Synthesis and Sorption Studies of Porous Metal-Organic Hosts

by

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Doctor of Philosophy

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Faculty of Science

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DECLARATION

By submitting this dissertation electronically, I, Eustina Batisai, declare that the entirety of the work contained therein is my own, original work, that I am the owner of the copyright thereof (unless to the extent explicitly otherwise stated) and that I have not previously in its entirety or in part submitted it for obtaining any qualification.

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March 2013

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ABSTRACT

The first part of this study describes the synthesis of new porous materials from basic building blocks. Five structurally related ligands namely: \(N,N^\prime\)-bis(3-pyridylmethyl)-naphthalene diimide (L1), \(N,N^\prime\)-bis(4-pyridylmethyl)-naphthalene diimide (L2), \(N,N^\prime\)-bis(4-pyridylmethyl)-pyromellitic diimide (L3), \(N,N^\prime\)-bis(3-pyridylmethyl)-pyromellitic diimide (L4) and 2-(pyridin-4-ylmethyl)-benzene tricarboxylic anhydride (L5) were synthesised. Ligands L1 and L2 were reacted with metal nitrates and carboxylates as co-ligands in a systematic manner with a view to obtaining potentially porous 3–D coordination polymers. Ten structurally diverse coordination polymers were obtained and they were characterised by single-crystal X-ray diffraction, powder X-ray diffraction and thermogravimetric analysis. Four of these compounds absorb moderate amounts of CO\(_2\) and, in addition, show sorption selectivity towards CO\(_2\) over N\(_2\). The reaction of L3 and L4 with transition metal halides yielded two 1–D chains, while the reaction of L5 with transition metal nitrates yielded seven coordination polymers of which four are 2–D and three are 1–D. Of the 2–D structures three are isostructural.

The second part of this work describes a variable pressure study of a flexible metal-organic framework \([\text{Zn}_2(\text{BDC})_2(\text{BPY})]\) (BPY = 4,4’-bipyridine and BDC = 1,4-benzenedicarboxylic acid). \([\text{Zn}_2(\text{BDC})_2(\text{BPY})]\) is one of the few examples of a flexible metal-organic framework that undergoes phase transformations in response to gas pressure. The high pressure sorption recorded for this metal-organic framework displays two inflection steps in the pressure range 0 to 30 bar, possibly indicating two phase transformations. The gas-loaded structures for each phase transformation were determined by means of single-crystal X-ray diffraction. High-pressure differential scanning calorimetry was also carried out on the system in order to determine accurate gate-opening pressures, as well as the energies involved with each phase transformation. The results correlate with those obtained from single-crystal X-ray diffraction and high-pressure sorption.

The final section reports the mechanochemical synthesis of two Werner complexes \([\text{NiCl}_2(4\text{-PhPy})_4]\) (1), \([\text{CoCl}_2(4\text{-PhPy})_4]\) (2) and their corresponding solid solution \([\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4\text{-PhPy})_4]\) (3) (PhPy = phenyl pyridine). The solid solution could only be formed by mechanochemical synthesis and not by conventional solution crystallisation methods. The solid solution exhibits sorption properties that differ from those of the pure compounds.
OPSOMMING

Die eerste deel van hierdie studie beskryf die sintese van nuwe poreuse stowwe uit basiese boublokke. Vyf struktureel verwante ligande naamlik: \(N,N'-\)bis(3-piridielmetiel)-naftaleen diimied (L1), \(N,N'-\)bis(4-piridielmetiel)-naftaleen diimied (L2), \(N,N'-\)bis(4-piridielmetiel)-piromellitien diimied (L3), \(N,N'-\)bis(3-piridielmetiel)-piromellitien diimied (L4) en 2-(piridiel-4-ielmetiel)benseen trianhidried (L5) is gesintetiseer. Ligande L1 en L2 is gereageer met metaal nitrate en karboksiesure as mede-ligande in 'n sistematiese wyse met 'n oog op die verkryging van potensieel poreuse 3–D koördinasie polimere. Tien struktureel diverse koördinasie polimere is verkry en hulle is gekarakteriseer deur enkel-kristal X-straal-diffraksie, poeier X-straal diffraksie en termo-analise (thermal analysis). Vier van hierdie verbindings het matige hoeveelhede \(\text{CO}_2\) geabsorbeer en, bykomend, wys sorpsie selektiwiteit van \(\text{CO}_2\) oor \(\text{N}_2\). Die reaksie van L3 en L4 met oorgangsmetaalhaliede het twee 1–D kettings gevorm, terwyl die reaksie van L5 met oorgangsmetaal nitrate sewe koördinasie polimere opgelewer het, waarvan vier 2–D en drie 1–D polimere is. Van die 2–D polimere het drie vergelykbare strukture.

Die tweede deel van hierdie werk beskryf 'n veranderlike druk studie van 'n buigsame metaal-organiese raamwerk \([\text{Zn}_2(\text{BDC})_2(\text{BPY})]\) (BPY = 4,4-bipiridien en BDC = 1,4-benseen dikarboksiesuur). \([\text{Zn}_2(\text{BDC})_2(\text{BPY})]\) is een van die min voorbeelde van 'n buigsame metaal-organiese raamwerk wat fase transformasies (phase transformations) ondergaan in respons op 'n verandering in gas druk. Die hoë-druk sorpsie aangeteken vir hierdie metaal-organiese raamwerk vertoon twee infleksie stappe in die gebestudeerde druk gebied (0 tot 30 bar), wat moontlik op twee fase transformasies dui. Die gas-gelaaide strukture vir elke fase transformasie is bepaal deur middel van enkel-kristal X-straal-diffraksie. Hoë-druk differensiële skandeer kalorimetrie (differential scanning calorimetry) is ook uitgevoer op die stelsel ten einde dié akkurate hek-openings druk, sowel as die energie betrokke by elke fase transformasie te bepaal. Die resultate stem ooreen met dié verkry vanaf enkel-kristal X-straal difffraksie en hoë-druk sorpsie.

Die finale afdeling bespreek die meganochemiese sintese van twee Werner komplekse \([\text{NiCl}_2(4-\text{PhPy})_4]\) (1) en \([\text{COCl}_2(4-\text{PhPy})_4]\) (2) en hul ooreenstemmende vaste oplossing (solid solution) \([\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4-\text{PhPy})_4]\) (3). Die vaste oplossing kan slegs gevorm word deur meganochemiese sintese en nie deur konvensionele oplossing kristallisasie metodes. Die vaste oplossing vertoon sorpsie eienskappe wat verskil van dié van die suiwre verbindings.
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my supervisor, Professor Len Barbour for his guidance, financial and academic support throughout the course of this study and in the preparation of this manuscript. I thank him for all he has taught me in this field of supramolecular chemistry and science in general. I would also like to extend my sincere gratitude to the following:

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PUBLICATION


CONFERENCES

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(ii) Indaba 7: Insights from Structure, Kruger National Park: 2 - 7 September 2012,  
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ATOM COLOUR KEY

<table>
<thead>
<tr>
<th>Colour</th>
<th>Element</th>
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</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
</tr>
<tr>
<td>Chlorine/bromine</td>
<td></td>
</tr>
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</table>
### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–D</td>
<td>One dimensional</td>
</tr>
<tr>
<td>2–D</td>
<td>Two dimensional</td>
</tr>
<tr>
<td>3–D</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>ASU</td>
<td>Asymmetric Unit</td>
</tr>
<tr>
<td>CIF</td>
<td>Crystallographic Information File</td>
</tr>
<tr>
<td>CPK</td>
<td>Corey-Pauling-Koltun</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge Structural Database</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>HPDSC</td>
<td>High-Pressure Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>L</td>
<td>Ligand</td>
</tr>
<tr>
<td>M</td>
<td>Metal</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-Organic Framework</td>
</tr>
<tr>
<td>PXR</td>
<td>Powder X-ray Diffraction</td>
</tr>
<tr>
<td>SBU</td>
<td>Secondary Building Unit</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>SC-SC</td>
<td>Single-Crystal to Single-Crystal</td>
</tr>
<tr>
<td>SCD</td>
<td>Single-Crystal X-ray Diffraction</td>
</tr>
<tr>
<td>Z</td>
<td>Number of formula units in the unit cell</td>
</tr>
<tr>
<td>H:G</td>
<td>Host-to-guest</td>
</tr>
</tbody>
</table>
CHAPTER 1: CRYSTAL ENGINEERING

1.1 INTRODUCTION

Crystal engineering is a relatively young and fast growing field of science encompassing chemistry and materials science.\textsuperscript{1,2} The aim of crystal engineering is to synthesise and develop new crystalline materials for various applications; examples include chemical separations, gas storage, molecular sensors and non-linear optics.\textsuperscript{2} A significant area of progress in crystal engineering is that of coordination polymers or metal-organic frameworks (MOFs).\textsuperscript{1} MOF materials have potential applications in gas storage, separation, catalysis and sensing.\textsuperscript{2,3} The first part of this chapter discusses some concepts in crystal engineering and the second part discusses two classes of crystal engineered materials (MOFs and inclusion compounds).

The formal definition of crystal engineering was proposed by Desiraju as “\textit{...the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties}”.\textsuperscript{4} However the term was first introduced by Pepinsky in 1955\textsuperscript{5} and later implemented by Schimdt\textsuperscript{6} in 1975 during a study of photodimerisation of cinnamic acid derivatives. Put in very simple terms, crystal engineering can be defined as “\textit{making crystals by design}”.\textsuperscript{7} The key to the design and synthesis of molecular crystals lies in understanding the strength and the nature of intermolecular interactions.\textsuperscript{4,8} Intermolecular interactions have been considered to be the \textit{glue} that holds molecules together in the solid state and a crystal has been described as a \textit{supermolecule par excellence}.\textsuperscript{9,10} Indeed, a crystal is a result of a delicate balance between numerous intermolecular interactions and is thus a thermodynamically stable 3–D assembly.\textsuperscript{9}

In molecular synthesis, the atom is the fundamental building block and the covalent bond is the design element. The covalent bond has been well studied and a variety of reactions in molecular synthesis have been discovered and refined, making it possible to synthesise even complex molecules such as natural products.\textsuperscript{9} Although there has been significant progress in crystal engineering in this regard, the ability to design molecular crystals from a set of building blocks still remains a challenge. Moreover, the occurrence of numerous weak intermolecular interactions means that many free energy minima are possible resulting in polymorphism and pseudo-polymorphism in crystal structures.\textsuperscript{11,12}

Organic chemists use retrosynthetic analysis to construct synthetic routes for the synthesis of target molecules using synthons as the building blocks. Similarly, crystal engineers have
borrowed this idea of synthons, whereby the crystal becomes the retrosynthetic target, and
building blocks are termed tectons. Tectons are able to recognize each other and to self-assemble
into crystals at the molecular level.\textsuperscript{13} The assembling node is termed a supramolecular synthon
and can be likened to a covalent bond in molecular synthesis.\textsuperscript{14} This idea of \textit{supramolecular synthons} was first described by Desiraju in 1995\textsuperscript{14} and it is based on analysing existing crystal
structures for certain repetitive units between the same functional groups and intermolecular
interactions. Supramolecular synthons are thus defined as “\textit{structural units within supermolecules which can be formed and/or assembled by known or conceivable synthetic
operations involving intermolecular interactions}”.\textsuperscript{14} A list of some commonly occurring synthons
is shown in Figure 1.1. Known crystal structures are stored in the Cambridge Structural Database
(CSD),\textsuperscript{15} which is a crystallographic database containing over half a million organic and
organometallic entries of crystal structures accumulated over a long period of time. Searches of
the CSD can be made for patterns of intermolecular interactions. The CSD is therefore an
indispensable tool in the field of crystal engineering.

\textbf{Figure 1.1} Some common supramolecular synthons.\textsuperscript{14}
1.2 SELF-ASSEMBLY
According to Whitesides, self-assembly can be defined as the process in which components, either separate or linked, spontaneously form ordered aggregates through non-covalent interactions.\textsuperscript{16} Nature uses self-assembly over covalent bond formation for assembling small building blocks into complex stable structures such as lipid bilayers, ribonucleic acid (RNA) and the tobacco mosaic virus. Non-covalent interactions are weak and reversible, and they can be easily broken and re-formed. Covalent bonds, on the other hand, would require a large amount of energy to be broken and reformed.\textsuperscript{13} The process of self-assembly is governed by steric factors, conformational preferences and entropic driving forces.\textsuperscript{13} In crystal engineering, tectons interact with one another \textit{via} non-covalent interactions by achieving a compromise between the attractive and repulsive forces in the system.\textsuperscript{16} Self-assembly allows for reversibility and adjustability, which are important for the formation of supramolecular systems.\textsuperscript{16}

1.3 INTERMOLECULAR INTERACTIONS
As mentioned earlier, intermolecular interactions are considered to be the glue that holds molecules together in the solid state. Generally, intermolecular interactions are weaker than covalent bonds and their strength ranges from 0.5-40 kcal mol\textsuperscript{-1}.\textsuperscript{17} Intermolecular interactions are classified into (1) long range forces and (2) medium range forces.\textsuperscript{14} Long range forces, which are also known as directional forces, form between heteroatoms N, S, O, Cl, Br, I, B, F, P, Se or between any one of the heteroatoms and either C or H.\textsuperscript{14} On the other hand, medium range forces are weak and non-directional. Even though intermolecular interactions are weaker than covalent bonds, their combined strength can be more important than a few strong interactions.\textsuperscript{14} A list of some of the intermolecular interactions and their strengths is given in Table 1.1.\textsuperscript{17}

<table>
<thead>
<tr>
<th>Intermolecular interaction</th>
<th>Energy (kcal mol\textsuperscript{-1})</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very strong hydrogen bonds</td>
<td>15-40</td>
<td>OH···O</td>
</tr>
<tr>
<td>Coordinative bonds</td>
<td>20-45</td>
<td>M···N, M···O</td>
</tr>
<tr>
<td>Strong hydrogen bonds</td>
<td>5-15</td>
<td>OH···O, NH···O</td>
</tr>
<tr>
<td>Weak hydrogen bonds</td>
<td>1-4</td>
<td>CH···O, OH···π</td>
</tr>
<tr>
<td>Van der Waals interactions</td>
<td>0.5-2</td>
<td>CH\textsubscript{3}···CH\textsubscript{3}, CH\textsubscript{3}···Ph</td>
</tr>
<tr>
<td>Heteroatom interactions</td>
<td>1-2</td>
<td>N···Cl, I···I, Br···Br</td>
</tr>
<tr>
<td>(\pi) interactions</td>
<td>2-10</td>
<td>Ph···Ph, nucleobases</td>
</tr>
</tbody>
</table>
1.3.1 Directional forces

1.3.1.1 The hydrogen bond
The definition of a hydrogen bond, as presented by Steiner in 2002, states that “an X–H···A interaction is called a hydrogen bond if (1) it constitutes a local bond, and (2) X–H acts as proton donor to A.” The X–H···A (X = donor and A = acceptor) bond is defined by the geometric parameters $d$, $D$, $r$, $\theta$ and $\phi$ as shown in Figure 1.2a. The hydrogen bond is one of the most important and commonly occurring interactions in nature - for example, in nucleic acids, proteins and polysaccharides. Hydrogen bonds are classified as (i) very strong, (ii) strong and (iii) weak, based on their strength. The terms bifurcated and trifurcated are used when one donor atom interacts with two or three acceptors, respectively (Figure 1.2b and 1.2c). A few examples of hydrogen bonds and their associated energies are given in Table 1.2.

![Figure 1.2](http://scholar.sun.ac.za)

**Figure 1.2** (a) The geometric parameters for a hydrogen bond, (b) bifurcated and (c) trifurcated hydrogen bonds.

1.3.1.2 Halogen bonds
A halogen bond is a non-covalent, directional interaction between a halogen atom acting as an electrophilic species and a neutral or anionic base. The term $D···X–Y$ is used to denote a halogen bond, where $X$ is the halogen, $D$ is an electron donor and $Y$ can be carbon, nitrogen or a halogen. Even though the concept of halogen bonding is still very new, the history of interactions such as I···N, I···O and Br···O dates back to the 1960s. Halogen bonds can be divided into two groups: (i) symmetrical ($X···X$, e.g. Cl···Cl, Br···Br, I···I) and (ii) asymmetrical ($X···Y$ where $Y$ is a halogen or a non-halogen e.g. I···Br, I···N, I···Cl). Halogen bonds are strong and directional interactions and these important properties have already been utilised in fields such as superconductors, liquid crystals and substrate receptor binding.
Table 1.2 Characteristics of very strong, strong and weak hydrogen bonds.1

<table>
<thead>
<tr>
<th></th>
<th>Very Strong</th>
<th>Strong</th>
<th>Weak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy (kcal mol⁻¹)</td>
<td>15-40</td>
<td>4-15</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Examples</td>
<td>[F···H···F]⁻</td>
<td>O–H···O=C</td>
<td>C–H···O</td>
</tr>
<tr>
<td></td>
<td>[N···H···N]⁺</td>
<td>N–H···O=C</td>
<td>O–H···π</td>
</tr>
<tr>
<td></td>
<td>P–OH···O=P</td>
<td>O–H···O–H</td>
<td>Os–H···O</td>
</tr>
<tr>
<td>Bond lengths</td>
<td>D–A ≈ D–H</td>
<td>H···A &gt; D–H</td>
<td>H···A &gt;&gt;&gt; D–H</td>
</tr>
<tr>
<td>Lengthening of D–H (Å)</td>
<td>0.05–0.2</td>
<td>0.01–0.05</td>
<td>≤ 0.01</td>
</tr>
<tr>
<td>Y(D···A) range (Å)</td>
<td>2.2–2.5</td>
<td>2.5–3.2</td>
<td>3.0–4.0</td>
</tr>
<tr>
<td>d(H···A) range (Å)</td>
<td>1.2–1.5</td>
<td>1.5–2.2</td>
<td>2.0–3.0</td>
</tr>
<tr>
<td>Bonds shorter than vdW</td>
<td>100%</td>
<td>Almost 100%</td>
<td>30–80%</td>
</tr>
<tr>
<td>θ(D–H···A) range (°)</td>
<td>175–180</td>
<td>130–180</td>
<td>90–180</td>
</tr>
<tr>
<td>Effect on crystal packing</td>
<td>Strong</td>
<td>Distinctive</td>
<td>Variable</td>
</tr>
<tr>
<td>Utility in crystal engineering</td>
<td>Unknown</td>
<td>Useful</td>
<td>Partly useful</td>
</tr>
<tr>
<td>Covalency</td>
<td>Pronounced</td>
<td>Weak</td>
<td>Vanishing</td>
</tr>
<tr>
<td>Electrostatics</td>
<td>Significant</td>
<td>Dominant</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

1.3.1.3 Coordination bonding

A coordination bond forms between a labile metal ion with a vacant site and a ligand that is capable of donating a lone pair of electrons. Its strength ranges from 20-45 kcal mol⁻¹.17 In the synthesis of coordination polymers the coordination bond is utilised as the primary interaction because of its strength and directionality.22 The coordination bond directs the formation of the network topology, while the other weaker interactions assume secondary functions, i.e. packing.22 In terms of strength, the strongest coordination bonds overlap in energy with the weakest covalent bonds, while the weakest coordination bonds overlap in energy with the strongest hydrogen bonds.23

1.3.2 Non directional forces

1.3.2.1 π···π interactions

π···π interactions are non-directional forces that occur in the energy range of 2-10 kcal mol⁻¹.17 They are common in crystal structures that contain aromatic systems. There are three common

*Table adapted from reference 19
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Types of interactions possible in aromatic compounds, viz, offset, edge-to-face and stacked motifs. The three motifs are show in Figure 1.3.

![Figure 1.3 Three types of interactions possible between phenyl rings. (a) Offset, (b) edge-to-face and (c) stacked.](image)

1.3.2.2 Van der Waal interactions

Van der Waals interactions are electrostatic and non-directional. The term includes the sum of all stabilising interactions and other anisotropic interactions in a molecular crystal. When considered individually, these interactions are relatively weak. However, because they are numerous, their combined effect accounts for the solubility, density and melting points of molecular crystals.

1.4 Metal-organic frameworks (MOFs)

Metal-organic frameworks (MOFs) are organic-inorganic hybrid microporous materials constructed from organic bridging ligands and metal ions or clusters. The most commonly used organic ligands are carboxylate and neutral nitrogen donor ligands (Figure 1.4). MOFs are a subclass of a much broader class of compounds known as coordination polymers or coordination complexes. The concept of coordination polymers was first introduced in the literature in 1965 by Tomic and Biondi, who referred to them as crystalline polymeric compounds. Three decades later, Yaghi and co-workers published the structure of MOF-5. Even though the concept of MOFs is still in its infancy remarkable progress has been made in terms of correlating structure-property relationships.
MOFs are interesting because of their exceptionally high surface area, low framework density and high pore volumes, which make them ideal candidates for a wide range of industrial applications such as gas storage, gas separation, gas purification and heterogeneous catalysis, among others. The chemistry of zeolites as catalysts has been developed for more than fifty years, and the use of zeolites in the above-mentioned applications, especially heterogeneous catalysis is well established. However, there are certain limitations to the use of zeolites. For example, zeolites have a low catalytic site density and a limited pore size.

The major disadvantage of using MOFs in some of the industrial applications is their low thermal and chemical stability. A large percentage of the reported MOFs decompose at temperatures around 300 °C, which implies that they cannot be used in vapour phase reactions, which are carried out at temperatures above 200 °C. However, in liquid phase reactions that are carried out under mild conditions, MOFs have been shown to perform better than zeolites.

1.4.1 Classification of MOFs
According to Kitagawa, MOFs are classified as 1\textsuperscript{st}, 2\textsuperscript{nd} and 3\textsuperscript{rd} generations (Figure 1.5). The classification is based upon the type of the host framework that results from desolvation. When guest removal results in complete and irreversible destruction of the framework, the MOF is termed 1\textsuperscript{st} generation. The 2\textsuperscript{nd} generation MOFs maintain their frameworks after guest removal, while in the 3\textsuperscript{rd} generation MOFs desolvation is accompanied by a reversible host
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rearrangement. MOFs of this type are flexible and dynamic and can respond reversibly to external stimuli such as temperature, light and guest molecules.

![Classification of MOFs](image)

**Figure 1.5 Classification of MOFs.**

1.5 POROSITY

Porosity in MOFs is associated with applications such as gas storage, molecular sensing and catalysis. According to Barbour, porosity can be classified into three distinct categories: virtual, transient and conventional porosity.

**Virtual porosity** is generated by deleting or ignoring small molecules i.e. solvent molecules or anions and, in some cases, even the ligand bridging two metal ions from a file containing the asymmetric unit (ASU) of a crystal structure.

**Transient porosity** (or porosity without pores) refers to a crystalline solid that possesses large voids without any channels leading to the voids and yet is still porous.

**Conventional porosity** is generated by completely removing or exchanging the solvent molecules situated in the channels of the host framework. The stability of the host framework after removal of the guest determines the permeability of the crystal.

Using the guidelines provided by the International Union of Pure and Applied Chemistry (IUPAC) in 1985, conventional porous materials can be classified into four categories based on the pore size: ultramicroporous (pore size < 5 Å), microporous (pore size 5-20 Å), mesoporous (pore size 20-500 Å) and macroporous (pore size > 500 Å). Porosity can be described in terms of adsorption or absorption behaviour. *Adsorption* is the enrichment of a substance.

† Figure adapted from reference 3
(adsorbate) at an interface (adsorbent), adsorption refers to the process whereby one substance is taken into the body of another. Desorption is the converse of adsorption and it is the process by which the amount of the adsorptive is decreased. In this thesis, the term sorption will be used to describe the combined action of adsorption and absorption. Sorption can be further divided into physi- and chemisorption. Physisorption occurs when a gas is in contact with a solid surface, and is characterised by long range and weak van der Waals forces. The enthalpy of adsorption is less than 40 kJ mol\(^{-1}\). Chemisorption is characterised by the formation of covalent bonds with an enthalpy of -110 kJ mol\(^{-1}\) to -400 kJ mol\(^{-1}\).\(^{43,45}\)

Gas adsorption is measured by determining the amount adsorbed at a constant temperature as a function of the equilibrium pressure of the gas; the amount adsorbed (in moles, grams or cm\(^3\)) is plotted against the relative equilibrium pressure (P/P\(_0\)), where P\(_0\) is the saturation pressure of the adsorptive at the specified temperature. This relationship is known as the adsorption isotherm. In most cases, the amount adsorbed and desorbed is often plotted in one isotherm, and if the adsorption and desorption curves do not coincide, then the system is said to display hysteresis.\(^{46,47}\)

There are six types of adsorption isotherms as classified by IUPAC (Figure 1.6) and only types I, II and IV are common.\(^{46,47}\) Type I isotherms are reversible and are characteristic of microporous solids with small surface areas such as zeolites or activated carbon. These are also known as Langmuir isotherms. Type II isotherms are also reversible and are characteristic of a nonporous or macroporous sorbent. Type IV isotherms display a characteristic hysteresis loop, which is attributed to capillary condensation in the mesopores and limited gas uptake at high P/P\(_0\). Type III isotherms display reversibility over the entire pressure range which can be attributed to weak host-guest interactions. The shape of Type V isotherm is similar to that of Type III, but it is not reversible. This is due to sorbent-sorbate interactions. Type VI isotherms display a stepwise profile which is attributed to layer-by-layer sorption on a uniform non-porous surface.
1.6 SOME APPLICATIONS OF MOFs

1.6.1 Catalysis

MOFs have been tested in a wide range of catalysis reactions such as the Ziegler-Natta type polymerisation,\textsuperscript{48} Diels-Alder reactions,\textsuperscript{49,50} transesterification,\textsuperscript{51} and cyanosilylation of aldehydes.\textsuperscript{52} Ongoing research seeks to find whether the differences in the metal centres, functionalised and unfunctionalised ligands and different metal ligand interactions can improve the efficacy of MOFs in terms of selectivity and activity.\textsuperscript{35} For example, the catalytic activity of MOF-2, which consists of zinc carboxylate clusters was tested in the reaction of propyne and methanol in cyclohexanol, to form methoxypropene.\textsuperscript{35} It was found that the conversion of propyne was 30\% with a selectivity of 80\% to 2-methoxypropene as compared to zinc silicate, which has a selectivity of 77\% with full conversion at temperatures between 180 and 200 °C.\textsuperscript{35,53,54}

1.6.2 Gas storage

With the world moving towards green chemistry, there is a need for clean energy with no greenhouse emissions or air pollution. For this reason natural gas, which consists of 95\% v/v of methane with the other 5\% being heavy hydrocarbons, carbon dioxide, nitrogen, water and sulphur compounds, has been identified as a viable clean energy source.\textsuperscript{3,55} On the other hand,
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the sequestration of CO$_2$ from flue gas is a global challenge.$^{56}$ Therefore, there is a need to develop porous materials that absorb gases such as methane, carbon dioxide and hydrogen. For CO$_2$ sequestration, current methods of capture involve the use of alkanol amine based solvents. However, one of the major disadvantages of this method is the high energy cost involved during regeneration.$^{57,58}$

Conventional porous materials such as activated carbon have been tested for storage of methane.$^3$ However, they do not possess the commercially viable gas storage capacity.$^3$ For useful storage and transportation of the gases, the porous materials should be able to absorb gases at ambient temperatures and low pressure.$^3$ Quite a large number of MOFs have been examined for the absorption of methane and hydrogen. For example, the compounds MOF-5, IRMOF-6 and IRMOF-8, which are based on the zinc-dicarboxylate cluster were tested for hydrogen absorbing capacity.$^59$ At 78 K MOF-5 absorbs 17.2 H$_2$ molecules per formula unit (4.5 weight %) and at room temperature and 20 atm MOF-5 absorbs 1.0 weight % H$_2$. $^{59}$

1.7 POST SYNTHETIC MODIFICATION (PSM) OF MOFs

Post synthetic modification (PSM) of MOFs can be broadly defined as the derivatisation of MOFs after the crystalline materials have already been formed.$^{61}$ PSM allows for certain functionalities, which would have been otherwise impossible to introduce before or during the formation of MOFs, to be introduced into the framework.$^{61}$ Moreover, a wide range of functionalities can be introduced into the MOF, generating diverse but structurally related MOFs.$^{61}$ Synthesis of MOF using ligands with different functionalities can be a daunting task as certain functionalities are not compatible with the MOF synthesis conditions. It is much easier to incorporate these functionalities after the MOF is formed.$^{61}$

1.7.1 Non-covalent interactions

Non-covalent modification of MOFs includes guest exchange, guest removal and anion exchange. Most MOFs can undergo a single-crystal to single-crystal (SC-SC) guest exchange. SC-SC transformation is a phenomenon where significant changes in the crystal structure occur in the solid state without destroying the integrity of the crystal such that it can still be analysed by means of single-crystal X-ray diffraction (SCD).$^{62,63}$ SC-SC transformations are interesting because they provide insight into the structural changes occurring at the molecular level as the crystal responds to either chemical or physical stimuli.
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During guest exchange the as-synthesised crystals are immersed in another solvent. If there are no strong interactions holding the guest molecules to the walls of the host framework, the as-synthesised solvent can simultaneously exchange with another solvent without compromising the integrity of the host framework. The mechanism by which the guest exchange takes place is not yet fully understood; It is not known whether the host framework deforms or dissociates during guest exchange.\textsuperscript{61} Guest removal, on the other hand, can be detrimental to the integrity of many MOFs. In some cases, guest removal coincides with decomposition of the framework, while in other cases, even if the guest can be removed, the framework is not robust enough to maintain single crystallinity.

1.7.2 Coordinative interactions
Post synthetic modification by coordinative interactions can be achieved in two ways, \textit{viz} generation of coordinatively unsaturated sites on the metal centre and exploring the coordination chemistry of organic components.\textsuperscript{61} Removal of auxiliary ligands can generate coordinatively unsaturated sites, whereas introducing new ligands can generate a MOF with modified properties.\textsuperscript{61} Incorporating unbound ligands onto a framework can be difficult as the unbound ligand tend to coordinate to the metal centre, thereby interfering with the synthesis. However, recent studies by Lin \textit{et al.} have shown that incorporating unbound ligands can indeed generate MOFs with enhanced catalytic properties.\textsuperscript{64} They synthesised a MOF from Cd(II) and 1,1′-bi-2-naphthol (BINOL) a homochiral ligand comprising both pyridine and hydroxyl groups. In this case, the pyridine coordinates to the metal centres, while the hydroxyl groups are non-coordinating. Treatment of the MOF with Ti(O\textsubscript{i}Pr)\textsubscript{4} resulted in coordinative interactions between the hydroxyl groups and the titanium centres. The Ti(O\textsubscript{i}Pr)\textsubscript{4} modified MOF was shown to have enhanced catalytic properties.\textsuperscript{64}

1.7.3 Covalent interactions
Covalent modification of MOFs is challenging when considering the relative strength of the covalent bond as compared to the weaker coordination bond.\textsuperscript{61} However, a large number of covalent transformations such as amide coupling,\textsuperscript{65,66} imine condensation,\textsuperscript{67} click reactions\textsuperscript{68} and protonation\textsuperscript{69} have been reported. For example, Kim \textit{et al.} constructed a 2–D homochiral framework that possesses free pyridyl moieties that are not coordinated to the metal centres.\textsuperscript{70} The MOF showed catalytic activity for the transesterification of 2,4-dinitrophenyl acetate and it was postulated that the free pyridyl rings are essential for this catalytic activity. Treatment of the
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crystal with CH$_3$I for two hours generated the alkylated MOF, which had little or no catalytic
activity for the transesterification of 2,4-dinitrophenyl acetate.\textsuperscript{70}

1.8 STIMULI-RESPONSIVE MOFs

Recently there has been growing interest in flexible and dynamic MOFs as compared to the more
rigid and robust structures.\textsuperscript{71-74} MOFs that can respond to external stimuli such as pressure and
temperature can be utilised in the creation of new generations of functional and smart
materials.\textsuperscript{71-74} The dynamic behaviour of these compounds is attributed to non-covalent
interactions such as $\pi$$\cdots$$\pi$ interactions, hydrogen bonding and van der Waals forces.\textsuperscript{72}

Stimuli-responsive materials are also known as soft porous materials.\textsuperscript{72} According to
Kitagawa soft porous crystals can be defined as porous solids that possess both a highly ordered
network and structural transformability.\textsuperscript{72} Soft porous crystals possess two characteristics,
namely permanent porosity and structural transformability.\textsuperscript{72} Structural transformability can
either occur progressively as in the case of MIL-88, which shows structural changes in response
to different guests,\textsuperscript{75,76} or it can occur abruptly between two mutually convertible structures of
the framework as in the case of MIL-53.\textsuperscript{76,77} Structural changes usually occur between nonporous
and porous phases of the crystals, but they can also occur from one porous phase to another.\textsuperscript{72}
Permanent porosity of the crystals arises when at least one of the phases has cavities that can
accommodate guests.\textsuperscript{72} The structural transformation of these materials is caused by motif
displacement and framework flexibility.\textsuperscript{72} In interpenetrated structures the frameworks are held
by weak interactions such as van der Waals forces or $\pi$$\cdots$$\pi$ interactions.\textsuperscript{72} This allows the
frameworks to slide together when an external stimulus is applied, resulting in either a decrease
or an increase in pore size. For example, the reported structure
\[ [\text{Zn}_2(\text{BDC})_2(\text{BPY})](\text{DMF})_2(\text{H}_2\text{O}), \text{BPY} = 4,4^\prime\text{-bipyridine and BDC} = 1,4\text{-benzene dicarboxylic}
\text{acid}] \]
also known as MOF-58 is a doubly interpenetrated 3–D structure.\textsuperscript{78} The as-synthesised
phase has channels that are occupied by solvent molecules. When the solvent molecules are
removed, the framework transforms into a nonporous phase that has no cavities. The porous
phase is capable of separating linear and branched alkanes.\textsuperscript{78}

1.9 ENGINEERING VOID SPACE

Molecules in the solid state naturally tend to close-pack so as to maximise the interactions
between them and, as a result, crystals with voids are rare.\textsuperscript{21} During MOF synthesis a solvent
(guest) that can be easily removed or exchanged is used as a template to fill these voids. The
porosity of the compound is then determined by whether the solvent can be removed or exchanged completely without damaging the framework of the host.42

Most research groups approach the synthesis of MOFs by using single metal ions and organic ligands. However, the main challenge of this approach is the difficulty in predicting the type of product that will result. As a result, unwanted 1–D polymeric chains that close pack, often form instead of the sought-after 3–D porous structures. Despite these challenges, a large number of functional MOFs have been synthesised using this approach.3 Yaghi and co-workers have been most successful in designing a synthetic strategy for the construction of robust MOFs.79 Their synthetic strategy is known as reticular synthesis and utilises metal carboxylate clusters instead of metal ions.79 The carboxylate locks the metal into a specific geometry and the carboxylate carbon forms the point of extension, which offers directionality. These points of extension are referred to as secondary building units (SBUs) and they impart rigidity to the framework.79 By using this strategy, Yaghi and co-workers have managed to synthesise MOFs that are robust and stable upon guest removal.79

Barbour et al. have developed the 0–D or doughnut shaped metallocycles.63,80-83 These metallocycles are constructed from imidazole-functionalised ditopic ligands and metal salts. Assuming the ligand adopts a C shape and two metal centres are shared between two chelating ligands, then a doughnut shape is formed, which packs inefficiently to leave voids or channels that are occupied by solvent molecules (Figure 1.7).

1.10 INCLUSION COMPOUNDS

The term inclusion compounds refers to the association between a molecule (host) that binds another molecule (guest).8,84 This association utilises non-covalent interactions and the supramolecular entity is known as host-guest complex or supermolecule.8 The host molecule is large and has a cavity that accommodates the guest molecule.8,84 The host molecule may be an enzyme, a synthetic organic molecule, a metal-organic framework or a zeolite, while the guest molecule is usually a small ion, solvent molecule or even a complex molecule such as a hormone.8,84
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Figure 1.7 (a) A schematic representation of a 0–D metallocycle, (b) the ideal packing arrangement in which individual metallocycles stack directly on top of one another forming channels templated by solvent molecules and (c) a side view showing continuous 1–D channel occupied by solvent molecules.

Host molecules can be divided into two categories, viz cavitands and clathrands. A cavitand is a host molecule possessing a large cavity both in solution and the solid state, while a clathrand is a host molecule whose cavity only exists in the solid state. The host-guest complexes formed are thus known as cavitates or clathrates, respectively. The host-guest systems can also be classified according to the strength and nature of the forces binding them. Host-guest aggregates held together by electrostatic forces such as hydrogen bonding and dipole-dipole interactions are referred to as ‘host-guest complexes’, while the terms ‘clathrates’ or ‘cavitates’ are used when the association is by non-directional forces such as van der Waals interactions.

A schematic representation of the processes of guest inclusion and removal is shown in Figure 1.8. The β phase can be obtained by any one of the following methods: (i) dissolution and crystallization of the apohost phase (the α-, nonporous phase) in the liquid guest, (ii) grinding the apohost phase with a few drops of the liquid guest and (iii) exposing the apohost phase to the vapour of the guest. In some instances, desolvation of the β phase is accompanied by rearrangement back to the α phase, whereas some inclusion compounds only partially desolvate with framework rearrangement to give the γ phase. Inclusion compounds can also desolvate completely without rearrangement of the framework to give the β₀ phase (Figure 1.8).
Figure 1.8 A schematic representation of (a) dissolution of the apohost phase in the liquid guest, (b) crystallization of the $\beta$ phase, (c) desolvation coupled with host rearrangement to yield the $\alpha$ phase, (d) partial desolvation to yield the $\gamma$ phase and (e) desolvation without host rearrangement, yielding the $\beta_0$ phase.\textsuperscript{85}

1.11 AIMS AND OBJECTIVES

The objectives of this work were:

(i) To synthesise new porous coordination polymers;

(ii) To identify MOFs with interesting sorption isotherms (e.g. stepwise gas absorption and hysteretic gas desorption behaviour) and to study them using analytical techniques such as powder X-ray diffraction (PXRD), single crystal diffraction (SCD), high pressure differential scanning calorimetry (HPDSC) and high pressure sorption. These materials are interesting because they undergo structural transformation between mutually convertible structures in response to external stimuli such as temperature, light and gas pressure. We are especially interested in those MOFs that undergo phase transformations in response to gas pressure in a SC-SC manner;

(iii) To prepare three inclusion compounds known as Werner complexes and to study their xylene sorption properties.
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1.13 THESIS OUTLINE
In Chapter 2, the instrumentation and computer packages that were used in this work are described.

Chapter 3 describes efforts to synthesise new porous materials from basic building blocks under ambient conditions as well as solvothermal conditions. For the study, five structurally related ditopic ligands L1-L5 were synthesised (Figure 1.9). L1 and L2 were reacted with metal nitrates and carboxylic acids with a view to obtaining 3–D porous MOFs. The porosity of some of the compounds obtained was tested using CO\(_2\) and N\(_2\) gases. L2 and L3 were reacted with metal halides in the hope of obtaining 0–D or discrete metallocycles, as discussed in section 1.9.

![Figure 1.9 Structures of the five ligands (L1-L5).](image)

Chapter 4 describes a rare phenomenon of two phase transformations in a flexible MOF [Zn\(_2\)(BDC)\(_2\)(BPY)] under different pressures of CO\(_2\). The system was studied extensively using PXRD, HPDSC and high pressure sorption. The ability of the compound to maintain single crystallinity allowed the different phases to be elucidated by means of SCD. The data obtained from SCD correlate well with those obtained from HPDSC and high pressure sorption.

Chapter 5 describes the mechanochemical synthesis of two Werner complexes [NiCl\(_2\)(4-PhPy)\(_4\)] (1), [CoCl\(_2\)(4-PhPy)\(_4\)] (2) and the solid solution [Ni\(_{0.5}\)Co\(_{0.5}\)Cl\(_2\)(4-PhPy)\(_4\)] (3) (PhPy = phenyl pyridine) that could not be obtained by solution synthesis (Figure 1.10). The solid solution exhibits vapour sorption properties that differ from those of the pure compounds.
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Figure 1.10 The preparation of the three Werner complexes \([\text{NiCl}_2(4\text{-PhPy})_4] \) (1), \([\text{CoCl}_2(4\text{-PhPy})_4] \) (2) and the solid solution \([\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4\text{-PhPy})_4] \) (3) by grinding, as well as their xylene sorption tendencies.

Chapter 6 provides a short summary of the outcomes of this work as well as suggestions for future work.
CHAPTER 2: EXPERIMENTAL TECHNIQUES

2.0 INSTRUMENTS AND COMPUTER PACKAGES

This chapter describes the analytical instruments as well as software packages used during the course of this study.

2.1 SINGLE CRYSTAL X-RAY DIFFRACTION (SCD)

Crystals were selected according to their transparency, morphology and ability to rotate plane-polarized light. Crystals that were too large were cut to the desired size. Suitable crystals were mounted at the tip of a MiTeGen mount using paratone oil. X-ray intensity data were collected on a Bruker SMART-APEX II or Bruker APEX II DUO X-ray diffractometer. The SMART is equipped with a molybdenum fine-focus sealed tube, a 0.5 mm Monocap collimator and an APEX II detector. The DUO is equipped with Incoatec μS molybdenum and copper microfocus X-ray sources and an APEX II detector. Both diffractometers are coupled to an Oxford Cryosystems Cryostat (700 Series Cryostream Plus), which is used as the temperature controller. Data reduction and absorption corrections were carried out using the SAINT\textsuperscript{88} and SADABS\textsuperscript{89} programmes, respectively. The unit cell dimensions were refined on all data and space groups were assigned based on systematic absences and intensity statistics. The structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97\textsuperscript{90} and refined with SHELXL-97\textsuperscript{90} using the X-seed\textsuperscript{91} graphical user interface. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Images of all crystal structures were generated using the programme POV-Ray\textsuperscript{92}.

2.2 GAS CELL FOR COLLECTION OF SINGLE-CRYSTAL DATA UNDER CONTROLLED ATMOSPHERE

A gas cell was developed by our group to allow collection of single-crystal data under controlled gas pressure. The gas cell consists of a Lindemann capillary, which is flame sealed at the narrow end, while the wider end is attached to a steel fitting using epoxy resin. The steel fitting has an internal diameter slightly larger than the external diameter of the capillary. The steel fitting is attached to a brass cell coated with nickel, which contains a gas inlet port. The entire gas cell assembly is shown in Figure 2.1; it fits onto a standard goniometer head, which is mounted on a diffractometer for data collection (Figure 2.1). The steel lock nut is used to secure the gas cell onto the goniometer head as well as for height adjustments during centering of the crystal. For a
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typical gas cell experiment, the crystal is glued at the tip of a glass fibre, which is inserted into the Lindemann capillary. The gas cell is then loaded with a particular gas by means of a detachable steel arm, which fits into the gas inlet port. The crystal is typically allowed to equilibrate for at least 24 h before proceeding with intensity data collection. The gas cell has been tested and found to be leak-proof and it can withstand gas pressures up to 80 bar.

![Diagram of gas cell assembly](image)

Figure 2.1 Left: The gas cell assembly attached to a standard goniometer head using the steel locknut and right: the gas cell mounted on a diffractometer.

2.3 POWDER X-RAY DIFFRACTION (PXRD)

Diffraction patterns were recorded on a PANalytical XPERT-PRO diffractometer. The diffractometer is equipped with Bragg-Brentano geometry and uses Cu Kα radiation (λ = 1.5418 Å) as the incident beam. Intensity data were collected by utilising a flat stage and capillary spinner. In the case of the flat stage, samples were gently pre-ground using a mortar and pestle, loaded onto a zero-background sample holder and levelled with a glass slide. The samples were scanned between 3° and 50° with a scan step size of 0.017° and a scan speed of 42 seconds per step. In order to record PXRD patterns under pressure, the samples were first ground and loaded into a Lindemann capillary fitted onto a gas cell as described above. The gas cell was then
fitted on a goniometer head, which was then attached to the capillary spinner of the diffractometer. For compounds that were analysed under gas pressure, the cell was pressurised to the desired gas pressure and allowed to equilibrate for at least 8 h prior to analysis. Unless otherwise noted, intensity data were collected at room temperature.

2.4 THERMOGRAVIMETRIC ANALYSIS (TGA)
TGA data were recorded on a TA Instruments Q500 thermogravimetric analyser. The samples were heated at a rate of 10 °C min⁻¹ under N₂ atmosphere (flow rate 50 ml min⁻¹) from room temperature to 598 °C.

2.5 GAS-SOLID REACTION KINETICS IN CONTROLLED ATMOSPHERES
An improved version of the microbalance designed by Barbour et al. was used for the study of solid-vapour reaction kinetics in a controlled atmosphere. The apparatus consists of a reaction vessel, solvent inlet port and a CI microelectronic balance. The reaction vessel encloses an aluminium sample pan, which hangs down a thin brass rod. The temperature and the pressure in the reaction vessel are monitored using a thermostat and a manometer respectively. For a typical experiment, the sample is loaded on the pan and the reaction vessel is evacuated until a constant sample weight is achieved. Then the liquid guest is injected and allowed to equilibrate to its temperature dependent vapour pressure. The weight increase is monitored until saturation. The data are graphically represented on the computer as a plot of weight vs time.

2.6 GRAVIMETRIC SORPTION
Gravimetric gas sorption experiments were carried out on an Intelligent Gravimetric Analyser (IGA) supplied by Hiden Isochema. The system is equipped with an advanced pressure rating that allows sorption measurements to be carried out up to 20 bar of gas pressure for which gas buoyancy effects are corrected. The temperature of the experiment is controlled by a refrigerated recirculation bath. The data are monitored by real time software that continually analyses the equilibrium using least-squares regression to extrapolate a value of the asymptote. A Linear Driving Force (LDF) relaxation model was used, with each point recorded once 95% fit with the model was achieved, or the time-out was reached (set at 120 minutes).
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2.7 PCT pro
Gas sorption isotherms were collected on a Hy-Energy PCTPro-2000. The system is equipped with a microdoser module connected in a 0-30 bar pressure range. The instrument employs the principles of gas sorption manometry whereby the pressure in a calibrated container (i.e. constant volume) is recorded at a stable temperature. For a typical experiment, the sample holder is filled with approximately 100 mg of sample. The free volume of the sample holder is determined before each experiment using helium absorption-desorption cycles. A reservoir of volume $0.58 \text{ cm}^3$ is used for a typical experiment and the free volume of the sample holder is normally around $0.7 \text{ cm}^3$. The pressure of the reservoir can be increased or decreased by 2 bar during sorption or desorption steps, so data points are collected at approximately 0.9 bar pressure intervals. The equilibrium for every step is checked with an equilibrium test after 30 minutes and a data point is recorded when equilibrium is reached.

2.8 HIGH-PRESSURE DIFFERENTIAL SCANNING CALORIMETRY (HPDSC)
Pressure-DSC measurements were carried out using a Setaram µDSC7 Evo module equipped with a high pressure sample holder. For constant pressure gradient measurement the DSC was coupled to a Teledyne ISCO 260D syringe pump, which was controlled with a computer using ‘in house’ developed software. For stepwise pressure increase the DSC was connected to the PCTPro-2000 to supply the required pressure doses. Data were collected and analysed using Calisto software from Setaram.

2.9 THE CAMBRIDGE STRUCTURAL DATABASE (CSD)
The CSD\textsuperscript{15} was used as a search tool for published structural data related to this work. The CSD records single crystal structures of compounds that have been determined by X-ray and neutron diffraction studies and deposited as published or unpublished results.

2.10 MERCURY
The programme Mercury\textsuperscript{101,102} is a crystal structure visualisation tool equipped with many utilities such as simulation of powder patterns, structure overlay, morphology calculations, as well as calculation and visualization of solvent-accessible voids.
Chapter 2: Experimental Techniques

2.11 PLATON/SQUEEZE

The programme PLATON\textsuperscript{103}/SQUEEZE\textsuperscript{104} sums electrons within the solvent-accessible voids of a crystal structure. The programme also calculates the volumes of the solvent-accessible voids. For accurate results, it is necessary to obtain high quality and complete data with high-angle reflections.
CHAPTER 3: STRUCTURAL ANALYSIS AND GAS SORPTION PROPERTIES OF MOFs DERIVED FROM PYRIDINE DONOR DIIMIDE LIGANDS

3.1. INTRODUCTION

Since the first appearance of the term “coordination polymer” in the literature in the early 1960s, remarkable progress has been made in the study of these organic–inorganic hybrid compounds. Interest in these materials is motivated by their potential applications in gas storage, catalysis, and molecular separation. To date, a large number of chemical industries have relied on the use of zeolites for these applications. However, there are certain limitations to the use of zeolites. For example, they have a low catalytic site density, and limited pore sizes, and, being purely inorganic, are also very rigid.

Coordination polymers have thus emerged as possible candidates for such applications where the use of zeolites has been limited. Unlike zeolites, coordination polymers possess high surface areas and flexibility, allowing tuneability of the physical and chemical properties such as pore size, surface area and guest binding capability. Even though the development of coordination polymers for industrial use is still impeded by their low thermal (most coordination polymers decompose at approximately 400 °C) and chemical stability, significant progress has been made in the design and synthesis of these materials.

Nitrogen donor ligands (e.g. pyridines and imidazoles) have been used extensively in the construction of coordination polymers. The major drawback of utilising pyridyl- or imidazole-derived ligands is that the anions usually block the channels. The use of mixed ligand systems of carboxylate-donor ligands and pyridine N-donor ligands has also been explored as a possible synthetic strategy for synthesising multi-dimensional compounds. This synthetic method offers the advantage that the anions, which usually occupy spaces in the channel, are excluded from the crystal structure. Moreover, the coordination requirements of a metal centre are satisfied, leading to higher dimensional frameworks.

For this study, five ligands namely \(N,N'-\text{bis}(3\text{-pyridylmethyl})\)-naphthalene diimide (L1), \(N,N'-\text{bis}(4\text{-pyridylmethyl})\)-naphthalene diimide (L2) \(N,N'-\text{bis}(4\text{-pyridylmethyl})\)-pyromellitic diimide (L3), \(N,N'-\text{bis}(3\text{-pyridylmethyl})\)-pyromellitic diimide (L4), 2-(pyridin-4-ylmethyl)-benzene tricarboxylic anhydride (L5) (Scheme 3.1) were targeted and synthesised. The ligands were crystallised with a variety of transition metal salts in the hope of obtaining potentially...
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porous coordination polymers. L1 and L2 contain naphthalene diimide functionality as the spacer unit and pyridyl groups for coordination. The nitrogen atom can be at the *meta* position (L1) or at the *para* position (L2). Ligands L3 and L4 contain the pyromellitic diimide functionality and the nitrogen atom can be at the *para* position (L3) or at the *meta* position (L4). Ligands L1–L5 contain a rotatable C–N single bond between the spacer unit and the pyridyl groups.

The pyridine donor ligands L1–L4 as well as their coordination chemistry with some metal salts have been reported.\(^{138-140}\) However, we believe that their coordination chemistry has not been fully exploited. For example, no coordination complexes combining either L1 or L2 with carboxylate coordinating ligands have been reported. The first section in this chapter describes the mixed ligand coordination polymers obtained from the reaction of L1 and L2 with nitrates of zinc and cobalt and six different carboxylic acid ligands, namely 2,6-naphthalene dicarboxylic acid (NDC), 4-[(E)-(4-carboxyphenyl)diazenyl]benzoic acid (AZO), 4,4’-oxybis(benzoic acid) (OBA), 1,3,5-benzene tricarboxylic acid (TMA), terephthalic acid (TRA) and fumaric acid (FMA) (Scheme 3.2). The second section describes the crystal structures obtained from the reaction of ligands L3 and L4 with metal halides. The last section describes the coordination polymers obtained from the reaction of L5 with metal (Mn, Co, Cd and Zn) nitrates.

![Scheme 3.1](image-url) The five different ligands synthesised for this study.
3.2 RESULTS AND DISCUSSION

3.2.1 Crystal structures obtained with L1

3.2.1.1 CP1

\[\text{[Zn(L1)_{0.5}(NDC)]·(DMF)_3}\]

\[P2_1/c\]

\[R1 = 0.051\]

\[
\begin{align*}
\alpha &= 10.205(7) \text{ Å} \\
b &= 19.689(1) \text{ Å} \\
c &= 17.112(1) \text{ Å} \\
\beta &= 100.576(1)^\circ \\
V &= 3379.6(4) \text{ Å}^3 \\
Z &= 8
\end{align*}
\]

CP1 was synthesised by the reaction of L1, NDC and zinc(II) nitrate tetrahydrate under solvothermal conditions (100 °C, DMF) (Figure 3.1a). CP1 crystallises in the monoclinic space group \(P2_1/c\). The asymmetric unit (ASU) consists of one zinc cation, one NDC ligand, half an L1 ligand and three DMF molecules. The framework is based on the paddle-wheel dinuclear zinc carboxylate units \([\text{Zn}_2(\text{COO})_4]\) (Figure 3.1b). The \([\text{Zn}_2(\text{COO})_4]\) are bridged by the NDC ligands to form a 2–D network. The 2–D nets stack on top of each other and are further linked into a 3–D network by bridging L1 ligands (Figure 3.2a). The structure is non-interpenetrated and contains large channels along the \(b\) and \(c\) axes and these channels are occupied by DMF molecules (Figure 3.2b and c). Two of the three DMF molecules are each disordered over two positions and one was modelled with 56:44 % site occupancy, while the other was modelled with 67:33 % site occupancy. TGA shows a 46.0% weight loss occurring in the temperature range of 60–130 °C, which corresponds to three DMF molecules per formula unit. Decomposition of the framework commences at 340 °C. Heating the solvent-filled phase at 150 °C under reduced pressure for 24 h generates the empty phase (Figure 3.3). Even though the process of desolvation
does not occur as a SC-SC transformation, the material still remains crystalline and PXRD analysis shows slight differences between the as-synthesised and the evacuated phases (Figure 3.4). However, it is postulated that the framework of the empty phase remains the same as that of the as-synthesised phase. Soaking the desolvated form in DMF for 24 h results in a powder pattern that is similar to that of the as-synthesised phase (Figure 3.4). A comparison of the powder patterns for the as-synthesised, simulated, evacuated and regenerated phases is shown in Figure 3.4.

Figure 3.1 (a) A reaction scheme showing the synthesis of CP1 from the solvothermal reaction of L1, NDC and zinc nitrate in DMF at 100 °C and the packing diagram of the crystal structure as viewed along the a axis and (b) the coordination geometry around the zinc centre.
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Figure 3.2 (a) 2–D nets formed from the coordination of the NDC ligands to the zinc centres, (b) a view along the c axis showing the channels occupied by DMF and (c) a view along the a axis showing the channels occupied by the DMF molecules (solvent molecules omitted for clarity).

Figure 3.3 TGA of the as-synthesised as well as the evacuated phases of CP1 (solid and broken green lines, respectively). The first derivatives of the weight % graphs are shown in blue.
Figure 3.4 PXRD patterns for the as-synthesised, simulated, evacuated and regenerated phases of CP1. Soaking the empty phase in DMF for 24 h regenerates the as-synthesised phase.

3.2.1.1 SC-SC guest exchange in CP1

SC-SC guest exchange was accomplished by immersing a single crystal of CP1 in the exchanging solvent. Exchange experiments were set up using a wide range of solvents such as toluene, xylene isomers, THF, dioxane, isopropanol, ethanol, methanol and benzene. Except in the case of the dioxane exchange, the DMF in CP1 was replaced by the exchanging solvents. However, methanol-, ethanol-, and THF-exchanged crystal structures could not be determined using SCD methods because of the poor quality of the guest-exchanged crystals.

**CP1-toluene**

\[
\text{[Zn(L1)_{0.5}(NDC)](toluene)_2} \quad \begin{align*}
\text{P2}_1/c & \quad a = 10.200(1) \text{ Å} \\
\text{RI} = 0.048 & \quad b = 19.959(2) \text{ Å} \\
& \quad c = 16.689(2) \text{ Å} \\
\end{align*}
\]

\[\beta = 100.316(2)^\circ \quad V = 3342.8(6) \text{ Å}^3 \quad Z = 8\]

The as-synthesised crystals of CP1 were immersed in toluene and then allowed to equilibrate over five days. The structure of CP1-toluene reveals complete exchange of the DMF molecules for toluene (Figure 3.5). There are no significant differences in the unit cell parameters of the as-synthesised crystals and that of CP1-toluene. The ASU consists of one zinc cation, one complete NDC ligand, half an L1 ligand and two toluene molecules. The toluene molecules interact with...
the NDC ligands as well as the ligand via edge-to-face \( \pi \cdots \pi \) interactions (distances = 2.748 and 2.803 Å, respectively) (Figure 3.5).

![Diagram of CP1-toluene](image)

**Figure 3.5** (a) The ASU of CP1-toluene; the toluene molecules interact with the host framework via \( \pi \cdots \pi \) interactions and (b) the packing diagram as viewed along the \( a \) axis. The toluene molecules occupy the channels previously occupied by the DMF molecules.

**CP1-\( m \)-xylene**

\[
[Zn(L1)_{0.5}(NDC)](m-xylene)_2
\]

\[
\begin{align*}
P2_1/c & \quad a = 10.250(7) \, \text{Å} \\
R1 & = 0.057
\end{align*}
\]

\[
\begin{align*}
b & = 19.896(2) \, \text{Å} \\
c & = 16.713(1) \, \text{Å}
\end{align*}
\]

\[
\beta = 97.431(1)^\circ \\
V = 3381.6(4) \, \text{Å}^3 \\
Z = 8
\]

The structure reveals that all of the DMF exchanges for \( m \)-xylene. The ASU consists of one zinc cation, one NDC ligand, half an L1 ligand and two \( m \)-xylene molecules (Figure 3.6). The three DMF molecules in the ASU are thus replaced by two \( m \)-xylene molecules (Figure 3.6) and the latter occupy the channels previously occupied by the DMF molecules, interacting with the host framework via \( \pi \cdots \pi \) interactions (Figure 3.6). There are no significant changes in the unit cell dimensions, although the \( \beta \) angle changes from 100.576(1)^\circ (as-synthesised) to 97.431(1)^\circ (CP1-\( m \)-xylene).
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Figure 3.6 (a) The ASU of CP1-\textit{m-xylene} and (b) the packing diagram as viewed along the \textit{a} axis.

**CP1-\textit{(m-xylene)(o-xylene)}**

\begin{align*}
\text{[Zn(L1)}_{0.5}(\text{NDC})] \cdot \text{(m-xylene)(o-xylene)} & \quad \begin{array}{c}
a = 10.250(7) \text{ Å} \\
b = 19.854(1) \text{ Å} \\
c = 16.825(1) \text{ Å}
\end{array} \\
P_{21/c} & \quad \beta = 99.099(1)^{\circ} \quad \gamma = 9.099(1)^{\circ} \\
R_I = 0.066 & \quad V = 3387.9(4) \text{ Å}^3
\end{align*}

The as-synthesised crystals were immersed in a 1:1:1 mixture of \textit{o-}, \textit{m-} and \textit{p-xylene} for a period of five days. The DMF molecules were completely exchanged for one \textit{m-xylene} and one \textit{o-xylene} molecule. The ASU consists of one zinc cation, half an \textbf{L1} molecule, one \textbf{NDC} ligand, one \textit{m-} and one \textit{o-xylene} molecules (Figure 3.7). The \textit{o-xylene} molecules occupy the channels previously occupied by the DMF molecules (Figure 3.7). The \(\beta\) angle changes from 100.576(1)\(^{\circ}\) (as-synthesised) to 99.099(1)\(^{\circ}\) (CP1-\textit{(m-xylene)(o-xylene)}).

**CP1-\textit{p-xylene}**

\begin{align*}
\text{[Zn(L1)}_{0.5}(\text{NDC})] \cdot \text{(DMF)(p-xylene)}_{1.5} & \quad \begin{array}{c}
a = 16.655(4) \text{ Å} \\
b = 20.235(5) \text{ Å} \\
c = 20.494(5) \text{ Å}
\end{array} \\
P_{21/c} & \quad \beta = 98.404(4)^{\circ} \quad \gamma = 98.404(4)^{\circ} \\
R_I = 0.0814 & \quad V = 6832(3) \text{ Å}^3
\end{align*}

The as-synthesised crystals were placed in \textit{p-xylene} and allowed to equilibrate for five days. The structure reveals that only two of three DMF molecules exchange for \textit{p-xylene}. The ASU consists of one and a half \textit{p-xylene} molecules, one DMF molecule, one zinc cation, half an \textbf{L1} molecule and one \textbf{NDC} ligand (Figure 3.8). The DMF and the \textit{xylene} molecules occupy the channels along the \textit{a} axis (Figure 3.8). The DMF is disordered over two positions, each with equal occupancy.

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Figure 3.7 (a) The ASU of CP1·(m-xylene)(o-xylene) and (b) the packing diagram as viewed along the a axis, showing channels occupied by xylene molecules.

Figure 3.8 (a) The molecular structure of CP1·p-xylene and (b) the packing diagram of CP1·p-xylene as viewed along the a axis.
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CP1-benzene, CP1-isopropanol and CP1-o-xylene

**CP1-isopropanol**

\[
[Zn(L_1)_{0.5}(NDC)](DMF)(isopropanol)_2
\]

\[
\begin{array}{lll}
c2/c & a = 23.542(3) \, \text{Å} & \beta = 123.134(2)^\circ \\
 & b = 19.464(3) \, \text{Å} & V = 6728(2) \, \text{Å}^3 \\
 & c = 17.534(2) \, \text{Å} & Z = 8 \\
\end{array}
\]

**CP1-benzene**

\[
[Zn(L_1)_{0.5}(NDC)](DMF)(benzene)_2
\]

\[
\begin{array}{lll}
c2/c & a = 16.908(4) \, \text{Å} & \beta = 99.728(6)^\circ \\
 & b = 19.843(5) \, \text{Å} & V = 6742(2) \, \text{Å}^3 \\
 & c = 20.389(6) \, \text{Å} & Z = 8 \\
\end{array}
\]

**CP1-o-xylene**

\[
[Zn(L_1)_{0.5}(NDC)](o-xylene)_2
\]

\[
\begin{array}{lll}
p2_1/c & a = 10.3378(8) \, \text{Å} & \beta = 101.573(1)^\circ \\
 & b = 19.680(2) \, \text{Å} & V = 3386.6(4) \, \text{Å}^3 \\
 & c = 16.992(1) \, \text{Å} & Z = 4 \\
\end{array}
\]

The as-synthesised crystals of CP1 were immersed in benzene, isopropanol and o-xylene in separate experiments and then allowed to equilibrate for five days. The packing diagrams for CP1-benzene, CP1-isopropanol and CP1-o-xylene are shown in Figure 3.9. The ASU of CP1-isopropanol consists of two independent halves of NDC ligand, one zinc cation, half an L1 ligand, one DMF molecule and two isopropanol molecules. One of the isopropanol molecules is disordered and was modelled as a two part disorder in a 0.54:0.46 ratio. The ligand L1 is also disordered over two positions; an attempt to model the disorder did not yield a satisfactory model; therefore, the highest populated orientation was refined as a full-occupancy molecule. The ASU of CP1-benzene consists of one zinc cation, one NDC ligand, two benzene molecules and half an L1 ligand. The electron density in the channels could not be modelled and was treated with SQUEEZE, resulting in an R1 of 0.0468. TGA of the exchanged crystal indicates that the solvent is lost readily at room temperature. In fact, the crystals disintegrate as soon as they are removed from the mother liquor. For CP1-o-xylene, the ASU consists of one zinc cation, half an L1 ligand, two o-xylene molecules and one NDC ligand. Both the guest molecules are disordered; however, only one of the guest molecules was modelled with full occupancy. The electron density contribution from the second guest molecule was treated with SQUEEZE, resulting in an R1 of 0.057.

In addition to the changes in the unit cell parameters mentioned for each guest-exchanged crystal, there is also structural variation in the NDC moiety. A comparative illustration of the differences in the shape and size of the NDC moiety is shown in Figure 3.10. By inspecting the NDC moieties in all the eight structures, it is apparent that the NDC ligands in the Zn-NDC moieties in the as-synthesised, benzene, p-xylene and isopropanol structures are somewhat linear as compared to the remaining four structures in which the NDC ligands appear to be bent.
inwards and outwards. The diagonal Zn···Zn through-space distance for the as-synthesised structure is 19.7 Å; this distance varies slightly in the other structures with the furthest deviation from that distance being observed in the toluene structure (17.0 Å). A similar but more profound dynamic response to guest inclusion was reported by Hupp and co-workers.\(^{141}\)

**Figure 3.9** The packing diagram of (a) 1-isopropanol, (b) CP1-benzene and (c) 1-\(\omega\)-xylene as viewed along the \(a\) axis. The guest molecules have been omitted for clarity.

**Figure 3.10** A view of the differences in shape of the NDC grid as it responds to the incoming guests.
3.2.1.1.2 Gravimetric gas sorption by CP1 using CO$_2$ and N$_2$ as test gases

To verify the porosity of the desolvated phase of CP1, the gas sorption properties were measured at 20 °C using CO$_2$ and N$_2$ (Figure 3.11). CP1 shows a classical Type I sorption behaviour for CO$_2$, absorbing approximately one equivalent of CO$_2$ (12.9 weight %) per ASU and a very small amount of N$_2$, i.e. < 0.05 mol per ASU.

![Figure 3.11](image_url)

Figure 3.11 CO$_2$ and N$_2$ sorption and desorption isotherms for CP1 at 20 °C. For CO$_2$ blue diamonds represent sorption while red squares represent desorption. For N$_2$ green triangles represent sorption while purple crosses represent desorption.

3.2.1.2 CP2

\[
[Zn(L1)_{0.5}(AZO)](DMF)_2 \quad P\bar{l}
\]

\[
\begin{align*}
R_I &= 0.060 \\
V &= 1575.5(6) \text{ Å}^3 \\
ap &= 7.758(2) \text{ Å} \\
b &= 13.096(3) \text{ Å} \\
c &= 16.498(4) \text{ Å} \\
\alpha &= 77.618(3)^\circ \\
\beta &= 81.183(3)^\circ \\
\gamma &= 76.176(3)^\circ \\
Z &= 2
\end{align*}
\]

Crystals of CP2 were grown from the solvothermal reaction of zinc(II) nitrate tetrahydrate, L1 and AZO at 100 °C (Figure 3.12a). CP2 crystallises in the triclinic space group $P\bar{l}$. The ASU consists of one zinc cation, half an L1 ligand, one AZO ligand and two DMF molecules. The structure is based on the [Zn$_2$(COO)$_4$] paddle-wheel whose equatorial positions are occupied by carboxylate oxygen atoms of the AZO ligand and the two axial positions are coordinated to the
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ligand via the pyridyl nitrogen atoms. The structure is similar to CP1 in that the coordination of the AZO ligands to the metal centres forms a 2–D network (Figure 3.12b). The 2–D nets then stack directly on top of one another and are linked into 3–D nets by bridging L1 ligands (Figure 3.12c). The linking of the 2–D nets by the ligand prevents interpenetration and the structure possesses channels along the a axis that are occupied by the DMF molecules. TGA shows that desolvation starts at room temperature and is complete at approximately 200 °C (Figure 3.13). The 28.1% weight loss corresponds to the loss of two DMF molecules per formula unit over that temperature range. The framework is stable up to 340 °C, after which decomposition commences. The purity of the as-synthesised phase was confirmed by PXRD (Figure 3.14). The as-synthesised crystals were heated at 150 °C for 24 h to generate the evacuated phase. PXRD analysis reveals that the evacuated phase differs from the as-synthesised phase, indicating a structural adjustment upon guest removal. Soaking the evacuated phase in DMF for 24 h generates the guest-filled phase, as confirmed by PXRD (Figure 3.14). Attempts were made to exchange the DMF for other solvents; however, the crystals disintegrated into small pieces that could not be analysed by SCD.

Figure 3.12 (a) A reaction scheme for the synthesis of CP2 and the packing diagram as viewed along the c axis, (b) 2–D nets formed by coordination of AZO to the zinc metal and (c) a spacefill model showing the channels that are generated after removal of the solvent, as viewed along the c axis (guest molecules omitted for clarity).
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**Figure 3.13** TGA of the as-synthesised as well as the evacuated phases of CP2 (solid and broken green lines, respectively). The first derivatives of the weight % traces are shown in blue.

**Figure 3.14** The PXRD patterns of the simulated, as-synthesised, evacuated and regenerated phases of CP2. The pattern of the as-synthesised phase matches that of the simulated pattern, indicating phase purity of the bulk sample.
3.2.1.1.2 Gravimetric gas sorption by CP2 using CO$_2$ and N$_2$ as test gases.

To verify the porosity of the evacuated phase of CP2, sorption isotherms were measured at 20 °C using CO$_2$ and N$_2$ as test gases. The isotherm for CO$_2$ shows Type I behaviour. Similar to CP1, CP2 also shows selectivity towards CO$_2$ over N$_2$ (Figure 3.15). CP2 absorbs one equivalent (9.62 weight %) CO$_2$ per ASU and 0.01 equivalent of N$_2$ per ASU. There is some hysteresis of the CO$_2$ desorption curve. As mentioned earlier, soaking the evacuated phase in DMF for 24 h generates the as-synthesised phase. This prompted an investigation of whether an incremental gas pressure loading experiment would transform the framework of the evacuated phase into the framework of the as-synthesised phase. The evacuated powder of CP2 was loaded into a capillary and attached to a gas cell (as described in Chapter 2). The cell was then loaded with CO$_2$ at pressures of 5 to 35 bar. At 5 bar there is a slight change in the powder pattern. However there is no further structural change when increasing gas loading to 10, 15 and 20 bar. Even at gas pressure as high as 35 bar there is no apparent framework transformation (Figure 3.16). This study also suggests that the hysteresis observed in the desorption curve may be due to interactions of the CO$_2$ molecules with the host framework rather than a structural change.

![Figure 3.15 CO$_2$ and N$_2$ sorption and desorption isotherms for CP2 at 20 °C. For CO$_2$ blue diamonds represent sorption while red squares represent desorption. For N$_2$ green triangles represent sorption while purple crosses represent desorption.](image-url)
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3.2.1.3 CP3

\[
\text{[Co(L1)}_{0.5}\text{(OBA)}]\text{·(DMF)₂} \\
P2_1/c \\
R_I = 0.062 \\
V = 3051.6(6) \text{ Å}^3
\]

\[ a = 7.881(1) \text{ Å} \]

\[ b = 17.000(2) \text{ Å} \]

\[ c = 22.083(3) \text{ Å} \]

\[ \beta = 97.842(2)^\circ \]

CP3 was synthesised by the reaction of L1, OBA and cobalt(II) nitrate hexahydrate under solvothermal conditions for 24 h (Figure 3.17a). CP3 crystallises in the monoclinic space group \( P2_1/c \) with one cobalt cation, one OBA ligand, two DMF molecules and half an L1 ligand molecule in the ASU. The framework is composed of \([\text{Co}_2(\text{COO})_4]\) units with the equatorial positions occupied by the carboxylate oxygen atoms of the OBA ligand while the axial positions are occupied by the pyridyl nitrogen atoms of L1. OBA ligands link the metal centres into a 2–D network (Figure 3.17b). The 2–D nets stack on top of one another and the L2 ligands link these 2–D nets into a 3–D network. The DMF molecules occupy channels along the \( a \) axis. Figure 3.17c shows a spacefill model as viewed along the \( a \) axis, illustrating the channels occupied by the DMF molecules. The PXRD analysis of the bulk sample indicates the presence of another unidentified powder, and efforts to produce CP3 exclusively were unsuccessful.
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Figure 3.17 (a) A reaction scheme for the synthesis of CP3 and the packing diagram as viewed along the $a$ axis, (b) the 2-D nets formed by the coordination of the OBA ligands to the zinc centre and (c) a spacefill model showing the channels that are occupied by the DMF molecules (guest molecules omitted for clarity).

3.2.1.4 CP4

$$[\text{Zn}_3(L1)_0.5(\text{TMA})_2(\text{DMF})_3](\text{DMF})_2$$

$P\bar{1}$

$R1 = 0.085$

$V = 2525.1(7) \, \text{Å}^3$

$a = 10.057(2) \, \text{Å} 
\quad a = 88.901(2)^\circ$

$b = 15.593(2) \, \text{Å} 
\quad \beta = 74.091(2)^\circ$

$c = 17.480(3) \, \text{Å} 
\quad \gamma = 73.685(2)^\circ$

$Z = 2$

CP4 crystallises in the triclinic space group $P\bar{1}$. The compound was synthesised by the reaction of L1, TMA and zinc(II) nitrate tetrahydrate in DMF under solvothermal conditions (Figure 3.18a). The ASU consists of three independent zinc atoms (Zn1, Zn2 and Zn3), two TMA ligands, three coordinated DMF molecules, half an L1 ligand and two non-coordinated DMF molecules. One of the non-coordinated DMF molecules is disordered over two positions with 60:40 % occupancy.
Figure 3.18 (a) A reaction scheme for the synthesis of CP4 and the packing diagram as viewed along the a axis, (b) the coordination geometry around Zn1; the axial positions are occupied by DMF molecules while the TMA ligands occupy the equatorial positions. (c) Zn2 and Zn3 coordination geometries; Zn2 is in an octahedral coordination geometry consisting of three TMA ligands and two DMF molecules and Zn3 is in a tetrahedral environment coordinated to three TMA ligands and one ligand molecule.

The Zn1 coordination environment is a [Zn₂(COO)₄] paddle-wheel with the axial positions occupied by the DMF molecules and the equatorial positions occupied by the TRA ligands (Figure 3.18b). Zn2 is in an octahedral environment, coordinated to three TMA ligands via the carboxylate oxygen atoms and two DMF molecules (Figure 3.18c). One of the TMA ligands coordinates in a bidentate fashion. Zn3 is in a tetrahedral environment with three of the sites occupied by TMA. The fourth site is coordinated to L1 via the pyridyl nitrogen atom (Figure 3.18c). The TMA ligands coordinate to the zinc metal centre to form columns with 1–D channels along the a axis and these channels are occupied by the coordinated DMF molecules (Figure 3.18a). The ligand molecules then link the columns, leaving channels that are occupied by the non-coordinated DMF molecules. CP4 crystallises concomitantly with another phase (of different crystal morphology), which appears to be a cubic MOF of zinc nitrate and TMA. In an attempt to produce phase-pure crystals of CP4, the experiments were repeated using an excess of the ligand instead of a 0.5 mol equivalent; however, these experiments only yielded polycrystalline material of another unidentified phase. A series of solvent-exchange experiments...
was carried out by immersing the as-synthesised crystals of CP4 in a variety of solvents such as ethanol, water, benzene, \( m \)-, \( o \)- and \( p \)-xylene. However, in all the experiments except that involving \( m \)-xylene, the crystal quality deteriorated such that a structure could not be elucidated by SCD. In the case of \( m \)-xylene, two of the coordinated DMF molecules were exchanged for water, which is believed to have originated from the wet xylene (Figure 3.19). The non-coordinated DMF is replaced by xylene, but the xylene could not be modelled to any reasonable geometry.

\[ \text{Figure 3.19 SC-SC exchange of DMF for } m \text{-xylene in CP4 (guest molecules omitted for clarity).} \]

3.2.1.5 CP5

\[ [\text{Co(L1)}(\text{NDC})_{0.5}](\text{DMF})_2 \]

\[
\begin{align*}
R_I &= 0.048 \\
V &= 1551.4(2) \text{ Å}^3
\end{align*}
\]

\[
\begin{align*}
a &= 9.0526(8) \text{ Å} & a &= 79.537(1)^\circ \\
b &= 11.519(1) \text{ Å} & \beta &= 75.305(1)^\circ \\
c &= 16.1582(1) \text{ Å} & \gamma &= 73.462(1)^\circ \\
Z &= 2
\end{align*}
\]

CP5 was synthesised by the solvothermal reaction of L1, NDC and cobalt(II) nitrate hexahydrate in DMF (Figure 3.20a). CP5 crystallises in the triclinic space group \( P\bar{1} \) with one cobalt cation, one L1 ligand, half an NDC ligand and one disordered NDC ligand in the ASU. The cobalt centre is coordinated to one ligand via the pyridyl nitrogen atom, one nitrate anion, which binds in a bidendate fashion, and one NDC ligand (Figure 3.20b). The NDC ligand bridges two metal centres and the two ligand molecules are stacked in close proximity, thus forming a 2–D network.
The ligand molecules interact by means of $\pi-\pi$ interactions (distance = 2.246 Å). \textbf{CP5} consists of channels along the $a$ axis that are occupied by the disordered \textbf{NDC} ligand (Figure 3.20c); however, owing to the large channels, the \textbf{NDC} ligand could not be modelled. TGA shows that loss of the \textbf{NDC} is concomitant with decomposition of the framework at 350 °C. The as-synthesised crystals of \textbf{CP5} were soaked in more volatile solvents such as acetone and ethanol. The TGA of the exchanged crystals shows the same thermal profile as that of the as-synthesised crystals of \textbf{CP5}, indicating that guest exchange was unsuccessful. As a result no further experiments were carried out on this compound.
3.2.1.6 CP6

\[
[Zn(L1)(OBA)](DMF)_3 \quad C2/c
\]

\[
R_1 = 0.054 \quad V = 8399(2) \text{ Å}^3
\]

\[
a = 49.026(2) \text{ Å} \quad b = 7.560(4) \text{ Å} \quad \beta = 112.479(4)^\circ \\
 c = 23.646(1) \text{ Å} \quad Z = 8
\]

**Figure 3.21** (a) A reaction scheme for the synthesis of CP6 and the packing diagram as viewed along the \( b \) axis. (b) A spacefill model for the packing diagram of CP6 as viewed along the \( b \) axis showing channels occupied by DMF molecules (guest molecules have been omitted for clarity).

CP6 was synthesised from the reaction of L1, OBA and zinc(II) nitrate tetrahydrate under solvothermal conditions (Figure 3.21a). CP6 crystallises in the monoclinic space group \( C2/c \). The ASU consists of two independent halves of L1, one zinc cation, three DMF molecules, one OBA ligand and three DMF molecules. The metal centre is coordinated to two NDC ligands via the carboxylate oxygen atoms and two L1 molecules via the pyridyl nitrogen atom. CP6 is a 1–D chain that folds onto itself, leaving channels that are occupied by solvent molecules along the \( b \) axis (Figure 3.21b). The assembly is facilitated by \( \pi \cdots \pi \) interactions between the OBA (2.349 Å) as well as weak edge-to-face \( \pi \cdots \pi \) interactions between the OBA and the ligand (3.979 Å).
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Figure 3.22 Green: TGA of the as-synthesised as well as the evacuated phases of CP6 (solid and broken green lines, respectively). The first derivatives of the weight % graphs are shown in blue.

TGA (Figure 3.22) of the compound shows that desolvation commences at room temperature and is complete at 190 °C. The compound remains stable up to 330 °C, after which decomposition of the framework begins. The as-synthesised crystals were heated to 100 °C under reduced pressure for 24 h to generate the empty phase. Desolvation was confirmed by TGA (Figure 3.22) and phase purity of the compound was confirmed by PXRD (Figure 3.23). Powder pattern of the evacuated phase is similar to that of the as-synthesised phase, indicating that the porous framework is maintained after desolvation.

3.2.1.6.1 Gravimetric gas sorption by CP6 using CO\textsubscript{2} and N\textsubscript{2} as test gases

CP6 possesses voids amounting to 24.4% of the unit cell volume (calculated with Mercury; probe radius 1.4 Å; grid spacing 0.7 Å). The porosity of the desolvated phase of CP6 was investigated using CO\textsubscript{2} and N\textsubscript{2} as test gases (Figure 3.24). Similar to CP1 and CP2, CP6 exhibits noticeable selectivity for CO\textsubscript{2} over N\textsubscript{2}; CP6 absorbs 0.8 equivalent (6.6 weight %) of CO\textsubscript{2} per ASU and 0.02 equivalent of N\textsubscript{2} at 20 °C per ASU.
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Figure 3.23 PXRD of the as-synthesised, simulated and evacuated phases of CP6.

Figure 3.24 CO₂ and N₂ sorption and desorption isotherms for CP6 at 20 °C. For CO₂ red squares represent sorption while green triangles represent desorption. For N₂ purple crosses represent sorption while blue stars represent desorption.
3.2.2 Crystal structures obtained with L2

3.2.2.1 CP7

\[
[Zn(L2)_{0.5}(NDC)(DMF)](H_2O)
\]

\[
\begin{align*}
\alpha &= 7.593(2) \text{ Å} \\
\beta &= 8.019(3) \text{ Å} \\
\gamma &= 21.267(7) \text{ Å} \\
V &= 1266.0(7) \text{ Å}^3 \\
R_I &= 0.058 \\
Z &= 2
\end{align*}
\]

CP7 was synthesised by the reaction of L2, NDC and zinc(II) nitrate tetrahydrate under solvothermal conditions. Pale yellow crystals were obtained after 24 h (Figure 3.25a). The compound crystallises in the triclinic space group P\(\overline{1}\) with half an L2 ligand, one coordinated DMF molecule, two independent halves of an NDC ligand, one water molecule and one zinc cation in the ASU. The zinc metal centre is coordinated to two NDC ligands via the oxygen atoms and one L2 ligand is coordinated via the pyridyl nitrogen atom and one DMF molecule. One of the NDC ligands coordinates in a bidentate fashion while the other coordinates via one oxygen atom (monodentate). CP7 consists of 2–D nets formed by six zinc centres, two L2 molecules and four NDC ligands (Figure 3.25b). The 2–D nets stack in an offset manner, leaving channels that are occupied by the coordinated DMF molecules. The TGA of the compound shows a 22.2% two-step weight loss occurring in the temperature range 25–230 °C (Figure 3.26). This is attributed to the loss of one water molecule and one coordinated DMF per formula unit. The as-synthesised crystals of CP7 were heated at 150 °C under reduced pressure to generate the desolvated phase; desolvation was confirmed by TGA (Figure 3.26). The as-synthesised crystals of CP7 were immersed in water and allowed to equilibrate for five days. However, the quality of the crystals deteriorated such that they could not be studied by means of SCD. TGA, however, suggests that exchange for water might have occurred (Figure 3.27). The phase purity of the as-synthesised crystals was confirmed by PXRD (Figure 3.28). The differences between the evacuated phase and as-synthesised phases indicate that the desolvation is accompanied by a structural change (Figure 3.28). The evacuated phase was soaked in DMF over a period of five days. However, PXRD analysis reveals that the evacuated phase does not revert back to the as-synthesised phase, implying that the process of desolvation is irreversible.
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Figure 3.25 (a) A reaction scheme for the synthesis of CP7 and the packing diagram as viewed along the a axis. (b) 2–D nets formed by the coordination of four NDC ligands, two L2 molecules and six zinc centres. (c) A spacefill model of CP7 showing the channels that are occupied by the DMF molecules as viewed along the a axis (guest molecules omitted for clarity).

Figure 3.26 Green: TGA of the as-synthesised as well as the evacuated phases of CP7 (solid and broken green lines, respectively). The first derivatives of the weight % graphs are shown in blue.
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**Figure 3.27** Green: TGA of the as-synthesised as well as the water-exchanged phases of CP7 (solid and broken green lines, respectively). The first derivatives of the weight % graphs are shown in blue.

![TGA graph](image1.png)

**Figure 3.28** PXRD patterns of the as-synthesised, simulated and evacuated phases of CP7; the patterns of the as-synthesised and evacuated crystals do not match, indicating a structural change upon desolvation.

![PXRD patterns](image2.png)
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3.2.2.1 Gravimetric gas sorption by CP7 using CO\textsubscript{2} and N\textsubscript{2} as test gases

CP7 was also tested for porosity using CO\textsubscript{2} and N\textsubscript{2} as test gases (Figure 3.29). However, unlike CP1, CP2, and CP6, CP7 shows little or no affinity for either CO\textsubscript{2} or N\textsubscript{2}. CP7 absorbs only 0.16 equivalent of CO\textsubscript{2} per ASU and <0.02 equivalent of N\textsubscript{2} per ASU at 20 °C. This could be attributed to surface adsorption. It was therefore concluded that CP7 is not porous.

![Figure 3.29 CO\textsubscript{2} and N\textsubscript{2} sorption and desorption isotherms for CP7 at 20 °C. For CO\textsubscript{2} blue diamonds represent sorption while red squares represent desorption. For N\textsubscript{2} green triangles represent sorption while purple crosses represent desorption.](image)

3.2.2.2 CP8

\[
[Zn(L2)_{0.5}(TRA)](DMF)_{2}
\]

\[P1\]

\[R_I = 0.065\]

\[V = 1223.0(9) \ \text{Å}^3\]

\[a = 8.534(4) \ \text{Å} \quad b = 12.55(5) \ \text{Å} \quad \alpha = 91.384(5)^\circ\]

\[c = 12.530(6) \ \text{Å} \quad \beta = 99.693(5)^\circ\]

\[\gamma = 106.788(5)^\circ \quad Z = 2\]

The complex was synthesised by the reaction of L2, TRA and zinc(II) nitrate tetrahydrate in a molar ratio of 0.5:1:1 under solvothermal conditions (100 °C, DMF) (Figure 3.30a). Light yellow crystals were obtained after 24 h. CP8 crystallises concomitantly with a monoclinic MOF of TRA and zinc. CP8 crystallises in the triclinic space group P\textsuperscript{1} with one zinc cation, half an L2 molecule, one TRA ligand and two DMF molecules in the ASU. The metal centre is coordinated
to one ligand molecule via the pyridyl nitrogen atom, two TRA ligands via the carboxylate oxygen atoms and one DMF molecule. The coordination polymer consists of six-connected 2–D nets formed by the coordination of two L₂ molecules and four TRA ligands to six metal centres (Figure 3.30b). The 2–D nets pack in a staggered arrangement, leaving two types of channels: one occupied by coordinated DMF molecules and the other by non-coordinated DMF molecules. This can be viewed along the a axis (Figure 3.30a).

Figure 3.30 (a) A reaction scheme for the synthesis of CP8 from the reaction of TRA, zinc nitrate and L₂ under solvothermal conditions. The structure consists of 2–D nets that are packed in an offset manner, leaving two types of channels: one occupied by coordinated DMF and the other by non-coordinated DMF molecules and (b) the six-connected 2–D network showing coordination around the metal centre.
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3.2.2.3 CP9

\[ \text{[Zn(L2)_{0.5}(OBA)]\cdot(DMF)} \]

\[
\begin{align*}
C2/c & \\
R1 &= 0.054 & c &= 17.008(1) \text{ Å} & Z &= 8 \\
V &= 10931.1(2) \text{ Å}^3 & \beta &= 113.168(1)^\circ
\end{align*}
\]

CP9 was synthesised by the solvothermal reaction of \( \text{L2, OBA} \) and zinc(II) nitrate tetrahydrate (Figure 3.31a). The metal centre is coordinated to two \( \text{L2} \) molecules via the pyridyl nitrogen atoms and to two \( \text{OBA} \) ligands via the oxygen atoms. Only one oxygen atom of the \( \text{OBA} \) coordinates to the metal centre.

![Reaction scheme](image)

**Figure 3.31** (a) A reaction scheme for the synthesis of CP9 and the packing diagram as viewed along the \( c \) axis, (b) 2–D nets from the coordination of six metal centres to four \( \text{OBA} \) and four \( \text{L2} \) molecules, (c) two of the 2–D chains interpenetrate leaving channels along the \( c \) axis that are occupied by DMF molecules. The two 2–D nets are coloured blue and red to distinguish them from each other and (d) a spacefill model of the packing as viewed along the \( c \) axis (guest molecules have been omitted for clarity).

The structure consists of 2–D nets that are formed by the coordination of four \( \text{L2} \) ligands and four \( \text{OBA} \) molecules to six metal centres (Figure 3.31b). Two of the 2–D nets interpenetrate, leaving two types of channels that are occupied by DMF molecules as viewed along the \( c \) axis (Figure 3.31c). Owing to the large channels that the structure possesses, the solvent molecules in the channels could not be modelled. The TGA shows that solvent is released at room temperature.
up to 200 °C (Figure 3.32). The as-synthesised crystals of CP9 were heated at 150 °C under reduced pressure to generate the desolvated phase, which maintains its framework until 400 °C, after which decomposition begins (Figure 3.32). The PXRD patterns of the as-synthesised and evacuated phases are shown in Figure 3.33. The PXRD patterns of the as-synthesised and the evacuated phases are different indicating a structural adjustment upon guest removal.

![Figure 3.32 Green: TGA of the as-synthesised as well as the evacuated phases of CP9 (broken and solid green lines, respectively). The first derivatives of the weight % graphs are shown in blue.](image)

**Figure 3.32** Green: TGA of the as-synthesised as well as the evacuated phases of CP9 (broken and solid green lines, respectively). The first derivatives of the weight % graphs are shown in blue.

### 3.2.2.3.1 Gravimetric gas sorption by CP9 using CO$_2$ and N$_2$ as test gases

The gas sorption capability of CP9 was tested using CO$_2$ and N$_2$ at 20 °C. CP9 absorbs approximately 0.65 equivalent (7 wt %) of CO$_2$ per ASU and 0.02 equivalent of N$_2$ per ASU.
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Figure 3.33 Comparison of the PXRD patterns of the as-synthesised, simulated and evacuated phases of CP9.

Figure 3.34 CO$_2$ and N$_2$ sorption and desorption isotherms for CP9 at 20 °C. For CO$_2$ blue diamonds represent sorption while red squares represent desorption. For N$_2$ green triangles represent sorption while purple crosses represent desorption.
3.2.2.4 CP10

\[
[\text{Zn}_2(L_2)(\text{FMA})_2](\text{DMF})_3
\]

\[
P\beta_1
\]

\[
R_I = 0.055
\]

\[
V = 1314.5(1) \text{ Å}^3
\]

\[
a = 8.832(4) \text{ Å}
\]

\[
b = 8.864(4) \text{ Å}
\]

\[
c = 17.040(7) \text{ Å}
\]

\[
\alpha = 96.450(6)^\circ
\]

\[
\beta = 92.418(6)^\circ
\]

\[
\gamma = 96.689(6)^\circ
\]

CP10 was synthesised by the solvothermal reaction of \( L_2, \text{FMA} \) and zinc(II) nitrate tetrahydrate under solvothermal conditions (Figure 3.35a). The crystallisation experiment yielded a mixture of crystals of CP10 and an unidentified powdered material. The compound crystallises in the triclinic space group \( P\beta_1 \), with one \( L_2 \) ligand, two \( \text{FMA} \) ligands, two zinc cations and five DMF molecules in the ASU. The structure is based on the paddle-wheel dinuclear zinc carboxylate units \( [\text{Zn}_2(\text{COO})_4] \), which are bridged by the \( \text{FMA} \) ligands to form a 2–D square grid. These 2–D nets are pillared by the \( L_2 \) ligands to form a non-interpenetrated 3–D network (Figure 3.35). The DMF molecules occupy channels along the \( a \) and \( b \) axes (Figure 3.35c).

**Figure 3.35** (a) A reaction scheme for the synthesis of CP10 and the packing diagram as viewed along the \( a \) axis, (b) the structure consists of paddle-wheel dinuclear zinc carboxylate units \( [\text{Zn}_2(\text{COO})_4] \), which are bridged by the \( \text{FMA} \) molecules to form a 2–D square grid as viewed along the \( c \) axis and (c) a spacefill model as viewed along the \( a \) axis showing the channels occupied by the DMF molecules (guest molecules omitted for clarity).
3.2.3 Summary of coordination polymers 1-10: Similarities and differences

The reaction of ligands L1 and L2 with metal salts and carboxylates yielded ten coordination polymers. Compounds CP1 to CP3 have a very similar framework topology. In all three compounds, the framework consists of the zinc paddle-wheel dinuclear cluster, which is bridged by the carboxylate units to form 2–D grids. The ligands then link these 2–D nets into 3–D networks. TGA of CP1 and CP2 indicates that the compounds maintain their structures after desolvation. In both cases, single crystallinity was lost during the process of desolvation. However, the polycrystalline material could still be analysed by PXRD. Gravimetric gas sorption indicates that both compounds absorb moderate amounts of CO\textsubscript{2} but not N\textsubscript{2}. While the bulk materials of CP1 and CP2 were pure, the bulk materials of CP3 and CP4 were contaminated with other phases and efforts to obtain the pure phases of CP3 and CP4 by altering experimental conditions (i.e. changing the temperature, solvent concentration and employing a mixed-solvent system—for example, DMF/ethanol) were unsuccessful. Therefore no further experiments were carried out on CP3 and CP4. Of the series of coordination polymers obtained with L1, CP4 has the most interesting structure. Three unique zinc centres exist in the structure. In addition to the zinc paddle-wheel dinuclear cluster, the structure also contains two other zinc centres; one of the zinc atoms is in a tetrahedral environment while the other is in an octahedral environment. CP5 also has interesting cobalt coordination geometry. The metal centre is six-coordinated, with the nitrate anion coordinating in a bidentate fashion. CP6 is the only compound in this series that is 1–D, despite which the structure possesses large channels and gas sorption proves the porosity of this compound.

Coordination polymers CP7 to CP10 represent the series of compounds obtained from L2. Self-assembly of L2 with carboxylic acids and metal salts yielded 2–D compounds (except for CP10, which is 3–D). CP7 and CP8 both consist of six-connected 2–D nets constructed from six metal centres, two ligand molecules and four carboxylate units. In CP9, the ligand is in a C conformation, this is the only compound with either L1 and L2 in which the ligand adopts such a shape.
3.2.4 Crystal structures obtained with L3

3.2.4.1 CP11

\[\text{[CoCl}_2\text{(L3)}_{n,5}(\text{MeOH})_2\text{(CHCl}_3)_2}\]

\[P\bar{1}\]

\(R_I = 0.032\)

\(V = 1031.11(9)\ \text{Å}^3\)

\(a = 6.4782(3) \ \text{Å}\)

\(b = 11.6594(6) \ \text{Å}\)

\(c = 14.0236(7) \ \text{Å}\)

\(\alpha = 87.380(1)^\circ\)

\(\beta = 77.076(1)^\circ\)

\(\gamma = 88.2970(1)^\circ\)

\(Z = 2\)

![Reaction scheme for the synthesis of CP11 and 1–D chains that stack along the a axis, leaving cavities that are occupied by chloroform molecules.](image)

Figure 3.36 (a) A reaction scheme for the synthesis of CP11 and (b) 1–D chains that stack along the a axis, leaving cavities that are occupied by chloroform molecules.

The coordination polymer was synthesised by layering a methanolic solution of cobalt(II) chloride hexahydrate onto a chloroform solution of L3. CP11 crystallises in the triclinic space group \(P\bar{1}\). The ASU consists of half an L3 ligand, two chloroform molecules, two coordinated chloride anions and two coordinated methanol molecules. One of the chloroform molecules is disordered over two positions with 60:40 % occupancy. A single bridging ligand links two metal centres into infinite 1–D chains running along the \(bc\) diagonal. The 1–D chains stack leaving cavities that are occupied by the chloroform molecules. The chloroform molecules interact with the chains by hydrogen bonding to one of the coordinated chloride anions. The 1–D chains interact with one another via hydrogen bonding between the coordinated chloride anion of one chain and the coordinated methanol of another chain (2.450(2) Å).
3.2.5 Crystal structures obtained with L4

3.2.5.1 CP12

\[ [\text{Ni}_{0.5} \text{Cl}_2 \text{(L4)}] \cdot (\text{MeOH})_2 \]

\[ P\bar{1} \]

\[ R_I = 0.044 \]

\[ V = 1099.0(1) \text{ Å}^3 \]

\[ a = 10.4601(8) \text{ Å} \quad \alpha = 87.8650(1)^\circ \]

\[ b = 10.6984(8) \text{ Å} \quad \beta = 64.9150(1)^\circ \]

\[ c = 10.9633(9) \text{ Å} \quad \gamma = 81.6750(1)^\circ \]

\[ Z = 2 \]

Figure 3.37 (a) A reaction scheme for the synthesis of CP12. The structure consists of looped 1–D chains running along the \( a \) axis (the methanol molecules occupy spaces between the 1–D chains) and (b) the looped 1–D chain running along the \( a \) axis.

Reaction of \textbf{L4} with \textit{NiCl}_2, \textit{CoCl}_2 and \textit{MnCl}_2 yielded isostructural structures; therefore only the structure obtained from the reaction with \textit{NiCl}_2 (\textbf{CP12}) will be discussed in detail. The coordination polymer was synthesised by layering a methanolic solution of nickel(II) chloride hexahydrate onto a chloroform solution of \textbf{L4}. \textbf{CP12} crystallises in the triclinic space group \( P\bar{1} \).

The ASU of \textbf{CP12} consists of one complete \textbf{L4} ligand, two methanol molecules, half a nickel cation and two chloride anions. The metal centre is in a distorted octahedral environment consisting of four ligands and two chloride anions. The ligand molecules link the metal centres into a looped 1–D chain, running along the \( b \) axis. The solvent molecules occupy the interstitial sites between the 1–D chains. TGA indicates the loss of two methanol molecules per formula unit in the temperature range of 100–150 °C. Decomposition of the polymer commences at 380 °C.
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3.2.6 Crystal structures obtained with L5

3.2.6.1 CP13

\[ \text{[Mn}_{0.5}(\text{L5})] \]

\( C2/c \)

\( R1 = 0.046 \)

\( V = 2611.4(7) \text{ Å}^3 \)

CP13 was synthesised by the reaction of manganese(II) nitrate hexahydrate and L5 (M:L ratio 2:1) in 4 ml DMF/EtOH mixed-solvent system under solvothermal conditions (Figure 3.38a). The coordination polymer crystallises in the monoclinic space group \( C2/c \) with one complete L5 ligand and half a cobalt cation in the ASU. The ligands link the metal centres along the \( a \) axis via coordination to the carboxylate and along the \( c \) axis via coordination to the pyridyl nitrogen atoms, thus forming a 2–D network. The metal centre is in an octahedral environment, coordinated to six ligand molecules via four carboxylate oxygen atoms and two pyridyl nitrogen atoms (Figure 3.38b). No solvent molecules are included in the structure. The TGA shows no solvent loss until 380 °C, after which decomposition of the framework commences.

Figure 3.38 (a) A reaction scheme for the synthesis of CP13 and the 2–D network running along \( a \) axis and (b) the coordination environment around the manganese centre.
3.2.6.2 CP14

\[
\text{[Cd(L5)\text{(DMF)}\text{(EtOH)}]} \quad P2_1/c \\
R_I = 0.045 \\
V = 3105(3) \ \text{Å}^3
\]

\[a = 19.157(1) \ \text{Å} \quad b = 21.032(1) \ \text{Å} \quad \beta = 101.861(3)^\circ \quad c = 7.874(4) \ \text{Å} \quad Z = 4\]

**Figure 3.39** (a) A reaction scheme for the synthesis of CP14 and the packing diagram showing the arrangement of the 2–D nets, leaving two types of channels. The 2–D nets have been coloured blue and red to distinguish them from each other, (b) coordination around the cadmium metal centre and (c) one of the 2–D nets formed by the coordination of four ligands to four metal centres.

CP14 was synthesised from a solvothermal reaction (DMF/EtOH, 100 °C) of L5 and cadmium(II) nitrate hexahydrate in a M:L ratio of 2:1. Crystals suitable for SCD were obtained after 24 h. CP14 crystallises in the monoclinic space group P2_1/c with one cadmium cation, two L5 ligands, one coordinated DMF and one ethanol molecule per ASU (Figure 3.39a). The metal centre is coordinated to four ligands and one DMF molecule (Figure 3.39b). Two ligands coordinate *via* the carboxylate group in a bidentate fashion, while the other two coordinate *via* the pyridyl nitrogen atom. The structure consists of 2–D nets that are stacked in an offset manner, leaving two types of channels: one channel is occupied by coordinated DMF molecules while the other is occupied by ethanol molecules (Figure 3.39a and b). The TGA shows a
two-step weight loss. The first weight loss, which commences at 25–60 °C is attributed to the loss of one ethanol molecule per formula unit, while the second weight loss, which occurs in the range 115–168 °C, is attributed to the loss of one coordinated DMF molecule per formula unit. The compound is stable up to approximately 400 °C, after which decomposition begins.

### 3.2.6.3 CP15

\[ \text{[Co(L5)_2(MeOH)](H}_2\text{O)} \]

\[ P2_1/c \]

\[ R1 = 0.059 \]

\[ V = 2887.6(3) \text{ Å}^3 \]

\[ a = 19.884(1) \text{ Å} \]

\[ b = 19.611(1) \text{ Å} \]

\[ c = 7.947(4) \text{ Å} \]

\[ \beta = 98.956(2)^\circ \]

\[ Z = 4 \]

**Figure 3.40** (a) A reaction scheme for the synthesis of CP15 and the packing diagram showing two types of channels, (b) the coordination environment around the cobalt metal centre and (c) the 2–D nets formed by the coordination of the ligand to the metal centre.

The coordination polymer was synthesised by the reaction of cobalt(II) nitrate hexahydrate and ligand L5 in a M:L ratio of 2:1 in 4 ml of ethanol/DMF mixed-solvent system under
solvothermal conditions at 100 °C (Figure 3.40a). Two different crystal forms were identified in
the reaction mixture, CP15 and CP16. CP15 crystallises in the monoclinic space group \( P2_1/c \).
The ASU consists of two \( \text{L5} \) ligands, one coordinated ethanol molecule, one water molecule and
one cobalt cation. The metal centre is octa-coordinated with two \( \text{L5} \) ligands coordinated \( \text{via} \) the
pyridyl nitrogen atom, two \( \text{L5} \) ligands coordinated \( \text{via} \) the carboxylate oxygen atoms and one
ethanol molecule (Figure 3.40b). The coordinated ethanol molecule is disordered over two
positions with 69.31 % occupancy. The ligand links the metal ion into a 2–D network as shown
in Figure 3.40c. The 2–D nets stack in an offset fashion such that the channels created by one 2–
D chain are occupied by the corners of another 2–D chain as shown in Figure 3.40a. Despite
the offset arrangement, there are still small cavities that are occupied by the water molecules. The
TGA shows a two-step weight loss occurring in the temperature range of 70–200 °C,
Corresponding to the loss of one water molecule and one ethanol molecule per formula unit. The
coordination polymer decomposes at 400 °C.

### 3.2.6.4 CP16

\[
\text{[Co(L5)2(H}_2\text{O)}_2]}_{\text{Pl}}
\]

\[
a = 10.449(1) \, \text{Å} \quad \beta = 95.696(2)^\circ \\
b = 12.016(1) \, \text{Å} \quad \gamma = 111.101(2)^\circ \\
c = 13.090(2) \, \text{Å} \quad Z = 2 \\
V = 1361.5(3) \, \text{Å}^3
\]

CP16 crystallises in the triclinic space group \( P\overline{1} \). The coordination polymer was synthesised from
the solvothermal reaction of \( \text{L5} \) with cobalt(II) nitrate hexahydrate in 4 ml DMF/EtOH solvent
system under solvothermal conditions (Figure 3.41a). The ASU consists of two independent
ligands, one cobalt cation and two coordinated water molecules. The metal centre is coordinated
to two ligand molecules \( \text{via} \) the pyridyl nitrogen atom, two ligand molecules \( \text{via} \) one of the
carboxylate oxygen atoms and to two water molecules. The metal centres and the ligand
molecules are joined into two distinct 1–D looped chains running almost perpendicular to each
other along the \( b \) axis. The packing diagram as viewed along the \( b \) axis is shown in Figure 3.41b.
TGA confirms the loss of two coordinated water molecules per formula unit in the temperature
range 96–100 °C. The polymer is stable up to 400 °C, after which decomposition begins.
3.2.6.5 CP17

\[
[Zn_{0.5}(L5)](\text{CH}_3\text{$_2$}\text{NH}_2^+) \\
C2/c \\
R1 = 0.047 \\
V = 2865.6(9) \, \text{Å}^3
\]

\[
a = 18.992(4) \, \text{Å} \\
b = 19.068(4) \, \text{Å} \\
c = 7.995(1) \, \text{Å} \\
\beta = 98.247(4)^\circ \\
Z = 8
\]

Crystallisation of zinc(II) nitrate tetrahydrate and L5 (M:L ratio 2:1) in 4 ml DMF/EtOH under solvothermal conditions yielded crystals of CP17 (Figure 3.42a). The compound crystallises in the monoclinic space group C2/c. The ASU consists of one complete L5 ligand, a zinc cation with half occupancy and one dimethylammonium ion ((CH$_3$)$_2$NH$_2^+$). The dimethylammonium ion is believed to have originated from hydrolysis of DMF under solvothermal conditions. As in the case of CP14 and CP15, the ligand links the metal centres into a 2–D net (Figure 3.42b). However, in CP17 the solvent molecules are not coordinated to the metal centre and thus the zinc metal adopts a tetrahedral environment with two ligands coordinated via the pyridyl nitrogen atoms and the other two via the carboxylate. The 2–D nets are arranged in an offset fashion, leaving channels that are occupied by the dimethylammonium. The structure solution of
the structure is uncertain as the data completeness is very low (38.1%). The TGA shows that the dimethylammonium ion is liberated in the range 58–250 °C and the compound is stable up to 400 °C, after which decomposition begins.

Figure 3.42 (a) A reaction scheme for the synthesis of CP17 and the packing diagram showing the 2–D nets that pack in an offset manner leaving small cavities that are occupied by (CH$_3$)$_2$NH$_2^+$ ion and (b) the 2–D nets have been coloured blue and red to distinguish them from each other.

3.2.6.6 CP18

\[
\text{[Zn(L5)$_2$(BPY)]} \quad a = 10.2071(6) \text{ Å} \\
P\bar{1} \\
R1 = 0.066 \\
V = 1666.9(2) \text{ Å}^3 \\
\]

\[a = 79.417(3)^\circ \quad \beta = 73.415(4)^\circ \quad \gamma = 67.645(3)^\circ \quad Z = 2\]

CP18 was grown from a solvothermal reaction (DMF/ethanol, 100 °C) of zinc(II) nitrate tetrahydrate, 4,4’-bipyridine (BPY) and L5 (Figure 3.43a). CP18 crystallises in the triclinic space group $P\bar{1}$ with two crystallographically independent L5 molecules, one BPY molecule and one zinc cation in the ASU. The zinc centre is coordinated to two ligands via the carboxylate oxygen atoms, two ligands via the pyridyl nitrogen atoms and one BPY molecule. Coordination
of the ligands to the metal centres forms a looped 1-D chain that runs along the c axis. The BPY molecules, however, point outside the plane of the 1-D chains and these 1-D chains are packed in such a way that the BPY molecule of one chain points into the space formed by another 1-D chain as shown in Figure 3.43b.

![Figure 3.43](image)

**Figure 3.43** A reaction scheme for the synthesis of CP18 and the 1-D chains formed by the coordination of L5 and BPY to the metal centre, (b) the packing diagram of CP18 as viewed along the a axis. The spaces formed by one 1-D chain are occupied by BPY molecules of another.

### 3.2.7 Summary of coordination polymers CP12 to CP17

CP12 to CP17 represent the series of compounds synthesised from the reaction of L5 with the metal nitrates of Mn, Co, Cd and Zn. Except for CP13, which crystallises in the monoclinic space group C2/c, CP14 to CP17 crystallise in the monoclinic space group P21/c and with similar unit cell parameters. The crystallisation of L5 with Co, Cd or Zn is almost predictable in that it yields 2-D nets that pack in an offset manner, leaving voids that are occupied by solvent molecules. However, it is quite interesting to note that, in the case of cadmium, the DMF molecule is coordinated to the metal centre while the ethanol molecule is included in the interstitial voids. In the case of cobalt, the ethanol molecule is coordinated to the metal centre and water molecules are included in the voids. Interestingly, the zinc metal centre prefers a
tetrahedral coordination environment consisting of only the four ligands, and the guest molecules are situated in the spaces created by the offset arrangement of the 2–D networks.

3.3 CONCLUSION

The reaction of the N-donor diimide ligands (L1-L5) and divalent metal salts yielded structurally diverse 1-D, 2-D and 3-D coordination polymers. With regard to coordination polymers obtained with L1 and L2, it can be concluded that the strategy of combining these flexible ligands with carboxylates proved to be feasible because the desired 3–D structures were obtained. In addition to being porous to CO$_2$, CP1, CP2, CP6 and CP9 were found to exhibit selectivity towards CO$_2$ over N$_2$. While CP3, CP4 and CP10 have interesting 3-D structures, no further porosity experiments were carried out on these because they could not be obtained in bulk phase purity. The gas sorption results indicate that these compounds can be used for CO$_2$ separation from mixtures of gases. This study has contributed 18 new coordination polymers to the field of crystal engineering. Further studies on these and other similar compounds may provide new insights into crystal engineering, which would help to engineer compounds better suited for practical industrial applications.

3.4 EXPERIMENTAL SECTION

3.4.1 Single crystal X-ray diffraction

Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX II or a Bruker Apex II Duo diffractometer. The SMART is equipped with a molybdenum fine-focus sealed tube, a 0.5 mm Monocap collimator and an APEX II detector. The DUO is equipped with Incoatec IµS molybdenum and copper microfocus X-ray sources and an APEX II detector. The temperature was controlled using an Oxford Cryosystems cryostat. Data reduction and absorption corrections were carried out using the SAINT$^{88}$ and SADABS$^{89}$ programmes, respectively. The structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97.$^{90}$ Non-hydrogen atoms were refined anisotropically by means of full-matrix least-squares calculations on $F^2$ using SHELXL-97$^{90}$ within the X-Seed graphical user interface.$^{91}$ Hydrogen atoms were placed in calculated positions. For CP1-o-xylene, CP1-benzene and CP5, CP6, CP9 and CP17 the contributions from disordered solvent molecules were removed by the SQUEEZE$^{104}$ routine within PLATON and the outputs from the SQUEEZE calculations are attached to each CIF file.
3.4.2 TGA and PXRD
Thermal analyses were carried at a heating rate of 10 °C min\(^{-1}\) under N\(_2\) atmosphere (flow rate 50 ml min\(^{-1}\)) using a TA instruments Q500 TGA. TGA was only performed on those compounds that were obtained in bulk phase purity. TGA traces for CP5, CP12, CP13, CP14, CP15, CP16 and CP17 can be found in the appendix. Diffraction patterns were recorded on a PANalytical X’PERT-PRO diffractometer system using Bragg-Brentano geometry and an incident beam of Cu K\(\alpha\) radiation (\(\lambda = 1.5418 \text{ Å}\)). The PXRD patterns presented in this chapter were collected at room temperature. The PXRD patterns for CP14, CP18 and CP17 can be found in the appendix.

3.4.3 Gas sorption studies
Gravimetric sorption isotherms (99.99% CO\(_2\) and N\(_2\)) were recorded at 20 °C by means of an Intelligent Gravimetric Analyser (IGA-002) supplied by Hiden Isochema (Ltd). The instrument is equipped with a high precision balance that facilitates precise measurement of sample mass change as a function of guest. The instrument is equipped with an advanced pressure rating, allowing measurement up to 20 bar. Prior to analysis, all the samples were first evacuated until a constant weight was achieved.

3.4.4 Synthesis of coordination polymers 1 to 18

**CP1:** A mixture of 26 mg of Zn(NO\(_3\))\(_2\)·4H\(_2\)O (0.1 mmol), 21 mg of NDC (0.1 mmol) and 22 mg of L1 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Orange-brown crystals were obtained after 24 h.

**CP2:** A mixture of 26 mg of Zn(NO\(_3\))\(_2\)·4H\(_2\)O (0.1 mmol), 27 mg of AZO (0.1 mmol) and 22 mg of L1 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Orange crystals were obtained after 24 h.

**CP3:** A mixture of 26 mg of Co(NO\(_3\))\(_2\)·6H\(_2\)O (0.1 mmol), 25 mg of OBA (0.1 mmol) and 22 mg of L1 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Brown crystals were obtained after 24 h.
Chapter 3: MOFs derived from pyridine donor diimide ligands

**CP4**: A mixture of 26 mg of Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol), 21 mg of TMA (0.1 mmol) and 22 mg of L1 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Brown crystals were obtained after 24 h.

**CP5**: A mixture of 26 mg of Co(NO$_3$)$_2$·6H$_2$O (0.1 mmol), 21 mg of NDC (0.1 mmol) and 22 mg of L1 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Red crystals were obtained after 24 h.

**CP6**: A mixture of 26 mg of Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol), 25 mg of OBA (0.1 mmol) and 22 mg of L1 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Yellow crystals were obtained after 24 h.

**CP7**: A mixture of 26 mg of Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol), 21 mg of NDC (0.1 mmol) and 20 mg of L2 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Yellow crystals were obtained after 24 h.

**CP8**: A mixture of 26 mg of Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol), 17 mg of TRA (0.1 mmol) and 22 mg of L2 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Colourless crystals were obtained after 24 h.

**CP9**: A mixture of 26 mg of Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol), 25 mg of OBA (0.1 mmol) and 20 mg of L2 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Brown crystals were obtained after 24 h.

**CP10**: A mixture of 26 mg of Zn(NO$_3$)$_2$·4H$_2$O (0.1 mmol), 12 mg of FMA (0.1 mmol) and 22 mg of L2 (0.05 mmol) in 10 ml DMF was heated to 100 °C. Brown crystals were obtained after 24 h.

**CP11**: A solution of 11.9 mg of CoCl$_2$·6H$_2$O (0.0502 mmol) in 4 ml methanol was carefully layered onto a solution of 20 mg of L3 (0.0502 mmol) in 4 ml chloroform. A 4 ml buffer of CHCl$_3$/MeOH was layered between the two solutions. Pink crystals were obtained after five days.

**CP12**: A solution of 11.9 mg of NiCl$_2$·6H$_2$O (0.0502 mmol) in 4 ml methanol was carefully layered onto a solution of 20 mg of L4 (0.0502 mmol) in 4 ml chloroform. A 4 ml buffer of
CHCl₃/MeOH was layered between the two solutions. Green crystals were obtained after five days.

**CP13**: A mixture of 46 mg of Mn(NO₃)₂·6H₂O (0.1422 mmol) and 20 mg of L₅ (0.071 mmol) in 4 ml DMF/EtOH solvent system was heated to 100 °C. Colourless crystals were obtained after 24 h.

**CP14**: A mixture of 44 mg of Cd(NO₃)₂·6H₂O (0.1422 mmol) and 20 mg of L₅ (0.071 mmol) in 4 ml DMF/EtOH solvent system was heated to 100 °C. Pink crystals were obtained after 24 h.

**CP15 and CP16**: A mixture of 41 mg of Co(NO₃)₂·6H₂O (0.1422 mmol) and 20 mg of L₅ (0.071 mmol) in 4 ml DMF/EtOH solvent system was heated to 100 °C. SCD reveals the presence of the two phases CP15 and CP16.

**CP17**: A mixture of 38 mg of Zn(NO₃)₂·4H₂O (0.1422 mmol) and 20 mg of L₅ (0.071 mmol) in 4 ml DMF/EtOH solvent system was heated to 100 °C. Colourless crystals were obtained after 24 h.

**CP18**: A mixture of 38 mg of Zn(NO₃)₂·6H₂O (0.1422 mmol), 11 mg of 4,4′-bipyridine (0.070 mmol) and 20 mg of L₅ (0.0711 mmol) in 4 ml DMF/EtOH solvent system was heated to 100 °C. Colourless crystals were obtained after 24 h.

### 3.4.5 Synthesis of ligands L1-L5

Ligands L₁ to L₅ were synthesised following a reported procedure.₁³⁸⁻¹⁴⁰ For L₁ and L₂ 1.34 g of 1,4,5,8 naphthalene dianhydride (0.005 mmol) and 1.08 g of the corresponding aminomethyl pyridine (0.01 mmol) in 40 ml DMF were heated to reflux with stirring for 7 h. The precipitate was filtered and washed with DMF, water, acetone and dichloromethane. For L₃ and L₄ 3.3 g of pyromellitic dianhydride (15 mmol) and 3.3 g of the corresponding aminomethylpyridine (31 mmol) in 40 ml DMF were heated to reflux with stirring for 7 h. L₅ was synthesised by the reaction of 1 g of 1,2,4-benzenetricarboxylic acid anhydride (5.2 mmol) and 0.5 ml of 4-(aminomethyl)pyridine (5.2 mmol) in 40 ml DMF. The reaction mixture was heated to reflux with stirring for 7 h.
### Crystallographic data for CPs 1-18

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<td>CP7</td>
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<td>R$_1$ = 0.054, wR$_2$ = 0.141</td>
<td>R$_1$ = 0.058, wR$_2$ = 0.160</td>
<td>R$_1$ = 0.065, wR$_2$ = 0.149</td>
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<tr>
<td>R indices (all data)</td>
<td>R$_1$ = 0.082, wR$_2$ = 0.13400</td>
<td>R$_1$ = 0.108, wR$_2$ = 0.166</td>
<td>R$_1$ = 0.078, wR$_2$ = 0.174</td>
<td>R$_1$ = 0.124, wR$_2$ = 0.174</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å$^{-3}$)</td>
<td>0.618 and -0.433</td>
<td>0.454 and -0.565</td>
<td>0.924 and -0.727</td>
<td>0.887 and -0.896</td>
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</table>
## Chapter 3: MOFs derived from pyridine donor diimide ligands

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>CP9 ( \text{C}<em>40\text{H}</em>{20}\text{N}_4\text{O}_9\text{Zn} )</th>
<th>CP10 ( \text{C}<em>40\text{H}</em>{20}\text{N}_4\text{O}_9\text{Zn} )</th>
<th>CP11 ( \text{C}_22\text{H}_0\text{N}_4\text{O}_2\text{Zn} )</th>
<th>CP12 ( \text{C}_22\text{H}_0\text{ClN}_4\text{NiO}_2 )</th>
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<tr>
<td>Formula weight</td>
<td>765.97</td>
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<td>100(2)</td>
<td>100(2)</td>
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</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
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<td>triclinic</td>
<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{C}2/\text{c} )</td>
<td>( \text{P} )</td>
<td>( \text{P} )</td>
<td>( \text{P} )</td>
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<tr>
<td>( \alpha )/Å</td>
<td>28.919(2)</td>
<td>8.832(4)</td>
<td>17.008(1)</td>
<td>90.00</td>
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<td>( \beta )/Å</td>
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<td>8.864(4)</td>
<td>17.040(7)</td>
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<tr>
<td>( \gamma )/Å</td>
<td>17.008(1)</td>
<td>17.040(7)</td>
<td>17.008(1)</td>
<td>96.689(6)</td>
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<tr>
<td>Volume (Å(^3))</td>
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<td>1314.5(1)</td>
<td>1031.11(9)</td>
<td>1099.1(2)</td>
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<td>( \alpha )/°</td>
<td>90.00</td>
<td>96.450(6)</td>
<td>96.450(6)</td>
<td>96.689(6)</td>
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<td>( \beta )/°</td>
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<td>11.659(6)</td>
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<tr>
<td>( \gamma )/°</td>
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<td>88.297(1)</td>
<td>81.675(1)</td>
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<td>( Z )</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td>2</td>
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<td>Calculated density (g cm(^{-3}))</td>
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<td>Absorption coefficient (mm(^{-1}))</td>
<td>0.491</td>
<td>1.904</td>
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<td>1.039</td>
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<td>( F_{000} )</td>
<td>3120</td>
<td>824</td>
<td>508</td>
<td>474</td>
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<tr>
<td>( \theta ) range for data collection (°)</td>
<td>1.14 to 28.27</td>
<td>2.33 to 29.47</td>
<td>1.75 to 27.90</td>
<td>1.92 to 27.96</td>
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<tr>
<td>Miller index ranges</td>
<td>-38 ≤ ( h ) ≤ 23, -32 ≤ ( k ) ≤ 31,</td>
<td>-8 ≤ ( h ) ≤ 12, -12 ≤ ( k ) ≤ 10,</td>
<td>-8 ≤ ( h ) ≤ 8, -15 ≤ ( k ) ≤ 15,</td>
<td>-13 ≤ ( h ) ≤ 13, -14 ≤ ( k ) ≤ 13,</td>
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<td>9143</td>
<td>11606</td>
<td>12461</td>
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<tr>
<td>Independent reflections</td>
<td>13071 [( R_{int} ) = 0.0849]</td>
<td>7976 [( R_{int} ) = 0.0275]</td>
<td>4486 [( R_{int} ) = 0.0182]</td>
<td>4804 [( R_{int} ) = 0.0248]</td>
</tr>
<tr>
<td>Completeness to ( \theta_{max} ) (%)</td>
<td>96.3</td>
<td>88.5</td>
<td>90.5</td>
<td>90.8</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
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<td>Data / restraints / parameters</td>
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<td>7976 / 3 / 704</td>
<td>4486 / 54 / 281</td>
<td>4804 / 0 / 327</td>
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<tr>
<td>Goodness-of-fit on ( F^2 )</td>
<td>1.524</td>
<td>0.945</td>
<td>1.031</td>
<td>1.003</td>
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<td>Final ( R ) indices [( I &gt; 2\sigma(I) )]</td>
<td>( R_1 = 0.054 ), ( wR2 = 0.141 )</td>
<td>( R_1 = 0.055 ), ( wR2 = 0.145 )</td>
<td>( R_1 = 0.032 ), ( wR2 = 0.076 )</td>
<td>( R_1 = 0.044 ), ( wR2 = 0.122 )</td>
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<tr>
<td>( R ) indices (all data)</td>
<td>( R_1 = 0.108 ), ( wR2 = 0.164 )</td>
<td>( R_1 = 0.069 ), ( wR2 = 0.158 )</td>
<td>( R_1 = 0.037 ), ( wR2 = 0.079 )</td>
<td>( R_1 = 0.051 ), ( wR2 = 0.128 )</td>
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<tr>
<td>Largest diff. peak and hole (e Å(^{-3}))</td>
<td>3.717 and -0.939</td>
<td>1.211 and -0.905</td>
<td>1.212 and -0.992</td>
<td>0.702 and -0.986</td>
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## MOFs derived from pyridine donor diimide ligands

<table>
<thead>
<tr>
<th>Empirical formula</th>
<th>CP13 ( C_{13}H_{27}Mn_{0.50}N_2O_4 )</th>
<th>CP14 ( C_{13}O_2N_2H_2Cd )</th>
<th>CP15 ( C_{28}H_23CoN_2O_{10} )</th>
<th>CP16 ( C_{28}H_23CoN_2O_{10} )</th>
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<tbody>
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<td>Formula weight</td>
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<td>517.01</td>
<td>682.47</td>
<td>657.45</td>
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<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
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<td>0.71073</td>
<td>1.54178</td>
<td>0.71073</td>
</tr>
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<td>Crystal system</td>
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<td>monoclinic</td>
<td>monoclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( C2/c )</td>
<td>( P2_1/c )</td>
<td>( P2_1/c )</td>
<td>( P )</td>
</tr>
<tr>
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<td>23.407(4)</td>
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<td>19.884(1)</td>
<td>10.449(1)</td>
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<tr>
<td>( b )/Å</td>
<td>4.7968(7)</td>
<td>21.032(1)</td>
<td>19.611(1)</td>
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<tr>
<td>( c )/Å</td>
<td>25.522(4)</td>
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<tr>
<td>( \alpha )/°</td>
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<td>90.00</td>
<td>90.00</td>
<td>95.696(2)</td>
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<tr>
<td>( \beta )/°</td>
<td>114.314(4)</td>
<td>101.861(3)</td>
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<td>90.00</td>
<td>90.00</td>
<td>112.508(2)</td>
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<tr>
<td>Volume (Å(^3))</td>
<td>2611.4(7)</td>
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<td>2887.6(3)</td>
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<tr>
<td>( Z )</td>
<td>8</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Calculated density (g cm(^{-3}))</td>
<td>1.56</td>
<td>1.659</td>
<td>1.57</td>
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<td>0.569</td>
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<td>( F_{000} )</td>
<td>1244</td>
<td>1570</td>
<td>1400</td>
<td>674</td>
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<tr>
<td>( \theta ) range for data collection (°)</td>
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<td>1.46 to 28.29</td>
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<td>1.91 to 26.12</td>
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<td>Miller index ranges</td>
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<td>(-25 \leq h \leq 25, ,-20 \leq k \leq 27,)</td>
<td>(23 \leq h \leq 19, ,-23 \leq k \leq 23,)</td>
<td>(-12 \leq h \leq 12, ,-14 \leq k \leq 14,)</td>
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<tr>
<td>Reflections collected</td>
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<td>19608</td>
<td>18849</td>
<td>15815</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1949 ([R_{int} = 0.0277])</td>
<td>7321 ([R_{int} = 0.0678])</td>
<td>5041 ([R_{int} = 0.0529])</td>
<td>5398 ([R_{int} = 0.0310])</td>
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<tr>
<td>Completeness to ( \theta_{\text{max}} ) (%)</td>
<td>60.4</td>
<td>94.9</td>
<td>98.8</td>
<td>99.7</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
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<td>7321 / 0 / 445</td>
<td>5041 / 0 / 440</td>
<td>5398 / 0 / 414</td>
</tr>
<tr>
<td>Goodness-of-fit on ( F^2 )</td>
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<td>0.858</td>
<td>1.047</td>
<td>1.149</td>
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<tr>
<td>Final ( R ) indices [( I &gt; 2\sigma(I) )]</td>
<td>( R_1 = 0.046, , wR_2 = 0.113)</td>
<td>( R_1 = 0.045, , wR_2 = 0.076)</td>
<td>( R_1 = 0.059, , wR_2 = 0.154)</td>
<td>( R_1 = 0.032, , wR_2 = 0.086)</td>
</tr>
<tr>
<td>R indices (all data)</td>
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<td>( R_1 = 0.092, , wR_2 = 0.089)</td>
<td>( R_1 = 0.076, , wR_2 = 0.164)</td>
<td>( R_1 = 0.039, , wR_2 = 0.098)</td>
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<tr>
<td>Largest diff. peak and hole (e Å(^{-3}))</td>
<td>0.594 and -0.210</td>
<td>0.760 and -1.228</td>
<td>0.742 and -0.512</td>
<td>0.919 and -0.495</td>
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</table>
### MOFs derived from pyridine donor diimide ligands

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<tr>
<th></th>
<th>CP17</th>
<th>CP18</th>
</tr>
</thead>
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<td>( \text{C}<em>{20}\text{H}</em>{13}\text{N}<em>{3}\text{O}</em>{4}\text{Zn}_{0.50} )</td>
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<td>100(2)</td>
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<tr>
<td><strong>Wavelength (Å)</strong></td>
<td>0.71073</td>
<td>1.54178</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>monoclinic</td>
<td>triclinic</td>
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<tr>
<td><strong>Space group</strong></td>
<td>( \text{C}2/c )</td>
<td>( \text{P}1 )</td>
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<tr>
<td><strong>a/Å</strong></td>
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<td>10.2071(6)</td>
</tr>
<tr>
<td><strong>b/Å</strong></td>
<td>19.068(3)</td>
<td>13.1390(8)</td>
</tr>
<tr>
<td><strong>c/Å</strong></td>
<td>7.996(1)</td>
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<td><strong>β/°</strong></td>
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<tr>
<td><strong>γ/°</strong></td>
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<tr>
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<td><strong>Z</strong></td>
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<td>4</td>
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<td><strong>Calculated density (g cm(^{-3}))</strong></td>
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<td><strong>Absorption coefficient (mm(^{-1}))</strong></td>
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<td>1.604</td>
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<td><strong>( F_{000} )</strong></td>
<td>1648</td>
<td>804</td>
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<td>2.14 to 28.10</td>
<td>4.82 to 64.27</td>
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<tr>
<td></td>
<td></td>
<td>-11 ≤ h ≤ 11, -15 ≤ k ≤ 12, -16 ≤ l ≤ 15</td>
</tr>
<tr>
<td><strong>Miller index ranges</strong></td>
<td>-16 ≤ h ≤ 13, -25 ≤ k ≤ 1, -3 ≤ l ≤ 8</td>
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<td><strong>Reflections collected</strong></td>
<td>1680</td>
<td>8775</td>
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<td><strong>Independent reflections</strong></td>
<td>1333 [( R_{	ext{int}} = 0.0205 )]</td>
<td>4975 [( R_{	ext{int}} = 0.0224 )]</td>
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<td><strong>Completeness to ( \theta_{\text{max}} ) (%)</strong></td>
<td>38.1</td>
<td>89.3</td>
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<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on ( F^2 )</td>
<td>Full-matrix least-squares on ( F^2 )</td>
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<tr>
<td><strong>Data / restraints / parameters</strong></td>
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<tr>
<td><strong>Goodness-of-fit on ( F^2 )</strong></td>
<td>1.111</td>
<td>1.099</td>
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<td><strong>Final R indices [( I &gt; 2σ(I) )]</strong></td>
<td>( R_1 = 0.072, \ wR_2 = 0.225 )</td>
<td>( R_1 = 0.066, \ wR_2 = 0.172 )</td>
</tr>
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<td><strong>R indices (all data)</strong></td>
<td>( R_1 = 0.084, \ wR_2 = 0.236 )</td>
<td>( R_1 = 0.070, \ wR_2 = 0.175 )</td>
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<tr>
<td><strong>Largest diff. peak and hole (e Å(^{-3}))</strong></td>
<td>1.043 and -0.461</td>
<td>0.462 and -1.229</td>
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</table>
4.1 INTRODUCTION

The recent interest in flexible and dynamic MOFs\textsuperscript{72,142,143} can be attributed to the potential applications of these materials in specific sensing and separation of gas molecules.\textsuperscript{73,144} These so-called third generation materials change their structures in response to external stimuli such as temperature and gas pressure. Interesting characteristics of these compounds include their stepwise gas sorption isotherms and hysteretic gas desorption behaviour. The latter is a consequence of the structural changes that occur during gas sorption.\textsuperscript{109} It has been postulated that the hysteresis might aid in storage of gases after the pressure is relieved.\textsuperscript{109}

Determination of the structures of gas-loaded porous materials by means of \textit{in-situ} single-crystal X-ray diffraction (SCD) can provide valuable insight into host-guest and guest-guest interactions, as well as dynamic structural changes in the host framework during the sorption process.\textsuperscript{80,145-148} Since sorption processes are still not well understood at the molecular level, improved structural insight can facilitate the design and development of materials with improved capture, storage and separation of gases. In this regard, Takamizawa, Kitagawa and several others have reported on the successful inclusion of CO\textsubscript{2},\textsuperscript{56,71,144,145,149} O\textsubscript{2},\textsuperscript{147,150} N\textsubscript{2},\textsuperscript{151,152} CH\textsubscript{4}\textsuperscript{114,153} and other gases in porous MOFs.

The reported MOF-508\textsuperscript{78} [Zn\textsubscript{2}(BDC)\textsubscript{2}(BPY)]·(DMF)\textsubscript{2}(H\textsubscript{2}O) is one of the rare examples of the third generation MOFs (BPY = 4,4′-bipyridine and BDC = 1,4-benzene dicarboxylic acid). MOF-508 is a 3–D framework comprising the dinuclear zinc paddle-wheel cluster. Desolvation to the solvent-free phase, which occurs \textit{via} a SC-SC transformation, is a reversible process and the fully solvated form can be regenerated upon soaking the empty crystal in DMF. Transformation from the fully solvated form to the empty nonporous phase does not involve any bond breaking. However, the zinc paddle-wheel cluster is severely distorted and the (Zn–Zn)–bpy–(Zn–Zn) linkage is non-linear, resulting in a 16.7% reduction in the unit cell volume per formula unit. It was also shown that the process of guest inclusion and removal can be repeated several times without loss in crystallinity. This is one of the rare examples of dynamic MOFs that can reversibly convert between the open and dense phases while retaining single crystallinity. Gas sorption isotherms (Figure 4.1) for N\textsubscript{2} and H\textsubscript{2} at 77 K and CO\textsubscript{2} at 195 K
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recorded for this MOF show hysteresis, which supports the notion of porous-nonporous network transformation.

![Figure 4.1 The N\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2} sorption isotherms for MOF-508b. The N\textsubscript{2} and H\textsubscript{2} sorption experiments were carried out at 77 K and the CO\textsubscript{2} sorption was recorded at 195 K.]

4.2 RESULTS AND DISCUSSION

The guest-filled (MOF-508a), hereafter referred to as 1\textsubscript{DMF}, was synthesised by the reaction of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O, BPY and BDC in a DMF/EtOH solvent system under solvothermal conditions.\textsuperscript{78} Compound 1\textsubscript{DMF} crystallises in the triclinic space group P\textbar. The zinc centres are coordinated to two BPY ligands via the pyridyl nitrogen atom and to four BDC ligands via the carboxylate groups, forming a dinuclear zinc paddle-wheel cluster. The BPY and the BDC link the zinc metal centres into an elongated primitive cubic net with large channels.\textsuperscript{78} These channels are occupied by another net, resulting in a doubly-interpenetrated structure. Despite the interpenetration, the structure still possesses isolated 2–D channels of 2.3×3.4 Å along the a axis and channels of 2.0×4.0 Å along the c axis; the latter are occupied by disordered DMF solvent.\textsuperscript{78} TGA of the as-synthesised crystals shows that the included solvent is released in the temperature range of 25–145 °C and the framework is thermally stable up to 360° C.
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Heating crystals of 1_{DMF} at 100 °C under vacuum for 24 h generates the nonporous phase 2. Desolvation of 1_{DMF} to 2 occurs via a SC-SC transformation. Even though the connectivity in 2 remains the same as that in 1_{DMF}, there is significant distortion of the framework. The zinc paddle-wheel secondary building unit (SBU) is severely distorted, as shown in Figure 4.2. As a result, the unit cell volume is reduced by 16.7%, with no solvent-accessible voids. Figure 4.2 shows the packing diagrams of 1_{DMF} and 2 as viewed along the a axis as well as the coordination geometries.

4.2.1 High pressure sorption

Chen et al. reported sorption isotherms for H₂ and N₂ at 77 K and for CO₂ at 195 K^{78} (Figure 4.1). As mentioned above, the system under study possesses two different forms (open and dense framework). As an extension of Chen’s work, we carried out gas sorption in the pressure range 0 to 30 bar at room temperature using CO₂ as the test gas (Figure 4.3). Interestingly, the sorption isotherm possesses two clear inflections, implying that the system undergoes at least two phase transformations in the pressure range tested. From 0 to 5 bar, the system adsorbs less than 0.75 equivalent of CO₂ per formula unit; as the pressure is increased to 7 bar the system takes up an additional 2 equivalents of CO₂ and this sorption is coupled with a
possible phase change as indicated by the large inflection on the sorption isotherm. At approximately 9 bar the system undergoes a second phase transformation, absorbing approximately 0.25 equivalent of CO$_2$. From 10 to 30 bar, the system gradually reaches saturation, taking up approximately one equivalent of additional CO$_2$ per formula unit.

![Figure 4.3](image_url) The high pressure sorption isotherm at room temperature. The sorption isotherm shows two inflection points, possibly indicating two phase transformations. The system takes up a total of four CO$_2$ molecules per formula unit. There is some hysteresis in the desorption curve, indicating a possible structural transformation during sorption.

**4.2.2 Single-crystal X-ray diffraction**

In order to understand these possible structural transformations as single-crystal transformations we employed our recently developed gas cell (described in Chapter 2). A suitable crystal of 2 was selected for SCD analysis and its crystal structures were determined under various pressures of CO$_2$. The crystal was glued at the tip of a glass fibre, which was inserted into the gas cell. In the pressure range 1 to 8 bar there is no significant change in the crystal structure. At 8 to 10 bar the crystal undergoes a SC-SC transformation to yield 1$_{CO2}$, which is analogous to the as-synthesised crystal structure 1$_{DMF}$. The transformation of 2 to 1$_{CO2}$ corresponds to the first inflection in the sorption isotherm (Figure 4.3). During the transformation from 2 to 1$_{CO2}$ there is a small change in the angle of the grid formed by the BDC ligands. The angle changes from 72.74(3)$^\circ$ to 75.57(2)$^\circ$. However, the most profound structural change is observed in the (Zn–Zn)–bpy–(Zn–Zn) linkages, which change from bent in 2 to straight in 1$_{CO2}$. This affects the relative positions of the grids, which in turn results in changes in the relative positions of the two
interpenetrating networks (Figure 4.4a and b). Similar to the as-synthesised structure 1\textsubscript{DMF}, a considerable amount of electron density is apparent in the channels of 1\textsubscript{CO2} but the density could not be modelled as individual CO\textsubscript{2} molecules. In an attempt to increase the chances of resolving the electron density, intensity data were collected at -20 °C. However, 1\textsubscript{CO2} (triclinic $P\bar{1}$) converts in a SC-SC manner to a new form 3, which is monoclinic with space group $P2_1/c$ (Figure 4.4c). The precise pressure-temperature conditions for this phase transformation from 1\textsubscript{CO2} to 3 could not be established by means of X-ray diffraction because, owing to the necessity for miniaturisation, the pressure within the gas cell cannot be monitored and is therefore unknown at any temperature other than room temperature (gas loading is carried out at room temperature). It is not possible to maintain a uniform temperature throughout the gas cell using the cryostat of the diffractometer.

Figure 4.4 Interpenetrating networks in (a) 2, (b) 1\textsubscript{CO2} and (c) 3. Note the difference in shapes of the BDC ligands.

It was also established that the structure 3 can be obtained at CO\textsubscript{2} pressure of approximately 15 bar at room temperature and that the structure persists up to 30 bar while the material maintains its single-crystal nature. The structure of 3 is consistent with the second inflection in the sorption isotherm (Figure 4.3). Therefore, it can be concluded that the transformation of 1\textsubscript{CO2} to 3 can be achieved either at low pressure and low temperature (-20 °C) or at high pressure (> 15 bar) and room temperature. Although the framework connectivity and interpenetration are maintained during the transformations from 2 to 1\textsubscript{CO2} to 3, these three structures differ significantly with regard to the guest-accessible volumes. These differences are derived from the
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shifting of the relative positions of the organic ligands. In order to show the extent of the distortion of the BDC and the BPY ligands, the three structures 1\textsubscript{CO2}, 2 and 3 were overlayed using the programme Mercury (Figures 4.5 and 4.6). Figures 4.5a and b show the structure overlay of 2 and 1\textsubscript{CO2}. Figure 4.5c and d shows the structure overlay of structures 3 and 1\textsubscript{CO2}.

**Figure 4.5** Top: Structure overlays of 2 and 1\textsubscript{CO2} (a) overlaying all four Zn\textsubscript{2} units, (b) overlaying only two Zn\textsubscript{2} units. Bottom: Structure overlays of 3 and 1\textsubscript{CO2} (c) overlaying all four Zn\textsubscript{2} units, (d) overlaying only two Zn\textsubscript{2} units.

**Figure 4.6** Top: Structure overlay of 2, 1\textsubscript{CO2} and 3 from different views and bottom: Structure overlay of interpenetrating networks of 1\textsubscript{CO2} and 3.
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Figure 4.6 shows the structure overlay of structures 2, 1_{CO2} and 3 from different views. The most interesting difference between the three structures is the presence of electron density in the small channels of 3. The electron density could be modelled as individual CO₂ molecules at full occupancy. The geometry of the CO₂ molecule (C=O bond lengths of 1.09(2) and 1.18(2) Å and, a bond angle of 173(2)°) is not ideal but corresponds well with the structures reported for CO₂ that are in the CSD. It therefore appears that the small size of the channels allows the solvent to be modelled. The CO₂ molecules are aligned in an offset manner to form dimers and they interact with each other via C···O interactions (3.13(2) Å). The CO₂ also interacts with one of the oxygen atoms of the carboxylate ligand (C···O = 3.07(2)) (Figure 4.7). It is important to note that these small channels are not occupied in 1_{CO2} or in 1_{DMF} as no electron density is observed in that space.

![Figure 4.6](image_url)

Figure 4.7 A view of the CO₂ molecules in the small channels of 3. The CO₂ molecules interact with the carboxylate oxygen atoms. The two CO₂ molecules also interact with each other, forming CO₂ dimers.

An inspection of the structures and angles in 1_{CO2} and 3 reveals some significant differences that can explain the creation of channels in 3. A view along the c axis in 3 shows that the BPY ligand is wave-like while it is somewhat straight in 1_{CO2}. In addition, the small channels represent a parallelogram in 1_{CO2} and in 3 the small channels are rectangular shaped (Figure 4.8). Furthermore, the change from a parallelogram shape to a rectangle shape of the channels is supported by the change in the γ angles of the unit cells; 104.331(7)° in 1_{CO2} to 90° in 3. There are also significant changes in the torsion angles of the carboxylate groups of the BDC ligands that accompany this phase transformation. A comparison of the torsion angles of the two structures is given in Table 4.1.
To further understand the differences in the structures $\text{1}_{\text{CO}_2}$ and 3, solvent-accessible voids were mapped using Mercury (Figure 4.9). The plot shows that in $\text{1}_{\text{CO}_2}$ there are 2–D solvent-accessible spaces, while in 3, the 2–D spaces are linked to the smaller channels to form a 3–D system of channels (Figure 4.9). It is well established that flexible MOFs can transform from a nonporous phase to a porous phase under gas pressure. Usually the porous phase is analogous to the solvated form, and the gas molecules occupy the channels previously occupied by solvent molecules. This phenomenon was indeed observed in the current system in the transformation of solvate $\text{1}_{\text{DMF}}$ into nonporous 2, followed by the transformation of 2 into gas-loaded $\text{1}_{\text{CO}_2}$. However, systems that convert from a nonporous phase to a porous phase that is not similar to any of the solvated phases are extremely rare. The system in question is indeed unique in that the phase transformation of $\text{1}_{\text{CO}_2}$ to 3 leads to formation of new channels that each incorporates two additional CO$_2$ gas molecules (one CO$_2$ per formula unit). These channels were not previously occupied by solvent molecules in the solvated structure $\text{1}_{\text{DMF}}$. 

**Figure 4.8** Left: a view along the $c$ axis of 3 illustrating the rectangular small channels and right: a view along the $c$ axis showing parallelogram shaped channels in $\text{1}_{\text{CO}_2}$. 

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Table 4.1 A comparison of the BDC torsion angles in the structures 1\textsubscript{CO2} and 3.

<table>
<thead>
<tr>
<th></th>
<th>Torsion angles for 1\textsubscript{CO2} (°)</th>
<th>Torsion angles for 3 (°)</th>
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</thead>
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<tr>
<td>BDC1</td>
<td>8.4(8)</td>
<td>9.4(3)</td>
</tr>
<tr>
<td></td>
<td>3.8(6)</td>
<td>8.0(3)</td>
</tr>
<tr>
<td>BDC2</td>
<td>4.9(8)</td>
<td>5.3(2)</td>
</tr>
<tr>
<td></td>
<td>3.2(1)</td>
<td>2.3(1)</td>
</tr>
</tbody>
</table>

Figure 4.9 A plot of solvent-accessible volume in (a) 1\textsubscript{CO2} and (b) 3. In 1\textsubscript{CO2} the voids are two-dimensional while in 3 the two-dimensional voids are further connected into the third dimension, accommodating two additional CO\textsubscript{2} molecules. (c) and (d) show spacefill models of the 1\textsubscript{CO2} and 3, respectively, illustrating the new guest-accessible space occupied by two additional CO\textsubscript{2} molecules shown in green.

4.2.3 Variable pressure powder X-ray diffraction

An incremental gas loading PXRD study was also carried out in order to observe the phase transformations in the powdered material. Powdered material of 2 was loaded into a 0.3 mm Lindemann capillary attached to a gas cell (described in Chapter 2) and powder patterns were determined under various pressures of CO\textsubscript{2} at room temperature. The powder was allowed to equilibrate with CO\textsubscript{2} for at least 8 h before intensity data were collected. From 0 to 12 bar the powder patterns remain unchanged. A phase change only becomes obvious at 15 bar (Figure 4.10). It is important to note that, unlike in the high pressure sorption and SCD, the
powder experiments do not show a clear distinction between the two phase transformations. The PXRD pattern at 15 bar shows the presence of peaks corresponding to both $1_{\text{CO}_2}$ and $3$. The three powder patterns are compared in Figure 4.11. This indicates that the phase transformation of $2$ to $1_{\text{CO}_2}$ occurs in a very narrow pressure range and hence PXRD does not accurately determine the onset pressure for the transformation of $2$ to $1_{\text{CO}_2}$. The PXRD patterns presented in Figures 4.12 to 4.14 show the comparisons between a powder pattern determined at 30 bar and simulated $3$, simulated powder patterns of $1_{\text{CO}_2}$ and $1_{\text{DMF}}$ and the experimental powder pattern of $2$ and the simulated pattern of $2$, respectively.

Figure 4.10 Variable pressure study of $2$. A phase change only becomes obvious at 15 bar.
Figure 4.11 A comparison of the simulated patterns of 3 and $I_{\text{CO}_2}$ and the experimental powder pattern determined at 15 bar.

Figure 4.12 A comparison of the experimental powder pattern determined at 30 bar and the simulated pattern of 3.
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Figure 4.13 A comparison of the simulated patterns of $I_{\text{CO}_2}$ and $I_{\text{DMF}}$.

Figure 4.14 A comparison of the experimental powder pattern of 2 and the simulated pattern of 2.
4.2.4 High pressure differential scanning calorimetry (HPDSC)*

In addition to the data obtained from high pressure sorption, SCD and PXRD, high-pressure differential scanning calorimetry (HPDSC) was also carried out in order to obtain more information about the system. HPDSC provides information about the gate-opening pressure and the energies involved in the sorption-desorption processes. HPDSC experiments were carried out in two different modes: (i) with a constant pressure gradient and (ii) at approximately 1 bar increments.

4.2.4.1 HPDSC with CO\textsubscript{2} at a constant pressure gradient.

The constant pressure gradient mode is analogous to conventional DSC except that the experiment involves heat flow plotted against pressure instead of temperature. The thermal events such as phase changes are indicated by either exo- or endotherms. The area under the exotherm/endotherm is therefore the sum of the energies evolved in the phase transformation as well as during the sorption/desorption processes. Figure 4.15 shows an HPDSC trace of 2 at 25 °C. In the sorption cycle, the large exotherm at approximately 7 to 10 bar corresponds to the conversion of 2 to 1\textsubscript{CO\textsubscript{2}}, while the broad exotherm at 11 to 16 bar corresponds to the conversion 1\textsubscript{CO\textsubscript{2}} to 3. The areas under the exotherm peaks indicate that conversion of 2 to 1\textsubscript{CO\textsubscript{2}} involves a larger enthalpy change than conversion of 1\textsubscript{CO\textsubscript{2}} to 3. The broad exotherm for the conversion of 1\textsubscript{CO\textsubscript{2}} to 3 also indicates that this phase transformation is slower than the phase transformation of 2 to 1\textsubscript{CO\textsubscript{2}}. The small endotherm in the desorption cycle occurring at around 7 bar and the large endotherm occurring at approximately 5 bar indicate the conversion of 3 to 1\textsubscript{CO\textsubscript{2}} and 1\textsubscript{CO\textsubscript{2}} to 2, respectively.

* The HPDSC experiments were carried out by Dr Prashant Bhatt at Stellenbosch University, South Africa.
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Figure 4.15 HPDSC at 25 °C with a constant pressure gradient of 0.2 bar min\(^{-1}\) in the pressure range 2 to 23 bar of CO\(_2\).

HPDSC experiments were also carried out at different temperatures (0, 15, 25 and 45 °C). It was found that the gate-opening pressures for both phase transformations increase with increasing temperature. At 0 °C the gate-opening pressure for conversion of 2 to 1\(_{\text{CO2}}\) is 3 bar, while at 45 °C the gate-opening pressure is approximately 13 bar. The peaks also become broader with increasing temperature, indicating that the conversion becomes difficult and occurs much slower at high temperatures (Figures 4.16 and 4.17). The increase in gate opening pressure with increasing temperature suggests that the transition from closed to open structure depends upon entropy of the gas.
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**Figure 4.16** HPDSC experiments carried out at 0, 15, 25 and 45 °C.

**Figure 4.17** An overlay of the HPDSC experiments at the four different temperatures; 0 °C (red), 15 °C (green), 25 °C (purple) and 45 °C (blue).
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To demonstrate the effect of the test gas on the gate-opening pressure, HPDSC experiments were also carried out on 2 using CH$_4$ as the test gas at 0 °C and at 25 °C (Figures 4.18 and 4.19). At 0 °C, the gate-opening pressure is 32 bar (Figure 4.18) and 59 bar at 25 °C (Figure 4.19). In both cases, the gate-opening pressure is higher than observed with CO$_2$.

![Graph](image)

**Figure 4.18** HPDSC at 0 °C with a constant pressure gradient of 1 bar min$^{-1}$ in the pressure range of 20 to 100 bar of CH$_4$.

A variable pressure powder diffraction study was carried out on the powdered material of 2 using CH$_4$ gas at room temperature. A phase transformation was only observed at 80 bar (Figure 4.20). The powder pattern at this pressure corresponds to the structure 3.
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Figure 4.19 HPDSC at 25 °C with a constant pressure gradient of 1 bar min\(^{-1}\) in the pressure range of 20 to 100 bar of CH\(_4\).

Figure 4.20 A comparison of the simulated powder pattern of 3, experimental pattern of 2 at 80 bar CH\(_4\) and the simulated pattern of 1\(\text{CO}_2\).
4.2.4.2 HPDSC experiment at 25 °C with approximately 1 bar increments of CO₂

The DSC trace was recorded from 0 to 30 bar CO₂ pressure range at approximately 1 bar pressure intervals. Figure 4.21 shows the HPDSC traces at approximately 1 bar increments of CO₂ pressure from 0 to 30 bar, followed by the desorption cycle. During the sorption cycle the energy released by the system for each step slowly decreases as the pressure increases until 5 bar. Between 5 and 7 bar the amount of energy released increases significantly, accounting for the phase transformation of 2 into 1_CO₂ as well as the sorption of CO₂. The amount of energy released decreases between 7 and 9 bar and then increases again significantly between 9 and 10 bar, accounting for the phase change from 1_CO₂ into 3. After 10 bar the energy released per step decreases smoothly with increasing pressure. A similar trend is observed during the desorption cycle but in this case the energy is absorbed by the system and the pressure at which the phase transformation occurs is lower because of the hysteresis. Figures 4.22 and 4.23 show the enthalpy values for each step in the sorption and desorption cycle, respectively.

![Graph for HPDSC experiment](image_url)

**Figure 4.21** HPDSC experiment for sorption and desorption cycles in the 0 to 30 bar pressure range.
Figure 4.22 HPDSC trace at 25 °C for sorption cycle at approximately 1 bar intervals in the pressure range 0 to 30 bar.

Figure 4.23 HPDSC trace at 25 °C for desorption cycle at approximately 1 bar intervals in the pressure range 30 to 0 bar.
4.3 CONCLUSION

In this Chapter we have

1. Shown that the system \([\text{Zn}_2(\text{BDC})_2(\text{BPy})]\) undergoes two phase transformations under \(\text{CO}_2\) pressure in the pressure range 0 to 30 bar.

2. Shown that the first phase transition is a transformation from the nonporous phase (2) to the gas-loaded phase (1\text{CO}_2), which is analogous to the as synthesised 1\text{DMF} structure and the second phase transition is a transformation from the 1\text{CO}_2 to a completely new structure 3. The second phase transformation is accompanied by creation of new space that accommodates an additional molecule of \(\text{CO}_2\) per formula unit.

3. Determined the gas-loaded structures concomitant with each phase transformation.

4. Established that the \(\text{CO}_2\) molecules in 3 interact with each other by forming dimers via hydrogen bonding and that they also interact with the host framework by hydrogen bonding to the oxygen atoms of the BDC ligands.

5. Developed and employed an HPDSC technique to determine gate-opening pressures as well as the energies involved in each phase transformation. HPDSC experiments carried out at different temperatures showed that the gate-opening pressure increases with increasing temperature.

MOFs such as the one in question in which new space is created under gas pressure to accommodate guest molecules are rare and the only other similar example in the literature is the system \([\text{M}_2(\text{O}_2\text{CPh})_4(\text{pyrazine})]_n\) (\(\text{M} = \text{Rh}^{2+}\)or \(\text{Cu}^{2+}\)), reported by Takamizawa and co-workers. In this system, small empty cages transform into channels by slippage of the chain skeleton under gas pressure. The channels thus formed are sufficient to hold guest molecules. However the structural transformations that occur in this system in order to accommodate the gas molecules are different to those occurring in the system under study.

The combination of high pressure sorption, HPDSC and SCD has provided a complete picture of the structural changes as well as the energies involved with each phase transformation. To the best of our knowledge, this is the first time HPDSC has been used to study flexible MOFs. Moreover, the information obtained from this system and other similar systems is essential for the design and development of MOFs that are better suited for their intended uses.
4.4 EXPERIMENTAL SECTION

4.4.1 Synthesis of 1DMF
Zn(NO$_3$)$_2$·4H$_2$O (140 mg), 4,4'-bipyridine (36.9 mg) and 1,4-benzene dicarboxylic acid (78 mg), were suspended in 4 ml of DMF/EtOH (1:1) solvent. The suspension was heated to 100 °C for one day. The resulting crystals were washed several times with DMF. To generate the desolvated form 2, crystals of 1 were heated at 120 °C under reduced pressure for 24 h.

4.4.2 X-ray crystallography
All intensity data were collected on a Bruker APEX II DUO. The crystals were loaded into a gas cell, and subjected to the CO$_2$ pressure for 24 h prior to analysis. Except for 3 for which data were collected at 253 K, all intensity data were collected at room temperature. Data were collected using omega scans and recorded using a CCD (charge coupled device) area detector. Data reduction and absorption corrections were carried out using the programs SAINT$^{88}$ and SADABS$^{89}$ respectively, which form part of the APEX II software package. Space groups were assigned based on systematic absences and intensity statistics using the program XPREP. The structures were solved by direct methods using SHELXS-97$^{90}$ and expanded/refined using SHELXL-97$^{90}$ within the X-Seed graphical user interface.$^{91}$ Unless otherwise stated, non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on $F^2$. In all cases, hydrogen atoms were placed in calculated positions using riding models.

4.4.3 Powder X-ray diffraction
PXRD studies were carried out using a PANalytical X'Pert PRO diffractometer. A sample of 2 was gently pre-ground before being transferred into the 0.3 mm glass capillary of the gas cell for variable pressure measurements. Before each measurement the sample was allowed equilibrate at a particular pressure for at least 8 h prior to analysis. Data were collected in the 2$\theta$ range 3 to 50°.

4.4.4 Sorption measurements
Sorption measurements were carried out using a Hy-Energy PCTPro-2000 in a 0 to 30 bar pressure range at 1 bar intervals using CO$_2$ as the test gas.
4.4.5 High pressure DSC measurements

High pressure DSC measurements were carried out using a Setaram µDSC7 Evo module equipped with a high pressure sample holder. For constant pressure gradient measurements, the DSC was coupled to a Teledyne ISCO 260D syringe pump. The syringe pump was controlled using a computer programme that was developed ‘in house’. For stepwise pressure increases the DSC was connected to a PCTPro-2000 to supply the required pressure doses. Data were collected and analysed using Calisto software from Setaram.
### 4.4.6 Crystallographic data

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<td>R$_1$ = 0.088, wR$_2$ = 0.212</td>
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<tr>
<td>R indices (all data)</td>
<td>R$_1$ = 0.073, wR$_2$ = 0.219</td>
<td>R$_1$ = 0.145, wR$_2$ = 0.261</td>
<td>R$_1$ = 0.141, wR$_2$ = 0.232</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å$^-3$)</td>
<td>1.256 and -1.250</td>
<td>1.874 and -1.340</td>
<td>2.296 and -0.731</td>
</tr>
</tbody>
</table>
CHAPTER 5: ENGINEERING SORPTION PROPERTIES OF A WERNER CLATHRATE: MECHANOCHEMICAL SYNTHESIS OF A SOLID SOLUTION

5.1 INTRODUCTION

Mechanochemistry refers to the solid-state powder process whereby reactions of solids take place by applying mechanical force.\textsuperscript{154,155} This can be achieved by ball-milling or by using a mortar and pestle. Mortar and pestle grinding is used for reactions that do not involve overcoming large energy barriers, while ball-milling is employed for those reactions that require longer reaction times.\textsuperscript{154,156} In some cases, catalytic amounts of solvent are required to initiate or accelerate the reaction between the solid reactants. In such instances, the reactions are often termed “kneading”, “solvent drop grinding” or “liquid assisted grinding” (LAG).\textsuperscript{157}

The milling time can range from a few hours to days depending on the type of reaction. During mechanochemical processing a number of processes take place \textit{viz}: reduction of particle size, thus increasing the surface area, formation of point defects and dislocations in crystals, exposing new reacting sites, and phase transformations.\textsuperscript{154,156} According to Takacs, the history of mechanochemistry can now be traced back to the end of the fourth century BC when the mechanochemical synthesis of elemental mercury from cinnabar and acetic acid was first reported.\textsuperscript{158,159} Nowadays, mechanochemistry is widely used in materials science, solid-state chemistry and in the pharmaceutical industry.\textsuperscript{159,160} Apart from being a simple and economical method of synthesis, mechanochemistry has another major advantage in that it is environmentally friendly since no solvent waste is generated.\textsuperscript{161}

It has recently been shown how mechanosynthesis can yield homogeneous solid solutions that are inaccessible by common wet chemistry. The formation of a solid solution phase allows control of some structural and physical properties such as polymorphism,\textsuperscript{162} photoemission spectra and unit cell dimensions.\textsuperscript{163,164} In these examples, the physical parameters assume values of either one of the pure phases or a linear combination of both, depending on whether the considered property can possess only certain values (e.g. space group) or can vary continuously (e.g. unit cell volume or emission band). In the latter case, the physical parameter can be tuned

\textsuperscript{*} The work described in this Chapter has recently been accepted for publication (\textit{Chem. Commun.} DOI:10.1039/c2cc37261d).
Chapter 5: Engineering sorption properties of a Werner clathrate

by varying composition of the solid solution. A recent study by the Barbour group concerned 2–D coordination polymers but the present work focuses on octahedral 0-D Werner complexes which usually have the general formula \([MX_2L_4]\) where \(M\) is a divalent metal salt, (\(M = \text{Co, Ni, Mn, Fe, Cu or Cd}\)) \(X\) is an anion (\(X = \text{Cl, SCN, NO}_2, \text{CN or NO}_3\)) and \(L\) is an organic coordinating ligand (\(L = \text{substituted pyridine, } \alpha\text{-arylalkylamine or isoquinoline}\)). These compounds are generally known for their ability to enclathrate a variety of guests and have therefore been employed in chromatographic separation of mixtures of aromatic compounds. The \(\alpha\) form refers to the empty phase whereas the clathrate phases are referred to as \(\beta, \gamma, \delta\ldots\) depending on the structural features.

Thus far, the most widely studied compounds have the general formula \([\text{Ni(NCS)}_2(4-R\text{Py})_4]\), where \(R\) is an alkyl or aromatic group. More specifically, the host compound \([\text{Ni(NCS)}_2(4-\text{MePy})_4]\) has been studied extensively and a review by Lipkowski describes several crystal structures and the physico-chemical properties of this host compound with a variety of guest molecules. The majority of the reported inclusion compounds were prepared by dissolving the host material in a suitable solvent and layering the guest, which would then be included upon crystallisation. Recently, our group reported a solid-vapour inclusion process of the host compound \([\text{Ni(NCS)}_2(4-\text{PhPy})_4]\) (PhPy = phenyl pyridine) as a means of separating xylene isomers.

This chapter describes (i) the mechanochemical synthesis of \([\text{NiCl}_2(4-\text{PhPy})_4]\) (1), \([\text{CoCl}_2(4-\text{PhPy})_4]\) (2) and the solid solution \([\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4-\text{PhPy})_4]\) (3), (ii) structures of the xylene clathrates obtained from solution synthesis and (iii) the vapour sorption kinetics for the uptake of xylene isomers by compounds 1-3.

5.2 RESULTS AND DISCUSSION

5.2.1 Synthesis of the hosts

When either the products from grinding (1 or 2), or a combination of the respective metal salt and ligand are dissolved in methanol, crystals of the Werner clathrates \([\text{NiCl}_2(4-\text{PhPy})_4]\cdot\text{MeOH} (1\cdot\text{MeOH})^{174}\) or \([\text{CoCl}_2(4-\text{PhPy})_4(4-\text{PhPy})]\cdot\text{MeOH} (2\cdot\text{MeOH})^{174}\) are obtained. The empty (\(\alpha\)) phases of 1 and 2 can be prepared by manual grinding of the respective metal chloride and 4-phenyl pyridine (M:L = 1:4). The solid solution 3 is produced by mechanochemical grinding of the ligand with a mixture of CoCl2 and NiCl2 (Co:Ni:L = 0.5:0.5:4). The three \(\alpha\) phases were analysed by powder X-ray diffraction (PXRD) (Figure 5.1) and thermogravimetric analysis (TGA) (Figure 5.2). PXRD analysis reveals that compound 3 adopts the structure of compound 1.
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while TGA analysis shows that, for all three compounds, the loss of the first two ligands occurs in the range of 70–160 °C. Scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDX) was used to produce elemental mapping images that show the distribution of the elements of interest. The analysis has the ability to differentiate between different elements that are present in a sample. Results of this technique are presented for the following samples: (1) the product of mechanochemical grinding of CoCl₂, NiCl₂ and 4-PhPy (3); (2) the product of solvent evaporation of CoCl₂, NiCl₂ and 4-PhPy; (3) the product of solvent evaporation of a 1:1 mixture of 1 and 2 and (4) the solid solution after exposure to p-xylene vapour. These analyses indicated that both cobalt and nickel ions are evenly distributed throughout the grind product 3 (Figure 5.3a). It was also established that the methanol solvent evaporation of a 0.5:0.5:4 mixture of CoCl₂, NiCl₂ and 4-PhPy, as well as the methanol solvent evaporation of a 1:1 mixture of 1 and 2 does not afford the solid solution 3. Indeed, both of these solution crystallisation techniques yielded a mechanical mixture of crystals of 1·MeOH and 2·MeOH (Figure 5.3b and c). Exposure of 3 to p-xylene also did not induce any phase separation, and the solid solution is maintained after the solid-vapour sorption reaction (Figure 5.3d).

Figure 5.1 The PXRD patterns of compounds 1-3. Compound 3 adopts the structure of 1.
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Figure 5.2 The TGA of compounds 1-3.

Figure 5.3 From left to right: SEM, cobalt and nickel EDX for (a) the product of grinding CoCl₂, NiCl₂ and 4-PhPy in a 0.5:0.5:4 ratio, (b) the product of solvent evaporation of CoCl₂, NiCl₂ and 4-PhPy in a 0.5:0.5:4 ratio, (c) the product of solvent evaporation of a 1:1 mixture of 1 and 2 and (d) the product of grinding CoCl₂, NiCl₂ and 4-PhPy in a 0.5:0.5:4 ratio which was then exposed to p-xylene vapour. These analyses indicate that both cobalt and nickel ions are evenly distributed throughout the grind product 3.
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5.2.2 Enclathration of xylene

5.2.2.1 Solution synthesis

The xylene clathrates were synthesised from solution by layering a methanolic solution of the metal salts with a xylene solution of the ligand.

5.2.2.1.1 Nickel chloride clathrates

The crystal structures for the \( m \)-xylene and \( p \)-xylene clathrates of \([\text{NiCl}_2(4\text{-PhPy})_4]\); \([\text{NiCl}_2(4\text{-PhPy})_4]\)\( (p\)-xylene)\(_4\) and \([\text{NiCl}_2(4\text{-PhPy})_4]\)\( (m\)-xylene)\(_2\) are reported elsewhere\(^1\) and hence their crystal structures will not be discussed here. The \( m \)-xylene clathrate crystallises in the triclinic space group \( P\overline{1} \) while the \( p \)-xylene clathrate crystallises in the monoclinic space group \( C2/c \) and it is isostructural to \([\text{CoCl}_2(4\text{-PhPy})_4]\)\( (p\)-xylene)\(_4\). The host-to-guest ratio (H:G) ratio in the \( m \)-xylene clathrate is 1:2 while it is 1:4 in the \( p \)-xylene clathrate case.

\[
[\text{NiCl}_2(4\text{-PhPy})_4]\( (o\)-xylene)\(_4\)
\]

<table>
<thead>
<tr>
<th>Space Group</th>
<th>( a ) (Å)</th>
<th>( b ) (Å)</th>
<th>( c ) (Å)</th>
<th>( \beta ) (°)</th>
<th>( Z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C2/c )</td>
<td>9.6749(5)</td>
<td>23.173(4)</td>
<td>28.2174(2)</td>
<td>95.5260(1)</td>
<td>4</td>
</tr>
</tbody>
</table>

\[ V = 6296.8(6) \text{ Å}^3 \]

Figure 5.4 (a) The molecular structure of \([\text{NiCl}_2(4\text{-PhPy})_4]\)\( (o\)-xylene)\(_4\), (b) the metal complex conformation and (c) the packing as viewed along the \( a \) axis. The guest molecules occupy the guest-accessible channels.

The clathrate crystallises in the monoclinic space group \( C2/c \) with a H:G ratio of 1:4. The ASU consists of a nickel cation with half occupancy, two 4-phenyl pyridine molecules, one chloride anion and two unique \( o \)-xylene molecules (Figure 5.4a). The nickel is in an irregular octahedral

\(^1\)The packing diagrams of these compounds and the CIF files are included in the appendix
environment consisting of four 4-phenyl pyridine molecules and two chloride anions (Figure 5.4b). The o-xylene molecules occupy the channels along the a axis (Figure 5.4c). The phenyl moiety of the 4-phenyl pyridine is disordered over two positions of 60:40 % occupancy, while the various positions of the disordered o-xylene could not be resolved. Therefore, the highest populated orientation was refined as a full occupancy molecule for both of the o-xylene molecules in the ASU.

5.2.2.1.2 Cobalt chloride clathrates
The crystallisation of 1 with p-xylene yielded two types of clathrates with composition [CoCl$_2$(4-PhPy)$_4$](4-PhPy)$_2$(p-xylene)$_2$ and [CoCl$_2$(4-PhPy)$_4$](p-xylene)$_4$ in the same experiment.

\[
\text{[CoCl}_2\text{(4-PhPy)}_4\text{](4-PhPy)}_2\text{(p-xylene)}_2 \quad a = 11.339(2) \text{ Å} \\
\quad \quad R_1 = 0.084 \\
\quad \quad V = 1617.7(5) \text{ Å}^3 \\
\quad \quad a = 64.278(2)^\circ \\
\quad \quad b = 12.958(2) \text{ Å} \\
\quad \quad c = 13.538(3) \text{ Å} \\
\quad \quad \beta = 78.322(2)^\circ \\
\quad \quad \gamma = 64.532(2)^\circ \\
\quad \quad Z = 4
\]

The clathrate crystallises in the monoclinic space group $P\bar{1}$ with four coordinated 4-phenyl pyridine molecules, two non-coordinated 4-phenyl pyridine molecules, two independent guest molecules, two chloride anions and one cobalt cation in the ASU (Figure 5.5a). The cobalt is in an irregular octahedral environment consisting of four 4-phenyl pyridine molecules and two chloride anions (Figure 5.5b). The p-xylene and the 4-phenyl pyridine guest molecules occupy the guest-accessible channels along the b axis (Figure 5.5c). The 4-phenyl pyridine guest interacts with the coordinated 4-phenyl pyridine via CH···π interactions (2.674 Å) (Figure 5.5d). The p-xylene molecules also interact with the coordinated 4-phenyl pyridine via weak edge-to-face interactions (CH···π = 3.013 Å).
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Figure 5.5 (a) The molecular structure of \([\text{CoCl}_2(4-\text{PhPy})_4] \cdot (4-\text{PhPy})_2(p\text{-xylene})_2\), (b) the metal complex conformation and (c) packing as viewed along the \(b\) axis showing channels occupied the \(p\text{-xylene}\) and the 4-phenyl pyridine guest molecules and (d) a view of the packing along the \(a\) axis.

\[
[\text{CoCl}_2(4-\text{PhPy})_4] \cdot (p\text{-xylene})_4
\]

\[
\begin{array}{ll}
C2/c & a = 9.555(4) \text{ Å} \\
R1 = 0.060 & b = 24.102(1) \text{ Å} \\
V = 6268(4) \text{ Å}^3 & c = 27.580(1) \text{ Å} \\
& \beta = 98.020(6)^\circ \\
& Z = 4
\end{array}
\]

The clathrate crystallises in the monoclinic space group \(C2/c\) with a H:G ratio of 1:4. The ASU consists of two unique \(p\text{-xylene}\) guest molecules, a cobalt cation with half occupancy, one chloride anion and two 4-phenyl pyridine ligands (Figure 5.6a). The cobalt is in an irregular octahedral environment consisting of four 4-phenyl pyridine molecules and two chloride anions (Figure 5.6b). The \(p\text{-xylene}\) molecules occupy the channels along the \(a\) axis (Figure 5.6c). The guest molecules interact with the host via \(\pi\cdots\pi\) interactions (3.706 Å) and they also interact with each other via CH\cdots\pi interactions (2.760 Å).
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Figure 5.6 (a) The molecular structure of $[\text{CoCl}_2(4\text{-PhPy})_4] \cdot (o\text{-xylene})_4$, (b) the metal complex conformation and (c) the packing as viewed along the $a$ axis. The guest molecules occupy the channels along the $a$ axis.

$$[\text{CoCl}_2(4\text{-PhPy})_4] \cdot (o\text{-xylene})_4$$

- $C2/c$
- $R_I = 0.010$
- $V = 6408(2) \text{ Å}^3$
- $a = 9.7131(2) \text{ Å}$
- $b = 23.566(4) \text{ Å}$
- $c = 28.167(5) \text{ Å}$
- $\beta = 96.357(1)^\circ$
- $Z = 4$

Figure 5.7 (a) The molecular structure of $[\text{CoCl}_2(4\text{-PhPy})_4] \cdot (o\text{-xylene})_4$, (b) the metal complex conformation and (c) the packing as viewed along the $a$ axis. The guest molecules are situated in the guest-accessible channels.

The clathrate crystallises in the monoclinic space group $C2/c$ with two 4-phenyl pyridine ligands, a cobalt cation with half occupancy, one chloride anion and two unique $o$-xylene molecules in the ASU (Figure 5.7a). The cobalt is in an irregular octahedral environment consisting of four 4-phenyl pyridine molecules and two chloride anions (Figure 5.7b). The H:G ratio in this
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cathrate is 1:4. The guest molecules occupy the channels along the \( a \) axis (Figure 5.7c). In this structure, there is disorder of both the ligand and the guest molecules. One of the ligand molecules is disordered over two positions with 55:45 \% occupancy. In one of the \( o \)-xylene molecules, the highest populated orientation was modelled as a full occupancy molecule, while the second \( o \)-xylene molecule was modelled as a three part disorder with 33:34:32 \% occupancy.

\[
[\text{CoCl}_2(4\text{-PhPy})_4] \cdot (m\text{-xylene})_4
\]

\[
\begin{align*}
C2/c & \quad a = 23.480(5) \text{ Å} \\
Rf = 0.068 & \quad b = 11.315(2) \text{ Å} \\
V = 6235.4(2) \text{ Å}^3 & \quad c = 23.479(3) \text{ Å} \\
\beta = 91.591(1)° & \quad Z = 4
\end{align*}
\]

Figure 5.8 (a) The molecular structure of \([\text{CoCl}_2(4\text{-PhPy})_4] \cdot (m\text{-xylene})_4\), (b) the metal complex conformation and (c) the packing as viewed along the \( b \) axis. The \( m \)-xylene guest molecules occupy the guest-accessible channels.

The clathrate crystallises in the monoclinic space group \( C2/c \). The ASU consists of one cobalt cation with half occupancy, two ligand molecules, two \( m \)-xylene molecules and one coordinated chloride anion (Figure 5.8a). The cobalt is in an irregular octahedral environment consisting of four 4-phenyl pyridine molecules and two chloride anions (Figure 5.8b). The \( m \)-xylene molecules are situated in the guest-accessible channels. A packing diagram along the \( b \) axis is shown in Figure 5.8c. The crystal was a non-merohedral twin, which was integrated in two twin domains after identification of the orientation matrices using the program CELL_NOW. The twin law is a twofold rotation about \([0 \ 1 \ 0]\).

5.2.2.2 Solid-vapour synthesis

Solid-vapour sorption reactions were carried out using a microbalance that monitors weight change as a function of time under controlled conditions of temperature and pressure.\(^93\) The
solid-vapour reactions of compounds 1-3 with the three xylene isomers were recorded in separate experiments at 20 °C. In each case, the reaction chamber was first evacuated until a constant weight was achieved. Then the liquid guest was injected and the weight increase was monitored until saturation, after which the resulting clathrates were analysed using TGA and PXRD.

\[ \text{[NiCl}_2(4-\text{PhPy})_4] \], \textbf{1}

For compound \textbf{1} the solid-vapour preparation of the \textit{m}-xylene clathrate reaches 100% completion while those for the \textit{o}- and \textit{p}-xylene clathrates reach approximately 80% completion (Figure 5.9). PXRD analysis confirms that, upon exposure of \textbf{1} to each of the three xylene isomers, the apohost \( \alpha \) phase transforms into the corresponding \( \beta \) phase, and these PXRD patterns are consistent with the simulated patterns for the clathrates resulting from solution growth (Figures 5.10 to 5.12). TGA reveals that guest release for the \textit{o}- and \textit{p}-xylene clathrates commences at approximately 25 °C while the \textit{m}-xylene clathrate starts to release the guest at approximately 65 °C (Figure 5.13).

![Figure 5.9](http://scholar.sun.ac.za)

**Figure 5.9** Sorption kinetics showing extent of reaction \( \alpha \) as a function of time for the uptake of the three isomers of xylene by compound \textbf{1} at 20 °C.
Figure 5.10 PXRD comparison for the α phase for compound 1, the o-xylene clathrate resulting from the solid-vapour synthesis and the simulated pattern for the o-xylene clathrate resulting from solution synthesis.

Figure 5.11 PXRD comparison for the α phase for compound 1, the m-xylene clathrate resulting from the solid-vapour synthesis and the simulated pattern for the m-xylene clathrate resulting from solution synthesis.
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Figure 5.12 PXRD comparison for the α phase for compound 1, the p-xylene clathrate resulting from the solid-vapour synthesis and the simulated pattern for the p-xylene clathrate resulting from solution synthesis.

Figure 5.13 TGA for the release of sorbed xylene isomers by compound 1.
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[CoCl$_2$(4-PhPy)$_4$], 2

![Graph showing sorption kinetics](image)

**Figure 5.14** Sorption kinetics showing extent of reaction $\alpha$ as a function of time for the uptake of the three isomers of xylene by compound 2 at 20 °C.

For compound 2, the solid-vapour preparation of the $p$- and $m$-xylene clathrates reach about 50% and 60% completion, respectively, while that of the $o$-xylene analogue proceeds to approximately 80% completion (Figure 5.14). PXRD analysis of the product of the solid-vapour reactions with $p$- and $m$-xylene reveals the presence of some peaks corresponding to the host $\alpha$ phase, which confirms only partial conversion of the material to its clathrate form (Figures 5.15 to 5.17).
Figure 5.15 Comparison of the PXRD patterns for the α phase for compound 2, o-xylene clathrate obtained from solid-vapour synthesis and the simulated pattern for the o-xylene clathrate obtained from solution synthesis.

Figure 5.16 Comparison of the PXRD patterns for the α phase of compound 2, m-xylene clathrate obtained from solid-vapour synthesis and the simulated pattern for the m-xylene clathrate of compound 1 obtained from solution synthesis.
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Figure 5.17 Comparison of the PXRD patterns for the α phase for compound 2, p-xylene clathrate obtained from solid-vapour synthesis and the simulated pattern for the p-xylene clathrate obtained from solution synthesis.

The TGA shows that, for all the three clathrates, guest release commences at 30 °C and is complete at 60 °C for the m- and o-xylene clathrates and for the p-xylene clathrate guest release is only complete at 75 °C (Figure 5.18).

Figure 5.18 TGA for the release of the sorbed xylene isomers by compound 2.
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$[\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4\text{-PhPy})_4]$, 3

In contrast to compounds 1 and 2, reaction of the solid solution 3 with $p$-xylene is only 10% complete after 220 minutes while for $o$- and $m$-xylene the reaction proceeds to about 80% completion (Figure 5.19). The PXRD pattern of 3 after exposure to $p$-xylene is very similar to that of the $\alpha$ phase, indicating that the amount of $p$-xylene absorbed by the host was insufficient to induce a substantial phase transformation to the $\beta$ phase. PXRD analyses of the $o$- and $m$-xylene clathrates are consistent with the simulated patterns of the structures of the corresponding clathrates of compound 1 (Figures 5.20 to 5.22). TGA of the xylene clathrates of 3 shows that guest release commences at 50 °C for the $p$-xylene clathrate, 30 °C for the $o$-xylene clathrate and 20 °C for the $m$-xylene clathrate. For all three clathrates guest release is complete at approximately 80 °C (Figure 5.23).

![Sorption kinetics showing extent of reaction $\alpha$ as a function of time for the uptake of the three isomers of xylene by compound 3 at 20 °C.](image)

Figure 5.19 Sorption kinetics showing extent of reaction $\alpha$ as a function of time for the uptake of the three isomers of xylene by compound 3 at 20 °C.
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Figure 5.20 PXRD analysis for the $\alpha$ phase of compound 3, the $m$-xylene clathrate prepared by solid-vapour synthesis and the simulated pattern for the $m$-xylene phase resulting from solution growth.

Figure 5.21 PXRD analysis for the $\alpha$ phase of compound 3, the $o$-xylene clathrate prepared by solid-vapour synthesis and the simulated pattern for the $o$-xylene phase resulting from solution growth.
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Figure 5.22 PXRD analysis for the α phase of compound 3, the p-xylene clathrate prepared by solid-vapour synthesis and the simulated pattern for the p-xylene phase resulting from solution growth.

Figure 5.23 TGA for the release of the sorbed xylene isomers by compound 3.

5.3 CONCLUSION

In summary, we prepared three compounds, namely [NiCl₂(4-PhPy)₄] (1), [CoCl₂(4-PhPy)₄] (2) and the solid solution [Ni₀.₅Co₀.₅Cl₂(4-PhPy)₄] (3) by grinding. We established that mechanochemical processing produces a homogeneous solid solution, whereas crystallisation from methanol produces a non-homogeneous product. Despite the structural similarity between
compounds 1 and 3, there is a remarkable difference in their sorption behaviour. In particular, the sorption tendency of \( o \)-xylene is consistent for all three compounds while that of \( p \)-xylene is significantly reduced for 3. Many hypotheses have been put forward to explain the clathratogenic behaviour of Werner complexes and to explain why a Werner complex would host some guests and not others. It was initially thought that the ability to enclathrate a guest is dependent upon the following factors: (i) the presence of substituents on the ligand that prevent the structure from close packing\(^{168}\) and (ii) the central ion must be a metal, that is involved in some kind of charge transfer between the host and the guest, thus enhancing clathrate stability,\(^{168}\) However subsequent reports seem to dispute these ideas.\(^{176,177}\) It has also been speculated that, for a Werner complex to host a guest, it must exhibit conformational flexibility.\(^{178}\) For each crystal structure such flexibility depends, among other things, upon the cooperative reorganization of the metal complex. We believe that, owing to presence of Co centres, compound 3, which is isostructural to 1 is unable to adopt the conformation required for it to host \( p \)-xylene, thereby preventing sorption. This study highlights the importance of exploring (a) solid solutions as a means of engineering bulk properties of crystalline materials and (b) mechanochemistry to prepare phases not accessible by solution synthesis.

### 5.4 EXPERIMENTAL SECTION

#### 5.4.1 Crystallographic data

Single-crystal X-ray diffraction data were collected on a Bruker Apex II Duo diffractometer employing Mo-K\( \alpha \) radiation. The temperature was controlled using an Oxford Cryosystems cryostat. Data reduction and absorption corrections were carried out using the SAINT\(^88\) and SADABS\(^89\) programmes, respectively. The structures were solved by direct methods or a combination of Patterson and partial structure expansion using SHELXS-97.\(^90\) Non-hydrogen atoms were refined anisotropically by means of full-matrix least-squares calculations on \( F^2 \) using SHELXL-97\(^90\) within the X-Seed graphical user interface.\(^91\) Hydrogen atoms were placed on calculated positions. In the \([\text{NiCl}_2(4-\text{PhPy})_4]\cdot(\text{m-xylene})_2\) structure one of the \( m \)-xylene molecules was refined as disordered over two positions in a ratio of 0.64 to 0.36. The \([\text{CoCl}_2(4-\text{PhPy})_4]\cdot(\text{m-xylene})_4\) crystal was a non-merohedral twin which was integrated in two twin domains after identification of the orientation matrices using the program CELL_NOW.\(^175\) The twin law is a twofold rotation about \([0 \ 1 \ 0]\). In the \([\text{NiCl}_2(4-\text{PhPy})_4]\cdot(\text{o-xylene})_4\) and \([\text{CoCl}_2(4-\text{PhPy})_4]\cdot(\text{o-xylene})_4\) structures there is disorder of both the ligand and the guest molecules. In \([\text{NiCl}_2(4-\text{PhPy})_4]\cdot(\text{o-xylene})_4\) the phenyl substituent of the ligand could be modelled as
disordered over two positions of 60:40% occupancy, while the various positions of the disordered o-xylene could not be resolved. Therefore, the highest populated orientation was refined as a full occupancy molecule for both of the o-xylene molecules in the ASU. In the [CoCl$_2$(4-PhPy)$_4$](o-xylene)$_4$ structure one of the ligand molecules is disordered and was modelled as two components in a 0.55 to 0.45 ratio. In one of the o-xylene molecules, the highest populated orientation was modelled as a full occupancy molecule, while the second o-xylene molecule was modelled as a three part disorder in a 0.33 to 0.34 to 0.32 ratio. In the 1·MeOH structure the methanol has an occupancy of 88% (as determined from an electron density summation in SQUEEZE), and it is disordered over two positions. However, an attempt to model the methanol as a two part disorder did not yield a satisfactory model, and therefore only the highest populated orientation was refined. In the 2·MeOH structure the unresolved electron density in the channels was treated with SQUEEZE, which resulted in an $R_1$ of 0.0478. The output from SQUEEZE has been attached to the CIF.

5.4.2 Solid-vapour reactions and kinetics

Solid-vapour sorption reactions at 20 °C were monitored using a microbalance that was constructed in-house.

5.4.3 Solid-state synthesis

[NiCl$_2$(4-PhPy)$_4$]: A mixture of 4-phenyl pyridine (62 mg; 0.4 mmol), nickel(II) chloride hexahydrate (23.71 mg; 0.1 mmol) and a few drops of methanol were ground together using a mortar and pestle. The paste was then allowed to dry in open air.

[CoCl$_2$(4-PhPy)$_4$]: A mixture of 4-phenyl pyridine (62 mg; 0.4 mmol), cobalt(II) chloride hexahydrate (23.71 mg; 0.1 mmol) and a few drops of methanol were ground together using a mortar and pestle. The paste was then allowed to dry in open air.

[Ni$_{0.5}$Co$_{0.5}$Cl$_2$(4-PhPy)$_4$]: A mixture of 4-phenyl pyridine (62 mg; 0.4 mmol), nickel(II) chloride hexahydrate (11.85 mg; 0.05 mmol), cobalt(II) chloride hexahydrate (11.85 mg; 0.05 mmol) and a few drops of methanol were ground together using a mortar and pestle. The paste was then allowed to dry in open air.
5.4.4 Solid-vapour reactions

The solid-vapour reactions were carried out using a microbalance, which monitors weight change as a function of time under controlled conditions of temperature and pressure.

\[\text{NiCl}_2(4-\text{PhPy})_4](\text{m-xylene})_2: \text{25.350 mg (0.034 mmol) of 1 were weighed on a microbalance under vacuum at 20 °C. 2 ml of m-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 32.540 mg, corresponding to 0.107 mmol of m-xylene sorbed.}\]

\[\text{NiCl}_2(4-\text{PhPy})_4](\text{o-xylene})_2: \text{21.540 mg (0.029 mmol) of 1 were weighed on a microbalance under vacuum at 20 °C. 2 ml of o-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 31.354 mg, corresponding to 0.116 mmol of o-xylene sorbed.}\]

\[\text{NiCl}_2(4-\text{PhPy})_4](\text{p-xylene})_4: \text{23.834 mg (0.032 mmol) of 1 were weighed on a microbalance under vacuum at a controlled temperature of 20 °C. 2 ml of p-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 35.210 mg, corresponding to 0.150 mmol of p-xylene sorbed.}\]

\[\text{CoCl}_2(4-\text{PhPy})_4](\text{o-xylene})_4: \text{11.055 mg (0.0147 mmol) of 2 were weighed on a microbalance under vacuum at 20° C. 2 ml of o-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 16.484 mg, corresponding to 0.0511 mmol of o-xylene sorbed.}\]

\[\text{CoCl}_2(4-\text{PhPy})_4](\text{m-xylene})_4: \text{22.876 mg (0.0305 mmol) of 2 were weighed on a microbalance under vacuum at 20 °C. 2 ml of m-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 31.950 mg, corresponding to 0.0910 mmol of m-xylene sorbed.}\]

\[\text{CoCl}_2(4-\text{PhPy})_4](\text{p-xylene})_4: \text{23.768 mg (0.032 mmol) of 2 were weighed on a microbalance under vacuum at 20 °C. 2 ml of p-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 31.835 mg, corresponding to 0.076 mmol of p-xylene sorbed.}\]

\[\text{Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4-\text{PhPy})_4](\text{o-xylene})_4: \text{21.609 mg (0.029 mmol) of 3 were weighed on a microbalance under vacuum at 20° C. 2 ml of o-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 32.553 mg, corresponding to 0.103 mmol of o-xylene sorbed.}\]
Chapter 5: Engineering sorption properties of a Werner clathrate

\[ \text{[Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4-\text{PhPy})_4]·(m-\text{xylene})_4: \] 24.513 mg (0.033 mmol) of 3 were weighed on a microbalance under vacuum at a controlled temperature of 20 °C. 2 ml of \textit{m}-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 35.418 mg, corresponding to 0.103 mmol of \textit{m}-xylene sorbed.

\[ \text{[Ni}_{0.5}\text{Co}_{0.5}\text{Cl}_2(4-\text{PhPy})_4]·(p-\text{xylene})_4: \] 18.407 mg (0.0245 mmol) of 3 were weighed on a microbalance under vacuum at a controlled temperature of 20 °C. 2 ml of \textit{p}-xylene was injected into the microbalance and the weight equilibrated for 220 minutes to 19.788 mg, corresponding to 0.01 mmol of \textit{p}-xylene sorbed.
### 5.4.5 Crystallographic data

<table>
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<tr>
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<th>NiCl$_2$(4-PhPy)$_4$·(o-xylene)$_4$</th>
<th>NiCl$_2$(4-PhPy)$_4$·(m-xylene)$_2$</th>
<th>NiCl$_2$(4-PhPy)$_4$·(p-xylene)$_4$</th>
<th>CoCl$_2$(4-PhPy)$_4$·(o-xylene)$_4$</th>
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<tr>
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<td>C$<em>{70}$H$</em>{76}$Cl$_2$N$_4$</td>
<td>C$<em>{76}$H$</em>{76}$Cl$_2$N$_4$</td>
<td>C$<em>{73}$H$</em>{76}$Cl$_2$CoN$_4$</td>
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<td>958.98</td>
<td>1175.02</td>
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<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
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<td><strong>Wavelength (Å)</strong></td>
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<td>0.71073</td>
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<td><strong>Space group</strong></td>
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<td>P</td>
<td>C2/c</td>
<td>C2/c</td>
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<td>9.5570(9)</td>
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<td><strong>b/Å</strong></td>
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<td>12.707(1)</td>
<td>23.899(2)</td>
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<td><strong>c/Å</strong></td>
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<td>15.954(2)</td>
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<td>89.157(2)</td>
<td>97.806(2)</td>
<td>96.357(3)</td>
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<td><strong>β/°</strong></td>
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<td>77.167(2)</td>
<td>88.118(2)</td>
<td>96.357(3)</td>
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<td><strong>γ/°</strong></td>
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<td>88.118(2)</td>
<td>88.118(2)</td>
<td>96.357(3)</td>
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<td>2498.8(4)</td>
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<td><strong>Calculated density (g cm$^{-3}$)</strong></td>
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<td>-13 ≤ h ≤ 13, -33 ≤ k ≤ 30,</td>
<td>-12 ≤ h ≤ 12, -31 ≤ k ≤ 30,</td>
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<td>-37 ≤ l ≤ 26</td>
<td>-22 ≤ l ≤ 22</td>
<td>-35 ≤ l ≤ 39</td>
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<td>23171</td>
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<td><strong>Independent reflections</strong></td>
<td>7824 [R$_{int}$ = 0.0260]</td>
<td>14497 [R$_{int}$ = 0.0378]</td>
<td>8844 [R$_{int}$ = 0.0415]</td>
<td>7934 [R$_{int}$ = 0.0803]</td>
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<tr>
<td><strong>Completeness to θ$_{max}$ (%)</strong></td>
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<td>92</td>
<td>99.1</td>
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<td><strong>Max. and min. transmission</strong></td>
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<td>0.9382 and 0.7897</td>
<td>0.9485 and 0.8669</td>
<td>0.9725 and 0.8743</td>
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<td><strong>Refinement method</strong></td>
<td>Full-matrix least-squares on F$^2$</td>
<td>Full-matrix least-squares on F$^2$</td>
<td>Full-matrix least-squares on F$^2$</td>
<td>Full-matrix least-squares on F$^2$</td>
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<td>14497 / 0 / 599</td>
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<td>0.921 and -0.627</td>
<td>0.386 and -0.462</td>
<td>1.091 and -0.559</td>
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<td>CoCl$_2$(4-PhPy)$_2$·(m-xylene)$_4$</td>
<td>CoCl$_2$(4-PhPy)$_2$·(p-xylene)$_4$</td>
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<td>C$<em>{36}$H$</em>{76}$Cl$_2$CoN$_4$</td>
<td>C$<em>{45}$H$</em>{36}$Cl$_2$N$_4$CoNiO$_1$</td>
<td>C$<em>{44}$H$</em>{36}$Cl$_2$N$_4$NiO$_1$</td>
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<td>C$_2$/c</td>
<td>P$_2_1$2$_1$2$_1$</td>
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<td>9.555(4)</td>
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<td><strong>b/Å</strong></td>
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<td>24.019(9)</td>
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<td>27.580(2)</td>
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<td><strong>γ/°</strong></td>
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<td>2484</td>
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<td>1556</td>
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<td>1.70 to 25.00</td>
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<td>1.71 to 28.43</td>
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<td><strong>Miller index ranges</strong></td>
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<td>-10 ≤ h ≤ 11, -28 ≤ k ≤ 28,</td>
<td>-16 ≤ h ≤ 16, -15 ≤ k ≤ 21,</td>
<td>-12 ≤ h ≤ 12, -22 ≤ k ≤ 31,</td>
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<td>16087</td>
<td>23493</td>
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<td>5519 [R$_{int}$ = 0.1056]</td>
<td>9179 [R$_{int}$ = 0.0296]</td>
<td>5825 [R$_{int}$ = 0.0422]</td>
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<td><strong>Completeness to θ$_{max}$ (%)</strong></td>
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<td>99.6</td>
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<td>Full-matrix least-squares on F$^2$</td>
<td>Full-matrix least-squares on F$^2$</td>
<td>Full-matrix least-squares on F$^2$</td>
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<td>0.436 and -0.524</td>
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### CoCl$_2$(4-PhPy)$_4$·(2p-xylene)(4-PhPy)

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<td>Wavelength (Å)</td>
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<td>Completeness to $\theta_{max}$ (%)</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
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<tr>
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<td>R indices (all data)</td>
<td>$R1 = 0.0911$, $wR2 = 0.2240$</td>
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<tr>
<td>Largest diff. peak and hole (e Å$^3$)</td>
<td>3.747 and -0.492</td>
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</table>
CHAPTER 6: CONCLUSIONS

SUMMARY AND CONCLUDING REMARKS

The work presented in this thesis has covered three interesting aspects of crystal engineering, viz (i) synthesis of new porous materials for a desired function, (ii) studying some known materials to obtain a better understanding of their behaviour and (iii) modification of properties of crystalline materials. Two different classes of metal-organic hosts were studied: MOFs and Werner clathrates. Eighteen new MOFs were synthesised and characterised and an already known flexible MOF was studied for its ability to undergo phase changes under gas pressure. Three Werner complexes were prepared and their xylene sorption tendencies were studied. With regard to the work presented in Chapter 3, the method of using ligands $L_1$ and $L_2$ concurrently with carboxylates proved to be a feasible strategy for synthesising porous MOFs. Ten coordination polymers were obtained of which four were found to be porous to CO$_2$. In addition, the compounds also exhibit selectivity of CO$_2$ over N$_2$. As might be expected, the sorption capacity of these compounds is enhanced at lower temperatures. It has been shown that the CO$_2$ sorption capability of naphthalene diimide based MOFs can be enhanced by lithium doping. Therefore, future studies on these compounds might involve doping the already formed MOFs with lithium and then studying their sorption properties. The reaction of $L_3$ and $L_4$ with metal halides yielded only 1–D structures instead of the desired 0–D metallocycles. The reaction of $L_5$ with metal nitrates yielded six coordination polymers, of which two are 1–D and four are 2–D. Of the four 2–D structures, three are isostructural with related unit cell parameters.

Flexibility and structural dynamism is an intriguing occurrence in MOFs. Flexible MOFs often exhibit stepwise sorption and hysteretic desorption isotherms and, although several structures have been reported, there is little experimental data explaining their behaviour. The work presented in Chapter 4 is a study of the flexible MOF [Zn$_2$(BDC)$_2$(BPy)], which undergoes phase changes in response to gas pressure. The absorption isotherm showed two inflection steps in the pressure range 0 to 30 bar. The ability of the system to maintain single crystallinity allowed the different phases to be elucidated by means of SCD. With the aid of a gas cell developed ‘in house’ the structural changes could be tracked at different pressure loadings. The incremental gas loading experiment revealed that the system undergoes two phase transformations, the first occurring at 8 bar (room temperature), which corresponds to the conversion of the nonporous phase (2) to the porous phase (1$_{CO_2}$) and the second occurring at 10 bar (-20 °C), which corresponds to the conversion of 1$_{CO_2}$ to 3. These results are consistent with...
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te the two inflection points observed in the sorption isotherms. An HPDSC technique was developed and used to determine the gate-opening pressures involved with each phase transformation, as well as the energies involved during the sorption and desorption processes. It was shown that the phase transformation of $\text{2 to 1}_{\text{CO}_2}$ involves more energy and it occurs much faster than the phase transformation of $\text{1}_{\text{CO}_2}$ to $\text{3}$. HPDSC was also used to determine the effect of temperature on the gate-opening pressures for both phase transformations, and it was observed that the gate-opening pressures increase with increasing temperature. Repeating the HPDSC experiments using CH$_4$ instead of CO$_2$ showed that the phase transformations occur at much higher pressures. This is the first time that such a technique has been used in the study of pressure induced phase transformation in flexible MOFs. Furthermore, there is a good correlation between the data obtained from HPDSC with those obtained from SCD and high pressure sorption. A combination of these techniques provides a more complete picture of the structural changes, phase transformation and the energies involved during the sorption and desorption processes and it also explains the inflection steps that occur in the sorption isotherm as well as the hysteresis in the desorption isotherm.

Finally, a mixed-metal strategy was used as a means of modifying properties in crystalline materials. The work presented in Chapter 5 describes the synthesis of two Werner complexes [NiCl$_2$(4-PhPy)$_4$] (1), [CoCl$_2$(4-PhPy)$_4$] (2) and the solid solution [Ni$_{0.5}$Co$_{0.5}$Cl$_2$(4-PhPy)$_4$] (3) that could not be obtained by solution synthesis. Scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy confirmed a homogeneous distribution of Ni and Co ions only in the grind product and not in the solvent evaporation products. The three Werner complexes were exposed to xylene vapours in separate experiments and the solid solution exhibits sorption properties that differ from those of the pure compounds. All three complexes absorb $o$- and $m$-xylene, however the sorption capability of the solid solution for $p$-xylene is significantly reduced. This interesting property of compound 3 can be employed in the separation of xylene isomers, an area of significant industrial importance. Future studies on this compound would be to expose it to a mixture of the xylene isomers to determine its selectivity over the three isomers. As a continuation of this work, it would also be interesting to prepare the [CuCl$_2$(4-PhPy)$_4$] complex which has not been explored in this regard, and the solid solution of Cu and Ni or Cu and Co and to study their xylene sorption properties.

Despite the fact that mechanochemistry is a simple, economical and eco-friendly method of synthesis, this study also highlights the importance of exploring mechanochemistry as a means of obtaining bulk phases that cannot be produced in bulk purity by solution synthesis. In addition,
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this study has also shown the importance of employing mixed-metal materials (solid solutions) as a means of engineering or modifying bulk properties in crystalline materials.
REFERENCES

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APPENDIX

The supplementary CD contains:

- CIFs and res files of structures described in Chapter 3
- Thermal ellipsoid plots for CP1 to CP18
- TGA for CP5, CP12-14, CP15, CP16 and CP17
- PXRD of CP14, CP17 and CP18
- CIFs and res files of structures described in Chapter 4
- CIFs and res files of structures described in Chapter 5
- Packing diagrams for structures 1·MeOH, 2·MeOH, [NiCl₂(4-PhPy)₄](p-xylene)₄ and [NiCl₂(4-PhPy)₄](m-xylene)₂