### Building solid-state approaches to metal-organic materials: a contribution to green, efficient synthesis

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This thesis is dedicated to the memory of Xiaoling Li, P.Eng.

Rest in peace, Dad.

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### i. Preface

This Thesis consists of four chapters, comprising an Introduction, two research-based Chapters, and a Conclusion. The contributions of other authors are acknowledged as follows:

### **Chapters 1 and 4: Introduction and Conclusion**

These chapters are primarily written by Shaodi Li, with contributions and editing from Prof. Tomislav Friščić.

### Chapter 2: Solid-state synthesis and chemical transformations of hexafluorosilicatecontaining metal-organic frameworks

This chapter is the basis of a manuscript currently being prepared for publication. Project design, material synthesis, and manuscript preparation was performed by Shaodi Li. Project guidance was provided by Dr. Cristina Mottillo, Dr. Hatem M. Titi, and Prof. Tomislav Friščić. Variable-temperature PXRD measurements were performed with the assistance of Dr. Hatem M. Titi and Dr. Steven P. Kelley. Synchrotron X-ray diffraction measurements were performed by Dr. Luzia S. Germann, Dr. Hatem M. Titi, and Patrick A. Julien at the Deutsches Elektronen-Synchrotron (DESY) facility in Hamburg, Germany.

# Chapter 3: Mechanochemical synthesis, accelerated aging and thermodynamic stability of the organic mineral paceite and its cadmium analogue

This chapter is duplicated in part from a paper published in the March 2019 issue of *ACS Omega*. Project design and synthesis of materials was performed by Shaodi Li. Some additional samples were prepared by co-first author Igor Huskić, as were single crystals and their analysis by XRD. Select thermochemical measurements were performed by Novendra Novendra and Prof. Alexandra Navrotsky of the University of California, Davis. Prof. Tomislav Friščić greatly assisted in the preparation and editing of the submitted manuscript. Co-first author Igor Huskić has granted permission for exclusive use by Shaodi Li in the present Thesis.

### ii. Abstract

Metal-organic frameworks (MOFs) and organic minerals are two categories of materials that have recently experienced a surge in interest. They offer interesting opportunities for judicious synthetic design and have gained increased attention for their potential commercial and industrial applications. However, their preparation has traditionally been accomplished by means of solution-based methods, which are often expensive, hazardous, and deleterious for the environment. Following the basic Principles of Green Chemistry, it is of environmental and commercial interest to investigate the possibility of preparing a wide range of synthetic materials in a manner that substantially reduces solvent use without compromising the products themselves.

In this work, a selection of solid-state synthetic methodologies is discussed in response to the need for an alternative to solution-based techniques. From mechanochemical processes that take advantage of physical force to promote reactions, to accelerated aging techniques that largely mimic natural mineral weathering processes, to more traditionally practiced techniques such as heating, a plethora of synthetic methods have become available to materials chemists in search of safer, less polluting ways to prepare not only extant materials, but entirely novel species as well.

Chapter 1 introduces several topics of importance regarding the work as a whole. Background information relating to the history and research of metal-organic frameworks, synthetic and natural organic minerals, green chemistry, and synthetic methodologies is presented.

Chapter 2 discusses the viability of mechanochemical ball milling and heating for the preparation of SIFSIX materials, a class of metal-organic framework that is distinguished simultaneously by its potential for gas separations and its intractability with regards to moisture.

Chapter 3 proceeds to extend the use of mechanochemistry to the preparation of a selection of synthetic organic minerals and their artificial analogues. In addition, accelerated aging processes are discussed as they relate to the preparation of these organic minerals.

#### iii. Résumé

Les solides hybrides poreux (SHP), autrement appelés « MOFs » ou « metal organic frameworks » en anglais, et les minéraux organiques sont deux genres de matériaux qui ont récemment connu une forte croissance d'intérêt. Ils offrent des opportunités intéressantes pour du design synthétique soigné et sont appréciés pour leur potentiel commercial et industriel. Cependant, leur préparation est typiquement réalisée à l'aide de processus axés sur l'utilisation de solvant, ce qui les rend coûteux, dangereux, et nocif pour l'environnement. Suivant les principes de base de la Chimie verte, il est dans l'intérêt environnemental et commercial d'enquêter sur la possibilité de préparer une large gamme de matériaux synthétiques d'une manière qui réduit de façon substantielle l'utilisation des solvants sans toutefois compromettre l'intégrité de ces produits.

Dans cette thèse, une sélection de méthodes synthétiques à l'état solide est présentée en réponse au besoin d'alternatives aux techniques à solution. Parmi celles-ci, on trouve les processus mécanochimiques qui utilisent la force physique pour promouvoir les réactions, les techniques de vieillissement accéléré qui imitent des processus minéralogiques naturels, et également des méthodes plus traditionnelles, dont le chauffage à four. Une véritable pléthore de techniques synthétiques est désormais disponible pour les chimistes en quête d'une manière plus sûre et moins polluante de préparer non seulement des matériaux déjà bien connus, mais également des structures tout à fait neuves.

Le premier chapitre présente de nombreux sujets importants relatifs aux recherches qui suivent, dont l'histoire de la mécanochimie, les minéraux organiques synthétiques et naturels, la chimie verte, et les méthodes de synthèse de matériaux.

Le deuxième chapitre discute de la viabilité de la mécanochimie et du chauffage afin de préparer les matériaux de type SIFSIX, une classe de solide hybride poreux distinguée à la fois par son potentiel comme filtre de gaz, et par sa stabilité marginale à l'humidité.

Le troisième chapitre décrit comment utiliser la mécanochimie pour la préparation d'une gamme de minéraux organiques synthétiques et leurs analogues artificiels. De plus, le vieillissement accéléré comme méthode de synthèse pour ce type de matériaux est discuté.

#### iv. Acknowledgments

I would like to extend my thanks and gratitude to all of those who have helped me and guided me through the course of my time at McGill University.

First, I would like to dedicate this work to my dad, Xiaoling Li, who passed away during the course of my graduate studies. He was the smart, generous, honourable, and loving person who had a profound impact on my character, my interests, and my direction. Words do not adequately convey the degree to which you have inspired our family, the mark you made on your journey to seek a better future, and the deep sadness that your absence has left all of us. You are truly missed. May you rest in peace.

To my mom, Situan Bao: Thank you for your tireless help, your wise advice, your dedication to move forward regardless of the situation, and your gentle reassurances that everything will be fine. You are the anchor that keeps our family steady through turbulent times, and Andy and I owe you a deep debt of gratitude.

To Andy Li, the best big little brother anyone can ask for: I know you'll become a fantastic electrical engineer!

To my wonderful supervisor, Prof. Tomislav Friščić, who is knowledgeable, affable, frank, and helpful: Your guidance and input have made all the difference in the projects I worked on, and your positivity radiates through everyone in the group.

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To friends in Montreal and beyond: Quentin, Philippe, Harrison, Jad, Ton of Clay, Ilias, Chris, Aidan, and all the folks of More housing. Thank you for all of the good times. I wish you all the best of luck in your adventures ahead.

### v. List of abbreviations

- API active pharmaceutical ingredient
- **bipy** 4,4'-bipyridine
- CMC Carbon Mineral Challenge, an initiative to promote the discovery of new carboncontaining mineral species
- CP coordination polymer
- DESY Deutsches Elektronen-Synchrotron, Hamburg, Germany
- DSC differential scanning calorimetry
- FTIR-ATR Fourier-transform infrared attenuated total reflectance (spectroscopy)
- ILAG ion- and liquid-assisted grinding
- IR infrared (spectroscopy)
- LAG liquid-assisted grinding
- MOF metal-organic framework
- MOM metal-organic material
- NMR nuclear magnetic resonance (spectroscopy)
- PCP porous coordination polymer
- PSM post-synthetic modification
- **pyz** pyrazine
- PXRD powder X-ray diffraction
- SBU secondary building unit
- SC-XRD single crystal X-ray diffraction
- SHP (French) "solides hybrides poreux," MOF
- SIFSIX a class of metal-organic frameworks featuring hexafluorosilicate building blocks, or alternatively, the hexafluorosilicate ion by itself
- SS-NMR Solid-state nuclear magnetic resonance (spectroscopy)
- TGA thermogravimetric analysis
- VT-PXRD variable temperature powder X-ray diffraction
- XRD X-ray diffraction

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### 1 Introduction

### 1.1 Coordination polymers, metal-organic frameworks

Within the field of inorganic chemistry, the subject of coordination chemistry is an area of active research. Although coordination chemistry has been occasionally applied for centuries, albeit without proper understanding, as in the case of dyes whose colourfastness was enhanced with chelating metal salts,<sup>1</sup> the subject remained obscure prior to the turn of the 20<sup>th</sup> century. Indeed, much of coordination chemistry owes its existence to the work of Nobel laureate Alfred Werner, who in the late 19<sup>th</sup> century first introduced the concept of the octahedral configuration of certain transition metal complexes.<sup>2</sup> Werner showed that for a number of six-coordinated metal complexes, only two isomers could be isolated, whereas hexagonal or trigonal prismatic geometries would necessarily yield three.<sup>1</sup> This discovery and its proof ushered in a new era of materials science, wherein novel compounds could be rationally designed, taking into consideration well-defined properties of the different metal species used, rather than merely encountered by chance. The thoughtful, deliberate combination of constituent bits and pieces of desired chemical complexes could then, in theory, yield not only those materials that were predicted, but indeed entirely novel structures never before observed.

The idea of coordination polymers comes in large part from Werner's deduction that transition metals tend to bind to specific, common numbers of ligands, a theory that is helpful when elaborating new structures. The concept of a "coordination polymer" was used as early as 1916,<sup>3</sup> and understood well before that time with species such as Prussian blue.<sup>4</sup> J. C. Bailar applied the term "coordination polymer" in 1964 to distinguish classical organic polymers from those with inorganic species.<sup>5</sup> In the simplest sense, coordination polymers (CPs) can be defined as polymers whose structure is composed of specific metal centres (whether alone or as a cluster), acting as "nodes," and ligands as "linkers."<sup>6</sup> More specifically, CPs can be one, two, or three-dimensional in nature.<sup>7</sup> Three-dimensional species in particular are of particular interest, since they can be porous and therefore amenable to the incorporation of guest molecules.<sup>8</sup> Those that feature organic ligands are commonly referred to as metal-organic frameworks (MOFs).<sup>9</sup>

The syntactical nuances between various terms used to describe these structures are a subject of discussion. It was not until the publication of key papers from Robson, Kitagawa, and Yaghi in the late 1980s and the 1990s that the idea of MOFs as a subset of CPs took hold.<sup>10-14</sup> The term MOF itself was coined by Yaghi to describe a copper-4,4'-bipyridyl complex he had prepared, which exhibited extended metal-organic "interactions."<sup>14</sup> This naming takes into consideration the importance of structure and morphology in a way the more general term "coordination polymer" does not, although the terms remain interchangeable in literature.<sup>15</sup> It has been proposed that the term "MOFs" be used to describe only three-dimensional structures, whereas "CPs" would be appropriate for 1-D and 2-D extended structures.<sup>16</sup>

Research in the area of MOFs is relatively nascent, having seen little interest prior to the seminal works of the 1990s. In the years following Bailar's original definition of coordination polymer, examples of porous inorganic frameworks had been published. For example, Gravereau and colleagues described in 1979 a porous mixed-metal framework, K<sub>2</sub>Zn<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>•xH<sub>2</sub>O containing cyanide bridging ligands.<sup>17</sup> They recognized that the cavities of this material were occupied, and that the structure, composed of tetrahedral zirconium(II) ions connected to octahedral hexacyanoferrate.<sup>17</sup> In 1989, Hoskins and Robson proposed that a "potentially extensive class" of new polymeric materials could be generated by connecting metal centres with rod-like segments.<sup>18</sup> Nowadays, such "rods" are understood to be ligands, and Robson published several early examples of such materials.<sup>10,18,19</sup>

It is widely considered that the field of MOFs evolved from interest in zeolites, which are aluminosilicate materials commonly found in nature. The porosity of zeolites is a defining characteristic, and synthetic samples with no naturally-occurring counterpart have been prepared from as early as 1948.<sup>20</sup> Although purely inorganic, zeolites had previously attracted considerable interest due to their porous nature; for example, certain zeolites can take up hydrogen gas up to 1.8% by weight under conditions of 77 K and 15 bar.<sup>21</sup> While zeolites have consequently found a variety of uses in applications such as molecular sieves,<sup>22</sup> they are difficult to engineer and modify.<sup>23</sup> One of the earliest MOFs, HKUST-1, a copper-benzenetricarboxylate MOF, was designed as an alternative that is simultaneously porous, stable, and readily

functionalized.<sup>24</sup> A class of MOFs called zeolitic imidazolate frameworks, or ZIFs, is isomorphous to zeolite materials<sup>25</sup> and carries similar potential applications.<sup>26-28</sup>



**Figure 1.1.** Structure of HKUST-1. (left) Dicopper(II) tetracarboxylate, a key component of HKUST-1; (right) HKUST-1 viewed down the [100] direction. Reproduced with permission from reference [24].



Figure 1.2. Structure of MOF-5 and its analogues. (a) MOF-5; (b) IRMOF-6; (c) IRMOF-8. Reproduced with permission from reference [29].

Like HKUST-1, many of the most well-known MOFs were developed only around the turn of the century. For example, MOF-5, composed of oxygen-centered, tetrahedral Zn<sub>4</sub>O clusters

joined by dicarboxylic acid linkers, is one of the most commonly studied frameworks.<sup>29</sup> First described in 2003, MOF-5 and its analogues were investigated for their potential to take up and store hydrogen gas, and in that respect, IRMOF-8, a derivative of MOF-5, showed an uptake of 2% by weight at room temperature.<sup>29</sup> Another porous material, MIL-53, comprised of *trans* chains of metal clusters linked by terephthalic acid, was described in the early 2000s as a candidate for gas absorption.<sup>30,31</sup>

As MOF-5 and MIL-53 demonstrate, considerable attention has been directed at the potential for MOFs to store and separate gases.<sup>32-38</sup> In recent years, MOFs with increasingly high surface areas and gas uptake capacities have been prepared, allowing for a wider range and higher quantities of gases to be sequestered.<sup>39</sup>



**Figure 1.3.** Progress in the porosity of synthetic MOFs, including a comparison against typical conventional materials (at left). The numbers given in parentheses represent the pore volume of the material, in units of cm<sup>3</sup>/g. From reference [39]. Reprinted with permission from AAAS.

In addition, MOFs can be useful materials for various other purposes, such as catalysis,<sup>40-43</sup> drug delivery,<sup>44,45</sup> chemical sensing,<sup>46</sup> heavy metal recovery,<sup>47,48</sup> and light harvesting.<sup>49,50</sup> Furthermore, the porosity of certain MOFs makes them suitable for emerging technologies, such as water capture from desert air.<sup>51</sup>

Indeed, the modular nature of MOFs has been a key factor in their popularity, as their size, structure, and chemical properties can be readily customized or developed entirely from scratch to suit their desired application.<sup>8</sup> As a result, these materials can be rationally designed; all that is theoretically required is to combine a metal centre that exhibits a rigid coordination geometry, while also possessing a vacant coordination site, with a bridging ligand; a polymer may, but not always, result.<sup>8</sup> Characterization by X-ray diffraction on a powder or single crystal sample is considered necessary to clearly establish the structure of any products prepared following this approach, but is often accompanied by other methods, notably surface area measurements, to establish any potential porosity in the material.

As is often the case with designing new structures, not all combinations of building blocks will yield materials as predicted. For example, structures that are presumed to be porous may be affected by interpenetration, where separate networks fill up the voids of each other.<sup>18,51,52</sup> On occasion, this can result in complete loss of porosity, or at least a considerable reduction in the size of any remaining open cavities. From the early days of MOF research, examples of two-fold, three-fold, four-fold, five-fold, and even nine-fold interpenetration have been reported.<sup>54-57</sup> To circumvent this problem, various methods have been proposed, most of which depend on proactively occupying any open cavity with some substance so as to inhibit the formation of an interpenetrating network. Robson originally speculated, correctly, that a charged framework, *i.e.* one that requires counterions to be present, could result in counterions occupying the pores.<sup>18</sup> [Hoskins 1990]. Alternatively, methods of incorporating aromatic molecules, such as pyrene and naphthalene, inside porous MOFs have also proved adequate in keeping interpenetration at bay.<sup>58</sup>



Figure 1.4. A selection of common MOF species. Reproduced from reference [59] with permission from The Royal Society of Chemistry.



Figure 1.5. Design of coordination polymers and MOFs from constituent building blocks or secondary building units (SBUs). Reproduced from reference [8] with permission from The Royal Society of Chemistry.

The wide array of potential applications for MOFs has led to increased commercial attention. In fact, a number of the most popular MOFs are now available for purchase from an ever-increasing number of manufacturers. BASF SE, for example, now manufactures such materials under the trade name Basolite®: HKUST-1 as Basolite C300®, ZIF-8 as Basolite Z1200®, to name a few. They are joined by offerings from MOF Technologies, Strem Chemicals, MOFapps, Promethean Particles, Acsynam, and many others.<sup>60</sup> It is expected that the range of such commercial products will continue to widen as research into the mass manufacture of MOF materials progresses.

### 1.1.1 The SIFSIX class of MOF materials



Figure 1.6. Representative SIFSIX material [Cu(bpy-n)<sub>2</sub>(SiF<sub>6</sub>)], where bpy-n is a ditopic ligand, consisting of copper centres connected by (left) 4,4'-bipyridine or (right) 1,2-bis(4-pyridyl)ethane ligands. Reproduced with permission from reference [61]. Copyright 2012 American Chemical Society.

We are interested in a specific class of metal-organic framework that has shown promise in the field of gas separations. Members of this class of MOF materials, called SIFSIX frameworks, are characterized by the presence of hexafluorosilicate anions acting as pillars between twodimensional metal-organic sheets.<sup>35</sup> To date, several examples of SIFSIX materials have been reported in the literature, featuring a number of metals (zinc, copper(II), and nickel(II), for example) and a range of ditopic ligands (such as bipyridines).<sup>37,61,62</sup> Depending on the identities of these constituents, the size and porosity of a SIFSIX framework can be tuned, providing an opportunity to design and apply the materials for the selective capture and separation of gases.<sup>34</sup> Additionally, steric and electronic effects of the various SBUs can impart specific qualities, such as improved water resistance, on the final material.<sup>63</sup>

An example of SIFSIX using zinc metal centers is the material  $Zn(4,4'-bipyridine)_2SiF_6$ , first described by Zaworotko and co-workers in 1995.<sup>64</sup> At the time of the discovery of this material, the SIFSIX structure was one of only a handful of known three-dimensional coordination polymers with octahedral metal nodes.<sup>65</sup> These materials are generated by essentially cross-

linking square planar sheets of metal centres and ditopic ligands with the aid of spacer ligands; in the case of the prototypical SIFSIX material, hexafluosilicate ions act as such pillars.<sup>64</sup>



Figure 1.7. Selected SIFSIX species with various metal centres and organic ligands plus associated PXRD patterns. (a,d) SIFSIX-1-Cu, using 4,4'-bipyridine as the organic linker; (b,e) SIFSIX-2-Cu-i, an interpenetrated framework featuring 1,2-bis-(4-pyridyl)acetylene ligands; (c,f) SIFSIX-14-Cu-I, an interpenetrated framework featuring 1,2-bis-(4-pyridyl)diazene ligands. Reproduced with permission from reference [63]. Copyright 2017 American Chemical Society.

The work of the Zaworotko group notes that SIFSIX materials often form interpenetrated framework structures, with excess hexafluorosilicate ions occupying the cube-shaped cavities of the material, in addition to an additional, independent metal-organic grid. The formation of such structures appears to be favoured unless specific mitigation procedures are applied. A synthesis of the open framework at the time required azeotropic distillation to remove water from a hydrated zinc hexafluorosilicate suspended in a mixture of benzene and 1,4-dioxane, followed by the addition of N,N-dimethylformamide and ligand.<sup>64</sup>

Despite the variety of SIFSIX materials described in the literature since the pioneering work of the Zaworotko group, little is known about their phase landscape. It is known that crystals of SIFSIX materials dissolve in water, and will also lose any included solvent of crystallization if left standing in air.<sup>64</sup> While several phases of the SIFSIX framework-based materials are known to exist,<sup>35,66</sup> little is known about their interconversion and topology. A recent study by the Zaworotko group demonstrated the collapse of the open SIFSIX framework (CSD codes WONZIJ, ZESFUY) to a non-porous, interpenetrated phase (CSD code JEZRUB) on contact with water,<sup>63</sup> owing to the weak nature of the metal-fluorine bonds between the cation and the hexafluorosilicate anion. This reaction is presumed to be irreversible,<sup>63</sup> which represents a problem for any commercial application of such materials, as it would result in short useful lifetime.

It is of relevant academic and commercial interest, therefore, to devise methods of preparing, storing, and applying members of the SIFSIX family of MOFs while maintaining the stability of these materials. In this regard, some pioneering work by the Eddaoudi group has shown that both optimized solvothermal and solvent-free methods can be used to prepare the nickel analogue of SIFSIX.<sup>67</sup> Moreover, their work has demonstrated that careful heating of such samples can induce structural changes within the material.<sup>67</sup> In addition, the work of Eddaoudi's group has suggested that SIFSIX structures with certain ligands, such as 1,2-bis-(4-pyridyl)acetylene, possess unusual CH--- $\pi$  interactions wherein their positioning locks in the structure of the MOF so that water is unable to displace the hexafluorosilicate moiety.<sup>63</sup> This phenomenon increases the stability of the material when it is exposed to moisture.

Chapter 2 will examine some approaches to address synthetic and stability challenges associated with the zinc SIFSIX material.

### 1.2 Geomimetic chemistry and artificial minerals

According to Nickel and Grice, a mineral is defined as a "naturally occurring solid that has been formed by geological processes, either on Earth or other extraterrestrial bodies."<sup>68</sup>

Alongside research in the field of MOFs, there has been increasing interest in finding examples of metal-organic materials that are naturally occurring, that is, metal-organic minerals. By convention, minerals are generally grouped by the identity of the anionic species, such as carbonates, chlorides, and sulfides.<sup>69</sup> In addition, one group is reserved for those minerals without anions, such as diamond.<sup>69</sup> A consequence of this classification system is that information about the presence or absence of metallic components within a mineral is obscured. In fact, relatively few organic minerals are known to exist, the vast majority of minerals being inorganic solids.<sup>70</sup> Some metal-organic minerals do exist, but they are generally uncommon.<sup>71</sup> Oxalates are one group of such minerals, and species such as humboldtine, an iron oxalate dihydrate mineral,<sup>72</sup> and moolooite, its copper analogue,<sup>73,74</sup> are found in areas where lichen, fungi, and certain plant species grow;<sup>75</sup> these organisms produce oxalates of heavy metals as a method to rid themselves of such metals.<sup>76,77</sup> Minerals containing components derived from formic acid,<sup>78</sup> cyanuric acid,<sup>79</sup> azoles,<sup>80</sup> and mellitic acid<sup>81</sup> have also been discovered.

While several metal-organic minerals are known, naturally-occurring three-dimensional MOFs are exceptionally rare. Recently, two naturally-occurring oxalate MOFs have been discovered in Siberia: zhemchuzhnikovite ( $[Mg(H_2O)_6][NaFe_xAl_{1-x}(C_2O_4)_3] \cdot 3H_2O$ , x~0.6) and stepanovite ( $[Mg(H_2O)_6][NaFe(C_2O_4)_3] \cdot 3H_2O$ ).<sup>82,83</sup> Comprised of two-dimensional metal-oxalate sheets separated by ordered water molecules and complemented by hexaaquomagnesium ions, these naturally-occurring materials have been shown to exhibit a topology similar to known oxalate MOFs.<sup>84-86</sup> Their existence shows that porous materials of a metal-organic nature can exist outside of a synthetic setting.

Zhemchuzhnikovite is of interest because it is a mixed-metal MOF. Such materials are often useful because the presence of multiple metals may lend them superior properties to similar materials with only one metal,<sup>87</sup> which make them useful in fields as diverse as battery components,<sup>88</sup> catalysis,<sup>89</sup> and waste remediation.<sup>90</sup> These exciting applications make mixed-

metal materials excellent candidates for geomimetic chemistry, which draws inspiration from natural substances and processes to design new materials or improve the properties of existing ones.<sup>91</sup>

The rational design of synthetic minerals in turn opens up an array of new materials and exciting applications. For example, it is known that vermiculite, a type of clay mineral, is capable of removing cesium from seawater.<sup>92,93</sup> By modifying phlogopite, a related mica material, to reduce its potassium content, Tamura and colleagues discovered that the new material was capable of taking up cesium and strontium ions, thereby offering a method to remediate nuclear fallout rich in radioactive isotopes of those elements.<sup>94</sup> In addition, some mineral species containing mellitates have been demonstrated as fluorescent materials,<sup>95</sup> which can be adapted to print invisible, fluorescent markings on media such as paper.<sup>96</sup> In order to promote the research and discovery of new organic minerals in general, an initiative called the Carbon Mineral Challenge (CMC) has recently been established, with over a dozen novel species having been found in the past three years.<sup>71</sup>

### 1.2.1 Paceite

One class of mixed-metal mineral involves species of the type M<sub>1</sub>M<sub>2</sub>(OCOCH<sub>3</sub>)4•6H<sub>2</sub>O, where M<sub>1</sub> and M<sub>2</sub> are metal (II) ions. These materials are comprised of one-dimensional (1-D) chains where alternating metal centers are bridged by acetate ligands,<sup>97</sup> and are in essence metal-organic coordination polymers. Importantly, the calcium-copper coordination polymer was discovered in the form of the mineral paceite in 2002, in New South Wales, Australia.<sup>98</sup> Forty years prior to its discovery in nature, the same material had been synthesized [Holden 1960] and characterized in a laboratory setting.<sup>99</sup> Its crystal structure was published in 1967 and subsequently reaffirmed in 1983 and 1999.<sup>97,99,100</sup> Paceite is readily soluble in water, but difficult to recrystallize owing to the solubility difference between calcium acetate and copper acetate, a phenomenon known as incongruent solubility.<sup>97</sup> In each case, it had been required to crystallize the materials in the presence of excess acetate in order to obtain the desired double salt, thereby generating large quantities of chemical waste.

The structure and properties of paceite make it an interesting starting point for the design of synthetic metal-organic minerals. Its cadmium analogue, CaCd(OCOCH<sub>3</sub>)4•6H<sub>2</sub>O, has been previously prepared and was reported to be isomorphous to paceite,<sup>99</sup> but its crystal structure has not yet been published. In Chapter 3, a solid-state synthesis and characterization of both copper-based paceite and this cadmium-based synthetic analogue are presented.

### 1.3 Green chemistry and solid-state synthesis

"We have no desire to do the best green chemistry. We will do the best chemistry, and it will happen to be green."

### - Paul Anastas

For as long as chemistry has been practiced, consideration of its impact on the environment has largely been relegated to an afterthought at best. However, it is not difficult to see how certain methodologies and reactions can be troublesome on that front, whether through solvent use, energy use, health hazards, or otherwise. For example, the Haber-Bosch process of nitrogen fixation, an extremely widespread and successful industrial process used to generate ammonia, is so energy intensive that it alone accounts for 1% of all worldwide energy consumption.<sup>101</sup> Given the increased attention to the environmental impacts of chemistry, a set of general guidelines is needed. In 1998, Paul Anastas and John Warner described an alternative approach to thinking about chemical processes; they put forth their "Twelve Principles of Green Chemistry," a comprehensive set of general guidelines to reduce the hazards and environmental impact posed by chemistry.<sup>102</sup> These Principles can be shortened to a mnemonic device – PRODUCTIVELY – as seen below.<sup>103</sup>

These Twelve Principles have sustained considerable academic interest. Since the turn of the millennium, new journals such as *Green Chemistry* have been founded,<sup>104</sup> and many existing chemical processes have been improved with the intention of reducing their impact on health and the environment. For example, several reactions relevant to organic synthesis and pharmaceutical development have been successfully modified to replace conventional organic solvents with water, a far less toxic and polluting solvent.<sup>105</sup> Yet, an important part of green chemistry is concerned with the reduction or outright elimination of solvent use. This is a tall order, especially given the prevalence of solvent; by some estimates, approximately 15 billion kilograms of organic and halogenated solvents are manufactured annually,<sup>106</sup> and some 90% by weight of the chemicals used in the pharmaceutical industry are attributed to solvents.<sup>107</sup> However, despite the problems inherent with a wide range of solvents, even including water,

chemistry is in general so closely intertwined with the idea of a liquid reaction medium that comparatively little interest has been afforded to the research of alternatives.

<b>Condensed Principles of Green Chemistry</b>
P – Prevent wastes
<b>R</b> – Renewable materials
<b>O</b> – Omit derivatization steps
<b>D</b> – Degradable chemical products
U – Use safe synthetic methods
C – Catalytic reagents
T – Temperature and pressure ambient
I – In-process monitoring
V – Very few auxiliary substances
E – E-factor, maximize feed in product
$\mathbf{L}$ – Low toxicity of chemical products
Y – Yes, it is safe!

**Figure 1.8.** Condensed principles of green chemistry, as represented by the mnemonic device "PRODUCTIVELY." Derived from reference [103].

Indeed, the idea of solvent as necessary for the purpose of enabling chemical reactions is not new. In fact, alchemists once dedicated themselves to the search for a substance that would dissolve everything, thereby streamlining their work in a way. This "alkahest," or universal solvent, would in theory dissolve gold, transmute base metals, heal ailments, and halt aging.<sup>108-110</sup> No true alkahest was ever found, but the focus on solvent as being essential to chemical reactions continues today. However, using solvent is not always ideal. Many common solvents, such as chloroform and dimethyl formamide, are noxious, and occupational exposure can lead to grave medical problems.<sup>111</sup> Furthermore, solvents can be flammable or otherwise pose handling hazards. As discussed earlier, they are also responsible for a large proportion of chemical waste,

which in turn needs to be addressed once a reaction is completed. These issues are addressed in the Twelve Principles, and the reduction or complete elimination of solvent use is therefore recommended. One way to accomplish this goal is to refrain from using bulk solvent in chemical reactions; this is called solid-state synthesis.<sup>112</sup> This can be accomplished in a variety of ways, from methods known since antiquity such as grinding with a mortar and pestle, to more modern approaches such as ball milling. It is also possible to draw inspiration from naturally-occurring processes to reduce solvent use; such methods include accelerated aging. The following sections will describe in more detail various synthetic methods relevant to the preparation of metal-organic materials.

### 1.4 Synthetic methods

#### 1.4.1 Solution-based synthesis

To the general public, and indeed to many chemists for that matter, chemistry is inextricably connected to the image of esoteric glassware filled with boiling, bubbling liquid. Regardless of the identity of the substance thus pictured, the notion that solvents are required to practice chemistry has not changed in millennia. Aristotle himself proclaimed that "no reaction occurs in the absence of solvent,"<sup>113</sup> and that guidance has survived largely intact into the era of modern chemistry. The challenges and problems posed with their use has increasingly been brought to the attention of chemists in the past decades, yet unfortunately the vast majority of chemical synthesis still takes place in solution. Classical syntheses have been accomplished with the aid of large volumes of solvent, often with heating. In the field of MOMs, solvothermal methods have been very successful for screening purposes; by changing solvents, substituting ligands, or adding templating agents, new materials can be created. Indeed, the original syntheses of solution.<sup>29,31,114</sup> Typically, reagents are added to solvent, and the mixture is heated for some time, before the product is removed and purified.

Frequently, the reaction conditions necessary for preparing MOFs in solution are tedious. In their synthesis of magnesium MOF-74 (Mg-MOF-74), Britt needed to keep a solution heated at 125 °C for a period of 26 hours, before washing the crude product in methanol for four days.<sup>115</sup> Moreover, in addition to the lengthy timeframe and high heat required, the methanol used needed to be exchanged on a daily basis, further accentuating the environmental impact of the synthesis.<sup>115</sup> While a number of other materials have since been prepared in less harsh conditions,<sup>114</sup> a generalized reliance on solvents persists. Moreover, it is sometimes necessary to use solvent diffusion techniques, also referred to as layering, to grow crystals of the desired material. In order to perform such a procedure, various reagents are dissolved in suitable solvents. Afterwards, the solutions are carefully layered in a container so that diffusion may occur at their phase boundary.<sup>63</sup> These methods are often lengthy and inefficient in terms of solvent use and product yield. As an example, O'Nolan and colleagues used both solvothermal and solution layering methods in their synthesis of interpenetrated copper SIFSIX structures:

heating a solution at 120  $^{\circ}$ C for one hour gave a bulk powder, while layering for one week yielded single crystals of the same material.<sup>63</sup>

Morevoer, other modern approaches for the preparation of MOF materials using solvent have been described. For example, supercritical carbon dioxide can be used as an alternative to conventional solvents in the manufacture of MOFs. In a 2018 paper, Marrett and co-workers demonstrated that the well-known frameworks MOF-5 and MIL-53 could be manufactured using a supercritical CO<sub>2</sub> process at up to kilogram scale.<sup>116</sup> While traditionally-used solvents are often highly polluting substances, supercritical carbon dioxide is a more environmentally-benign fluid, solvent-like medium<sup>117</sup> that can be readily recycled and reused in a wide range of reactions encountered at large scale.<sup>118</sup>

While MOF manufacturing in particular on an industrial scale (*i.e.* tens of kilograms or more) is still not widespread, existing methods of preparing such quantities of MOFs continue to rely on solvent, although green chemistry considerations have helped ameliorate the safety and environmental impact of such syntheses. One example of an industrially relevant MOF is Basolite A520®, an aluminum fumarate material. The manufacturer, BASF SE, uses a waterbased method to prepare that material at ton-scale, wherein dimethylformamide (DMF), a toxic solvent, is replaced by water in the manufacturing process.<sup>119</sup> Moreover, the product was able to be prepared with aluminum sulfate instead of aluminum chloride or aluminum nitrate, which are more difficult to handle.<sup>119</sup> However, solvent use is frequently required even after the initial synthesis of a material, during processing, purification, and activation steps as applicable. For example, post-synthetic modification (PSM) is important for the preparation of materials with constituent groups that are incompatible with the original reaction conditions. In PSM, such functional groups are introduced after the original material is prepared, thereby enabling the preparation of a wide variety of materials otherwise inaccessible by means of conventional synthesis.<sup>120</sup> In the context of MOF materials, solvent can serve as a medium facilitating ligand exchange while conserving the parent topology.<sup>121,122</sup>



**Figure 1.9.** Synthetic methods for Basolite A520®, an aluminum fumarate MOF commercialized by BASF SE. Prior to the development of a water-based method (right), preparation required toxic solvent and hazardous metal precursors such as aluminum nitrate. The new synthetic method also afforded improved yields, both in terms of absolute and space-time

yields. Reproduced with permission from reference [119].

Post-synthetic modifications are also commonly encountered as one way of preparing artificial mineral-based materials such as zeolites or clays. Following in the footsteps of Komarneni's work, Tamura and co-workers described a hydrothermal synthesis of sodium, magnesium, calcium, and aluminum analogues of phlogopite, a magnesium mica material.<sup>94</sup> These artificial minerals proved favourable in capturing and immobilizing cesium and strontium ions and are therefore interesting candidates for remediating hazardous waste contamination. This type of application could prove useful in situations such as the scrubbing of radioactive cesium from the fallout of the 2011 Fukushima nuclear disaster.<sup>94</sup>

### 1.4.2 Mechanochemical synthesis

An alternative to conventional solution-based synthetic methods makes use of mechanical force to induce or propagate a chemical reaction; this approach is called mechanochemistry.<sup>123</sup> Although this concept has been put into practice well before the advent of modern chemistry,<sup>124,125</sup> mechanochemistry was not widely recognized at all until the late 19<sup>th</sup> century, when Belgian chemist Spring and American chemist Lea independently described chemical reactions exclusively attributable to mechanical action.<sup>126-128</sup> Common examples of mechanochemical apparatus include the mortar and pestle, the ball mill, and the screw extruder.<sup>129</sup> Of such implements, the mortar and pestle have been in use since the Stone Age,<sup>126</sup> with specific examples dating as far back as the 4<sup>th</sup> century B.C., when Theophrastus of Eresus briefly noted the reduction of cinnabar (HgS) to elemental mercury in a copper mortar.<sup>130</sup> In 1820, Faraday discovered that silver chloride could be reduced by grinding in the presence of an assortment of metals, including zinc, copper, iron, and tin.<sup>131</sup> Since then, many chemical reactions have been found to be activated by these simple tools, such as Grignard reactions.<sup>132</sup> In 2002, Orita and co-workers described the near quantitative preparation of platinum and palladium-containing molecular squares by grinding reagents together for ten minutes at room temperature, whereas preceding solution-based methods produced only 80% yield after more than four weeks' heating.<sup>133-135</sup> This represents one of the earliest known metal-organic reactions conducted mechanochemically.

However, reactions conducted using manual grinding alone may sometimes suffer from poor reproducibility owing to the variances in grinding speed, force, and time.<sup>136</sup> The use of a ball mill, which is a relatively modern invention, offers an opportunity to mitigate those factors, allowing for the precise control of reaction environment, time, and input force.<sup>136</sup> Likewise, screw extrusion devices, which operate on the basis of forcing the combination of reagents through a restricted space, allow for improved control of reaction parameters, and are particularly well suited for flow chemistry.<sup>120,137</sup> It is evident that mechanochemical techniques offer the potential to circumvent the use of bulk solvent, which constitutes a major advantage in many industrial and environmental respects. It is, consequently, not surprising that interest in mechanochemistry has steadily increased in recent times, with exciting applications not only in
areas where reductions in solvent use carry economic and safety benefits, but also in situations where solvent may actively interfere with the reaction course, selectivity, as well as formation or isolation of a desired product.<sup>138</sup>



**Figure 1.10.** Common mechanochemical apparatus. Clockwise from top left: a mortar and pestle, a linear "mixer" mill, a screw extrusion device, and an *in situ* PXRD monitoring apparatus for milling reactions. Figure reproduced with permission from reference [129].

To illustrate the first case, many pharmaceutical ingredients have been successfully adapted for mechanochemistry. In one example, it was shown that bismuth subsalicylate, an organometallic pharmaceutical that is used for gastro-intestinal difficulties and is the active pharmaceutical ingredient (API) in the over-the-counter medication Pepto-Bismol, can be prepared by mechanochemical solvent-free ion- and liquid-assisted grinding (ILAG, cf. Section 1.4.3). The commercial preparation of the bismuth subsalicylate API typically relies on toxic and corrosive reagents, such as bismuth(III) nitrate, and must be conducted under carefully controlled pH conditions.<sup>139</sup> In contrast, the proposed adaptation of bismuth subsalicylate synthesis into a mechanochemical process offered a considerable simplification of the procedure, a reduction in

reaction time, the ability to use safe, inexpensive reagents and the precise, directed synthesis of several stoichiometrically different forms of the compound.<sup>139</sup> As another example, it was reported that the manufacture of sildenafil, the active ingredient found in Viagra, can be translated to the mechanochemical domain, leading to a sharp decrease in solvent usage.<sup>140</sup>

Mechanochemistry can also be highly useful in the creation of pharmaceutically-relevant crystals, *i.e.* molecular crystals composed of at least two chemically distinct components. The development of mechanochemical cocrystal screening and synthesis is an increasingly important field because conventional solution-based methods are hampered by the problems of incongruent solubility, where solubility differences between individual cocrystal components cause one to be preferentially deposited from the reaction mixture. This has the effect of precipitating the least soluble component, rather than yielding the desired cocrystal.<sup>141</sup> Ball milling has been shown to readily circumvent this problem; a 2009 study featuring cocrystals of nicotinamide and a selection of dicarboxylic acids shows that milling allowed for improved control of the reaction products as a function of reagent stoichiometry.<sup>142</sup> Furthermore, ball milling allows poorly soluble components to be used, whereas that property precludes their use in conventional solution-based techniques.<sup>142</sup>

The advantages and applications of mechanochemistry are not confined to the pharmaceutical domain. The first mechanochemical synthesis of a coordination polymer,  $ZnBr_2(\mathbf{pyz})_2$ , where **pyz** is the pyrazine ligand, was published in 2001 by Bourne and co-workers.<sup>143</sup> In that pioneering work, an existing polymer,  $ZnBr_2(\mathbf{pyz})$ , was milled with an extra equivalent of pyrazine without the aid of additional additives or solvents. More recently, Do and colleagues demonstrated that ball milling can be used in the extraction and recycling of various noble metals, a field still largely dominated by the use of harsh acids and toxic cyanide reagents.<sup>144</sup>

Mechanochemistry can generally allow for the use of reagents that are poorly soluble or otherwise inactive in solution chemistry. For instance, metal oxides can be used in the synthesis of MOFs by ball milling.<sup>145</sup> Previously, such syntheses required more reactive starting materials, such as metal hydroxides, which in turn necessitated higher costs and increased hazards.<sup>145</sup>



**Figure 1.11.** tris(1,3-bis(trimethylsilyl)allyl)aluminum obtained via ball milling reaction. Previous attempts to prepare this compound in solution have failed to yield an isolable product. Reproduced with permission from reference [146].

Mechanochemistry is also used to develop entirely new materials. Depending on the circumstances, such techniques have been demonstrated to elicit previously unreported or seemingly improbable products or behaviours from reactions of known starting materials.<sup>146</sup> Lea himself described this occurrence in a paper relating to the behaviour of silver and mercury halides, among other substances; whereas heating resulted in their sublimation, grinding leads to their decomposition.<sup>147</sup> In more recent times, ball milling has been instrumental in the synthesis of so-called "impossible" compounds – substances that have only been theorized but not prepared experimentally, or those that are considered chemically impossible to prepare in the laboratory. One such example comes from the work of Rightmire *et al.*, who in 2014 published the mechanochemical synthesis of a tris(allyl)aluminum complex incorporating the bis(trimethylsilyl)allyl ligand, which is sterically hindered.<sup>146</sup> That steric effect had previously precluded the solvent-based preparation of the complex, as it was impossible to isolate it uniquely from a solution. Ball milling, on the other hand, using the potassium salt of the ligand along with aluminum chloride, generated the "impossible" complex in 88% yield.<sup>146</sup>

As a result of the exciting possibilities engendered by solid-state mechanochemistry, it is not surprising that research in this field has continued to grow. Later in this Thesis, a number of new mechanochemical syntheses used to prepare metal-organic materials will be presented.

### 1.4.3 Grinding with additives

A growing body of evidence suggests that certain mechanochemical reactions, in particular those conducted by ball milling, benefit from the addition of small quantities of liquids, whether generated *in situ* or added during the course of sample preparation.<sup>139,148</sup> It has been speculated that the presence of such liquids imparts favourable qualities to the reactions being performed, whether by promoting reagent mobility within the reaction vessel,<sup>149,150</sup> favouring certain reaction pathways,<sup>148</sup> or some combination of these. This technique is referred to as liquid-assisted grinding (LAG). The quantities of liquid involved for a LAG reaction must necessarily be small, so as to not appreciably introduce solvent effects that cause deviations from the mechanical effects of milling. While it remains difficult to clearly assess the boundary between purely mechanical effects and the introduction of thermodynamic solubility effects for any given reaction, the *eta* parameter,  $\eta$ , can be used as a guide. This quantity is defined as the ratio of solvent volume, usually given in microliters, to the total mass of solid reagents, written in milligrams. In general, for reaction conditions where  $\eta \leq 2 \mu L/mg$ , the reaction can be reasonably considered outside the scope of solvent effects.<sup>136</sup>



**Figure 1.12.** Mechanochemical reaction of zinc oxide with fumaric acid gives different products in the presence of various liquid additives in the context of liquid-assisted grinding. Reproduced with permission from reference [151].

The presence of liquids in trace amounts can have a tangible effect on the outcome of a mechanochemical reaction. In their study of mechanochemically-induced cocrystallization, Friščić and co-workers determined that LAG can improve the synthesis of three-component co-

crystals to quantitative yields, or yield entirely new cocrystals altogether.<sup>148</sup> Furthermore, the addition of a sub-stoichiometric amount of salt in addition to liquid can be beneficial to a mechanochemical reaction; such a technique is called ion and liquid assisted grinding (ILAG). This technique was found to be useful in many situations; for instance, the mechanochemical synthesis of bismuth subsalicylate described previously made use of simple nitrates (such as ammonium or potassium nitrate) to ensure a full conversion of starting materials where neat grinding previously failed.<sup>139</sup> In this particular study, it was found that milling bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) with solid salicylic acid in ratios of 1:6, 1:4, and 1:2 but in the absence of liquid additive produced no XRD evidence of subsalicylate formation, whereas the addition of water yielded a mixture of the desired product and unreacted bismuth oxide. The addition of 5% (by weight) of salts, such as ammonium nitrate or potassium nitrate, promoted the complete conversion of the starting materials.<sup>139</sup> Examination of the ILAG process has demonstrated that templating effects introduced by the added salt help direct the formation of specific products.<sup>152</sup>

# 1.4.4 Accelerated aging

An alternative to mechanochemical or solution-based methods draws inspiration from naturally occurring geological phenomena to arrive at the solid-state synthesis of materials. Specifically, accelerated aging methods attempt to simulate the action of weathering processes that lead to the formation of minerals in nature.<sup>153</sup> By combining certain reagents in the presence of moisture and surrounding these mixtures in a slightly elevated ambient temperature (ca. 45 °C), it is possible to observe chemical transformations taking place over a timespan of hours to days.<sup>129</sup> Contrary to ball milling, accelerated aging processes do not require high capital expenditures and do not create pollution from noise, vibrations, or dust. They are therefore attractive options for solid-state synthesis in settings where such factors are important considerations to take into account.



**Figure 1.13.** Overview of accelerated aging reactions. In this specific example, the reaction of zinc or cobalt oxides with a selection of imidazoles in the presence of solvent vapours yields the well-known MOF species ZIF-8, ZIF-67, and a RHO framework. Reproduced with permission from reference [153].

Several examples of accelerated aging reactions exist; for instance, Cliffe and co-workers recently described the synthesis of an array of zinc imidazolate frameworks (ZIFs) by aging the metal oxide with variously substituted imidazoles in the presence of protic salts.<sup>154</sup> This introduced a novel method of employing metal oxides in MOF synthesis, an advantage since such reagents tend to be plentiful, safe, and inexpensive.<sup>153</sup> In a related study, Qi and colleagues described the synthesis of metal oxalate coordination polymers by aging mixtures of oxalic acid and metal oxide species at 98% relative humidity.<sup>155</sup> In addition, Užarević and colleagues expanded on this procedure by using accelerated aging techniques to prepare UiO-66 type MOFs, a zirconium-based material that exhibit a high degree of porosity and catalytic activity.<sup>156</sup> Outside the scope of MOF synthesis, accelerated aging has been used to prepare a range of materials, including palladium-based photosensitizers.<sup>157</sup>

### 1.5 Outlook: Toward greener synthesis of metal-organic materials

Over the course of the past few decades, the field of metal-organic materials has seen a continuously increasing level of interest and development. The combination of metal nodes and organic linkers to form highly customizable, tunable materials has opened the door toward exciting industrial and commercial opportunities. Metal-organic materials have found use in a diverse range of applications, such as gas filters and reaction catalysts. Parallel to the development of porous metal-organic frameworks, the area of organic minerals has experienced a similar uptick in interest. This Thesis will address several examples of such metal-organic materials, and specifically address their syntheses.

Importantly, the conventional methods used to prepare these materials leave considerable room for improvement. Currently, both metal-organic materials (such as the SIFSIX class of MOFs) and synthetic samples of organic mixed-metal minerals (such as paceite) are generally made using solution-based methods that very often exhibit poor efficiency in terms of reaction yield and phase purity. Such solution techniques are often time-consuming due to the long times required to obtain a crystalline product, and wasteful in terms of energy and reagent use. For example, the laboratory solution-based synthesis of the synthetic samples of the mineral paceite, which contains copper(II) and calcium ions in a 1:1 stoichiometric ratio, requires the use of a large, four-fold excess of calcium salts due to incongruent solubility of individual components. On the other hand, the laboratory, solution-based synthesis of SIFSIX materials often leads to only partial yields. It is, therefore, clear that there is plenty of room to improve the syntheses of such materials, by exploring alternative reaction environments such as solvent-free mechanochemistry. This is the principal focus of the work presented in this Thesis, which will specifically explore how such materials can be synthesized quickly, cleanly, and safely by taking advantage of solid-state methodologies while ensuring high yields and phase purity of the targeted products. As a result of the work described in this Thesis, it is now possible to use ball milling to fabricate these materials in greener ways that are compatible with the Twelve Principles of Green Chemistry, as well as hint to how coordination polymers like the mineral paceite could form in geological environments.

Chapter 2 deals with the solid-state synthesis of SIFSIX materials, a class of metal-organic frameworks that have been presented as potential candidates for tunable gas filters. Specifically, this Chapter will outline the exploration and development of mechanochemical, solvent-free approaches for the synthesis of two distinct members of the SIFSIX class of frameworks. These materials were selected because they present specific, yet unexplored, challenges in mechanochemical synthesis. In the course of this work it was discovered that the materials also exhibit sensitivity to ambient atmospheric conditions, specifically a high tendency to undergo structural rearrangements in the presence of moisture, which should negatively impact their commercial viability. In light of this unexpected problem, a part of the work in Chapter 2 has been dedicated to thermal properties of the SIFSIX frameworks, and in particular the structural transformations that take place upon heating as a means to both discover new materials, as well as revert the hydration process that yields interpenetrated materials of low porosity, to form more open structures.

Chapter 3 is focused on mechanochemistry and solvent-free reactivity as geomimetic synthetic methodologies that can provide simple, easy access to samples of synthetic minerals, as well as provide an insight into how organic minerals, an unusual and still considered rare class of minerals, may be forming in geological environments. Specifically, this chapter develops a mechanochemical, "green" synthesis of synthetic samples of the naturally-occurring mineral paceite, demonstrating the ability to form the material using only stoichiometric amounts of reagents, as well as directly from simple mineral-like precursors such as calcium carbonate (calcite) and copper(II) acetate monohydrate (hoganite). The chapter also demonstrates how the mechanochemical procedure can be expanded to a cadmium-based analogue of paceite, and also reports the detailed crystallographic investigation of this material. While most of the work in Chapter 3 relies on the use of ball milling, it also provided an inspiration to explore accelerated aging as a synthetic methodology in which commercial samples of the known minerals calcite and hoganite spontaneously convert to the paceite structure under mild conditions of temperature and atmosphere. Whereas such accelerated aging did not provide in all cases quantitative reaction yields, it is important as an illustration of a possible pathway through which paceite could form naturally.

Chapter 4 concludes this Thesis by reviewing the results described in Chapters 2 and 3, investigating the successes and challenges faced in the course of the projects described therein, and highlighting opportunities for future work.

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# 2 Solid-state synthesis and chemical transformations of hexafluorosilicate-containing metal-organic frameworks

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The work described in this chapter is a part of a manuscript that is currently in preparation, and this chapter contains additional information not yet included in the original manuscript.

#### 2.1 Rationale

As the discussion in Chapter 1 highlighted, interest in metal-organic frameworks (MOFs) has been rapidly growing since their introduction in the early 1990s. The reason for this lies in their surprisingly high degree of customizability, which stems from their modular design in which a variety of metal centres that can be used as framework nodes, and a wide range of differently functionalized organic molecules that can be used as linkers. In addition, numerous MOFs exhibit microporosity and high surface area, often exceeding 1000 m<sup>2</sup>/g, which makes them promising candidates for industrial applications like gas separation and storage. The microporous nature of MOFs can also readily be combined with other advanced physicochemical properties (e.g. conductivity, catalysis, luminescence, etc.) which provides an entry to advanced, multifunctional materials. However, the advanced design and range of potential applications for MOFs are in contrast with the methods used in their synthesis, which remain poorly efficient. Most MOFs in scientific literature and technical reports are still prepared through solvothermal or, at best, solution-based approaches which tend to be low-yielding, time-consuming and, importantly, based on environmentally-taxing and toxic metal reagents such as chlorides and nitrates. Collectively, these issues present a significant challenge in the commercial development of MOF materials, as their synthesis becomes difficult to scale-up and produces considerable amounts of waste. The goal of the current Chapter, therefore, is to explore and establish the ability to use cleaner, safer and faster synthetic methodologies based on ball milling mechanochemistry for the preparation of the SIFSIX class of MOF materials. Whereas SIFSIX materials have been documented as highly attractive for use in gas separation, and are therefore

of commercial interest, their synthesis using greener, more environmentally-friendly solid-state techniques has not yet been reported.

### 2.2 Abstract

Herein, we introduce the use of solid-state reaction techniques, based on ball milling mechanochemistry, as well as thermally-induced phase transformations, for the efficient synthesis of materials belonging to the SIFSIX class of MOFs. In particular, the work outlined in this chapter describes the first methodologies for the assembly of SIFSIX materials by ball milling, and also establishes previously unreported SIFSIX phases, obtained through thermally-induced conversion. Two mechanochemical synthesis strategies are presented, enabling the synthesis of zinc-based SIFSIX structures either from a zinc hexafluorosilicate salt, or from basic zinc carbonate, an alternative that is more readily available and safer to handle. These synthetic techniques represent the very first reports of mechanochemistry in SIFSIX synthesis, providing small amounts (hundreds of milligrams) of materials at room temperature, without bulk solvent, and rapidly (minutes to an hour). The accessibility of SIFSIX materials established in this work by using mechanochemistry has also permitted extensive investigation of their thermal properties, revealing previously not documented temperature-induced transformations, leading to at least two new phases in the system involving 4,4'-bipyiridine as the bridging ligand of the SIFSIX framework.

### **2.3 Introduction**

Solvent-free methods can serve as promising avenues for the synthesis of a wide range of materials.<sup>1-3</sup> As the name implies, such procedures eschew the use of bulk solvent in chemical reactions, and potentially constitute greener alternatives to more traditional routes for various chemical reactions.<sup>4</sup> For certain materials, reactions performed in the solid state have considerable advantages over solvent-based approaches in terms of solvent use, reactant hazards, and reduced reagent waste.<sup>5</sup> Novel methods, such as mechanochemical ball milling, have been utilized to great success in this area, both as replacements for extant syntheses,<sup>6,7</sup> and as routes toward new materials otherwise unobtainable by conventional methods.<sup>8,9</sup> In effect, solid-state synthesis plays a key role at the confluence of green chemistry and the development of emerging materials.

Among the latter, metal-organic frameworks (MOFs) are a class of three-dimensional hybrid materials comprised of metal centers and organic bridging ligands.<sup>10</sup> As classical examples illustrate, <sup>11-14</sup> the arrangement of these components in three dimensions can cause these materials to be porous. This property permits them to take up a wide variety of guest molecules, such as carbon dioxide, acetylene, hydrogen, or sulfur dioxide.<sup>15-21</sup> As a result of this behavior, MOFs are promising candidates for industrially relevant applications such as gas separation and storage, in addition to exciting new prospects such as water capture from otherwise dry environments.<sup>22</sup>

One class of MOFs that has been identified as a potential gas filter is characterized by the presence of hexafluorosilicate groups acting as pillars between two-dimensional metal-organic sheets. These materials, collectively known as SIFSIX frameworks (shown in **Figure 2.1**), have been demonstrated to selectively take up gases such as carbon dioxide from streams comprised of mixtures of gases.<sup>18</sup> Such frameworks can also be fine-tuned so that the substitution of different metal centers and organic ligands results in the selective uptake of different gaseous species.<sup>18,19</sup> On the other hand, the preparation of SIFSIX materials is challenging in terms of synthetic methodology, and expensive with regard to time and solvent use.<sup>23</sup> Like many other MOFs,<sup>24</sup> SIFSIX frameworks are also hygroscopic and poorly stable in the presence of water.<sup>25</sup> These difficulties render large-scale synthesis and adoption of these materials currently

impractical. However, these challenges could be resolved or otherwise circumvented by the judicious choice of nodes and/or linkers used for the creation of the SIFSIX structure.



**Figure 2.1.** Structure of a representative SIFSIX material. The black bars represent any of a number of ditopic ligands such as pyrazine and 4,4'-bipyridine (**bipy**).

An example of SIFSIX using zinc metal centers is  $Zn(bipy)_2SiF_6$ , first described by the Zaworotko group in 1995.<sup>26</sup> This system, based on data available in the Cambridge Structural Database (CSD), features two distinct types of structure. One is the open net (CSD code WONZIJ), while the other is an interpenetrated structure of low expected porosity (CSD code JEZRUB). Although a wide range of SIFSIX materials have subsequently been described in the literature,<sup>20,27</sup> less is known about their phase landscape. While several phases, or polymorphs, for some of the SIFSIX materials are known to exist,<sup>18,28</sup> their interconversion and morphology are not well documented. A recent study by the Zaworotko group demonstrated that exposure to

moisture is sufficient to induce the collapse of an open SIFSIX framework to an interpenetrated phase,<sup>25</sup> owing to the weak nature of the metal-fluorine coordination bonds. While this reaction is presumed to be irreversible,<sup>25</sup> the loss of water can be induced by heating. We believe that a porous material, though not necessarily identical to the one previously reported, could be obtained if the water molecules are removed.

The goal of this study was therefore to address these issues by exploring solid-state properties and reactions of selected SIFSIX structures. First, the use of mechanochemical ball milling greatly reduces energy and solvent use;<sup>29</sup> this technique of MOF synthesis has been well documented.<sup>5</sup> The use of liquid-assisted grinding (LAG) during the course of such reactions has further enabled the synthesis of these materials from less reactive starting materials, such as metal oxides.<sup>30</sup> In addition, the impact of milling can be enhanced by choosing milling media of larger diameter or choosing milling apparatus made from materials of higher density.

Specifically, we were interested in applying mechanochemistry to the synthesis of the SIFSIX material  $Zn(bipy)_2SiF_6$ , a model system based upon simple, readily available commercial compounds. This system, based on data available in the Cambridge Structural Database (CSD), forms two distinct types of structures. One is the open net structure (CSD code WONZIJ), while the other is an interpenetrated structure of low expected porosity (CSD code JEZRUB), which also contains water. We decided to explore its solid-state reactivity, in particular its sensitivity to moisture and temperature. We were also attracted to the possibility of using mechanochemical pathways to develop a simple, inexpensive route to this model framework, and possibly other SIFSIX materials as well.



Figure 2.2. (left) Open SIFSIX framework WONZIJ; (right) interpenetrated framework JEZRUB.

In order to achieve the synthesis of target  $Zn(bipy)_2SiF_6$  in the absence of bulk solvent, we envisaged two different mechanochemical approaches, illustrated in Reaction Equations 1 and 2.

$$ZnSiF_{6} \bullet n H_{2}O + 2 \text{ bipy} \xrightarrow{\bigcirc} Zn(bipy)_{2}SiF_{6} (SIFSIX) + n H_{2}O \qquad (Eq. 1)$$

$$[ZnCO_{3}]_{2} \bullet [Zn(OH)_{2}]_{3} + 5 (H_{2}bipy)SiF_{6} + 5 bipy \xrightarrow{\bigcirc} 5 Zn(bipy)_{2}SiF_{6} (SIFSIX) + 8 H_{2}O + 2 CO_{2} \qquad (Eq. 2)$$
where bipy = 4,4'-bipyridine

In the process described by Equation 1, the commercially available salt zinc hexafluorosilicate hydrate,  $ZnSiF_6 \cdot n H_2O$ , is used as a source of needed  $Zn^{2+}$  nodes and  $SiF_6^{2-}$  linkers, with two equivalents of 4,4'-bipyridine required for assembly of the SIFSIX structure.

The alternative approach, illustrated by Equation 2, simplifies the choice of metal reagent to inexpensive, safe zinc oxide or basic zinc carbonate, but uses two different types of bipyridine reagents. One is simply the solid 4,4'-bipyridine (**bipy**), in an amount stoichiometrically equal to the amount of zinc reagent used; the other is the salt of 4,4'-bipyridine and fluosilicic acid, with formula (H<sub>2</sub>**bipy**)SiF<sub>6</sub>. This reagent is not readily available commercially, so it needs to be prepared. While this requirement makes the synthesis of  $Zn(bipy)_2SiF_6$  following the process of Equation 2 more cumbersome, designing a reaction around simple salts such as oxides and carbonates should in principle permit the synthesis of analogous structures using a variety of other metals. For certain alternatives, such as  $Co^{2+}$  and  $Cu^{2+}$ , the hexafluorosilicate salts might not be commercially available, or incur higher costs than the corresponding oxides or carbonates.

### 2.4 Results and discussion

#### 2.4.1 Solid-state approach

Several attempts to prepare the framework were carried out in neat grinding and LAG scenarios. From these data, it is apparent that the open framework WONZIJ was only partially synthesized at best, in conjunction with the interpenetrated phase JEZRUB.

Using previous literature<sup>26</sup> as a guideline, we started by attempting to mechanochemically prepare  $Zn(bipy)_2SiF_6$  using zinc hexafluorosilicate hydrate as a starting material. It became apparent that this approach, described in solution syntheses, was not readily amenable to mechanochemical adaptation. As Figure 2.3 and Figure 2.4 show, this starting material was not fully reacted after up to 30 minutes of milling at a frequency of 30 Hz. Furthermore, there is scant diffraction evidence (Figure 2.5, Figure 2.6) that the open framework WONZIJ was obtained at all amongst the reaction products, while the majority of new diffraction signals was consistent with the formation of interpenetrated material. These results were consistently observed across varying choices of LAG additives (including neat reactions) and milling times.

In order to examine whether the volume of added liquid played any role in promoting the reaction, and to determine the degree to which this additive plays a role in directing the formation of the desired framework topology, various volumes of liquid additives were screened. Selected results of this mechanochemical LAG screening are shown in **Figure 2.8**.



**Figure 2.3.** Overlay of selected PXRD patterns for mechanochemical syntheses of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> by neat (*i.e.* solvent-free) milling of zinc hexafluorosilicate and 4,4'-bipyridine (**bipy**).



 $2\Theta$  / degrees

**Figure 2.4.** Overlay of selected PXRD patterns for mechanochemical LAG syntheses of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> by milling of zinc hexafluorosilicate hydrate and 4,4'-bipyridine in the presence of methanol as the LAG milling additive.



**Figure 2.5.** Overlay of selected PXRD patterns for mechanochemical LAG syntheses of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> by milling of zinc hexafluorosilicate hydrate and 4,4'-bipyridine in the presence of ethanol as the LAG additive.



 $2\Theta$  / degrees

**Figure 2.6.** Overlay of selected PXRD patterns for mechanochemical LAG syntheses of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> by milling of zinc hexafluorosilicate hydrate and 4,4'-bipyridine in the presence of N,N-dimethylformamide as the LAG additive.



**Figure 2.7.** Overlay of selected PXRD patterns for mechanochemical LAG syntheses of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> by milling of zinc hexafluorosilicate hydrate and 4,4'-bipyridine in the presence of water as the LAG additive.



Figure 2.8. Overlay of selected PXRD patterns for mechanochemical LAG syntheses of Zn(bipy)<sub>2</sub>SiF<sub>6</sub> in the presence of ethanol as the liquid milling additive, illustrating the effect of solvent volume on the reaction. Each sample was milled for 30 minutes.

The PXRD analysis of the mechanochemical reactions revealed that the open  $Zn(bipy)_2SiF_6$ framework (CSD code WONZIJ) was difficult to prepare by milling, with the mechanochemical experiments consistently yielding the interpenetrated structure. Next, we explored if different results could be obtained by changing the sources of zinc and hexafluorosilicate ions. Instead of using zinc hexafluorosilicate hydrate reagent, a combination of basic zinc carbonate (zinc carbonate hydroxide) and bipyridinium hexafluorosilicate was used. The latter salt was prepared in the laboratory following a method previously described in the literature [Gelmboldt 2014], namely, by precipitation from a solution of hexafluorosilicic acid and 4,4'-bipyridine. Substitution of the zinc hexafluorosilicate salt with the two separate reagents in stoichiometric amounts also yielded incomplete and mixed conversion, as evidenced by **Figure 2.9**. Zinc oxide was also explored as a potential precursor of zinc ions, but no improvement was observed either (see **Figure 2.10**).

Mechanochemical LAG experiments were conducted using different liquids as milling additives, and in systematically varying amounts. Such screening of LAG reaction conditions revealed that regardless of the additive used, or even in the absence of a liquid additive altogether, it was not impossible to isolate the open Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> structure (CSD code WONZIJ) as a pure solid phase. Specifically, the reactions in each case led to the concomitant appearance of different amounts of the non-porous, interpenetrated hydrate form of the framework (CSD code JEZRUB). Notably, using water as the LAG liquid yielded exclusively the latter framework. Likewise, modification of milling time, frequency, and solvent volume appeared to have little effect on the quality of the milling products. We speculate that this problem may arise from the fact that both synthetic approaches (detailed earlier in Equations 1 and 2) generate water as a byproduct, which cannot be readily removed during the course of a milling reaction. Since the interpenetrated structure JEZRUB contains water within its structure, it is unsurprising that the excess moisture would tend to favour its formation over the open structure. Given this important limitation, we directed our attention to potential post-synthetic methods of removing water incorporated into the products.





**Figure 2.9.** Overlay of selected PXRD patterns for mechanochemical LAG syntheses of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> framework materials. The reactions were performed using **bipy**, bipyridinium hexafluorosilicate and basic zinc carbonate as precursors. Each sample was milled with a

different LAG additive (indicated for each pattern); each sample was milled for 30 minutes at

30 Hz.



**Figure 2.10.** Overlay of selected PXRD patterns for the mechanochemical LAG synthesis of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> framework materials. The milling reactions were conducted using ZnO as the zinc precursor. Each sample was milled with a different liquid additive, as indicated on each pattern; each sample was milled for 30 minutes at a frequency of 30 Hz.



**Figure 2.11.** Overlay of selected PXRD patterns for mechanochemical LAG synthesis of Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> framework materials. Milling reactions were conducted with water as the LAG additive; each sample was milled for 30 minutes, at a frequency of 30 Hz.



### 2.4.2 In situ reaction monitoring with PXRD

**Figure 2.12.** Modified milling apparatus designed for *in situ* powder X-ray diffraction monitoring. In this setup, the moving arms of a commercial mixer mill are positioned such that the centre of a poly(methyl methacrylate) milling jar is exposed to a synchrotron X-ray source. A robotic mechanism, comprised of a motor and a "finger," is mounted above the mill to remotely control its operation. Reproduced with permission from reference [31].

In order to achieve a better understanding of the mechanochemical reactions to form  $Zn(bipy)_2SiF_6$  frameworks, a series of selected milling experiments was repeated at the DESY synchrotron facility in Hamburg, Germany. An in-house ball mill apparatus had previously been assembled for the purpose of *in situ* reaction monitoring.<sup>31</sup> Using solid ZnSiF<sub>6</sub> and **bipy** accompanied by dry methanol under ambient conditions, the reaction was observed by repeatedly recording PXRD patterns. The resulting time-domain XRD patterns for this reaction are reproduced in **Figure 2.13**. This data clearly shows the formation of a transient phase corresponding to the open framework (CSD code WONZIJ), before rearranging to the
interpenetrated phase (CSD code JEZRUB) upon continued milling and exposure to moisture. A similar reaction, documented in **Figure 2.14**, substituted water in place of the methanol previously used for LAG. This again resulted in the formation of the interpenetrated material, although the intermediate step in which the open framework appears is more short-lived.



**Figure 2.13.** Time-resolved synchrotron powder X-ray diffraction patterns for a LAG milling experiment involving solid zinc hexafluosilicate and 4,4'-bipyridine in the presence of methanol as the grinding liquid. The observed sequence of phases indicates a fast transformation within a period of *ca.* 3 minutes.



**Figure 2.14.** Time-resolved synchrotron powder X-ray diffraction patterns for a milling experiment involving dry zinc hexafluorosilicate and 4,4'-bipyridine in the presence of water. Unlike the experiment shown in **Figure 2.13**, the reaction sequence observed herein indicates the appearance of the interpenetrated material (CSD code JEZRUB) after a period of only *ca*. 30 seconds.

From both experiments, it is evident that the reaction proceeds rapidly, taking approximately three minutes to generate the open framework material if methanol is used as a milling additive, or as little as 30 seconds if water is used for LAG. However, this open framework structure rapidly re-arranged upon continued milling, leading to a final product that contained no evidence of porous material. In addition, if water was used as the liquid additive in LAG, it was not

possible to observe the open framework as a pure phase; instead, the diffractograms indicate the presence of the interpenetrated material (CSD code JEZRUB) as well as residual starting materials simultaneously with the desired porous material. These results suggest that the reaction environments, particularly those in our laboratory, were not sufficiently devoid of water, and therefore the formation of the interpenetrated framework would have been strongly preferred over that of the open, porous material. Furthermore, the short timeframes in which the open framework can be observed create challenges in their preparation and scale-up, as the mechanochemical reaction must be precisely timed in addition to being kept completely dehydrated.

## 2.4.3 Thermal transformations

As the interpenetrated polymorph of the Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> framework (CSD code JEZRUB) forms from the corresponding open framework polymorph (CSD code WONZIJ) by inclusion of water, we speculated that removal of water through thermal means could lead to the rearrangement of the interpenetrated material back to the open structure. Indeed, previous work suggested that a crystalline nickel(II)-based SIFSIX framework could be prepared by a combination of mechanochemical mixing and wetting followed by heating.<sup>32</sup> While the authors noted that the zinc analogue was not amenable to such a synthesis, we were interested to see if similar results could be obtained with a modified method. To that end, samples of the interpenetrated material (CSD code JEZRUB) were placed in a conventional oven set to a temperature of 140 °C. These samples were kept heated for periods of 24 hours, 48 hours, 7 days, and 10 days. From powder X-ray diffraction data, we found that a new phase was obtained after heating, as shown in **Figure 2.15**. Additionally, by lowering the oven temperature and extending the heating time, it was possible to observe this thermally-induced transformation on a daily basis, whereby the sample was collected every 24 hours and a PXRD pattern obtained before returning the sample to the oven.

**Figure 2.16** shows that this thermal conversion proceeds via the transient formation of the open  $Zn(bipy)_2SiF_6$  framework (CSD code WONZIJ). However, it was not possible to observe this phase cleanly via PXRD, again likely due to water exposure. In addition, this type of experiment proved highly irreproducible, and we are yet unable to determine exactly the reason why similar samples failed to undergo the same kind of thermal transformation. As **Figure 2.17** illustrates, a sample of the interpenetrated  $Zn(bipy)_2SiF_6$  material (CSD code JEZRUB) can remain structurally unchanged at 140 °C for more than three weeks, whereas other samples placed under seemingly identical conditions resulted in pronounced changes in their crystal structures.



Figure 2.15. Formation of new phases during heating. In order from top to bottom, PXRD patterns represent the same sample heated at 140 °C for zero, one, two, and seven days. Evidence of two new phases is observed, represented as new phases A and B. New phase A is not isolated and is observed as part of a mixture that also includes new phase B, whose structure appears to be structurally unchanged over the course of three weeks.



Figure 2.16. Overlay of PXRD patterns illustrating the structural changes to mechanochemically prepared interpenetrated Zn(bipy)<sub>2</sub>SiF<sub>6</sub> material (CSD code JEZRUB) upon heating at 140 °C in air. The original sample was prepared by milling bipyridinium hexafluorosilicate, basic zinc carbonate, and 4,4'-bipyridine with 50 μL water for a period of 30 minutes. The sample was analyzed immediately *via* PXRD, then placed in the oven. The sample was retrieved every day for a period of one week for additional PXRD scans, after which the sample was returned to the





In order to investigate the dehydration process in more detail, an *in situ* PXRD monitoring experiment was set up with the aid of a variable-temperature auxiliary on a laboratory X-ray diffractometer. The experiment was performed with the expectation that, if the structural rearrangement of different  $Zn(bipy)_2SiF_6$  structures is sufficiently slow, it would be possible to observe the process with regard to both time and temperature. A clean sample of the interpenetrated framework JEZRUB was placed in the hot stage sample holder and heated to 140 °C for a period of up to 12 hours. The collected diffractograms are represented in Figure 2.18. Unfortunately, it was not evident that any major structural change was effected.



**Figure 2.18.** Attempted dehydration at 140 °C of interpenetrated framework JEZRUB as monitored by variable-temperature powder X-ray diffraction. No evidence of any structural transformation was observed over a period of five hours.

Following this observation, the sample of interpenetrated  $Zn(bipy)_2SiF_6$  (CSD code JEZRUB) was then analyzed *via* thermogravimetric analysis (TGA) to observe its behaviour up to a temperature of 800 °C. Two separate measurements were performed, with one conducted on the product of the VT-PXRD analysis and the other on a different sample of the non-heated interpenetrated material. As **Figure 2.19** shows, the sample subjected to the VT-PXRD heating sequence exhibited a higher residual mass than the sample not previously heated, which suggests that the VT-PXRD study did cause the loss of material while apparently keeping the crystal structure intact. It is believed that the majority of this lost material corresponds to water present in the interpenetrated phase. Consequently, it appears that the loss of at least some of the water found in the interpenetrated structure does not by itself drive the rearrangement of the material back to an open phase.

Despite the tendency to retain its structure upon heating, the interpenetrated SIFSIX material has indeed undergone rearrangements. The exact cause or catalyst of such structural changes remains unknown and is the subject of continued investigation.



**Figure 2.19.** Samples of the interpenetrated Zn(**bipy**)<sub>2</sub>SiF<sub>6</sub> material (CSD code JEZRUB) were heated in air up to 800 °C. Two trials were performed with the same source material: one sample was run prior to the VT- PXRD study, while the other sample was run after being exposed to the heating conditions outlined in **Figure 2.18**.

#### 2.5 Conclusion

The mechanochemical preparation of SIFSIX materials explored herein illustrates both advantages and challenges of using ball milling as a synthetic route to complex materials. On the one hand, we were able to determine that the process of milling does indeed generate an array of phases corresponding to both the open  $Zn(bipy)_2SiF_6$  framework (CSD code WONZIJ) and the corresponding non-porous interpenetrated structure (CSD code JEZRUB). In addition, these phases can be observed in a way that is not practical with conventional solution-based methods. However, while mechanochemical ball milling does yield characteristic open frameworks, the sensitivity of the targeted materials to water impedes their stability. Indeed, we were unable to properly isolate the porous material, even though we were able to observe its formation and rearrangement *in situ*. This represents a major drawback of mechanochemistry relative to slow solution-based techniques, such as layering, as a method for the preparation of the industrially attractive open framework material.

Thermal conversions show that water can be removed from the interpenetrated frameworks, leading to the formation of new materials. However, the process is exceptionally difficult to control and reproduce, to the point where we are unable to explain why some samples exhibited morphological changes while others of the same material remained stable under heating. We detected a new phase of the  $Zn(bipy)_2SiF_6$  SIFSIX material that is obtainable upon careful heating of the interpenetrated structure in air; however, this does not demonstrate the reversibility of the original process of interpenetration.

Unfortunately, it appears that the most desirable form of the SIFSIX material, an open net, is transient in nature upon mechanochemical treatment. It appears briefly as an intermediate phase in both the formation of the interpenetrated structure during ball milling, and again as an intermediate in the formation of a new phase by thermal dehydration. Since the open framework is the only SIFSIX phase explored herein known to have potential industrial and commercial applications as a gas filter, we conclude that the solid-state techniques we have so far explored are unable to overcome the central problem of these materials, namely, their structural sensitivity in the presence of moisture.

#### 2.6 Experimental

Zinc hexafluorosilicate hydrate, zinc oxide, basic zinc carbonate, and concentrated hexafluorosilicic acid were purchased from Sigma-Aldrich and used as received. 4,4'-bipyridine was purchased from Alfa Aesar and used without further purification.

Solid bipyridinium hexafluorosilicate was prepared following a method described in literature.<sup>33</sup> One equivalent of 4,4'-bipyridine was dissolved in methanol and added to three equivalents of fluosilicic acid. Solid precipitate was obtained upon addition of acetone. The filtered and dried salt was collected and used in associated experiments.

Mechanochemical synthesis of the interpenetrated  $Zn(bipy)_2SiF_6$  framework (CSD code JEZRUB) was accomplished by milling equal parts bipyridinium hexafluorosilicate, 4,4'bipyridine, and basic zinc carbonate in a 10 mL Retsch stainless steel jar. The total amount of reagents totaled approximately 300 mg per jar. In addition, 50 µL of water was added to facilitate reagent mobility; this process is known as liquid-assisted grinding (LAG).<sup>34,35</sup> Two 7 mm stainless steel balls (1.38 g each) were added to each jar, which was then agitated at 30 Hz on a Retsch MM400 mixer mill for 30 minutes. The product was collected and analyzed by powder X-ray diffraction and IR spectroscopy and used as-is without further processing.

For thermal studies, samples were placed in an oven set to 140 °C and exposed to air.

Powder X-ray diffraction studies were completed using a benchtop Bruker D2 benchtop diffractometer with a copper X-ray source,  $K\alpha = 1.508$  Å.

For the purpose of variable temperature PXRD studies, an Anton-Paar hot stage was used. Hotstage studies were conducted on a Bruker D8 Advance diffractometer using the same X-ray source, with the temperature range set between 25-250 °C.

*In situ* PXRD measurements were conducted at DESY (Hamburg, Germany) using synchrotron X-ray radiation of wavelength  $\lambda = 0.20709$  Å.

#### 2.7 Outlook: Expanding the scope of mechanochemistry

We demonstrated that the mechanochemical reaction of selected zinc-containing precursors and sources of hexafluorosilicate anions provides framework materials, and progresses through a multistep process. On the other hand, our investigation into the solid-state synthesis of SIFSIX materials also highlighted the challenges of using mechanochemistry to resolve certain aspects of their synthesis. Notably, the high selectivity of zinc SIFSIX materials upon exposure to moisture could not yet be adequately remediated by modifying the method through which they are synthesized. Despite efforts to adjust the reaction conditions so that exposure to water is either minimized or rendered ineffective, we were so far unable to produce an entirely stable structure by using mechanochemistry alone.

In our efforts to remove water from interpenetrated frameworks, we also discovered that solidstate syntheses can lead to unexpected and novel products. In Chapter 3, the feasibility of solidstate chemistry to generate synthetic analogues of naturally-occurring materials is investigated.

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# 3 Mechanochemical synthesis, accelerated aging and thermodynamic stability of the organic mineral paceite and its cadmium analogue

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\* For the purpose of this Thesis, the work contained in this Chapter is the exclusive intellectual property of S. Li (see Preface).

#### 3.1 Rationale

The preceding Chapter has described the development of mechanochemical and thermochemical methods for the synthesis and discovery of advanced SIFSIX-type metal-organic framework (MOF) materials. That work has revealed the possibility of synthesizing an advanced MOF using a mineral-like metal carbonate starting material. This chapter now pursues the use of mechanochemistry, and another type of simple solvent-free reactivity, known as "accelerated aging", to investigate the transformation of synthetic minerals into samples of a coordination polymer that appears as a rare organic mineral paceite. Consequently, the work outlined in this chapter will establish the relevance of mechanochemistry in the preparation of synthetic mineral samples, which is particularly important in investigations of rare minerals where pure samples cannot be naturally obtained in large enough amounts to permit detailed characterization. At the same time, the success of mechanochemistry in preparing synthetic paceite samples has permitted the design of accelerated aging reactions in which substances known to appear naturally as minerals (calcium carbonate as calcite, copper(II) acetate monohydrate as hoganite) spontaneously convert into samples of synthetic paceite mineral. This provides potential insight into solvent-free transformations not only as routes for the synthesis of MOFs and synthetic minerals, but also as potential ways through which organic minerals could form geologically.

#### **3.2 Abstract**

We demonstrate the use of ball milling mechanochemistry for rapid, simple and materialsefficient synthesis of organic mineral paceite, with the composition CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O (where OAc<sup>-</sup> is the acetate ion), which is based on coordination polymer chains comprising alternating Ca<sup>2+</sup> and Cu<sup>2+</sup> ions, as well as its cadmium-based analogue CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O. Whereas the preparation of synthetic paceite in aqueous solutions requires a high, at least four-fold, excess of the calcium acetate precursor, mechanochemistry permits the use of stoichiometric amounts of reagents, as well as the use of poorly soluble, and readily accessible calcium carbonate or hydroxide reactants. As established by thermochemical measurements, enthalpies of formation of both synthetic paceite and its cadmium analogue relevant to the mechanochemical reactions are highly exothermic. Importantly, the mechanochemical reactivity can also be adapted to an accelerated aging process in which calcium carbonate (naturally occurring as the mineral calcite) and copper(II) acetate monohydrate (naturally occurring as the mineral hoganite) spontaneously transform into synthetic paceite under very mild conditions of temperature and atmosphere. While not all explored accelerated aging reactions provided complete conversion to synthetic paceite, the herein reported results highlight a potential role of accelerated aging in natural formation of paceite and perhaps other similar organic minerals. In this work, we have also demonstrated mechanochemical routes for the synthesis of the cadmium-based analog of paceite, which has now also been fully structurally characterized using single crystal X-ray crystallography.

#### **3.3 Introduction**

Over the past ten years, structural studies of geological samples have identified an increasing number of organic minerals, broadly defined as carbon-bearing mineral species other than carbonates.<sup>1,2</sup> Principal representatives of such organic minerals are transition metal and lanthanide oxalates,<sup>3,4</sup> as well as metal formats,<sup>5</sup> mellitates,<sup>6</sup> acetates,<sup>1,2</sup> and organic molecules such as uric acid.<sup>7-9</sup> The search for organic minerals and a deeper understanding of their structures and origins has been additionally promoted by the recent "Carbon Mineral Challenge" initiative, which considers organic minerals, while extremely poorly investigated, as nevertheless central to understanding mineral evolution and carbon cycle on Earth and other planetary systems.<sup>10,11</sup> The vibrant investigations of organic minerals have recently led to the structural characterization of geoporphyrins,<sup>12</sup> discovery of naturally-occurring metal-organic frameworks (MOFs),<sup>13,14</sup> and proposed geological appearance of organic cocrystals<sup>15</sup> in extraterrestrial environments such as Titan.<sup>16</sup>

A recent addition to the library of organic minerals are copper(II) acetate monohydrate, Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, found as the mineral hoganite in the Potosi Mine in New South Wales (Australia), as well as paceite, the related double salt of calcium copper(II) acetate hexahydrate, CaCu(OAc)<sub>4</sub>·6H<sub>2</sub>O, found as dark blue crystals growing on surface of hoganite specimens.<sup>17</sup> The structures of both of these minerals are unique in the context of organic minerals, and are also of relevance to modern metal-organic materials chemistry. In particular, hoganite consists of the well-known copper(II) acetate "paddlewheel" dimers, which are also important secondary building units (SBU) in the design and synthesis of coordination polymers and metal-organic frameworks (MOFs).<sup>18</sup> Calcium copper(II) acetate hexahydrate is a synthetic compound that has been known since at least 1960,<sup>19</sup> and its single crystal X-ray diffraction structure was reported first by Langs and Hare in 1967,<sup>20</sup> who described the structure without detailed crystallographic data. The structure was subsequently re-determined by Klop et al.<sup>21</sup> and by El-Bali et al.,<sup>22</sup> and consists of one-dimensional (1-D) coordination polymer chains of alternating square-coordinated copper(II) ions and hydrated, octahedrally-coordinated calcium ions, bridged by acetate ions. Such regular alternation of metal ions is also of relevance for the development of metal-organic materials based on more than one type of metal ion. In particular, whereas a number of designs

have recently emerged for such mixed-metal materials,<sup>23,24</sup> these are usually based on the formation of solid solutions in which different metal ions are randomly distributed, rather than placed on distinct crystallographic sites<sup>25</sup> as in paceite. The potentially broader relevance of this structure in metal-organic chemistry is highlighted by its cadmium- and calcium-based analogue,  $CdCa(OAc)_2 \cdot 6H_2O$ . This compound was described by Balarew and Stoilova,<sup>26</sup> as well as by Langs and Hare, who also conducted a structural characterization.<sup>20</sup> The compound was reported to be isomorphous to  $CuCa(OAc)_2 \cdot 6H_2O$ , but detailed crystallographic information was never provided.



Figure 3.1. a) Structure of the paddlewheel unit found in the crystal structure of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (hoganite mineral) and b) fragment of the crystal structure of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O, with cadmium ions represented as yellow polyhedra. c) Fragment of a single bimetallic coordination polymer chain in the crystal structure of paceite, CdCa(OAc)<sub>2</sub>·6H<sub>2</sub>O.

Consequently, we recognized paceite and its synthetic cadmium analogues as excellent targets for our ongoing investigation of the properties and potential origin of naturally-occurring metalorganic materials.<sup>13,27</sup> Specifically, we targeted the structure, thermal and thermodynamic stability of synthetic paceite and its cadmium analogue, as well as potential routes through which such materials could assemble from geologically-relevant precursors, *via* mechanochemical<sup>28</sup> or accelerated aging<sup>29</sup> reactions.

#### 3.4 Results and discussion

#### 3.4.1 Mechanochemical synthesis of paceite

Synthesis of artificial paceite from water was described in 1960 by Holden and Singer, using copper(II) acetate monohydrate and calcium acetate as starting materials.<sup>19</sup> The synthesis is a textbook example of non-congruent cocrystallization, as the aqueous solubility of calcium acetate is significantly higher than that of  $Cu(OAc)_2 \cdot H_2O$ , which requires the two components to be used in a non-stoichiometric, approximately 4:1 ratio. Mechanochemistry by ball milling has been demonstrated to provide access to solubility-independent reactions, in which the stoichiometric composition of the product can be readily controlled by composition of the reaction mixture.<sup>30,31</sup> Such stoichiometric control was observed for mechanochemistry by neat (dry) milling, as well as by liquid-assisted grinding (LAG), a methodology that uses a small amount of a liquid phase (measured in the form of  $\eta$ , the ratio of liquid additive to reactant weight) to enable and accelerate mechanochemical reactions.<sup>32</sup> Consequently, we decided to explore whether mechanochemistry can be used to obtain synthetic paceite samples using stoichiometric amounts of  $Cu^{2+}$  and  $Ca^{2+}$  precursors.

For that purpose, and with the intention to explore potential routes through which paceite could be formed in a geological environment, we envisaged a two-step synthetic protocol that would use mineral-like substances as precursors. We chose copper(II) acetate monohydrate,  $Cu(OAc)_2 \cdot H_2O$ , as a source of  $Cu^{2+}$  ions, while the calcium acetate material required for the synthesis would be obtained in a mechanochemical reaction of either  $CaCO_3$  or  $Ca(OH)_2$  in combination with acetic acid (AcOH) (Equations 1 and 2). The resulting hydrated calcium acetate was then expected to form paceite in a mechanochemical reaction with one equivalent of  $Cu(OAc)_2 \cdot H_2O$  (Equation 3).

$$CaCO_{3}(s) + 2AcOH(l) \rightarrow Ca(OAc)_{2} \cdot H_{2}O(s) + CO_{2}(g)$$
(Eq. 1)

$$Ca(OH)_{2}(s) + 2AcOH(l) \rightarrow Ca(OAc)_{2} \cdot H_{2}O(s) + H_{2}O(g)$$
(Eq. 2)

$$Ca(OAc)_{2} \cdot H_{2}O(s) + Cu(OAc)_{2} \cdot H_{2}O(s) + 4H_{2}O(l) \rightarrow CaCu(OAc)_{4} \cdot 6H_{2}O(s)$$
(Eq. 3)

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All mechanochemical reactions were performed using the LAG methodology [Friščić 2009], using a small amount of water as an additive (typically 10-12  $\mu$ L, see SI), and analysis of reactants by PXRD confirmed that the used CaCO<sub>3</sub> was in the calcite form. The LAG reactions of either Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> with a small excess (under 5 mol%) of glacial acetic acid led to the formation of calcium acetate monohydrate as the sole crystalline product. In particular, milling 0.5 mmol Ca(OH)<sub>2</sub> for 30 minutes with 60  $\mu$ L AcOH and 10  $\mu$ L water led to complete disappearance of the solid reactant and formation of a hydrated calcium acetate of the formula Ca(OAc)<sub>2</sub>·H<sub>2</sub>O (CSD code CEJLIM), identified by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (Figure 3.2, also see SI). In contrast, complete conversion of CaCO<sub>3</sub> into Ca(OAc)<sub>2</sub>·H<sub>2</sub>O required 80 minutes milling, on 1 mmol scale (see SI). Shorter milling times revealed the formation of a mixed hydrate and acetic acid solvate of calcium acetate, of composition Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH, which was identified by PXRD reflections matching those simulated for the published structure (CSD code COKJUH), along with unreacted CaCO<sub>3</sub>. Upon longer milling the initially formed Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH reacted with remaining CaCO<sub>3</sub> to provide Ca(OAc)<sub>2</sub>·H<sub>2</sub>O (Figure 3).

In the next step, one equivalent of  $Cu(OAc)_2 \cdot H_2O$  was added to the mechanochemically prepared  $Ca(OAc)_2 \cdot H_2O$  and the reaction mixture milled for an additional 30 minutes. Analysis by PXRD revealed the complete disappearance of Bragg reflections of the starting materials, and appearance of new reflections consistent with the diffraction pattern calculated for the crystal structure of paceite. Identical outcomes were obtained regardless of whether the  $Ca^{2+}$  source in this two-step process was calcium carbonate or hydroxide (Figure 3.2). The formation of the paceite structure was also possible in a one-pot, one-step process, by milling calcium carbonate or hydroxide and acetic acid in the presence of an equimolar amount of  $Cu(OAc)_2 \cdot H_2O$  and water. After 30 minutes of milling, the PXRD pattern of the reaction mixture exhibited only X-ray reflections of the mixed coordination polymer  $CuCa(OAc)_4 \cdot 6H_2O$  (Figure 3.2). The formation of paceite by both one- and two-step mechanochemical routes was also confirmed by Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra, which were identical for the products of both synthetic methods (see SI).

The described two-step and one-step mechanochemical routes to  $CuCa(OAc)_4 \cdot 6H_2O$  clearly demonstrate that the synthesis of this material can be readily performed through LAG using only stoichiometric amounts of metal precursors.



**Figure 3.2.** Comparison of PXRD patterns for Ca(OAc)<sub>2</sub>·H<sub>2</sub>O mechanochemically prepared from Ca(OH)<sub>2</sub> or CaCO<sub>3</sub>, and for samples of CaCu(OAc)<sub>4</sub>·6H<sub>2</sub>O (synthetic paceite) prepared in a one- or two-step mechanochemical procedure, to corresponding patterns of starting materials and simulated patterns of targeted products.

### 3.4.2 Stoichiometric control in mechanochemical synthesis of calcium acetate solvates

The observed formation of Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH as an intermediate in the mechanochemical synthesis of Ca(OAc)<sub>2</sub>·H<sub>2</sub>O from CaCO<sub>3</sub> is consistent with previously reported formation of highly solvated compounds as intermediates in mechanochemical synthesis of coordination compounds and MOFs.<sup>33-35</sup> It also suggests the possibility for selective synthesis of different solvates of calcium acetate, Ca(OAc)2·H2O or Ca(OAc)2·H2O·AcOH, depending on the stoichiometric composition of the reaction mixture. Specifically, we speculated that simply using the calcium-based precursor and acetic acid in the respective stoichiometric ratio of 1:3 should enable the selective formation of Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH. Indeed, milling of 1 mmol Ca(OH)<sub>2</sub> with 3 mmol AcOH led to complete disappearance of Bragg reflections of the solid reactant in the PXRD pattern of the reaction mixture, and the appearance of reflections of Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH (Figure 3). The formation of Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH was also verified by TGA. Similarly, milling of CaCO<sub>3</sub> with three equivalents of AcOH led to quantitative conversion within 60 minutes of milling. Energetic constraints on these reactions and observed intermediates are discussed below from the point of view of thermochemical data. The demonstrated ability to selectively obtain either Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH or Ca(OAc)<sub>2</sub>·H<sub>2</sub>O provides an additional illustration of the effectiveness of mechanochemical methods in controlling stoichiometric composition of products.



**Figure 3.3.** Overlay of PXRD patterns for Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH mechonchemicaly synthesized from Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> to relevant patterns of reactants and simulated patterns for Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH and Ca(OAc)<sub>2</sub>·H<sub>2</sub>O.

# 3.4.3 Formation of paceite by accelerated aging: a potential route for geochemical synthesis

The formation of paceite by two-step or one-step milling reaction of  $CaCO_3$  and  $Cu(OAc)_2 \cdot H_2O$ , both of which are known mineral species, suggests a possible geochemical route to paceite, either through mechanical impact<sup>36</sup> or through mineral weathering reactions. In order to explore this possibility, we conducted "accelerated aging" reactions,<sup>37</sup> inspired by mineral weathering processes<sup>38</sup> in which the exposure of inorganic minerals to small organic molecules under suitable conditions of temperature and atmosphere leads to the formation of organic minerals.

Two designs of accelerated aging reactions were explored. In one design, the reaction mixtures of either Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> with one equivalent of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O were manually mixed, followed by addition of a slight excess (10 mol%) of liquid AcOH and then left to age for seven days in 100% relative humidity (100% RH, *i.e.* saturated water vapor). In the second reaction design, the mixtures of Cu(OAc)<sub>2</sub>·2H<sub>2</sub>O with either CaCO<sub>3</sub> or Ca(OH)<sub>2</sub> as the calcium source were left to age for seven days in an atmosphere saturated by vapors of a 50% aqueous solution of acetic acid (v/v). The reactions were conducted either at room temperature or in an incubator set to 45 °C. Visual observation of reaction mixtures over time in most cases revealed partial deliquescence and change in reactions in which mixtures of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O with CaCO<sub>3</sub> or Ca(OH)<sub>2</sub> were left to age in vapors of the 50% aqueous acetic acid solution. Even after seven days, these mixtures clearly consisted of a white powder with dispersed dark green particles of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O reactant.

The visual observations are confirmed by PXRD analysis of the aged reaction mixtures (**Figure 5**), which were briefly manually ground before recording a diffractogram. The analysis revealed the formation of the paceite structure in all experiments, except in the aforementioned reactions of aging in vapors of 50% aqueous AcOH solution (v/v) at room temperature. Importantly, whereas reaction mixtures exhibited deliquescence, in no case was complete dissolution of samples observed.



**Figure 3.4.** Optical images of equimolar mixtures of  $Cu(OAc)_2 \cdot H_2O$  and either  $Ca(OH)_2$  or  $CaCO_3$  upon six days of aging under different conditions: a)  $Cu(OAc)_2 \cdot H_2O$  and  $Ca(OH)_2$  with

1.1 equivalent of AcOH added directly to the mixture, and aged at 100% RH and 45 °C; b)
Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and Ca(OH)<sub>2</sub> with 1.1 equivalent of AcOH added directly to the mixture, and aged at 100% RH and room temperature; c) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and Ca(OH)<sub>2</sub>, aged in vapors of 50% aqueous AcOH at 45 °C; d) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and Ca(OH)<sub>2</sub>, aged in vapors of 50% aqueous AcOH at room temperature; e) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and Ca(OH)<sub>2</sub>, aged in vapors of 50% aqueous AcOH at che mixture, and aged at 100% RH and 45 °C; f) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and CaCO<sub>3</sub> with 1.1 equivalent of AcOH added directly to the mixture, and aged at 100% RH and 45 °C; f) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and CaCO<sub>3</sub> with 1.1
equivalent of AcOH added directly to the mixture, and aged at 100% RH and room temperature; g) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and CaCO<sub>3</sub>, aged in vapors of 50% aqueous AcOH at 45 °C and h)
Cu(OAc)<sub>2</sub>·H<sub>2</sub>O and CaCO<sub>3</sub>, aged in vapors of 50% aqueous AcOH at room temperature.

In addition to paceite, the reaction mixtures also exhibited X-ray reflections consistent with different amounts of  $Ca(OAc)_2 \cdot H_2O$  or  $Ca(OAc)_2 \cdot H_2O \cdot AcOH$ . The observation that both of these phases participate in the solid-state formation of paceite was verified by real-time monitoring of the reaction of  $Cu(OAc)_2 \cdot H_2O$  with  $Ca(OH)_2$  in an atmosphere containing vapors of water and AcOH. An analogous measurement was not possible for  $CaCO_3$  as the calcium source due to

formation of the gaseous  $CO_2$  in the reaction. A detailed description of the experimental set-up, and its use in monitoring cocrystal formation has been recently published.<sup>39,40</sup>



Figure 3.5. PXRD patterns for mixtures of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O with either Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> after seven days aging under different conditions, compared to simulated patterns of CaCu(OAc)<sub>4</sub>·6H<sub>2</sub>O, Ca(OAc)<sub>2</sub>·H<sub>2</sub>O and Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH. Reactions were kept either at 45 °C, or at room temperature (RT).

Real-time *in situ* X-ray diffraction monitoring of changes in a mixture of equimolar amounts of  $Ca(OH)_2$  and  $Cu(OAc)_2 \cdot H_2O$  upon exposure to vapors of acetic acid and water revealed (Figure 6) the interconversion of at least five crystalline phases:  $Ca(OH)_2$ ,  $Cu(OAc)_2 \cdot H_2O$ , as well as paceite, calcium acetate monohydrate (CSD code CEJLIM) and  $Ca(OAc)_2 \cdot H_2O \cdot AcOH$  (CSD code COKJUH). Rietveld refinement of *in situ* PXRD data revealed a continuous drop in the content of  $Ca(OH)_2$  and  $Cu(OAc)_2 \cdot H_2O$  reactants over *ca*. 14 hours. The first new crystalline phase observed in the reaction is the mixed hydrate and acetic acid solvate  $Ca(OAc)_2 \cdot H_2O \cdot AcOH$ , which is detected already in the first experimental datasets. The crystalline monohydrate  $Ca(OAc)_2 \cdot H_2O$  appears considerably later in the reaction, after *ca*. 3.5 hours of aging, and is soon followed by the appearance of the paceite structure after *ca*. 5 hours aging. The initial formation of  $Ca(OAc)_2 \cdot H_2O \cdot AcOH$ , followed by  $Ca(OAc)_2 \cdot H_2O$ , is consistent with previous general observations on mechanochemical reactions of oxides with carboxylic acids, which reveal the initial formation of the more solvated intermediate phases.

Rietveld analysis suggests that the disappearance of  $Ca(OH)_2$  takes place faster than that of  $Cu(OAc)_2 \cdot H_2O$ . While quantitative analysis is hindered by significant potential for preferred orientation and crystal size effects in such a non-mixed reaction system, these observations may be explained by multiple possible reaction pathways available for calcium hydroxide, forming three different calcium-containing products, in contrast to copper(II) acetate converting only to paceite.



Figure 3.6. a) Time-resolved X-ray powder diffractogram for the againg reaction of Ca(OH)<sub>2</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O in an atmosphere of water and acetic acid and b) corresponding reaction profile based on Rietveld refinement of the PXRD data.

#### 3.4.4 Cadmium analogue of paceite

We next explored the potential to use analogous reactivity to synthesize the previously reported cadmium analogue of paceite.<sup>20</sup> Indeed, the two-step mechanochemical reactions involving milling of  $Ca(OH)_2$  or  $CaCO_3$  in the presence of a small excess of acetic acid, followed by milling of resulting  $Ca(OAc)_2$ ·H<sub>2</sub>O with commercially available  $Cd(OAc)_2$ ·2H<sub>2</sub>O led to the quantitative formation of the targeted  $CaCd(OAc)_2$ ·6H<sub>2</sub>O paceite analogue (Figure 7). Formation of  $CaCd(OAc)_2$ ·6H<sub>2</sub>O was verified by PXRD pattern analysis, which revealed a product isostructural to paceite. As observed in case of synthetic paceite, its cadmium analogue could also be obtained by a one-pot mechanochemical procedure starting from either  $CaCO_3$  or  $Ca(OH)_2$  in the presence of commercial  $Cd(OAc)_2$ ·2H<sub>2</sub>O, acetic acid and a small amount of water. Again, the formation of  $CaCd(OAc)_2$ ·6H<sub>2</sub>O was confirmed by PXRD analysis (Figure 7), as well as TGA (see SI). In this case also, the formation of the same product by both one- and two-step mechanochemical routes was confirmed by FTIR-ATR spectroscopy (see SI).



**Figure 3.7.** Comparison of PXRD patterns for CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O prepared from Ca(OH)<sub>2</sub> or CaCO<sub>3</sub> in a one- or two-step mechanochemical procedure, to corresponding patterns of starting materials and simulated patterns of targeted products.

As the crystallographic data for  $CaCd(OAc)_2 \cdot 6H_2O$  have previously not been reported, we also conducted a single crystal X-ray diffraction study of the structure of this mixed-metal coordination polymer (Table 1). Single crystals for  $CaCd(OAc)_2 \cdot 6H_2O$  were obtained through an accelerated aging process, from a deliquescent mixture of equimolar amounts of  $Ca(OH)_2$ ,  $Cd(OAc)_2 \cdot 2H_2O$  and a small excess (10%) acetic acid that was aged over 2 days at 45 °C and 100% RH. Crystal structure analysis revealed coordination polymer chains of alternating  $Cd^{2+}$  and  $Ca^{2+}$  ions propagating along the 4<sub>1</sub>-screw axis parallel to the crystallographic *c*-axis (Figure 8). The chains are isostructural to those of copper(II)- and calcium-based chains found in paceite.

As in paceite,  $Ca^{2+}$  ions adopt an octahedral coordination geometry involving four equatorial acetate ions (Ca···O distances 2.30 Å), each forming a bridge to one of the two nearest-neighbor  $Cd^{2+}$  ions in a chain (Cd···O distance 2.29 Å). The apical coordination positions on each  $Ca^{2+}$  ion are occupied by oxygen atoms of two water molecule ligands (Ca···O distances 2.34 Å). Also analogous to  $Cu^{2+}$  ions, the  $Cd^{2+}$  ions in the structure of CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O adopt a roughly square-planar coordination geometry (O···Cd···O angle 90.7°), established through four monodentate oxygen ligands, each coming from a different acetate ion, which is also associated to a nearest-neighbor  $Ca^{2+}$  ion.

formula	$C_4H_{12}Ca_{0.5}Cd_{0.5}O_7$
Mr	248.4
Т / К	298(2)
crystal system	tetragonal
space group	I4/m
a / Å	11.3440(4)
c / Å	16.0488(6)
$V/Å^3$	2065.3(2)
Ζ	8
$\rho_{\rm calc}  {\rm g/cm^3}$	1.598
$\mu / \mathrm{mm}^{-1}$	1.362
F(000)	1008
crystal size / mm <sup>3</sup>	0.3  imes 0.15  imes 0.15
λ/Å	0.71073 (ΜοΚα)
$2\theta$ range for data collection / °	7.18 - 66.21
No. reflections	17744
No. independent reflections	1825
No. restraints	9
No. parameters	70
S	0.994
R1, wR2 $(l \ge 2\sigma(l))$	0.063, 0.099
R1, wR2 (all data)	0.034, 0.080
Largest difference electron density peak/hole / e $Å^{-3}$	0.71; -0.40

Table 3.1. Crystallographic a	nd general data for	CaCd(OAc) <sub>2</sub> ·6H <sub>2</sub> O
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Each of the two water ligands on a  $Ca^{2+}$  ion also acts as a hydrogen bond donor to two neighboring water molecules (O-H···O distance 2.77 Å), which are further hydrogen-bonded to their symmetry-related counterparts (O-H···O separation 2.78 Å) across a 4<sub>1</sub>-screw axis to form 12-membered cages based on O-H···O hydrogen bonds.



**Figure 3.8.** The CaCd(OAc)<sub>4</sub>· $6H_2O$  crystal stucture viewed along the 4<sub>1</sub> screw axis parallel to the crystallographic *c*-direction: a) highlighting the hydrogen-bonded (H<sub>2</sub>O)<sub>12</sub> cluster situated between four bimetallic coordination polymer chains and b) similar orientation of the structure, with metal coordination polyhedra outlined (Cd:yellow, Ca:green).

# 3.4.5 Enthalpies of formation of paceite structures and thermodynamic driving force for the mechanochemical and aging formation of paceite structures from CaCO<sub>3</sub>

In order to achieve deeper insight into the formation of paceite and its cadmium analogue from calcium carbonate, we evaluated the enthalpies of formation  $(\Delta H_f)$  for both CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O using acid dissolution calorimetry<sup>41</sup> in 5 N aqueous hydrochloric acid as the solvent. For this purpose, dissolution enthalpies for both CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O, as well as for Cu(OAc)<sub>2</sub>·H<sub>2</sub>O, Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O, calcium acetate hydrate, Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH and CaCO<sub>3</sub> were experimentally determined at 25 °C. The details of experiments and collected thermodynamic data are provided in the SI, and a summary of the data is given in Table 2. Together with measured and literature values for the dissolution enthalpy of glacial acetic acid and water, these measurements enabled the evaluation of  $\Delta H_f$  for CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O from reacting the corresponding transition metal acetates with either CaCO<sub>3</sub> and acetic acid, or with hydrated calcium acetate, following equations 4-7. The sample of hydrated calcium acetate used in calorimetric measurements was

found to contain a slight excess of water, corresponding to the overall formula of  $Ca(OAc)_2 \cdot 1.1H_2O$ , which was then used instead of the ideal composition  $Ca(OAc)_2 \cdot H_2O$  for thermodynamic calculations of equations 5 and 7.

$$Cu(OAc)_{2} \cdot H_{2}O_{(s)} + CaCO_{3(s)} + 2AcOH_{(l)} + 4H_{2}O_{(l)} \rightarrow CuCa(OAc)_{4} \cdot 6H_{2}O_{(s)} + CO_{2(g)}$$
(Eq. 4)

$$Cu(OAc)_{2} H_{2}O_{(s)} + Ca(OAc)_{2} I I H_{2}O_{(s)} + 3.9H_{2}O_{(l)} \rightarrow CuCa(OAc)_{4} H_{2}O_{(s)}$$
(Eq. 5)

$$Cd(OAc)_{2} \cdot 2H_{2}O_{(s)} + CaCO_{3(s)} + 2AcOH_{(l)} + 3H_{2}O_{(l)} \rightarrow CdCa(OAc)_{4} \cdot 6H_{2}O_{(s)} + CO_{2(g)}$$
(Eq. 6)

$$Cd(OAc)_{2} \cdot 2H_{2}O_{(s)} + Ca(OAc)_{2} \cdot 1.1H_{2}O_{(s)} + 2.9H_{2}O_{(l)} \rightarrow CdCa(OAc)_{4} \cdot 6H_{2}O_{(s)}$$
(Eq, 7)

The measurement of enthalpies of dissolution also enabled the calculation of  $\Delta H_{\rm f}$  for CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O from hydrated calcium acetate, in a process corresponding to the second step of the herein reported two-step mechanochemical synthesis starting from either CaCO<sub>3</sub> or Ca(OH)<sub>2</sub>. In this case also, the formation of copper(II)- and cadmium-based paceite structures was clearly exothermic, which agrees with the ease of forming CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O by mechanochemical milling of corresponding metal acetates. The  $\Delta H_{\rm f}$  for the formation of CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O from Ca(OAc)<sub>2</sub>·6H<sub>2</sub>O are more exothermic than values when starting from CaCO<sub>3</sub>, which might be related to the high stability of the carbonate ion in the reactant. The measured thermodynamic data also reveal that the  $\Delta H_{\rm f}$  for the formation of synthetic paceite is in each case more exothermic than for its cadmium-based analogue, indicating a destabilization effect introduced by the incorporation of CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O are not identical, as well as that the crystal structures of the starting materials Cu(OAc)<sub>2</sub>·6H<sub>2</sub>O and Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O are different water content.

Compound	$\Delta H_{s}$ (kJ/mol) –	$\Delta H_{f}$ (kJ/mol)	
		From carbonate	From acetate
CuCa(CH <sub>3</sub> COO) <sub>4</sub> ·6H <sub>2</sub> O <sub>(s)</sub> (synthetic paceite)	2.77 ± 0.13 (4)	$\textbf{-27.14} \pm 0.30^{a}$	$\textbf{-31.45}\pm0.25^{b}$
$CdCa(CH_3COO)_4 \cdot 6H_2O_{(s)}$	$-24.69 \pm 0.25 \ (5)$	$\textbf{-16.14}\pm0.36^{c}$	$\textbf{-20.46} \pm 0.32^d$
Ca(CH <sub>3</sub> COO) <sub>2</sub> ·1.1H <sub>2</sub> O <sub>(s)</sub>	$-30.00 \pm 0.15~(6)$		
$Cu(CH_3COO)_2 \cdot H_2O_{(s)}$	$2.68 \pm 0.15 \; (13)$		
$Cd(CH_3COO)_2 \cdot 2H_2O_{(s)}$	$-14.14 \pm 0.13$ (4)		
$Ca(CH_{3}COO)_{2} \cdot H_{2}O \cdot CH_{3}COOH_{(s)}$	$-9.24 \pm 0.04$ (3)		
$(Cu(CH_3COO)_2 \cdot H_2O +$			
$Ca(CH_3COO)_2 \cdot 1.1H_2O)$	$-27.08 \pm 0.89$ (2)		
(mechanical mixture)			
CaCO <sub>3(s)</sub>	$-25.23 \pm 0.22 \ (29)$		
CH <sub>3</sub> COOH <sub>(1)</sub>	$-0.21 \pm 0.01^{e}$		
H <sub>2</sub> O <sub>(1)</sub>	-0.35 <sup>f</sup>		

**Table 3.2.** Thermodynamic data obtained and calculated from acid solution calorimetry in 5N HCl, provided by N. Novendra and A. Navrotsky, University of California, Davis.

<sup>a</sup>for Equation 4; <sup>b</sup>for Equation 5; <sup>c</sup>for Equation 6; <sup>d</sup>for Equation 7; <sup>c</sup>Ref [42]; <sup>t</sup>Calculated from dilution enthalpy of HCl [43]. Error is two standard deviations of the mean, value in brackets is number of experiments performed.

Tentatively, the difference in  $\Delta H_{\rm f}$  for synthetic paceite and its cadmium analogue might be attributed to the difference in change of transition metal coordination during the reaction: in Cu(OAc)<sub>2</sub>·H<sub>2</sub>O starting material the Cu<sup>2+</sup> ions are five coordinated with oxygen-based ligands, whereas in Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O the Cd<sup>2+</sup> ions adopt a coordination number seven.<sup>44,45</sup> However, in CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O and CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O the transition metal ions adopt a coordination number of four. Consequently, cadmium ions undergo a more significant change in coordination number upon transformation into the paceite structure, compared to copper(II) ions.<sup>20</sup> Such a difference might be a significant factor contributing to a diminished exothermic enthalpy of formation of CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O compared to synthetic paceite.

An energy diagram explaining the reaction steps that occurs during the formation of  $CaCu(OAc)_2 \cdot 6H_2O$  is given in Figure 9. It is drawn to conserve mass in all the reactions, thus excess acetic acid and carbon dioxide appear in the final products together with the paceite. The top diagram shows the reaction steps when  $CaCO_3$  is first milled with acetic acid to form  $Ca(OAc)_2 \cdot H_2O \cdot AcOH$ , followed by formation of  $Ca(OAc)_2 \cdot 1.1H_2O$ , which is then followed by subsequent milling with  $Cu(OAc)_2 \cdot H_2O$  to form paceite. Formation of the first intermediate

 $Ca(OAc)_2 \cdot H_2O \cdot AcOH$  was seen after short milling times and the ease of this reaction is supported here by the exothermic enthalpy change (-16.62 ± 0.23 kJ/mol). The formation of the second possible intermediate is accompanied by an endothermic enthalpy change (20.94 ± 0.35 kJ/mol), which resulted in an intermediate that has higher energy than the reactants. The highly endothermic enthalpy is consistent with the evolution of  $CO_2$  gas or the loss of other volatile reaction components, where the positive enthalpy is compensated by a large positive entropy, making the overall reaction favorable in free energy. The last step of paceite formation from  $Ca(OAc)_2 \cdot 1.1H_2O$  is accompanied by a strong exothermic enthalpy change of -31.45 ± 0.25 kJ/mol.

Comparison of the formation of paceite directly from either of the intermediates can be seen in the bottom diagram in Figure 3.9. The black line indicates the formation through the Ca(OAc)<sub>2</sub>.H<sub>2</sub>O.AcOH intermediate, while the blue line indicates the formation through the Ca(OAc)<sub>2</sub>·1.1H<sub>2</sub>O intermediate. It can be seen that the Ca(OAc)<sub>2</sub>·1.1H<sub>2</sub>O intermediate has higher enthalpy than the bulk reactants, compared to the other intermediate which has lower enthalpy than the reactants. The formation of Ca(OAc)<sub>2</sub>·1.1H<sub>2</sub>O is accompanied by small positive enthalpy change of  $4.32 \pm 0.27$  kJ/mol. Based on these two figures, the pathway with the formation of Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH appears to be the more favorable one, because the intermediate lies energetically between the reactants and the products, slightly closer to the products. The reactions proceed toward lower energy and more stable forms, where the first reaction step forming the intermediate is accompanied by enthalpy change of  $-16.62 \pm 0.23$  kJ/mol and the subsequent step of paceite formation is accompanied by enthalpy change of  $-10.51 \pm 0.20$  kJ/mol.


Figure 3.9. Energy diagram for the formation reaction of CaCu(OAc)<sub>2</sub>·6H<sub>2</sub>O from CaCO<sub>3</sub> and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O by considering the participation of either: (top) both intermediates or (bottom) one intermediate. Each step corresponds to one of the following compositions: (1) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O<sub>(s)</sub> + CaCO<sub>3(s)</sub> + 3AcOH<sub>(l)</sub> + 4H<sub>2</sub>O<sub>(l)</sub>; (2) Cu(OAc)<sub>2</sub>·H<sub>2</sub>O<sub>(s)</sub> + Ca(OAc)<sub>2</sub>·H<sub>2</sub>O<sub>(s)</sub> + Ca(OAc)<sub>2</sub>·H<sub>2</sub>O(s) + Ca(OAc)<sub>2</sub>·H<sub>2</sub>O(s) + Ca(OAc)<sub>2</sub>·H<sub>2</sub>O(s) + Ca(OAc)<sub>2</sub>·H<sub>2</sub>O(s) + Co<sub>2(g)</sub> + AcOH<sub>(l)</sub> + 3.9H<sub>2</sub>O<sub>(l)</sub> and (3) CuCa(OAc)<sub>4</sub>·6H<sub>2</sub>O<sub>(s)</sub> + AcOH<sub>(l)</sub> + CO<sub>2(g)</sub>. This diagram was prepared by N. Novendra and A. Navrotsky, University of California, Davis.

Analogous diagrams for the cadmium analogue of paceite are given in Figure 3.10. The intermediates also have the same energyas previously, because their formation does not depend on the presence of the copper(II) or cadmium acetate. In the bottom diagram, interesting behavior is observed. The product has essentially the same enthalpy as the Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH intermediate, or perhaps slightly higher. The formation reaction of the product from Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH is accompanied by an enthalpy change of  $0.48 \pm 0.29$  kJ/mol. (essentially zero). Thus, while the Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH is indeed intermediate in enthalpy between reactants and products in the case with copper, with cadmium the Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH

intermediate appears to be essentially the same in enthalpy as the final product. The reason for this difference is not yet clear.



Figure 3.10. Energy diagram of the formation reaction of CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O from CaCO<sub>3</sub> and Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O by considering the participation of either: (top) both intermediates or (bottom) one intermediate. Each step corresponds to one of the following compositions: (1) Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O<sub>(s)</sub> + CaCO<sub>3(s)</sub> + 3AcOH<sub>(l)</sub> + 3H<sub>2</sub>O<sub>(l)</sub>; (2) Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O<sub>(s)</sub> + Ca(OAc)<sub>2</sub>·H<sub>2</sub>O·AcOH<sub>(s)</sub> + CO<sub>2(g)</sub> + 3H<sub>2</sub>O<sub>(l)</sub>; (2\*) Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O<sub>(s)</sub> + Ca(OAc)<sub>2</sub>·1.1H<sub>2</sub>O<sub>(s)</sub> + CO<sub>2(g)</sub> + AcOH<sub>(l)</sub> + 2.9H<sub>2</sub>O<sub>(l)</sub>; (3) CdCa(OAc)<sub>4</sub>·6H<sub>2</sub>O<sub>(s)</sub> + AcOH<sub>(l)</sub> + CO<sub>2(g)</sub>. This diagram was prepared by N. Novendra and A. Navrotsky, University of California, Davis.

#### **3.5 Conclusion**

We have demonstrated the use of mechanochemistry for the rapid, simple and materials-efficient preparation of synthetic samples of the organic mineral paceite, as well as its cadmium analogue, CaCd(OAc)<sub>2</sub>·6H<sub>2</sub>O. Importantly, whereas the synthesis of synthetic paceite from aqueous solutions containing copper(II) acetate and calcium acetate requires the use of ca. four-fold excess of the calcium reagent, mechanochemistry permits the synthesis of this material using only stoichiometric amounts of metal precursors. Furthermore, the use of mechanochemical techniques also permitted the use of readily available calcium hydroxide or carbonate as a source of Ca<sup>2+</sup>, which would be difficult to achieve using simple solution-based chemistry. Consequently, the described mechanochemical approaches illustrate benefits of ball milling mechanochemistry in improving the control over product stoichiometry in the synthesis of coordination polymers based on two different types of metal centers, and in expanding the scope of starting materials in such syntheses to poorly soluble solids. At the same time, these syntheses of synthetic paceite illustrate a poorly explored, but fast, simple and efficient route for making synthetic samples of organic minerals. The exploration of mechanochemical reactivity also provided hints at how analogous reactions could take place in a non-agitated system, by aging of reactant mixtures at high humidity and mild temperature. Such accelerated aging experiments, which mimic mineral weathering processes in geological environment, provide a potential route for the formation of organic minerals. Importantly, thermodynamic studies based on acid dissolution calorimetry confirm that the mechanochemical syntheses of synthetic paceite, and analogous aging reactions involving known mineral species Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (hoganite) and CaCO<sub>3</sub> (calcite), are highly exothermic. It is expected that the exothermic nature of such transformations provides sufficient driving force for the formation of paceite in a natural environment. We are currently investigating the use of mechanochemistry for the synthesis of synthetic samples of other known organic minerals.

### 3.6 Supplemental information

### 3.6.1 Synthetic procedures

Mechanochemical syntheses were conducted using either a Retsch MM200 mixer mill operating at 25 Hz, or a FormTech Scientific 1000 shaker mill operating at 30 Hz. All reactions were performed using stainless steel milling media, including a milling jar of 15 mL volume equipped with two milling balls of 7 mm diameter (1.37 grams each).

# Mechanochemical synthesis of calcium acetate monohydrate from calcium hydroxide

Calcium acetate monohydrate was prepared by combining 37 mg (0.5 mmol) of calcium hydroxide, 60  $\mu$ L (~1.1 mmol) acetic acid, and 10  $\mu$ L water in a milling jar. The sample was then milled for 30 minutes at 25 Hz.

#### Mechanochemical synthesis of calcium acetate monohydrate from calcium carbonate

The synthesis of calcium acetate monohydrate from CaCO<sub>3</sub> was accomplished by combining 100 mg (1.0 mmol) of calcium carbonate, 120  $\mu$ L (~2.0 mmol) of acetic acid, and 12  $\mu$ L water in a milling jar. The sample was then milled for 80 minutes at 30 Hz.

# Mechanochemical two-step synthesis of synthetic paceite from calcium hydroxide

Synthetic paceite was prepared mechanochemically in a stepwise manner. First, 37 mg (0.5 mmol) calcium hydroxide, 62  $\mu$ L (~1.1 mmol) acetic acid, and 10  $\mu$ L water were added to a milling jar. The sample was milled for 30 minutes at 25 Hz. Subsequently, 100 mg (~0.5 mmol) copper(II) acetate monohydrate and 60  $\mu$ L water were added, and the sample milled for another 30 minutes at 25 Hz.

#### Mechanochemical two-step synthesis of synthetic paceite from calcium carbonate

Synthetic paceite was prepared mechanochemically in a stepwise manner. First, 50 mg (0.5 mmol) calcium carbonate, 62  $\mu$ L (~1.1 mmol) acetic acid, and 10  $\mu$ L water were added to a milling jar. The sample was milled for 30 minutes at 25 Hz. Subsequently, 100 mg (~0.5 mmol) copper(II) acetate monohydrate and 67  $\mu$ L water were added, and the sample milled for another 30 minutes at 25 Hz.

#### Mechanochemical one-step synthesis of synthetic paceite from calcium hydroxide

Synthetic paceite was prepared mechanochemically in a direct one-pot method. To a milling jar were added 37 mg (0.5 mmol) calcium hydroxide, 100 mg (~0.5 mmol) copper(II) acetate monohydrate, 62  $\mu$ L (~1.1 mmol) acetic acid, and 62  $\mu$ L water. The sample was milled for 30 minutes at 25 Hz.

# Mechanochemical one-step synthesis of synthetic paceite from calcium carbonate

Synthetic paceite was prepared mechanochemically in a direct one-pot method. To a milling jar were added 50 mg (0.5 mmol) calcium carbonate, 100 mg (~0.5 mmol) copper(II) acetate monohydrate, 62  $\mu$ L (~1.1 mmol) acetic acid, and 60  $\mu$ L water. The sample was milled for 30 minutes at 25 Hz

# Mechanochemical two-step synthesis of CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O from calcium hydroxide

The cadmium paceite analogue CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O was prepared mechanochemically in a stepwise manner. First, 37 mg (0.5 mmol) calcium hydroxide, 63  $\mu$ L (~1.1 mmol) acetic acid, and 10  $\mu$ L water were added to a milling jar. The sample was milled for 30 minutes at 25 Hz. Subsequently, 133 mg (~0.5 mmol) cadmium(II) acetate dihydrate and 60  $\mu$ L water were added, and the sample milled for another 30 minutes at 25 Hz.

# Mechanochemical two-step synthesis of CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O from calcium carbonate

The cadmium paceite analogue CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O was prepared mechanochemically in a stepwise manner. First, 50 mg (0.5 mmol) calcium carbonate, 62  $\mu$ L (~1.1 mmol) acetic acid, and 10  $\mu$ L water were added to a milling jar. The sample was milled for 30 minutes at 25 Hz. Subsequently, 133 mg (~0.5 mmol) cadmium(II) acetate dihydrate and 60  $\mu$ L water were added, and the sample milled for another 30 minutes at 25 Hz.

# Mechanochemical one-step synthesis of CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O from calcium hydroxide

The cadmium paceite analogue CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O was prepared mechanochemically in a direct one-pot method. To a milling jar were added 37 mg (0.5 mmol) calcium hydroxide, 133 mg

(~0.5 mmol) cadmium(II) acetate dihydrate, 60  $\mu$ L (~1.1 mmol) acetic acid, and 60  $\mu$ L water. The sample was milled for 30 minutes at 25 Hz.

#### Mechanochemical one-step synthesis of CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O from calcium carbonate

The cadmium paceite analogue CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O was prepared mechanochemically in a direct one-pot method. To a milling jar were added 50 mg (0.5 mmol) calcium carbonate, 133 mg (~0.5 mmol) cadmium(II) acetate dihydrate, 62  $\mu$ L (~1.1 mmol) acetic acid, and 60  $\mu$ L water. The sample was milled for 30 minutes at 25 Hz.

#### 3.6.2 Real-time *in situ* reaction moniotring using powder X-ray diffraction (PXRD)

In situ PXRD monitoring was performed on the PROTO AXRD Benchtop diffractometer equipped with a DECTRIS Mythen 1K strip detector. Measurements were collected using a custom designed sample holder.(ref) A homogenized mixture of  $Ca(OH)_2$  and  $Cu(OAc)_2 \cdot H_2O$  was placed in the middle and a 200 mL of 50% aqueous solution (by volume) of acetic acid were placed in the sample holder grooves. Consecutive powder diffractograms were collected over the course of 12 hours, with a temporal resolution of 5 min 50 seconds. Rietveld fitting was performed in TOPAZ6 analytical program.

3.6.3 Selected Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectra of mechanochemically prepared materials



**Figure 3.11.** Overlay of selected FTIR-ATR spectra for mechanochemical syntheses of synthetic paceite samples and its cadmium analogue CaCd(OAc)<sub>4</sub>·6H<sub>2</sub>O.

### 3.6.4 Thermal analysis for water content determination

Differential scanning calorimetry coupled with thermogravimetric analysis (DSC-TG) was performed on a Netzsch 449 instrument to determine the water content of the samples. In each experiment the samples were heated from 25 to 800  $^{\circ}$ C under O<sub>2</sub> atmosphere (heating rate 10  $^{\circ}$ C/min, Pt crucible).



Figure 3.12. Example DSC-TG thermograms for all samples.

Sample	Mass loss (weight %)			
	First step (complete dehydration)	Expected value	Total (formation of binary oxides)	Expected value
Cu(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O	9.06	9.02	60.55	60.16
Cd(CH <sub>3</sub> COO) <sub>2</sub> ·2H <sub>2</sub> O	13.70	13.52	51.40	51.82
Ca(CH <sub>3</sub> COO) <sub>2</sub> ·1.1H <sub>2</sub> O	11.55	11.06	68.09	68.47
Ca(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O. CH <sub>3</sub> COOH	32.94	33.05	75.89	76.26
CdCa(CH <sub>3</sub> COO) <sub>4</sub> ·6H <sub>2</sub> O	21.34	21.76	62.00	62.86
CuCa(CH <sub>3</sub> COO) <sub>4</sub> ·6H <sub>2</sub> O	24.3	24.13	69.28	69.72

**Table 3.3.** Summary of sample composition, the expected stoichiometric mass loss and the experimental mass loss observed from DSC-TG measurements

#### 3.7 Outlook: Broadening the reach of solid-state reactions

Although the field of mechanochemistry is still in its early stages of development, it has already expanded along several general branches, including those pertaining to metal-organic frameworks, those related to pharmaceutical research, and those focused on the development of greener alternatives to conventional solution-based processes. Chapter 3 has illustrated that mechanochemical ball milling techniques are applicable to reproducing reactions that occur naturally in the environment, namely in the formation of organic minerals. Indeed, a careful consideration of mineral species found in the environment, along with their interactions *via* weathering processes, has served to guide the design of a geomimetic synthesis of paceite and its cadmium analogue. It is also apparent that translating the natural mineral weathering process into an accelerated aging procedure was also successful in yielding these materials. Taken together, these reactions contribute to an expansion of known solid-state techniques used in the laboratory setting to recreating the natural processes that define the environment outside the research laboratory.

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#### 4 Conclusion

Solid-state chemistry, particularly in the field of materials synthesis, is rapidly evolving, and the challenges that have historically posed difficulties in the preparation of materials such as metalorganic frameworks and synthetic samples of organic minerals (e.g. paceite) are being addressed through the use of novel but simple, clean and efficient synthetic methods such as mechanochemistry and accelerated aging. These solvent-free methodologies have the potential to produce a wide assortment of materials, both extant and novel, while greatly reducing the need for solvent use in the course of the reaction. Chapter 1 provided an overview of relevant areas, including MOF chemistry and design, as well as mechanochemical synthesis, while highlighting in some detail several examples across a wide range of applications, from pharmaceuticallyrelevant products, such as the metallodrug component bismuth subsalicylate, to materials such as MOF-based gas filters that show tremendous industrial and commercial potential. It is clear that mechanochemistry can be used to not only reduce waste and reaction time, but also drive reactions that would otherwise be difficult, hazardous or inefficient to perform in solution, by way of initiating reactions between less reactive reagents or enabling transformations previously thought to be impossible. These advances, highlighted and discussed in Chapter 1, served as the basis of the research through which this Thesis contributes to the body of scientific knowledge. Chapters 2 and 3, respectively, build upon these known advantages of mechanochemistry and elements of MOF design to create new approaches for synthesizing both commercially attractive MOFs as well as synthetic samples of rare organic minerals based on coordination bonds.

Chapter 2 examined the possibility of using ball milling mechanochemistry, as well as temperature-induced (thermochemical) transformations for the synthesis and discovery of selected members of the popular SIFSIX class of water-sensitive metal-organic frameworks. Notably, mechanochemistry alone was demonstrated to be highly efficient in the synthesis of SIFSIX structures, leading to two distinct strategies which permit the assembly of a SIFSIX material either from a pre-made metal hexafluorosilicate salt, or from significantly less costly and much more accessible metal carbonate reactant. However, a phase-pure microporous SIFSIX material was not yet synthesized using mechanochemistry. While it was possible to distinguish the mechanochemical formation of the targeted open framework SIFSIX material thanks to *in* 

*situ* powder X-ray diffraction monitoring, it was evident that the presence of moisture invariably led to the formation of a competing hydrated phase of interpenetrated, non-porous structure. Since the interpenetrated material was consistently obtained in the course of ball milling reactions, efforts were made to effect a structural rearrangement in the product by thermal means. However, this process did not produce a definitive result. While heating the interpenetrated material failed to cause its rearrangement to the desired open framework, it did lead to the formation of an entirely new phase that is not described in the literature. It will be important to determine the crystal structure of this material, as its porosity and composition remain currently unknown.

Consequently, the important results and contributions to knowledge of Chapter 2 can be summarized as follows:

- a) Confirmation of the possibility to use mechanochemistry for the synthesis of SIFSIX structures
- b) Development of two distinct mechanochemical strategies for the synthesis of SIFSIX materials
- c) Discovery of a previously not reported sequence of thermal transformations in the 4,4'bipyridine member of the zinc-based SIFSIX class of materials
- d) Discovery of at least two new structurally different phases for the 4,4'-bipyridine member of the zinc-based SIFSIX class of materials

However, the work described in Chapter 2 has also highlighted the following challenges that should be resolved in future work:

a) SIFSIX-type frameworks of high surface areas and open, microporous structure are not readily accessible through mechanochemistry. The development of mechanochemical approaches to such frameworks is expected to require a more extensive screening of mechanochemical reaction conditions (based on different liquid-assisted and ion- and liquid-assisted grinding strategies), possibly accompanied by further *in situ* reaction studies.

b) Structures of new SIFSIX frameworks reported herein, which are based on zinc nodes and 4,4'-bipyridine linkers, have not yet been determined. The elucidation of these structures will be a significant contribution to the understanding of the design, energetics and phase landscapes of SIFSIX materials – and should be accessible through application of powder X-ray diffraction structure determination methods, either on their own, or in combination with other solid-state analytical techniques, such as thermogravimetric analysis, solid-state nuclear magnetic resonance, infrared spectroscopy, *etc*.

Following the preceding investigations, Chapter 3 applied the use of solid-state methodologies to the field of geologically significant organic minerals, a class of rare, naturally-occurring materials. Specifically, mixed-metal minerals, whose syntheses are traditionally complicated by considerations of incongruent solubility, were targeted for synthesis using solid-state techniques. In that regard, mechanochemical ball milling and accelerated aging were successfully used in the preparation of paceite, a copper-calcium acetate mineral that was recently discovered in nature. These syntheses were notable for resolving two synthetic challenges; in addition to avoiding the problem of incongruent solubility and thereby drastically reducing the amount of reagents needed, solid-state approaches were able to enable the reaction of widely available but poorly soluble carbonate and hydroxide salts. Furthermore, it was demonstrated that the same techniques could be used to prepare a synthetic mineral with no currently known natural analogue, substituting cadmium for the copper found in paceite.

In summary, Chapter 3 has contributed the following to the overall understanding of solid-state preparation of synthetic organic mineral samples:

- a) Confirmation of the viability of using ball milling mechanochemistry and mild accelerated aging techniques to produce synthetic paceite samples without concern for incongruent solubility and reagent reactivity
- b) Application of solid-state methodologies to prepare synthetic, non-naturally-occurring analogues of paceite, featuring cadmium in place of copper
- c) Determination of the crystal structure of the cadmium analogue of paceite
- d) Evaluation of the thermodynamic characteristics of paceite materials

While the project accomplished several key goals pertaining to the solid-state synthesis of mixed-metal organic minerals, there remain many potential avenues for further research:

- a) The establishment of effective and efficient synthetic methods allows for new materials featuring the paceite structure to be designed and constructed by using alternative reagents, such as other metal salts or anionic species. While paceite is already a rare mineral, and consequently poorly investigated, it and its analogues featuring different metals may possess yet unknown properties of practical relevance. This is an area that is ripe for further investigation; for instance, we have already identified a new mixed-metal structure of barium and cadmium acetate that falls under this class of material.
- b) It is possible to extend the use of ball milling and accelerated aging techniques to encompass the preparation of similarly complex organic minerals, whether naturallyoccurring or otherwise. Accelerated aging, as a geomimetic technique, could be an attractive option to better understand the mechanisms of natural mineral formation.

In conclusion, the overall goals of this Thesis are two-fold: it aims to demonstrate the viability of solid-state methods, such as ball milling and accelerated aging, to generate a range of metalorganic materials in an environmentally conscious manner, with consideration for waste reduction and reaction efficiency, while simultaneously expanding the library of materials accessible by solid-state techniques. The research presented herein indeed demonstrates that these methodologies are powerful synthetic tools for a range of relevant metal-organic materials. It also demonstrates that these techniques are still far from being a panacea for challenges inherent to the materials being prepared. Notably, the work described in Chapter 2 highlights the difficulty of generating an open framework material when such materials are water-sensitive; additional work is needed to more thoroughly characterize the materials prepared by heating the products derived from ball milling. Yet, moving forward, there is an increasing need to take environmental impacts into account when developing new experimental techniques; this Thesis clearly demonstrates that mechanochemistry and accelerated aging are certainly attractive ways to address those considerations.