that functionality of the material can be modified by the structure containing more than one type of ligand. In ZIFs, such mixed-ligand architectures are readily made in situ by solvothermal synthesis or post-synthetically via solvent-assisted linker exchange on pre-made materials. This section is dedicated to demonstrating that squarate-based SIF design exhibits sufficient robustness and simplicity of synthesis to permit facile formation of mixed-linker square-grid structures. Much like the mixed-ligand ZIFs, we sought to demonstrate how isostructural SIFs could be built from chemically distinct linkers. To test this, HMelm and HEtIm were reacted with squaric acid in a 1:1:1 ratio, in a mixture of acetonitrile and water. The resulting white precipitate exhibited a diffraction pattern similar to that of (H2EtIm)2sq. The same product could also be obtained by reacting a 1:1 stoichiometric mixture of HMelm and HEtIm mechanochemically with squaric acid.

![Figure 7.8 Schematic of one layer of the crystal structure of (H2EtIm)1.34(H2Melm)0.66sq, depicting a random placement of H2EtIm+ (pink) and H2Melm+ (blue) linkers, which are disordered with relative occupancies of 0.67 and 0.33, respectively.](image-url)
By using single crystal X-ray diffraction, crystals obtained from the mechanochemically synthesized product recrystallized in MeOH upon slow evaporation in air revealed a material isostructural to \((\text{H}_2\text{EtIm})_2\text{sq}\), composed of both \(\text{H}_2\text{MeIm}^+\) and \(\text{H}_2\text{EtIm}^+\) ligands. The presence of both ligands was suggested by the appearance of an electron density peak adjacent to the CH\(_2\) carbon of the ethyl group. When this peak was assigned as a methyl carbon, the R-value reduced from 10.4% to 4.6% upon least-squares refinement. This was indicative of the replacement of some \(\text{H}_2\text{EtIm}^+\) linkers with \(\text{H}_2\text{MeIm}^+\) linkers. The least-squares refinement of the disorder of methyl and ethyl groups to determine the relative occupancy parameters of the carbon atoms belonging to both substituents suggested that 67% of linkers in the framework consist of \(\text{H}_2\text{EtIm}^+\) and 33% of linkers consist of \(\text{H}_2\text{MeIm}^+\) (Figure 7.8). Comparison of the unit cell parameters of both structures revealed that replacement of one third of \(\text{H}_2\text{EtIm}^+\) linkers with \(\text{H}_2\text{MeIm}^+\) linkers afforded a reduction in \(\beta\) angle from 94.656(7)º to 93.797(4)º. Comparison of the simulated pattern from the crystal structure of the salt \((\text{H}_2\text{EtIm})_{1.34}(\text{H}_2\text{MeIm})_{0.66}\text{sq}\) with the experimental patterns from the solution-made powder as well as that from mechanochemical synthesis demonstrated they were the same due to similar peak positions and relative intensities. Analysis of the FTIR-ATR spectrum of \((\text{H}_2\text{EtIm})_{1.34}(\text{H}_2\text{MeIm})_{0.66}\text{sq}\) made mechanochemically and comparison with that of squaric acid revealed an absorbance profile consistent with deprotonation of \(\text{H}_2\text{sq}\) and formation of the salt. The spectrum of \(\text{H}_2\text{sq}\) contained a broad absorption band centered at 1272 cm\(^{-1}\) tentatively assigned to the vibrational frequencies of the C-C stretch. This absorption band was not evident in the spectrum of \((\text{H}_2\text{EtIm})_{1.34}(\text{H}_2\text{MeIm})_{0.66}\text{sq}\), and was replaced by a broad absorption band at 1444 cm\(^{-1}\). The disappearance of absorption bands found at 1801 cm\(^{-1}\) and 1651 cm\(^{-1}\) for \(\text{H}_2\text{sq}\), corresponding to the asymmetric and symmetric C-O stretch, and appearance of a weak C-O stretching frequency at 1638 cm\(^{-1}\) were consistent with the formation of the squarate anion in the salt. The disappearance of the broad and weak O-H stretch centered at 2312 cm\(^{-1}\) in the spectrum of \((\text{H}_2\text{EtIm})_{1.34}(\text{H}_2\text{MeIm})_{0.66}\text{sq}\) was also indicative of deprotonation of \(\text{H}_2\text{sq}\).

7.2.5 Future analysis still required for the mixed-linker SIF described above

The bulk sample of the mixed-linker SIF obtained from solution synthesis will be analyzed by solution-state \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy to determine the initial ratio of \(\text{H}_2\text{EtIm}^+\) linkers and \(\text{H}_2\text{MeIm}^+\) linkers found in the initially synthesized SIF. The single crystal used for the XRD analysis described herein has also been saved for solution \(^1\text{H}\) and \(^{13}\text{C}\) NMR
spectroscopy, such that the relative stoichiometry of H$_2$EtIm$^+$ linkers and H$_2$MeIm$^+$ linkers suggested the occupancy parameters obtained by refinement of the disorder in the crystal structure can be confirmed by NMR data. The stoichiometric ratio between H$_2$EtIm$^+$ linkers and H$_2$MeIm$^+$ linkers will be determined by integrating the signals corresponding to the methyl protons of H$_2$EtIm$^+$ and of H$_2$MeIm$^+$, and comparing their values.

7.2.6 Conclusion

Herein was presented the synthesis of a new class of SIFs based on squarate nodes and imidazolium linkers. In the case of imidazole derivatives, structures based on five imidazoles assembled open square-grid frameworks. Greater steric bulk on the 2-position did not prevent squarate nodes from hydrogen-bonding to imidazolium linkers in a four-connected manner. Investigation of derivatives of benzimidazole revealed it forms distorted four-fold 2-D nets with squarate anions. Distortion in structures from benzimidazole and 2-methylbenzimidazole were induced by pi-interactions and C-H-pi interactions. In the case of 2-phenylbenzimidazole, bulky phenyl groups induced the easier formation of hydrates and solvates which did not form framework structures. However, synthesis of 2-phenylbenzimidazolium squarate by milling revealed the formation of an anhydrous structure which formed 2-D nets. Further work revealed the robustness of squarates at forming 2-D nets resistant to chemically different ligands incorporated into the structure.

7.3 Detailed solid-state analysis of the squarate-based SIFs described in Section 7.2

All solution-based syntheses of squarate-based SIFs were conducted in a mixture of acetonitrile and water. Based on experience from the synthesis of sulfate and selenate SIFs, the salts formed in the reactions were expected to be poorly soluble in the water/acetonitrile mixture and precipitate, allowing for simple separation. Any unreacted reagent was expected to remain in solution and be readily washed away. In keeping with the node-and-linker approach, the ratio of squarate nodes to imidazolium linkers was kept at 1:2, in order to form a 2-D square-grid framework (Scheme 7.1). Therefore, the reaction of squaric acid and imidazole should ideally have resulted in the full deprotonation of squaric acid to form the di-imidazolium salt. Product formation was at first implied by the appearance of a precipitate. Subsequent PXRD analysis of the powder was conducted to verify if the formation of phases distinct from the starting materials had occurred. To support evidence by PXRD that a reaction between the imidazole derivative and H$_2$sq had occurred, the powders were further analyzed in the solid state using single crystal
X-ray diffraction (XRD), Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectroscopy, and thermogravimetric analysis (TGA). The following section thus describes the detailed analysis of each SIF mentioned in Section 7.2.

7.3.1 Solid-state analysis of imidazolium squarate

The white precipitate obtained from the reaction of two equivalents of imidazole and H$_2$sq was analyzed by PXRD. Comparison of the PXRD pattern with those of the starting materials determined that the precipitate was a phase distinct from that of either two reagents. After recrystallization of the powder from pyridine and structure determination by single crystal X-ray diffraction, the simulated pattern for the SIF structure was compared with the experimental pattern of the product. As seen in Figure 7.9, the reflection intensities in both patterns were different, and rightward shift of 1.0° 2θ diffraction angle was observed in the simulated pattern with respect to the PXRD. The difference in reflection intensity was most likely due to preferred orientation effects and the geometry of the PXRD experiment, which was conducted on a flat, static sample. Single crystal data were collected at 150 K, whereas PXRD data was collected at room temperature, offering a suitable explanation for the shift in measured and calculated diffraction angles.
Figure 7.9 Selected PXRD patterns for the synthesis of (H$_2$Im)$_2$sq: a) HIm; b) H$_2$sq; c) experimental PXRD pattern of (H$_2$Im)$_2$sq; d) simulated pattern for the structure of (H$_2$Im)$_2$sq.

Thermogravimetric analysis of imidazolium squarate in dynamic atmosphere of N$_2$ revealed a first decomposition step of 16.1% weight loss at ca. 200 °C. This value may be consistent with the loss of one CO$_2$ molecule, which when calculated, accounts for 17.6% of the total mass of imidazolium squarate (Figure 7.10). While this would result in unusual fragmentation of the squarate anion, the release of CO$_2$ during the thermal decomposition of squarate-based salts and coordination polymers has been reported. The second weight loss step at ca. 290 °C corresponds to the complete decomposition and carbonization of the material.
FTIR-ATR spectroscopy provided further confirmation that the synthesis of a squarate salt had occurred upon the reaction of imidazole with $\text{H}_2\text{sq}$. The FTIR-ATR spectrum for $(\text{H}_2\text{Im})_2\text{sq}$ is shown in Figure 7.11, compared with the spectra for both $\text{HIm}$ and $\text{H}_2\text{sq}$ reactants. The spectrum of $\text{H}_2\text{sq}$ shows several absorption bands consistent with the vibrational modes of C-O and C-C bonds in the molecule. Namely, an absorption band corresponding to the C=C stretching frequency was observed at 1497 cm$^{-1}$. In addition, two absorption bands at 1651 cm$^{-1}$ and 1801 cm$^{-1}$ were observed, and are respectively consistent with the symmetric and asymmetric C=O stretch. A strong, broad absorption band at 1272 cm$^{-1}$ and another weaker one at 2289 cm$^{-1}$ were tentatively assigned to the C-C and O-H stretch, respectively. Analysis of the FTIR-ATR spectrum of $(\text{H}_2\text{Im})_2\text{sq}$ revealed the disappearance of the absorption bands corresponding to the symmetric and asymmetric C=O stretch at 1651 cm$^{-1}$ and 1801 cm$^{-1}$, and the appearance of a new, weaker one at 1658 cm$^{-1}$. In addition, the broad C-C absorption band at 1272 cm$^{-1}$ in $\text{H}_2\text{sq}$ is shifted to 1345 cm$^{-1}$ in the spectrum of $(\text{H}_2\text{Im})_2\text{sq}$. The O-H stretch at 2289 cm$^{-1}$ was no longer visible in the spectrum of $(\text{H}_2\text{Im})_2\text{sq}$, consistent with deprotonation of the acid. These observed differences between the FTIR-ATR spectra of $(\text{H}_2\text{Im})_2\text{sq}$ were consistent with what has previously been reported on the infrared spectroscopic analysis of squaric acid and its salts.$^{14}$

Figure 7.10 TGA thermogram of $(\text{H}_2\text{Im})_2\text{sq}$. The first weight loss step of 16.1% possibly corresponds to the loss of one CO$_2$ molecule, whose molar mass accounts for 17.6% of the molar mass of $(\text{H}_2\text{Im})_2\text{sq}$. 

Figure 7.11
The PXRD, TGA, and FTIR-ATR data presented herein was supplemented with solid-state $^{15}$N CP-MAS NMR spectroscopy to confirm the protonation of both N atoms on the imidazole linkers. Analysis of the $^{15}$N ssNMR spectrum of (H$_2$Im)$_2$sq revealed the presence of one signal at -341.77 ppm, suggesting that both N atoms are in the same chemical environment (Figure 7.12).

While this spectrum could not be compared to the spectrum of neutral HIm due to the extensive acquisition times needed for that sample, the appearance of only one signal is consistent with the protonation of both nitrogen atoms of HIm.

Figure 7.11 FTIR-ATR spectra pertaining to the synthesis of (H$_2$Im)$_2$sq: a) HIm; b) H$_2$sq; c) (H$_2$Im)$_2$sq, synthesized from solution.

Figure 7.12 Solid-state $^{15}$N CP-MAS NMR spectrum of (H$_2$Im)$_2$sq.
7.3.2 Solid-state analysis of 2-methylimidazolium squarate

![Scheme 7.2 Reaction of squaric acid and HMeIm in solution.](image)

The synthesis of 2-methylimidazolium squarate, \((\text{H}_2\text{MeIm})_2\text{sq}\), was achieved in the same manner as \((\text{H}_2\text{Im})_2\text{sq}\). Single crystals of the product were obtained by growth from hot MeOH upon cooling, and the structure elucidated by single crystal XRD. The experimental PXRD pattern of the bulk product was compared to the pattern simulated from crystal structure data. A visual comparison of both patterns revealed that the bulk product is the same phase as the single crystal (Figure 7.13).

![Figure 7.13 Selected PXRD patterns for the synthesis of \((\text{H}_2\text{MeIm})_2\text{sq}\): a) HMeIm; b) Hsq; c) bulk \((\text{H}_2\text{MeIm})_2\text{sq}\); d) simulated pattern for \((\text{H}_2\text{MeIm})_2\text{sq}\).](image)

Thermogravimetric analysis in dynamic atmosphere of N\(_2\) of \((\text{H}_2\text{MeIm})_2\text{sq}\) revealed that it has a higher thermal stability than \((\text{H}_2\text{Im})_2\text{sq}\). Specifically, the methylimidazole salt did not
show any evidence for release of CO₂ before its decomposition, and the TGA thermogram revealed a single decomposition step at ca. 270 °C (Figure 7.14).

![TGA thermogram of (H₂MeIm)₂sq in dynamic atmosphere of N₂, showing decomposition at ca. 270 °C.](image)

**Figure 7.14** TGA thermogram of (H₂MeIm)₂sq in dynamic atmosphere of N₂, showing decomposition at ca. 270 °C.

A visual comparison of FTIR-ATR spectrum of (H₂MeIm)₂sq with that of commercial reactants HMeIm and H₂sq was consistent with the protonation of HMeIm by H₂sq to form a salt. As in the case of (H₂Im)₂sq, the appearance of a weak absorption band at 1643 cm⁻¹ was evident with the simultaneous disappearance of bands at 1651 cm⁻¹ and 1801 cm⁻¹ corresponding to the C=O stretch in H₂sq. Likewise, the absorption band at 1272 cm⁻¹ corresponding to the C-C stretch was no longer observable and was replaced by a broad band centered at 1446 cm⁻¹. The broad O-H stretch at 2316 cm⁻¹ was no longer apparent in the spectrum of (H₂MeIm)₂sq.
As discussed in Section 7.2, (H$_2$MeIm)$_2$sq was employed as the model SIF to confirm full protonation of the imidazole derivatives in squarate-based SIFs. The relaxation times of nitrogen atoms in HMeIm were sufficiently short such that the solid-state CP-MAS $^{15}$N NMR spectrum could be collected in a short time. The CP-MAS $^{15}$N NMR spectra of HMeIm and (H$_2$MeIm)$_2$sq are shown in Figure 7.16. While the spectrum of neutral HMeIm demonstrated signals corresponding to two independent nitrogen species, the spectrum of (H$_2$MeIm)$_2$sq only revealed one, positioned at 24.74 ppm. This suggested that the 2-methylimidazole species in (H$_2$MeIm)$_2$sq are fully protonated, which is consistent with crystal structure data.

**Figure 7.15** Comparison of the FTIR-ATR spectra relating to the squarate salt of HMeIm: a) HMeIm; b) H$_2$sq; c) (H$_2$MeIm)$_2$sq bulk powder.
7.3.3 Solid-state analysis of 2-ethylimidazolium squarate

Solution synthesis of 2-ethylimidazolium squarate, (H$_2$EtIm)$_2$sq, from H$_2$EtIm and H$_2$sq resulted in the precipitation of a white solid, which by PXRD was found to be crystalline and structurally distinct from each of the starting materials. Recrystallization of the product from EtOH upon evaporation resulted in translucent crystals which were isostructural to the bulk product, as established by comparing the experimental and simulated PXRD patterns (Figure 7.17).

![Figure 7.16](image)

**Figure 7.16** Solid-state $^{15}$N CP-MAS NMR spectra consistent with full protonation of HMelm in the SIF (H$_2$Melm)$_2$sq: a) HMelm; b) bulk (H$_2$Melm)$_2$sq, synthesized in solution.

**Scheme 7.3** Reaction of squaric acid and HEtIm in solution.
Thermal decomposition of (H$_2$EtIm)$_2$sq in dynamic atmosphere of N$_2$ resembled that of (H$_2$MeIm)$_2$sq, displaying one single decomposition step at ca. 280 ºC (Figure 7.18).

Figure 7.17 PXRD patterns for the reaction between HEtIm and H$_2$sq: a) HEtIm; b) H$_2$sq; c) powder sample of (H$_2$EtIm)$_2$sq made from solution; d) simulated pattern for (H$_2$EtIm)$_2$sq crystal structure.

Figure 7.18 TGA thermogram of (H$_2$EtIm)$_2$sq in dynamic atmosphere of N$_2$, revealing a single decomposition step at ca. 280 ºC.
A comparison of the FTIR-ATR spectra of neutral HEtIm, H₂sq, and (H₂EtIm)₂sq revealed they were consistent with the deprotonation of H₂sq. The absorption band at 1272 cm⁻¹ found in the spectrum of H₂sq which corresponds to the C-C stretch was shifted to 1441 cm⁻¹ in the spectrum of (H₂EtIm)₂sq. The absence of absorption bands at 1651 cm⁻¹ and 1801 cm⁻¹ corresponding to the C=O stretch in H₂sq was simultaneous with the observation of a weak band at 1636 cm⁻¹.

**Figure 7.19** FTIR-ATR spectra for the squarate SIF made with HEtIm: a) HEtIm; b) H₂sq; c) (H₂EtIm)₂sq, synthesized from solution.

7.3.4 *Solid-state analysis of 2-isopropylimidazolium squarate*

![Scheme 7.4 Reaction of squaric acid and Hi-PrIm in solution.](image)

The PXRD pattern of bulk 2-isopropylimidazolium squarate (H₂i-PrIm)₂sq, synthesized from solution by reacting H₂i-PrIm and H₂sq in a mixture of acetonitrile and water, was consistent with the formation of a crystalline product. Single crystals of the solid, obtained from hot MeOH upon cooling, were analyzed by single crystal X-ray diffraction analysis at 150 K. Comparison of the room temperature experimental PXRD pattern with the PXRD pattern
simulated from crystal structure data revealed the two were identical, despite a leftward shift in diffraction angles, probably caused by the temperature discrepancy between experimental PXRD data and single crystal X-ray data collection (Figure 7.20).

In the case of (H$_2$i-PrIm)$_2$sq, thermal analysis revealed two overlapping weight loss steps, one at 240 °C and the other at 290 °C (Figure 7.21). The percent weight loss of the first step could not be readily correlated with the loss of any particular component of the salt, nor by loss of CO$_2$ or CO gas.

Figure 7.20 Powder X-ray diffraction patterns for the synthesis of the SIF (H$_2$i-PrIm)$_2$sq: a) H$i$-PrIm; b) H$_2$sq; c) (H$_2$i-PrIm)$_2$sq; d) simulated pattern for the structure of (H$_2$i-PrIm)$_2$sq.
Analysis of the FTIR-ATR spectrum of (H$_2$-PrIm)$_2$sq revealed a C-C bond stretching frequency at 1436 cm$^{-1}$ and a weak absorption band at 1633 cm$^{-1}$, corresponding to the C=O stretch. This is consistent with an increase in the double bond character of the C-C bonds and a decrease in the double bond character of the C=O bonds respectively, upon formation of squarate ions. The O-H stretch observed at 2316 cm$^{-1}$ in the FTIR-ATR spectrum of H$_2$sq was also no longer visible in the spectrum of (H$_2$-PrIm)$_2$sq.

**Figure 7.21** TGA thermogram of (H$_2$-PrIm)$_2$sq, showing two unresolved decomposition steps at 240 °C and 290 °C.

Analysis of the FTIR-ATR spectrum of (H$_2$-PrIm)$_2$sq revealed a C-C bond stretching frequency at 1436 cm$^{-1}$ and a weak absorption band at 1633 cm$^{-1}$, corresponding to the C=O stretch. This is consistent with an increase in the double bond character of the C-C bonds and a decrease in the double bond character of the C=O bonds respectively, upon formation of squarate ions. The O-H stretch observed at 2316 cm$^{-1}$ in the FTIR-ATR spectrum of H$_2$sq was also no longer visible in the spectrum of (H$_2$-PrIm)$_2$sq.

**Figure 7.22** FTIR-ATR spectra for the synthesis of (H$_2$-PrIm)$_2$sq from solution: a) H$_2$sq; b) (H$_2$-PrIm)$_2$sq.
7.3.5 Solid-state analysis of 2-phenylimidazolium squarate

The reaction of H\textsubscript{PhIm} and H\textsubscript{2}\textsubscript{sq} in a mixture of acetonitrile and water led to the formation of a white precipitate which, by thermal analysis, showed a weight loss of 4.5% at ca. 100 °C. Due to the similarity in temperature onset of the first weight loss transition to the temperature at which water most likely is removed from a crystal structure, the formation of a hydrate was investigated as a possibility (Figure 7.23). The calculated percent weight loss for the removal of one water molecule is 4.3%, suggesting that the product is a monohydrate of 2-phenylimidazolium squarate ((H\textsubscript{2}\textsubscript{PhIm})\textsubscript{2}\textsubscript{sq}·H\textsubscript{2}O).

![Scheme 7.5 Reaction of squaric acid and HPhIm in solution.](image)

**Scheme 7.5** Reaction of squaric acid and HPhIm in solution.

**Figure 7.23** TGA thermogram of the solid product of the solution reaction between HPhIm and H\textsubscript{2}\textsubscript{sq}. The first weight loss step of 4.5% is consistent with the loss of one water molecule, which theoretically accounts for 4.3% of the molar mass of (H\textsubscript{2}\textsubscript{PhIm})\textsubscript{2}\textsubscript{sq}·H\textsubscript{2}O.

This conclusion was supported by single crystal X-ray diffraction structure analysis of crystals grown from MeOH at 150 K. The asymmetric unit of phenylimidazolium squarate consists of half a squarate molecule, half a water molecule, and one phenylimidazolium molecule, consistent
with the formula \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\). Importantly, the single crystal and the bulk material were identical, as confirmed by comparing the room temperature experimental PXRD pattern of powder \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\) with the simulated pattern calculated from crystal structure data (Figure 7.24).

![Figure 7.24 PXRD patterns comparing the powder form of \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\) synthesized in solution and the simulated pattern of the structure, calculated from crystal structure data: a) \(\text{HPhIm}\); b) \(\text{H}_2\text{sq}\); c) bulk \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\); d) simulated pattern for \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\).](image)

Analysis of the FTIR-ATR spectrum of \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\) revealed a weak absorption band at 3503 cm\(^{-1}\) corresponding to the O-H stretching frequency, consistent with the presence of water. The deprotonation of \(\text{H}_2\text{sq}\) was suggested by the shift of the broad absorption band at 1272 cm\(^{-1}\) in the spectrum of \(\text{H}_2\text{sq}\), corresponding to the C-C stretch, which is shifted to 1404 cm\(^{-1}\) in the spectrum of \((\text{H}_2\text{PhIm})_2\text{sq} \cdot \text{H}_2\text{O}\). Furthermore, a weak absorption band at 1642 cm\(^{-1}\) corresponding to form the C=O stretch is consistent with deprotonation of \(\text{H}_2\text{sq}\) to the \(\text{sq}^{2-}\) dianion (Figure 7.25).
7.3.6 Solid-state analysis of benzimidazolium squarate

The solution synthesis of benzimidazolium squarate, \((\text{H}_2\text{BIm})_2\text{sq}\) in a mixture of acetonitrile and water from \(\text{H}_{2}\text{BIm}\) and \(\text{H}_2\text{sq}\) resulted in a white crystalline powder, as established by PXRD analysis. Single crystals of the product, obtained from MeOH upon slow evaporation, were analyzed by XRD and the structure determined to be \((\text{H}_2\text{BIm})_2\text{sq}\). Low temperature (150 K) of the single X-ray crystal diffraction experiment caused the experimental PXRD pattern to be shifted with respect to the one simulated from the crystal structure. Visual comparison of the simulated and experimental PXRD patterns led to the conclusion that the two samples are identical (Figure 7.26).

![FTIR-ATR spectra](image)

**Figure 7.25** FTIR-ATR spectra for \((\text{H}_2\text{PhIm})_2\text{sq}\cdot\text{H}_2\text{O}\): a) \(\text{HPhIm}\); b) \((\text{H}_2\text{PhIm})_2\text{sq}\cdot\text{H}_2\text{O}\) in powder form.

![Reaction Scheme](image)

**Scheme 7.6** Reaction of squaric acid and \(\text{HBlm}\) in solution.

The solution synthesis of benzimidazolium squarate, \((\text{H}_2\text{BIm})_2\text{sq}\) in a mixture of acetonitrile and water from \(\text{HBlm}\) and \(\text{H}_2\text{sq}\) resulted in a white crystalline powder, as established by PXRD analysis. Single crystals of the product, obtained from MeOH upon slow evaporation, were analyzed by XRD and the structure determined to be \((\text{H}_2\text{BIm})_2\text{sq}\). Low temperature (150 K) of the single X-ray crystal diffraction experiment caused the experimental PXRD pattern to be shifted with respect to the one simulated from the crystal structure. Visual comparison of the simulated and experimental PXRD patterns led to the conclusion that the two samples are identical (Figure 7.26).
Thermal analysis of the powder of under (H$_2$BIm)$_2$sq in dynamic atmosphere of N$_2$ revealed a principal weight loss step corresponding to the partial decomposition of the salt at ca. 270 ºC (Figure 7.27). The subsequent, minor step probably represents further calcination of carbonaceous residue at higher temperatures.

Figure 7.26 Powder X-ray diffraction patterns pertaining to the synthesis and crystal structure elucidation of (H$_2$BIm)$_2$sq: a) HBIm; b) H$_2$sq; c) (H$_2$BIm)$_2$sq, synthesized in solution; d) simulated pattern calculated from the crystal structure of (H$_2$BIm)$_2$sq.

Figure 7.27 TGA thermogram of (H$_2$BIm)$_2$sq, showing a principal decomposition step at 270 ºC.
Comparison between the FTIR-ATR spectra (Figure 7.28) of neutral HBlm, Hsq, and (H2BIm)2sq revealed that the latter was consistent with the deprotonation of Hsq and formation of a salt. A broad absorption band at 1453 cm\(^{-1}\) corresponding to the C-C stretch of the aromatic cyclobutene ring was observed in the spectrum of (H2BIm)2sq. Furthermore, the absence of C=O stretching frequencies at 1651 cm\(^{-1}\) and 1801 cm\(^{-1}\) were consistent with deprotonation of Hsq and the formation of the squarate salt of HBlm.

![Figure 7.28](image)

**Figure 7.28** FTIR-ATR spectra for the synthesis of (H2BIm)2sq in solution: a) HBlm; b) Hsq; c) (H2BIm)2sq bulk powder sample.

7.3.7 Solid-state analysis of 2-methylbenzimidazolium squarate

![Scheme 7.7](image)

**Scheme 7.7** Reaction of squaric acid and HMeBIm in solution.

The synthesis of (H2MeBIm)2sq was conducted in a solution of acetonitrile and water, and the resulting precipitate was analyzed by PXRD (Figure 7.29). The solid product was recrystallized in MeOH upon evaporation and the structure elucidated by single crystal XRD. A
comparison of the experimental powder pattern of the bulk product \((H_2MeBIm)_2sq\) with the simulated PXRD pattern calculated from crystal structure data revealed that the single crystals used for XRD analysis were identical to the bulk powder.

**Figure 7.29** Series of PXRD patterns comparing the product \((H_2MeBIm)_2sq\) made from solution and the crystal structure elucidated from single crystal XRD: a) \(HMeBIm\); b) \(H_2sq\); c) bulk powder sample of \((H_2MeBIm)_2sq\); d) simulated pattern of \((H_2MeBIm)_2sq\) calculated from crystal structure data.

Thermal analysis and FTIR-ATR spectroscopy of \((H_2MeBIm)_2sq\) have not been conducted yet,

7.3.8 Solid-state analysis of 2-phenylbenzimidazolium squarate

**Scheme 7.8** Reaction of squaric acid and \(HPhBIm\) in solution.

The attempted synthesis of 2-phenylbenzimidazolium squarate was conducted by adding an acetonitrile solution of \(HPhBIm\) to aqueous \(H_2sq\) in a 2:1 stoichiometric ratio. The resulting
white precipitate was analyzed by PXRD, which indicated that the powder consisted of a crystalline product distinct from either of the starting materials (Figure 7.30). Recrystallization of the solid from N,N-dimethylformamide (DMF) yielded single crystals. Analysis of single crystals by XRD revealed that they are a dihydrate of (H₂PhBIm)₂sq. Crystal structure determination revealed that (H₂PhBIm)₂sq·2H₂O does not form a framework structure, due to the water molecules interacting with the squarate nodes via O-H---O hydrogen bonds. Comparison between the simulated PXRD pattern for (H₂PhBIm)₂sq·2H₂O and the experimental PXRD pattern of the initial solid product revealed that the single crystal and bulk product are identical phases (Figure 7.30). Recrystallization of bulk (H₂PhBIm)₂sq·2H₂O from MeOH upon evaporation, and subsequent XRD analysis of these single crystals resulted in the discovery of a methanol solvate of (H₂PhBIm)₂sq. In this structure, MeOH molecules interact with the squarate nodes through O-H---O hydrogen bonds, thus preventing the assembly of H₂PhBIm⁺ linkers and sq²⁻ nodes into a square-grid framework.

![Figure 7.30](image-url) PXRD patterns comparing the reaction product of HPhBIm and H₂sq from solution and the solid phases obtained upon recrystallization in various solvents: a) HPhBIm; b) H₂sq; c) (H₂PhBIm)₂sq·2H₂O, from solution synthesis; d) simulated pattern for (H₂PhBIm)₂sq·2H₂O; e) simulated pattern for (H₂PhBIm)₂sq·2MeOH; f) (H₂PhBIm)₂sq·2H₂O, thermally treated at 150 °C overnight.
The bulk powder of \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\), obtained from solution synthesis, was analyzed by TGA in dynamic atmosphere of N\(_2\). The thermogram of \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\) revealed a weight loss step of 7.1\% with an onset at \(\sim 95 \, ^\circ\text{C}\), which was consistent with the loss of two water molecules per formula unit (\textbf{Figure 7.31}). Following this step, the sample exhibited no change in the thermogram until full decomposition occurred at 300 \(^\circ\text{C}\). To determine the identity of the product of dehydrating \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\), a sample of bulk \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\) was kept at 150 \(^\circ\text{C}\) overnight. PXRD analysis (\textbf{Figure 7.30}) of the sample after heat treatment revealed that it consisted of a crystalline phase distinct from \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\) or \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{MeOH}\), and was presumed to be the anhydrous form, \((\text{H}_2\text{PhBIm})_2\text{sq}\) (Polymorph 1). Attempts to recrystallize this phase in various solvents were unsuccessful, and yielded single crystals of either the hydrate or other solvate forms which have not yet been fully characterized.

\textbf{Figure 7.31} TGA thermogram of \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\), showing a first weight loss step of 7.1\% at \textit{ca.} 125 \(^\circ\text{C}\), consistent with the loss of two water molecules per formula unit. The two water molecules account for 6.8\% of the total molar mass of \((\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}\).

Analysis of both the dihydrate and anhydrous form of \((\text{H}_2\text{PhBIm})_2\text{sq}\) by FTIR-ATR spectroscopy was consistent with the presence of squarate salts. In both spectra, strong absorption bands at 1478 cm\(^{-1}\) and 1482 cm\(^{-1}\) were observed, consistent with the C-C stretch of the \text{sq}^-\ anion (\textbf{Figure 7.32}). In addition, the strong bands at 1651 cm\(^{-1}\) and 1801 cm\(^{-1}\) corresponding to the C=O stretch, were no longer visible in the FTIR-ATR spectra of
(H₂PhBIm)₂sq·2H₂O and (H₂PhBIm)₂sq (Polymorph 1). In addition, the O-H stretching frequency at 3381 cm⁻¹ was observed in the FTIR-ATR spectrum of (H₂PhBIm)₂sq·2H₂O, whereas the FTIR-ATR spectrum of (H₂PhBIm)₂sq (Polymorph 1) after thermal treatment at 150 ºC did not show an absorption band at this frequency. This was consistent with the complete loss of water upon heating, and the presumed isolation of an anhydrous form.

Figure 7.32 FTIR-ATR spectra demonstrating the formation of (H₂PhBIm)₂sq·2H₂O upon reacting HPhBIm and H₂sq in solution, and the subsequent transformation to an anhydrate, (H₂PhBIm)₂sq, upon thermal treatment at 150 ºC overnight: a) HPhBIm; b) H₂sq; c) (H₂PhBIm)₂sq·2H₂O made from solution; d) (H₂PhBIm)₂sq, Polymorph 1.

Comparison of the propensities of squarate and sulfate SIFs towards forming hydrates and solvates suggests that the increased steric bulk in H₂PhBIm⁺ linkers leads to more frustrated crystal packing. The increased frustration in these structures makes them more susceptible to interfering solvent interactions which may hinder assembly into sql-hydrogen-bonded frameworks, as has been seen in the above cases and in Chapter 6. However, this increased flexibility can also lead to higher structural diversity in HPhBIm-based SIFs, heightening the potential for polymorphism and solvate formation. While attempts to isolate Polymorph 1 of (H₂PhBIm)₂sq or other solvates by recrystallization repeatedly resulted in formation of the dihydrate or no single crystals at all, mechanochemistry was identified as a more promising route
to potentially isolate new polymorphs or solvates of (H₂PhBIm)₂sq. Therefore, HPhBIm and H₂sq were milled mechanochemically in the presence of μL amounts of varying liquid additives, as well as with no additive at all. The results from this screen are summarized in Scheme 7.8. Milling HPhBIm and H₂sq in a 2:1 stoichiometric ratio without salt additive resulted in the formation of no crystalline products, as established by analyzing the PXRD pattern of the solid mixture after 30 minutes grinding (Figure 7.33).

Scheme 7.9 Schematic summarizing the mechanochemical synthesis of various polymorphs and solvates of the salt (H₂PhBIm)₂sq. Milling in the presence of 50 μL water or MeOH resulted in the formation of (H₂PhBIm)₂sq·2H₂O and (H₂PhBIm)₂sq·2MeOH, respectively. Overnight thermal treatment of (H₂PhBIm)₂sq·2H₂O at 150 ºC resulted in transformation to Polymorph 1 of (H₂PhBIm)₂sq, the structure of which has not yet been elucidated. Milling HPhBIm and H₂sq in the presence of 50 μL EtOH or n-BuOH resulted in the synthesis of a second polymorph of anhydrous (H₂PhBIm)₂sq.

Milling HPhBIm and H₂sq in the presence of 50 μL water for 30 minutes resulted in the formation of the dihydrate, as seen by comparing the PXRD of the reaction mixture with the simulated PXRD pattern calculated from crystal structure data of (H₂PhBIm)₂sq·2H₂O. Using 50 μL MeOH as the LAG additive, on the other hand, resulted in the formation of a triphasic mixture of (H₂PhBIm)₂sq·2H₂O, (H₂PhBIm)₂sq·2MeOH, and an unknown phase which could not be associated with the starting materials or Polymorph 1 of (H₂PhBIm)₂sq. Comparing the PXRD pattern of the reaction mixture with the simulated patterns for (H₂PhBIm)₂sq·2H₂O and
(H$_2$PhBIm)$_2$sq·2MeOH revealed distinct diffraction peaks at 12.5° and 13.5° 2θ, which indicated that a new, unidentified crystalline phase had also formed (Figure 7.33). Conducting the reaction in the presence of 50 μL EtOH or n-butanol (n-BuOH) resulted in the conversion of HPhBIm and H$_2$sq to this unknown crystalline phase as the major product. Low-intensity reflections corresponding to the starting materials and (H$_2$PhBIm)$_2$sq·2H$_2$O were also observed in the PXRD patterns of these reaction mixtures.

**Figure 7.33** PXRD patterns for the mechanochemical LAG synthesis of squarate-based salts and SIFs based on HPhBIm: a) HPhBIm; b) H$_2$sq; c) simulated pattern for (H$_2$PhBIm)$_2$sq·2H$_2$O; d) simulated pattern for (H$_2$PhBIm)$_2$sq·2MeOH; e) bulk (H$_2$PhBIm)$_2$sq, polymorph 1; solid-state reaction between HPhBIm and H$_2$sq for 30 min at 30 Hz by: f) neat milling; g) with 50 μL H$_2$O; h) with 50 μL MeOH; i) with 50 μL EtOH; j) with 50 μL n-BuOH.

The reaction mixtures obtained by milling in the presence of MeOH, EtOH, and n-BuOH were analyzed by FTIR-ATR spectroscopy to corroborate phase identification by PXRD. The FTIR-
ATR spectra of all LAG samples were consistent with the formation of squarate salts, as established by a visual comparison with the FTIR-ATR spectrum of solution-made $(\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{H}_2\text{O}$ (Figure 7.34). In each case, a strong absorption band was observed around 1480 cm$^{-1}$ consistent with the C-C stretch, in addition to the absence of absorption bands at 1561 cm$^{-1}$ and 1801 cm$^{-1}$ corresponding to the C=O stretch. In the FTIR-ATR spectrum of the sample made by milling with EtOH additive, the absence of any O-H stretching frequencies was consistent with the majority of the unknown sample consisting of an anhydrous form. This form, appearing to be a crystalline phase, distinct from $(\text{H}_2\text{PhBIm})_2\text{sq}$ (Polymorph 1) by PXRD data, has been referred to as anhydrous Polymorph 2. A low-intensity band at 3384 cm$^{-1}$, consistent with the O-H stretch, was observed in the FTIR-ATR spectrum of the reaction mixture using n-BuOH as an additive. This could possibly be due to the presence of small amounts of surface-adsorbed solvent or water in the sample. Analysis of the FTIR-ATR spectrum of the reaction mixture obtained in the presence of MeOH revealed an O-H stretch 3293 cm$^{-1}$, which is consistent with PXRD data suggesting the formation of $(\text{H}_2\text{PhBIm})_2\text{sq} \cdot 2\text{MeOH}$ as the major product.
The product of the milling reaction between HPhBIm and H$_2$sq in the presence of 50 μL n-BuOH, named anhydrous Polymorph 2, was analyzed by thermogravimetric analysis. The TGA

Figure 7.34 FTIR-ATR spectra for the products of the mechanochemical reaction between HPhBIm and H$_2$sq: a) HPhBIm; b) H$_2$sq; c) (H$_2$PhBIm)$_2$sq·2H$_2$O synthesized from solution; d) (H$_2$PhBIm)$_2$sq, Polymorph 1; e) (H$_2$PhBIm)$_2$sq, Polymorph 2 from milling with EtOH; f) (H$_2$PhBIm)$_2$sq, Polymorph 2 from milling with nBuOH; g) mixture of (H$_2$PhBIm)$_2$sq and (H$_2$PhBIm)$_2$sq·2MeOH from milling with MeOH.

The product of the milling reaction between HPhBIm and H$_2$sq in the presence of 50 μL n-BuOH, named anhydrous Polymorph 2, was analyzed by thermogravimetric analysis. The TGA
thermogram (Figure 7.35) of the product demonstrated only one decomposition step at ~305 °C, consistent with the formation of anhydrous (H₂PhBIm)₂sq, as also suggested by FTIR-ATR spectroscopy.

![TGA thermogram of (H₂PhBIm)₂sq, Polymorph 2.](image)

**Figure 7.35** TGA thermogram of (H₂PhBIm)₂sq, Polymorph 2.

Structure determination of (H₂PhBIm)₂sq, Polymorph 2, was achieved by single crystal X-ray diffraction. Single crystals were obtained by recrystallizing the product obtained by milling with n-BuOH upon cooling from n-BuOH. The composition of the anhydrous Polymorph 2 was thus confirmed to be (H₂PhBIm)₂sq, with the structure consisting of 2-D SIF sheets based on H₂PhBIm⁺ linkers and sq²⁻ nodes. Analysis of the simulated PXRD pattern for the (H₂PhBIm)₂sq, Polymorph 2 single crystal, and comparison with the experimental PXRD patterns of the products of mechanosynthesis in the presence of either EtOH or n-BuOH revealed that they are the same crystalline phase (Figure 7.36).
The mixed-linker SIF composed of H$_2$EtIm$^+$ and H$_2$MeIm$^+$ linkers was synthesized from solution using the protocol described for the synthesis of (H$_2$EtIm)$_2$sq. In this case, however, both HEtIm and HMeIm were used, in a 1:1 stoichiometric ratio, with H$_2$sq, while maintaining an overall imidazole-to-squaric acid ratio of 2:1. Analysis of the PXRD pattern of the resulting precipitate revealed that the product consisted of a crystalline phase very similar to (H$_2$EtIm)$_2$sq (Figure 7.37). This was consistent with single crystal XRD data, which revealed that the mixed linker SIF of HEtIm and HMeIm crystallizes in a similar space group and unit cell as 

\[ (H_2EtIm)_{1.33}(H_2MeIm)_{0.67}(sq) \]
(H₂EtIm)²sq, with H₂Mel⁺ linkers replacing one third of all H₂EtIm⁺ linkers. Refinement of this solid solution as a disordered structure revealed a methyl group occupancy of 0.33 relative to 0.66 for the ethyl group, which is consistent with the formula (H₂EtIm)₁.₃₄(H₂Mel)₀.₆₆sq. The mixed-linker SIF (H₂EtIm)₁.₃₄(H₂Mel)₀.₆₆sq could also be synthesized in the solid state, by milling equal parts of HEtIm and HMel with H₂sq in a 2:1 imidazole-to-squaric acid ratio overall, using water as the liquid additive (Figure 7.37).

Figure 7.37 Powder X-ray diffraction data demonstrating the similarity between the experimental and simulated PXRD patterns of (H₂EtIm)²sq and the mixed linker SIF (H₂EtIm)₁.₃₄(H₂Mel)₀.₆₆sq: a) commercial HMel; b) commercial HEtIm; c) commercial H₂sq; d) bulk powder of (H₂EtIm)²sq from solution synthesis; e) simulated PXRD pattern for (H₂EtIm)²sq; f) pattern for (H₂EtIm)₁.₃₄(H₂Mel)₀.₆₆sq synthesized from solution; g) experimental pattern for (H₂EtIm)₁.₃₄(H₂Mel)₀.₆₆sq synthesized mechanochemically; h) simulated pattern for experimental pattern for (H₂EtIm)₁.₃₄(H₂Mel)₀.₆₆sq from single crystal data.
7.4 Conclusion

The node-and-linker approach has been applied for the reliable synthesis of squarate-based supramolecular imidazolium frameworks (SIFs). Open square-grid frameworks assemble from negatively charged squarate nodes and cationic imidazolium linkers which are held together by charge-assisted hydrogen bonds. The node-and-linker relationship between the tetratopic nodes and ditopic linkers is retained in a family of seven structures despite increasingly bulk 2-position modification of the imidazole and competing interactions from hydrogen-bonds donating solvents. Potential voids within the square-grid networks are either occluded by adjacently stacked networks or obstructed by interdigitation of adjacent sheets by 2-position moieties. Squarate-based SIFs represent a new class of molecular solids and the second of which have been reliably assembled using the node-and-linker design strategy. Moreover, the design of mixed-linker SIF composed of 2-methylimidazole and 2-ethylimidazole further solidifies the potential of this strategy for the predicted synthesis of molecular framework solids. While there has been very little research in this area, the successful introduction of a completely altered linker has been achieved. This concept has potential for the further design of two-dimensional and three-dimensional molecular solids, with the possibility of linker modification as well as the formation of solid solutions.

7.5 References


CHAPTER 8
EXPERIMENTAL DETAILS

This chapter outlines the synthetic and analytical methods used in all experiments discussed within this Dissertation. Synthetic details are divided by publication, and thus, by chapter, while detailed instrumental analysis has been generalized for all chapters in the interest of concision.

8.1 Experimental details for Chapter 2: Accelerated aging: a low energy, solvent-free alternative to solvothermal and mechanochemical synthesis of metal–organic materials

8.1.1 Preparation of accelerated aging samples

In a typical reaction, a mixture of 0.163 g (2.0 mmol) ZnO and 0.306 g (4.5 mmol) HIm was gently ground manually using a mortar and pestle. For accelerated aging experiments, 10.00 mg (3.8 mol%) of (NH₄)₂SO₄ were added to the reaction mixture. The ground mixtures were placed in an open vial and aged at room temperature and humidity, or room temperature and 98% RH, or at 45°C and 98% RH. Experiments conducted at 98% RH were placed in a glass desiccator in which a constant humidity level was maintained by equilibrating the inside atmosphere with a saturated K₂SO₄ solution. For controlled temperature reactions, the desiccator was placed in a large volume incubator set at 45 °C. The same procedure was repeated for reactions involving all other imidazole ligands, typically using a 1:2 stoichiometric ratio of zinc oxide to imidazole ligand. For reactions with HMeIm on a 10 gram scale 3.47 g (42.6 mmol) ZnO was mixed with 7.01 g (85.3 mmol) HMeIm and 0.52 g (5% w/w) (NH₄)₂SO₄. For the 10 gram scale reaction with HEtIm, 2.96 g (36.4 mmol) ZnO was mixed with 7.00 g (72.8 mmol) HEtIm and 0.50 g (5%w/w) (NH₄)₂SO₄. Following complete disappearance of ZnO, the samples were washed with distilled water to remove the salt additive or its degradation products and dried in air. Power consumption of the incubator was measured using the BluePlanet AC Electronic Energy Meter.

8.1.2 Synthesis of imidazolium sulfate dihydrate ((H₂Im)₂SO₄·H₂O):

Imidazole (4.0 mmol, 0.27 g) was dissolved in a 1:9 water:ethanol (v/v) mixture. Concentrated sulfuric acid (2.1 mmol, 111 µL) was added and a white precipitate formed. The product was collected over vacuum and dried over air. Elemental analysis for (H₂Im)₂(SO₄)·2H₂O: C (calculated: 26.67%, measured: 26.41%), H (calculated: 5.22%; measured: 5.54%), N (calculated: 20.73%, measured: 20.38%).

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8.2 Experimental details for Chapter 3: Mineral neogenesis as an inspiration for mild, solvent-free synthesis of bulk microporous metal–organic frameworks from metal (Zn, Co) oxides

8.2.1 Synthesis of salt additives

8.2.1.1 Caffeinium hydrogensulfate ((H\text{Caf})(HSO₄)):

For the synthesis of (H\text{Caf})(HSO₄) caffeine (3.0 mmol, 0.58 g) was dissolved in acetonitrile. Concentrated sulfuric acid (3.0 mmol, 160 µL) was added, and upon stirring, a white precipitate formed. The solid was filtered and dried over vacuum. The product was isolated in 90% yield and analyzed by PXRD, solid-state \(^{13}\)C CP-MAS NMR, FTIR-ATR, and determined to be (H\text{Caf})(HSO₄) by elemental analysis. Storage in dry atmosphere was necessary to prevent conversion to (H\text{Caf})(HSO₄)·H₂O, observable by PXRD. Single crystals for single crystal X-ray diffraction structure determination were obtained by dissolving (H\text{Caf})(HSO₄) in a 1:4 v/v solution of nitromethane and anhydrous EtOH and allowing the solvent to evaporate slowly overnight. X-ray single crystal structure determination confirmed the composition (H\text{Caf})(HSO₄), and crystallographic data has been deposited with the Crystal Structure Database. The bulk composition of the product was confirmed by comparison of experimental powder X-ray diffraction patterns to the one simulated for the determined crystal structure. Elemental analysis for (H\text{Caf})(HSO₄): C (calculated: 32.88%, measured: 32.87%), H (calculated: 4.14%, measured: 4.14%), N (calculated: 19.17%, measured: 19.02%).

8.2.1.2 Caffeinium hydrogensulfate hydrate ((H\text{Caf})(HSO₄)·H₂O):

(H\text{Caf})(HSO₄) was allowed to sit in 98% RH atmosphere overnight to obtain (H\text{Caf})(HSO₄)·H₂O. The product was analyzed by FTIR-ATR spectroscopy, PXRD and TGA. Experimental powder X-ray diffraction pattern matched to that simulated from the known crystal structure.

8.2.1.3 Benzimidazolium sulfate ((H₂BIm)₂SO₄):

Benzimidazole (8.0 mmol, 0.55 g) was dissolved in acetonitrile. Concentrated sulfuric acid (8.1 mmol, 520 µL) was added to form a beige precipitate. The product was collected, dried over vacuum, and characterized by PXRD and FTIR-ATR spectroscopy.

8.2.2 Preparation of accelerated aging samples

In a typical experiment, 2.0 mmol of metal oxide (ZnO or CoO), 4.0 mmol of the imidazole ligand (HMeIm or HEtIm), and 4 mol% (unless otherwise specified) of the salt
additive [(NH₄)₂SO₄], KH₂SO₄, (H₂Im)₂SO₄·H₂O, (HCaf)(HSO₄), (HCaf)(HSO₄)·H₂O, or (H₂BIm)₂(SO₄), percentage calculated with respect to ZnO] were added to a 10 mL stainless steel milling jar along with one stainless steel ball of 7 mm diameter, weighing 1.3 grams. Unless specified otherwise, the mixtures were briefly milled using a Retsch MM400 ball mill for 5 minutes at 29.5 Hz. The samples not containing ammonium salt were left to age in a Secador® controlled humidity chamber at 98% RH or 100% RH, which was situated in an incubator set at 45°C. Samples containing ammonium sulfate as the additive were placed in a separate controlled humidity glass chambers under the same conditions, so as to avoid possible absorption of NH₃ within the container walls and contamination of subsequent samples. Saturated K₂SO₄ solution (for 98% RH) or just water (for 100% RH) were used to maintain humid atmosphere. Upon complete disappearance of X-ray reflections representing the metal oxides in PXRD patterns, samples were washed overnight and filtered over vacuum in H₂O, MeOH, or acetonitrile to remove trace amounts of catalyst or organic ligand. Samples for gas adsorption analysis were evacuated in a vacuum oven at 80 °C overnight.

8.3 Experimental details for Chapter 4: Carbon dioxide sensitivity of zeolitic imidazolate frameworks

8.3.1 Stability analysis of zeolitic imidazolate frameworks

In a typical stability experiment, 1.0 mmol of the ZIF (ZIF-8 (Basolite Z1200®), ZIF-67, dia-Zn(MeIm)₂, zni-Zn(Im)₂, dia-Cd(Im)₂, SOD-Zn(AldIm) (ZIF-90), RHO-Zn(EtIm)₂, and qtz-Zn(EtIm)₂ was added to a 6 dram glass vial. For reactions conducted in air, the open vial was placed in a plastic Secador® chamber of 22 dm³ volume set at 100% RH using pure water as the humidity source. For reactions in controlled atmosphere of CO₂ or argon, a 1 dram vial containing distilled water was placed inside the 6 dram vial. The vial was capped with a rubber septum, sealed with Parafilm M®, and flushed with either CO₂ or argon. Samples in controlled atmosphere were flushed again after collecting PXRD patterns. For reactions containing 4 mol% NH₄NO₃ the reagents were placed in a 10 mL stainless steel jar with one 7 mm (1.3 g) stainless steel ball. The samples were milled at 29.5 Hz for 5 min using a Retsch MM400 shaker mill prior to aging. Glass humidity chambers were used for samples containing ammonium salts. The humidity chambers and individual vials were placed in the same walk-in incubator set at 45°C.

8.3.2 Synthesis of ZIFs for stability analysis

8.3.2.1 Synthesis of dia-Zn(MeIm)₂:

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Synthesis of dia-Zn(MeIm)$_2$ was achieved through a method based on a previously described accelerated aging transformation. To increase the speed of the transformation, 16 mol% of (NH$_4$)$_2$SO$_4$ additive (with respect to ZnO) was used as opposed to the usual 4 mol%. ZnO (2.0 mmol, 1.62 g), HMeIm (4.0 mmol, 3.28 g), and (NH$_4$)$_2$SO$_4$ (0.32 mmol, 0.01 g) were milled for 5 minutes at 29.5 Hz in a 10 mL stainless steel jar with one 7 mm (1.3 g) stainless steel ball using a Retsch MM400 shaker mill and left to age at 45°C and 100% RH. The white powder was stirred overnight in distilled H$_2$O, and dried in vacuo at 80°C overnight. The composition and purity of the product was confirmed by powder PXRD, FTIR-ATR, and TGA.

8.3.2.2 Synthesis of zni-Zn(Im)$_2$

In a synthesis adapted from previously published work, Zn(NO$_3$)$_2$·6H$_2$O (9.9 mmol, 2.94 g) and HIm (79.0 mmol, 5.38 g) were dissolved in 150 mL MeOH. Triethylamine (79.0 mmol, 11.0 mL) was added dropwise, leading to the formation of a white amorphous precipitate which crystallizes upon filtering and drying over vacuum. The product was washed three times with MeOH and dried using vacuum filtration. The composition of the product was confirmed by PXRD, FTIR-ATR, and TGA.

8.3.2.3 Synthesis of dia-Cd(Im)$_2$

In a method adapted from previously published work, Cd(NO$_3$)$_2$·4H$_2$O (9.9 mmol, 3.04 g) and HIm (79.0 mmol, 5.38 g) were dissolved in 150 mL MeOH. Triethylamine (79.0 mmol, 11.0 mL) was added dropwise, leading to the formation of a white precipitate. The solid product was filtered, washed two times with MeOH and dried at 80°C in vacuo overnight. The composition of the product was confirmed by PXRD, FTIR-ATR, and TGA.

8.3.2.4 Synthesis of SOD-Zn(AldIm)$_2$ (ZIF-90)

SOD-Zn(AldIm)$_2$ (ZIF-90) was synthesized using an unpublished method developed by M. J. Cliffe. ZnO (1.0 mmol, 0.81 g) and imidazole-2-carboxaldehyde (HAlldIm) (2.0 mmol, 0.19 g) were milled in the presence of 10 mg CH$_3$NH$_4$Cl and 75 μL DMF in a 10 mL stainless steel milling jar with two 7 mm diameter (1.3 g) stainless steel balls. Milling was conducted at 29.5 Hz for 30 minutes. The resulting product was stirred in MeOH overnight and subsequently activated in vacuo at 80 °C overnight. Confirmation of product composition and purity was established using PXRD and TGA.

8.3.2.5 Synthesis of RHO-Zn(EtIm)$_2$
Synthesis of $\text{RHO-Zn(EtIm)}_2$ was achieved through a method based on a previously described accelerated aging transformation. ZnO (2.0 mmol, 0.16 g), H$\text{EtIm}$ (10.0 mmol, 0.96 g), and (H$\text{Caf}$)(HSO$_4$) (0.08 mmol, 0.23 g) were milled for 5 minutes at 29.5 Hz in a 10 mL stainless steel jar with one 7 mm (1.3 g) stainless steel ball using a Retsch MM400 shaker mill and left to age at 45°C and 100% RH. Powder X-ray diffraction data collected after 1 day demonstrated the complete disappearance of X-ray reflections pertaining to ZnO. The product was then stirred overnight in distilled MeOH, and dried $in\ vacuo$ at 80°C overnight. The composition of the product was confirmed by PXRD, FTIR-ATR, and TGA.

8.3.2.6 Synthesis of qtz-$\text{Zn(EtIm)}_2$

Synthesis of qtz-$\text{Zn(EtIm)}_2$ was achieved through a method based on a previously described accelerated aging transformation. ZnO (2.0 mmol, 0.16 g), H$\text{EtIm}$ (4.0 mmol, 0.34 g), and NH$_4$SO$_4$ (0.08 mmol, 0.01 g) were milled for 5 minutes at 29.5 Hz in a 10 mL stainless steel jar with one 7 mm (1.3 g) stainless steel ball using a Retsch MM400 shaker mill and left to age at 45°C and 100% RH. The white powder, which in a PXRD collected after two days demonstrated no more reflections pertaining to ZnO, was stirred overnight in distilled H$_2$O, and dried $in\ vacuo$ at 80°C overnight. The composition of the product was confirmed by powder PXRD, FTIR-ATR, and TGA.

8.3.3 Synthesis of $\mathbf{1}$

8.3.3.1 Synthesis of $\mathbf{1}$ derived from Basolite $\text{Z1200}^\text{®}$

Basolite $\text{Z1200}^\text{®}$ (1.0 mmol, 0.23 g) was suspended in 1.5 mL H$_2$O in a sealed vial. The vial was flushed with CO$_2$ and allowed to stand for 2 hours. The white precipitate was collected over vacuum, rinsed twice with water and dried $in\ vacuo$ at room temperature. The phase identity and absence of any remaining ZIF-8 in the product was confirmed by PXRD, and $\mathbf{1}$ was subsequently analyzed by FTIR-ATR, and TGA. Elemental analysis for $\mathbf{1}$: C: 33.01%, N: 16.98%, H: 3.15%

8.3.3.2 Synthesis of $\mathbf{1}$ from solution

10 mL of a saturated aqueous solution of Na$_2$CO$_3$ was added to 10 mL of a saturated solution of H$\text{MeIm}$, after which the solution turned slightly opaque. A 10 mL saturated solution of Zn(NO$_3$)$_2$$\cdot$$6$H$_2$O was immediately added, leading to the formation of a white precipitate. The product was filtered over vacuum, stirred in H$_2$O for 2 hours, and dried over vacuum again. PXRD analysis revealed the product is a mixture of ZIF-8 and $\mathbf{1}$. 

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8.4 Experimental details for Chapter 5: *Ex-situ* monitoring of accelerated aging synthesis of Cd-based ZIFs by X-ray powder diffraction and $^{111}$Cd solid-state NMR

8.4.1 Preparation of CdIFs by accelerated aging

8.4.1.1 Typical accelerated aging experiments

The synthesis of CdIFs by accelerated aging was conducted in a manner similar to that of ZIFs (see Chapter 8, Section 8.2.2). Solid CdO (4.0 mmol, 0.51 g) was mechanically pre-milled with 8 mmol of the selected imidazole derivative (HIm, HMeIm, or HEtIm) for 5 minutes using a Retsch MM400® shaker mill in 10 mL stainless steel milling jars containing one 7 mm (1.3 g) stainless steel ball. In the case of reactions requiring a salt catalyst, 4 mol% (with respect to CdO) of a protic salt additive consisting of either NH$_4$NO$_3$, (NH$_4$)$_2$SO$_4$, or (HCAF)(HSO$_4$) was also added to the reaction mixture prior to pre-milling. The solid mixtures were placed in open glass vials and kept in a chamber equilibrated at 100% RH with the use of an open beaker of distilled water. All reactions containing ammonium salts were placed in glass desiccators separate from ammonia-free reactions to prevent cross-contamination with ammonia gas. The reaction mixtures were periodically removed from the humidity chambers and analyzed by PXRD and FTIR-ATR spectroscopy to determine the extent of conversion.

8.4.1.2 Synthesis and analysis of Cd(MeIm)$_2$·HMeIm

A pure sample of Cd(MeIm)$_2$·HMeIm was obtained by pre-milling CdO (4.0 mmol, 0.51 g) and HMeIm (12.0 mmol, 0.99 g) in a 1:3 molar ratio for five minutes in the presence of 4 mol% NH$_4$NO$_3$ with respect to CdO. The solid mixture was aged at 100% RH for several days until the appearance of reflections corresponding to CdO was no longer evident by PXRD. The product was stirred in MeOH for one hour to remove traces of unreacted ligand or salt additive, and was dried by vacuum filtration. The sample of Cd(MeIm)$_2$·HMeIm was analyzed by PXRD, TGA, FTIR-ATR, and solid-state $^{13}$C, $^{113}$Cd, and $^1$H NMR spectroscopy.

8.4.2 Solid-state NMR Experimental Parameters

All multinuclear ($^{13}$C, $^{111}$Cd, $^1$H) solid-state NMR (ssNMR) experiments were conducted at the University of Windsor Department of Chemistry and Biochemistry in the laboratory of Prof. R. Schurko. Samples of CdIFs used for preliminary ssNMR spectroscopy analysis were synthesized by C. Mottillo. All ssNMR experiments on pre-synthesized samples were conducted by C. O’Keefe, a PhD candidate in the group of Prof. R. Schurko. Monitoring the accelerated aging synthesis of CdIFs by *ex situ* ssNMR were conducted at the University of Windsor.
Department of Chemistry and Biochemistry in the laboratory of Prof. R. Schurko, in collaboration between C. Mottillo and C. O’Keefe, during a one-week research trip. The Retsch MM400 shaker mill used for preparing samples to be monitored by ex situ ssNMR was sent to and from McGill University and the University of Windsor by courier.

### 8.4.2.1 $^{13}$C ssNMR Experimental Parameters

The $^{13}$C ssNMR experiments were conducted on a Chemagnetics 4mm HX T3 Style MAS probe using the variable-amplitude cross polarization (VACP) experiment under MAS conditions ($\nu_{\text{rot}} = 10$ kHz). Optimized contact times and recycle delays were used and are shown below. The $\pi/2(1\text{H})$ pulse width was 7.4 $\mu$s. The spinning locking powers were 34 kHz for $^1\text{H}$ and 24 kHz for $^{13}\text{C}$. 46 kHz of TPPM decoupling was used. 8k of points were collected with a dwell time of 16.67 $\mu$s (spectral width of 60 kHz). Spectra were referenced to TMS using adamantane as a secondary reference ($\delta_{\text{iso}} = 38.57$ ppm).

<table>
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<th>Recycle delay (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{dia-Cd(Im)_2}$</td>
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<td>5</td>
</tr>
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<td>$\text{yqt1-Cd(MeIm)_2}$</td>
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<td>5</td>
</tr>
<tr>
<td>$\text{dia-Cd(MeIm)_2\cdot HMeIm}$</td>
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<td>5</td>
</tr>
<tr>
<td>$\text{Cd(Im)_6CO}_3\cdot 3\text{H}_2\text{O}$</td>
<td>2</td>
<td>7.5</td>
</tr>
</tbody>
</table>

### 8.4.2.2 $^{111}$Cd ssNMR Experimental Parameters

$^{111}$Cd ssNMR experiments were conducted on a Chemagnetics 4mm HX T3 Style MAS probe using the variable-amplitude cross polarization (VACP) experiment under both MAS ($\nu_{\text{rot}} = 5$ kHz) and static conditions. Optimized contact times and recycle delays were used and are shown below. The $\pi/2(1\text{H})$ pulse width was 3.5 $\mu$s. The spinning locking powers were 52 kHz for $^1\text{H}$ and 42 kHz for $^{111}\text{Cd}$. 58 kHz of TPPM decoupling was used. 2k of points were collected with a dwell time of 20 $\mu$s (spectral width of 50 kHz). Spectra were referenced to Cd(ClO$_4$)$_2\cdot 6\text{H}_2\text{O}$ using Cd(NO$_3$)$_2\cdot 4\text{H}_2\text{O}$ as a secondary reference ($\delta_{\text{iso}} = -100$ ppm).

<table>
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<td>$\text{yqt1-Cd(MeIm)_2}$</td>
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<td>$\text{dia-Cd(MeIm)_2\cdot HMeIm}$</td>
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<td>5</td>
</tr>
<tr>
<td>$\text{Cd(Im)_6CO}_3\cdot 3\text{H}_2\text{O}$</td>
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<td>7.5</td>
</tr>
<tr>
<td>Reaction Monitoring</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

### 8.4.2.3 $^1$H ssNMR Experimental Parameters
Experiments were conducted on a Chemagnetics 4mm HX T3 Style MAS probe. A one pulse experiment under MAS ($\nu_{\text{rot}} = 16 \text{ kHz}$) with calibrated $\pi/2$ pulse widths of 3.56 $\mu$s (70 kHz of rf) was used. 4k of points were collected with a 6.67 $\mu$s dwell (150 kHz spectral width). The recycle delays were calibrated for each sample and are shown below. Spectra were referenced to TMS using adamantane as a secondary reference ($\delta_{\text{iso}} = 1.87 \text{ ppm}$).

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<th>Compound</th>
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<td>$\text{dia-Cd(Im)}_2$</td>
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</tr>
<tr>
<td>$\text{yqt1-Cd(MeIm)}_2$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{dia-Cd(MeIm)}_2 \cdot \text{HMeIm}$</td>
<td>5</td>
</tr>
<tr>
<td>$\text{Cd(Im)}_6\text{CO}_3 \cdot 3\text{H}_2\text{O}$</td>
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<td>Reaction Monitoring</td>
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</tbody>
</table>

8.5 Experimental details for Chapter 6: Ex-situ monitoring of accelerated aging synthesis of Cd-based ZIFs by powder diffraction and $^{111}\text{Cd}$ solid-state NMR

8.5.1 Synthesis of supramolecular imidazolium frameworks

8.5.1.1 2-ethylimidazolium sulfate ((H$_2$EtIm)$_2$SO$_4$):

A sample of 2-ethylimidazole (16.0 mmol, 1.53 g) was dissolved in EtOH. Concentrated H$_2$SO$_4$ (8.1 mmol, 0.44 mL) was added dropwise. A 10 mL aliquot of the reaction mixture was dried under rotary evaporation, resulting in a viscous liquid. The formation of large, highly deliquescent diffraction-quality crystals was observed after 24 months in a closed vial. The resulting crystals were too deliquescent to be handled in air. As a result, they were unsuitable for general solid-state analysis, and needed to be encased in epoxy glue for the duration of the diffraction experiment.

8.5.1.2 Benzimidazolium sulfate ((H$_2$BIm)$_2$SO$_4$):

Benzimidazole (8.0 mmol, 0.95 g) was dissolved in acetonitrile. Concentrated H$_2$SO$_4$ (4.1 mmol, 0.2239 mL) was added dropwise, inducing the formation of a white precipitate. The product was filtered, washed three times with acetonitrile, dried over vacuum filtration, and analyzed by PXRD, FTIR-ATR, TGA, $^{15}$N solid-state CP-MAS NMR, and N$_2$ Brunauer-Emmett-Teller sorption measurements. Diffraction-quality crystals were obtained by recrystallizing the product from hot MeOH by cooling.

8.5.1.3 2-methylbenzimidazolium sulfate ((H$_2$MeBIm)$_2$SO$_4$):

A sample of 2-methylbenzimidazole (4.0 mmol, 0.53 g) was dissolved in acetonitrile. Concentrated H$_2$SO$_4$ (2.1 mmol, 0.11 mL) was added dropwise, inducing the formation of a
white precipitate. The product was filtered, washed three times with acetonitrile, and dried over vacuum filtration. Diffraction quality crystals were obtained by recrystallizing the product from DMF upon cooling. These crystals were gently crushed in a mortar and pestle and analyzed by PXRD, FTIR-ATR, and TGA.

8.5.1.4 2-phenylbenzimidazolium sulfate ethanol solvate ((H2PhBIm)2SO4∙EtOH):

A sample of 2-phenylbenzimidazole (4.0 mmol, 0.78 g) was dissolved in acetonitrile. Concentrated H2SO4 (2.1 mmol, 0.11 mL) was added dropwise, inducing the formation of a beige precipitate. The product was filtered, washed three times with acetonitrile, and dried over vacuum filtration. Diffraction-quality crystals were obtained by recrystallization from EtOH upon cooling. The crystals of rapidly decomposed upon removal from their mother liquor, making them unsuitable for further solid-state analysis. X-ray diffraction analysis of ten crystals selected from the same crystallization vial revealed the same unit cell parameters as the reported structure.

8.5.1.5 2-phenylbenzimidazolium sulfate methanol solvate ((H2PhBIm)2SO4∙2MeOH):

A sample of 2-phenylbenzimidazole (4.0 mmol, 0.78 g) was dissolved in acetonitrile. Concentrated H2SO4 (2.1 mmol, 0.11 mL) was added dropwise, inducing the formation of a beige precipitate. The product was filtered, washed three times with acetonitrile, and dried over vacuum filtration. Diffraction quality crystals were obtained by recrystallization from MeOH upon cooling. The crystals of rapidly decomposed upon removal from their mother liquor, making them unsuitable for further solid-state analysis. Single crystal X-ray diffraction analysis of ten crystals selected from the same vial revealed they possessed the same unit cell parameters and Bravais lattice as the reported structure.

8.5.1.6 Benzimidazolium selenate ((H2BIm)2SeO4):

Benzimidazole (4.0 mmol, 0.47 g) was dissolved in acetonitrile. Selenic acid‡ (2.1 mmol, 0.51 ml) was added dropwise to form a white precipitate. The precipitate was filtered over vacuum and washed three times with acetonitrile. The product was analyzed by PXRD, FTIR-ATR, TGA, and 15N solid-state CP-MAS NMR. Diffraction-quality crystals were obtained by recrystallizing from MeOH upon cooling.

‡ Heat should be avoided in the synthesis and recrystallization of selenate salts, due to potential reduction of the selenate anion.
8.5.1.7 2-methylbenzimidazolium selenate methanol solvate hemihydrate 

\((\text{H}_2\text{MeBIm})_2\text{SeO}_4\cdot\text{MeOH} \cdot 0.5\text{H}_2\text{O})\):

A sample of 2-methylbenzimidazole (4.0 mmol, 0.53 g) was dissolved in MeOH. Selenic acid (2.1 mmol, 0.52 ml) was added dropwise, after which the addition of adequate amounts of acetonitrile induced the precipitation of a white solid. The product was filtered, washed three times with acetonitrile, and dried over vacuum. Diffraction-quality crystals were obtained by recrystallization from MeOH and acetone upon cooling, crushed, and subsequently analyzed by PXRD while still in their mother liquor. The crystals decomposed upon removal from their mother liquor, making them unsuitable for further solid-state analysis. X-ray diffraction analysis of ten crystals selected from the same vial revealed they possessed the same unit cell parameters as the reported structure.

8.5.1.8 2-phenylbenzimidazolium selenate \((\text{H}_2\text{PhBIm})_2\text{SeO}_4)\):

A sample of 2-phenylbenzimidazole (4.0 mmol, 0.78 g) was dissolved in MeOH. Selenic acid (2.1 mmol, 0.52 ml) was added dropwise, after which the addition of adequate amounts of acetonitrile induced the precipitation of a white solid. The product was filtered, washed three times with acetonitrile, and dried over vacuum. Diffraction-quality crystals were obtained by recrystallization from DMSO upon cooling. Crystals were crushed in their mother liquor by mortar and pestle and analyzed by PXRD. They decomposed upon removal from their mother liquor, making them unsuitable for further solid-state analysis. X-ray diffraction of ten crystals selected from the same vial revealed they possessed the same unit cell parameters and Bravais lattice as the reported structure.

8.5.1.9 2-phenylbenzimidazolium selenate methanol solvate \((\text{H}_2\text{PhBIm})_2\text{SeO}_4\cdot2\text{MeOH})\):

A sample of 2-phenylbenzimidazole (4.0 mmol, 0.7769 g) was dissolved in MeOH. Selenic acid (2.1 mmol, 0.52 ml) was added dropwise, after which the addition of adequate amounts of acetonitrile induced the precipitation of a white solid. The product was filtered, washed three times with acetonitrile, and dried over vacuum. Diffraction-quality crystals were obtained by recrystallization from MeOH upon cooling. Crystals were crushed in their mother liquor by mortar and pestle and analyzed by PXRD. They decomposed upon removal from their mother liquor, making them unsuitable for further solid-state analysis. X-ray diffraction analysis of ten crystals selected from the same vial revealed they possessed same unit cell parameters and Bravais lattice as the reported structure.
8.6 Experimental details for Chapter 7: Reliable design and self-assembly of squarate-based supramolecular imidazolium frameworks

8.6.1 Synthesis of squarate-based supramolecular imidazolium frameworks

8.6.1.1 Imidazolium squarate ((H₂Im)₂sq):

Imidazole (4.0 mmol, 0.27 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂Im)₂sq was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from MeOH solution upon evaporation.

8.6.1.2 2-methylimidazolium squarate ((H₂MeIm)₂sq):

A sample of 2-methylimidazole (4.0 mmol, 0.33 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the acetonitrile solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂MeIm)₂sq was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from hot EtOH solution by cooling.

8.6.1.3 2-ethylimidazolium squarate ((H₂EtIm)₂sq):

The reactant 2-ethylimidazole (4.0 mmol, 0.39 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂EtIm)₂sq was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from EtOH solution by evaporation.

8.6.1.4 2-isopropylimidazolium squarate ((H₂-iPrIm)₂sq):

Solid 2-isopropylimidazole (4.0 mmol, 0.44 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂-iPrIm)₂sq was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from MeOH solution by evaporation.
8.6.1.5 2-phenylimidazolium squarate hydrate ((H₂PhIm)₂sq·H₂O):

A sample of 2-phenylimidazole (4.0 mmol, 0.58 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂PhIm)₂sq·H₂O was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from i-PrOH solution by evaporation.

8.6.1.6 Benzimidazolium squarate ((H₂Blm)₂sq):

Benzimidazole (4.0 mmol, 0.47 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂Blm)₂sq was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from aqueous solution by evaporation.

8.6.1.7 2-methylbenzimidazolium squarate ((H₂MeBlm)₂sq):

A sample of 2-methylbenzimidazole (4.0 mmol, 0.53 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂MeBlm)₂sq was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from hot MeOH solution by cooling.

8.6.1.8 2-phenylbenzimidazolium squarate hydrate ((H₂PhBlm)₂sq·H₂O):

Solid 2-phenylbenzimidazole (4.0 mmol, 0.78 g) was dissolved in acetonitrile. Squaric acid (2.1 mmol, 0.23 g) was dissolved in H₂O and added to the imidazole solution, resulting in the immediate formation of a white precipitate. The product was filtered over vacuum, washed three times with acetonitrile, dried, and stored under vacuum. (H₂PhBlm)₂sq·H₂O was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from MeOH solution by evaporation.

8.6.1.9 2-phenylbenzimidazolium squarate ((H₂PhBlm)₂sq) Polymorph 1:
A sample of \((\text{H}_2\text{PhBIm})_2\text{sq}\cdot\text{H}_2\text{O}\) synthesized from solution was heated to 150 °C for 4 hours, and stored under vacuum. \((\text{H}_2\text{PhBIm})_2\text{sq}\) was analyzed by PXRD, TGA, FTIR-ATR, and natural abundance solid-state \(^{15}\text{N}\) CP-MAS NMR.

8.6.1.10 2-phenylbenzimidazolium squarate \((\text{H}_2\text{PhBIm})_2\text{sq}\) Polymorph 2:

Solid 2-phenylbenzimidazole (4.0 mmol, 0.78 g) was milled with 2.1 mmol (0.23 g) squaric acid in the presence of 50 μL \(n\)-BuOH in a 10 mL stainless steel jar with one 7 mm diameter (1.3 g) stainless steel ball using a Retsch MM400 shaker mill set at a frequency of 29.5 Hz for 30 minutes. The white crystalline product was stored under vacuum. \((\text{H}_2\text{PhBIm})_2\text{sq}\) was analyzed by PXRD, TGA, and FTIR-ATR. Crystals for single crystal X-ray diffraction experiments were obtained from \(n\)-BuOH upon cooling.

8.7 General instrumental analysis

8.7.1 Powder X-ray diffraction (PXRD)

Typical powder patterns were collected on either a Bruker D2 Phaser benchtop powder diffractometer or a Bruker D8 Discovery diffractometer. Prof. D. Scott Bohle from McGill University and Prof. Xavier Ottenwaelder from Concordia University are acknowledged for the gracious use of their single crystal diffractometers.

8.7.1.1 Bruker D2 Phaser benchtop diffractometer

Powder patterns were collected using a Cu-K\(\alpha\) (\(\lambda = 1.54056 \text{ Å}\)) source operating at a power setting of 30 kV and 10 mA, in the range of 4° to 50° for samples containing CoO and 4° to 40° for all others. The lower discriminal of the detector was increased from 0.110 V to 0.200 V to mitigate X-ray fluorescence from Co-based samples, which exhibits X-ray fluorescence under Cu radiation. Analysis of PXRD patterns was conducted using Panalytical X’Pert Highscore software.

8.7.1.2 Bruker D8 Discovery diffractometer

Data collection was achieved using a Cu-K\(\alpha\) (\(\lambda = 1.54056 \text{ Å}\)) source, with the X-ray tube operating at a power setting of 40 kV and 40 mA. Patterns were collected from 4° to 50° for samples containing CoO and 4° to 40° for all others. Analysis of PXRD patterns was conducted using Panalytical X’Pert Highscore software.

8.7.2 Single crystal X-ray diffraction (XRD)

Single crystal X-ray diffraction data was collected on a Bruker APEX II diffractometer with MoK\(\alpha\) (\(\lambda=0.71073 \text{ Å}\)) source and CCD detector at room 293 K, 150 K, or 100 K. Low
temperature was achieved using liquid N₂ stream. The structures were determined by least squares refinement against F² using SHELX-2014 software running under the WinGX user interface. All non-hydrogen atoms were refined anisotropically. Placement of hydrogen atoms was modeled using idealized positions based on the hybridization of the parent atom. Position of hydrogen atoms connected to oxygen atoms were calculated by determining the most ideal position based on neighbouring hydrogen-bond acceptors.

8.7.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

8.7.3.1 Solution NMR

Solution ¹H and ¹³C NMR spectra were collected in D₂O on a 300 MHz Varian Mercury spectrometer equipped with an autosampler and a 5 mm AutoSW PFG ¹H/X[¹⁵N-³¹P] probe.

8.7.3.2 Solid-state ¹³C NMR (ssNMR)

Solid-state ¹³C cross-polarization magic-angle spinning (CP-MAS) NMR spectra were collected on a 400 MHz Varian VNMR equipped with a 7.5 mm CP-MAS probe at a spin rate of 5 KHz. All spectra were collected with a contact time of 2 to 5 ms and recycle delay of 2 s. Spectra were referenced to the carbonyl chemical shift of glycine at 176.46 ppm, with respect to tetramethylsilane.

8.7.3.3 Solid-state ¹⁵N NMR (ssNMR)

Natural abundance CP-MAS ¹⁵N ssNMR spectra were collected on a 400 MHz Varian VNMR using a 7.5 mm or 4 mm MAS probe. All spectra were collected at a spin rate of 5 kHz with a contact time of 2 ms and a recycle delay of 2 to 5 s, depending on the sample. Spectra were referenced to the chemical shift of glycine at -347.7 ppm, with respect to nitromethane. NMR spectra were analysed using MestreNova software.

8.7.4 Fourier transform infrared attenuated total reflection (FTIR-ATR)

All FTIR-ATR spectra were collected in the solid state either using a Perkin Elmer Fourier Transform-Infrared Attenuated Total Reflection spectrometer or a Bruker Vertex 70 FTIR-ATR spectrometer in the range 400 cm⁻¹ to 4000 cm⁻¹. FTIR spectra were analysed using Bruker OPUS software.

8.7.5 Thermogravimetric analysis (TGA)

Thermograms were collected on either of these two instruments: a TA Instruments Q500 Thermogravimetric System with a Pt pan or a Mettler Toledo TGA/DSC 3+ with high-temperature furnace using an alumina pan. Samples were heated under dynamic atmosphere of
air or N₂ to an upper temperature limit ranging from 500°C to 900°C at a rate of 10 °C/min to 20 °C/min. The balance and purge flow were 40 mL/min and 60 mL/min respectively.

8.7.5.1 Thermal analysis of ZIFs synthesized by accelerated aging and conversion calculation

Thermal analysis of ZIF samples made by accelerated aging reactions was typically conducted after the samples were washed overnight in MeOH and evacuated overnight at 80 °C. TGA thermograms of ZIF samples were collected at a temperature range from 25 °C to 600 °C under dynamic atmosphere of air. Under these conditions, the residue of calcination consisted of ZnO, in the case of zinc-based ZIFs, and Co₃O₄ in the case of cobalt-based ZIFs. The percent conversion of ZnO or CoO in accelerated aging reactions was calculated from the percent residue remaining after complete calcination, according to the formulae:

\[
x = \frac{M_{\text{ZnO}}}{w_{\text{ZnO}}(M_{\text{ZIF}}-M_{\text{ZnO}})} - \frac{M_{\text{ZnO}}}{M_{\text{ZIF}}-M_{\text{ZnO}}}, \text{ for zinc-based ZIFs and}
\]

\[
x = \frac{M_{\text{CoO}}}{w_{\text{Co₃O₄}}(M_{\text{ZIF}}-M_{\text{CoO}})} - \frac{M_{\text{CoO}}}{M_{\text{ZIF}}-M_{\text{CoO}}}, \text{ for cobalt-based ZIFs.}
\]
Framework solids, which include metal-organic frameworks (MOFs) and molecular materials, are being extensively investigated for their potential use in a variety of industrial applications. The design of MOFs has been an area of particular interest, with enhanced porosity, functionality, and stability being pivotal to their use in the areas of gas storage, molecular separation, and catalysis. In addition to designing MOFs with improved functionality, developing sustainable routes to their synthesis has been highlighted as an important factor in the adoption of MOFs for industrial scale use. The current routes to synthesize MOFs being relatively low-yielding, energy-intensive and waste-generating, these impinge on the feasibility of producing MOFs on industrial scales due to the negative environmental impact and low cost-effectiveness. In addition, despite the abundance of research describing novel and well-studied MOFs, the long-term solid-state behaviour of such materials under variable conditions resembling their desired application environment is understudied.

This has highlighted the need for developing a methodology which would provide a more environmentally-friendly route for the synthesis of MOFs, as well as serve as a unique tool to study their behavior in the solid state. Inspired by previous literature describing the high-yielding solvent-free synthesis of zeolitic imidazolate frameworks, accelerated aging was devised as a milder, more atom-efficient, and less energy-intensive synthetic route for the synthesis of metal-organic materials. Building on previous work regarding the activation of metal oxides by slow reactivity in the presence of moisture, accelerated aging has been presented as a sustainable alternative for the synthesis of ZIFs. The diffusion-based self-assembly of porous three-dimensional ZIFs has been achieved from mild metal oxides entirely in the solid state, minimizing energy consumption and waste production, and resulting in water being the only byproduct. A series of ZIFs bearing differing porosities, metal centers, and ligands, were synthesized in near-quantitative yields, in a matter of days. As a result, accelerated aging provides a simple, solvent-free method for the synthesis of ZIFs, from low-cost starting materials. Further studies should involve the development of accelerated aging as a route to obtain ZIFs with higher functionality, including those bearing mixed linkers and reactive sites on which to do post-synthetic modification. Preliminary experiments have suggested that mixed-linker ZIFs incorporating both HEtIm and HMeIm can be synthesized by aging and adopt different topologies upon collapse depending on the ratio of linkers used. Additionally,
accelerated aging should be investigated as a method to synthesize ZIFs with modifiable functional groups (aldehyde, vinyl, ethynyl, -OH). Recent preliminary results have demonstrated that this is feasible with 2-vinylimidazole, and the post-synthetic modification of such functionalizable ZIFs should be attempted by aging through simple vapour-asisted organic reactions (eg. aldehyde-amine condensation). The synthesis of fluorescent ZIFs by \textit{in-situ} incorporation of BODIPY fluorophores was demonstrated in collaboration with the group of Prof. Gonzalo Cosa at McGill University. This project should be completed and the \textit{in-situ} incorporation of donor-acceptor pairs of fluorophores into ZIFs by accelerated aging should be investigated as an extension of this project.

The unprecedented reactivity of metal oxides, usually considered too insoluble and unreactive for conventional methods, was achieved using structure-templating salt additives. The selection of salt additives demonstrated that accelerated aging can enable the templated synthesis of various polymorphs of the same metal-imidazolate. In the process of investigating the role of salt-catalyst in accelerating aging reactions, it was discovered that ZIFs, previously thought to be highly stable, were prone to collapse in the presence of small amounts of such protic salts. A systematic investigation of this effect led to the conclusion that ZIF-8, as well as the RHO-Zn(EtIm)$_2$, readily collapse to their non-porous polymorphs within days of being exposed to humidity and salt additives. This discovery bears significant importance to the applicability of ZIFs, and highlights the need for further study despite previous reports of high ZIF stability under high-temperature, hydrothermal, and solvothermal conditions.

Accelerated aging, or simply aging, involves the exposure of solid reagents or materials to varying conditions of temperature, humidity, atmosphere and chemical additives. While the viability of accelerated aging as a synthetic method was demonstrated, the discovery of ZIF collapse emphasized the ability to observe surprising structural changes in ZIF materials subjected to aging conditions. Evaluating the viability of ZIFs for industrial use requires knowledge of their stability under dynamic conditions. For example, the use of ZIFs for sequestration of CO$_2$ from flue gas streams would subject the material to any combination of high temperatures, moisture, CO$_2$, as well as SO$_2$. Aging conditions were explored as a medium for evaluating the stability of ZIFs under conditions of moisture, mild temperature, and CO$_2$ gas. When subjected to moist CO$_2$, non-porous and porous ZIFs based on zinc, cadmium and cobalt, converted to complex imidazole-based carbonates. All ZIFs tested, except for the dense zni-
Zn(Im)_2, were unstable in CO₂ gas. These results call for further investigation of long-term MOF stability under different conditions of moisture, acidity, and atmosphere (CO₂, SO₂, NOₓ), as well as provide a powerful yet simplistic tool for determining their solid-state behaviour. Elucidating the structural or chemical variables leading to CO₂ (in)stability will enable the synthesis of ZIFs with greater resistance to environmental factors, and allow the design of more applicable metal-organic materials. The first structural investigation of the CO₂ degradation products of ZIF-8, ZIF-90, and RHO-Zn(EtIm)_2 is currently under way with the collaboration of Prof. Kenneth D. M. Harris from Cardiff University. Igor Huskić, a doctoral student in our group, is leading a project whereby the degradation of ZIF-8 in moist CO₂ has been observed, for the first time, by in situ PXRD. These preliminary results will provide the groundwork for an extensive analysis of the processes leading to the degradation of ZIF-8 in CO₂ and will assist in understanding why and how this degradation occurs for different ZIF structures.

The initial proof-of-principle investigation of accelerated aging focused on the synthetic design and thus, the synthesis of previously-described zinc- and cobalt(II)-based ZIFs was selected to optimize accelerated aging as a synthetic methodology. However, the relatively unknown nature of class of cadmium-based materials called CdIFs and the increased possibility of polymorphism rendered this system interesting to investigate by accelerated aging. Much like in the first accelerated aging studies, the synthesis of CdIFs from HIm, HMeIm, HEtIm using ammonium or xanthine salts resulted in the initial formation of open structures which rapidly converted to a previously known non-porous CdIF. In the case of HMeIm, however, the isolation of a new open CdIF of diamondoid topology was possible. The discovery of a new phase implies that accelerated aging processes are poorly understood at a fundamental level, and that determination of the factors governing the mechanisms and structure templating effects involved was necessary. While analytical methods such as powder X-ray diffraction were useful for phase identificaion, ¹¹¹Cd solid-state NMR was exploited as an analysis tool to monitor the progression of the Cd²⁺ coordination environment during CdIF synthesis. New, intermediate species of Cd²⁺ were observed by solid-state NMR where no change in the starting materials was observed by laboratory powder X-ray diffraction analysis. While the identity of these species is still unknown, it highlights the lack of understanding of accelerated aging mechanisms. Extensive solid-state analysis (PXRD, FITR-ATR, ssNMR, TGA, DSC) of the unknown phase observed in small quantities at the onset of aging reactions in the presence of NH₄NO₃ will be
conducted in order to elucidate its composition and structure. As a natural extension of the investigation into accelerated aging synthesis of CdIFs, PXRD and ssNMR will be used complimentarily to investigate the mechanosynthesis of CdIFs, again in collaboration with the group of Prof. Robert Schurko at the University of Windsor.

The development and design of MOFs and ZIFs has been fuelled by the node-and-linker approach strategy. The development of molecular framework materials has, however, been hindered by a lack of reliable design principles due to the relatively flexible nature of non-covalent interactions. With the goal of developing a robust strategy for the design of hydrogen-bonded frameworks, the node-and-linker approach was adapted for the synthesis of supramolecular imidazolium frameworks (SIFs), charged-inverted analogues of metal-azolate frameworks (MAFs). Employing sulfate, selenate, dichromate, and squarate nodes, a class of over 20 two- or three-dimensional open frameworks which are resistant to competing interactions by hydrogen-bond donating solvents was described. A robust method has been outlined for the synthesis of molecular frameworks, which can, in the future, be extended towards the design of porous hydrogen-bonded materials. This extension should include a research program targeting the synthesis of new SIFs with structural, topological, and chemical diversity. Namely, new in-house-made organic molecules such as 2-vinylimidazole, 2-ethynylimidazole, and 4-\((1\text{H}-\text{pyrrol-3-yl})\)-pyridin-1-ium will be investigated as linkers for SIFs incorporating \(\text{SO}_4^{2-}\), \(\text{SeO}_4^{2-}\), squarate, and dichromate nodes. Attempts to make novel SIFs with nodes of diverse sizes and charges (e.g. acetylene dicarboxylic acid, 2,5-dihydroxybenzoquinone, and deltic acid) have been initiated and should be pursued. The search for node-and-linker relationships leading to three-dimensional SIF structures is an important avenue for this project. Since the dichromate anion is thus far the only node which yielded a three-dimensional SIF, the synthesis of a set of dichromate SIFs utilizing diverse imidazolium linkers should be attempted in order to expand this new class of hydrogen-bonded materials. Investigating the role of hydrogen-bonded dimers as extended linkers in the formation of structurally diverse three-dimensional SIFs should also be included in future work on this project.
APPENDIX A
TABLES OF CRYSTALLOGRAPHIC DATA FOR CHAPTER 6

Table A1. General and crystallographic data for (H\textCaf)(HSO\textsubscript{4})

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C\textsubscript{8}H\textsubscript{12}N\textsubscript{4}O\textsubscript{6}S</td>
</tr>
<tr>
<td>(M_r)</td>
<td>292.27</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>(a/\AA)</td>
<td>6.406(1)</td>
</tr>
<tr>
<td>(b/\AA)</td>
<td>8.167(1)</td>
</tr>
<tr>
<td>(c/\AA)</td>
<td>23.311(4)</td>
</tr>
<tr>
<td>(V/\AA^3)</td>
<td>1219.6(3)</td>
</tr>
<tr>
<td>(T/K)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P\textsubscript{2}1\textsubscript{2}1\textsubscript{2}1</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK(_\alpha)</td>
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<td>(\mu/\text{mm}^{-1})</td>
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<tr>
<td>No. of reflections measured</td>
<td>13570</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2616</td>
</tr>
<tr>
<td>(R_{int})</td>
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<td>(R_I) (for (I &gt; 2\sigma(I)))</td>
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</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
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</tr>
<tr>
<td>(R_I) (all data)</td>
<td>0.0712</td>
</tr>
<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.1006</td>
</tr>
<tr>
<td>(S)</td>
<td>0.955</td>
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</table>

Table A2. Hydrogen bond parameters for (H\textCaf)HSO\textsubscript{4}

<table>
<thead>
<tr>
<th>Bond</th>
<th>D-H (\AA)</th>
<th>H--A (\AA)</th>
<th>D--A (\AA)</th>
<th>Angle (DHA) (\degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-H2--O6</td>
<td>0.86</td>
<td>2.02</td>
<td>2.804(7)</td>
<td>150.6</td>
</tr>
<tr>
<td>O4-H4A--O5 (a)</td>
<td>0.82</td>
<td>1.79</td>
<td>2.590(7)</td>
<td>163.3</td>
</tr>
</tbody>
</table>

Symmetry operator: \(a = -x+1, y-1/2, z+1/2\)
Table A3. General and crystallographic data for \((H_2\text{EtIm})_2\text{SO}_4\)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C(<em>{10}H</em>{16}N_4O_4S)</td>
</tr>
<tr>
<td>(M_r)</td>
<td>288.33</td>
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<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
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<tr>
<td>(a/\text{Å})</td>
<td>9.642(11)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>15.986(17)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>9.334(10)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>1437.11(3)</td>
</tr>
<tr>
<td>(T/\text{K})</td>
<td>293(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK(_{\alpha})</td>
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<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.241</td>
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<td>No. of reflections measured</td>
<td>7178</td>
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<tr>
<td>No. of independent reflections</td>
<td>1484</td>
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<tr>
<td>(R_{int})</td>
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<tr>
<td>(R_1) (for (I &gt; 2\sigma(I)))</td>
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</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
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<tr>
<td>(R_1) (all data)</td>
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<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.1499</td>
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<tr>
<td>(S)</td>
<td>1.081</td>
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</table>

Table A4. Hydrogen bond parameters for \((H_2\text{EtIm})_2\text{SO}_4\)

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1A--O2</td>
<td>0.88</td>
<td>1.79</td>
<td>2.659(4)</td>
<td>168.5</td>
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<tr>
<td>N2-H2A--O1\text{a}</td>
<td>0.88</td>
<td>1.81</td>
<td>2.668(3)</td>
<td>163.4</td>
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</table>

Symmetry operator: \(a = x-\frac{1}{2}, y-\frac{1}{2}, z\)
Table A5. General and crystallographic data for (H₂BIm)₂SO₄

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₁₄H₁₄N₄O₄S</th>
</tr>
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<tr>
<td>( M_r )</td>
<td>334.35</td>
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<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
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<td>( a/Å )</td>
<td>14.6766(8)</td>
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<tr>
<td>( b/Å )</td>
<td>18.8388(14)</td>
</tr>
<tr>
<td>( c/Å )</td>
<td>11.8862(7)</td>
</tr>
<tr>
<td>( V/Å³ )</td>
<td>3286.4(4)</td>
</tr>
<tr>
<td>( T/K )</td>
<td>293(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>Fdd2</td>
</tr>
<tr>
<td>( Z )</td>
<td>8</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
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<tr>
<td>( \mu/\text{mm}^{-1} )</td>
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<td>No. of reflections measured</td>
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<td>No. of independent reflections</td>
<td>1962</td>
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<td>( R_{int} )</td>
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<td>( R_1 ) (for ( I &gt; 2\sigma(I) ))</td>
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<td>0.0828</td>
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<td>( S )</td>
<td>1.069</td>
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Table A6. Hydrogen bond parameters for (H₂BIm)₂SO₄

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<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-H2--O1_a</td>
<td>0.86</td>
<td>1.79</td>
<td>2.6397(19)</td>
<td>172.0</td>
</tr>
<tr>
<td>N1-H1A--O2</td>
<td>0.86</td>
<td>1.83</td>
<td>2.665(2)</td>
<td>164.1</td>
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</table>

Symmetry operator: a = -x, -y-1/2, z-1/2
Table A7. General and crystallographic data for (H₂MeBIm)₂SO₄

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<tr>
<th></th>
<th>C₁₆H₁₈N₄O₄S</th>
<th>362.40</th>
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<td>Formula</td>
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<td>Crystal system</td>
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<td>a/Å</td>
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<tr>
<td>b/Å</td>
<td>7.4436(11)</td>
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<tr>
<td>c/Å</td>
<td>14.051(2)</td>
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<tr>
<td>V/Å</td>
<td>1754.5(4)</td>
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</tr>
<tr>
<td>T/K</td>
<td>293(2)</td>
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<tr>
<td>Space group</td>
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<td>Z</td>
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<td>Radiation type</td>
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<td>R₁ (all data)</td>
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<td>wR(F²) (all data)</td>
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Table A8. Hydrogen bond parameters for (H₂MeBIm)₂SO₄

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<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
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</thead>
<tbody>
<tr>
<td>N1-H1--O1</td>
<td>0.88</td>
<td>1.82</td>
<td>2.669(2)</td>
<td>161.2</td>
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<tr>
<td>N2-H2--O2</td>
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<td>1.81</td>
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Symmetry operator: a = -x+1, y, -z+1/2, b = x, -y, z+1/2
Table A9. General and crystallographic data for (H$_2$PhBIm)$_2$SO$_4$·EtOH

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<tr>
<td>Formula</td>
<td>C$<em>{26}$H$</em>{22}$N$_4$O$_4$S·C$_2$H$_6$O</td>
</tr>
<tr>
<td>$M_r$</td>
<td>532.60</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>16.620(4)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>8.218(2)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>19.159(5)</td>
</tr>
<tr>
<td>$V$/Å</td>
<td>2616.8(11)</td>
</tr>
<tr>
<td>$T$/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbcn</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK$_\alpha$</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>0.170</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>23489</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2314</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.1162</td>
</tr>
<tr>
<td>$R_1$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.1023</td>
</tr>
<tr>
<td>$wR(F^2)$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.1497</td>
</tr>
<tr>
<td>$R_1$ (all data)</td>
<td>0.2031</td>
</tr>
<tr>
<td>$wR(F^2)$ (all data)</td>
<td>0.2235</td>
</tr>
<tr>
<td>$S$</td>
<td>1.095</td>
</tr>
</tbody>
</table>

Table A10. Hydrogen bond parameters for (H$_2$PhBIm)$_2$SO$_4$·2EtOH

<table>
<thead>
<tr>
<th>Bond</th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O1$_b$</td>
<td>0.86</td>
<td>1.82</td>
<td>2.669(10)</td>
<td>170.4</td>
</tr>
<tr>
<td>N2-H2--O2$_a$</td>
<td>0.86</td>
<td>1.70</td>
<td>2.514(12)</td>
<td>156.5</td>
</tr>
<tr>
<td>N1A-H1A--O2$_a$</td>
<td>0.86</td>
<td>1.77</td>
<td>2.609(11)</td>
<td>164.3</td>
</tr>
<tr>
<td>N2A-H2A--O1$_b$</td>
<td>0.86</td>
<td>1.80</td>
<td>2.651(9)</td>
<td>169.3</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x, -y+1, z+1/2, b = x+1/2, -y+1/2, -z
Table A12. General and crystallographic data for \((H_2\text{PhBIm})_2\text{SO}_4 \cdot 2\text{MeOH}\)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(C_{26}H_{22}N_4O_4S \cdot 2(C_2H_4O))</td>
</tr>
<tr>
<td>(M_r)</td>
<td>550.62</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>16.933(4)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>8.0337(18)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>19.688(4)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>2678.2(10)</td>
</tr>
<tr>
<td>(T/\text{K})</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbcn</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK(\alpha)</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.171</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>24911</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2444</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.1050</td>
</tr>
<tr>
<td>(R_1) (for (I &gt; 2\sigma(I)))</td>
<td>0.0650</td>
</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
<td>0.1590</td>
</tr>
<tr>
<td>(R_1) (all data)</td>
<td>0.1148</td>
</tr>
<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.1915</td>
</tr>
<tr>
<td>(S)</td>
<td>1.045</td>
</tr>
</tbody>
</table>

Table A13. Hydrogen bond parameters for \((H_2\text{PhBIm})_2\text{SO}_4 \cdot 2\text{MeOH}\)

<table>
<thead>
<tr>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.84</td>
<td>1.98</td>
<td>2.814(4)</td>
<td>174.4</td>
</tr>
<tr>
<td>0.88</td>
<td>1.79</td>
<td>2.635(6)</td>
<td>161.3</td>
</tr>
<tr>
<td>0.88</td>
<td>1.78</td>
<td>2.652(5)</td>
<td>169.2</td>
</tr>
<tr>
<td>0.88</td>
<td>1.84</td>
<td>2.710(7)</td>
<td>169.2</td>
</tr>
<tr>
<td>0.88</td>
<td>1.78</td>
<td>2.641(7)</td>
<td>167.3</td>
</tr>
</tbody>
</table>

Symmetry operator: \(a = -x+1/2, y-1/2, z\)
Table A14. General and crystallographic data for (H₂BIm)₂SeO₄

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₁₄H₁₄N₄O₄Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_r )</td>
<td>381.25</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>( a/\text{Å} )</td>
<td>18.5107(19)</td>
</tr>
<tr>
<td>( b/\text{Å} )</td>
<td>18.5107(19)</td>
</tr>
<tr>
<td>( c/\text{Å} )</td>
<td>18.953(2)</td>
</tr>
<tr>
<td>( V/\text{Å}³ )</td>
<td>6494.2(12)</td>
</tr>
<tr>
<td>( T/\text{K} )</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P4₁2₁2₁</td>
</tr>
<tr>
<td>( Z )</td>
<td>16</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK( \alpha )</td>
</tr>
<tr>
<td>( \mu/\text{mm}^{-1} )</td>
<td>2.338</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>68473</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>6722</td>
</tr>
<tr>
<td>( R_{int} )</td>
<td>0.0679</td>
</tr>
<tr>
<td>( R_1 ) (for ( I &gt; 2\sigma(I) ))</td>
<td>0.0290</td>
</tr>
<tr>
<td>( wR(F^2) ) (for ( I &gt; 2\sigma(I) ))</td>
<td>0.0605</td>
</tr>
<tr>
<td>( R_1 ) (all data)</td>
<td>0.0449</td>
</tr>
<tr>
<td>( wR(F^2) ) (all data)</td>
<td>0.0663</td>
</tr>
<tr>
<td>( S )</td>
<td>1.034</td>
</tr>
</tbody>
</table>

Table A15. Hydrogen bond parameters for (H₂BIm)₂SeO₄

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1A--O8_a</td>
<td>0.88</td>
<td>1.82</td>
<td>2.677(4)</td>
<td>162.8</td>
</tr>
<tr>
<td>N2-H2--O1</td>
<td>0.88</td>
<td>1.78</td>
<td>2.649(4)</td>
<td>166.9</td>
</tr>
<tr>
<td>N1A-H9--O5_b</td>
<td>0.88</td>
<td>1.81</td>
<td>2.674(4)</td>
<td>167.5</td>
</tr>
<tr>
<td>N2A-H10--O4_c</td>
<td>0.88</td>
<td>1.78</td>
<td>2.655(4)</td>
<td>176.3</td>
</tr>
<tr>
<td>N1B-H1BA--O6_d</td>
<td>0.88</td>
<td>1.81</td>
<td>2.675(4)</td>
<td>165.6</td>
</tr>
<tr>
<td>N2B-H2B--O3</td>
<td>0.88</td>
<td>1.80</td>
<td>2.671(4)</td>
<td>168.8</td>
</tr>
<tr>
<td>N1C-H1CA--O2_e</td>
<td>0.88</td>
<td>1.80</td>
<td>2.673(4)</td>
<td>173.3</td>
</tr>
<tr>
<td>N2C-H2C--O7_c</td>
<td>0.88</td>
<td>1.79</td>
<td>2.666(5)</td>
<td>170.1</td>
</tr>
</tbody>
</table>

Symmetry operator: a = -y, -x, -z+1/2, b = y, x, -z, c = -y+1/2, x+1/2, z-1/4, d = x+1/2, -y+1/2, -z+1/4, e = x+1/2, -y+3/2, -z+1/4
Table A16. General and crystallographic data for (H₂MeBIm)₂SeO₄·MeOH·0.5H₂O

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₆H₁₈N₄O₄Se·CH₄O·0.5(H₂O)</td>
</tr>
<tr>
<td>$M_r$</td>
<td>450.35</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>25.917(2)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>8.7717(7)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>17.5915(14)</td>
</tr>
<tr>
<td>$V$/Å</td>
<td>3933.8(5)</td>
</tr>
<tr>
<td>$T$/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>C₂/c</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>$\mu$/mm⁻¹</td>
<td>1.948</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>22811</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>4797</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.0499</td>
</tr>
<tr>
<td>$R_1$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.0387</td>
</tr>
<tr>
<td>$wR(F^2)$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.0850</td>
</tr>
<tr>
<td>$R_1$ (all data)</td>
<td>0.0625</td>
</tr>
<tr>
<td>$wR(F^2)$ (all data)</td>
<td>0.0936</td>
</tr>
<tr>
<td>$S$</td>
<td>1.0458</td>
</tr>
</tbody>
</table>

Table A17. Hydrogen bond parameters for (H₂MeBIm)₂SeO₄·MeOH·0.5H₂O

<table>
<thead>
<tr>
<th>Bond</th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1-H5A--O2_a</td>
<td>0.976(2)</td>
<td>1.902(2)</td>
<td>2.827(3)</td>
<td>157.27(10)</td>
</tr>
<tr>
<td>O6-H6A--O1_b</td>
<td>0.84</td>
<td>1.97</td>
<td>2.801(4)</td>
<td>172.8</td>
</tr>
<tr>
<td>O6-H6A--O1B_b</td>
<td>0.84</td>
<td>2.32</td>
<td>3.04(3)</td>
<td>144.4</td>
</tr>
<tr>
<td>N1-H1--O3_c</td>
<td>0.88</td>
<td>1.80</td>
<td>2.662(3)</td>
<td>166.9</td>
</tr>
<tr>
<td>N2-H2--O2B</td>
<td>0.88</td>
<td>1.81</td>
<td>2.65(3)</td>
<td>159.0</td>
</tr>
<tr>
<td>N2-H2--O1</td>
<td>0.88</td>
<td>2.02</td>
<td>2.835(3)</td>
<td>154.4</td>
</tr>
<tr>
<td>N3-H3--O4_d</td>
<td>0.88</td>
<td>1.80</td>
<td>2.667(3)</td>
<td>169.0</td>
</tr>
<tr>
<td>N3-H3--O4B_d</td>
<td>0.88</td>
<td>1.91</td>
<td>2.76(3)</td>
<td>161.6</td>
</tr>
<tr>
<td>N4-H4A--O2_a</td>
<td>0.88</td>
<td>1.79</td>
<td>2.669(3)</td>
<td>177.2</td>
</tr>
<tr>
<td>N4-H4A--O1B_a</td>
<td>0.88</td>
<td>2.08</td>
<td>2.77(3)</td>
<td>135.0</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x, y+1, z, b = -x+1/2,y+1/2, z-1/2, c = x, -y-1, z-1/2, d = x, y+2, z
### Table A18. General and crystallographic data for (H₂PhBIm)₂SeO₄

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₂₆H₂₂N₄O₄Se</td>
</tr>
<tr>
<td>$M_r$</td>
<td>533.44</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>9.611(4)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>10.852(4)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>11.918(5)</td>
</tr>
<tr>
<td>$V$/Å</td>
<td>1175.2(8)</td>
</tr>
<tr>
<td>$T$/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>$\mu$/mm⁻¹</td>
<td>1.639</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>12318</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>4683</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.0883</td>
</tr>
<tr>
<td>$R_1$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.0631</td>
</tr>
<tr>
<td>$wR(F^2)$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.1337</td>
</tr>
<tr>
<td>$R_1$ (all data)</td>
<td>0.1047</td>
</tr>
<tr>
<td>$wR(F^2)$ (all data)</td>
<td>0.1514</td>
</tr>
<tr>
<td>$S$</td>
<td>1.003</td>
</tr>
</tbody>
</table>

### Table A19. Hydrogen bond parameters for (H₂PhBIm)₂SeO₄

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O3_b</td>
<td>0.88</td>
<td>1.74</td>
<td>2.604(5)</td>
<td>166.5</td>
</tr>
<tr>
<td>N2-H2--O2</td>
<td>0.88</td>
<td>1.81</td>
<td>2.672(5)</td>
<td>166.2</td>
</tr>
<tr>
<td>N1A-H1A--O1</td>
<td>0.88</td>
<td>1.74</td>
<td>2.578(9)</td>
<td>159.2</td>
</tr>
<tr>
<td>N2A-H2A--O1_a</td>
<td>0.88</td>
<td>1.75</td>
<td>2.622(9)</td>
<td>171.1</td>
</tr>
<tr>
<td>N1B-H1B--O4_c</td>
<td>0.88</td>
<td>1.77</td>
<td>2.633(10)</td>
<td>164.6</td>
</tr>
<tr>
<td>N2B-H2B--O4_b</td>
<td>0.88</td>
<td>1.81</td>
<td>2.671(10)</td>
<td>165.9</td>
</tr>
</tbody>
</table>

Symmetry operator: a = -x+3,-y,-z+1, b = x-1, y, z, c = -x+3, -y+1, -z
Table A20. General and crystallographic data for (H₂PhBIₘ)₂SeO₄·2MeOH

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₂₆H₂₆N₄O₄Se·2(CH₄O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_r)</td>
<td>597.52</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>17.3442(12)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>8.0712(6)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>19.5768(14)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>2740.5(3)</td>
</tr>
<tr>
<td>(T/\text{K})</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>Pbcn</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>1.419</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>27923</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2818</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0653</td>
</tr>
<tr>
<td>(R_1) (for (I &gt; 2\sigma(I)))</td>
<td>0.0376</td>
</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
<td>0.0772</td>
</tr>
<tr>
<td>(R_1) (all data)</td>
<td>0.0619</td>
</tr>
<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.0866</td>
</tr>
<tr>
<td>(S)</td>
<td>1.043</td>
</tr>
</tbody>
</table>

Table A21. Hydrogen bond parameters for (H₂PhBIₘ)₂SeO₄·2MeOH

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O2 a</td>
<td>0.86</td>
<td>1.86</td>
<td>2.708(6)</td>
<td>170.5</td>
</tr>
<tr>
<td>N2-H2--O1 b</td>
<td>0.86</td>
<td>1.79</td>
<td>2.637(5)</td>
<td>166.9</td>
</tr>
<tr>
<td>N2A-H2A--O2 a</td>
<td>0.86</td>
<td>1.79</td>
<td>2.642(4)</td>
<td>169.4</td>
</tr>
<tr>
<td>N1A-H1A--O1 b</td>
<td>0.86</td>
<td>1.83</td>
<td>2.662(4)</td>
<td>161.1</td>
</tr>
<tr>
<td>O3-H2O--O1 c</td>
<td>1.068(2)</td>
<td>1.754(2)</td>
<td>2.808(3)</td>
<td>167.72(18)</td>
</tr>
</tbody>
</table>

Symmetry operator: a = 2-x, 1-y, -z, b = -x+3,-y,-z+1, c = x-1, y, z
APPENDIX B
TABLES OF CRYSTALLOGRAPHIC DATA FOR CHAPTER 7

Table B1. General and crystallographic data for \((\text{H}_2\text{Im})_2\text{sq}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>(\text{C}<em>{10}\text{H}</em>{10}\text{N}_4\text{O}_4)</td>
</tr>
<tr>
<td>(M_r)</td>
<td>250.22</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>4.7754(16)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>8.680(3)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>13.985(5)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>571.4(3)</td>
</tr>
<tr>
<td>(T/K)</td>
<td>293(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK(_\alpha)</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.115</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>6848</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2622</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0733</td>
</tr>
<tr>
<td>(R_1) (for (I &gt; 2\sigma(I)))</td>
<td>0.0567</td>
</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
<td>0.1229</td>
</tr>
<tr>
<td>(R_1) (all data)</td>
<td>0.1087</td>
</tr>
<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.1484</td>
</tr>
<tr>
<td>(S)</td>
<td>0.968</td>
</tr>
</tbody>
</table>

Table B2. Hydrogen bond parameters for \((\text{H}_2\text{Im})_2\text{sq}\)

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O4 a</td>
<td>0.86</td>
<td>1.81</td>
<td>2.664(3)</td>
<td>176.2</td>
</tr>
<tr>
<td>N2-H2--O2 b</td>
<td>0.86</td>
<td>1.81</td>
<td>2.667(3)</td>
<td>178.8</td>
</tr>
<tr>
<td>N3-H3--O1</td>
<td>0.86</td>
<td>1.81</td>
<td>2.661(3)</td>
<td>177.2</td>
</tr>
<tr>
<td>N4-H4--O3</td>
<td>0.86</td>
<td>1.81</td>
<td>2.668(3)</td>
<td>177.4</td>
</tr>
</tbody>
</table>

Symmetry operator: \(a = x+1, y-1, z-1, b = -x+1, -y+1, -z+1\)
Table B3. General and crystallographic data for (H₂MeIm)₂sq

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₁₂H₁₄N₄O₄</td>
</tr>
<tr>
<td><strong>M₀</strong></td>
<td>278.27</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>6.418(7)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>14.522(13)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>7.863(8)</td>
</tr>
<tr>
<td><strong>V/Å³</strong></td>
<td>701.2(1)</td>
</tr>
<tr>
<td><strong>T/K</strong></td>
<td>293(2)</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>P₂₁/c</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>Radiation type</strong></td>
<td>MoKα</td>
</tr>
<tr>
<td><strong>μ/mm⁻¹</strong></td>
<td>0.101</td>
</tr>
<tr>
<td><strong>No. of reflections measured</strong></td>
<td>7850</td>
</tr>
<tr>
<td><strong>No. of independent reflections</strong></td>
<td>1542</td>
</tr>
<tr>
<td><strong>R_{int}</strong></td>
<td>0.0589</td>
</tr>
<tr>
<td><strong>R_{I} (for I &gt; 2σ(I))</strong></td>
<td>0.0479</td>
</tr>
<tr>
<td><strong>wR(F²) (for I &gt; 2σ(I))</strong></td>
<td>0.1190</td>
</tr>
<tr>
<td><strong>R_{I} (all data)</strong></td>
<td>0.0841</td>
</tr>
<tr>
<td><strong>wR(F²) (all data)</strong></td>
<td>0.1384</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>1.004</td>
</tr>
</tbody>
</table>

Table B4. Hydrogen bond parameters for (H₂MeIm)₂sq

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O1_a</td>
<td>0.88</td>
<td>1.78</td>
<td>2.658(3)</td>
<td>176.2</td>
</tr>
<tr>
<td>N2-H2--O2</td>
<td>0.88</td>
<td>1.80</td>
<td>2.672(3)</td>
<td>171.7</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x-1, -y+3/2, z+1/2
### Table B5. General and crystallographic data for (H₂EtIm)₂sq

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₁₄H₁₈N₄O₄</td>
</tr>
<tr>
<td>M_r</td>
<td>306.32</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.959(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.815(7)</td>
</tr>
<tr>
<td>c/Å</td>
<td>7.157(3)</td>
</tr>
<tr>
<td>V/Å</td>
<td>735.4(6)</td>
</tr>
<tr>
<td>T/K</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.104</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>6270</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>1099</td>
</tr>
<tr>
<td>R_int</td>
<td>0.1182</td>
</tr>
<tr>
<td>R₁ (for I &gt; 2σ(I))</td>
<td>0.0577</td>
</tr>
<tr>
<td>wR(F²) (for I &gt; 2σ(I))</td>
<td>0.1197</td>
</tr>
<tr>
<td>R₁ (all data)</td>
<td>0.1087</td>
</tr>
<tr>
<td>wR(F²) (all data)</td>
<td>0.1417</td>
</tr>
<tr>
<td>S</td>
<td>1.064</td>
</tr>
</tbody>
</table>

### Table B6. Hydrogen bond parameters for (H₂EtIm)₂sq

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O2_a</td>
<td>0.88</td>
<td>1.80</td>
<td>2.675(4)</td>
<td>171.7</td>
</tr>
<tr>
<td>N2-H2--O1_b</td>
<td>0.88</td>
<td>1.82</td>
<td>2.698(4)</td>
<td>173.8</td>
</tr>
</tbody>
</table>

Symmetry operator: a = -x, -y+1, -z+1, b = -x+1, y+1/2, -z+3/2
Table B7. General and crystallographic data for (H$_2$-PrIm)$_2$sq

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{16}$H$</em>{22}$N$_4$O$_4$</td>
</tr>
<tr>
<td>$M_r$</td>
<td>334.38</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>7.492(3)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>14.821(6)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>7.965(4)</td>
</tr>
<tr>
<td>$V$/Å</td>
<td>862.6(7)</td>
</tr>
<tr>
<td>$T$/K</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P$_c$</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK$_\alpha$</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>0.094</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>10270</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>4132</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.0451</td>
</tr>
<tr>
<td>$R_1$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.0449</td>
</tr>
<tr>
<td>$wR(F^2)$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.0985</td>
</tr>
<tr>
<td>$R_1$ (all data)</td>
<td>0.0618</td>
</tr>
<tr>
<td>$wR(F^2)$ (all data)</td>
<td>0.1083</td>
</tr>
<tr>
<td>$S$</td>
<td>1.023</td>
</tr>
</tbody>
</table>

Table B8. Hydrogen bond parameters for (H$_2$-PrIm)$_2$sq

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H3A--O2</td>
<td>0.88</td>
<td>1.81</td>
<td>2.682(2)</td>
<td>174.0</td>
</tr>
<tr>
<td>N2-H4--O4</td>
<td>0.88</td>
<td>1.79</td>
<td>2.663(2)</td>
<td>170.5</td>
</tr>
<tr>
<td>N3-H1--O1</td>
<td>0.88</td>
<td>1.83</td>
<td>2.771(2)</td>
<td>173.8</td>
</tr>
<tr>
<td>N4-H2A--O3</td>
<td>0.88</td>
<td>1.85</td>
<td>2.703(2)</td>
<td>162.7</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x+1, -y+2, z+1/2, b = x, -y+2, z-1/2, c = x+1, y-1, z
Table B9. General and crystallographic data for (H₂PhIm)₂sq·H₂O

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C₂₂H₂₀N₄O₅</td>
</tr>
<tr>
<td><strong>Mr</strong></td>
<td>420.42</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Monoclinic</td>
</tr>
<tr>
<td><strong>a/Å</strong></td>
<td>11.031(3)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>13.207(3)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>14.601(3)</td>
</tr>
<tr>
<td><strong>V/Å³</strong></td>
<td>2015.7(9)</td>
</tr>
<tr>
<td><strong>T/K</strong></td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>C₂/c</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>Radiation type</strong></td>
<td>MoKα</td>
</tr>
<tr>
<td><strong>μ/mm⁻¹</strong></td>
<td>0.100</td>
</tr>
<tr>
<td><strong>No. of reflections measured</strong></td>
<td>12023</td>
</tr>
<tr>
<td><strong>No. of independent reflections</strong></td>
<td>2509</td>
</tr>
<tr>
<td><strong>R_int</strong></td>
<td>0.0466</td>
</tr>
<tr>
<td><strong>R_1 (for I &gt; 2σ(I))</strong></td>
<td>0.0469</td>
</tr>
<tr>
<td><strong>wR(F²) (for I &gt; 2σ(I))</strong></td>
<td>0.1354</td>
</tr>
<tr>
<td><strong>R_1 (all data)</strong></td>
<td>0.0642</td>
</tr>
<tr>
<td><strong>wR(F²) (all data)</strong></td>
<td>0.1485</td>
</tr>
<tr>
<td><strong>S</strong></td>
<td>1.003</td>
</tr>
</tbody>
</table>

Table B10. Hydrogen bond parameters for (H₂PhIm)₂sq·H₂O

<table>
<thead>
<tr>
<th>N1-H1--O2_a</th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.86</td>
<td>1.81</td>
<td>2.664(16)</td>
<td>176.2</td>
</tr>
<tr>
<td>N2-H2--O1_b</td>
<td>0.86</td>
<td>1.81</td>
<td>2.667(16)</td>
<td>178.8</td>
</tr>
<tr>
<td>N3-H3O--O2</td>
<td>0.86</td>
<td>1.81</td>
<td>2.661(18)</td>
<td>177.2</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x, -y, z+1/2, b = -x+1/2, -y+1/2, -z+1
Table B11. General and crystallographic data for (H$_2$BIm)$_2$sq

<table>
<thead>
<tr>
<th>Formula</th>
<th>C$<em>{18}$H$</em>{14}$N$<em>{4}$O$</em>{4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_r$</td>
<td>350.33</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>7.280(9)</td>
</tr>
<tr>
<td>$b$/Å</td>
<td>9.538(12)</td>
</tr>
<tr>
<td>$c$/Å</td>
<td>11.696(14)</td>
</tr>
<tr>
<td>$V$/Å</td>
<td>802.5(2)</td>
</tr>
<tr>
<td>$T$/K</td>
<td>100(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>$\mu$/mm$^{-1}$</td>
<td>0.106</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>3795</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>1390</td>
</tr>
<tr>
<td>$R_{int}$</td>
<td>0.0545</td>
</tr>
<tr>
<td>$R_f$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.0499</td>
</tr>
<tr>
<td>$wR(F^2)$ (for $I &gt; 2\sigma(I)$)</td>
<td>0.1104</td>
</tr>
<tr>
<td>$R_f$ (all data)</td>
<td>0.0958</td>
</tr>
<tr>
<td>$wR(F^2)$ (all data)</td>
<td>0.1410</td>
</tr>
<tr>
<td>$S$</td>
<td>1.038</td>
</tr>
</tbody>
</table>

Table B12. Hydrogen bond parameters for (H$_2$BIm)$_2$sq

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1A--O1_a</td>
<td>0.88</td>
<td>1.75</td>
<td>2.606(4)</td>
<td>164.9</td>
</tr>
<tr>
<td>N2-H2--O2_b</td>
<td>0.88</td>
<td>1.80</td>
<td>2.670(4)</td>
<td>171.2</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x, y, z-1, b = -x+1, y-1/2, -z+1/2
Table B13. General and crystallographic data for \((\text{H}_2\text{MeBIm})_2\text{sq}\)

<table>
<thead>
<tr>
<th>Formula</th>
<th>C_{20}\text{H}_{18}\text{N}_4\text{O}_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_r)</td>
<td>378.39</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>7.9097(18)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>14.231(3)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>15.988(4)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>1799.8(7)</td>
</tr>
<tr>
<td>(T/\text{K})</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_12_12_1)</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoK(_\alpha)</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.100</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>17793</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>3194</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0696</td>
</tr>
<tr>
<td>(R_I) (for (I &gt; 2\sigma(I)))</td>
<td>0.0523</td>
</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
<td>0.1207</td>
</tr>
<tr>
<td>(R_I) (all data)</td>
<td>0.0753</td>
</tr>
<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.1350</td>
</tr>
<tr>
<td>(S)</td>
<td>1.068</td>
</tr>
</tbody>
</table>

Table B14. Hydrogen bond parameters for \((\text{H}_2\text{MeBIm})_2\text{sq}\)

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O2(_a)</td>
<td>0.86</td>
<td>1.83</td>
<td>2.664(3)</td>
<td>164.8</td>
</tr>
<tr>
<td>N2-H2--O1</td>
<td>0.86</td>
<td>1.82</td>
<td>2.644(3)</td>
<td>160.5</td>
</tr>
<tr>
<td>N3-H3--O3</td>
<td>0.86</td>
<td>1.81</td>
<td>2.640(3)</td>
<td>162.8</td>
</tr>
<tr>
<td>N4-H4A--O4(_b)</td>
<td>0.86</td>
<td>1.78</td>
<td>2.621(3)</td>
<td>165.5</td>
</tr>
</tbody>
</table>

Symmetry operator: \(a = -x+1/2, -y+2, z+1/2, b = -x+1/2, -y+1, z-1/2\)
Table B15. General and crystallographic data for (H₂PhBIm)₂sq, Polymorph 2

<table>
<thead>
<tr>
<th></th>
<th>C₃₀H₂₂N₄O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td></td>
</tr>
<tr>
<td>Mr</td>
<td>502.52</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>5.449(3)</td>
</tr>
<tr>
<td>b/Å</td>
<td>14.002(8)</td>
</tr>
<tr>
<td>c/Å</td>
<td>16.237(9)</td>
</tr>
<tr>
<td>V/Å</td>
<td>1213.9(12)</td>
</tr>
<tr>
<td>T/K</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>MoKα</td>
</tr>
<tr>
<td>μ/mm⁻¹</td>
<td>0.187</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>13155</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>2534</td>
</tr>
<tr>
<td>R_int</td>
<td>0.1517</td>
</tr>
<tr>
<td>R₁ (for I &gt; 2σ(I))</td>
<td>0.0863</td>
</tr>
<tr>
<td>wR(F²) (for I &gt; 2σ(I))</td>
<td>0.2043</td>
</tr>
<tr>
<td>R₁ (all data)</td>
<td>0.2101</td>
</tr>
<tr>
<td>wR(F²) (all data)</td>
<td>0.2670</td>
</tr>
<tr>
<td>S</td>
<td>0.962</td>
</tr>
</tbody>
</table>

Note: The thermal parameters of atoms belonging to H₂PhBIm⁺ ions could not be refined anisotropically without significant breakdown of the crystal structure model. The isotropic refinement of these thermal parameters, in addition to the crystals being of poor diffraction quality, resulted in higher refinement parameters (R_int, R₁, wR, and S) than is normally acceptable for publication by the International Union of Crystallography. Single crystal X-ray diffraction data will be collected again with longer acquisition times, so as to obtain the publication quality crystal structure of (H₂PhBIm)₂sq, Polymorph 2.

Table B16. Hydrogen bond parameters for (H₂PhBIm)₂sq

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1_a-H1_a--O1</td>
<td>0.86</td>
<td>1.85</td>
<td>2.713(5)</td>
<td>177.0</td>
</tr>
<tr>
<td>N2_a-H2_a--O2_a</td>
<td>0.86</td>
<td>1.82</td>
<td>2.667(5)</td>
<td>165.7</td>
</tr>
<tr>
<td>N1A_b-H1A_b--O2_a</td>
<td>0.86</td>
<td>1.82</td>
<td>2.64(3)</td>
<td>160.3</td>
</tr>
<tr>
<td>N2A_b-H2A_b--O1</td>
<td>0.86</td>
<td>1.75</td>
<td>2.64(3)</td>
<td>152.0</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x, -y-1/2, z+1/2
Table B17. General and crystallographic data for \((\text{H}_2\text{EtIm})_{1.34}(\text{H}_2\text{MeIm})_{0.66}\text{sq}\)

<table>
<thead>
<tr>
<th>Formula</th>
<th>((\text{C}_5\text{H}_9\text{N}<em>2)</em>{1.33}(\text{C}_4\text{H}_7\text{N}<em>2)</em>{0.67}\text{C}_4\text{O}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_r)</td>
<td>296.97</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>(a/\text{Å})</td>
<td>6.897(3)</td>
</tr>
<tr>
<td>(b/\text{Å})</td>
<td>14.675(5)</td>
</tr>
<tr>
<td>(c/\text{Å})</td>
<td>7.188(3)</td>
</tr>
<tr>
<td>(V/\text{Å}^3)</td>
<td>725.9(5)</td>
</tr>
<tr>
<td>(T/\text{K})</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
</tr>
<tr>
<td>(Z)</td>
<td>2</td>
</tr>
<tr>
<td>Radiation type</td>
<td>(\text{MoK}_\alpha)</td>
</tr>
<tr>
<td>(\mu/\text{mm}^{-1})</td>
<td>0.105</td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>8599</td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>1812</td>
</tr>
<tr>
<td>(R_{int})</td>
<td>0.0422</td>
</tr>
<tr>
<td>(R_1) (for (I &gt; 2\sigma(I)))</td>
<td>0.0459</td>
</tr>
<tr>
<td>(wR(F^2)) (for (I &gt; 2\sigma(I)))</td>
<td>0.1132</td>
</tr>
<tr>
<td>(R_1) (all data)</td>
<td>0.0720</td>
</tr>
<tr>
<td>(wR(F^2)) (all data)</td>
<td>0.1252</td>
</tr>
<tr>
<td>(S)</td>
<td>1.057</td>
</tr>
</tbody>
</table>

Table B18. Hydrogen bond parameters for \((\text{H}_2\text{EtIm})_{1.34}(\text{H}_2\text{MeIm})_{0.66}\text{sq}\)

<table>
<thead>
<tr>
<th></th>
<th>D-H (Å)</th>
<th>H--A (Å)</th>
<th>D--A (Å)</th>
<th>Angle (DHA) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1--O1_a</td>
<td>0.88</td>
<td>1.81</td>
<td>2.6862(18)</td>
<td>177.1</td>
</tr>
<tr>
<td>N2-H2--O2</td>
<td>0.88</td>
<td>1.79</td>
<td>2.6580(18)</td>
<td>170.8</td>
</tr>
</tbody>
</table>

Symmetry operator: a = x+1, -y+1/2, z+1/2