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Structural Behaviour and Adsorption Properties of Sc-based Metal-Organic Frameworks

Jorge Sotelo

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy to the School of Chemistry,

University of Edinburgh

2015
Declaration

I declare that this Thesis has been written by me and that the work carried out is my own, or I have made a substantial contribution towards it except where specific reference is made to another. This work has not been submitted for another degree or professional qualification.

Jorge Sotelo
Abstract

Some of the challenges faced when developing novel functional materials, cannot be resolved without the correct understanding of their structure-property relationships. Metal-organic frameworks (MOFs) constitute a representative example where in-depth structural knowledge can greatly help improve and optimise their application into industrially relevant settings. Fortunately, the inherent crystalline nature of MOFs allows for analysis using the wide range of crystallographic experimental techniques that are currently available.

This work covers the study of the structural properties of a particular family of MOFs, which have shown significant potential as molecular sieves and for gas storage. Sc-based MOFs first attracted attention for their particularly robust and inert nature, bypassing some of the physical challenges many MOFs have when undergoing industrial implementation.

After an initial review of the state of the art in the field of MOFs and the techniques utilised to analyse their properties, this work then focuses on the mechanical properties of a series of functionalised and unfunctionalised Sc-dicarboxylate MOFs. Using nano-indentation techniques and high-pressure crystallography, the hardness and elasticity of these materials are correlated to their different structural features, confirming their relative robustness when compared to other MOFs in the literature.

An interesting property of Sc\textsubscript{2}BDC\textsubscript{3} is its selective uptake of CO\textsubscript{2} over other fuel-related gases such as CH\textsubscript{4} and CO. In this context, the \textit{in situ} adsorption crystallographic analysis of Sc\textsubscript{2}BDC\textsubscript{3} and its amino-functionalised derivative Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3} (BDC-NH\textsubscript{2} = 1,4-amino-2-benzenedicarboxylate) is described, as performed using the gas cell set up of beamline I19 at the Diamond Light Source synchrotron. This study is the first example of a mixed gas atmosphere experiment using single-crystal diffraction, which in conjunction with \textit{in silico}, adsorption and breakthrough experiments, provides direct insight into the interactions that drive the selective behaviour of both frameworks.
Following this, the MOF Sc₂BDC₃ (BDC = 1,4-benzenedicarboxylate), is selected as a case study for branched and unbranched alkane separation. Here, high-pressure crystallography shows how these relatively oversized guest molecules, can be forced at thousands of atmospheres of pressure inside the narrow triangular channels (< 4 Å diameter) of the framework. It is also possible to resolve the structural changes the framework undergoes upon uptake of the different guests, as well as locate the adsorption sites of the hydrocarbons in the pores of Sc₂BDC₃, which can be then correlated to the gas adsorption behaviour of the different guests.

To conclude, the high-pressure inclusion study of both CO₂ and CH₄ inside Sc₂BDC₃ shows how combining cryoloading techniques and molecular crystallography for the first time, can provide improved models of the adsorbed gaseous guests inside Sc₂BDC₃. This example not only provides a novel alternative in which to study more easily the adsorption sites in MOFs via diffraction techniques, but also reveals some of the interesting structural behaviour MOFs can have in these extreme conditions.
Para Lola, el Sol de tantos y mi gran inspiración.
Acknowledgements

Words are not enough to express my gratitude to everyone that has joined me throughout these incredible three years. Through the good, the bad and ugly times many have come and gone, but without each and every one of them my experience in Edinburgh would have not been the same.

Of course, without Stephen this would have not have happened altogether. Even though I was only hired because I claimed to be able to play football, we have since done that and many other great things together. Your understanding and generally amazing ability to put yourself in the place of others, has really left an enduring mark on me. Sometimes being like the big brother I never had, your advice, knowledge and, of course, your friendship is something I look forward to for many more years.

It has been very funny how, despite not technically my supervisor, I have had the privilege to enjoy the wisdom of Simon for the last three years. This has not been limited to crystallography by any means, and I will remember with particular fondness the many moments of laughter, political and general life lessons you have shared with me. I hope for many more and enrich what is already a great admiration for you.

There were four of us when I started, Jack, Andy and Scott, who I have had the joy to share a friendship which can be hardly summarised in two lines, but I will try in three words: “pure dead brilliant”. Those that joined afterwards, starting with Claire, whose bravery and brilliance demonstrated in dealing with an all-boys office I will admire endlessly, and Charlie, whose ability and seemingly useless but immense knowledge of the oddest subjects will not cease to amaze me, have also been truly enjoyable to work with: to Gary, Chris, Solveig, Tom, Mark, Becky, Philippa, Jurgita, Thom, Mark and Anna, Mike, Odin, Jamie my dancing partner Chris and everyone in St. Andrews, Alex, John, Berenice and especially Paul, thank you.

Those who have put up with me outside work, through their own choice, probably deserve a whole book to themselves. Sam, Linz, Koke, Ben, Ivan, they don’t give PhDs for being friends with you, but what I have learned, shared and laughed with you would probably fill a few bookshelves.

My family have no choice but to deal with me, but what a great job they have done at making so many miles seem so few. Mum, Dad, Guille, Elisa, you have all done so much to make this possible, especially Mum and Dad, but you all know why that is.
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<thead>
<tr>
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<th>Full Form</th>
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<tbody>
<tr>
<td>ATZ</td>
<td>3-amino-1,2,4-triazole</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BDC</td>
<td>1,4-benzenedicarboxylate</td>
</tr>
<tr>
<td>BDC-NH₂</td>
<td>2-aminobenzene-1,4-dicarboxylate</td>
</tr>
<tr>
<td>BDP</td>
<td>1,4-benzenedipyrazolate</td>
</tr>
<tr>
<td>BFGS</td>
<td>Broyden-Fletcher-Goldfarb-Shanno</td>
</tr>
<tr>
<td>BTC</td>
<td>1,3,5-benzenetricarboxylate</td>
</tr>
<tr>
<td>CCD</td>
<td>charged-coupled device</td>
</tr>
<tr>
<td>CPO</td>
<td>coordination polymer</td>
</tr>
<tr>
<td>CSD</td>
<td>Cambridge structural database</td>
</tr>
<tr>
<td>DAC</td>
<td>diamond anvil cell</td>
</tr>
<tr>
<td>DEF</td>
<td>diethylformamide</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DMF</td>
<td>dimethylformamide</td>
</tr>
<tr>
<td>DOBDC</td>
<td>2,5-dioxidobenzene-1,3-dicarboxylate</td>
</tr>
<tr>
<td>DOBPDC</td>
<td>4,4’-dioxidobiphenyl-3,3’-dicarboxylate</td>
</tr>
<tr>
<td>EH</td>
<td>experimental hutch</td>
</tr>
<tr>
<td>EoS</td>
<td>equation of state</td>
</tr>
<tr>
<td>FSE</td>
<td>framework strain energy</td>
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<tr>
<td>GCMC</td>
<td>grand canonical Monte Carlo</td>
</tr>
<tr>
<td>GOE</td>
<td>geometry optimised energy</td>
</tr>
<tr>
<td>HKUST</td>
<td>Hong Kong University of Science and Technology</td>
</tr>
<tr>
<td>IA</td>
<td>1,3-benzenedicarboxylate (from isophthalic acid)</td>
</tr>
<tr>
<td>IA-NH₂</td>
<td>1,3-amino-2-benzenedicarboxylate</td>
</tr>
<tr>
<td>MIE</td>
<td>mean interaction energy</td>
</tr>
<tr>
<td>MIL</td>
<td>Matériaux de l’Institut Lavoisier</td>
</tr>
<tr>
<td>MOF</td>
<td>metal–organic framework</td>
</tr>
<tr>
<td>Melm</td>
<td>2-methylimidazole</td>
</tr>
<tr>
<td>NBE</td>
<td>net binding energy</td>
</tr>
<tr>
<td>NLC</td>
<td>negative linear compressibility</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>OX</td>
<td>oxalate</td>
</tr>
<tr>
<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
</tr>
<tr>
<td>PTM</td>
<td>pressure transmitting medium</td>
</tr>
<tr>
<td>SAV</td>
<td>solvent accessible volume</td>
</tr>
<tr>
<td>UiO</td>
<td>University of Oslo</td>
</tr>
<tr>
<td>UPLC</td>
<td>ultra performance liquid chromatography</td>
</tr>
<tr>
<td>TS</td>
<td>Tkatchenko-Scheffler</td>
</tr>
<tr>
<td>ZIF</td>
<td>zeolitic imidazolate framework</td>
</tr>
<tr>
<td>atm[^a][^d]</td>
<td>bar</td>
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<td>49346</td>
<td>50000</td>
</tr>
<tr>
<td>98692</td>
<td>100000</td>
</tr>
</tbody>
</table>

[^a]: atm – standard atmosphere
[^b]: Torr – essentially equivalent to mmHg
[^c]: Pascal – SI unit of pressure
[^d]: psi – pounds per square inch
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Introduction
1.1 Structure-property relationships

Defining the structure of a system, the parts it is made of and how they are connected and interact with each other, is the root to comprehending the functions of many things. This is as important in the case of particle physics or macromolecular biology as it is in mechanical engineering or building architecture, and of course, it is central to our understanding of chemistry.

Structure-function relationships form the basis of our knowledge of the subject, from atomic structure to the chemical and physical properties of materials. The differentiation we make between the elements in the periodic table, could not be done without knowing the structure of atoms: how electrons are organised into different orbitals, and how they interact between each other and with the nucleus to give each element its unique properties. Chemical properties, like for example $pK_a$, can also be rationalised on the basis of the chemical structure of the different species. The electron donating or withdrawing ability of different parts of the molecule (determined by its atoms and the way they are bonded together), can be related to how easily the hydrogen atom can dissociate from the rest of the molecule into solution.

More complex properties depend on more variables, hence more knowledge of the structure of the different parts of the system is required. Explaining the reactivity, conductivity or even the adsorption properties of a material requires an increasing amount of understanding of the electronic and bonding structure, including the intermolecular interactions in place in the system.

1.2 Sorbent (or adsorbent) materials

In this thesis, where the adsorption properties of porous metal-organic frameworks (MOFs) are investigated, special emphasis is placed on understanding how the structure of MOFs change when molecules penetrate into their pores. For the purpose of this work, it is therefore important to clarify the concept of adsorption, the process by which atoms, ions or molecules in the gas or liquid phase adhere to a surface. It is more formally defined by the IUPAC as the “increase in the concentration of a
dissolved substance at the interface of a condensed and a liquid (or gaseous) phase due to the operation of surface forces” and should not be confused with absorption.[1] Absorption refers to the process whereby a material (absorbate) is retained by another (absorbent).[2] In simple terms, adsorption can be seen as surface-based process whilst absorption refers to the whole volume of the material.

Sorption is commonly used to encompass both phenomena, and sorbent materials are the systems utilised to absorb or adsorb liquids and gases in separation and storage technologies. On occasion sorbent materials are also referred to as adsorbents in the literature, since it is generally adsorption phenomena that dictate uptake mechanisms, and surface-based theories (like Langmuir or BET\(^1\) theory) that are used to explain such processes.

In light of this, one tends to see terminology such as adsorbate or guest used to refer to the molecular species of gas or liquid being adsorbed, and consequently adsorbent or host as the condensed phase on which adsorption occurs.[1] The phenomenon of adsorption occurs in many natural, physical, biological or chemical systems, but in the context of this work it is its relevance in separation and storage technologies that will be discussed.

The invention of synthetic zeolites in 1959 marked the beginning of adsorbent development and has made adsorption a key tool in chemical, petrochemical and pharmaceutical industries.[3] From hydrogen storage and carbon capture to paraffin or hydrocarbon separations, many porous materials have been utilised to tackle different industrial challenges. The aforementioned zeolites, activated carbon, silica gels or aqueous amine solutions are just some examples of adsorbents, and each type targets certain storage or separation applications. A brief summary of some of the adsorbents and their storage and separation processes they are used for can be found in Table 1.1

---

\(^1\) BET - Brunauer–Emmett–Teller
Table 1.1 - Examples of the most commonly used adsorbents and some of their storage and separation applications (modified and expanded from Bird et al.)[3]

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolites</td>
<td>Air drying</td>
</tr>
<tr>
<td></td>
<td>CO₂ removal (from C₆H₁₄, natural gas, etc.)</td>
</tr>
<tr>
<td></td>
<td>Liquid bulk separations (p-xylene/o-xylene and m-xylene, paraffins, fructose/glucose)</td>
</tr>
<tr>
<td></td>
<td>CO₂ storage</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>Gas bulk separations (hydrocarbons/vent streams)</td>
</tr>
<tr>
<td></td>
<td>Gas purification (SO₂/vent streams, hydrocarbons/halogenated organics)</td>
</tr>
<tr>
<td></td>
<td>Liquid purifications (organics/water, inorganics/water, drug detoxification in the body)</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>Air drying</td>
</tr>
<tr>
<td></td>
<td>Polar separations</td>
</tr>
<tr>
<td>Metal and non-metal hydrides</td>
<td>H₂ storage</td>
</tr>
<tr>
<td>Amines and amine coated materials</td>
<td>H₂S and CO₂ removal</td>
</tr>
<tr>
<td></td>
<td>CO₂ storage</td>
</tr>
<tr>
<td></td>
<td>H₂ storage</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>Water treatment</td>
</tr>
<tr>
<td></td>
<td>H₂ storage</td>
</tr>
</tbody>
</table>

The mechanisms whereby different adsorbent materials work depend on the nature of both the adsorbate and the adsorbent. Liquid amine solutions for example, are used for carbon capture, and generally absorb CO₂ via the reversible chemical formation of compounds such as ammonium carbamate, ammonium carbonate, and ammonium bicarbonate. Activated carbons on the other hand, tend to adsorb through physisorption of different adsorbates through weak van der Waals and London dispersion forces. For these materials, large surface areas are much more important for maximising CO₂ uptake.

Zeolites are anionic crystalline aluminosilicates usually contain cationic alkali or alkaline earth metals inside their generally porous architecture. In general, the chemistry of zeolites, and in particular their behaviour on uptake of adsorbents, can be complicated, partly due to a combination of their unique anionic surface chemistry and the presence of cations inside the pores.[3] This results in many more factors determining the uptake properties, including dispersion, van der Waals and electrostatic interactions as well as molecular sieving effects.
Characterisation and measurement of the adsorption properties of zeolites, like many other adsorbents, tends to be done by measuring their adsorption isotherms. There are several approaches to measuring adsorption isotherms, but all based on the principle of monitoring guest uptake (either by mass or volume) as function of increasing pressure at a constant temperature. Adsorption isotherms can be used to determine the maximum capacity of a particular adsorbent, as well as the mechanisms dictating the uptake of the different species. Based on the shapes of the curves obtained it is possible to classify isotherms into different types (Figure 1.1). Comparing the isotherms of the different adsorbate/adsorbent systems helps determine what storage or separation applications each system is best suited for.

Figure 1.1 - Six main types of adsorption isotherms. On the y-axis represents coverage or uptake and on the x-axis P represents pressure (IUPAC, 1985).
Chapter 1 - Introduction

Gas adsorption in zeolites tends to be explained using some form of the Langmuir adsorption model, since monolayer coverage is the main adsorption mechanism in microporous materials such as zeolites. In simple terms one can describe the adsorption on a solid surface using the following equilibrium:

\[ A(g) + B(s) \overset{\text{Adsorption}}{\underset{\text{Desorption}}{\rightleftharpoons}} AB \]  \hspace{1cm} (1.1)

Where \( A(g) \) is the gas adsorbate, \( B(s) \) is the solid adsorbent and \( AB \) is the guest-host complex. From this, Langmuir defined coverage as the fraction of the adsorption sites occupied, which at equilibrium results in:

\[ \Theta = \frac{KP}{1 + KP} \]  \hspace{1cm} (1.2)

where \( \Theta \) is the fractional coverage, \( K \) is the equilibrium constant of Equation 1.1 and \( P \) is the pressure of the adsorbate.

At low pressures \( KP \) is so small that \( \Theta \approx KP \), thus behaving like a simple linear adsorption isotherm, otherwise referred to as Henry’s adsorption isotherm.[4] At high pressures, maximum coverage is approached when \( \Theta \approx 1 \) and hence full capacity is reached. An ideal Langmuir isotherm corresponds to a Type 1 adsorption isotherm (Figure 1.1), but in reality many adsorption processes deviate from this ideal Langmuir isotherm behaviour, like for example adsorption in microporous materials such as zeolites. Modifications to the theory can be made and other models like BET theory can be used to explain different effects, such as multicomponent or multilayer adsorption for example, whilst more complex models can be used to describe liquid adsorption.[5, 6] However, the Langmuir model remains the most widely used for practical purposes, with the general concept that higher pressures will lead to higher coverage (at constant temperature).

To underpin the factors that drive a particular adsorption behaviour, it is important to be able to understand the nature of \( AB \). The wide range of zeolites, and structural derivatives (or zeotypes) such as aluminophosphates (AlPOs) has opened the possibility of tuning the properties of the adsorbent to best target a particular
separation or storage application. For this it becomes important to analyse the structure of $AB$ at different pressure conditions, and determine the structural features that allow for more optimal adsorption properties.

The rise in the past two decades of a new generation of microporous materials commonly referred to as metal-organic frameworks (MOFs), has increased several orders of magnitude the number of materials that can be tested for adsorption. The even greater degrees of chemical tuning available in MOFs, together with a more varied range of porous architectures, make them an interesting alternative to traditional adsorbent systems allowing to tackle even more challenging separations. The characterisation and understanding of the guest-host structures of MOFs has thus become a very important avenue to explain some of their more complex adsorption behaviours.
1.3 Metal-organic frameworks (MOFs)

The wide variety of terminologies and definitions used in this relatively young field of research, led to IUPAC setting up a task group to recommend a unified definition for MOFs. Initially they defined coordination polymer as “a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions” and the subgroup of coordination network as “a coordination compound extending, through repeating coordination entities, in 1 dimension, but with cross-links between two or more individual chains, loops, or spiro-links, or a coordination compound extending through repeating coordination entities in 2 or 3 dimensions”.[7] These lead to metal-organic framework or MOFs being “a coordination network with organic ligands containing potential voids”.

In a more general sense, MOFs can be seen as compounds consisting of metal ions or clusters (nodes) coordinated by organic linkers (struts) connected into framework architectures that tend to be porous and crystalline. Two archetypical examples include MOF-5 ([Zn₄(μ₄-O)(BDC)₃], BDC = benzene-1,4-dicarboxylate) or HKUST-1 ([Cu₃(BTC)₂], BTC = benzene-1,3,5-tricarboxylate)² (Figure 1.2), where Zn and Cu clusters respectively are connected by organic linkers to form 3-dimensional porous frameworks.[8, 9]

Like in the case of MOF-5 and HKUST-1, carboxylate linkers are commonly used as the organic nodes, but azole-based MOFs are also highly recurrent. The wide variety of types of metal nodes and organic linkers that can be combined together, has given rise to an ever increasing number of MOFs, with varying degrees of porosity, network topologies and a rich chemical diversity. This has contributed to the synthesis and characterisation of MOFs becoming a very prolific area of research.[10]

² The terminology of MOFs is complex, with many acronyms for the linkers and the materials themselves, which in some cases relate to the laboratory in where the material was first synthesised, like HKUST-1 from Hong Kong University of Science and Technology. The list of abbreviations references the different linkers and materials discussed in this work.
Figure 1.2 - Ball and stick representation of MOF-5 and HKUST-1. MOF-5 is composed of Zn$_4$O$_{13}$ clusters (ZnO$_4$ tetrahedra represented in blue) connected by BDC linkers, whilst HKUST-1 is connected Cu$_2$O$_{10}$ paddle-wheel nodes linked by BTC linkers. Cu-atoms appear in brown, O-atoms in red and C-atoms in grey. H-atoms are omitted for clarity. Yellow, green, orange and purple spheres represent the different type of voids present in the frameworks.

Several books and reviews have been written on the field, particularly highlighting the wide variety of potential applications MOFs have, including catalysis, sensing, biomimicry and separation and storage.[11-13] Despite the promising prospects of MOFs, there are still many challenges that need addressing. Concerns with regards to their stability and mechanical properties have surrounded MOFs since their inception, particularly in comparison with other adsorbents such as zeolites, for which a more extensive literature on their physical properties exists. Additionally, some MOFs present a degree of flexibility unobserved in previous porous materials, giving rise to the subclass of “soft porous crystals”. [14] These include materials which can undergo significant structural changes, such as expansion in volume of over 100 %, negative linear compressibility or rearrangements of their porous structure.
when exposed to varying conditions of temperature, pressure and other external stimuli.[15-18]

These structural features have a direct influence on the properties of the materials, and particularly on their adsorption and uptake properties relevant to separation and storage applications. In addition, the inherent crystalline nature of many MOFs, which arises from their highly ordered structure, has facilitated their characterisation using crystallographic techniques. The fact they often retain this crystallinity when undergoing structural changes or on uptake of different adsorbate molecules, has driven the further development of in situ structural techniques, allowing MOFs to be investigated when exposed to varying pressures and increasing guest content, for both gases and liquids. From direct observation of the effects of guest inclusion it has been possible to gain invaluable insight into the adsorption mechanisms in MOFs.

This work aims to explore further the techniques used for this purpose, and build upon the current technologies in order to explore and better understand the adsorption behaviour of MOFs. The techniques of high-pressure crystallography, gas cell single-crystal diffraction and nanoindentation have been utilised to determine the adsorption and mechanical properties of Sc-based frameworks – some of which have shown promising CO₂ adsorption and separation properties. More details on the experimental methods used can be found in Chapter 2, which have also been backed by computational simulations to support some of the conclusions reached.

This approach is increasingly common in the field, particularly with developments in computational techniques, and the possibility of obtaining accurate atomistic models of the systems studied (including adsorption sites and any structural rearrangements that the framework may undergo), allowing more complex problems to be tackled using simulations. The marriage of experimental with theoretical studies has thus become a necessary step towards quantifying and understanding the energetics of the adsorption processes in MOFs.
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1.4 MOFs under pressure

Recently, several reviews about the latest advances in the field of non-ambient crystallography, as well as a special issue of *Acta Crystallographica Section B* have been published.[19-21] To date, numerous studies at different conditions of temperature and pressure have been carried out on MOFs, including gas sorption and high-pressure crystallographic studies. Details of the technical and methodological outline of these techniques will be described in the following chapter, and a brief review of some of the MOFs already studied will now follow. In particular, this introduction is focused on what might be considered the main archetypical MOFs, including MOF-5, HKUST-1, ZIF-8, MOF-74 and MIL-53 as they have been by far, the most studied MOFs to date.

**MOF-5**

Being one of the most representative MOFs, MOF-5 has been studied in great depth. The porous framework of MOF-5, which arises from connecting Zn₄(μ-O)₆⁺ clusters with BDC linkers in a cubic structure with *Fm3m* symmetry, is dominated by a large central cavity of approximately 1600 Å³ interconnected by channel windows of ~ 7.6 Å. *In situ* single-crystal and powder X-ray and neutron diffraction experiments have been carried out under atmospheres of N₂, H₂, D₂, He, Ar and CD₄ gases.[22-26] In these studies, it has been possible to identify up to eight symmetry-independent adsorption sites, with five of them in close contact with the framework surface and three forming a secondary layer. It is worth mentioning the temperature dependence of the uptake observed for N₂ and Ar, where location of the sites was unambiguous at 30 K, below the freezing point of the gases, but at 293 K little electron density could be found around the positons of the adsorption sites.[26] This is one of the challenges faced when performing these experiments closer to temperature at which separation and storage applications take place – the decrease in uptake associated with increasing temperature requires increasingly high pressures to be able to observe the adsorption with crystallographic methods.
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Diamond anvil cell (DAC) technology has been used to investigate the behaviour of MOF-5 at much higher pressures. Comparing the work by Graham et al. with the work of Hu et al. shows that whilst the latter demonstrated the amorphisation of the framework upon grinding under non-hydrostatic conditions, the former achieved stabilisation of the framework up to pressures of over 32 kbar when compressed with DEF (diethylformamide).[27, 28] This exemplified the pore filling mechanism observed when compressing MOFs using a penetrating pressure-transmitting medium (PTM), which is a common recurrence in high-pressure studies of microporous materials.

These results were followed by the calculation of the direct compressibility of MOF-5 using \textit{ab initio} computational methods (Figure 1.3). The effect of using a penetrating PTM (that is essentially forced inside the pores), causes both an initial expansion in the unit cell volume below 8 kbar and an eventual compression of the framework. In contrast, the simulated direct compression shows no sign of expansion and a greater compressibility, highlighting how the pore-filling mechanism alters the compressibility of MOF-5.

![Figure 1.3 - Compressibility of MOF-5 at high-pressures as measured from compression with DEF (green circles) and by DFT simulations (red circles).](image-url)
HKUST-1

Sometimes referred to as Cu-btc, HKUST-1 has attracted considerable attention for its adsorption properties. These are dominated by the open-metal site of the Cu-paddlewheels, which usually hosts a water molecule. *In situ* neutron and X-ray diffraction studies have explored the uptake of gases such as D₂, CD₄, CO₂, Ar, Xe and Kr.[29-34] Work on CD₄ and D₂ revealed HKUST-1 to have up to 8 or 9 adsorption sites respectively, with some of the sites only filling at higher gas loading, establishing a hierarchy of occupation for the different sites with those closer to the metal-sites filling preferentially.[29-32] The importance of the open-metal site in guest adsorption is also pertinent in the uptake of CO₂, however in the case of noble gases, no evidence of interaction with these sites can be found.[33, 34]

The effect of hydrostatic compression has also been investigated on HKUST-1, where both powder and single-crystal high-pressure X-ray diffraction experiments have been carried out by Chapman et al. and Graham et al. respectively.[35, 36] Initially, Chapman and co-workers highlighted the difference in compressibility of the framework, depending on the PTM used. Compression with non-penetrating Fluorinert resulted in a direct compression of HKUST-1 in a similar fashion to the behaviour observed when compressed in the absence of any liquid medium. However, when a penetrating PTM such as isopropyl alcohol (i-propanol) was used, a reduction in the compressibility was observed indicating a stabilising effect against compression. This is caused by the permeation of the PTM molecules inside the pores of the framework and was similarly observed when using MEW (Methanol:Ethanol:Water mixture in 16:3:1 ratio).[35]

In both cases where a penetrating PTM was used a sudden change in compressibility was observed. This transition occurred at different pressures depending on the PTM (~ 0.8 GPa with i-propanol and ~ 2.2 GPa with MEW), indicating a difference in response depending on the PTM. The smaller molecules in MEW cause the compressibility of HKUST-1 to be reduced further than with i-propanol and also delayed amorphisation, which for i-propanol and MEW occur at ~ 4 GPa and 7.5 GPa.
respectively. The transition between the two regions of compressibility was attributed to a change from a pore filling to a pore emptying process.[35]

Using single-crystal high-pressure X-ray diffraction, Graham et al. provided a more detailed analysis of the structural consequences under the compression in MEW.[36] The pore content analysis, obtained from the SQUEEZE routine, showed the gradual increase in guest molecules up until the aforementioned phase change, at which point the electron count in the pores was reduced. This was coupled to a sudden change in the Cu-O bond lengths, which consisted of a reduction of the equatorial Cu-O1 distances and an elongation of the axial Cu-O2. This indicated that the pore emptying mechanism was associated with the compression of the stiffer equatorial Cu–O1 bonds being responsible for the reduction in volume during the pore-filling to pore-emptying transition. It is also worth noting that the phase change occurred at a higher pressures in the single-crystal (5 GPa) than in powder (~2 GPa), which could be attributed to a particle-size effect. This has been observed in the MOF ZIF-8, though more work would be required to establish whether this is the case here.[37]
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ZIF-8

Another commonly studied MOF is ZIF-8 ([Zn(MeIm)₂], where MeIm = 2-methylimidazolate), a framework with a sodalite topology that arises from the interconnection of MeIm linkers with Zn centres into a cubic structure with \( I\bar{4}3m \) symmetry.[38, 39] ZIF-8 has a single pore of \( \sim 2500 \, \text{Å}^3 \) in volume which is connected by two channels through 4-ring and 6-ring windows. Neutron and X-ray powder diffraction experiments have been performed on ZIF-8 under gaseous atmospheres of \( \text{D}_2, \text{CD}_4 \) and \( \text{N}_2 \).[23, 25, 40, 41]

The work performed with \( \text{D}_2 \) and \( \text{CD}_4 \) using neutron radiation initially showed ZIF-8 to have 4 different \( \text{D}_2 \) sites and just 2 for \( \text{CD}_4 \) at low loadings. At increasing loadings, up to six sites were found for each gas.[25, 40] Unlike in MOF-5, the two strongest adsorption sites were found to be directly associated with the imidazolate linkers, instead of the Zn centres, which was the case in MOF-5 where the primary adsorption sites are found closer to the metal-oxygen clusters.

Interestingly, the narrow 6-ring windows of \( \sim 3.4 \, \text{Å} \) in diameter should be too small for molecules such as methane (with a kinetic diameter of \( \sim 3.8 \, \text{Å} \)) or nitrogen (\( \text{N}_2 \) \( \sim 3.6 \, \text{Å} \)).[21] Assuming a rigid framework, ZIF-8 should be an ideal candidate for separation of \( \text{H}_2 \) from \( \text{CH}_4 \) and \( \text{N}_2 \). However, the fact that both \( \text{CD}_4 \) and \( \text{N}_2 \) are clearly adsorbed into ZIF-8 indicates the framework must have a certain degree of flexibility around the channel openings.

When loaded in a DAC with a 4:1 mixture by volume of methanol and ethanol, increasing the pressure in a step-wise manner leads to a gradual filling of the framework pores – in a similar fashion to MOF-5 – with the corresponding initial increase in the unit cell volume. However, at 14.7 kbar, a single-crystal to single-crystal phase transition takes place, in which the MeIm linkers rotate by \( \sim 25^\circ \) around the vector connecting the two imidazolate nitrogen atoms (Figure 1.5).[42] This change in channel structure allows for further uptake of guest molecules into the framework, causing an increase in both the unit cell volume and pore content. Under ambient pressure conditions, some evidence for linker rotation in ZIF-8 is present and
manifests itself in the N$_2$ adsorption isotherm at 77 K, which has a sigmoidal shape (Type IV). The presence of such a step in the isotherm is often indicative of a change in the pore structure on uptake of guest species, particularly for microporous MOFs. This so-called ‘gating effect’ is fully reversible. In conjunction with in situ X-ray powder diffraction studies and GCMC methods, it was demonstrated that the high-pressure structure obtained at 14.7 kbar could be used to model the N$_2$ uptake after the step in the isotherm (and was identical to the crystalline phase obtained at 0.4 atm. in a powder sample purged with N$_2$ gas), whilst the ground state structure could be used to model the lower pressure regime.[43]

Figure 1.5 - Representation of the phase change adopted by ZIF-8 at 1.47 GPa in methanol, leading to the channels to open through the rotation of the MeIm linkers. ZnN$_4$ tetrahedra are represented in dark blue, N-atoms in cyan and C-atoms in grey. H-atoms are omitted for clarity. Bottom right graph shows the isotherms calculated using both the ambient pressure model (grey circles) and the high-pressure model (white circles), in comparison to the experimentally measured Type 4 isotherm (black circles).
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**MOF-74**

Otherwise referred to as CPO-27-M, the M-MOF-74 (\([\text{M}_2(\text{DOBDC})]\) family, where DOBDC is 2,5-dioxido-1,4-benzenedicarboxylate and \(M = \text{Mg}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}\) or \(\text{Zn}\)) are also characterised by the open-metal sites present in their ~11 Å hexagonal channels.[44] The adsorption behaviour shown by these materials has marked differences to that observed in the previous examples, due to the possibility to chemically bind guest species and hence form stronger guest-host interactions. CO₂ adsorption in the M-MOF-74 family has been thoroughly studied under different conditions of temperature and pressure using both X-rays and neutron diffraction methods.[33, 45-47] Recently, work carried out by Long and co-workers on many of the M-MOF-74 derivatives have demonstrated the versatility of these systems by studying the inclusion of hydrocarbons, \(\text{H}_2\), \(\text{CH}_4\), \(\text{N}_2\) and \(\text{CO}\).[48-51] The potential application of these materials in separation applications, lies in their selective binding of guests such as CO, CO₂ or even \(\text{N}_2\) over \(\text{H}_2\) and \(\text{CH}_4\), or through the shape selectivity shown in the case of C₆ hydrocarbons with different degrees of branching. Furthermore, their investigations involving the functionalisation of the Mn-MOF-74 with appended diamines has brought further insight into possibilities of functionalising MOFs to enhance separation.[52]

Bringing together some of the working principles in the use of amine solutions for carbon capture and using MOFs as a high-surface area solid support, allows for the cooperative insertion of CO₂ into Mn-MOF-74. This enhances the possibility of using temperature swing adsorption processes in carbon capture technologies, by having highly selective CO₂ materials with large capacities and appreciably lower regeneration energies than state-of-the-art aqueous amine solutions.[52]

In addition to gas separation and storage applications, the MOF-74 family has been investigated by Morris and co-workers for this gas delivery properties, specifically the Ni and Co derivatives.[53-55] The open-metal site readily binds water, which can in turn be removed through heating in what is called the activation process. Upon exposure to either H₂S or NO, the activated framework readily uptakes either species
and retains it at ambient pressure and temperature conditions in the absence of any moisture. Re-exposure to water vapour results in the exchange of the coordinated species with water, releasing either H₂S or NO back into the atmosphere (Figure 1.6). This behaviour has attracted significant attention due to the biological activity of both H₂S and NO. In the case of NO, the incorporation of MOF-74 into plaster-like materials and subsequent exposure to NO, can be used to treat open wounds and avoid infections.[55]

Figure 1.6 - Representation of the NO delivery mechanism of MOF-74 as proposed by Morris and co-workers.[55] In the top left, the as synthesised Co or Ni versions of MOF-74 can be activated by heating to release the coordinated water. This leads to the activated empty structure (bottom), which upon exposure to NO uptakes the gas to form the NO-bound structure (top right). Exposure to moisture causes the exchange of NO with water and subsequent delivery of the gas. MO₅ (where M – Co or Ni) centres have the M-atoms represented in green and O-atoms in red. C-atoms are in grey and H-atoms removed for clarity.
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**MIL materials**

The final family of MOFs that will be discussed are those commonly referred to as MILs (*Matériaux de l’Institut Lavoisier*). A wide range of MIL materials have been synthesised giving rise to an spectrum of topologies and properties, but some of the most representative examples are particularly known for their high flexibility, and are thus usually included under the MOF subgroup of soft porous crystals (SPCs).[14]

One of the most characteristic examples of extreme flexibility is the MIL-88B ([M\(\text{III}O(H_2O)_2X(BDC)_3\)], where \(X = \text{F, Cl acetate}\)) series, which can undergo an expansion of 165% of its unit cell volume upon uptake of diethylformamide (DEF).[56] However, perhaps the most studied subgroup of the MIL family in terms of adsorption properties is the MIL-53 ([M\(\text{III}OH(BDC)_3\)])) series, which have shown a considerable thermal stability in comparison to other MOF materials.[57] From gases such as CO\(_2\), H\(_2\) and CH\(_4\) and other fuel related hydrocarbons, to liquid separations such as xylenes and other aromatics, several studies have shown the MIL-53 materials to have a remarkable potential in separation and storage applications.[58-61]

In particular, functionalisation of the BDC linker has been used to investigate the effect different chemical groups have on the uptake of small hydrocarbons in Fe-MIL-53.[62] The selective uptake of CO\(_2\) over CH\(_4\) has also been studied in the Sc, In, Ga, Al, Fe, and Cr-MIL-53, as well as amino functionalised derivatives, revealing guest-driven phase changes occurring upon uptake of CO\(_2\), and demonstrating its potential in carbon capture technologies.[63, 64]

MILs, in particular MIL-53 has also been used in the separation of different xylene isomers.[65, 66] For these experiments, suspensions of different MIL-53 materials (Al, Cr, and Fe) were packed into separate stainless steel columns and used as the static phase in a high performance liquid chromatography (HPLC) set up. In this study, it was shown that Fe-MIL-53 shows the best retention sequence and is able to separate \(p\)-xylene, \(m\)-xylene and \(o\)-xylene from each other efficiently. More detailed structural analysis revealed the different packing arrangements of xylene isomers in the...
included structures, as well as the structural changes induced on the framework upon uptake of the different isomers.

*In situ* energy-dispersive X-ray diffraction (EDXRD) were used to perform time-resolved experiments to monitor the phase changes upon increasing guest uptake. These results were then correlated with the powder X-ray diffraction structures obtained for the different included guests, determining the different host-guest interactions of the *para* isomer compared to the *meta* and *ortho* isomers (Figure 1.8).[66] MIL materials are of special relevance in this thesis since much of it focuses on a material which is closely related to the MIL series, Sc₂BDC₃.[67] Following a brief description of the experimental methods, the four experimental chapters in this thesis will aim to explain and further the understanding of the physical, mechanical and adsorption properties of Sc₂BDC₃, some of its derivatives, and related materials.

![Figure 1.7 - Structural transitions observed in Fe-MIL-53 upon increasing uptake of m-xylene. From top left to bottom right increasing equivalents of m-xylene cause the framework to undergo phase changes which increase its channel openings to accommodate more guest.](image)

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1.5 References


- Chapter 2 -

Materials and Methods
2.1 Synopsis

This chapter aims to provide a brief summary of the key experimental and theoretical methods used throughout this thesis, and precedes four research studies that form the experimental body. Non-ambient crystallographic methods have been central to the research undertaken herein, thus an outline of the experimental set-ups utilised is presented, including the gas cell on station I19 in the Diamond Light Source and diamond anvil cell technologies. This is followed by a brief discussion of the experimental methods used to obtain mechanical properties measurements, in particular bulk and elastic moduli.

2.2 Gas cell

Capillary gas cells are environmental cells that permit crystalline samples to be exposed to a gaseous environment. To date, gas cells have been available at a number of synchrotrons, in particular those which are dedicated to small molecule single-crystal diffraction, including ID15 at the ESRF in France and station 11.3.1 at the ALS in the United States. In the past few years, on station I19 in the Diamond Light Source in the UK, significant developments have been made to establish a state-of-the-art gas cell set-up.[1]

The gas cell equipment is located in the Experimental Hutch 2 (EH2), after a few years of prior development in EH1 (Figure 2.1). The experiments performed as part of this work (mainly Chapter 4), have been carried out in both enclosures and have been performed in close collaboration with the beamline scientists, thus forming an integral part of the testing and development of the set-up. The facilities in EH1 and EH2 differ slightly and thus the experimental protocol has evolved throughout the lifetime of this project. One of the main differences is the diffractometer, where EH1 has a Crystal Logic four-circle goniometer with kappa geometry and a Rigaku Saturn 724+ CCD detector, EH2 has a Newport four-circle kappa geometry goniometer with a Pilatus 300K detector.[1]
Chapter 2 – Materials and Methods

Figure 2.1 - Distribution of the I19 beamline layout, showing the two experimental hutches in which the single-crystal diffraction experiments are carried out. Picture from I19 website.

There are several types of gas-cell available including a quartz static (or flow) cell (Figure 2.2a and 2.2b), both of which are 5 mm in outer diameter and 22 mm in length, and are tested up to 80 bar of pressure. In addition there is a 1 mm sapphire cell which is 30 mm in length and has an inner diameter of 0.6 mm, which can be used to 200 bar (Figure 2.2c). Each can be attached to a goniometer head containing either a standard Mitegen® mount or a glass capillary to which single-crystals are glued in order to avoid sample movement on application of pressure. They are connected to the gas rig through flexible 1/16 inch PFA tubing (Cole-Parmer WZ-06407-41) for low pressures (< 25 bar) and stainless steel capillary tubing (Swagelok SS-T1-S-014-6ME) for higher pressures (> 25 bar). The static cells have a single fitting, whilst the flow cell has two.[2]

The gas control rig used to control the gases delivered into the cell allows users to operate the set-up remotely and permits studies remote changes and monitoring of pressure and temperature without having to enter the enclosure. A wide variety of gases are available including: Ar, CO₂, CO, H₂S, Kr, Ne, NO, N₂, N₂O, CH₄, O₂ and SO₂. Mixtures of any of these gases can also be used, and controlled remotely using the control rig.

The data collections are generally $\phi$-scans (either hemispheres or full spheres depending on symmetry) to minimise the possible tangling of the tubing coming off the cell. Data processing can be carried out using the Rigaku CrystalClear software or
CCP4 Xia2 with which the diffractometers in EH1 and EH2 respectively are controlled, however in all cases the frames were converted using ECLIPSE or CBF2SFRM to Bruker images to be processed with APEX 2 software.[3-5]

Figure 2.2 - Representation of the 5 mm quartz static cell (a), the 5 quartz mm flow cell (b) and the 1 mm sapphire capillary (c) with 5 or 1 mm glass capillaries containing Mitogen® mount and either one or two fittings respectively to the control rig (d). Figures taken from Warren et al.[2]
2.3 High-pressure crystallography

Diamond anvil cell (DAC) technology is a mature science with wide applications in fields such as geoscience, biology, condensed matter physics as well as materials science and chemistry. Particularly since the developments of the Merril-Bassett cell (Figure 2.3a), DACs have opened up the possibility of performing a variety of experiments on samples under conditions of extreme pressures (higher than 1 kbar, or 0.1 GPa).[6] These include spectroscopic measurements (Raman, IR, UV), magnetic measurements (SQUID) and of course X-ray diffraction experiments, both powder and single-crystal.

The modified Merril-Bassett DAC used for the experiments in this thesis, comprises two opposing diamond anvil which are each held in a tungsten carbide backing disc.[7] Between the two diamonds (which have a flat surface or culet ground onto them), a metal gasket (usually made of tungsten or steel) with a hole of 200-300 μm diameter is placed, creating a small cylindrical chamber in which the sample can be contained. The backing discs are held in position by two steel plates which have a conical hole at its centre (half-opening angle of usually 40°) to allow the sample to be viewed whilst under pressure, and of course to permit diffraction measurements to be made. The two steel plates are tightened together using three allen screws which force the two diamonds closer together.

The sample chamber usually contains a single crystal (or powder) surrounded by a small amount of pressure transmitting medium (PTM, Figure 2.3b), which is used to apply pressure hydrostatically to the sample when the two diamonds are brought together. The cell loading depends on the PTM of choice, which can either be a liquid, gas or even a soft solid. Liquid media are simply pipetted into the chamber, whilst gases can be loaded using more complex methodologies such as cryoloading or using a gas loader (see Chapter 6). Together with the sample a small ruby chip is placed inside the chamber since its characteristic fluorescence transition is dependent on pressure, thus making ruby fluorescence one of the most commonplace pressure calibration methods[8]
The high-pressure diffraction experiments described in this work were either carried out using a Bruker-Nonius APEX-II diffractometer with a CCD detector, or on station I19 using EH1 and a Crystal Logic four-circle goniometer and a Rigaku Saturn 724+ CCD detector. In both cases a modified data collection strategy is required to account for the shading of the body of the cell and optimise the data collection times. Based on the work by Dawson et al. a typical data collection is outlined in Table 2.1, where 8 runs of $0.3^\circ\omega$ scans are performed at different values of $\phi$ and $2\Theta$ to ensure the angle between the incident beam and the cell axis is less than 40$^\circ$ and less than 80% of the detector is shaded.[9]
Table 2.1 - Strategy for data collection in DAC designed by Dawson et al.[9]

<table>
<thead>
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<th>Run #</th>
<th>$\omega$ range (°)</th>
<th>$2\Theta$ (°)</th>
<th>$\phi$ (°)</th>
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<td>-28</td>
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<td>2</td>
<td>40 to -25</td>
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<td>3</td>
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<td>8</td>
<td>40 to -25</td>
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<td>270</td>
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</table>

Data obtained from high-pressure single-crystal diffraction requires a significant amount of data manipulation to process the data, compared to routine single-crystal diffraction experiments. Indexing of the unit cell requires for the harvested reflections to be ‘cleaned up’, as the images from the detector are contaminated with scattering from the diamond anvils, the ruby chip and the WC backing disks. In addition, dynamic masks are required so that areas of the detector which are shaded by the body of the pressure cell are not included during integration of the data. During data reduction, it is also important that poorly measured reflections (either due to partial shading from the cell, or overlap by strong diamond reflections) are deleted. These can be determined semi-automatically using the program SHADE, which will automatically highlight reflections with poor correlations that lie within a few degrees of the opening angle of the DAC body.[10]

When all of these aspects are taken into account, data quality obtained from high-pressure data nowadays can be of very good quality and, despite the lack of completeness obtained for low symmetry systems, the errors on the structural parameters are often comparable to data obtained under ambient conditions.
2.4 **Mechanical properties**

Beyond the atomistic structure, it is as important to analyse and understand the bulk properties of materials. To this avail, several techniques can be used to monitor properties such as stress or shear tension, or as will be covered in this work, hardness, elasticity and bulk compressibility.

**Nanoindentation**

In order to experimentally measure the uniaxial compressibility and the hardness of materials, nanoindentation measurements are required. The technique consists of pressing a tip made of a very hard material (usually diamond, and of a few hundred nanometres in diameter) onto a single-crystal of the material of interest, and one in which the crystalline faces have been pre-indexed, in order to evaluate the direction of compression directly with the crystal structure. By measuring the load placed on the tip against the displacement one obtains a load-displacement curve from which the mechanical properties of the material analysed can be extracted (Figure 2.4). These include primarily the hardness and elastic modulus, which can be calculated using, for example the Oliver and Parr method.[11]

![Figure 2.4 - Example of a load displacement curve. In this case S represents the stiffness of the sample being indented, $h_{max}$ is the maximum displacement, $h_{f}$ is the final depth and $P_{max}$ the maximum load. Modified from Oliver and Parr.[11]](image-url)


**Chapter 2 – Materials and Methods**

**Hardness**

The hardness \((H)\) of a material can be estimated from the following relationship:

\[
H = \frac{P_{\text{max}}}{A}
\]  
(2.1)

where \(P_{\text{max}}\) is the maximum load and \(A\) is the contact area. The contact area can be obtained by using an area function \(F(d)\) that describes the projected area of the indenter at a distance \(d\).\[11\] This can be done as the shape of the tip is accurately known (usually a Berkovich triangular pyramid), as well as its tensile strength. The value of \(H\) tends to be reported either for the whole experiment or as function of the indented depth.

**Elastic modulus**

Otherwise referred to as Young’s modulus, the elastic modulus provides a measure of the resistance of a material to deform elastically when a linear force is applied to it. The effective Young’s modulus \((E_{\text{eff}})\) is related to the slope of the curve upon unloading, which is the stiffness \((S)\) by:

\[
S = \beta \frac{2}{\sqrt{\pi}} \frac{E_{\text{eff}}}{A} \sqrt{A}
\]  
(2.2)

where \(\beta\) is a dimensionless constant (usually unity) and \(A\) is again the contact area at a given indentation depth. This accounts for the elastic modulus of both the indented material and the tip used for indentation. The elastic modulus of the material under examination \((E)\) can therefore be extracted by:

\[
\frac{1}{E_{\text{eff}}} = \frac{1}{E} + \frac{1 - v^2}{E_i}
\]  
(2.3)

where \(E_i\) and \(v\) are respectively the Young’s modulus and the Poisson’s ratio of the indenter tip and \(v\) is Poisson’s ratio of the material being examined. The Poisson’s ratio is the negative ratio of the transverse to axial strain.\[11\] For a higher value of \(E\) the material will be stiffer and less prone to compression.
Bulk modulus

Finally, the last physical property discussed will be the resistance of a material to uniform (or hydrostatic) compression, which is characterised by the bulk modulus \( K \) or \( B \). This can be measured by means of high-pressure X-ray diffraction and is defined as:

\[
K = -V \left( \frac{\delta P}{\delta V} \right)_T
\]  

(2.4)

where \( V \) = volume, \( P \) = pressure and \( T \) = temperature. It is possible to determine \( K \) by fitting and ideal equation of state (EoS) to the pressure-volume data. Several EoS exist, with Birch-Murnaghan (B-M) EoS being one of the most widely used.\[12\] B-M theory is based on a Taylor expansion, whereby adding increasing truncation order allows to model more complex behaviour. It is however the 2\textsuperscript{nd} or 3\textsuperscript{rd} order B-M EoS that are most commonly used when comparing bulk moduli with either one and three parameters being refined respectively to fit the pressure-volume data.
2.5 References


- Chapter 3 -

Mechanical Properties of Sc-based Metal-organic Frameworks
3.1 Synopsis

This first experimental chapter covers the synthesis and characterization of the physical properties of a series of Sc-based metal-organic frameworks (MOFs). Specialist techniques described in the previous chapter, together with standard experiments and computational models, are used to develop a full picture of the physio-mechanical behaviour of the Sc-MOF family.

3.2 Introduction

Besides the functional chemical properties that many MOFs are designed to incorporate, it is important to understand some of the more basic physical properties that these novel materials have. For successful implementation in industrial settings, MOFs must maintain their structural integrity when operating within a reasonable range of different physical conditions. This presents one of the challenges that many MOFs have faced, and it is not uncommon for many of them to degrade in mildly humid conditions, or to have lower thermal stabilities than other porous materials such as zeolites. MOF-5 and HKUST-1, two of the archetypical MOFs that were first synthesised, have a limited hydrothermal stability and only remain crystalline up to temperatures of 573 K and 513 K respectively.[1, 2]

This is perhaps unsurprising from a thermodynamic stand-point, as open-pore MOFs are not the lowest energy products of combining the metals and organic linkers they are made of. Synthetic parameters are carefully chosen to avoid thermodynamically more stable dense structures, and instead produce open frameworks through kinetic control.[3] The large porous cavities present in MOFs are not the most efficient use of space, this being one of the reasons these materials have relatively low thermodynamic barriers towards denser forms with higher entropies. Additionally, the coordination bonds that hold together linkers and metal nodes are considerably labile in mildly acidic conditions, with hydrolysis being a common decomposition pathway for MOFs.[4] However, it is possible to synthesise MOFs that bypass such challenges and are capable of sustaining harsher thermal and atmospheric conditions.[5]
Some of the more pressing aspects of MOFs that need to be understood in the context of industrial processes are their mechanical properties. In the course of bulk synthesis or when incorporating MOFs into membranes or columns for separation and storage applications, the materials experience a wide range of different conditions of stress and pressure that have to be controlled.

There are several measurements that can be made to assess the different mechanical properties of a material, and in Figure 3.1 some of the most common modes of mechanical loading usually considered can be found. Each provides different insights depending on the application of the target material, and some examples of the most relevant properties studied in MOFs include hydrostatic compression (relevant in gas sorption applications) or mechanical stiffness to assure the endurance of the MOF materials incorporated into films or membranes.[6] In the previous chapter, a more detailed description of the methods of measuring some of these properties can be found, including nanoindentation and high-pressure crystallography.

Figure 3.1 - Schematic representations of the common modes of mechanical compression: (a) uniaxial tension, (b) uniaxial compression, (c) torsion, (d) bending, (e) shear and (f) hydrostatic compression. Adapted from Tan et al.[6]
Mechanical properties of MOFs

To date, several studies on the mechanical stability of MOFs have been performed, and it has been possible to identify certain structure-property relationships in several MOF families. Zeolitic Imidazolate Frameworks (ZIFs), which combine the thermal and chemical stability of zeolites with the wide topological and functional range of MOFs, have been the subject of extensive study with respect to their mechanical properties. [7, 8] Significant correlations were observed between the elastic modulus ($E$) and solvent accessible volume (SAV)\(^3\), and, to a lesser extent, the physical density ($\rho$). In general, materials that are either denser or with smaller pore volumes have higher Young’s moduli and are thus more rigid. The effect of chemical functionalisation on their mechanical properties has also been investigated, though in general the family possesses moderately high $E$ values of 8-9 GPa for the densest ZIF-zni, but as low as 3.5 GPa for ZIF-8. [8] These are however, slightly higher than those measured for MOF-5 and the zeolitic analogues ZMOFs. [9, 10]

Consideration of the hydrostatic compression of ZIFs using high-pressure crystallography has yielded bulk moduli of 14 GPa for ZIF-zni and 6.5 GPa for ZIF-8, about on order of magnitude lower than nanoporous zeolites. [6, 11, 12] These and related studies have also highlighted some unusual phenomena such as the tendency to amorphise and consequently loose porosity upon compression with non-penetrating pressure transmitting media (PTMs), or indeed the ‘hyperfilling’ of the porous frameworks when using PTMs small enough to fit inside the channels of the MOF, as discussed in the previous chapter.[13, 14]

In contrast, Zr-based UiO-66 and MIL-140 type frameworks exhibit relatively high mechanical stabilities, owing to strong bonds between the carboxylate linkers and the Zr\(^{4+}\) centres. [15, 16] The importance of the strength of coordination bonds in their mechanical stability has been highlighted by the delay in amorphisation rate by ball-

\[^3\text{Solvent accessible volume is a measure of the accessible pore volume of the framework. It is calculated as the sum of all void space large enough to accommodate a H- atom (1.2 Å).}\]
milling, which was achieved by introducing monodentate acidic modulators that increased the Zr–O bond strength.[17] Ongoing work on the UiO-67 and analogues indicate these superior mechanical properties are also reflected in the values obtained for both Young’s and bulk modulus.[18]

Other MIL materials, like the MIL-53 series, have also shown remarkable physical properties. Different MIL-53 analogues (Cr, Fe, Ga, In and Sc) show good thermal stability, though the Al variant maintains one of the highest decomposition temperatures of the MIL-53 series at 773 K.[19-24] When incorporated into a membrane structure the framework was measured to have a Young’s modulus in between 60.9 GPa and 94.7 GPa (depending on the direction of indentation), which corresponds to a remarkable mechanical strength for a MOF structure.[25]

Structural anisotropy, as present in the MIL-53 series, requires more careful consideration than in cubic frameworks like the MOF-5, ZIFs and UiO examples. Having lower symmetry structures in many occasions leads to more complex crystal habits, and thus compressibility along different directions can vary significantly. This is in fact one of the challenges of nanoindentation studies, especially when dealing with small crystals where access to the different faces of the crystals is more difficult.[9] An approach to circumvent this, is to study these systems using computational models, using first-principle calculations to simulate the elastic constants along different crystallographic directions.[26] In some cases, particularly in ‘wine-rack’ MOFs such as the MIL-53 series, Negative Linear Compressibility (NLC) has been found to be a common occurrence, a rare phenomenon in inorganic crystals, but relatively recurrent in MOF chemistry.[27, 28] The mechanical properties and NLC behaviour of ‘wine-rack’ MOFs has been studied extensively using computational approaches, and has also been observed experimentally under different external stimuli, including on application of hydrostatic pressure or upon guest uptake. [27, 29, 30]
Sc-based MOFs

A modification of synthesis conditions of MIL-53(Sc), where the terephthalate linker to metal ratio is increased to 3:2, yields the Sc₂BDC₃ framework (Sc₂(O₂CC₆H₄CO₂)₃).[31] The incorporation of an additional BDC linker, connects opposing Sc atoms in the vertices of the rhomboidal channels of MIL-53(Sc), effectively bisecting the channels into two (see Figure 3.2a). With a denser structure and fully coordinated metal centres, Sc₂BDC₃ has an increased decomposition temperature than MIL-53(Sc) – 703 K for MIL-53(Sc) compared to 773 K in Sc₂BDC₃.[32] Sc₂BDC₃ has orthorhombic Fddd symmetry with two different types of symmetry independent BDC linkers (Group 1 and Group 2), which are arranged to form triangular channels along the a-axis measuring less than 4 Å across.

Sc₂BDC₃ has shown promising adsorption properties, including significant CO₂ uptake (6.5 mmol g⁻¹), as well as room temperature selectivity of CO₂ over other fuel related gases such as CH₄ or C₂H₆.[33] Furthermore, the functionalisation of Sc₂BDC₃ to yield amino-, nitro- or bromo-derivatives and the effect this has on its adsorption properties has also been investigated.[34] In particular, the isostructural amino-derivative, Sc₂(BDC-NH₂)₃ (Sc₂(O₂CC₆H₄NH₂CO₂)₃), has shown the most promising selective properties, which are discussed further in the following chapter. For this reason, a more complete understanding of the mechanical properties of Sc₂BDC₃ and Sc₂(BDC-NH₂)₃ would be of use before their application in separation technologies.

Additionally, using the isomeric isophthalate linkers (1,3-benzene dicarboxylate or IA) instead of the terephthalate linkers (1,4-benzene dicarboxylate or BDC), two new Sc-based framework materials can be formed: Sc(IA)-1 (Sc(μ-O)(OH)(O₂CC₆H₄CO₂) and Sc(IA)-2 (Sc(O₂CC₆H₄CO₂)₃). Using 5-aminoisophthalate as a linker (5-amino-1,3-benzenedicarboxylate) it is also possible to form a functionalised analogue, Sc(IA-

---

4 The terephthalate linker is commonly referred to in the literature as BDC (1,4-benzene dicarboxylate), and will be referred to as such throughout. The isomeric isophthalate linker (1,3-benzene dicarboxylate) will be referred to as IA (isophthalate).
NH₂) (Sc₂(O₂CC₆H₄NH₂CO₂)₃), which is structurally related to Sc(IA)-2 having identical connectivity.

Nothing is known about the structural and adsorption properties of these three structures. To compare the physical properties of all of the Sc-based MOFs, and to study the consequences of amino-functionalisation on the mechanical properties, the crystal structures of Sc(IA)-1, Sc(IA-2) and Sc(IA-NH₂) have been determined. The elasticity and bulk compressibility of Sc₂BDC₃, Sc₂(BDC-NH₂)₃, Sc(IA)-1, Sc(IA-2) and Sc(IA-NH₂) have also been analysed by nanoindentation and high-pressure single crystal X-ray diffraction.
Comparison of the structures of Sc$_2$BDC$_3$ (a) and Sc$_2$(BDC-NH$_2$)$_3$ (b), as viewed along the a-axis of their orthorhombic Fddd unit cell. The two symmetry independent linkers are labelled 1 and 2 for Group 1 and Group 2 respectively. Green octahedra represent ScO$_6$ coordination sphere, C-atoms are coloured in grey, blue for N-atoms and light grey for H-atoms.

Figure 3.2 - Comparison of the structures of Sc$_2$BDC$_3$ (a) and Sc$_2$(BDC-NH$_2$)$_3$ (b), as viewed along the a-axis of their orthorhombic Fddd unit cell. The two symmetry independent linkers are labelled 1 and 2 for Group 1 and Group 2 respectively. Green octahedra represent ScO$_6$ coordination sphere, C-atoms are coloured in grey, blue for N-atoms and light grey for H-atoms.
3.3 Experimental

Note: the synthesis of materials was carried out by Dr. John Mowat, Berenice Gonzalez and Dr. Alex Greenaway from the University of St. Andrews.

Synthesis

Sc:BDC₃: scandium nitrate (Sc(NO₃)₃:3H₂O, 99.9%, 0.269 mmol, 0.0768 g, Metall Rare Earth Limited) and terephthalic acid (1,4-benzenedicarboxylic acid, 98%, 0.539 mmol, 0.0895 g, Aldrich) in diethylformamide, (DEF, Alfa Aesar, 98% 6 mL) were transferred into a Teflon-lined steel autoclave and heated at 463 K for 72 h. Resulting solid was washed with ethanol and dried at 333 K for 12 h.

Sc(BDC-NH₂): scandium oxide (Sc₂O₃, 99.9%, 0.310 mmol, 0.126 g, Stanford Chemical Compounds) and 2-aminoterephthalic acid (2-amino-1,4-benzenedicarboxylic acid, 99%, 0.465 mmol, 0.0841 g, Aldrich) in H₂O (6 mL) were transferred into a Teflon-lined steel autoclave and heated at 463 K for 72 h. Resulting solid was washed with ethanol and dried at 333 K for 12 h.

Sc(IA)-1: scandium chloride (ScCl₃, 1.45 M aqueous solution, 1.16 mmol, 0.8 mL) and isophthalic acid (1,3-benzenedicarbocyclic acid, 1.20 mmol, 0.19 g, Aldrich) in DMF:H₂O (1:20, 0.77:3.6 mL) were transferred into a Teflon-lined steel autoclave and heated at 403 K for 12 h. After heating the autoclave was cooled and the mixture filtered. The resulting solid yielded colourless cube-shape crystals, the product was washed with water and dried at 333 K for 12 h.

Sc(IA)-2: scandium oxide (Sc₂O₃, 99.9%, 0.32 mmol, 0.132 g, Stanford Chemical Compounds) and isophthalic acid (1,3-benzenedicarbocyclic acid, 0.65 mmol, 0.10 g) in H₂O (3mL) were transferred into a Teflon-lined steel autoclave and heated at 493 K for 48h. The resulting solid was washed with water and dried at 333 K for 12 h.

Sc(IA-NH₂): scandium chloride (ScCl₃, 1.45 M aqueous solution, 0.65 mmol, 0.45 mL) and 5-aminoisophthalic acid (5-amino-1,3-benzenedicarbocyclic acid, 1.26 mmol) in H₂O (4 mL) were transferred into a Teflon-lined steel autoclave and heated at 433 K for 12 h. After heating, the autoclave was cooled and the mixture filtered. The
synthesis yielded red cubic crystals which were washed with water and dried at 333 K for 12 h.

**Nanoindentation**

Nanoindentation measurements of Sc$_2$BDC$_3$, Sc$_2$(BDC-NH$_2$)$_3$, Sc(IA)-1 and Sc(IA-NH$_2$) were performed using a MTS Nanoindenter XP and data analysed following the method described in the previous chapter. Unfortunately, single-crystals of Sc(IA)-2 were too small (< 30 μm) to carry out the nanoindentation experiments. Indentations were conducted under the dynamic displacement-controlled “continuous stiffness measurement” mode. $E$ and $H$ mechanical properties were subsequently determined as a function of the surface penetration depth. A 2-nm sinusoidal displacement at 45 Hz was superimposed onto the system’s primary loading signal, and the loading and unloading strain rates were set at $5 \times 10^{-2}$ s$^{-1}$. All tests were performed to a maximum indentation depth of 500 nm using a Berkovich (i.e., three-sided pyramidal) diamond tip of radius *ca.* 100 nm. A Poisson’s ratio of 0.2 was used, in accordance with prior nanoindentation studies on ZIFs. The raw data (load-displacement curves) obtained were analysed using the Oliver and Pharr method.[35] Data from depths under 100 nm were not included because of tip-surface contact variance.

**Face-indexing**

Face-indexing measurements used to determine the crystal faces being indented were performed at room temperature, using an Oxford Diffraction SuperNova X-ray diffractometer, with Cu Kα radiation ($\lambda = 1.540598$ Å) and equipped with an Atlas CCD detector. Data were collected in $\omega$-scans in four settings of $2\theta$ and $\varphi$ with a step size of 1°. Exposure times were 30 s at low angle and 90 s at high-angle. Data processing, unit cell determination and face indexing were carried out using the program CrysAlisPro. Figure 3.3 contains the main crystallographic parameters and different views of the indexed crystals.
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Table

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Unit cell dimensions</th>
<th>Volume</th>
<th>Crystal size</th>
<th>Main crystal faces</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Sc}_2 \text{BDC} )</td>
<td>Orthorhombic</td>
<td>( \text{Fddd} )</td>
<td>( a = 8.756(3) , \text{Å} )</td>
<td>( V = 6250.1(3) , \text{Å}^3 )</td>
<td>0.058 x 0.067 x 0.160 mm</td>
<td>( (1 , 1 , 1 , 3) , (1 , -1 , 1 , 3) , (1 , 1 , -1 , 3) , (-1 , 1 , 1 , 3) )</td>
</tr>
<tr>
<td>( \text{Sc}_2 \text{BDC-NH}_2 )</td>
<td>Orthorhombic</td>
<td>( \text{Fddd} )</td>
<td>( a = 8.720(4) , \text{Å} )</td>
<td>( V = 6247(4) , \text{Å}^3 )</td>
<td>0.039 x 0.050 x 0.134 mm</td>
<td>( (0 , 0 , 1) , (0 , 0 , 1) , (0 , 1 , 1) , (0 , 1 , 1) )</td>
</tr>
<tr>
<td>( \text{Sc} ) (IA)-1</td>
<td>Cubic</td>
<td>( \text{Pn} )</td>
<td>( a = 19.478(4) , \text{Å} )</td>
<td>( V = 7390.2(6) , \text{Å}^3 )</td>
<td>0.089 x 0.090 x 0.091 mm</td>
<td>( (1 , 0 , 0) , (0 , 1 , 0) , (-1 , 0 , 0) )</td>
</tr>
<tr>
<td>( \text{Sc} ) (IA-NH)_2</td>
<td>Cubic</td>
<td>( \text{F} )</td>
<td>( a = 13.876(2) , \text{Å} )</td>
<td>( V = 2671.8(3) , \text{Å}^3 )</td>
<td>0.068 x 0.074 x 0.099 mm</td>
<td>( (1 , 1 , 0) , (1 , 0 , 1) , (0 , 1 , 1) , (1 , 0 , 1) )</td>
</tr>
</tbody>
</table>

Figure 3.3 - Summary for the face-indexing statistics for the four crystals examined using nanoindentation. From bottom to top: \( \text{Sc}_2 \text{BDC-NH}_2 \), \( \text{Sc} \) (IA)-1, \( \text{Sc} \) (IA)-2 and \( \text{Sc} \) (IA-NH)_2.
High-pressure crystallography

High-pressure single-crystal diffraction experiments on Sc$_2$(BDC-NH$_2$)$_3$, Sc(IA)-1, Sc(IA)-2 and Sc(IA-NH$_2$) were performed using the diamond anvil cell (DAC) methodology covered in the previous chapter. Using FC-77 (a mixture of perfluorooctane (C$_8$F$_{18}$) and perfluoroxyclononane (C$_8$F$_{16}$O) as the PTM, data collections were performed on station I19 at Diamond Light Source, using radiation of wavelength of 0.48590 Å on a four-circle Crystal Logic diffractometer equipped with a Rigaku Saturn 724+ CCD detector. Data were collected using the strategy described in the previous chapter for data collections on I19. Unit cell indexing and data processing were carried out using the Bruker APEX II suite, with the Rigaku frames obtained on I19 being converted to Bruker compatible frames using the program ECLIPSE.[36] Integration was carried out using SAINT, with dynamic masks generated using ECLIPSE. The absorption correction was carried both with SHADE (to account for shading by the DAC) and SADABS.[37, 38]

Structure solution and space group determination were carried our using SHELXT and SHELXL was used for structure refinement within Olex2.[39-41]. Hydrogen atoms on the framework were placed geometrically and 1,2 and 1,3 thermal restraints were applied on the disordered parts of the structure. The SQUEEZE routine within PLATON was used to account for any residual electron density in the pores.[42] For the higher-pressure datasets, which suffered from significant resolution loss, no structural information was obtained and only the unit cell parameters were recorded.
3.4 Results and discussion

Structural characterisation of Sc-isophthalate MOFs

Similarly to the MIL-53 series, in Sc(IA)-1 there is a single isophthalate linker for every Sc-centre, but in addition to having a water molecule to complete the octahedral coordination sphere of Sc, groups of three ScO₆ octahedra are connected by a μ₃-O atom (Figure 3.4). This leaves each isophthalate linker connecting two pairs of Sc-centres.

With cubic $Pd\overline{3}$ symmetry, Sc(IA)-1 has a very similar density to Sc$_2$BDC$_3$ (1.243 vs 1.238 g cm$^{-3}$ for Sc(IA)-1 and Sc$_2$BDC$_3$ respectively), and a similar porosity (48.9% compared to 48.4% of Sc$_2$BDC$_3$). However, due to the different framework topology, Sc(IA)-1 has reduced SAV (29.9%) than Sc$_2$BDC$_3$ (35.2%). In fact, unlike Sc$_2$BDC$_3$, the pore structure of Sc(IA)-1 is not interconnected by channels, leading to isolated voids that have a distorted trigonal-bipyramidal shape (see Figure 3.5). Some of these voids lie in the centre of the unit cell connecting opposing vertices, whilst others are arranged around the 3-fold rotation axis (see Figure 3.6). The crystal analysed had the cavities filled with solvent molecules, which were modelled as disordered water molecules, however the presence of residual dimethylformamide (DMF) from the synthesis could not be discarded.

It is also worth noting that the isophthalate linkers appeared disordered over two positions, which occurs through the libration around the axis made by the C-atoms in the 1 and 3 positions of the phenyl ring (Figure 3.4).

---

5 Porosity is defined as the percentage volume of the unit cell that is unoccupied by the van der Waals volumes of the atoms in it, and tends to be slightly higher value than the SAV. Both porosity and SAV have been calculated using the VOID routine in the PLATON software.
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Figure 3.4 - Main connectivity present in Sc(IA)-1 showing how groups of three ScO$_6$ octahedra (green) are connected by a $\mu_3$-O (red) and how these are in turn connected through the isophthalate linkers (grey - C-atoms, light grey - H-atoms) with other groups of ScO$_6$ octahedra. The two disordered components of the linker are also highlighted and broken off bonds indicate additional isophthalate linkers connected to the ScO$_6$ octahedra.

Figure 3.5 - Representation of the trigonal-bipyramidal-shaped voids of the Sc(IA)-1 showing how the central void extends across the cubic unit cell of the connecting opposing vertices. Dashed yellow lines represent the outline of the pore and the disordered components of the isophthalate linker have been removed for clarity. Green octahedra represent ScO$_6$ coordination sphere, C-atoms are coloured in grey, blue for N-atoms and light grey for H-atoms.
Figure 3.6 - View along the (1 1 1) showing how the pores are placed compared to each other. The central void is represented by the dashed yellow lines, and the dashed blue lines outline one half of each of the six equivalent pores that are closest to the central pore. Isophthalate linkers have been removed for clarity, green octahedra represent ScO$_6$ coordination sphere (O-atoms in red).
Tuning the synthetic conditions by performing the reaction in water and increasing the metal to linker molar ratio to 1:2 leads to the formation of Sc(IA)-2. The structure of this material is also cubic but has \( P2_13 \) symmetry and has a completely different porous structure to Sc(IA)-1. Sc(IA)-2 is of particular relevance due to having a significant resemblance to the framework obtained when 5-aminoisophthalatic acid is used as a linker instead. The amino substituted Sc(IA-NH₂), which is also cubic and with \( I2_13 \) symmetry, is slightly distorted with respect to Sc(IA)-2, however the two structures share a general topology that leads to a similar porous architecture.

Both Sc(IA)-2 and Sc(IA-NH₂) are formed using a 1:1.5 metal to linker ratio, like Sc₂BDC₃ and Sc₂(BDC-NH₂). This results in each isophthalate linker bonding four different Sc atoms, whilst each Sc is in turn connected to six isophthalate linkers. This leads to much denser materials (1.601 g cm\(^{-3}\) for Sc(IA)-2 and 1.562 g cm\(^{-3}\) for Sc(IA-NH₂), excluding solvent) with the connectivity producing a complex porous framework. Both MOFs have small cavities which are not interconnected by channels, creating small isolated voids (Figure 3.7). In the case of Sc(IA)-2 these cavities were empty, whilst in Sc(IA-NH₂) they contained a single water molecule which forms hydrogen bonds with the amino group on the linker that point into the cavity.

Without taking into account the water molecules, it is possible to compare the porosities of both frameworks and show how the functionalisation reduces the size of the pores. Sc(IA)-2 has a SAV of 15 \% and a porosity of 33 \%, whilst Sc(IA-NH₂) has a SAV of only 10.1 \% with a porosity of 34.6 \%. Despite the voids in Sc(IA)-2 being larger than those in Sc(IA-NH₂), the reduced porosity makes Sc(IA)-2 slightly denser than its functionalised derivative, with a density of 1.60 and 1.56 g cm\(^{-3}\) for Sc(IA)-2 and Sc(IA-NH₂) respectively.
Figure 3.7 - View along the a-axis of Sc(IA)-2 (a) and Sc(IA-NH₂) (b). Orange and yellow spheres represent the voids in the framework structures. Green octahedra represent ScO₆ units, C-atoms are coloured in grey, blue for N-atoms and light grey for H-atoms.
Uniaxial compressibility

As seen in Figure 3.3, single-crystals of the different Sc-based MOFs have different crystals habits. This could be expected in species with significantly different structures, but in the case of ScBDC₃ and Sc( BDC-NH₂)₃, where they both crystallise in Fddd and are isostructural, it is worth considering more carefully.

Figure 3.8 - Comparison of the BFDH calculated morphologies and the different crystal faces of (a) Sc₂BDC₃ and (b) Sc₂(BDC-NH₂)₃ as obtained using the CCDC Mercury® software. Red arrow depicts the direction of indentation, highlighting the crystal face on which the load is applied.

As highlighted in more detail in Figure 3.8, the crystal morphology of both analogues are very different. The rhomboidal shaped crystals of Sc₂BDC₃ have only one of type of face (1 1 3), whilst the blocks of Sc₂(BDC-NH₂)₃ have more facets, with the main ones being the (0 0 1) and (0 1 1). The consequences of this is that difference parts of the structure are exposed on the faces, and when exerting pressures on the crystals, the stress will be distributed differently within each framework. In the case of Sc(IA)-
1 and Sc(IA-NH₂), this effect is not as significant since the isotropic habit of both materials only allows for a single face to be indented, the (1 0 0) for Sc(IA)-1 and the (1 1 0) for Sc-(IA-NH₂).

The load displacement curves obtained from the nanoindentation studies are detailed in Figure 3.9, and show how the different materials behave under uniaxial compression. The $E$ and $H$ values calculated from these experiments on both Sc₂BDC₃ and Sc₂(BDC-NH₂)₃ are plotted in Figures 3.10a and 3.10b, together with the values obtained for the isophthalate frameworks Sc(IA)-2 and Sc(IA-NH₂).

The hardness of the Sc-based frameworks is largely higher than those reported for ZIFs and ZMOFs using a similar set up.[8, 9] Values for $H$ are highest for the amino substituted frameworks with 1.43 and 1.15 GPa for Sc(IA-NH₂) and Sc₂(BDC-NH₂)₃ respectively. The unfunctionalised frameworks Sc(IA)-1 and Sc₂BDC₃ have hardness of 0.99 and 0.76 GPa, just under the value reported for the strongest ZIF, the dense ZIF-zni framework with a $H$ of 1.1 GPa.

The calculated elastic constants $E$, are also higher than those previously reported for other MOFs, where again Sc(IA-NH₂) and Sc₂(BDC-NH₂)₃ have the highest values at
14.98 and 11.24 GPa, whilst the unfunctionalised derivatives are 10.32 and 9.8 GPa for Sc-(IA)-1 and Sc:BDC3 respectively.

In order to rationalise these observations, it is possible to identify particular structural traits of the frameworks analysed, and correlate them with $E$ and $H$. To put them in context with other MOFs on which mechanical properties have been measured, in Figure 3.11 $E$ and $H$ values for different frameworks are plotted against properties such as $SAV$, $\rho$ and porosity ($P$). Sc-based frameworks are generally denser and less porous than the zeolitic type MOFs, thus it is expected for them to be harder and stiffer if they were to follow previous trends, which is largely what is observed.
Comparison of the $E$ and $H$ values for different MOFs in correlation with solvent area volume ($SAV$), porosity ($P$) and physical density ($\rho$). The materials are grouped into their respective families by the different coloured ovals.

However, the relationships of both $E$ and $H$ with the various physical parameters do not exactly follow those obtained for ZIFs and ZMOFs. With the exception perhaps of $H$ vs $P$ and $H$ vs $SAV$, Sc-MOFs seem to behave slightly differently to previously reported frameworks. The results also confirm that correlation between $\rho$ and mechanical properties is not very strong, whilst $P$ and – more significantly – $SAV$ have stronger correlations with $H$ and $E$. 

Figure 3.11 - Comparison of the $E$ and $H$ values for different MOFs in correlation with solvent area volume ($SAV$), porosity ($P$) and physical density ($\rho$). The materials are grouped into their respective families by the different coloured ovals.
It is worth pointing out that within the Sc-based MOFs there is a significant $E$ vs $SAV$ correlation (over 90%), which is also seen in the case of ZIFs and less significantly in UiOs. This indicates that although certain trends can be found in the mechanical properties within families, it seems to be the framework chemistry which mostly determines absolute values.

Another observation that can be made is the effect different ligands have on the mechanical properties. In the case of functionalisation, the amino derivatives had both higher values of $E$ and $H$ than the respective unfunctionalised materials. Yet, a direct comparison between Sc-(IA)-2 and Sc(IA-NH$_2$) would provide an even better indication of the effect of introducing –NH$_2$ groups into MOFs.

Considering the difference between terephthalate and isophthalate linkers, it can be concluded that the latter yield more robust frameworks, even though the amino-functionalisation of the terephthalate linkers makes Sc(IA-NH$_2$) a stronger framework than the Sc(IA)-1 in terms of uniaxial compressibility.

**Bulk compressibility**

Previous work on Sc$_2$BDC$_3$ and its nitro-derivative Sc$_2$(BDC-NO$_2$)$_3$ highlighted the marked influence of functionalisation and the choice of PTM on hydrostatic compressibility.[43] Whilst non-penetrating media such as FC-77 caused the direct reversible amorphisation of Sc$_2$BDC$_3$ above 0.1 GPa, in the case of Sc$_2$(BDC-NO$_2$)$_3$ the framework underwent a displacive phase change from $C2/c$ to $Fdd2$ and remained crystalline up to 2.5 GPa. On the other hand, when using methanol as the PTM neither amorphisation nor a phase change occurred. Instead the MOFs were filled with increasing amounts of methanol molecules, which stabilised the frameworks up to pressures of 3 GPa.

The stabilisation brought about by the use of a penetrating PTM has been observed in other MOFs such as ZIF-8 or MOF-5, sometimes referred to as ‘super-filling’, ‘super-solvation’ or ‘super hydration’ in zeolites.[44] However this was the first instance in which functionalisation had been used to reduce the bulk compressibility.
of the single-crystal of a MOF. [14, 45] To explore if this effect translated to the amino-functionalised Sc(BDC-NH₂)₃ and how it compared with Sc-isophthalate MOFs, high-pressure single-crystal experiments using FC-77 as PTM were carried out on Sc(BDC-NH₂)₃, Sc(IA)-1, Sc(IA)-2 and Sc(IA-NH₂).

In order to obtain the bulk modulus for the different systems, it is necessary to monitor the change in cell volume with applied pressure. Figure 3.12 shows the unit cell compressibility of the four systems considered together with Sc:BDC₃ and Sc(BDC-NO₂)₃.

![Figure 3.12 - Comparison of the percentage change of unit cell volume upon compression in FC-77 for different Sc-based MOFs. Inset focuses on the lower pressure regime, where most terephthalate frameworks collapse and undergo a reversible amorphisation. Error bars are smaller than the symbols.](image-url)
Similarly to Sc\textsubscript{2}BDC\textsubscript{3}, the isostructural Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3} undergoes reversible amorphisation at low pressures. However, the fact that this occurs above 0.4 GPa instead of at 0.1 GPa indicates that the functionalisation makes Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3} slightly more resilient than Sc\textsubscript{2}BDC\textsubscript{3}.

In the case of the isophthalate containing frameworks, the results indicate that they maintain their crystallinity up to much higher pressures, before undergoing a similar amorphisation process. Comparison of the isostructural Sc(IA)-2 and Sc(IA-NH\textsubscript{2}), also reveals that the amino-functionalisation seems to delay the amorphisation significantly, with Sc(IA)-2 remaining crystalline until 1.7 GPa whilst Sc(IA)-NH\textsubscript{2} remains crystalline to nearly 4 GPa.

A more detailed analysis of the hydrostatic compressibility of a material can be obtained by calculating the isothermal equation of state (EoS). This is characterised by the bulk modulus of the material (K), as discussed in the previous chapter. Using a 2\textsuperscript{nd} and 3\textsuperscript{rd} order Birch-Murnaghan equation of states (B-M) depending on the number of data points collected, bulk moduli for all four systems were determined (Figure 3.13). Care must be taken when fitting K due to small number of data points, however meaningful information can still be extracted from them.

In the case of Sc\textsubscript{2}BDC\textsubscript{3} and Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3} bulk moduli were calculated from 2 and 3 data points respectively, since they undergo reversible amorphisation at low pressures. For these systems only a 2\textsuperscript{nd} order B-M was used to calculate K, with the values obtained for both frameworks being very similar; 17.3 ± 1.8 GPa for Sc\textsubscript{2}BDC\textsubscript{3} and 18.5 ± 1.1 GPa for Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3}. This suggests that the similar structure of both MOFs dictates the similarities in bulk compressibility, with functionalisation resulting in a marginal improvement in resistance to compression. However more data points would be required to support this conclusion.

On the other hand, the isophthalate-based frameworks appear to be much more compressible, with bulk moduli (calculated using 3\textsuperscript{rd} order B-M) of 10.8 ± 0.5 GPa for Sc(IA)-1, 8.3 ± 0.2 GPa for Sc(IA)-2 and 11.9 ± 0.4 GPa Sc\textsubscript{2}(IANH\textsubscript{2}). The increase in
available data points for these materials allows for more accurate and more precise estimations of $K$, and helps differentiate between the isostructural Sc(IA)-2 and the Sc(IA-NH$_2$). It appears that the amino-functionalisation leads to a slightly less compressible framework, an effect which can also be associated to the additional water molecule present in the pores of Sc(IA-NH$_2$) but not in those of Sc(IA)-2. Sc(IA)-1 is also slightly less compressible than Sc(IA)-2, however it is harder to draw direct relationships between both materials due to large differences in their structures and the difference in pore content.

Figure 3.13 - Unit cell volumes and the respective 2nd (dark green) and 3rd (light green) order Birch-Murnaghan EoS for Sc$_2$(BDC-NH$_2$)$_3$, Sc(IA)-1, Sc(IA)-2 and Sc(IA-NH$_2$). Note that for Sc$_2$(BDC-NH$_2$)$_3$ the scale is considerably smaller and in the case Sc(IA-NH$_2$) a third 2nd order EoS has been added to fit the higher pressure point at which a phase change takes place. Error bars are smaller than the symbols.
With the exception of Sc(IA-NH2), the samples did not diffract beyond 1.5 Å, and hence extracting good quality structural data was not possible. It is also worth noting, that at higher pressures, Sc(IA-NH2) underwent a phase transition. This resulted in no change in symmetry but did lead to significant loss in diffraction quality and a clear change in the compressibility. This may also occur in Sc(IA)-2, however due to the smaller crystal size, the data quality was already compromised at low pressures, and above 2 GPa only very low resolution data could be collected.

Overall, the more porous ScBDC3 and Sc(BDC-NH2)3 have comparable bulk compressibilities to the densest ZIFs, and although they are less compressible than the isophthalate derivatives, when using a non-penetrating PTM they amorphise more readily. Sc(IA)-1, Sc(IA)-2 and Sc(IA-NH2) are more easily compressed and undergo a reduction in volume of ~ 10 %, remaining crystalline to much higher pressures. There is also an indication that the amino-functionalisation of the dicarboxylic linkers tends to yield slightly harder materials, which are in general more stable under direct hydrostatic compression.
3.5 Conclusions

To summarise, the structural characterisation of three new Sc-based MOFs has been carried out. The isophthalate linkers used as struts to connect the different Sc-nodes yield markedly different structures, which have a reduced porosity when compared to the Sc-based terephthalate MOFs. Consequently some differences in the mechanical properties between the two sets of frameworks have also been observed.

Isophthalate-based MOFs have a greater resilience to direct hydrostatic compression, contrasting with the tendency of ScBDC$_3$ and Sc(BDC-NH$_2$)$_3$ to amorphise at relatively moderate pressures. Amino-functionalisation of the frameworks seems to lead to a reduced compressibility when compared to the unfunctionalised isostructural frameworks, although further investigation is required in this respect.

In terms of uniaxial compressibility, the isophthalate frameworks tend to be harder and less elastic than the terephthalate-based MOFs, and again amino-functionalisation exacerbates both these features. It is also possible to confirm trends between certain structural features, such as porosity and $SAV$, with the elastic modulus within families of MOFs, but framework chemistry appears to dominate the absolute values. Structural anisotropy should also be considered further, perhaps by computational simulations, particularly for both ScBDC$_3$ and Sc(BDC-NH$_2$)$_3$.

Overall, the Sc-based frameworks considered show promising mechanical properties when compared to other MOFs, providing added value in their potential industrial applications.
3.6 References

Chapter 3 – Mechanical Properties of Sc-based Metal-organic Frameworks


Chapter 4 – Structural Studies of Gas Uptake in Sc₂BDC₃ and Sc₂(BDC-NH₂)₃

- Chapter 4 -

Structural Studies of Gas Uptake in
Sc₂BDC₃ and Sc₂(BDC-NH₂)₃
4.1 Synoptic

Following the analysis of the mechanical properties of Sc-based MOFs, this chapter covers the study of one of their main functional applications, gas adsorption. In particular, this work focuses on the effect functionalisation has on the CO₂ selective uptake properties of MOFs. Using the gas cell set-up on station I19 at the Diamond light source, an in situ structural study of the uptake of CO₂, CH₄ and different mixtures of both gases in Sc₂BDC₃ and Sc₂(BDC-NH₂)₃ has been carried out. This, together with some complementary computational experiments, provides a detailed analysis of the selective behaviour of both MOFs.

4.2 Introduction

The study of microporous metal-organic frameworks (MOFs) has attracted considerable interest due to their applications in a wide variety of different fields such as catalysis, sensing, drug delivery or biomimicry.[1-4] However, their use as new generation adsorbents has probably received the greatest attention, and has therefore been the subject of many research efforts.[5-7] The experimental methods used to investigate uptake in traditional adsorbents like zeolites, activated carbons or mesoporous silicas, include gravimetric or volumetric adsorption measurements, which are still an important avenue for determining the capacities of MOFs at different pressures and temperatures.[8] However, their inherent crystalline nature also provides a host of structural techniques that can give detailed insight into the different adsorption mechanisms in place in MOFs.

The possibility of modifying their structures by changing the building blocks that constitute them, leads to a wide range of functional properties that can be used to tune the properties of MOFs. Additionally, the flexible nature of many of them can result in significant structural changes upon uptake of different guests, directly influencing their adsorption behaviour.[9] Understanding and quantifying these effects, and the guest-host interactions that drive their adsorption properties, is where a detailed structural analysis (in combination with conventional adsorption
measurements) is necessary to gain a complete picture. Thus the use of *in situ* structural techniques is becoming more commonplace in the study of MOFs.

*In situ* Raman and IR spectroscopy, inelastic neutron scattering or solid-state NMR can all be used to infer the adsorption processes in MOFs.[10-12] However, diffraction techniques that provide atomic resolution information remain instrumental in the characterisation of these systems. The improvements in the last decade of gas cell set ups - both for in-house and central facilities - have made *in situ* crystallographic adsorption studies in MOFs more available.[13] Using both neutron and X-ray radiation for both powder and single-crystal diffraction, many systems have been investigated in the last decade. With knowledge of the adsorption sites and any phase changes induced in the framework, it has been possible to directly measure and predict adsorption capacities, as well as obtaining invaluable starting models for computational studies that can help quantify the energetics of adsorption processes.[14]

On station I19 at the Diamond Light Source, a new gas cell has been recently developed. As described in Chapter 2, this experimental set-up allows single-crystal diffraction experiments under different gaseous atmospheres up to pressures of hundreds of bars to be carried out. Furthermore, it has the capability of performing experiments using gas mixtures, which is particularly important for investigating the separation properties of porous materials. To date, mixed gas atmosphere diffraction experiments have only been reported once using powder samples, and considering the improved resolution and quality of data generally obtained *via* single-crystal diffraction experiments, it is envisaged for this to be an area of growth for *in situ* diffraction experiments.[15]

A material that is well suited for *in-situ* gas studies is Sc₂BDC₃⁶. Sc₂BDC₃ has remarkable thermal stability (crystalline up to 850 K in N₂) and has shown significant

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* BDC = 1,4 benzenedicarboxylate
Chapter 4 – Structural Studies of Gas Uptake in Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$

CO$_2$ uptake and selectivity at room temperature. In particular, its selectivity over CH$_4$ could be exploited for carbon capture or in CO$_2$/CH$_4$ separation for enhanced fuel recovery. Separation and capture of CO$_2$ is one of the most pressing scientific challenges, and many MOFs are considered as a viable alternative to current technologies to tackle such issues.[16] The optimisation of these materials cannot be done without understanding the structural features that favour this behaviour, particularly when CO$_2$ uptake in different MOFs can be driven by markedly different mechanisms. Recently, for example, two separate studies by Long et al. have shown the different CO$_2$ adsorption processes in place in two related MOFs, M$_2$(DOBDC)$^7$ and M$_2$(DOBPD)$^8$, where insertion of diamine groups on the latter causes step-shaped isotherm, compared the more common Langmuir type of the former.[11, 17]

This approach is particularly sought after in MOFs, where the ease of chemical modification of certain parts of the frameworks allows for the inclusion of functionality that may enhance particular selective behaviour, such as introducing amine groups to enhance carbon capture.[18] Recently an amino-functionalised derivative of Sc$_2$BDC$_3$ (Sc$_2$(BDC-NH$_2$)$_3$)$^9$, was synthesised.[19] Comparison of the CO$_2$ adsorption isotherms up to 0.9 bar at 197K and 273K for both Sc$_2$(BDC-NH$_2$)$_3$ and Sc$_2$BDC$_3$ respectively, revealed that even though Sc$_2$(BDC-NH$_2$)$_3$ has a 13% reduced maximum capacity at 197 K, at 273 K it takes up to 30% more CO$_2$. This promising result at higher temperature motivated the work presented herein, in which we investigate the structural factors that lead to the differences in adsorption behaviour of both frameworks at room temperature. Furthermore, and based on the selective properties of Sc$_2$BDC$_3$ demonstrated in previous in situ diffraction experiments, the first mixed gas single-crystal adsorption experiments have been carried out on both

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$^7$ DOBDC = 2,5-dioxidobenzene-1,3-dicarboxylate
$^8$ DOBPDC = 4,4’-dioxidobiphenyl-3,3’-dicarboxylate
$^9$ BDC-NH$_2$ = 1,4 amino-2-benzenedicarboxylate
frameworks in order to investigate if the selective behaviour extends to Sc$_2$(BDC-NH$_2$)$_3$.[20]

Both Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$ are isostructural, with orthorhombic $Fddd$ symmetry. Two symmetry-independent BDC linkers form small triangular channels (less than 4 Å in diameter) that run along the $a$-axis direction. These linkers are referred to as Group 1 and Group 2 (Figure 4.1a). The phenyl rings on these BDC linkers have a relatively low energetic barrier to rotation, and give the framework a certain degree of flexibility (see Chapter 5). In fact, the work by Miller et al. showed that Sc$_2$BDC$_3$ undergoes a guest-driven structural phase transition from orthorhombic ($Fddd$) symmetry to monoclinic (C2/c) upon uptake of CO$_2$ (Figure 4.1b) at room temperature.[20] In this transition (which is also observed upon cooling of Sc$_2$BDC$_3$
below 225 K), some of the Group 2 linkers rotate by ~11°, leading to three symmetry independent BDC linkers (Group 1, 2a and 2b) and two types of triangular channels.[20] In each of these channels it is possible to locate two different CO$_2$ sites – Site 1 and Site 2. The CO$_2$ at Site 1 lies parallel to the Group 1 linkers and across two sets of Group 2a with short C-H⋯O contacts of 2.88 Å. Site 2, is disordered over two positions which are half-occupied and only 2.2 Å away from each other. The CO$_2$ in Site 2 have their shortest C-H⋯O contacts to the framework at 2.87 Å with Group 1 and 2.93 Å with Group 2b.

From the refined occupancies of this structure, the calculated uptake of Sc$_2$BDC$_3$ at 1 bar and 235 K is 3.4 mmol g$^{-1}$ (corresponding to 8 CO$_2$ molecules per unit cell). This is only half of the maximum uptake of 6.5 mmol g$^{-1}$, measured both at 1 bar and 195K and at 0.0006 bar and 150 K, indicating there must be a packing rearrangement to accommodate increasing loadings of CO$_2$. This will be investigated further in Chapter 6 using extreme pressures (>2000 bars), but here using more moderate pressures (1-10 bar) and room temperature, the first indications of the possible pathways to increase the CO$_2$ capacity in Sc$_2$BDC$_3$ have been observed. Together with computational simulations, it has been possible to quantify and explain both the phase change and the appearance of a third site that accounts for the maximum loading of CO$_2$. 
4.3 Experimental

Synthesis
Single crystals of Sc$_2$BDC$_3$ were prepared following the synthetic procedure detailed in Chapter 3.

Gas cell set up
The gas cell set up in I19 was utilised to perform single-crystal diffraction under the different gaseous conditions. The 5 mm static cell used for this work allows the build-up of gas pressure up to 80 bar around a single-crystal held in a standard Mitegen® mount, which is encapsulated by a quartz capillary with 5 mm of outer diameter and 22 mm height. The capillary is mounted onto a goniometer head and connected through flexible tubing to a gas rig, which is used to control the gases delivered into the cell. The gas cell control apparatus allows us to operate the set-up remotely and offers the possibility to perform studies at different pressures, temperatures and gas mixtures without having to enter the Experimental Hutch (EH). A more detailed description of the set-up can be found in Chapter 2. Table 4.1 summarises the different samples and conditions tested as part of this study.

Data processing and structure refinement
Diffraction data were collected through the course of two different beamtime trips to station I19. First experiments where performed in EH1 using a four-circle goniometer with a Rigaku Saturn 724+ CCD detector. The second set were performed using a four-circle goniometer with a Pilatus 300K detector in EH2. In all cases a full sphere of data was collected for each pressure point. Data processing was carried out using the APEX II suite and integrated with SAINT after conversion of the raw frames using ECLIPSE and CBF2SFRM.[21, 22] Adsorption corrections were performed using SADABS or TWINABS.[23, 24]

Datasets with the highest loadings of gas molecules were used to obtain the most accurate models for gas molecules included in the pores. SHELXT was used for structure solution and SHELXL for structure refinement within Olex2.[25-27] The
atomic coordinates obtained for the highest loadings were then used as a starting model for the lower pressure datasets, allowing the occupancies of the adsorbed molecules to freely refine to account for any decrease in guest content. Gas molecules were refined isotropically with thermal similarity, distance and angle restraints. Hydrogen atoms on the framework were placed geometrically. The SQUEEZE routine within PLATON was performed to analyse the solvent accessible volume and calculate the electron density in the pores.[28] This was used in conjunction with the refined occupancy values of the guest molecules to determine the uptake of gas molecules at each pressure.

Note: DFT calculations were carried out by Jamie McHardy under the supervision of Dr. Carole Morrison from the University of Edinburgh and are included here for completeness.

**DFT calculations**

Calculations were carried out using the Cambridge Serial Total Energy Package (CASTEP v. 7.01) simulation package.[29] Calculations were performed on the primitive cell for better optimisation of the computational resources and in \( P1 \) symmetry in order to allow free movement to all atomic positions. The crystal structures obtained from *in situ* diffraction experiments were used as starting models. Approximation of the Hamiltonian operator was done using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional with the Tkatchenko-Scheffler (TS) van der Waal correction scheme.[30, 31] The plane wave cut-off energy for the finite basis set was 600 eV, giving a convergence within 3 meV per atom. The initial models were optimised by means of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm with convergence criteria for energy per atom, maximum force, maximum stress, and maximum atomic displacement of 0.02 meV/atom, 0.05 eV/Å, 0.1 GPa, and 0.002 Å, respectively.[32-35]

A series of different energy values have been obtained including the Mean Interaction Energy (MIE), Framework Strain Energy (FSE) and the Net Binding Energy (NBE). These have been calculated following these formulae:
Chapter 4 – Structural Studies of Gas Uptake in Sc₂BDC₃ and Sc₂(BDC-NH₂)₃

\[ MIE = GOE_{\text{framework+guest}} - SPE_{\text{framework}} - SPE_{\text{isolated guest}} \]  (4.1)

where \( GOE_{\text{framework+guest}} \) is the geometry optimised energy of the framework with the included guest, \( SPE_{\text{framework}} \) is the single-point energy of the framework coordinates obtained from the included framework calculation without the guest and \( SPE_{\text{isolated guest}} \) is the single-point energy of the isolated guest in an empty unit cell.

\[ FSE = SPE_{\text{framework}} - GOE_{\text{empty framework}} \]  (4.2)

where \( GOE_{\text{empty framework}} \) is the geometry optimised energy of the empty monoclinic ground state framework with no guest present in the optimisation.

\[ NBE = FSE + MIE \]  (4.3)
### Table 4.1 Summary of the gas cell experimental conditions tested for both Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sc$_2$BDC$_3$ Pressure (bar)</th>
<th>Sc$_2$BDC$_3$ Temperature (K)</th>
<th>Sc$_2$(BDC-NH$_2$)$_3$ Pressure (bar)</th>
<th>Sc$_2$(BDC-NH$_2$)$_3$ Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0 1.2 1.5 2 2.2 2.5 3 6 10 10</td>
<td>0 298 298 298 298 298 298 298 298 298</td>
<td>0 1.1 1.1 4.6 4.6 208</td>
<td>0 298 298 298 298 298 298 298 298 298</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0 11 19 4.6 4.6 208</td>
<td>0 298 298 298 298 298</td>
<td>0 11 11 3 3 208</td>
<td>0 298 298 298 298 298</td>
</tr>
<tr>
<td>CO$_2$/CH$_4$ (90/10)</td>
<td>2.2 4.4 4.4 208</td>
<td>2.2 4.4 4.4 208</td>
<td>11 3 3 208</td>
<td>11 3 3 208</td>
</tr>
</tbody>
</table>
4.4 Results and discussion

CO$_2$ adsorption experiments on Sc$_2$BDC$_3$

The first set of experiments aimed to investigate the room temperature CO$_2$ uptake behaviour of Sc$_2$BDC$_3$. In order to identify the pressure at which the previously reported CO$_2$ induced phase transition took place, small pressure increments of CO$_2$ (0.2 to 0.5 bar) were applied initially. The orthorhombic to monoclinic phase transition occurred at 3 bar, above which larger pressure steps of approximately 3 bar were applied until a maximum pressure of 10 bar.

At the first pressure point measured at 1.2 bar, uptake of CO$_2$ was already observed, despite Sc$_2$BDC$_3$ retaining the original $Fddd$ structure. CO$_2$ molecules were seen to clearly occupy two distinct sites, which although not in very high-occupancy (below 15%), indicated CO$_2$ uptake in Sc$_2$BDC$_3$ at low pressures and 298 K can occur without inducing the phase change.

The sites (henceforth referred to as Site 1 and Site 2, in keeping with the nomenclature in Miller et al.) due to constraints of the higher orthorhombic symmetry, lie in the same channel – unlike in the case of the monoclinic structure, where two symmetry independent channels can be identified (cf. Figure 4.1). Site 1 lies parallel to the Group 1 BDC ligand, whilst Site 2 is disordered through a 2-fold rotation axis, keeping a close resemblance to the arrangement reported by Miller et al. at 1 bar and 235 K but in the monoclinic phase.[20] However, the fact that both sites are in the same channel results in very close O–O contacts (< 1.8 Å) between them, which indicate that both sites may not be occupied simultaneously (Figure 4.2). This is also observed from the partial occupancies refined for both positions which indicate that both sites remain below 20% occupied up to 2.2 bar, with Site 2 showing marginally higher occupancy across the entire pressure range (see Table 4.2).
Figure 4.2 - CO₂ adsorption sites in the orthorhombic Fddd (a) and the monoclinic C2/c (b) structures of Sc₂BDC₃. Disordered CO₂ sites are shaded for clarity. ScO₆ octahedra coloured in green, H-atoms are coloured in light grey, C-atoms in grey and O-atoms in red.

Table 4.2 - Refined occupancies for CO₂ sites in Sc₂BDC₃.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Site occupancy</th>
<th>Molecules per unit cell</th>
<th>CO₂ uptake (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site 1</td>
<td>Site 2</td>
<td>Site 3</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1.2</td>
<td>0.114(8)</td>
<td>0.129(7)</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>0.131(9)</td>
<td>0.141(7)</td>
<td>-</td>
</tr>
<tr>
<td>1.75</td>
<td>0.147(11)</td>
<td>0.155(7)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.167(13)</td>
<td>0.171(11)</td>
<td>-</td>
</tr>
<tr>
<td>2.2</td>
<td>0.178(14)</td>
<td>0.179(13)</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td>0.235(17)</td>
<td>0.177(14)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.39(3)</td>
<td>0.316(17)</td>
<td>0.18(2)</td>
</tr>
<tr>
<td>6</td>
<td>0.552(19)</td>
<td>0.381(17)</td>
<td>0.17(2)</td>
</tr>
<tr>
<td>10</td>
<td>0.68(2)</td>
<td>0.59(3)</td>
<td>0.15(3)</td>
</tr>
</tbody>
</table>
At 1.75 bar the first signs of the phase transition from \( Fddd \) to \( C2/c \) on uptake of \( \text{CO}_2 \) were observed. Splitting of the diffraction peaks is a clear indication of the phase transition induced twinning, which occurs on lowering symmetry from \( Fddd \) to \( C2/c \) (see Figure 4.4). The transition occurs gradually and although it was still possible to obtain an acceptable monoclinic model from 2 bar onwards, it is not until 3 bar that the change to the monoclinic phase is complete. The occupancies of \( \text{CO}_2 \) molecules at Sites 1 and 2 kept increasing with each pressure step reaching around 20% occupancy at 2.5 bar. From the refined occupancies it is possible to calculate the number \( \text{CO}_2 \) molecules per unit cell and hence the uptake of Sc\(_2\)BDC\(_3\) (Figure 4.3). The calculated uptake from our refined model, and the experimental isotherm show good agreement between each other (Figure 4.8).

![Figure 4.3](image-url) - Refined occupancy values for the three \( \text{CO}_2 \) sites in Sc\(_2\)BDC\(_3\) at 298 K as a function of pressure. Up until 2.5 bar (\( Fddd \)) there are only two distinct sites, Site 1 (red) and Site 2 (green). Above 3 bar the phase change to the monoclinic phase takes place and a third site can be observed (blue). The dotted line represents the total uptake in mmol g\(^{-1}\) as calculated from the summation of all sites.
Chapter 4 – Structural Studies of Gas Uptake in \( \text{Sc}_2\text{BDC}_3 \) and \( \text{Sc}_2(\text{BDC-NH}_2)_3 \)

Snapshots from the diffraction pattern of \( \text{Sc}_2\text{BDC}_3 \) at different pressure detailing the peak splitting arising from the twinning during the phase transition from orthorhombic Fddd and monoclinic C2/c.

Figure 4.4 - Snapshots from the diffraction pattern of \( \text{Sc}_2\text{BDC}_3 \) at different pressure detailing the peak splitting arising from the twinning during the phase transition from orthorhombic Fddd and monoclinic C2/c.

\[
R_{\text{int}} \text{ for } \text{Sc}_2\text{BDC}_3 \text{ as function of CO}_2 \text{ pressure for triclinic, C-centred monoclinic and F-centred orthorhombic. Data quality increasingly worsens above 1.75 bar, coinciding with the beginning of the phase change. Refinement in both space groups C2/c and Fddd is possible up to 3 bar, at which point the C-centred monoclinic setting is clearly favoured over the F-centred orthorhombic setting.}
\]

Figure 4.5 - \( R_{\text{int}} \) for \( \text{Sc}_2\text{BDC}_3 \) as function of CO\(_2\) pressure for triclinic, C-centred monoclinic and F-centred orthorhombic. Data quality increasingly worsens above 1.75 bar, coinciding with the beginning of the phase change. Refinement in both space groups C2/c and Fddd is possible up to 3 bar, at which point the C-centred monoclinic setting is clearly favoured over the F-centred orthorhombic setting.
Further indication that the phase transition is completed at 3 bar can be found from the diffraction intensities statistics, specifically $R_{int}$. The results for $R_{int}$ from data integrated in both the orthorhombic and the monoclinic settings, clearly show a preference for the monoclinic $C2/c$ above 3 bar (see Figure 4.5).

By means of *ab initio* solid-state DFT simulations, the thermodynamics of this phase change were studied further. Firstly, comparison of the optimised energies of the empty orthorhombic $Fddd$ and the monoclinic $C2/c$ structure showed that the $C2/c$ phase is 13 kJ mol$^{-1}$ lower in energy than the $Fddd$ phase (Table 4.3). Therefore, on undergoing the $Fddd$ to $C2/c$ transition, this subtle rotation of the BDC ligands occurs due to the $C2/c$ structure having a lower internal energy at 225 K. Since at low temperatures the internal energy ($U$) dominates the Gibbs free energy (as the difference in volume ($V$) between the two states varies by only 0.2%, and the $pV$ term is negligible), the monoclinic structure becomes the most thermodynamically stable phase below 225 K.

Table 4.3 - Summary of the DFT calculation results.

<table>
<thead>
<tr>
<th></th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Fddd$</td>
</tr>
<tr>
<td><strong>Geometry Optimised Energy of Empty Framework (GOE)$_{ef}$ (kJ mol$^{-1}$)</strong></td>
<td>-2274309.3</td>
</tr>
<tr>
<td><strong>Mean Interaction Energy (MIE) per CO$_2$ molecule (kJ mol$^{-1}$)$^a$</strong></td>
<td>-60.3</td>
</tr>
<tr>
<td><strong>Framework Strain Energy (FSE) (kJ mol$^{-1}$)$^b$</strong></td>
<td>19.7</td>
</tr>
<tr>
<td><strong>Net Binding Energy (NBE) per CO$_2$ molecule (kJ mol$^{-1}$)$^c$</strong></td>
<td>-40.6</td>
</tr>
</tbody>
</table>

$^a$MIE = GOE$_{framework}$ + SPE$_{framework} - $ SPE$_{isolated}$-guest  
$^b$FSE = SPE$_{framework} - $ GOE$_{ef}  
$^c$NBE = FSE + MIE
With increasing temperature, the entropic term ($TS$) gains a higher weighting. Since the orthorhombic crystal structure has a higher symmetry than the monoclinic form, it is possible to state that the $Fddd$ structure will have a higher entropy than the $C2/c$ form. Thus, as the temperature increases (in this case above 225 K), the entropic contribution drives the phase change from the monoclinic to the orthorhombic phase.

Combining this with calculations on the CO$_2$ included structures, it is possible to understand how CO$_2$ uptake drives the phase change to the $C2/c$ phase (Table 4.3). Despite the mean interaction energies being higher for the monoclinic phase, the framework strain energies obtained indicate there is a smaller penalty to place the CO$_2$ in the orthorhombic structure. Therefore, at temperatures above 225 K where the $Fddd$ structure is more stable, upon initial filling with CO$_2$, the monoclinic structure remains unobserved - as the net energy benefit achieved from guest-host interactions is not sufficient to counteract the effect of the strain and entropic factors. Above a certain threshold however, increasing the guest content starts to invert this trend and both the entropic and strain factors become less significant than the guest-host interactions, favouring the transition to monoclinic phase.

The relatively small differences in energies between both phases may also explain why the symmetry change occurs gradually. As stated in Table 4.3, the net benefit from adopting the $C2/c$ structure is only of 3.4 kJ mol$^{-1}$, so at higher temperatures, where the entropic contribution is more significant, more CO$_2$ and higher pressures are required to drive the phase change. For these reasons Miller et al. observed the monoclinic structure at only 1 bar when performing the experiment at 235 K, and in this work performed at 300 K, it is only above 3 bar the monoclinic phase is clearly observed.[20] One could postulate that at even higher temperatures the monoclinic phase may not be observed at all, when the entropic factors may be too big to be overcome by the net interaction energy gain obtained from the phase change.

Comparing the $C2/c$ structure obtained at 3 bar and 298 K and that reported by Miller et al. at 1 bar and 230 K, shows they are both equivalent, with the associated reduction
in symmetry from \textit{Fddd} resulting in two distinct channels, one hosting Site 1 and the other Site 2 (see Figure 4.2b).[20] This way Site 1 and Site 2 are not in close proximity anymore, and thus can be further occupied, effectively allowing for a greater uptake of CO$_2$ in the pores. Furthermore, above 3 bar a third site was seen to appear in the same channels as Site 1. This third site (Site 3), lies closer than Site 1 to the wall of Group 1 BDC linkers, occupying the space directly in-between subsequent linkers along the channels. The closest O···O contact between Site 1 and Site 3 was measured to be 2.889 Å, which still provides enough space for both molecules to be present simultaneously.

The occupancies of Site 1 and 2 were observed to increase with pressure. At 3 bar, Site 1 reached an occupancy of 0.39(3) and Site 2 0.316(17), whilst Site 3 was 0.18(2). Increasing pressure to 6 bar, filled Sites 1 and 2 to 0.552(19) and 0.381(17) respectively, whilst site 3 remained statistically unchanged at 0.17(2). These observations indicated that, even though in the orthorhombic structure no major distinction could be made about the filling order of the sites, in the monoclinic case Site 1 appeared to fill up more promptly than Site 2, whilst Site 3 seemed to be the less favoured of all three CO$_2$ positions.

![Figure 4.6 - View of Site 3 as observed in the C2/c phase of Sc$_2$BDC$_3$ at pressures above 3 bar, showing the shortest contacts of CO$_2$ molecule with the framework (blue dashed lines) and with the neighbouring CO$_2$ molecules in Site 1 (yellow dashed lines), which are shown in lighter shade for clarity. Distances in Å.](image)
In the final pressure point at 10 bar, the refined occupancies for Sites 1, 2 and 3 were 0.68(3), 0.59(3) and 0.15(3) respectively. Note that Site 2 appeared to be occupied more than half of the time, contradicting the conclusion by Miller et al., which suggested that the distance between the two CO$_2$ sites was too short for both to be simultaneously occupied. This is certainly the case at lower pressures, where the separation between each disordered molecule was ~ 1.3 Å. After the phase transition to the monoclinic form, at 298 K this distance increases to ~ 2 Å (still a very close O—O contact when compared to other reported structures in the CSD containing CO$_2$). [36] However, a final measurement at 230 K to maximise the CO$_2$ loading, increased the separation further to 2.13 Å. The increase in O—O distance is coupled by an increase in occupancy of 0.68(3) at 230 K, confirming that in order to accommodate higher loadings, the CO$_2$ molecules in symmetry equivalent Site 2-positions have to move apart in order that the two sites can be filled simultaneously (Figure 4.7).

The maximum calculated uptake at 10 bar and 298 K obtained from the refined occupancy values was 3.45 mmol g$^{-1}$. This can be compared with the results obtained from calculating the residual electron density in the pores using the SQUEEZE algorithm.[37] From the residual electron density it was possible to calculate the number of CO$_2$ molecules present per unit cell, which yielded a maximum uptake of 3.3 mmol g$^{-1}$. Figure 4.8 compares the calculated uptake at different pressures using both the refined occupancies and the residual electron density. The good agreement between both methods helps validate both the SQUEEZE routine and the refined occupancy and positions for CO$_2$ from our models.

Comparison of the CO$_2$ uptake obtained from the single-crystal analysis (3.3-3.45 mmol g$^{-1}$) with the recorded isotherm values (2.95 mmol g$^{-1}$ maximum uptake) results in a slight overestimation of the capacity of Sc$_2$BDC$_3$. However, the agreement is still remarkable and the differences could arise from particle size effects, which have been previously reported to cause differences in uptake of gaseous species in the porous zeolitic imidazolate framework ZIF-8.[38]
Chapter 4 – Structural Studies of Gas Uptake in Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$

Gradual increase in the O···O distance (yellow in Å) between CO$_2$ molecules Site 2 with increasing pressure. The separation increases with increasing occupancy of the site.

Figure 4.7 - Gradual increase in the O···O distance (yellow in Å) between CO$_2$ molecules Site 2 with increasing pressure. The separation increases with increasing occupancy of the site.
Calculated uptake of CO₂ in Sc₂BDC₃ as calculated using the refined occupancies (white) and SQUEEZE (grey) as function of pressure at 298 K.

**CO₂ adsorption experiments on Sc₂(BDC-NH₂)₃**

Similar experiments were carried out on the functionalised analogue of Sc₂BDC₃, Sc₂(BDC-NH₂)₃, which previous adsorption work indicated to have a higher uptake of CO₂ than Sc₂BDC₃ at 273 K, but a lower maximum capacity than Sc₂BDC₃ at 197K (as shown by adsorption isotherms).[19] The structure of Sc₂(BDC-NH₂)₃ is similar to the native framework, adopting the same space group Fddd, however, as discussed in the previous chapter, the presence of the amino groups induces a certain degree of static disorder in the structure. Like in Sc₂BDC₃, two symmetry independent linkers can be identified (also termed Group 1 and Group 2). Group 2 has two positions for the amino group, which are related by the inversion centre in the middle of the linker, hence each position is half occupied. Probably to minimise contact between adjacent linkers along the channel, the BDC rings in Group 2 are rotated subtly when compared to their position in the native Sc₂BDC₃ structure. In Sc₂BDC₃ the plane of
Chapter 4 – Structural Studies of Gas Uptake in Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$

the Group 1 linkers forms an angle of 7.5° with the (022) plane, whilst in the Sc$_2$(BDC-NH$_2$)$_3$ the rotation is 12.9° (Figure 4.9a).

Group 1 has a similar positional disorder caused by the three 2-fold axes that bisect the linker. However, in this case, the ring is rotated by 20° when comparing the plane made by the BDC linker in Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$, again to avoid close contacts between the amino groups of adjacent Group 1 linkers. This rotation causes the ring to be disordered over two positions in a similar fashion to that observed upon inclusion of hydrocarbons in the native Sc$_2$BDC$_3$ framework (see Chapter 5). As a consequence, the amino groups are disordered over four positions (Figure 4.9b).

![Side view of the BDC groups in Sc$_2$(BDC-NH$_2$)$_3$, showing the different type of disorder that arises from the presence of the NH$_2$ functionality in both Group 1 (a) and Group 2 linkers (b). The fainter tones of blue are used to represent the disorder of the NH$_2$ groups, whilst the dashed bonds are used to represent the 50:50 disorder of the Group 1 BDC linker.](image)

Figure 4.9 - Side view of the BDC groups in Sc$_2$(BDC-NH$_2$)$_3$, showing the different type of disorder that arises from the presence of the NH$_2$ functionality in both Group 1 (a) and Group 2 linkers (b). The fainter tones of blue are used to represent the disorder of the NH$_2$ groups, whilst the dashed bonds are used to represent the 50:50 disorder of the Group 1 BDC linker.
The disorder complicates the calculation of the pore volume of the framework. However, by deleting redundant amino groups and one of the disordered rings of Group 1, using the void analysis tool in Mercury it is possible to estimate a solvent accessible volume (SAV) of 1582.4 Å per unit cell (25.5% of the unit cell volume) for Sc₂(BDC-NH₂)₃. This is less than the 2203 Å³ (35.2%) in Sc₂BDC₃, in line with the greater maximum capacity of Sc₂BDC₃ observed at lower temperatures, as more space is available to the guest.

In the case of Sc₂(BDC-NH₂)₃, only three 298 K datasets were collected: an empty ground state under vacuum, one at 2.1 bar and another at 10 bar. At 2 bar, it was already possible to observe CO₂ present in the pores of the framework. A single site can be found, and similarly to Site 2 in the native framework, the site is disordered by a 2-fold axis leading to two CO₂ sites present per triangular channel (Figure 4.10). At 2.1 bar, this site was not fully occupied and refined to an occupancy of 0.225(19). This corresponds to a calculated uptake at 2.1 bar of 1.43 mmol g⁻¹, in comparison to the 1.28 mmol g⁻¹ recorded at 2.2 bar for Sc₂BDC₃ at the same temperature.

At 10 bar the refined occupancy for CO₂ increased significantly to 0.460(13). This equates to an uptake of 2.92 mmol g⁻¹, which is in this case inferior to the 3.35 mmol g⁻¹ reported for Sc₂BDC₃ at the same temperature and pressure. Unfortunately, due to the heavily disordered structure, the usage of the SQUEEZE routine to estimate the uptake from the residual electron density is not as effective in Sc₂(BDC-NH₂)₃, since the disorder actually masks the CO₂ sites as they are too close to the NH₂ groups.[28] The void mapping underestimates the real solvent accessible space, hence resulting in lower electron density counts. It is still possible to observe an increase in guest content with increasing pressure, but the total number of electrons obtained do not accurately resemble the values obtained with the refined occupancies for CO₂ or the experimental adsorption isotherms. Despite this, and although there are only two pressure points to compare, these results are a first indication that in the lower pressure regimes at 298 K, Sc₂(BDC-NH₂)₃ shows a greater uptake of CO₂ over Sc₂BDC₃. This then reverts at higher pressures, where the larger pores of Sc₂BDC₃...
accommodate more CO₂, however indicating that there must be a greater drive for CO₂ uptake in Sc₂(BDC-NH₂)₃ than in Sc₂BDC₃ at low pressures.

Further evidence that different guest-host interactions are in place in Sc₂(BDC-NH₂)₃ can be found in the orientation and short contacts of the CO₂ molecules with the framework. These CO₂ molecules show a particular directionality towards the amino groups of the BDC linkers, with a C=O···N angle of 151° between the amino group and Group 1 and 174° with Group 2 BDC ligands respectively (Figure 4.10). The O···N distances are 3.145 Å and 2.994 Å for Group 1 Group 2 respectively, which could indicate some form of interaction between the CO₂ molecules and the framework. However, the only prior study of an amino-functionalised MOF (Zn₂(Atz)₂(ox), where Atz is 3-amino-1,2,4-triazole and ox is oxalate) with CO₂ in the pores showed that, rather than a head-on’ O···N contacts, a ‘side-on’ C···N contact dominated the guest-host interactions.[39] In the case of Sc₂(BDC-NH₂)₃, similar ‘side-on’ contacts can be found with a similar C···N contact of 3.154 Å, suggesting that such interactions may also be in place here as well. Which interaction dominates need to be further studied.
using computational approaches, however, the significant disorder of the framework here complicates such analysis and we have not succeeded in obtaining reliable results yet.

Additionally, a final dataset at 230 K and 10 bar was collected to attempt to maximise the CO\textsubscript{2} content inside Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3}. The 2.92 mmol g\textsuperscript{-1} recorded at 298 K and 10 bar are still below the maximum capacity of Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3}, which from the isotherm work is estimated at ~ 5 mmol g\textsuperscript{-1}. For this reason, it is necessary for a second site or a rearrangement of CO\textsubscript{2} molecules in Site 1 to take place, as Site 1 cannot be further occupied. From the data at 230 K, a tentative second site appears between the Group 1 BDC linkers. Significant residual electron density peaks can be found, and a heavily constrained model of a second CO\textsubscript{2} site with an occupancy of ~ 0.2, can be refined. This is sensible in terms of achieving the maximum capacity, which with the second site would be closer to 5 mmol g\textsuperscript{-1}, however the quality of the model obtained at 230 K is poor. Better data would be needed before more definitive conclusions can be made.

**CH\textsubscript{4} adsorption experiments on Sc\textsubscript{2}BDC\textsubscript{3} and Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3}**

Analogously to the experiments with CO\textsubscript{2}, single-crystal *in situ* studies were performed on both Sc\textsubscript{2}BDC\textsubscript{3} and Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3} using methane gas (CH\textsubscript{4}). Previous reports revealed Sc\textsubscript{2}BDC\textsubscript{3} to have comparatively low uptake at room temperature, but no prior work on CH\textsubscript{4} uptake on Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3} had been done. Both framework materials were studied in four different conditions: vacuum and 298 K, 1.1 bar and 298 K, 4.6 bar and 298 K, and 4.6 bar and low temperature (230 K for Sc\textsubscript{2}BDC\textsubscript{3} and 130 K for Sc\textsubscript{2}(BDC-NH\textsubscript{2})\textsubscript{3}).

As expected, Sc\textsubscript{2}BDC\textsubscript{3} showed no significant uptake at 1.1 bar. Analysis of residual electron density using SQUEEZE showed no change when compared with the empty ground state. Increasing the pressure to 4.6 bar revealed a marginal increase in the residual electron density. As calculated by SQUEEZE, 70 electrons per unit cell could be found in the pores of Sc\textsubscript{2}BDC\textsubscript{3}, which equates to a CH\textsubscript{4} uptake of 1.5 mmol g\textsuperscript{-1}. It was possible to refine a single CH\textsubscript{4} site with an occupancy of 0.11(2), which itself
equates to a CH₄ uptake of 0.79 mmol g⁻¹. These values are a significantly higher than the measured uptake at room temperature and 4.2 bar of CH₄ from previous isotherm experiments (0.34 mmol g⁻¹), yet these experiments still confirmed the low uptake for CH₄ at room temperature in comparison to CO₂.

At 230 K CH₄ uptake increased to the point that it was possible to locate CH₄ sites in the pores of Sc₂BDC₃. The two sites found are analogously to the previous structure determined by Miller et al. However, the occupancies reported in this work correspond to 0.306(14) and 0.155(11) for Sites 1 and 2 respectively, which are greater than those found by Miller et al., despite their experiment being collected at 9 bar instead of 4.6 bar. The residual electron density calculated using SQUEEZE also demonstrated the increase in CH₄ content at 230 K, equating to 101 electrons per unit cell. The calculated uptake from the refined occupancy of both CH₄ sites, and that calculated from those modelled using the SQUEEZE approach, equate to 2.12 and 2.17 mmol g⁻¹ respectively.

![Figure 4.11 - Sc₂BDC₃ structure with included CH₄, showing the same site distribution as that reported by Miller et al.[20]](image)

In the case of Sc₂(BDC-NH₂)₃ functionalisation renders the material even less prone to uptake of CH₄ than Sc₂BDC₃. Not only is there no significant structural change or sign of increase in electron density in the pores at 1.1 or 4.6 bar at 298 K, but even on
cooling to 230 K, no indication of uptake of CH₄ could be detected. The residual electron density calculated with SQUEEZE also reflected this, remaining essentially constant. Overall, these results indicate a high selectivity for CO₂ over CH₄ for both frameworks, and particularly for Sc₂(BDC-NH₂)₃, which shows negligible uptake of CH₄ at room temperature.

**Mixed gas experiments**

Based on the observed selectivity under single gas atmospheres, a series of mixed gas experiments were carried out to determine whether such behaviour was maintained under competing conditions. Mixtures of CO₂ and CH₄ at 50:50 (50% CO₂) and 20:80 (20% CO₂) ratios were exposed to single-crystals of both Sc₂BDC₃ and Sc₂(BDC-NH₂)₃ at 298 K.

In the case of Sc₂BDC₃, mixed gas experiments were carried out to only 4.5 bar due to limitations in the CH₄ regulator. For Sc₂(BDC-NH₂)₃, measurements up to 11 bar were possible. The results for the different experiments are shown in Figure 4.9 together with the values obtained for the single-component experiments discussed earlier.

Using the 50:50 mixture it was possible to observe the guest-driven phase transition in Sc₂BDC₃, however this occurs at a higher pressure (above 4 bar). This is not unexpected as it is at this point that the partial pressure of CO₂ (pCO₂) is of the order of 2 bar, corresponding to where the phase change was observed using 100% CO₂ (Figure 4.10c). With a 20:80 mixture of CO₂ and CH₄, the phase transition was not observed despite a significant uptake of CO₂ being observed, however this is not unsurprising since the pCO₂ never exceeds 1 bar, which is below the phase transition pressure.

For Sc₂(BDC-NH₂)₃, the mixed gas experiments revealed a constant uptake of CO₂, which was, as expected, lower for the 20:80 mixture than for the 50:50 mixture. Comparison with the single-component gas experiments must be done with care, since only 2 pressure points were collected. However, using a logarithmic fit, it was
possible to plot the expected isotherm at 100% CO₂ which closely resembles the uptake trend observed at 50% and 20% when plotted against pCO₂ (Figure 4.12c)

Figure 4.12 - CO₂ uptake as measured from the occupancy of the CO₂ sites in Sc₂BDC₃ (a and c) and Sc₂(BDC-NH₂)₃ (b and d). Top graphs (a and b) are plotted against total pressure, whilst bottom graphs (c and d) are as function of the partial CO₂ pressure (pCO₂).

Comparison of the uptake behaviour of both Sc₂BDC₃ and Sc₂(BDC-NH₂)₃ in the mixed components, leads to the corroboration of the observations made under 100% atmosphere of CO₂. As seen in Figure 4.13, at low loadings of CO₂, Sc₂(BDC-NH₂)₃ takes up more CO₂ than Sc₂BDC₃. With increasing pressure, the order reverses and Sc₂BDC₃ uptakes more CO₂ than Sc₂(BDC-NH₂)₃ as seen in the 50:50 mixture. This coincides with the phase change of Sc₂BDC₃ from Fddd to C2/c, highlighting how the selective phase transition enhances the uptake of CO₂.
Chapter 4 – Structural Studies of Gas Uptake in $\text{Sc}_2\text{BDC}_3$ and $\text{Sc}_2(\text{BDC-NH}_2)_3$

Comparison of the CO$_2$ uptake in $\text{Sc}_2\text{BDC}_3$ (yellow) and $\text{Sc}_2(\text{BDC-NH}_2)_3$ (green) in a 20:80 (a) and a 50:50 (b) mixture of CO$_2$ and CH$_4$ at 298 K.

What can be extracted from these results is that both in the case of $\text{Sc}_2\text{BDC}_3$ and $\text{Sc}_2(\text{BDC-NH}_2)_3$, the presence of CH$_4$ does not hinder uptake of CO$_2$. If anything it enhances CO$_2$ adsorption as for both MOFs, uptake of CO$_2$ at the same partial pressures is higher for the gas mixtures than for single gases.
4.5 Conclusions

Overall, this study presents an in-depth analysis of the adsorption of both CO$_2$ and CH$_4$ into Sc$_2$BDC$_3$ and Sc$_2$(BDC-NH$_2$)$_3$ at room temperature. The structural evidence obtained indicates that the previously observed behaviour at low temperatures for Sc$_2$BDC$_3$ is reproducible at higher temperatures, if the higher pressures available with the I19 gas cell set up are used. Additionally, further insights into the benefits of introducing amine functionality in MOFs, particularly to maximise the CO$_2$ separation properties have been obtained.

The information obtained from the mixed gas experiments indicates that the observed uptake behaviour of both frameworks is also in place at different concentrations of both CO$_2$ and CH$_4$. They also help elucidate the structural traits behind the increased uptake observed for Sc$_2$(BDC-NH$_2$)$_3$ at lower pressures, and why Sc$_2$BDC$_3$ has a greater capacity at higher pressures following the guest-driven phase change and the increased number of sites.

Valuable information such as the filling mechanisms, and the location of the sites can be extracted from single-crystal experiments, and although exact values for uptake capacities may have to be treated with caution, perhaps due to particle size effects, these in situ experiments present and invaluable approach to further our understanding of gas adsorption in MOFs.
4.6 References


5.1 Synopsis

Using pressures of up to 1 GPa, a range of sterically ‘oversized’ C5-C8 alkane guest molecules have been forced into the cavities of Sc2BDC3. Guest inclusion causes a pronounced reorientation of one third of the aromatic rings of the terephthalate linkers, which act as ‘torsion springs’, resulting in a dramatic and fully reversible change in the local pore structure. The study demonstrates how pressure-induced guest uptake can be used to investigate framework flexibility and understand the uptake in MOFs of guest molecules relevant to hydrocarbon separation.

5.2 Introduction

One of the major drivers for the current intensive research into porous metal-organic frameworks (MOFs) is the potential they offer for applications in separation technologies.[1, 2] The wide variety of chemical environments, pore sizes and shapes, and flexible behaviour found in MOFs may improve current separation technologies, or enable previously unfeasible separations.[3] For example, a recent study has shown that the framework Fe2BDP3 (BDP = 1,4-benzenedipyrzolate) can separate isomers of hexane according to their degree of branching.[4] Notably, the triangular channel topology of Fe2BDP3, which imparts the selectivity, is not observed in zeolites. This has potential application in gasoline production, where the separation of C6 isomers is a crucial step.

Understanding the role that a MOF has on controlling the kinetics and selectivity of gas uptake is crucial for exploitation in separation technologies.[5] Molecular simulations are an important part of this process as they offer insight into the gas adsorption sites and diffusivity through a framework.[6, 7] However, it is becoming increasingly clear that it is not only the framework geometry that determines the uptake behaviour, but also the dynamics and structural response of a framework in the presence of adsorbates. In particular, ligands in MOFs have been observed to show rotation and tilting around an axis and the ability to hinge at the points of their connection to metal cations, all in response to uptake of adsorbates. This can lead to
gate opening without a change in the time-averaged structure, to distortions and tilts of the framework structure, or major breathing phenomena, with very large changes in the pore volumes, sometimes over 100%.\[8, 9\] To predict adsorption behaviour for any given MOF, for example by molecular simulation, the nature and energetics of its structural response must first be measured and quantified.[\(10-14\)]

Structural changes of these types have been observed over a wide range of conditions in cases where significant guest uptakes occur, ranging from low temperatures and pressures to room temperature and very high pressures.[\(15-17\)] At very high pressures, the \(P\Delta V\) energy associated with the ingress of molecules from fluids into pores becomes comparable with typical energies of adsorption. For example, in ZIF-8 a similar structural response has been observed for different adsorbates under very different conditions. The structure was observed by X-ray diffraction to undergo a transition involving a rotation of the imidazolate linkers, increasing the porosity of the framework and allowing more guest molecules to enter the pores. This occurs at 0.02 bar in \(\text{N}_2\) gas at 77 K and also at 1.5 GPa in liquid methanol at 298 K. The latter was observed for a single crystal of ZIF-8 loaded into a diamond anvil cell (DAC) and surrounded with methanol as a pressure-transmitting liquid (PTM), to ensure pressure is applied hydrostatically to the sample.[\(15, 18-20\)] The high-pressure structure was used to model the ambient-pressure structural changes responsible for the increased \(\text{N}_2\) uptake.[\(15\)] Therefore, as well as directly giving information on the structural response of the MOF to high adsorbate pressures – itself relevant to potential applications of MOFs in high pressure applications such as ultra-performance liquid chromatography (UPLC) or gas storage – such diamond anvil studies can shed light on the structural behaviour (adsorption site energies; flexibility) during adsorption at lower pressures.[\(10-12\)]

Like ZIF-8, the scandium 1,4-benzenedicarboxylate MOF Sc-BDC\(_3\), is a highly stable 3D-connected small pore MOF.[\(21\)] The structure comprises isolated ScO\(_6\) octahedra, in which all O-atoms are part of the linking BDC ligands. The framework possesses one-dimensional channels with a triangular cross-section of ~4 Å in free diameter
giving a similar topology to that observed in Fe₂BDP₃ (see Figure 5.1). [4] Adsorption isotherms have shown that the framework has adsorption capacity for small fuel-related molecules, namely CO₂ (kinetic diameter ~ 3 Å) and normal alkanes (methane, ethane, propane; ~ 4 Å).[22] Crystallographic studies at low temperature show that methane and ethane fit closely into the available channel space of the Sc₂BDC₃, though adsorption sites for ethane are also observed in gaps in the channel walls between the aromatic rings. Preliminary packed column experiments indicated markedly shorter retention times over a packed column of Sc₂BDC₃ crystals for branched alkanes compared with normal alkanes of similar boiling points, suggesting a greater uptake of straight chain than of branched chain alkanes.[23] To determine whether this resulted from size exclusion, the adsorption behaviour of normal and branched alkanes not only up to saturated vapour pressures at room temperature, but also at extreme pressures in a diamond anvil cell has been investigated. The aim was to elucidate if guest uptake is limited to linear hydrocarbons, or if pressure could be used as a tool to overcome steric limitations. For this, a series of structural and adsorption studies on a selection of hydrocarbons with varying chain lengths (from C₅ to C₈) and different degrees of branching have been performed.
Figure 5.1 - Comparison of the structures of (a) Sc₂BDC₃ and (b) Fe₂BDP₁ highlight the similarities in the pore structure when viewed parallel to the crystallographic a-axis, with ScO₆ octahedra coloured in green and FeN₆ octahedra coloured in dark red. H atoms are omitted for clarity, C-atoms coloured in grey, O-atoms in red and N-atoms in blue.
5.3 Experimental

Synthesis

Single crystals of Sc₂BDC₃ were prepared following the synthetic procedure detailed in Chapter 3.

*Note: gas adsorption measurements were carried out by Dr. Alex Greenaway from the University of St. Andrews and are included here for completeness.*

Gas adsorption isotherms.

Gas isotherms for the different alkanes (2-methylbutane, n-pentane, n-hexane, 2,2-dimethylbutane, 2,3-dimethylbutane, n-heptane, 2-methylheptane and 2,2,4-trimethylpentane (Table 5.1)) were measured volumetrically at 298 K for Sc₂BDC₃ using a custom-built vacuum line. The Sc₂BDC₃ sample was degassed at 438 K under vacuum for ca. 2 h prior to measurement of each isotherm. The alkane was degassed using a repeated freeze/thaw process using liquid N₂. The alkane uptake was determined as a function of increasing equilibrium pressure, up to pressures close to their saturated vapour pressures. A more detailed scheme of the apparatus used can be seen in Figure 5.2.

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**Figure 5.2 -** Schematic of manually assembled porosimeter used for construction of gas adsorption isotherms.
Table 5.1 - Chemical structures and kinetic diameters of the linear and branched alkanes examined as guest species in Sc$_2$BDC$_3$ at low and high pressures.

<table>
<thead>
<tr>
<th>Guest</th>
<th>Molecular structure</th>
<th>Kinetic diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>n-heptane</td>
<td></td>
<td>4.3</td>
</tr>
<tr>
<td>2-methylheptane</td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>2,3-dimethylbutane</td>
<td></td>
<td>6.0</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,2,4-trimethylpentane</td>
<td></td>
<td>6.2</td>
</tr>
</tbody>
</table>

**Single-crystal X-ray diffraction experiments.**

All single-crystal X-ray diffraction data were collected on a Bruker APEX II diffractometer (Bruker, 2002) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).

Single-crystal X-ray diffraction experiments were performed on Sc$_2$BDC$_3$ crystals in a capillary, immersed in both n-pentane and 2-methylbutane, using a method described previously in Chapter 2.[24] A crystal was attached to the tip of a MiTeGen 100 µm Microloop™ using a small amount of Araldite™ epoxy resin. The loop was mounted on a goniometer head and covered with a MicroRT™ polyester capillary. The capillary was stuck to the goniometer head and sealed around the base using Araldite™. When the epoxy resin was dry, the capillary was filled with the solvent in
question by injection through the top of the capillary using a 0.6 mm needle. The resultant hole was sealed with a drop of molten beeswax. Diffraction data were then collected at room temperature.

High-pressure single-crystal diffraction data were obtained using the set-up described in Chapter 2. A single-crystal of Sc₂BDC₃ - together with a ruby chip for pressure calibration – was placed in a Merril-Bassett Diamond Anvil Cell (DAC) with 600 μm culet diamonds and a tungsten gasket. For each pressure series the gasket chamber was filled with a different solvent as hydrostatic medium and the DAC closed carefully. Diffraction data were then collected at room temperature. The data collection strategy was based on that described by Dawson et al as described in Chapter 2.[25] Data were integrated with SAINT using ‘dynamic masks’ to avoid integration of regions of the detector shaded by the body of the pressure cell. Absorption corrections for the DAC and sample were carried out with the programs SHADE and SADABS, respectively.[26]

Structure solutions were performed using SUPERFLIP and in the cases where no satisfactory solution was obtained, the atomic coordinates of the previous pressure point were used as a starting model. [27] Refinements were carried out against |F| using data with an I>2σ cut off in the program CRYSTALS.[28] Vibrational restraints were applied on all non-hydrogen atoms (except for Sc). 1,2 and 1,3 restraints were also applied to the guest molecules and on the disordered Group 2 BDC ring. Hydrogen atoms attached to carbon atoms were placed geometrically and not refined. Where possible, the highest electron density peaks within the pores were assigned dummy C-atoms, and refined, with restraints (including occupancies), in order to model the disordered guest molecules. Because of loss in resolution at higher pressures, 1,2 and 1,3 distances on the BDC linker were also restrained to the values observed at ambient temperature and pressure in the highest pressure data sets. All metal-ligand distances and angles, and all torsion angles were refined freely. H-atoms attached to carbon were placed geometrically and not refined. Upon increasing pressure, sample deterioration resulted in loss of resolution. Structure refinements
were carried out to the maximum resolution of each sample as determined from the intensity statistics. Analysis of the solvent accessible volume and the residual electron density was performed using the SQUEEZE algorithm within PLATON.[29] An artificial resolution cut off of 1.1 Å was applied to each data set in order to compare the electron density in the pores, following the procedure described by Graham et al.[16] The results of the residual electron density calculations were used in conjunction with the refined occupancy values for the solvent molecules to determine the uptake of guest molecules at each pressure. After each pressure study, the Sc₂BDC₃ crystal was downloaded from the DAC and diffraction data collected at 250K.

Note: DFT calculations were carried out by Odin Kvam under the supervision of Dr. Carole Morrison from the University of Edinburgh and are included here for completeness.

DFT calculations.

A series of density functional theory single-point energy calculations were performed to generate potential energy surfaces dependant on rotation of Group 1 and 2 linkers in Sc₂BDC₃. The CASTEP (version 5.50 1) simulation code was used throughout, with starting coordinates taken from the ambient pressure, room temperature crystal structure determination by Graham et al., 2014. [30-32] The PBE DFT functional, augmented with the Tkatchenko-Scheffler (TS) dispersion correction scheme was employed to model the Hamiltonian operator, while the molecular wave function was generated with a plane-wave/pseudopotential basis set generated ‘on the fly’. [33, 34] Plane waves were expressed up to an energy cut-off of 600 eV, which gave convergence to within 3 meV per atom.

To save computational time, the experimentally determined structure of Sc₂BDC₃ was converted from space group symmetry Fddd (volume = 6238.25 Å³) to the primitive cell setting (volume = 1562.52 Å³). To allow the structure to relax without constraints, all symmetry was removed, giving a P1 unit cell. The structure was then subjected to an atom-only minimisation (i.e. unit cell parameters are held fixed at experimental values) using the BFGS algorithm (convergence criteria: maximum change in system
energy $2.0 \times 10^{-5} \text{ eV/atom}$ maximum force $0.05 \text{ eV/Å}$, and maximum root-mean square (RMS) atomic displacement $0.002 \ \text{Å}$. The resulting structure was then used to generate a series of models, where the two phenyl group linkers were subjected to rotations based on $10^\circ$ increments. These structures were obtained by calculating a best-fit plane through each phenyl ring using mass-weighted RMS distances. The axes of rotation were defined as parallel to these planes, allowing the remaining $4 \times \text{CH}$ fragments of the rings to be rotated as required (see Figure 5.3).

Figure 5.3 - Rotation of a single phenyl group. Best fit plane (rectangle), plane normal (arrow) and the 1,4 axis of rotation (dotted line) are indicated. The figure shows the phenyl ligand rotated by (A) $0^\circ$, (B) $45^\circ$ and (C) $90^\circ$. All other atoms remain fixed during the rotation.
5.4 Results and discussion

Immersion diffraction experiments and adsorption isotherms

The adsorption isotherms for alkanes on Sc₂BDC₃ obtained volumetrically at 298 K are shown in Figure 5.4. The straight-chain alkanes n-pentane, n-hexane and n-heptane show strong uptake at low partial pressures (0.14 – 0.18 mmol g⁻¹ at 40 mbar) indicating the molecules are taken up readily into the MOF. By contrast the geminal dimethylalkanes (2,2-dimethylbutane and 2,2,4-trimethylbutane) show very low uptakes (<0.02 mmol g⁻¹ at 40 mbar). These low uptakes are not unexpected, considering the bulky t-butyl groups at the end of the molecules which must prevent these from penetrating into the pores of Sc₂BDC₃.

![Figure 5.4 - Adsorption isotherms on Sc₂BDC₃ for un-, mono- and di-branched hydrocarbon species.](image)

The mono-branched 2-methylbutane and the vicinal dimethyl 2,3-dimethylbutane uptakes are intermediate between n- and geminal dibranched alkanes. In particular 2-methylbutane shows considerable uptake. By contrast, 2-methylheptane shows
very low uptake, possibly in part due to its low saturated vapour pressure at 298 K.
In order to understand the uptake behaviour of Sc2BDC3 at low pressures and
determine whether branched hydrocarbons can enter the pores under ambient
conditions, two immersion in situ single-crystal X-ray diffraction experiments were
performed, where a single-crystal of Sc2BDC3 was immersed in a linear alkane (n-
pentane) and a branched alkane (2-methylbutane) and in-situ diffraction data
collected.

Immersion in n-pentane induced subtle structural changes to the framework
structure. Though the adsorbed linear hydrocarbons could not be modelled
crystallographically, a rotation of 14° of the Group 2 BDC linkers was observed.
Together with a slight increase in the residual electronic density in the pores, these
immersion experiments suggest that upon soaking, Sc2BDC3 easily adsorbs linear
hydrocarbons. By contrast, no crystallographic evidence for uptake of the branched
and bulkier 2-methylbutane was obtained: when compared to the native Sc2BDC3
structure, neither structural changes in the framework nor significant increases in the
residual electron density in the pores were observed.

These observations expose the limitations of the in situ immersion diffraction
experiments. These measurements have an inherently low sensitivity due to the very
low uptake of guest species into the pores at ambient pressure and temperature
making these experiments extremely challenging for modelling guest species. In
order to increase uptake, a series of high-pressure single-crystal X-ray diffraction
experiments was performed to see whether very high pressures could be used to force
larger amounts of sterically hindered and oversized guest molecules into the pores.

**High-pressure inclusion experiments**

All alkanes listed in Table 5.1 were used as the pressure transmitting medium in high-
pressure single-crystal diffraction experiments on Sc2BDC3. In each case the pressure
was increased from ca. 0.2 GPa until the samples became amorphous. While still
crystalline, Sc2BDC3 was observed to retain its orthorhombic Fddd symmetry in all
cases. The results of the variation of unit cell volume are given in Figure 5.5. The
inclusion of molecules into MOFs is found not only to reduce the degree of unit cell contraction upon compression, but also to stabilize the frameworks against collapse. As discussed in Chapter 3, compression of Sc$_2$BDC$_3$ in methanol has little physical effect on the framework structure, rather the pores become super-filled with methanol molecules and guest-guest interactions throughout the channels stabilizes the MOF at high pressures.[32]

![Figure 5.5 - Unit cell volume as a function of pressure for the different hydrocarbons considered. Error bars are smaller than the symbols.](image)

For the experiments using n-pentane, which is known to be readily adsorbed, there is strong resistance to compression and the structure remains crystalline until 0.8 GPa. By contrast, for 2,2,4-trimethylpentane, amorphisation occurred immediately upon loading the cell at 0.2 GPa, and for the germinal 2,2-dimethylbutane the structure contracts strongly under pressure and loses crystallinity above 0.2 GPa, consistent with these molecules being too large to access the pores and stabilize the structure, even at elevated pressures. For all the other alkanes, the behaviour is intermediate, suggesting some pore filling occurs under pressure. For 2-methylbutane, when the
pressure was increased beyond 0.4 GPa the crystals became amorphous and underwent a change from colourless to black. As discussed in Chapter 3 a similar effect was observed upon compression with FC-77. When the crystals were removed from the DAC after releasing the pressure, in all cases the samples became colourless and fully crystalline again, which is consistent with previous reports.[32]

High-pressure single crystal diffraction data allowed us not only to monitor how the framework responded to external pressure, but also to understand how the framework adapted to increasing guest content. In the cases where guest uptake had occurred, the extra-framework electron density could be modelled by disordered alkane adsorbates. Some details of the measured crystal structures are given in Table 5.2, where the extra-framework electron density (modelled using the SQUEEZE algorithm within PLATON) is given in terms of adsorbate molecules per pore. In line with the adsorption data, these results confirm that n-pentane is most readily taken up whilst 2,2-dimethylbutane is not adsorbed at all. As well as locating extra framework electron density in the pores, these single crystal structures show that the Sc₂BDC₃ MOF can adapt to facilitate the uptake of alkanes through a ligand rotation.

This modification is best explained in terms of the native empty structure. Under ambient temperature and pressure conditions, Sc₂BDC₃ crystallises in the orthorhombic space group Fddd, having two independent BDC linker molecules (Groups 1 and 2) the phenyl rings of which are parallel to the a-axis (i.e. parallel to the principal framework channel direction). Upon uptake of either linear or di-branched hydrocarbons, the Group 2 BDC rings are rotated along [010] into two statically disordered (50:50 occupancy) positions (Figure 5.6a).
Table 5.2 Summary of rotation angle of BDC Group 2 linkers and pore content in the high-pressure Sc$_2$BDC$_3$ crystal structures for various hydrocarbon guest species calculated from the PLATON SQUEEZE routine

<table>
<thead>
<tr>
<th>Branching</th>
<th>Solvent</th>
<th>Structure reference</th>
<th>Pressure (GPa)</th>
<th>Rotation angle (°)</th>
<th>Electrons per unit cell</th>
<th>Number of molecules per pore</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono-branched</td>
<td>$i$-pentane</td>
<td>Sc$_2$BDC$_3$(i$p$)</td>
<td>0.4</td>
<td>52.4</td>
<td>292</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>2-methylheptane</td>
<td>Sc$_2$BDC$_3$(mh-I)</td>
<td>0.2</td>
<td>15.3</td>
<td>143</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sc$_2$BDC$_3$(mh-II)</td>
<td>0.5</td>
<td>28.2</td>
<td>183</td>
<td>0.35</td>
</tr>
<tr>
<td>secondary di-branched</td>
<td>2,3-dimethylbutane</td>
<td>Sc$_2$BDC$_3$(2,3-dmb-I)</td>
<td>0.2</td>
<td>10.9</td>
<td>125</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sc$_2$BDC$_3$(2,3-dmb-II)</td>
<td>0.4</td>
<td>21.2</td>
<td>204</td>
<td>0.51</td>
</tr>
<tr>
<td>unbranched</td>
<td>$n$-pentane</td>
<td>Sc$_2$BDC$_3$(np-I)</td>
<td>0.2</td>
<td>20.6</td>
<td>158</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sc$_2$BDC$_3$(np-II)</td>
<td>0.5</td>
<td>43.7</td>
<td>365</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sc$_2$BDC$_3$(np-III)</td>
<td>0.8</td>
<td>35.0</td>
<td>370</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>$n$-heptane</td>
<td>Sc$_2$BDC$_3$(nh-I)</td>
<td>0.3</td>
<td>46.7</td>
<td>208</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sc$_2$BDC$_3$(nh-II)</td>
<td>0.7</td>
<td>50.0</td>
<td>312</td>
<td>0.67</td>
</tr>
<tr>
<td>tertiary di-branched</td>
<td>2,2-dimethylbutane</td>
<td>Sc$_2$BDC$_3$(2,2-dmb)</td>
<td>0.2</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 5.6 - (a) Scheme of the ring rotation along [010] of Group 2 BDC with respect to the (001) plane. On the left, the native Sc$_2$BDC$_3$ structure, on the right, the high-pressure guest-included structure Sc$_2$BDC$_3$(ip). Only one of the statistically disordered rings is shown for clarity. (b) SAV (yellow) in one unit cell of Sc$_2$BDC$_3$. (c) SAV (yellow) in one unit cell of Sc$_2$BDC$_3$(ip). 2-Methylbutane molecules are not shown in (c) to allow clear representation of modified pore space.
This effect is most significant in the case of 2-methylbutane inclusion (henceforth referred to as Sc₂BDC₃(ip); Figure 5.6c and 5.7b), where the rings rotate by 52.4° (and -52.4° by symmetry) with respect to the (001) plane on which the Group 2 linkers lie in the empty Sc₂BDC₃. *Fddd* symmetry is maintained. The phase transition has a profound effect on the pore size and shape. Sections of adjacent triangular channels – originally partitioned by the Group 2 BDC ‘walls’ in the parent Sc₂BDC₃ structure amalgamate to give eight rhomboidal cavities per unit cell in the high-pressure Sc₂BDC₃(ip) phase (Figure 5.6b, 5.6c, and 5.8b).

The intermolecular distance between adjacent Group 2 BDC linkers along the *a*-axis in empty Sc₂BDC₃ is ~4.5 Å (CH···HC; normalized values), whereas in Sc₂BDC₃(ip) the distance between the two closest disordered BDC positions is ~6.3 Å. This significantly increases the depth of the pores, allowing the bulky 2-methylbutane molecules to sit in the isolated pores between adjacent rotated rings along [100]. The pore volume indicates that the volume of each large pore in the high-pressure phase is ~240 Å³, compared with ~137 Å³ for each of the two equivalent sections of triangular channel in the ambient pressure structure that merge, allowing the bulky 2-methylbutane molecules to be incorporated into the framework (Figure 5.7b).

A comparison can be made between these high-pressure guest-included Sc₂BDC₃ structures and the high pressure behaviour of ZIF-8.[20] In ZIF-8, a pressure-induced ring rotation was observed when using methanol as a hydrostatic liquid at 1.5 GPa, causing the volume (and accessible pore volume) to increase with pressure. However, the overall accessible pore volume in the different high-pressure structures of Sc₂BDC₃ is actually reduced by around 10%. Instead, the radical change in local pore structure shows that the ring rotation can be attributed to the shape of the guest molecule, not the requirement of the system to increase the pore volume.
Figure 5.7 - Crystal structures of (a) Sc$_2$BDC$_3$ with the included guest molecules of (b) 2-methylbutane (Sc$_2$BDC$_3$(ip)), (c) n-pentane (Sc$_2$BDC$_3$(np-I)), (d) 2,3-dimethylbutane (Sc$_2$BDC$_3$(2,3-dmb-II)), (e) n-heptane (Sc$_2$BDC$_3$(nh-II) and (f) 2-methylheptane (Sc$_2$BDC$_3$(mh-II)). Groups 1 and 2 are coloured blue and yellow, respectively. The disordered positions of the guests are shown in lighter grey for clarity.
Amorphisation of the crystal in 2-methylbutane occurs above 0.4 GPa, substantially lower in pressure than in methanol. As the 2-methylbutane-bearing structure at 0.4 GPa can no longer accommodate any more 2-methylbutane, it would appear that on increasing pressure further, direct compression and amorphisation occurs for Sc₂BDC₃(ip). Sc₂BDC₃(ip) does not therefore experience the stabilizing effect of channel ‘super-filling’ which occurs with methanol, which also occurs in other MOFs with one, two and three-dimensional channel connectivity.[16, 24, 35]

Larger di-branched hydrocarbons can also penetrate into the pores of Sc₂BDC₃ at high pressures. Using 2,3-dimethylbutane and 2-methylheptane as hydrostatic media, a similar transformation is observed (see Figure 5.7d and 5.7f), though in each case the rotation is not as significant as in Sc₂BDC₃(ip): 21.2° for 2,3-dimethylbutane and 28.2° for 2-methylheptane. This can be explained by the amount of alkane that is being adsorbed into the framework. In the case of Sc₂BDC₃(ip) one 2-methylbutane molecule is present in each pore at high pressure. On the other hand, at the highest pressure measured for both larger species (0.4 GPa for 2,3-dimethylbutane and 0.5 GPa for 2-methylheptane) the hydrocarbon uptake equates to less than half-occupancy for each guest molecule in the framework pores (see Table 5.2). For guests larger than 2-methylbutane a reduced uptake capacity results, which is coupled to a less substantial rotation angle of the Group 2 BDC ligands. This agrees well with trends observed in the gas adsorption experiments.

High-pressure diffraction experiments on n-pentane and n-heptane, show a similar structural transition to that observed with mono-branched secondary hydrocarbons. However the shape of the molecules and their location within the cavity results in distinct differences in the structural behaviour of Sc₂BDC₃. These differences are particularly evident between 2-methylbutane and n-pentane.

The longer chain and increased flexibility of n-pentane, in comparison to 2-methylbutane, causes the molecule to occupy additional adsorption sites, extending across both the existing channel space (along the [100] direction) and the deepened
voids between the rotated BDC rings (as shown in Figure 5.7c). The longer, narrower shape of n-pentane results in three key differences between the structural response of Sc₂BDC₃ to n-pentane and 2-methylbutane uptake at high pressure. Firstly, the Group 2 BDC rings initially do not rotate to the same extent as in Sc₂BDC₃(ip). There is slight variation over the pressure regime (from 20.8° in Sc₂BDC₃(np-I) to 35.0° in Sc₂BDC₃(np-III)), but the rotation of 54.6° in Sc₂BDC₃(ip) is far more extreme. Secondly, the framework channels do not become ‘closed’ in Sc₂BDC₃(np-I), as is the case in Sc₂BDC₃(ip). This is shown in Figure 5.8c and is a direct result of the lesser degree of BDC rotation in Sc₂BDC₃(np-I). Finally, and related wholly to the two previous points, the disordered sites of the n-pentane increase in occupancy as pressure is increased on the Sc₂BDC₃ crystal. Essentially, more n-pentane is forced into the framework as the pressure is increased, with a subsequent increase in rotation angle of the BDC linker. In the previous pressure study using methanol, an increase in occupancy of two disordered methanol adsorption sites could also be followed as a function of pressure, however no change in framework geometry occurred.
Chapter 5 – High-Pressure Inclusion of Hydrocarbons in Sc\textsubscript{2}BDC\textsubscript{3}

Figure 5.8 - Solvent accessible surface (yellow) in (a) Sc\textsubscript{2}BDC\textsubscript{3}, (b) Sc\textsubscript{2}BDC\textsubscript{3}(ip-I) and (c) Sc\textsubscript{2}BDC\textsubscript{3}(np-II) viewed down [110]. The channels in (b) but not (c) become closed as a result of the phase transition. Isopentane molecules are not shown in (b) and (c) to allow clear representation of modified pore space. SAV using the CCDC Mercury\textsuperscript{®} software.
Inclusion of n-heptane yields similar effects to those observed with n-pentane. However in this case, the rotation angle recorded for both n-heptane included structures, Sc:BDC$_3$(hp-I) and Sc:BDC$_3$(hp-II) is more pronounced, measuring 46.7° and 50.0° respectively. This results from the longer chain length which extends not only along the channels but also between them. Comparing the uptake of n-heptane (0.65 molecules per pore) with that recorded for the monobranch 2-methylheptane (0.35 per pore) shows again the different behaviour of unbranched and branched hydrocarbons upon inclusion into Sc:BDC$_3$.

Both in the case of n-pentane and n-heptane, crystallinity is maintained beyond 0.5 GPa, unlike in the case of branched hydrocarbons. With n-pentane it was possible to keep increasing the pressure without significant loss in the diffraction quality up until 0.8 GPa. Amidst a gradual loss of resolution, it is not until 1.7 GPa that amorphisation is complete, however, only unit cell dimensions could be obtained above 0.8 GPa. As mentioned previously, in both Sc:BDC$_3$(np-II) and Sc:BDC$_3$(np-III) the occupancy of the included n-pentane molecules gradually increases to 100%, and coincides with the Group 2 BDC rotation angle increase, resulting in a single molecule of n-pentane per rhomboidal pore. Thus, the possibility to continue filling the framework results in a delay in the amorphisation, showing a markedly different behaviour between the compression with branched and unbranched hydrocarbons.

Using 2,2-dimethylbutane or 2,2,4-trimethylpentane as hydrostatic media, no evidence of guest uptake was detected in Sc:BDC$_3$. Whilst for 2,2-dimethylbutane the only high-pressure crystal structure collected at 0.2 GPa (Sc:BDC$_3$(2,2-dmb)), revealed no obvious structural change. Additionally, the unit cell volume was substantially reduced; a clear indication of direct framework compression in tertiary branched hydrocarbons.

This indicates that tertiary branched alkanes are too big to enter the framework pores, even at high pressures, and that the secondary di-branched hydrocarbons represent the upper diameter limit for a guest species under pressure in Sc:BDC$_3$. This in
principle could enable Sc₂BDC₃ to act as a molecular sieve between secondary and tertiary branched alkanes under pressure.

The results show that the very high pressures in the DAC are required to achieve high adsorbate loadings of branched alkanes in Sc₂BDC₃. At these pressures, significant $P\Delta V$ work is available to give rise to rotation of phenyl groups of the linker and to maintain them in a rotated, ‘high energy’, state, to allow hydrocarbon uptake. At 0.1 GPa this is of the order of 10 kJ mol⁻¹, for example, increasing linearly with pressure.

To calculate the energy associated with the rotation of Group 2 linker phenyl groups, we performed density functional theory single-point energy calculations of the potential energy of rotation in 10° rotation increments (Figure 5.9). For observed rotations in the 10–50° range, energies of 5–20 kJ mol⁻¹ of linker are observed, which could readily be offset by the work performed on the included hydrocarbons in the GPa regime.

It is also of interest to understand why it is the Group 2 linker phenyl groups, and not those of the Group 1 linker, that rotate, especially when the adsorption of CO₂ is observed to cause a minor tilt of the Group 1 rings while the Group 2 ring remains unperturbed. Comparison of the rotation energies (Figure 5.9) indicates that there is a higher energy required for significant rotation of the Group 1 linkers. Consideration of the steric limitations of different BDC groups indicates that concerted rotation of equivalent and adjacent Group 1 linkers (to a greater degree than the minor rotation already reported) could result in unfavourably close edge-to-edge contacts (<1.25 Å) between aromatic rings. The Group 2 BDC has less steric restriction to rotate since all adjacent BDC linkers are Group 1. The larger Tkatchenko-Scheffler dispersion correction term for Group 2, especially at higher rotation angles, also indicates that there may be additional van der Waals stabilization, which is not the case for the Group 1 linkers.
Figure 5.9 - Relative unit cell energy as a function of rotational angle of Group 1 (green circles) and Group 2 (blue circles) BDC linkers. Solid lines denote values corrected with the Tkatchenko-Scheffler (TS) dispersion correction and dotted lines denote values without the dispersion correction.
5.5 Conclusions

In summary, this work shows how sterically ‘oversized’ hydrocarbon molecules, can be squeezed into accessible cavities of the small-pore MOF, Sc₂BDC₃, using high-pressure. Since C₅-C₈ hydrocarbons cannot penetrate or diffuse through the framework in the same way as shorter unbranched hydrocarbons, inclusion results in a structural phase transition which alters the shape and size of the individual pores with relatively little change to the overall porosity. As a result of the ring rotation, guest molecules of an awkward shape are able to be admitted. Since this transition is fully reversible (no damage, fractures or polycrystallinity is imparted on the crystal), this result is akin to ‘breathing’ mechanisms in frameworks, exemplifying how high-pressure X-ray diffraction can be used to probe the structural flexibility of MOFs, and is a powerful tool for understanding the structural effect of guest uptake. The framework responds differently to inclusion of linear, mono-branched, secondary di-branched or tertiary branched hydrocarbons and so this material may have application in alkane separations. For instance, mono-branched hydrocarbons can penetrate the framework void space under relatively moderate pressures, while tertiary branched hydrocarbons cannot. Similarly, only linear molecules are readily adsorbed under ambient conditions. Such a potential application of Sc₂BDC₃ in the high-pressure separation of alkane isomers would be facilitated by the complete reversibility of the adsorption/desorption process.
5.6 References


6.1 Synopsis

This final experimental chapter describes a new alternative approach to loading MOFs with gas molecules at high pressures. The technique, which uses liquefied gases of industrial relevance as the PTM in a DAC, is demonstrated to have considerable advantages over other gas-loading methods when investigating host-guest interactions. Loading Sc\textsubscript{2}BDC\textsubscript{3} with liquefied CO\textsubscript{2} reveals the presence of three fully occupied adsorption sites resolving previous inconsistencies between structural data and adsorption isotherms. Compression studies using liquid CH\textsubscript{4} demonstrates hyperfilling of the Sc\textsubscript{2}BDC\textsubscript{3} pores with CH\textsubscript{4} and two new high-pressure displacive and reversible phase transitions.

6.2 Introduction

The importance of understanding how guest molecules in metal-organic framework (MOFs) interact with each other and the framework they occupy upon adsorption, has been highlighted throughout the body of this work, and is particularly vital for the development and commercial application of MOFs in carbon capture and gas sequestration technologies.[1, 2]

Some of the current methods for probing these interactions include infra-red spectroscopy, solid-state NMR and others mentioned previously.[3, 4] Crystallographic studies, both X-ray and neutron diffraction, utilising various environmental cells have proven invaluable in determining the nature of host-guest interactions within MOFs and their guest-driven structural flexibility.[5] This is particularly important in the many cases where the uptake behaviour, which can include conformational changes in the framework itself, can be perturbed by the type and amount of guest adsorbed.[6, 7]

One of the main reasons why so little data is available is that experimentally locating gas molecules in MOFs is challenging. The gas molecules are usually disordered and exhibit high thermal motion which is often difficult to model crystallographically even when cooled close to the condensation temperature of the gas adsorbed. In-situ
cells like the one used in Chapter 4 have been developed for collecting crystallographic data whilst exposing a MOF to a gaseous environment at tens, or even hundreds of bars of pressure in an effort to saturate the pores with gas molecules. Yet even in this approach, the gas molecules are often difficult to model. Because of these challenges, despite the intensive research in carbon capture technologies, relatively few crystallographic studies have been reported where CO₂ molecules have been unambiguously located within MOFs.[8-18]

The use of condensed gases as pressure transmitting media (PTM) in diamond anvil cells (DACs) is commonplace in the fields of condensed matter physics and high-pressure mineralogy, particularly due to their excellent hydrostatic properties at very high pressures (> 10 GPa) relative to other common liquid PTM.[19, 20] He, Ar and Ne are typically used because they are chemically inert, whilst other gases have been studied for their diverse structural behaviour. High temperature and pressure phases of CO₂ and CH₄ are of interest for understanding planetary interiors for example, while the formation and decomposition of methane-hydrates, which are only stable at pressure, have been studied in great detail.[21, 22] Of course, both CO₂ and CH₄ are also of obvious industrial and environmental interest.

Combining the techniques developed in high-pressure science with the study of MOFs has been the purpose of this last piece work, leading to the high-pressure study of the MOF Sc₂BDC₃ (BDC = benzene-1,4-dicarboxylate) using both CO₂ and CH₄ as PTM. The active role that the PTM plays in high-pressure studies of porous materials, where the ability of the PTM to penetrate the framework can be used to “hyperfill” the pores, has been previously reported and exemplified in the previous chapter.[23] Additionally, earlier work on Sc₂BDC₃ using methanol as a PTM, showed how the pores were hyperfilled with methanol molecules at 16 kbar, achieving a guest density 2.5 times larger than possible under ambient pressure conditions.[24] Similarly, a previous high-pressure study on the zeolitic imidazolate framework, ZIF-8 (Zn(MeIm)₂, MeIm = 2-methylimidazole), showed how an unobserved framework conformation, driven by the inclusion of the PTM inside the framework, could be
used to explain a step in its adsorption isotherm observed for a number of gases and its increased loading capacity.[25-28]

In the case of Sc₂BDC₃, the work by Miller et al. and that described in Chapter 4, revealed interesting features worthy of further investigation.[29] Adsorption of CO₂ into Sc₂BDC₃ both at 1 bar and 235 K and above 3 bar at 298 K leads to a phase transition, which results in a change in space group symmetry from Fddd to C2/c. The transition is characterized by a subtle rotation of one of the two symmetry independent BDC linkers upon exposure to CO₂. This results in three symmetry independent linkers (Group 1, 2a and 2b) and gives rise to two crystallographically independent channels with one absorption site in each channel (Site 1 and Site 2, Figure 4.1 and Figure 4.2). Site 1 lies across two Group 2a linkers with host-guest C-H⋅⋅⋅O distances of ~ 2.9 Å and Site 2 is disordered over two positions and also has close C-H⋅⋅⋅O contacts that range from 2.87 to 2.98 Å. At 235 K and 1 atm, Site 1 and Site 2 are fully and half-occupied respectively, giving a calculated CO₂ adsorption capacity of ~ 3 mmol g⁻¹ which differs significantly from the experimentally measured maximum uptake of 6.5 mmol g⁻¹ from adsorption isotherm data.

On the other hand, on exposure to CH₄ no phase transition has been observed, with the framework retaining the orthorhombic Fddd symmetry.[29] Even at 9 bar and 230 K, Sc₂BDC₃ shows low affinity for CH₄, with two crystallographically-distinct adsorption sites (also termed Site 1 and Site 2) showing very low fractional occupancy (~ 0.15 and ~ 0.25 respectively for Site 1 and 2). This implied that there was potential available capacity in the channels for further adsorption, motivating the performance of high-pressure experiments on Sc₂BDC₃ with both CO₂ and CH₄ as the PTM.
6.3 Experimental

Synthesis

Single crystals of Sc$_2$BDC$_3$ were prepared following the synthetic procedure detailed in Chapter 3.

Gas loading of carbon dioxide

A single crystal of Sc$_2$BDC$_3$ was loaded together with a chip of ruby (for pressure calibration) into a modified DAC with 600 μm culet diamonds and a tungsten gasket. The cell was placed inside an in-house gas loading chamber based on that reported by Mills et al. (Figure 6.1).[30] The DAC is loaded into the gas loader in a pre-calibrated open position. The system was pressurised with CO$_2$ (BOC research grade 99.9% purity) to 2000 bar in the gas loader using a two stage compressor (the first stage of the compressor feeds the second stage with a gas pressure of 200 bar). Once pressurised, the DAC was closed via a gear system, closing the cell at 2 kbar, confirmed by ruby fluorescence and observation of the Raman signal of CO$_2$.

![Multistate gas compressor set up: (a) First stage of the compressor, (b) high-pressure chamber and (c) whole set up with second stage compressor under the high-pressure chamber.](image)

Figure 6.1 - Multistate gas compressor set up: (a) First stage of the compressor, (b) high-pressure chamber and (c) whole set up with second stage compressor under the high-pressure chamber.
Cryogenic loading of methane

A single crystal of Sc$_2$BDC$_3$ together with a chip of ruby (for pressure calibration) was loaded in a modified Merrill-Bassett DAC with 600 μm culet diamonds and a tungsten gasket. Springs were placed on the pins of the DAC and a calibration performed to determine the open and closed positions of the DAC. The DAC was then placed inside a cryogenic gas loading chamber (Figure 6.2), in the calibrated closed position and placed in a bath of liquid N$_2$ to equilibrate to 77 K. CH$_4$ (BOC 100 % research grade) was purged through the chamber until condensation occurred. The DAC was opened to a pre-calibrated open position in the bath of liquefied CH$_4$ and the sample chamber exposed for approximately 30 seconds before closing. The DAC was then removed from the bath and allowed to warm to room temperature. Pressure inside the cell was measured using the ruby fluorescence method to give an initial loading pressure of 3 kbar.

Figure 6.2 - Cryogenic loading chamber set up: a) side view showing the brass coils through which the CH$_4$ gas is pumped into the chamber, b) top view showing the inside of the chamber with a DAC immersed in liquid CH$_4$, with the whole set up surrounded in liquid nitrogen in a polystyrene box.
Data collection and processing

Single-crystal X-ray diffraction data for the CO2 loaded structure were collected on a modified version of the XIPHOS diffractometer utilising a microfocus Ag source with multilayer optics.[31] Data were collected using ϕ-scans in eight different settings of 2θ and ω in three different cell orientations with a frame time of 40 s. Single-crystal X-ray diffraction data for the CH4 loaded structures were collected on a Bruker APEX II diffractometer with graphite-monochromated Mo Ka radiation for pressure points at 3, 6, 10 and 12 kbar. For pressure data collected at 13, 18 and 25 kbar data were collected on station I19 at The Diamond Light Source, using synchrotron radiation of wavelength of 0.4859 Å on a four-circle Crystal Logic diffractometer equipped with a Rigaku Saturn 724+ CCD detector. In both cases, data were collected as ω-scans in eight settings of 2θ and ϕ with a frame time of 40 s and 1 s for both in-house and synchrotron data respectively.

Cell indexing and data processing were carried out using the Bruker APEX II suite.[32] Integration was carried out using the programme SAINT, with dynamic masks generated with ECLIPSE to account for the shading of the pressure cell. [32, 33] The absorption correction was carried out using both the program SHADE (to account for cell shading) and SADABS. [34, 35] Structure solution and space group determination were carried our using SHELXT for the structures at 3 and 13 kbar.[36] The final structure at 25 kbar was solved using SHELXS and space group determination determined using the program XPREP and checked using the ADDSYM routine within PLATON.[37]

Refinement

Refinements were carried out using SHELXL through Olex2.[38] 1,2 and 1,3 restraints distance were applied to the BDC linkers for the datasets collected above 10 kbar. All metal-ligand distances and angles, and all torsion angles were refined freely and thermal and vibrational similarity restraints applied to all non-hydrogen atoms.[39] H-atoms where placed geometrically, while phenyl rings were constrained geometrically in the two structures with Fdd2 and P21/c symmetry. For the Fddd and
For \( Fdd2 \) structures, H-atoms attached to methane C-atoms had four H-atoms added geometrically to form an idealised tetrahedral \( \text{CH}_4 \) molecule. The H-atoms were held by distance and angle restraints and their occupancy and thermal parameters linked to the C-atoms. The positions, occupancy and isotropic thermal parameters of the CH\(_4\) molecules were then allowed to freely refine. At higher pressures the refined occupancies increased beyond 100% yielding chemically unreasonable models, hence the thermal parameters and occupancies where held fixed, essentially placing dummy atoms to account for the electron density in the pores. Additionally, the residual electron density and pore volumes were calculated using the SQUEEZE algorithm in PLATON.[37] A summary of the main structural parameters can be found in Table 6.1.
Table 6.1  Main crystallographic information for the different phases of Sc₂BDC₃ as synthesised, with CO₂ and CH₄ at different pressures.

<table>
<thead>
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<th>Method</th>
<th>Sc₂BDC₃</th>
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<th>Sc₂BDC₃ CH₄ (3 kbar)</th>
<th>Sc₂BDC₃ CH₄ (6 kbar)</th>
<th>Sc₂BDC₃ CH₄ (10 kbar)</th>
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<td>7.8 mmol g⁻¹</td>
<td>9.49 mmol g⁻¹</td>
<td>10.31 mmol g⁻¹</td>
<td>10.2 mmol g⁻¹</td>
<td>-</td>
</tr>
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</table>

[^1] SAV – solvent accessible volume as calculated using the VOID routine in the PLATON software.
6.4 Results and discussion

High-pressure CO$_2$ inclusion

The CO$_2$ compression study on Sc$_2$BDC$_3$ was performed at a pressure of 2 kbar. Single-crystal X-ray analysis revealed that upon sealing the DAC, CO$_2$ entered the MOF, immediately inducing the expected $Fddd$ to $C2/c$ phase transition. At 2 kbar, CO$_2$ positions appeared similar to those previously observed by Miller et al., with both Site 1 and Site 2 occupied (Figure 6.3).[29] At 2 kbar, Site 1 was fully occupied, and Site 2 was observed to have an occupancy refining to 0.83(3). The partial occupancy of Site 2 had previously been justified as a form of static disorder, where the two symmetry-related positions of Site 2 could not be occupied simultaneously due to short (<2.2 Å) intermolecular O···O distances. However, as speculated in Chapter 4, at these extreme pressures, the distance between the two symmetry equivalent sites increased further to 2.46 Å, allowing for an increased occupancy of CO$_2$ at Site 2.

![Diagram of CO$_2$ included structure of Sc$_2$BDC$_3$.](image)

Figure 6.3 - View along the a-axis of the CO$_2$ included structure of Sc$_2$BDC$_3$. The positions of the three different adsorption sites (Site 1 in blue, Site 2 in yellow and Site 3 in lilac) as well as the disorder in the framework of Group 1 are shown.
Furthermore, a third site (Site 3) (similar to that reported in Chapter 4) was observed. However, at such extreme pressures Site 3, which is in the same channel as Site 1 but closer to the Group 1 linker, appears in two different orientations at 90° with respect to each other, disordered over a two-fold rotation axis (Figure 6.4). Both positions lie very close to each other (<0.2 Å apart), ruling out the possibility of both being occupied simultaneously. This was confirmed by the refinement of occupancies in the two orientations – 0.58(4) when the CO$_2$ molecule is aligned perpendicular to the channels (Site 3a), and 0.42(4) when parallel to it (Site 3b).

Site 3b closely resembles the orientation and position to Site 3 discussed in Chapter 4 at 2.998 Å away from Site 1, but Site 3a lies closer to the Group 1 BDC linkers. The close proximity between the phenyl rings and the CO$_2$ molecule induces a disorder of
the Group 1 BDC linker, which appears in two orientations (Figure 6.4). Refinement of the occupancy of the two orientations of the linker closely matches the obtained values for Site 3 CO₂ molecules (i.e. 0.56(4) and 0.44(4)) – indicating the disorder is induced by the presence of the new CO₂ site.

By modelling Site 3 and the re-ordering of Site 2, the calculated uptake of CO₂ in Sc₂BDC₃ equates to 6.2 mmol g⁻¹. This value is much closer to the maximum capacity of 6.5 mmol g⁻¹ reported by Miller et al., and much better than their previous estimate from their original structural work (of 3.4 mmol g⁻¹).[29] This approach therefore provides direct structural evidence of the expected packing re-arrangement of guest molecules required to reach maximum CO₂ capacity.

Application of further pressure beyond 6 kbar resulted in a significant loss of diffraction, most likely due to the freezing of CO₂. Nevertheless, the structural data already obtained exemplified the use of liquefied, near supercritical gases, as an excellent method for “hyper-filling” MOFs, to the extent of allowing the location of all the adsorption sites, including ones not previously visible with X-ray diffraction.

**High-pressure CH₄ inclusion**

CH₄ was loaded using a similar principle to CO₂ but using a different method: cryogenically cooling CH₄ to liquefy into the sample chamber of a standard Merrill-Bassett DAC before sealing at 3 kbar (Figure 6.2). The initial loading showed the immediate inclusion of CH₄ molecules inside the framework, and two adsorption sites were found in similar positions to those previously reported but now fully occupied.[29] Site 1 was close to the Group 1 linker (C-H···H-C shortest contact of 2.62 Å), and Site 2 and its symmetry equivalent positions appeared next to Group 2 linkers (C-H···H-C shortest contact of 2.44 Å). Refinement of CH₄ molecules including the hydrogen positions was possible, a rarity in gas adsorption structural studies, and even rarer for high-pressure phases of CH₄ at much higher pressures, where the molecules tend to show several rotational degrees of freedom.[40] The data collected at 3 kbar provided an excellent model for the estimation of the adsorbed CH₄ from the refined occupancies (0.91(2) for Site 1 and 0.68(2) for Site 2) corresponded to 7.8
mmol g⁻¹, beyond the uptake capacity of 6.8 mmol g⁻¹ previously reported for Sc₂BDC₃. The increased uptake shown here, beyond what was measured previously provides further evidence of the hyper-filling of the framework at elevated pressures.

Figure 6.5 - Change in unit cell parameters of native Fddd phase of Sc₂BDC₃ as a function of pressure up to 18 kbar: a) Volume, b) a-axis, c) b-axis and d) c-axis.

It was possible to continue the compression study to 25 kbar before freezing of the CH₄ occurred, resulting in a loss of hydrostaticity and deterioration of diffraction quality. Up until 10 kbar the framework remained unaltered, with CH₄ occupancy of both sites increasing until all sites were fully occupied, yielding a maximum capacity of 10.7 mmol g⁻¹. A small increase in the unit cell volume of <1% was observed at 3 kbar, which is a frequent observation in other high-pressure inclusion studies on other MOFs including ScBDC₃.[24, 41] As seen with the inclusion of methanol, the expansion seemed to rely mostly on an increase along the a-axis, which corresponds to the channel directions (Figure 6.5). The continued increase of the a-axis with
increasing pressure is in line with further CH₄ being forced inside the framework, but overall the unit cell volume started to decrease above 6 kbar.

At 10 kbar, an increase in the libration of both Group 1 and 2 BDC linkers was observed, suggesting both linkers were adopting more than one orientation. On increasing pressure to 12 kbar, the appearance of new weak reflections indicated the onset of a phase change, which is clear at 13 kbar and results in a tripling of the b-axis and reduction in symmetry to Fdd2 (Figure 6.6 and 6.7). On increasing pressure further to 25 kbar, another displacive phase transition occurs to a previously unobserved form of Sc₂BDC₃ (with the same topology), which has monoclinic symmetry (space group P2₁/c).

![Figure 6.6](image1.png)

*Figure 6.6 - Precession images showing the 1kl plane of the CH₄-included Sc₂BDC₃ datasets at different pressures. The gradual phase transition that causes a tripling of the F-centred orthorhombic cells can be seen by the appearance of additional reflections along the b-direction.*

![Figure 6.7](image2.png)

*Figure 6.7 - Comparison of the two unit cells of the Fddd phase (left) and the Fdd2 phase (right), viewed along the a-axis to show the tripling along the b-axis.*
Both phase transitions change the pore structure of Sc$_2$BDC$_3$. At 13 kbar, the transition from $Fdd$ to $Fdd2$ results in an increase from one to three different Sc environments. The tripling of the $b$-axis and lowering in symmetry is driven by the rotation of some of the ScO$_6$ octahedra, with one rotating clockwise, the other anti-clockwise and the last remaining largely unaltered (Figure 6.8). On increasing pressure further to 25 kbar, the transition from $Fdd2$ to $P2_1/c$ causes a further rotation of the two symmetry independent ScO$_6$ octahedra. In the final phase, all octahedra are twisted, allowing Sc$_2$BDC$_3$ to adopt a higher density form. Analysis of the subgroup-group relations of the two phases showed that the transition from $Fdd2$ and $P2_1/c$ symmetry is forbidden and must go via an unobserved intermediate phase, possibly with $Fddd$ symmetry.[42]

These structural changes are coupled to a marginal reduction in the percentage pore volume of Sc$_2$BDC$_3$ – reducing from 34.9% to 34.8 % from 10 to 13 kbar respectively, followed by a more significant decrease to 29.2 % in the final phase at 25 kbar. On increasing pressure to 13 kbar, the refined occupancies of the CH$_4$ molecules decreased, indicating that the amount of CH$_4$ in the pores started to reduce on undergoing the first phase transition. The driving force for the formation of the high-pressure phases above 10 kbar would therefore appear to be to form denser crystalline phases of Sc$_2$BDC$_3$, with CH$_4$ trapped in the pores.

Atomic positions for the CH$_4$ sites were unambiguously determined for all three phases. The initial two CH$_4$ sites, which become ten independent CH$_4$ positons in the $Fdd2$ structure, revert back to six different sites in the $P2_1/c$ phase. In both phases, two different sites per channel were maintained, with a similar arrangement to those observed in the original $Fddd$ structure. From fully occupied sites in the $Fddd$ structure at 10 kbar, 5 out of the 10 sites in the $Fdd2$ structure at 13 kbar refine to an occupancy of ca. 0.9, revealing a reduction in the number of CH$_4$ molecules per channel upon increasing pressure (Table 6.2). Unfortunately, extracting definitive conclusions from the pore content analysis in the $P2_1/c$ phase was not possible, since data quality was seriously compromised at such high pressures, partly due to CH$_4$ having frozen around the crystal. For this reason, the above mentioned evidence of a reduction in
pore volume is the only indication of reduced pore content in the final $P2_1/c$ phase. On decreasing pressure, and recovering the crystal from the pressure cell, the crystal reverts to the original $Fddd$ structure.

Table 6.1 - Table outlining the pore content analysis of CH$_4$ in Sc$_2$BDC$_3$ at high-pressure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Refined occupancies</th>
<th>CH$_4$ molecules per unit cell</th>
<th>uptake (mmol/g$^\text{\textsuperscript{a}}$)</th>
<th>SQUEEZE</th>
<th>CH$_4$ molecules per unit cell</th>
<th>uptake (mmol/g$^\text{\textsuperscript{a}}$)</th>
<th>Volume (Å$^3$)$^\text{\textsuperscript{b}}$</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc$_2$BDC$_3$CH$_4$ (3 kbar)</td>
<td>S1 = 0.91(3) S2 = 0.09(2)</td>
<td>36.36</td>
<td>7.81</td>
<td>333</td>
<td>32.1</td>
<td>6.90</td>
<td>2240</td>
<td>35.75</td>
</tr>
<tr>
<td>Sc$_2$BDC$_3$CH$_4$ (6 kbar)</td>
<td>S1 = 1.00(4) S2 = 0.88(2)</td>
<td>44.17</td>
<td>9.49</td>
<td>371</td>
<td>34.9</td>
<td>7.50</td>
<td>2333</td>
<td>37.41</td>
</tr>
<tr>
<td>Sc$_2$BDC$_3$CH$_4$ (10 kbar)</td>
<td>S1 = 1 S2 = 1</td>
<td>48</td>
<td>10.31</td>
<td>379</td>
<td>37.4</td>
<td>8.03</td>
<td>2242</td>
<td>36.15</td>
</tr>
<tr>
<td>Sc$_2$BDC$_3$CH$_4$ (13 kbar)</td>
<td>S1 = 0.95(3) S2 = 1.53 = 0.98(3) S4 = 1 S5 = 0.92(3) S6 = 1 S7 = 0.95(3) S8 = 1 S9 = 0.93(3) S10 = 1</td>
<td>138</td>
<td>9.88</td>
<td>684</td>
<td>68.4</td>
<td>4.90</td>
<td>6373</td>
<td>34.77</td>
</tr>
<tr>
<td>Sc$_2$BDC$_3$CH$_4$ (25 kbar)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>839</td>
<td>29.26</td>
</tr>
</tbody>
</table>

$^\text{a}$ SF - Site $\tau$

$^\text{b}$ Volume corresponds to the solvent accessible volume defined in Table 6.1
Figure 6.8 - Structural transitions upon high-pressure compression of Sc$_2$BDC$_3$ in CH$_4$. Red and blue arrows represent the rotation of the ScO$_6$ octahedra for each phase, with red representing anti-clockwise motion and blue clockwise. CH$_4$ adsorption sites are coloured by symmetry equivalence, with 2, 10, and 6 independent sites in the Fddd (left), Fdd2 (middle) and P2$_1$/c (right) respectively. Red numbers represent the different channel types present in each phase change.
6.5 Conclusions

Overall, these results highlight the potential of using gases as PTM in high-pressure single-crystal diffraction experiments to explore the maximum gas uptake of porous MOFs at room temperature using laboratory single crystal X-ray diffractometers. Not only is it possible to determine adsorption sites within the pores, but the technique also reveals sites unoccupied at lower pressures, where low uptake or large thermal motion may have made determining guest positions within the pores extremely challenging, or impossible. These cryogenic loading DAC studies can be of direct relevance to possible applications of MOFs at high pressures, such as ultra-high performance liquid chromatography (UPLC) or the storage of mechanical energy.[43] Finally, this is a new experimental approach to monitoring gas uptake with associated changes in the framework, which are expected to be widely applicable to other MOFs and help obtain improved atomistic models of the gas molecules inside the pores.
Chapter 6 – Extreme-Pressure Loading of Fuel Related Gases into Sc₂BDC₃

6.6 References

32. Bruker. 2007, Bruker AXS Inc.: Madison, Wisconsin, USA.
34. Parsons, S., SHADE. 2004: The University of Edinburgh, Edinburgh, UK.
- Chapter 7 -

Concluding Remarks
Looking at the main body of this thesis, the main achievements can be summarised by sub-dividing the successes of each of the experimental chapters.

Starting with Chapter 3, in which the mechanical properties of five Sc-based MOFs have been analysed, including their hardness, elastic modulus and bulk modulus. The results indicate that, in general, these materials are close to the regime of the hardest known MOFs with relatively high elastic moduli. Correlations between structural features such as their solvent accessible volume or their porosity are in line with similar studies on MOFs, indicating materials with smaller voids tend to be harder and with a higher elastic modulus. However, comparison with other families of MOFs confirm that the chemical nature of the framework, including its connectivity and type of metal centre, have a much more significant effect on the hardness and elastic properties. In terms of bulk compressibility, Sc-based frameworks showed a much more varied response, ranging from significantly high bulk moduli and low pressure amorphisation for the more porous examples, to intermediate compressibility and higher resilience to amorphisation for the densest MOFs. However, further work is required in this area; particularly owing to the varied response the choice of pressure transmitting medium can have on the compressibility of porous materials.

The fourth chapter built upon previous structural studies on the CO$_2$ adsorption of ScBDC$_3$, confirming that uptake of CO$_2$ is similar at ambient temperature compared to previous low-temperature crystallographic studies. Work on Sc(BDC-NH$_2$)$_3$ has also provided further insight into the benefits of functionalising MOFs with amino groups to enhance CO$_2$ uptake within the framework, highlighting the role of NH$_2$:CO$_2$ guest-host interactions in the increased uptake of CO$_2$ at lower pressures and room temperature. The experiments performed using gas mixtures have also provided a novel approach in examining the selective uptake behaviour of both frameworks, confirming the potential application of these two MOFs in CO$_2$/CH$_4$ separation technologies.
Chapter 7 – Concluding Remarks

The work carried out in Chapter 5 provides extensive examples of the varied response the pressure transmitting medium (in this case, a series of linear and branched hydrocarbons) can have on the structure of Sc\textsubscript{2}BDC\textsubscript{3} under compression in a DAC. It has allowed correlating the extent of the pore modification to their shape and size and degree of branching. It has also been possible to then link the framework behaviour on uptake of hydrocarbons at high‐pressures with the hydrocarbon gas adsorption isotherms of Sc\textsubscript{2}BDC\textsubscript{3}, confirming the insights high‐pressure crystallographic analysis can bring to understanding the adsorption properties of MOFs.

The final chapter has brought together some of the principles outlined in the previous chapters, together with the well‐established techniques of gas loading (in this case, CO\textsubscript{2} ad CH\textsubscript{4}) into a DAC along with Sc\textsubscript{2}BDC\textsubscript{3}, in order to open a novel avenue to explore gas inclusion in microporous materials. One of the advantages of such an approach is the possibility of locating and being able to model accurately adsorption sites that can be hard to find using current gas cell methodologies. In addition it provides a new way of exploring the structural flexibility of MOFs by bringing the possibility of performing high‐pressure crystallography with a host of different gases as pressure transmitting media.

In all, this thesis has touched upon and furthered the techniques used to characterise \textit{in situ} guest inclusion in MOFs. The work has focused on Sc‐based frameworks and in particular on Sc\textsubscript{2}BDC\textsubscript{3}, since it has shown very interesting responses on uptake of different guest, perhaps due to its comparatively small pore size, good crystal quality and its stable nature. There is, however, further evidence that many of the approaches outlined here are applicable and have indeed been applied to other MOFs. Thus it is likely that further utilisation of these techniques will improve and further the understanding of adsorption processes in microporous materials.