Solid State NMR Spectroscopic Studies of Metal-Organic Frameworks

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Graduate Program in Chemistry
A thesis submitted in partial fulfillment of the requirements for the degree in Master of Science
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Solid State NMR Spectroscopic Studies of Metal-Organic Frameworks

(Thesis format: Integrated Article)

by

Peng He

Graduate Program in Chemistry

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

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Abstract

Metal–organic frameworks (MOFs) are a class of novel porous materials with a wide range of chemical applications. Structural characterization is important because understanding the relationship between the properties of these industrially relevant materials and their structures allows one to develop new applications and improve current performance. In this thesis $^{17}$O solid state NMR (SSNMR) spectroscopy is used to differentiate chemically and, under favorite circumstances, crystallographically nonequivalent oxygens and to follow the phase transitions in MOF-based materials. Several cost-effective approaches were used to prepare $^{17}$O-labelled MOFs. The metal centers of MOFs, including $^{47/49}$Ti, $^{67}$Zn, $^{91}$Zr, $^{115}$In and $^{139}$La, are also studied by SSNMR spectroscopy. It is demonstrated that SSNMR of metal ions is sensitive to the environment of metal cations. As a result, SSNMR is a useful tool to refine MOF structure, differentiate non-equivalent metal sites and probe the local structure of metal cations. SSNMR spectroscopy of the metal ions should be added to the arsenal of the techniques for MOFs characterization.

Keywords

Solid state NMR, MOFs, QCPMG, unreceptive nuclei, ultrahigh field, $^{17}$O-enrichment, metal center cation, CASTEP, Gaussian.
Co-Authorship Statement

This thesis contains materials from a previously published manuscript (Peng He, Jun Xu, Victor V. Terskikh, Andre Sutrisno, Heng-Yong Nie and Yining Huang. Identification of Nonequivalent Framework Oxygen Species in Metal-Organic Frameworks by $^{17}$O Solid-State NMR, *J. Phy. Chem. C* **2013**, *117*(33), 16953-16960). Dr. Yining Huang was the corresponding author on the presented paper and was responsible for the supervision of Peng He over the course of his Master of Science study. For copyright releases see the Appendix.

Qi Shi and Zhengwei Song (Taiyuan University of Technology) are credited for preparing the Zn-MOFs samples used in Chapter 3.
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<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>B3LYP</td>
<td>Becke’s 3-parameter hybrid density exchange functional with Lee, Yang and Parr correlation functional</td>
</tr>
<tr>
<td>BDC</td>
<td>1,4-benzendicarboxylate</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2’-bipyridyl</td>
</tr>
<tr>
<td>BTC</td>
<td>1,3,5-benzenetricarboxylate</td>
</tr>
<tr>
<td>CP</td>
<td>cross-polarization</td>
</tr>
<tr>
<td>CSA</td>
<td>chemical shielding anisotropy</td>
</tr>
<tr>
<td>ct</td>
<td>contact time</td>
</tr>
<tr>
<td>CT</td>
<td>central transition</td>
</tr>
<tr>
<td>DMBIM</td>
<td>5,6-dimethylbenzimidazolate</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>EFG</td>
<td>electric field gradient</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier transformation</td>
</tr>
<tr>
<td>IM</td>
<td>imidazole</td>
</tr>
<tr>
<td>IRMOF</td>
<td>isoreticular metal-organic framework</td>
</tr>
<tr>
<td>MAS</td>
<td>magic angle spinning</td>
</tr>
<tr>
<td>MIM</td>
<td>2-methylimidazolate</td>
</tr>
<tr>
<td>MIL</td>
<td>materiauxs de l’Institut Lavoisier</td>
</tr>
<tr>
<td>MOF</td>
<td>metal-organic framework</td>
</tr>
</tbody>
</table>
phen 1,10-phenantroline

ppm parts per million

QCPMG quadrupolar Carr-Purcell-Meiboom-Gill pulse sequence

RHF restricted Hartree-Fock

SBU secondary building units

SSNMR solid state nuclear magnetic resonance

ST satellite transition

TGA thermographic analysis

UiO University of Oslo

WURST wideband uniform-rate smooth truncation

XRD X-ray diffraction

ZIF zeolitic imidazolate framework
Chapter 1

1 General Introduction

1.1 MOFs

1.1.1 Composition of MOFs

Metal-Organic frameworks (MOFs) are a new family of porous solids, emerged approximately two decades ago and have been developed into a fruitful research field since then. MOFs are organic-inorganic hybrid solids with infinite, but uniform framework structures built from organic linkers and inorganic metal cation or metal-containing cluster centers. Following the tradition of zeolite science, some researchers have used an acronym of the laboratory where the MOFs were prepared to name them.\(^1\) For example, some MOFs that appear in this report are named as MIL (materiaux de l’Institut Lavoisier), UiO (University of Oslo) and HKUST (Hong-Kong University of Science and Technology).

Before the emergence of MOFs there were only two types of porous solid materials that were widely applied in industry, zeolites and carbon-based materials. Zeolites and activated carbons are now widely used in industry, reflecting the importance of porous materials. Since mid-1990s, MOFs have been regarded as advanced porous materials thanks to their regularity, rigidity/flexibility, variety and designability in both structure and properties. There are enormous possibilities of combining inorganic and organic moieties to yield a porous material compared with traditional inorganic and carbon-based porous materials. Thus MOFs provide scientists with more unique properties, including high thermal stability, permanent porosity, a flexible framework and exceptionally high surface areas, which are important to many applications in selective adsorption\(^1\), catalysis\(^2\), luminescence\(^3\), chemical sensors\(^4\), drug delivery\(^5\) and magnetism\(^6\).

The last decade has seen an explosive increase in new MOFs. In order to have a better understanding of MOFs, it is necessary to classify them into different categories based on
their structural differences. Many MOFs are classified into several series of MOFs for the similarities in structure. For example, IRMOFs (isoreticular metal-organic frameworks) are a series of MOFs that display primitive cubic (pcu) net topology, which resembles the boron net of CaB$_6$.

IRMOFs are based on prototypical IRMOF-1 and numerous other extended/functionalized analogues assembled from the 6-connected octahedral basic zinc acetate molecular building block and linear dicarboxylates of various lengths and functionalities. It is worth introducing the structure of IRMOF-1, which is also denoted MOF-5, to better understand the construction of IRMOFs. The formula of IRMOF-1 is Zn$_4$O(BDC)$_3$ (BDC: benzenedicarboxylate). Zn$^{2+}$ is coordinated by three carboxylate oxygens and one μ$_4$-O$_2^-$, as Figure 1.1a shows. ZnO$_4$ tetrahedra form secondary building units (SBUs), which connect by sharing a μ$_4$-O$_2^-$ to form a tetra-SBU cluster (Figure 1.1b). The clusters are connected by BDC linkers extending to three dimensions to form a finite framework (Figure 1.1c).

Figure 1.1 Frameworks (a), a pore surrounded by eight tetra-SBUs clusters (b) and Zn coordination environment (c) of IRMOF-1.

Another important series is zeolitic imidazolate frameworks (ZIFs), which are a series of porous crystalline materials consisting of tetrahedral SBUs and imidazolate (IM) linkers. The tetrahedral SBUs are ZnN$_4$ and CoN$_4$ tetrahedra. The organic linkers are limited to IM and its derivatives such as benzimidazolate and 5-chlorobenzimidazole. The structure of ZIFs shares similarity with that of zeolites, which has been widely used in industry. In ZIFs, IM bridges make an Zn–IM–Zn angle close to 145°, which is
coincide with the Si–O–Si angle that is preferred and commonly found in many zeolites. Transition metals (Zn, Co) of ZIFs replace tetrahedrally coordinated atoms (for example, Si) of zeolites, and imidazolate linkers replace oxygen bridges.\textsuperscript{11} Compared with zeolites, a striking feature of ZIF is that the structure is determined by the interactions between SBUs and linkers, rather than by the structure directing agents used in zeolite synthesis. As a result, systematic variations of linker substituents have yielded many different ZIFs that exhibit known or predicted zeolite topologies.\textsuperscript{11} A good example of ZIFs is ZIF-8, which is a promising candidate for gas storage for its tunable pore size, chemical stability and thermal robustness. Figure 1.2a shows the framework of ZIF-8, which possesses a pore in the middle. In ZIF-8, Zn is coordinated by four nitrogens from four 2-methylimidazolate linkers (Figure 1.2c) and form ZnN\textsubscript{4} tetrahedra, which connect with each other through linkers (Figure 1.2b).

Figure 1.2 Framework (a), connection of ZnN\textsubscript{4} tetrahedra (b) and Zn coordination of ZIF-8.

There are also some other important series such as MIL and UiO. Unlike IRMOFs or ZIFs, these series do not have very strict definitions. MOFs are classified into a certain series either because they are synthesized by the same research group or because they share structure similarities. For example, many MOFs of MIL series are discovered by Ferey and Serre \textit{et al}. They employed Group 13 elements as metal centers and BDC/BTC (BTC: benzenetricarboxylate) as organic linkers.\textsuperscript{12-18} Another example is UiO-66, 67 and
68, where metal cations are all Zr\(^{4+}\) while organic linkers are BDC, BPDC (4,4’-biphenyldicarboxylate) and TPDC (4,4’,4’’-triphenyldicarboxylate).\(^{19}\) Such common features belonging to each series help us understand these MOFs, but are not crucial requirements.

Besides different MOF series, the concept of secondary building units (SBUs) can serve as an organizing concept for the classification of the MOF structures into their underlying topology\(^20\). The construction of SBUs depends on the properties of metal cations including the d electron configuration and lone electron pairs. Numerous SBUs have been found and display diversity. Tranchemontagne \textit{et al} reported the connectivity and composition of 131 SBUs.\(^{20}\) Among the many species of SBUs, such as triangular, square pyramid and trigonal prism SBUs, two typical constructions, tetrahedron and octahedron, are widely present in MOFs. Figure 1.3 shows ZnO\(_4\) tetrahedron and AlO\(_6\) octahedron.

![ZnO\(_4\) tetrahedron (a) and AlO\(_6\) octahedron (b).](image)

MOFs can also be classified based on the structure of organic linkers. In many organic linkers, carboxylate is used to coordinate metal cations and build SBUs. Figure 1.4 displays three typical carboxylate linkers. In some MOFs, amide groups are employed to bond metal cations via nitrogen atoms. For example, in In(BDC)\(_{1.5}\)(bipy), the nitrogens of 2,2’-bipyridine (bipy) molecules bond to In\(^{3+}\).\(^{21}\) In ZIFs, nitrogens of imidazolate play the role in forming SBUs with metal cations.
1.1.2 Various oxygen species in MOFs

Many of the key questions concerning the property of MOFs require an understanding of the structure and bonding, involving oxygen atoms which usually appear at key positions in the structure. There are various species of oxygens in MOFs. Various carboxylate ligands are used to coordinate metal cations and build SBUs in many MOFs. Oxygen present in the carboxylate ligands is a key component in such MOFs. In many MOFs, bridge hydroxyl (μ₂-OH$^{22}$ and μ₃-OH$^{23}$), oxygen anion (μ₃-O$^{2-}$ and μ₄-O$^{2-}$)$^{8,14}$ and water molecules$^{21}$ bond to metal centers. Certain organic linkers have phenol groups, where oxygens can also bond to metal center cations upon deprotonation.$^{24}$

1.1.3 Metal center cations in MOFs

Metal cations are the center of secondary building units (SBUs) in MOFs. The local structure of metal center cations, such as coordination number and coordination geometry, has profound influence on the structure and potential application of MOFs. For example, Zn$^{2+}$ is usually four-coordinated in MOFs. As a result, Zn based MOFs often display tetrahedral networks. Al$^{3+}$ and In$^{3+}$, on the other hand, are six-coordinated and form octahedral SBUs in MOFs. In UiO-66, Zr$^{4+}$ cations are eight-coordinated and form big and complicated SBUs (Zr₆O₄(OH)₄ octahedra)$^{25}$. In MIL-140, however, Zr$^{4+}$ cations are seven coordinated and form infinite Zr oxide chains instead of isolated SBUs.$^{14}$ The coordination number of La$^{3+}$ can reach nine$^{26}$ due to its large radius. Metal cations usually
form single-center SBUs, but Cu$^{2+}$ may form a copper dimer with a short Cu-Cu distance.$^{27,28}$

Besides those in the center of polyhedral SBUs, some metal centers are unsaturated, and located on pore surface exposed to the channel. The open metal sites are typically obtained by removing solvent molecules (e.g. H$_2$O, DMF) losly occupying a coordination site upon desolvation.$^{29}$ Open metal sites can offer extra and usually strong binding sites to guest molecules.$^{30}$ A good example is CPO-27-Mg, which bears open Mg$^{2+}$ site upon activation. Figure 1.5a shows the framework of Mg in CPO-27-Mg. Mg$^{2+}$ is five-coordinated upon removing the coordinated water molecule (Figure 1.5c) and the open metal site is exposed to tunnel (Figure 1.5b). The strong interaction between the open metal site and CO$_2$ makes CPO-27-Mg an extraordinary MOF for CO$_2$ adsorption.$^{31}$

Figure 1.5 Structure (left) and coordination of Mg (middle and right) of CPO-27-Mg.

1.2 Solid state NMR study of MOFs

1.2.1 $^{17}$O SSNMR study of MOFs

In this thesis, I synthesized $^{17}$O-enriched MOFs: MIL-53(Al), Zr-Uio-66 and MIL-96(Al). These three MOFs are important and frequently studied due to their unique structure features. Ultrahigh magnetic field 21.1 T is utilized to get better $^{17}$O solid state NMR (SSNMR) spectra, from which NMR parameters are extracted and spectral signatures of various nonequivalent framework oxygen species are established.
1.2.2 SSNMR study of metal center cations in MOFs

In this thesis, I synthesized MOFs whose metal centers are Ti (MIL-125(Ti)), Zr (MIL-140A), In (MIL-68(In), In(BDC)1.5(bipy) and In(BTC)(H2O)(phen)) and La (La2(BDC)3(H2O)4 and La2(C4H4O4)3(H2O)2·(H2O)). Shi et al provide several Zn-MOFs including TIF-1, TIF-5, Zn-zni and Zn-dia. Ultrahigh filed of 21.1 T is utilized to acquire good SSNMR spectra of these metal center cations, which reveal the relationship between the structure and NMR parameters. Magnetic fields of 14.1 T and 9.4 T are also utilized to acquire 139La and 115In spectra of La-MOFs and In-MOFs. The spectra acquired at multiple fields help get accurate NMR parameters.

1.3 Solid state NMR

1.3.1 Physical background of SSNMR

The foundation of the technology of solid state NMR (SSNMR) is the spin of nuclei. Spin is a form of angular momentum which is not induced by the rotation of the particle under external stimulation, but an intrinsic property of the nuclei, decided by the number of nuclear spin angular momentum \((I)\). The angular momentum \(P\) of a spin-\(I\) nuclei can only have \((2I+1)\) projections on a reference axis, which is z axis. \(P_z = m_I \hbar\), where \(m_I\) is the magnetic quantum number with only \((2I+1)\) values: \(I, I-1, I-2, \ldots, -I+1, -I\). The magnetic moment of a nucleus \((\mu)\) is linearly related to its spin angular momentum by magnetogyric ratio \((\gamma)\), so the projection of \(\mu\) is also quantized: \(\mu_z = \gamma P_z = \gamma m_I \hbar\).

For some isotopes, like \(^{12}\)C and \(^{16}\)O, \(I\) equals to 0, leaving the nuclear with no angular momentum (i.e. no nuclear movement), thus no NMR spectra. For \(^1\)H and \(^{13}\)C, \(I\) equals to \(\frac{1}{2}\), so there are only two energy levels: \(\frac{1}{2} \hbar\) and \(-\frac{1}{2} \hbar\) and there is only one energy gap for NMR measurement. And the distribution of positive charges in the nucleus is spherical. But for many other nuclei with \(I > \frac{1}{2}\), such as \(^{17}\)O \((I=5/2)\), \(^{23}\)Na \((I=3/2)\) and \(^{115}\)In \((I=9/2)\), the distribution of positive charges in the nuclei is non-spherical and there is a nuclear electric quadrupole moment. The quadrupole moment interacts with non-zero electric field gradient (EFG) which makes the NMR patterns much boarder.
These energy levels are generally degenerate in the absence of magnetic field, but when locating in magnetic field \((B_0)\), they will split. Assuming only Zeeman interaction between \(\mu\) and \(B_0\) takes effect, the energy of interaction between the magnetic moment and the applied magnetic field is:

\[-\mu \cdot B_0 = -\mu_z B_0 = -\gamma m_I \hbar B_0 \quad (m_I= I, I-1, I-2, \ldots, -I+1, -I).\]

So the energy gap induced by Zeeman interaction is proportional to both \(\gamma\) and \(B_0\). Therefore, higher \(\gamma\) value of a nucleus results in a larger energy separation between the two energy levels and makes it easier to detect its NMR signal. Also, for a given nucleus, higher magnetic fields would have the same effect. For example, in a magnetic field \(B_0 = 9.4\) T, the energy separation of \(^1\text{H}\) corresponds to a frequency of 400 MHz; when \(B_0 = 21.1\) T, the energy separation of \(^1\text{H}\) corresponds to 900 MHz.

Zeeman interaction, however, is not the only interaction that has effect on NMR patterns. Table 1.1 compares the typical magnitudes of all the nuclear spin interactions in typical solids and liquids.

**Table 1.1 Typical magnitudes of nuclear spin interactions**

<table>
<thead>
<tr>
<th>Spin Interactions</th>
<th>Magnitude in Solids (Hz)</th>
<th>Magnitude in Liquids (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeeman</td>
<td>(10^7 - 10^9)</td>
<td>(10^7 - 10^9)</td>
</tr>
<tr>
<td>Chemical Shielding</td>
<td>(10^2 - 10^5)</td>
<td>(\delta_{iso})</td>
</tr>
<tr>
<td>Dipolar</td>
<td>(10^3 - 10^5)</td>
<td>0</td>
</tr>
<tr>
<td>J-coupling</td>
<td>(1 - 10^3)</td>
<td>(1 - 10^3)</td>
</tr>
<tr>
<td>Quadrupolar</td>
<td>(10^3 - 10^7)</td>
<td>0</td>
</tr>
</tbody>
</table>

This table indicates that the special features of SSNMR are attributed to chemical shielding, dipolar and quadrupolar interactions. These three interactions are the key to understand SSNMR spectra. It is clear that Zeeman interaction is the much larger than others. Thus, Zeeman interaction is responsible for the initial splitting of the energy levels. But other interactions, especially quadrupolar interaction, also have profound
influence on the energy level splitting and the SSNMR spectra.

Chemical shielding results from the interaction between nuclear spins and a local secondary magnetic field.\textsuperscript{35} It represents the response of electronic cloud around the nucleus to an applied magnetic field. As the applied field induces a circulation of the electrons, the induced electronic movement produces a small field, which modifies the total field experienced by the nucleus.

The orientation dependence of the chemical shielding is described by a second-rank tensor. The shielding tensor can be diagonalized to a diagonal 3x3 matrix in a principal axis system (PAS).

\[
\sigma = \begin{pmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & \sigma_{33}
\end{pmatrix}
\]

The shielding is characterized by three principle values $\sigma_{11}$, $\sigma_{22}$ and $\sigma_{33}$ ($\sigma_{11} \leq \sigma_{22} \leq \sigma_{33}$) along three orthogonal directions fixed in molecular framework. In NMR study they are often converted to Herzfeld-Berger conventions\textsuperscript{36}. The conversion equations are listed below. ($\sigma_{iso}$: isotropic shielding tensor. $\delta_{iso}$: isotropic chemical shift. $\Omega$: span. $\kappa$: skew.)

Another three important parameters are the Euler angles ($\alpha$, $\beta$ and $\gamma$). They are used to describe the orientation of the principal axes with respect to an arbitrary frame.

\[
\sigma_{iso} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3}
\]

\[
\delta_{iso} = \sigma_{iso} - \sigma_{reference}
\]

\[
\Omega = \sigma_{33} - \sigma_{11}
\]

\[
\kappa = \frac{3 \times (\sigma_{22} - \sigma_{iso})}{\Omega}
\]

Figure 1.6 displays the effects of $\Omega$ and $\kappa$ on the $^{13}$C pattern at 9.4 T. It is clear that $\Omega$ decides the width of and $\kappa$ determines the shape the pattern.
Figure 1.6 Simulated $^{13}$C spectra at 9.4 T with various $\Omega$ and $\kappa$ ($\delta_{\text{iso}} = 0$ ppm).

It is worth noting that when $\kappa$ equals to 1 or -1, $\sigma_{22}$ equals to $\sigma_{11}$ or $\sigma_{33}$, indicating an axial symmetry of the CS tensor.

Beside the Zeeman and the CS interaction, another important interaction that has profound effect on the spectra of MOFs is the quadrupolar interaction, which is the interaction between the nuclear quadrupole moment (Q) and the EFG.\textsuperscript{35, 37} This interaction broadens resonances in the SSNMR spectra of quadrupolar nuclei. Unlike spin -$1/2$ nuclei which have spherical charge distribution within the nuclei, quadrupolar nuclei ($I > 1/2$) have asymmetric charge distribution, giving rise to a nuclear quadrupole moment. As a result, the nuclei look like ellipsoids as shown below. Larger Q value corresponds to more distorted sphere. The quadrupole moment is therefore an index of the deviation of the nuclear charge distribution from spherical symmetry and an internal property of a nuclear.

Table 1.2 lists the NMR properties of several important quadrupolar isotopes in MOFs, which are the metal centers of the MOFs examined in this thesis. It is noticed that $^{47/49}$Ti, $^{67}$Zn and $^{91}$Zr are challenging due to the very low natural abundances and small
magnetogyric ratios. $^{47/49}$Ti is especially challenging, primarily because the magnetogyric ratios of two isotopes, $^{47}$Ti and $^{49}$Ti, are almost identical, making it almost impossible to separate their patterns. For some nuclei, the quadrupole moments are also large. For example, the $^{115}$In has a very large quadrupole moment, making its NMR spectra extremely wide.

Table 1.2 NMR properties of several metal isotopes

<table>
<thead>
<tr>
<th>Isotopes</th>
<th>Natural abundance (%)</th>
<th>Spin number, $I$</th>
<th>Quadrupole moment (mb)</th>
<th>Magnetogyric ratio, $\gamma$ ($10^7 , \text{T}^{-1} \cdot \text{s}^{-1}$)</th>
<th>Frequency relative to $^1\text{H}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{47}$Ti</td>
<td>7.44</td>
<td>5/2</td>
<td>302</td>
<td>-1.5105</td>
<td>5.6375</td>
</tr>
<tr>
<td>$^{49}$Ti</td>
<td>5.41</td>
<td>7/2</td>
<td>247</td>
<td>-1.5110</td>
<td>5.6390</td>
</tr>
<tr>
<td>$^{67}$Zn</td>
<td>4.10</td>
<td>5/2</td>
<td>150</td>
<td>1.6767</td>
<td>6.2568</td>
</tr>
<tr>
<td>$^{91}$Zr</td>
<td>11.22</td>
<td>5/2</td>
<td>-176</td>
<td>-2.4974</td>
<td>9.2963</td>
</tr>
<tr>
<td>$^{115}$In</td>
<td>95.70</td>
<td>9/2</td>
<td>770</td>
<td>5.8972</td>
<td>21.9125</td>
</tr>
<tr>
<td>$^{139}$La</td>
<td>99.91</td>
<td>7/2</td>
<td>200</td>
<td>3.8083</td>
<td>14.1256</td>
</tr>
</tbody>
</table>

The EFG is described by a second-rank tensor, which is a traceless and symmetric $3 \times 3$ matrix which can be diagonalized to determine the principle components of the tensors in its own principle axis system. The principle tensors are in an order of $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$. $V_{XX} + V_{YY} + V_{ZZ} = 0$. The nuclear quadrupolar interaction depends on both quadrupole moment and the EFG. Two parameters are used to characterize the quadrupolar interaction: nuclear quadrupolar coupling constant ($C_Q$) and asymmetry parameter ($\eta_Q$) which are defined as below.

$$C_Q = \frac{eQV_{zz}}{\hbar} = \frac{e^2Qq_{zz}}{\hbar} \quad \eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}$$
C_Q value describes the magnitude of the quadrupolar interaction of the nucleus. When \( C_Q = 0 \), it means that the environment of the nucleus has a perfectly spherical symmetry (i.e., tetrahedral, octahedral and cubic). The asymmetry parameter (\( \eta_Q \)), on the other hand, describes the axial (cylindrical) symmetry of the EFG tensors. It ranges from \( 0 \leq \eta_Q \leq 1 \). An \( \eta_Q \) value of 0 means that the EFG tensors are axial symmetric (corresponding to a C_3 or higher site symmetry). Figure 1.7 displays the effect of \( C_Q \) and \( \eta_Q \) on the solid NMR pattern of \(^{17}\text{O}\) at 9.4 T. A larger \( C_Q \) results in a broader pattern and \( \eta_Q \) affects the shape of the NMR resonance.

**Figure 1.7** \(^{17}\text{O}\) static NMR spectra with various \( C_Q \) and \( \eta_Q \) at 21.1T.

**Figure 1.8** Influence of quadrupolar interaction on the energy gap of I=3/2 nucleus.
Figure 1.9 CT and ST due to first-order quadrupolar interaction (a) and CT due to second-order quadrupolar interaction.

Figure 1.8 shows the energy diagram of a spin 3/2 nucleus. CT is the central transition and STs are satellite transitions. The energy splitting is primarily due to the Zeeman interaction and then perturbed by first- and second-order quadrupolar interaction. Figure 1.9 shows the effect of first- and second-order quadrupolar interactions. The CT is unaffected by the first-order quadrupolar interaction, while the STs are significantly broadened. Therefore the ST patterns usually have very low intensity compared to that of CT (Figure 1.9a). Thus ST patterns are so wide that they are not observed on NMR spectra. CT pattern, however, is affected by the second-order quadrupolar interaction (Figure 1.9b). The width of CT pattern due to second-order quadrupolar interaction is inversely proportional to the magnetic field $B_0$. Figure 1.10 displays the $^{17}$O SSNMR spectra at various fields ($C_Q=7$ MHz, $\eta_Q= 0.1$, $\delta_{iso}= 0$ ppm, only considering CT). High field reduces the width of NMR pattern and enhances its intensity.
1.3.2 Techniques of SSNMR

Both first-quadrupolar interaction and the chemical shielding interaction contain components that have the orientational dependance of \((3\cos^2\theta-1)\). For quadrupolar interaction, \(\theta\) is the angle between the \(V_{ZZ}\) and \(B_0\). For chemical shielding interaction, \(\theta\) is the angle between the \(B_0\) and the principle axis frame about which the chemical shielding tensor is defined. When \(\theta = 54.74^\circ\), the term \((3\cos^2\theta-1)\) equals to zero and the spatial dependencies will be averaged out to zero, resulting in significant line narrowing in NMR spectra (Figure 1.11). Second-order quadrupolar interaction, however, has a more complicated spatial dependence term. So the NMR patterns will display certain shapes rather than a sharp peak (Figure 1.11c).
In order to achieve higher resolution, the magic-angle spinning (MAS) technique is widely used in NMR study. MAS technique involves a fast spinning of the rotor which is filled with powdered sample with frequencies on the range of kHz. The sample rotation axis forms an angle of 54.74° with respect to the external magnetic field (Figure 1.12).

To average out the anisotropic interactions, the spinning speed of the sample should be greater than the order of the magnitude of the anisotropy. Most conventional SSNMR probes can only rotate the rotor to 3 - 65 kHz. At limited spinning speed, these interactions cannot be averaged out completely and the periodical rotation of rotor will produce spinning sidebands in the frequency-domain spectrum. These sidebands appear

**Figure 1.11** MAS at 10 kHz and static spectra of $^{17}$O ($C_Q = 9$ MHz, $\eta_Q = 0$, $\delta_{iso} = 0$ ppm) and $^{31}$P ($\delta_{iso} = 8$ ppm, $\Omega = 150$ ppm, $\kappa = -0.5$). *: sidebands.
at both sides of isotropic peak, with a distance equalling to spinning frequency from each other. In the NMR spectra of this report, sidebands are marked with asterisk. Figure 1.13 displays the NMR patterns of $^{13}$C at variable spinning rates. It is demonstrated that MAS works only when the spinning rate is greater than the magnitude of anisotropy (Figures 1.13a and b). Otherwise the pattern would be very complicated (Figure 1.13c). When the pattern is too wide for MAS, static spectra should be acquired (Figure 1.13d).

**Figure 1.12** Schematic diagram of magic-angle spinning.

**Figure 1.13** Static and MAS spectra of $^{13}$C at 9.4 T ($\delta_{iso} = 0$ ppm, $\Omega = 150$ ppm, $\kappa = -1$). MAS spectra at acquired at variable spinning rates. *: sidebands.
The procedure of acquiring NMR signal is applying a second $B_1$ field in x direction (assuming $B_0$ is along z direction) to turn the magnetization vector toward y direction, and acquire the signal along y direction. The signal is in time-domain and will be transformed to frequency-domain by Fourier transform (FT). To enhance the signal of insensitive nuclei, other important SSNMR techniques, such as cross-polarization (CP), which transfers magnetization from sensitive and abundant spin (i.e., $^1$H) to insensitive and dilute spin (i.e., $^{13}$C), are applied. CP is based on dipolar interaction between the magnetic moments of $^1$H and $^{13}$C. The pulse sequence is shown below.

There is dipole-dipole interaction between $^1$H and $^{13}$C during the contact time (ct), and the signal of the insensitive nucleus ($^{13}$C) is enhanced. The length of contact time required depends on the distance between hydrogen and the insensitive nuclei. Thus the CP method can be used to detect the distance between hydrogen and the insensitive nuclei. Thus the CP method can be used to detect the distance between hydrogen and the insensitive nuclei. Since at shorter ct, only signal of those close to hydrogen is enhanced. By applying CP method with a range of contact time, the peak that exists on the spectra at very short ct can often be assigned to atoms that are bonded to hydrogen.

Another important technique in SSNMR is spin echo. The NMR signal observed following an initial excitation pulse (usually 90° pulse) decays with time due to inhomogeneous effects which cause different spins in the sample to precess at different rates. Such inhomogeneous dephasing can be removed by applying a 180° pulse. When we run spin echo NMR, we apply a 180 degree pulse after a delay time ($\tau$) following 90 degree pulse, then wait another $\tau$ before starting acquiring signal. The 180 degree pulse has different effect on the x and y axis projection of magnetization vector: it does not affect the x component but rotates the y component to the opposite axis (+y to -y).
Figure 1.14 displays a typical procedure of spin echo. The magnetization vector is rotated from z axis to y axis upon 90° pulse (Figure 1.14a and 1.14b). Then the vector will spread on xy plane (Figure 1.14c). A 180° is applied and the vector and the y component of the vector is rotated to −y axis immediately (Figure 1.14d). After that the vector will refocus on xy plane (Figure 1.14e and 1.14f). In another word, the evolution during the first delay \( \tau \) is undone by the second delay upon 180° pulse, which helps cancel the inhomogeneous effects of the decaying on xy plane.

1.4 References


Chapter 2

2 $^{17}$O SSNMR Study of MOFs

2.1 Introduction

SBUs of many MOFs are built from metal center cations and oxygen-containing ligands, where oxygen atoms are the joints where organic linkers bind to SBUs. The local chemical environment of oxygen is sensitive to such binding. SSNMR would be a useful tool to probe the local environment, since the changes of the NMR parameters of oxygen, induced by bond length, bond angle and local symmetry, reflect the change of local environment sensitively. As a result, $^{17}$O NMR should be used as an ideal tool to study the local environment of oxygens, probe the structure of MOFs and follow the phase transition of MOFs. As is known, X-ray diffraction (XRD) is not sensitive to hydrogen atoms, so the location of hydrogen is sometimes not certain, especially when both hydroxyl group (OH$^-$) and oxygen anion (O$^{2-}$) may be present in the same structure.$^{1, 2}$ In such cases, $^{17}$O NMR can be utilized to distinguish the closely related oxygen species.

$^{17}$O solid state NMR study is relatively scarce compared with commonly studied nuclei such as $^{13}$C, $^{27}$Al and $^{29}$Si. There are two reasons. One is the extremely low natural abundance of $^{17}$O. There are three stable isotopes of oxygen: $^{16}$O (99.76%), $^{17}$O (0.037%) and $^{18}$O (0.20%). But only $^{17}$O possesses a non-zero nuclear spin quantum number ($I=5/2$). Hence, $^{17}$O SSNMR study usually requires $^{17}$O enrichment, which is both expensive and difficult. The second problem with $^{17}$O SSNMR is the significant line broadening due to the quadrupolar interaction.$^{3}$ The $^{17}$O peaks of different sites may overlap and are difficult to be distinguished.

Despite the disadvantages of $^{17}$O nucleus for SSNMR, $^{17}$O SSNMR attracts attention because it allows the measurements of the NMR parameter such as chemical shift and nuclear quadrupole coupling constant, which are directly correlated to molecular structure.$^{3-6}$ Wu et al employed $^{17}$O SSNMR to study different functional groups in organic and biological molecules, and demonstrated the $^{17}$O NMR parameters, such as
$C_Q$, $\eta_Q$ and $\delta_{iso}$, of various oxygen-containing groups.\textsuperscript{7,8} Besides organic molecules, $^{17}$O SSNMR has been utilized to study inorganic compounds including crystalline ionic oxides\textsuperscript{9}, glasses\textsuperscript{10} and phosphates\textsuperscript{11}. For example, Oldfield \textit{et al} developed $^{17}$O cross-polarization (CP) NMR and acquired CP spectra of various $^{17}$O-labelled solids including Mg(OH)$_2$, boehmite (AlO(OH)) and amorphous SiO$_2$\textsuperscript{12}

$^{17}$O SSNMR has also been used to study the chemical environment of oxygen sites in zeolites, which are a family of porous materials based on networks of corner sharing AlO$_4$ and SiO$_4$ tetrahedra. An important aspect of zeolite study is the binding (both position and strength) of extra framework cations and adsorbed molecules. It is of particular importance for the understanding of the application of zeolites as heterogeneous catalysts. In zeolites adsorbed species often bind to the oxygens. The application of $^{17}$O SSNMR enables detailed study of such binding and probes the framework structure through the sensitivity of the chemical shift and the quadrupolar parameters to the local chemical environment of oxygens.\textsuperscript{3}

Inspired by the $^{17}$O SSNMR study on zeolites, we started to apply $^{17}$O SSNMR to study the $^{17}$O environment of MOFs. This area is novel and such study remains sparse. To our best knowledge, there is only one recent report which showed that it is possible to incorporate $^{17}$O into specific sites in MOF-5 structures.\textsuperscript{13} $^{17}$O enrichment is the key to solve this problem and all our $^{17}$O SSNMR studies start from there.

In this chapter, I synthesized $^{17}$O-enriched MOFs: MIL-53(Al)-lp, MIL-53(Al)-np, Zr-Uio-66 and MIL-96(Al). These four MOFs are important and frequently studied due to their unique structure features. At a magnetic field of 9.4 T, $^{17}$O peaks of the MOFs overlap with each other. To separate $^{17}$O peaks and get better $^{17}$O NMR spectra, ultrahigh magnetic field 21.1 T is utilized. NMR parameters are extracted and spectral signatures of various nonequivalent framework oxygen species are established.
2.2 Experimental

2.2.1 Synthesis of MOFs

*MIL-53(Al)*\textsuperscript{14}

To prepare \(^{17}\text{O}\)-enriched MIL-53(Al)-\textit{lp}, or Al(OH)(O\textsubscript{2}C-C\textsubscript{6}H\textsubscript{4}-CO\textsubscript{2})\cdot (HO\textsubscript{2}C-C\textsubscript{6}H\textsubscript{4}-CO\textsubscript{2})\cdot 0.7H\textsubscript{2}O (Sigma-Aldrich, 98 %) and 5.9 mmol terephthalic acid (1,4-benzenedicarboxylic acid, Sigma-Aldrich, 98 %), both of which are solids, was first placed into a small Teflon cup. The cup was then put in a 23 mL Teflon-lined autoclave with 0.4 mL \(^{17}\text{O}\)-enriched H\textsubscript{2}O (CortecNet, 41.8% \(^{17}\text{O}\) atom) at the bottom and heated in an oven at 473 K for 3 days (Dry-gel method, Figure 2.1). The product was washed using deionized water and recovered by vacuum filtration to obtain a white powder. The powder was finally dried at 353 K for 12 h to get MIL-53(Al)-\textit{lp}. MIL-53(Al)-\textit{np}, or Al(OH)(O\textsubscript{2}C-C\textsubscript{6}H\textsubscript{4}-CO\textsubscript{2})\cdot H\textsubscript{2}O was prepared by calcinating the MIL-53(Al)-\textit{lp} at 603 K under dynamic vacuum for 3 days in air and cooling it to room temperature. The sample was sealed in a glass tube.

![Figure 2.1 Diagram of reaction vessel for dry-gel method.](image)
In a typical synthesis of $^{17}$O-enriched Zr-UiO-66, or Zr$_6$O$_4$(OH)$_4$(BDC)$_6$, 2.3 mmol ZrCl$_4$ (Sigma-Aldrich, 99.5 %), 2.3 mmol terephthalic acid and 0.25 mL $^{17}$O-enriched water (CortecNet, 41.8% $^{17}$O atom) were dissolved in 25 mL N,N’-dimethylformamide (DMF, Reagent grade, Caledon). The solution was then added into a 30 mL Teflon-lined autoclave and heated at 473 K for 16 h. The product was recovered by vacuum filtration as a white powder. The white power was washed in DMF for 6 h and then recovered by vacuum filtration as a white powder.

MIL-96(Al)

To prepare MIL-96(Al), or Al$_{12}$O(OH)$_{18}$(H$_2$O)$_3$(Al$_2$(OH)$_4$)(BTC)$_6$·24H$_2$O, a mixture of 0.7 mmol Al(NO$_3$)$_3$·9H$_2$O (Sigma-Aldrich, 98 %) and 0.9 mmol trimethyl 1,3,5-benzenetricarboxylate (Me$_3$BTC, Alfa, 98 %) was first added into a small Teflon cup. The cup was then placed in a 23 mL Teflon-lined autoclave with 0.50 g deionized water at the bottom and heated in an oven at 483 K for 1 day. The product was washed using deionized water and recovered by vacuum filtration to obtain a grey powder. In order to get a $^{17}$O-enriched product, 0.15 g product was sealed in Teflon-lined autoclave with 0.1 g $^{17}$O-enriched water (CortecNet, 41.8% $^{17}$O atom) and heated at 423 K for 24 h. The product was then heated at 423 K for 4 h under vacuum to remove the water molecules in the pores.

2.2.2 Powder X-ray characterization

The purity of MIL-53(Al)-lp, MIL-53(Al)-np, Zr-UiO-66 and MIL-96(Al) confirmed by powder XRD characterization. Powder XRD patterns were recorded on a Rigaku diffractometer using Co Kα radiation ($\lambda=1.7902$ Å). Samples were scanned at $5^\circ \leq 2\theta \leq 45^\circ$ at a scan rate of $10^\circ$/min with a step-size of 0.02$^\circ$. Then the patterns were converted to Cu Kα radiation ($\lambda=1.5405$ Å) to be compared with literature. The XRD patterns are shown in Figure 2.2.
2.2.3 Thermal gravity analysis (TGA)

TGA spectra were used to determine the thermal stability of MOFs, which were crucial to decide the activation temperatures. TGA measurement was fulfilled with Mettler Toledo TGA/SDTA 851e. The samples were heated from 298 K to 773 K at a rate of 10 K/min.

2.2.4 $^{17}$O solid state NMR spectroscopy

All $^{17}$O SSNMR experiments were conducted at 21.1 T ($v_0$ ($^{17}$O) = 122.0 MHz) on a Bruker Avance II spectrometer at the *National Ultrahigh-Field NMR Facility for Solids* in Ottawa, Canada. The magic-angle spinning spectra were acquired by using the Hahn-echo pulse sequence with a 4 mm H/X MAS Bruker probe. The samples were packed in a Si$_3$N$_4$ and a ZrO$_2$ rotor for 10 and 18 kHz MAS experiment, respectively. The pulse delay was 1-5 s. For selected samples, the MAS spectra were also obtained by using one-pulse
sequence with a 15-degree solid pulse angle to ensure quantitative information of multiple sites in the samples. The pulse delay was 2 s. The $^{17}$O chemical shifts were referenced to H$_2$$_{17}$O ($\delta_{iso} = 0$ ppm). The selective $\pi/2$ pulse lengths for the central transition were determined on H$_2$$_{17}$O. Detailed experimental conditions are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>Spinning rate (kHz)</th>
<th>90° pulse length ((\mu)s)</th>
<th>SW (kHz)</th>
<th>Pulse delay(s)</th>
<th>Number of scan ((\times 1024))</th>
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</thead>
<tbody>
<tr>
<td>MIL-53(Al)-lp</td>
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<td>200</td>
<td>5</td>
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<tr>
<td>MIL-53(Al)-lp</td>
<td>Static Echo</td>
<td>/</td>
<td>4</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
<td>MIL-53(Al)-np</td>
<td>Echo</td>
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<td>4</td>
<td>200</td>
<td>5</td>
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<tr>
<td>MIL-53(Al)-np</td>
<td>Static Echo</td>
<td>/</td>
<td>4</td>
<td>200</td>
<td>5</td>
</tr>
<tr>
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<td>200</td>
<td>2</td>
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<td>Zr-UiO-66</td>
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<td>/</td>
<td>4</td>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td>MIL-96(Al)</td>
<td>Echo</td>
<td>20</td>
<td>2</td>
<td>200</td>
<td>10</td>
</tr>
</tbody>
</table>

2.2.5 Estimation of $^{17}$O-enrichment

Estimation of the degree of $^{17}$O-enrichment in MOFs was a challenging task as these MOFs do not dissolve in solvents. We established a protocol to evaluate $^{17}$O-enrichment in MOFs by using time-of-flight secondary ion mass spectrometry (TOF-SIMS). The $^{17}$O/$^{16}$O isotope ratios estimated for the two $^{17}$O-enriched samples of MIL-53-Al and Zr-UiO-66 are 5.8±0.1% and 2.4±0.2% respectively. When comparing with the $^{17}$O/$^{16}$O ratio
of 0.0381% at natural abundance, the degrees of the enrichment are estimated at 152 and 63 times the natural abundance of $^{17}$O for MIL-53-Al and Zr-UiO-66 respectively. Note that Zr-UiO-66 used was the as-synthesized sample with solvent DMF and a small amount of water which are not $^{17}$O labeled. Using the TGA data, the $^{17}$O/$^{16}$O ratio in the framework was adjusted to be 3.38%, corresponding to 88 times of the natural abundance of $^{17}$O.

2.2.6 Gaussian and CASTEP calculation

Ab initio calculations were conducted using the Gaussian 09 program on SHARCNET (www.sharcnet.ca). The EFG tensors of $^{17}$O in all the model clusters were calculated using hybrid density functional theory (DFT) at the B3LYP level\(^{17}\) of theory using the GIAO method. The basis sets used were 6-311G* for Al atoms, 6-311+G* for O atoms bonded directly and 6-31G* for other atoms. The basis sets were chosen based on previous studies in literature, which showed good agreement with experimental values in similar systems.\(^{18-20}\)

Gauge including projector augmented wave (GIPAW) quantum chemical calculations\(^{35,36}\) were conducted using the Cambridge Serial Total Energy Package (CASTEP) code program\(^{21,22}\) (version 4.4, Accelrys Materials Studio). The NMR module\(^{23-25}\) was used to calculate the $^{17}$O NMR parameters. Unit cell parameters and atomic coordinates were taken from the crystal structures of the MOFs examined. When necessary, the geometry optimization was performed. The unit cell parameters were not allowed to change since the unit cell dimensions are well-defined from the powder XRD. The solvent/guest molecules were kept in the pores whenever possible. The calculations were performed using ultrasoft pseudopotentials generated from the “on-the-fly” method implemented within the CASTEP. The generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) functional was used. The $C_Q(^{17}$O) values were calculated from the EFG tensor produced by the CASTEP calculation using $Q(^{17}$O) = -2.558 × 10\(^{-30}\) m\(^2\).\(^{26}\) The isotropic chemical shift for $^{17}$O was computed using the correlation $\delta_{iso} = 287.5 - \sigma_{iso}$ (all in ppm), where 287.5 ppm is the absolute shielding value of liquid H\(_2\)O ($\delta_{iso} = 0$ ppm).\(^{27}\)
2.2.7 Simulation of NMR spectra

SSNMR parameters, including $C_Q$, $\eta_Q$, $\delta_{\text{iso}}$, $\kappa$, $\Omega$, $\alpha$, $\beta$ and $\gamma$ of objective nuclei were determined by analytical simulations of NMR spectra using the DMFIT$^{28}$, WSOLIDS and QUEST$^{29}$ simulation package. DMFIT is used to simulate the spin sidebands in MAS spectra. The experimental error for each measured parameter was determined by visual comparison of experimental spectra with simulations. The parameter of concern was varied bidirectionally starting from the best fit value and all other parameters were kept constant, until noticeable differences between the spectra were observed.

In this chapter, all the experimental spectra are in blue or red and all simulated spectra are in black if there is no special note.

2.3 Results and discussion

2.3.1 MIL-53(Al)

MIL-53(Al) is a MOF with significant flexibility.$^{30,31}$ The building unit of MIL-53(Al) is AlO$_6$ octahedron. Aluminium is coordinated to four carboxylate oxygens from four different –COO$^-$ groups and two $\mu_2$-OH oxygens. The organic linker is 1,4-benzenedicarboxylate (BDC). In the as-made phase (also referred as large pore phase, or $lp$), the AlO$_6$ octahedron is connected to another two AlO$_6$ octahedra through $\mu_2$-OH groups, forming infinite Al-O chains along $b$ direction (Figure 2.3a). Adjacent AlO$_6$ octahedra are connected by carboxylate groups from BDC linkers, which extend on $ac$ plane. Such connection forms 1D tunnel along $b$ direction (Figure 2.3b). For low temperature phase (also referred as narrow pore phase, or $np$)$^{14}$, the connection is similar, as is shown in Figure 2.3c. However, the atom coordination is not resolved from single crystal XRD pattern, but simulated from powder XRD pattern.$^{14}$ And the presence of $\mu_2$-OH groups is extrapolated based on $^1$H NMR results, where a broad peak at around 2.9 ppm is assigned to $\mu_2$-OH hydrogen. These facts make it necessary to further confirm the structure with $^{17}$O SSNMR technique.
An interesting feature of MIL-53(Al) is the breathing effect. MIL-53(Al)-lp undergoes a phase transition from an orthorhombic to a monoclinic phase (MIL-53(Al)-np) upon calcination and subsequent water adsorption. Such transformation is accompanied by one-third reduction in the unit cell volume without breaking chemical bonds. Figure 2.3c displays the network of MIL-53(Al)-np. In MIL-53(Al)-np, the building unit is consistent with MIL-53(Al)-lp, but the aluminum chain and tunnel are along $c$ axis. The mechanism of the breathing effect has been studied with $^1$H, $^{13}$C and $^{27}$Al SSNMR. Such phase change will change the chemical environment of oxygens as well, which should be detected by $^{17}$O SSNMR.

The $^{17}$O NMR spectra of MIL-53(Al)-lp and MIL-53(Al)-np are shown in Figure 2.4. The spectra of MIL-53(Al)-lp are on top (Figures 2.4 a and b), where two peaks can be seen clearly. The stronger one at about 230 ppm can be assigned to the oxygen atoms in the BDC linkers, for the $\delta_{iso}$ is consistent with $-\text{COO}^-$ in literature. 
Comparing with previous $^{17}$O NMR spectra in literature, the peak at around 20 ppm might be due to either the bridging OH group in the proposed structure or the oxygen in a simple Al-O-Al linkage.\textsuperscript{33} To identify the specie of this oxygen, we further carried out $^1$H $\rightarrow$ $^{17}$O cross-polarization (CP) experiments with a variety of contact time (ct). As is shown in Figure 2.5, at long contact time (10 ms), the spectrum is similar to the MAS spectrum (Figure 2.4b). When contact time is shortened, the intensity of the peak at 230 ppm decreases. As is mentioned in Chapter 1, such phenomenon indicates that this oxygen is not bonded to hydrogen directly. This observation confirms that this peak is due to $-\text{COO}^-$ oxygen. When ct equals to 0.2 ms, however, a peak of low intensity
remains in the spectrum. This is because there is unreacted terephthalic acid in the tunnel, which bears –COOH.

The peak at 20 ppm, on the other hand, has a higher intensity when ct is shorter. Such phenomenon indicates that this oxygen site is directly bonded to hydrogen. So this peak is due to bridging OH group instead of Al-O-Al linkage. When simulating the MAS spectrum with DMFIT package\textsuperscript{28}, the oxygen site of unreacted terephthalic acid and those of the framework are so close that they can hardly be distinguished. Thus they are simulated as one signal. The EFG parameters extracted are given in Table 2.2.

Figure 2.5 \textsuperscript{17}O CPMAS spectra of MIL-53(Al)-lp with different contact time. *: spinning sidebands. All spectra are experimental results.

Another method to confirm the assignment of peaks is the theoretical calculation using the CASTEP program. The background of CASTEP is mentioned in Chapter 2. There are two –COO\textsuperscript{−} oxygen sites in the lp phase. Ideally we should see two signals in the NMR spectrum. But CASTEP calculation results show that the two oxygen sites display almost identical $C_Q$, $\eta_Q$ and $\delta_{iso}$, which explains why there is only one –COO\textsuperscript{−} signal observed in the NMR spectrum. Table 2.3 displays the calculation results.
**Table 2.2 Experimental $^{17}$O NMR parameters of MIL-53(Al)**

| O Signal | $|C_Q|(\text{MHz})$ | $\eta_Q$ | $\delta_{iso}$ (ppm) | $\Omega$ (ppm) | $\kappa$ |
|----------|-------------------|----------|-----------------------|----------------|---------|
| MIL-53(Al)-lp | | | | | |
| $\mu_2$-OH | 6.1(3) | 0.60 (5) | 22 (5) | / | / |
| -COO$^-$ | 7.9(3) | 0.58(5) | 240(5) | 100(20) | -0.7(1) |
| MIL-53(Al)-np | | | | | |
| $\mu_2$-OH | 6.5(3) | 0.81(5) | 24(5) | / | / |
| -COO$^-$ signal 1 | 6.9(3) | 0.85(5) | 256(5) | 160(20) | 0.5(1) |
| -COO$^-$ signal 2 | 6.0(3) | 0.72(5) | 210(5) | 160(20) | 0.5(1) |
| H$_2$O | 3.0(3) | 0.30(5) | -8(5) | / | / |

* $\alpha$, $\beta$ and $\gamma$ are 0
### Table 2.3 CASTEP results of MIL-53(Al)-lp and MIL-53(Al)-np

| O Site  | O position | \(|C_Q| (MHz)| \(\eta_Q\) | \(\delta_{iso} \) (ppm) | \(\Omega \) (ppm) | \(\kappa\) |
|--------|------------|----------------|---------|----------------|----------------|--------|
| MIL-53(Al)-lp |
| O1     | \(\mu_2\)-OH | 8.25          | 0.74    | 12.7          | 39.4          | 0.34   |
| O2     | -COO\(^{-}\) site1 | 7.23          | 0.79    | 242.0         | 385.5         | -0.62  |
| O3     | -COO\(^{-}\) site2 | 7.16          | 0.83    | 239.0         | 374.4         | -0.58  |
| MIL-53(Al)-np |
| O1     | \(\mu_2\)-OH | 8.24          | 0.74    | 6.9           | 31.9          | 0.65   |
| O2     | -COO\(^{-}\) site1 | 7.84          | 0.73    | 235.7         | 365.7         | -0.74  |
| O2b    | -COO\(^{-}\) site2 | 8.02          | 0.70    | 239.3         | 373.7         | -0.75  |
| O3     | -COO\(^{-}\) site3 | 7.12          | 0.73    | 261.8         | 399.4         | -0.68  |
| O3b    | -COO\(^{-}\) site4 | 7.27          | 0.72    | 264.4         | 404.4         | -0.69  |

Besides MAS spectra, static spectrum of MIL-53(Al)-lp is also acquired. Figure 2.6 displays the static experimental spectrum and simulated spectra. The same \(C_Q\), \(\eta_Q\) and \(\delta_{iso}\) extracted from the MAS spectrum were used to simulate the static spectrum. The CSA parameters are listed in Table 2.2, which show the same trend of \(\Omega\) comparing with the calculation results (Table 2.3).
Figures 2.4c, d and e display the NMR spectrum of MIL-53(Al)-np, which looks distinctly different from that of MIL-53(Al)-lp. The peak at around 20 ppm is assigned to $\mu_2$-OH oxygen. When simulating with DMFIT package\textsuperscript{28}, the shoulder on the high-field side of the 20 ppm peak is difficult to be well simulated. Considering the existence of guest water molecules in the tunnel (Figure 2.3c), this shoulder is assigned to the oxygen of guest water. From the CP spectrum we notice that with short ct, the peak of $\mu_2$-OH oxygen is strong because this oxygen is bonded to a hydrogen directly. Oxygen of guest water is also bonded to hydrogen, but the cross-polarization efficiency is low due to its mobility. So the shoulder is absent at short ct. The peak at around 250 ppm splits into two peaks, which is indicative of the lowering of the crystal symmetry. Comparing the CP spectra of large pore phase and narrow pore phase, it is noticed that the peak due to unreacted acid is absent in narrow pore phase, consistent with the absence of terephthalic acid in the tunnel upon calcination. Taking all the information into consideration, the MAS spectrum can be fitted with four oxygen sites (two crystallographically non-
equivalent carboxylate oxygens, one $\mu_2$-OH group and one from water molecules). The EFG parameters extracted are given in Table 2.2.

### Table 2.4 Bond lengths and bond angles of –COO’ oxygens in MIL-53(Al)-np

<table>
<thead>
<tr>
<th>Bonds</th>
<th>O2</th>
<th>O2b</th>
<th>O3</th>
<th>O3b</th>
</tr>
</thead>
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<tr>
<td>Al-O (Å)</td>
<td>1.912</td>
<td>1.925</td>
<td>2.003</td>
<td>2.006</td>
</tr>
<tr>
<td>C- O (Å)</td>
<td>1.226</td>
<td>1.226</td>
<td>1.299</td>
<td>1.281</td>
</tr>
<tr>
<td>Al-O-C (°)</td>
<td>134.5</td>
<td>130.6</td>
<td>129.1</td>
<td>124.7</td>
</tr>
</tbody>
</table>

There are four crystallographically non-equivalent carboxylate oxygens in the framework of the np phase (Figure 2.7).\(^{14}\) However, O2 and O2b have similar geometrical environment, and the other two (denoted O3 and O3b) share similar geometrical environment. (Table 2.4) Thus in the experimental spectrum there are only two peaks present. CASTEP calculation is employed to assign the peaks. The CASTEP calculations using optimized geometry show that O2 and O2b have similar $C_Q$ and $\delta_{\text{iso}}$, which holds true for O3 and O3b as well. The $\eta_Q$ values are almost identical to all four

---

\(^{14}\) Reference number.
Based on the CASTEP calculations, we can assign the observed signal at 206 ppm to O2 and O2b, whereas the resonance at 256 ppm to O3 and O3b. This example shows that under favorable conditions, crystallographically non-equivalent oxygen sites can be separated at high field.

![Diagram of O spectra](image)

**Figure 2.8** $^{17}$O static spectra of MIL-53(Al)-$np$.

Besides MAS spectra, static spectrum of MIL-53(Al)-$np$ is also acquired. Figure 2.8 displays the static experimental spectrum and simulated spectra. The same EFG parameters extracted from MAS spectra were used to simulate the solid spectrum. The CSA parameters are listed in Table 2.2. The $\Omega$ values show the same trend comparing with the calculation results (Table 2.3).
2.3.2 Zr-Uio-66

One of the important issues for MOFs is their thermal stability. Zr-Uio-66 is a MOF with exceptionally high thermal stability.\textsuperscript{15} The structure is built upon from polyhedra containing eight-coordinated zirconium atoms, which are connected by 1,4-BDC linkers. The basic building unit of Zr-Uio-66, $\text{Zr}_6\text{O}_4(\text{OH})_4$, consists of an octahedron formed by six Zr atoms. The eight triangular faces of the octahedron are capped alternately by four $\mu_3$-$\text{O}^{2-}$ anions and four $\mu_3$-OH groups.

![Figure 2.9 The network (a) and the basic unit (b) of Zr-Uio-66. (Copyright 2013 American Chemical Society)](image)

The crystal structure of Zr-Uio-66 was determined from the powder XRD data. Since X-ray could not distinguish two different capping species, the evidence for $\mu_3$-OH groups initially comes from IR spectroscopy.\textsuperscript{34} As shown below, they can be easily differentiated by $^{17}$O SSNMR. Figure 2.10 displays $^{17}$O MAS and CP MAS spectra of as-synthesized Zr-Uio-66. The strong peak at around 278 ppm is due to the carboxylate oxygen in 1,4-BDC ligands. The resonance appearing at 60 ppm is also seen in the CP MAS spectrum with very short contact time, indicating that this peak is due to the capping $\mu_3$-OH. In addition, there is a very sharp line at 388 ppm. Based on the chemical shift, this peak can be assigned to the capping $\mu_3$-$\text{O}^{2-}$ species.\textsuperscript{35} The sharpness of this peak suggests that the capping $\text{O}^{2-}$ likely has very high mobility. It is possible that the four $\text{O}^{2-}$ anions undergo fast inter-exchange at room temperature.
Figure 2.10 $^{17}$O MAS and CPMAS spectra of Zr-Uio-66. *: spinning sidebands.

(Copyright 2013 American Chemical Society)$^{32}$

Table 2.5 Experimental $^{17}$O NMR parameters of Zr-Uio-66

| O Site   | $|C_Q|$(MHz) | $\eta_Q$ | $\delta_{iso}$(ppm) | $\Omega$ (ppm) | $\kappa$ |
|----------|-------------|----------|---------------------|---------------|----------|
| $\mu_3$-OH | 6.6(3)     | 0.49(5)  | 60(5)               | 50 (10)       | 1.0 (1)  |
| -COO$^-$  | 7.3(3)     | 0.81(5)  | 278(5)              | 0             | 0        |
| $\mu_3$-O$^2$ | 2.4(3)   | 0.87(5)  | 388(5)              | 200 (20)      | 0        |

* $\alpha$, $\beta$ and $\gamma$ are 0

Besides MAS spectra, static spectrum of Zr-Uio-66 is also acquired. Figure 2.11 displays the static experimental spectrum and simulated spectra. The CSA parameters obtained from the static spectrum are listed in Table 2.5.
2.3.3 MIL-96(Al)

MIL-96(Al) is also a MOF with several oxygen species.\(^{16}\) It is a porous aluminum trimesate MOF constructed from a hexagonal network of 18-membered rings and \(\mu_3\)-O\(^{2}\)-centered units. The three-dimensional (3D) framework contains isolated trinuclear \(\mu_3\)-oxo (O1) bridged aluminum (Al1) clusters and infinite chains of AlO\(_6\)(OH)\(_2\), (Al2) and AlO\(_2\)(OH)\(_4\), (Al3) octahedra. AlO\(_6\) octahedra of Al2 and Al3 form a honeycomb lattice based on 18-membered rings. The octahedra are connected to each other through the trimesate species, which induce corrugated chains of aluminum octahedra, linked via \(\mu_2\)-hydroxo (O2) bonds with the specific -cis-cis-trans- sequence. There are three –COO\(^{-}\) oxygen species. O7, O8 and O6 bond to Al1, Al2 and Al3, respectively. There is a disordered site Al4 and some water molecules in the structure. The guest water can be removed upon calcination. The 3D framework of MIL-96 has three types of cages (Figure 2.12). Two of them have estimated pore volumes of 417 and 635 Å\(^3\) (Figures 2.12a and 2.12b), respectively, and encapsulate free water molecules. The diameters are estimated
to 8.8 and 10.1 Å. The third one is small (Figure 2.12c) and contains disordered aluminum site. The size of this pore is estimated to a range of 2.5~3.5 Å. The pores exhibit the potential for molecule separation and gas adsorption upon activation.

![Figure 2.12 Three cages in MIL-96(Al) (Copyright 2006 American Chemistry Society)](image)

![Figure 2.13 Framework of MIL-96(Al) (a) and coordination of three ordered Al sites (b, c, d).](image)
Figure 2.13 presents the framework and three Al sites of MIL-96(Al), which bears various oxygen species, including –COO’, μ₂-OH, μ₃-O²⁻ and coordinated H₂O. The 18-membered rings are built by AlO₆ octahedra of Al2 and Al3. Octahedra of Al1 are in the rings. The variety of oxygen species makes the ¹⁷O NMR spectrum more complicated comparing with those of MIL-53(Al) and Zr-UiO-66. To reduce the complexity, the MOF is heated at 150 °C under vacuum to remove the water in the pore and coordinated to Al. Figure 2.14 shows the ¹⁷O MAS echo spectrum, where four peaks are present. The signal/noise ratio is lower than those in previous section, though the acquisition time is as long as 17 h. This is primarily because there are more oxygen sites in MIL-96(Al). These peaks are simulated with DMFIT package to display the spinning sidebands.²⁸ Simulation results are in Table 2.6.

**Figure 2.14** ¹⁷O MAS NMR spectrum at 20 kHz of MIL-96(Al). *: spinning sidebands.
To assign the oxygen peaks, theoretical calculations are required. The structure of MIL-96(Al) is more complicated than that of MIL-53(Al) and Zr-UiO-66. As a result, the unit cell is very large for CASTEP calculation. So I employed Gaussian calculation to predict the NMR parameters of oxygens in MIL-96(Al). Gaussian calculation is first applied to MIL-53(Al)-np, since the NMR parameters of the oxygens have been obtained. Figure 2.15 shows the cluster used for calculation. Table 2.7 shows the calculation results. The calculated $\delta_{\text{iso}}$ are higher than the experimental values, but their trend is correct.

![Figure 2.15 The cluster for Gaussian calculation of MIL-53(Al)-np.](image)

$[\text{Al}_2(\text{BDC})_6(\text{OH})_3]^9$. 

Table 2.6 Experimental $^{17}$O EFG parameters of MIL-96(Al)

| O Signal | $|C_Q|$/MHz | $\eta_Q$ | $\delta_{\text{iso}}$/ppm |
|----------|------------|----------|--------------------------|
| Signal 1 | 10.0(5)    | 0.66(5)  | 255(5)                   |
| Signal 2 | 8.0(5)     | 0.50(5)  | 30(5)                    |
| Signal 3 | 8.0(5)     | 0.30(5)  | 165(5)                   |
| Signal 4 | 9.0(5)     | 0.40(5)  | 315(5)                   |
Table 2.7 Gaussian calculation results of MIL-53(Al)-np

<table>
<thead>
<tr>
<th>O Site</th>
<th>O species</th>
<th>Calculated $\delta_{iso}$ (ppm)</th>
<th>Experimental $\delta_{iso}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>$\mu_2$-OH</td>
<td>61</td>
<td>24(5)</td>
</tr>
<tr>
<td>O2</td>
<td>-COO$^-$</td>
<td>305</td>
<td>210(5)</td>
</tr>
<tr>
<td>O2b</td>
<td>-COO$^-$</td>
<td>281</td>
<td>210(5)</td>
</tr>
<tr>
<td>O3</td>
<td>-COO$^-$</td>
<td>363</td>
<td>256(5)</td>
</tr>
<tr>
<td>O3b</td>
<td>-COO$^-$</td>
<td>342</td>
<td>256(5)</td>
</tr>
</tbody>
</table>

Then I apply Gaussian calculation to MIL-96(Al). Figure 2.16 shows the clusters for calculation. Table 2.8 shows the calculated $^{17}$O EFG parameters. By comparing with the experimental $\delta_{iso}$ displayed in Table 2.6, signals 1, 3, 4 are assigned to O8, O7 and O6 respectively. The calculated $\delta_{iso}$ values of O1 (103 ppm) and O2 (80 ppm) are relatively close to that of signal 2 (30 ppm). As a result, both O1 and O2 should contribute to signal 2. And the spinning sideband of O8 overlaps with signal 2 (Figure 2.14). So the signal 2 may be mixture of O1, O2 and spinning sideband of O8.

**Figure 2.16** Clusters used for Gaussian calculation of MIL-96(Al). $[\text{Al}_3(\text{BTC})_6(\text{O})(\text{H}_2\text{O})_3]^{11-}$ (a) and $[\text{Al}_5(\text{BTC})_4(\text{OH})_3]^{2-}$ (b).
### Table 2.8 Gaussian calculation results of MIL-96(Al)

| O Site | O species | \( |C_Q| \) (MHz) | \( \eta_Q \) | \( \delta_{iso} \) (ppm) |
|--------|-----------|-----------------|-------------|--------------------|
| O2     | \( \mu_2\)-OH | 7.64            | 0.55        | 103                |
| O1     | \( \mu_3\)-O\(^2\^-\) | 3.74            | 0           | 80                 |
| O7     | -COO\(^-\) | 7.24            | 0.88        | 257                |
| O8     | -COO\(^-\) | 7.57            | 0.72        | 289                |
| O6     | -COO\(^-\) | 7.81            | 0.75        | 301                |

### 2.4 Summary

In this chapter, I successfully prepared several prototypical \(^{17}\)O-enriched MOFs. Because of the diversity of MOF-based materials, different types of MOFs may require different isotopic enrichment methods to effectively incorporate \(^{17}\)O from \(^{17}\)O-enriched H\(_2\)O. Several synthetic strategies for \(^{17}\)O enrichment were discussed. Using these \(^{17}\)O-enriched MOFs, we were able to acquire \(^{17}\)O SSNMR spectra at a magnetic field of 21.1 T. They provide distinct spectral signatures of various key oxygen species commonly existing in representative MOFs. We demonstrate that \(^{17}\)O SSNMR can be used to differentiate chemically and, under favorable circumstances, crystallographically nonequivalent oxygens and to follow the phase transitions. The synthetic approaches for preparation of \(^{17}\)O-enriched sample described in this chapter are fairly simple and cost-effective. It is hoped that this work will encourage other researchers to use \(^{17}\)O SSNMR for MOF characterization.

### 2.5 References


Chapter 3

3 SSNMR Study of Metal Center Cations in MOFs

3.1 Introduction

3.1.1 SSNMR study of metal center cations

To better understand the relationship between the property and structure of MOFs, we need to get the precise structure information. Although the accurate structures of some MOFs have been determined based on single X-ray diffraction, many other MOF structures are refined from more limited powder X-ray diffraction patterns due to the difficulty in getting suitable single crystal. In these cases, information from complementary techniques is required to refine structures more accurately. SSNMR can provide such complementary information since it is sensitive to the short range order of the structure and the local chemical environment of metal center. The changes in bond length and bond angle around the metal cation will induce detectable difference in NMR parameters, therefore the appearance of the spectrum will change. The combination of SSNMR and XRD data will help optimize the structure of MOFs.

Among the applications in optimizing the structure of MOFs, obtaining information on the local geometry around metal center is of importance. NMR spectrum reflects local geometry around the cations sensitively. More often than not, the local environment of metal cations is affected by processes including dehydration, desolvation and adsorption of guest molecules, even though the framework remains intact. Such change is due to the interaction between metal cations and the solvent/guest molecules, and can be detected by SSNMR.

Some obstacles, however, limit the application of SSNMR on metal centers. First, many metal centers in MOFs are quadrupolar nuclei. The quadrupolar interaction between the quadrupole moment of a nucleus and local electric field gradient (EFG) often results in very broad NMR pattern. Second, some metal nuclei have low magnetogyric
ratio ($\gamma$), making it difficult to detect their NMR signal. Last but not the least, the natural abundances of many metal nuclei are very low, resulting in weak NMR signal.

Due to these problems, SSNMR study on metal centers in MOFs is largely limited to some nuclei with high $\gamma$ and high natural abundance, including $^{27}$Al, $^{71}$Ga and $^{45}$Sc. For example, Loiseau et al employed $^{27}$Al SSNMR to differentiate the four Al sites in MIL-96(Al). As is discussed in Chapter 3, there are four Al sites in the framework. Three ordered Al sites and one disordered site. The four Al sites were clearly differentiated by $^{27}$Al SSNMR, providing evidence for their existence. Beside the highly receptive nuclei, some more challenging nuclei including $^{25}$Mg, $^{67}$Zn, which have both low $\gamma$ and low natural abundance, have recently been studied at ultrahigh magnetic field of 21.1 T.

In this thesis, I synthesized MOFs whose metal centers are Ti (MIL-125(Ti)), Zr (MIL-140A), In (MIL-68(In), In(BDC)$_{1.5}$(bipy) and In(BTC)(H$_2$O)(phen)) and La (La$_2$(BDC)$_3$(H$_2$O)$_4$ and La$_2$(C$_4$H$_8$O$_4$)$_3$(H$_2$O)$_2$·(H$_2$O)). Shi et al provide several Zn-MOFs including TIF-1, TIF-5, Zn-zni and Zn-dia. Ultrahigh filed of 21.1 T is utilized to acquire good SSNMR spectra of these metal center cations including $^{47/49}$Ti, $^{67}$Zn, $^{91}$Zr, $^{115}$In and $^{139}$La, which reveal the relationship between the structure and NMR parameters. Magnetic fields of 14.1 T and 9.4 T are also employed to acquire $^{139}$La and $^{115}$In spectra of La-MOFs and In-MOFs. Spectra acquired at multiple fields are helpful to get accurate CSA parameters.

3.1.2 $^{91}$Zr SSNMR study of MIL-140A

Recent years have seen growing interest in Zr compounds for their novel properties. Layered and three dimensional zirconium phosphates display potential in the areas of catalysis, sorption, protonic conductors, solar energy storage, crystal engineering and ion exchange. Several Zr-MOFs such as Zr-Uio-66, P1ZOFS, MOF-525, MOF-535 and MOF-545 have been reported. An outstanding feature of these Zr-MOFs is the high thermal and chemical stability, enabling them to be employed under rough conditions in further application, including catalysis and molecules adsorption. For some of the MOFs, the structure is resolved from single-crystal X-ray diffraction or synchrotron single-crystal data. For the rest, however, the structure is merely simulated from powder X-
ray diffraction (PXRD) patterns.\textsuperscript{9, 11} Since the relative intensity of the peaks in PXRD may not be accurate, the structure determined from PXRD simulation may deviate from the actual structure. To solve the problem, solid state \textsuperscript{91}Zr NMR can be used to refine the structure.

\textsuperscript{91}Zr is a challenging nucleus for solid state NMR, primarily for the large quadrupole moment, 176 mb\textsuperscript{12}. The low natural abundance (11.2\%) and low magnetogyric ratio $\gamma$ (-2.49×10\textsuperscript{7} rad·T\textsuperscript{-1}·s\textsuperscript{-1}, which is only 9.3\% that of \textsuperscript{1}H) also limit the application of \textsuperscript{91}Zr NMR. In order to overcome these obstacles, ultrahigh magnetic field 21.1 T is employed to enhance the intensity and narrow the width of the resonances. Beside, Quadrupolar CarrPurcell Meiboom-Gill (QCPMG) method is adopted to obtain better spectrum when the $T_2$ is long enough to acquire multiple spin echo cycles. QCPMG technique consists of a series of $\pi$ pulses which refocus the transverse magnetization, thereby allowing a spin echo to be recorded multiple times per scan. Fourier transformation of the resultant echo train results in a spectrum composed of narrow lines called spikelets.\textsuperscript{13}

Despite the unfavorable properties, \textsuperscript{91}Zr NMR has proved to be a good tool to study the local environment and structure of zirconium compounds. Lapina et al. employed \textsuperscript{91}Zr NMR to directly reveal the nature of Zr sites in silica fiberglass modified with zirconia.\textsuperscript{14} Zhu et al. utilized \textsuperscript{91}Zr NMR to study the local environment of Zr cation a serial of zirconium silicates through QCPMG method.\textsuperscript{15} \textsuperscript{91}Zr NMR also provides information about the ion-exchange in zirconium phosphates.\textsuperscript{6} However, \textsuperscript{91}Zr SSNMR study of MOFs has not been reported yet.

In this chapter, I employed \textsuperscript{91}Zr SSNMR to study the metal center and refine the structure of MIL-140A. MIL-140A, originally synthesized by Guillerm et al., is a MOF with high stability and high amount of Lewis acid sites.\textsuperscript{16} The structure of the MOF is determined through simulation of PXRD pattern, making the reliability of the fine structure open to doubt. \textsuperscript{91}Zr NMR and Cambridge Serial Total Energy Package (CASTEP) calculation are employed to obtain refined structure.
3.1.3 $^{115}$In SSNMR study of In-MOFs

Indium salts and indium coordination complexes have found many important applications, such as superconductor, semiconductor and catalyst. For example, some indium-phosphorus semiconductors have drawn attention for their potential application as light-emitting diodes. $^{115}$In solid state NMR (SSNMR) has been applied to study these systems despite the large Q of $^{115}$In (Table 1.2). For example, Jung et al employed $^{115}$In MAS NMR to study the band gap in wurtzite indium nitrite. Chen et al applied $^{115}$In static NMR to reveal the relationship between $^{115}$In chemical shift and different ligands in In coordination complexes. They also studied how the EFG parameters such as $C_Q$ and $\eta_Q$ are influenced by the symmetry of indium environment. Such work proves that $^{115}$In is a useful tool to study the structure of In-containing systems.

Indium is a Group 13 element. The most stable oxidation state of In is In(III), which displays spherical symmetry of electron shells with $d^{10}$ formation. In(III) cation is a hard acid in the hard and soft (Lewis) acids and bases (HSAB) system. Based on HSAB theory, “hard likes hard and soft likes soft”, which means hard atoms prefer to bond hard atoms. As a result, In(III) can strongly bond to the ligands to form coordination compounds with hard donor atoms including N, O and F. At the same time, indium is capable of forming stable complexes with softer bases (P, S, Cl, Br, and I), which provides for In(III) the existence of heteroleptic species with donor atoms of various HSAB series. Due to the above reasons, In$^{3+}$ can be coordinated by a variety of organic ligands, and adopts a wide range of coordination numbers. In recent years, a lot of indium containing MOFs have drawn attention for their potential for hydrogen storage, CO$_2$ adsorption, small molecule separation and catalysis. Encouraged by the $^{115}$In NMR work on indium salts and indium coordination complexes, I utilize $^{115}$In NMR to study the In local environment in MOFs.

The NMR parameters of $^{115}$In are listed in Table 1.2. The natural abundance and magnetogyracy ratio are high, and spin number is also very large. The quadrupole moment, however, is very large, making the NMR resonance very wide. In this chapter I focus on three kinds of In-MOFs: MIL-68(In)$^{24}$, In(BDC)$_{1.5}$(bipy) and In(BTC)(H$_2$O)(phen).
BDC is terephthalate, BTC is benzenetricarboxylate, bipy is 2,2'-bipyridyl and phen is 1,10-phenanthroline. MIL-68(In) displays tunnels with large diameters of 16 and 6 Å. It draws attention for its capability in gas adsorption.\textsuperscript{24,27} The other two MOFs are active and selective acid catalysts in acetalization of aldehydes. The structures of all the MOFs were revealed by single crystal XRD.\textsuperscript{24,26}

### 3.1.4 \textsuperscript{139}La SSNMR study of La-MOFs

Lanthanum compounds have attracted attention for their intense luminescence and potential application in luminescent materials and devices. They can be used in electroluminescent devices, integrated optics\textsuperscript{28} and biological labels\textsuperscript{29}. Numerous MOFs employing La as metal center have been reported for their outstanding properties. For example, La\textsubscript{2}(BDC)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{4} (BDC: benzenedicarboxylate) exhibits luminescent property as nanoscale particles\textsuperscript{30}. Another property of Lanthanum compounds is the potential catalytic activity. Rare-earth containing compounds are widely used as effective catalysts.\textsuperscript{31,32} For example, lanthanum succinates could be used as heterogeneous catalysts in many organic reactions of industrial importance such as the acetalization of aldehydes and the oxidation of sulfides.\textsuperscript{33} Lanthanides have also been explored in many other catalytic reactions such as oxidation of thioethers\textsuperscript{34}, cyanosilylation of aldehydes and ring opening of meso-carboxylic anhydrides\textsuperscript{35}.

\textsuperscript{139}La SSNMR has been employed to study La primarily due to its favorable NMR properties. There are two isotopes of Lanthanum: \textsuperscript{138}La and \textsuperscript{139}La. The natural abundance of \textsuperscript{139}La is 99.91\%. So the NMR study on La-MOFs focuses on \textsuperscript{139}La. The spin number (I) of \textsuperscript{139}La is 7/2 and magnetogyric ratio is 3.81×10\textsuperscript{7} rad·T\textsuperscript{-1}·s\textsuperscript{-1} (14.1\% of \textsuperscript{1}H). The nuclear quadrupole moment (Q) is 200(6) millibarn (1 millibarn = 10\textsuperscript{-31} m\textsuperscript{2}). The advantage of \textsuperscript{139}La NMR is that the natural abundance is very large. And magnetogyric ratio and spin number are also high. The disadvantage of \textsuperscript{139}La NMR is that the quadrupole moment is large. MAS NMR is not applicable for La-MOFs in most cases because the \textsuperscript{139}La resonance is often too broad.\textsuperscript{36-40} As a result, the potential of lanthanum NMR in the solid state has not been thoroughly explored.\textsuperscript{40}
In this chapter I focus on two kinds of La-MOFs, La$_2$(BDC)$_3$(H$_2$O)$_4$ and La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O. BDC is terephthalate and C$_4$H$_4$O$_4$ is succinate. La$_2$(BDC)$_3$(H$_2$O)$_4$ is a MOF with luminescent property. La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O is a catalytic MOF for acetalization of aldehydes and the oxidation of sulfides. The structures of these MOFs were determined by single crystal XRD. La NMR was used to study the environment of La nuclei in the framework.

3.1.5 $^{47/49}$Ti SSNMR study of MIL-125(Ti)

Titanium compounds have attracted much attention for their application in many areas. TiO$_2$, in particular, has seen many applications in hydrogen production, catalysis, protonic conductors and photocatalyst. Besides TiO$_2$, other titanium compounds such as titanium phosphates and titanium nitrides are also widely used in areas of electrode materials, photocatalysts and acid catalysts. Titanium is a very attractive metal cation due to its low toxicity, redox activity, and photocatalytic properties. The incorporation of titanium in MOFs should also benefit from the porosity of the structure, though Ti-MOFs remain sparse.

Titanium is a challenging nucleus for solid state NMR, primarily because there are two NMR active isotopes with extremely low and almost identical magnetogyric ratio. The spin numbers of $^{47}$Ti and $^{49}$Ti are 5/2 and 7/2, respectively. The Natural abundances are 7.44% and 5.41%. The nuclear quadrupole moments are 302 and 247 mb. Their magnetogyric ratios are very low, -1.5105×10$^7$ rad·T$^{-1}$·s$^{-1}$ (5.638 % of $^1$H) and -1.5110×10$^7$ rad·T$^{-1}$·s$^{-1}$ (5.639 % of $^1$H). Since the magnetogyric ratios are almost identical, the resonances of the two isotopes can hardly be distinguished. As $^{49}$Ti has a larger spin number and a smaller quadrupole moment, the observed resonance is mainly contributed by $^{49}$Ti.

Despite the difficulty due to the unfavorable properties of the nuclei, $^{47/49}$Ti NMR has been employed to study the local chemical environment of titanium cations. Zhu et. al. examined the $^{47/49}$Ti static NMR spectra of several titanium phosphates, including α-, β- and γ-TiP, to characterize the local structure around Ti in these materials. Ballesteros et. al. examined the correlations between the structure of some titanium alkoxide and...
chloride precursors immobilized by grafting or tether procedures.53 Titanium coordination complexes were studied through $^{47/49}$Ti NMR. For example, Rossini et al. utilized $^{47/49}$Ti MAS and static NMR to relate the anisotropic NMR tensor parameters to the molecular and electronic structures of titanocene chlorides.54

To our best knowledge, there is no $^{47/49}$Ti NMR study of Ti-MOFs yet. But previous work on Ti compounds inspires us to apply the technique to study the local environment of Ti cations in MOFs. My work in this chapter focuses on MIL-125(Ti)51.

### 3.1.6 $^{67}$Zn SSNMR study of Zn-MOFs

Zinc is an important metal center in MOFs. It is the center of IRMOFs55,56, ZIFs57-59 as well as many other MOFs60, 61. Information of the local Zn environment would help understand the structure of such MOFs. In principle, Zn SSNMR should be ideal to probe the Zn environment. However, the only NMR active isotope of zinc is $^{67}$Zn, which exhibits very challenging NMR properties. Its natural abundance is only 4.1 % and the magnetogyratic ration is only 6.3 % that of $^1$H. Such obstacles make it difficult to get high-quality NMR spectra.

Despite the unfavorable NMR properties, $^{67}$Zn SSNMR has proved to be a useful tool to probe the local Zn environment of MOFs. Sutrisno et al acquired $^{67}$Zn SSNMR spectra at ultrahigh field of 21.1 T.5 They demonstrated that $^{67}$Zn NMR was sensitive to the local Zn environment and could differentiate nonequivalent Zn sites. They also demonstrated that $^{67}$Zn SSNMR was sensitive to the guest molecules present inside the cavities of ZIF-8.

Inspired by the literature work, I employed $^{67}$Zn SSNMR at 21.1 T to study the local environment of several other Zn-MOFs: TIF-1, TIF-5, Zn-zni and Zn-dia.
3.2 Experimental

3.2.1 Synthesis of MOFs

*MIL-140A*\(^{16}\)

In a typical synthesis of MIL-140A or ZrO(BDC), 4 mmol ZrCl\(_4\) (Sigma-Aldrich, 98 \%) and 5 mmol H\(_2\)BDC (Sigma-Aldrich, 98 \%) were dissolved in 25 mL anhydrous DMF. The solution was added into a 50 mL Teflon-lined autoclave and heated at 493 K for 20 h. Then 1 g product was recovered by vacuum filtration. After being washed in 80 mL DMF and 80 mL acetone in the filter, the product was recovered as a white powder.

*MIL-68(In)*\(^{24}\)

In a typical synthesis of MIL-68(In), or In(OH)(BDC), 2.4 mmol In(NO\(_3\))\(_3\)-5H\(_2\)O (Alfa, 98 \%) and 3 mmol H\(_2\)BDC were dissolved in 12 mL DMF. The solution was added into a 30 mL Teflon-lined autoclave and heated at 403 K for 22 h. 0.8 g product was recovered by vacuum filtration as a white powder. The powder was calcined at 523 K under vacuum for 5 h to remove DMF in the tunnel and get activated MIL-68(In).

*In(BDC)\(_{1.5}\)(bipy)*\(^{26}\)

In a typical synthesis of In(BDC)\(_{1.5}\)(bipy), 2.5 mmol In(NO\(_3\))\(_3\)-5H\(_2\)O (Alfa, 98 \%), 7.5 mmol H\(_2\)BDC (Sigma-Aldrich, 98 \%), 7.5 mmol 2,2’-bipyridyl (bipy, Alfa, 98\%), 0.4 mL Et\(_3\)N (Triethylamine, 99.5 \%) and 25 mL H\(_2\)O were added into a 50 mL Teflon-lined autoclave and heated at 443 K for 48 h. 1 g product was recovered by vacuum filtration as a white powder. After being washed in 80 mL H\(_2\)O and 80 mL ethanol, the product was recovered by vacuum filtration.

*In(BTC)(H\(_2\)O)(phen)*\(^{26}\)

In a typical synthesis of In(BTC)(H\(_2\)O)(phen), 1.2 mmol In(NO\(_3\))\(_3\)-5H\(_2\)O (Alfa, 98 \%) and 2.5 mmol H\(_3\)BTC (Sigma-Aldrich, 98 \%), 2.5 mmol 1,10-phenantroline (phen, Sigma-Aldrich, 98\%), 0.4 mL Et\(_3\)N (Triethylamine, 99.5 \%) and 25 mL H\(_2\)O were added
into a 50 mL Teflon-lined autoclave and heated at 443 K for 48 h. 1 g product was recovered by vacuum filtration as a white powder. After being washed in 80 mL H$_2$O and 80 mL ethanol, the product was recovered by vacuum filtration.

$La_2(BDC)_3(H_2O)_4^{30}$

In a typical synthesis of $La_2(BDC)_3(H_2O)_4$, 1.5 mmol LaCl$_3$·7H$_2$O (Sigma-Aldrich, 99.9 %) and 2 mmol Na$_2$BDC were dissolved in 25 mL H$_2$O. White precipitate formed upon stirring. 0.4 g product was obtained by vacuum filtration.

Na$_2$BDC was prepared by mixing NaOH and H$_2$BDC (2:1 molar ratio) in water and heated to remove the water. The product was further purified by refluxing in ethanol.

$Ld_2(C_4H_4O_4)_3(H_2O)_2·(H_2O)^{33}$

In a typical synthesis of $Ld_2(BDC)_3(H_2O)_4$, 2 mmol LaCl$_3$·7H$_2$O (Sigma-Aldrich, 99.9 %), 3 mmol succinic acid (C$_4$O$_4$H$_6$, or HOOCCH$_2$CH$_2$COOH, Alfa, 99 %), 1 mL Et$_3$N and 10 mL H$_2$O were added into a 50 mL Teflon-lined autoclave and heated at 453 K for 5 days. 0.35 g product was recovered as white powder by vacuum filtration.

$MIL$-$125(Ti)^{51}$

In a typical synthesis of MIL-125(Ti), 0.75 g H$_2$BDC and 0.9 mL Ti(OPr)$_4$ (liquid) were dissolved in a mixture of 13.5 mL DMF and 1.5 mL MeOH. The solution was put in a Teflon-lined autoclave and heated at 423 K for 17 h. The product was recovered by vacuum filtration. After washing in acetone, the product was recovered by vacuum filtration as a white powder. The as-synthesized MIL-125(Ti) powder was further calcined in air at 473 K for 20 h to remove the DMF in the tunnel and get activated MIL-125(Ti).
The following Zn-MOFs are prepared by Qi Shi et al.

**TIF-1**

Zn(OAc)$_2$·2H$_2$O (0.22 g, 1.0 mmol) and 5,6-dimethylbenzimidazole (0.29 g, 2.0 mmol) were dissolved in 2-amino-1-butanol (10 mL) and benzene (5 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 150 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

**TIF-5**

Zn(OAc)$_2$·2H$_2$O (0.22 g, 1.0 mmol), imidazole (0.068 g, 1.0 mmol) and 5,6-dimethylbenzimidazole (0.146 g, 1.0 mmol) were dissolved in methanol (15 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

**Zn-zni**

Zn(OAc)$_2$·2H$_2$O (0.22 g, 1.0 mmol) and imidazole (0.20 g, 3.0 mmol) were dissolved in methanol (15 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 72 h. After cooling to room temperature, the solid products were separated by filtration and washed with ethanol.

**Zn-dia**

Zn(OAc)$_2$·2H$_2$O (0.11 g, 0.5 mmol) and 2-methylimidazole (0.41 g, 5.0 mmol) were dissolved in H$_2$O (8 mL) in a 30 mL Teflon-lined stainless steel autoclave. The autoclave was then sealed and heated at 120 °C for 24 h. After cooling to room temperature, the solid products were separated by filtration and washed with distilled water.
Figure 3.1 XRD patterns of MOFs
3.2.2 Powder X-ray Diffraction Measurements

The purity of the MOFs is confirmed by powder XRD characterization. The XRD patterns are shown in Figure 3.1.

3.2.3 Simulation of NMR spectra

NMR parameters are determined by simulations of NMR spectra using the WSOLIDS and QUEST program. To simulate the spectra of MIL-125(Ti) and TIF-5, QUADFIT program is employed to simulate the local disorder of $^{47/49}$Ti and $^{67}$Zn. The experimental error for each measured parameter was determined by visual comparison of experimental spectra with simulations. The parameter of concern was varied bidirectionally starting from the best fit value and all other parameters were kept constant, until noticeable differences between the spectra were observed. In this chapter, experimental and simulated spectra are displayed in blue and black, respectively.

3.2.4 $^{91}$Zr SSNMR spectroscopy

$^{91}$Zr NMR spectrum of MIL-140A is acquired at 21.1 T using WURST-QCPMG method due to the extremely large width of the resonance. A home-built 7 mm H/X static probe is used. The Larmor frequency is 83.6 MHz. WURST-QCPMG is similar to normal frequency stepped QCPMG, but employs a single frequency offset. And the excitation bandwidth of the WURST pulses is much wider. We run two WURST-QCPMG experiments on MIL-140A. The offset is from low frequency to high frequency for one, and from high to low frequency for the other. Then we add the two spectra to get the $^{91}$Zr NMR spectrum. The reference sample is BaZrO$_3$(solid) at 316 ppm relative to saturated Zr(C$_5$H$_5$)$_2$Cl$_2$ solution in CH$_2$Cl$_2$ at 0 ppm. The 90° pulse lengths for all nuclei in this chapter are calibrated with the corresponding reference samples. The 90° pulse length is 1 $\mu$s, spectrum width (SW) is 1 MHz, pulse delay is 0.5 s and number of scan is 49,152. Proton decoupling is applied to remove the dipolar coupling interaction. The decoupling field is 30 kHz.
3.2.5 $^{115}$In SSNMR spectroscopy

The Larmor frequency of $^{115}$In at 21.1 T is 197.2 MHz. The probe is a home-built 7 mm H/X static probe. $^{115}$In NMR chemical shifts were referenced with respect to an external solution of 0.1 M In(NO$_3$)$_3$ in 0.5 M HNO$_3$ at 0 ppm. Proton decoupling is applied at the decoupling field of 25 kHz. For $^{115}$In static echo spectrum of In(BDC)$_{1.5}$(bipy), the $90^\circ$ pulse length is 4 $\mu$s, SW is 200 kHz, pulse delay is 5 s and number of scan is 4,096. For $^{115}$In stepwise static echo spectrum of In(BTC)(H$_2$O)(phen), the $90^\circ$ pulse length is 4 $\mu$s, SW is 200 kHz, pulse delay is 1 s and number of scan is 32,768. The spectrum of added from 2 pieces. The frequency offset is 1 MHz. Stepwise $^{115}$In static echo spectra of the two In-MOFs are also acquired at 9.4 T. The probe is a 5 mm H/X static Varian probe. The reference sample is saturated In(NO$_3$)$_3$ solution at 0 ppm. The Larmor frequency is 87.5 MHz. The $90^\circ$ pulse length is 0.5 $\mu$s, SW is 200 kHz, pulse delay is 0.5 s and number of scan is 61,440 for each piece. The spectrum of In(BDC)$_{1.5}$(bipy) is co-added from 8 pieces and the spectrum of In(BTC)(H$_2$O)(phen) is co-added from 7 pieces. The frequency offset is 250 kHz for both MOFs.

Stepwise $^{115}$In static echo spectra of as-synthesized and activated MIL-68(In) are also acquired at 21.1 T. The spectra are both co-added from 9 pieces. SW of each piece is 500 kHz. The $90^\circ$ pulse length is 20 $\mu$s, pulse delay is 0.5 s and number of scan is 4,096 for each piece. Proton decoupling is also applied at the decoupling field of 25 kHz.

3.2.6 $^{139}$La SSNMR spectroscopy

The Larmor frequency of $^{139}$La static echo spectrum of La-MOFs at 21.1 T is 127.1 MHz. The probe used for static spectra is a home-built 5 mm H/X static probe. The probe for 22 kHz MAS experiments is a 3.2 mm H/X MAS Bruker probe. A 1 M aqueous LaCl$_3$ solution is used as reference sample at 0 ppm. For $^{139}$La static echo spectrum of La$_2$(BDC)$_3$(H$_2$O)$_4$, the $90^\circ$ pulse length is 1 $\mu$s, SW is 500 kHz, pulse delay is 1 s and number of scan is 4,096. The MAS spectrum is also acquired. The the $90^\circ$ pulse length is 2 $\mu$s, SW is 500 kHz, pulse delay is 1 s and number of scan is 8,192. The spinning rate is 22 kHz. For $^{115}$In static echo spectrum of La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O, the $90^\circ$ pulse length
is 1 μs, SW is 500 kHz, pulse delay is 1 s and number of scan is 24,576. $^1$H decouple is applied for static spectra. The decoupling field is 70 kHz. Stepwise $^{139}$La static echo spectra of the two La-MOFs are also acquired at 14.1 T. The probe is a 5 mm H/X static Varian probe. The reference sample is a saturated aqueous LaCl$_3$ solution at 0 ppm. The Larmor frequency is 84.6 MHz. The 90° pulse length is 3.5 μs, SW is 500 kHz, pulse delay is 0.5 s and number of scan is 15,360 for each piece. Each spectrum is added from two pieces. The frequency offset is 67.7 kHz for both MOFs.

3.2.7 $^{47/49}$Ti SSNMR spectroscopy

The $^{47/49}$Ti static echo spectra of MIL-125(Ti) are acquired at 21.1 T using a home-built 7 mm X static probe. The Larmor frequency is 50.75 MHz. Pulse delay is 0.5 s. Number of scan is 184,320 for as-made phase and 196,608 for activated phase. The reference sample is a Cp$_2^{49}$TiCl$_2$ solution in CH$_2$Cl$_2$ at -773 ppm relative to neat TiCl$_4$ at 0 ppm. No signal is observed from WURST-QCPMG method. It is possibly due to the short T$_2$. Static spectra are acquired because the peaks are too wide for MAS.

3.2.8 $^{67}$Zn SSNMR spectroscopy

The $^{67}$Zn spectra of Zn-MOFs are acquired at 21.1 T. The Larmor frequency is 56.4 MHz. The probe used for static spectra is a home-built 7 mm H/X static probe. The probe for 5 kHz MAS experiments is a 7 mm H/X MAS Bruker probe. A 1 M aqueous Zn(NO$_3$)$_2$ solution was used as a standard for referencing $^{67}$Zn chemical shifts ($\delta_{iso}=0.0$ ppm) and also for pulse calibration. NMR measurement conditions for static echo (echo), static WURST-QCPMG (QCPMG)$^{13}$ and MAS one-pulse (one-pulse) are listed in Table 3.1. In the WURST-QCPMG spectra, the offset between peaks is 5 kHz. Proton decoupling is applied at the decoupling field of 60 kHz.
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<th>SW (kHz)</th>
<th>Pulse delay(s)</th>
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<td>50</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Zn-zni Echo</td>
<td>4</td>
<td>100</td>
<td>1</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Zn-dia Echo</td>
<td>4</td>
<td>100</td>
<td>1</td>
<td>46</td>
<td></td>
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<tr>
<td>Zn-dia QCPMG</td>
<td>50</td>
<td>500</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

### 3.2.9 Gaussian calculation

*Ab initio* calculations were conducted using the Gaussian 09 program on SHARCNET (www.sharcnet.ca). The EFG tensors of $^{17}$O in all the model clusters were calculated using hybrid density functional theory (DFT). Several methods were tried, including RHF, B3LYP$^{69}$, TPSSTPSS$^{70}$ and PBE1PBE$^{71}$. For Zn, In and La, several basis sets including 6-31G*, 6-311G*, 3-21G and LAN2DZ were tried and the best combinations of methods and basis sets are displayed in Table 3.2. The basis sets used for other atoms in all the MOFs were 6-311+G* for O and N, and 6-31G* for C and H. These basis sets were chosen based on previous studies in literature, which showed good agreement with experimental values in similar systems.$^{72-74}$ For Ti, B3LYP and several basis sets
(3F(4333/43/4), 3F(5333/53/5), 5F(4333/43/4), 5F(5333/53/5)) were used because previous literature work showed that such level and basis sets gave results in good agreement with experimental values in layered Ti compounds. The results of B3LYP/3F(4333/43/4) showed the best agreement, which is consistent with literature work.52

**Table 3.2 Gaussian calculation conditions of metal nuclei**

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Method</th>
<th>Basis set</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>B3LYP</td>
<td>3F(4333/43/4)</td>
</tr>
<tr>
<td>Zn</td>
<td>RHF</td>
<td>6-31G*</td>
</tr>
<tr>
<td>In</td>
<td>PBE1PBE</td>
<td>3-21G</td>
</tr>
<tr>
<td>La</td>
<td>B3LYP</td>
<td>LAN2DZ</td>
</tr>
</tbody>
</table>

In this chapter, the CASTEP calculation is performed by Dr. Anmin Zheng.

### 3.3 Results and discussion

#### 3.3.1 \(^{91}\)Zr SSNMR study of MIL-140A

The crystal symmetry of MIL-140A is monoclinic.16 The space group is \(C2/c\).16 Zr is seven coordinated with four oxygens from carboxylate of BDC (benzenedicarboxylate) and three \(\mu_3\)-\(\text{O}^2\) (Figure 3.2a). The site symmetry of Zr is \(C_i\). In the framework, ZrO\(_7\) clusters connect with each other through \(\mu_3\)-\(\text{O}^2\) to form zirconium oxide chains along \(c\) axis (Figure 3.2c). The structure of the framework along \(c\) axis is shown in Figure 3.2b.
Figure 3.2 Zr coordination (a, c) and framework (b) of MIL-140A

Figure 3.3 illustrates the $^{91}$Zr SSNMR experimental spectra of MIL-140A at 21.1 T. The NMR parameters are displayed in Table 3.3. The $C_Q$ is very large compared with other zirconium compounds.\textsuperscript{6,14,15,75,76} This is due to the low symmetric environment of Zr$^{4+}$ cations. Zr is seven coordinated and Zr is at the center of ZrO$_7$ SBU. The symmetry of such SBU is lower than tetrahedral and octahedral.
To better understand the relationship between the local structure and the EFG at the Zr sites, CASTEP calculation was carried out. Previous literature work has proved that CASTEP calculation results are in good agreement with the experimental results. The CASTEP calculations were performed by using the crystal structure proposed by Guillerm et al (Structure a)\(^{16}\), yielding the following EFG parameters: \(C_Q = 62.1\ \text{MHz}, \ \eta_Q = 0.63\). The same CSA parameters extracted from experimental spectrum were used to plot the spectrum based on structure a (Figure 3.3 and Table 3.3). Surprisingly, the

**Table 3.3 \(^{91}\text{Zr} \) NMR parameters of MIL-140A**

| \(|C_Q|/\text{MHz} \) | \(\eta_Q\) | \(\delta_{\text{iso}}\) | \(\Omega/\text{ppm}\) | \(\kappa\) | \(\alpha\) | \(\beta\) | \(\gamma\) |
|-----------------|---------|-----------------|-----------------|-------|-------|-------|-------|
| Experimental    | 35.0    | 0.85            | 100             | 200   | 0     | 35    | 25    | 0     |
| Structure a     | 62.1    | 0.63            | 100             | 200   | 0     | 35    | 25    | 0     |
| Structure b     | 39.8    | 0.82            | 100             | 200   | 0     | 35    | 25    | 0     |

**Figure 3.3 \(^{91}\text{Zr} \) static spectra of MIL-140A.**
calculated $C_Q$ value is drastically larger than the experimental value (35.0 MHz), and the peak based on Structure a is much broader than the experimental one as a result.

To examine if the discrepancy might result from the inaccuracy in the crystal structure, which is simulated from powder XRD rather than single-crystal XRD$^{16}$, the geometry of all the atoms in the unit cell is optimized (Structure b). CASTEP calculation is then performed based on the optimized structure. The calculation predicts $C_Q = 39.8$ MHz, $\eta_Q = 0.82$, which are in much better agreement with measured EFG parameters. Figure 3.3 displays the NMR spectrum using the calculated $C_Q$ and $\eta_Q$. The same CSA parameters extracted from experimental spectrum were also used (Table 3.3). The NMR spectrum based on the optimized structure is in good agreement with the experimental one.

![Figure 3.4 Illustration of structure from iteration (a) and optimized structure (b)
(Zr-O bond length unit: Å and O-Zr-O angle unit: °).](image)

Figure 3.4 displays the local environment of Zr in structure of literature by Guillerm et al (structure a)$^{16}$ and optimized structure (structure b). The bond length distribution of structure a (2.018 Å ~ 2.348 Å) is larger than that of structure b (2.038Å ~ 2.221Å), resulting in a larger $C_Q$ value of structure a.
Figure 3.5 shows the XRD spectra simulated based on structure a and structure b. The locations of the XRD peaks are identical. The intensities of peaks, which are determined by the coordination of the atoms in the structure\textsuperscript{77}, are almost identical. As a result, the structural difference of structure a and b cannot be differentiated by powder XRD. It is demonstrated that SSNMR is sensitive to the structural difference that cannot be detected by powder XRD.

3.3.2  \textsuperscript{115}In SSNMR study of In-MOFs

\textit{In(BDC)}\textsubscript{1.5}(bipy) and \textit{In(BTC)}(H\textsubscript{2}O)(phen)

The crystal symmetry of \textit{In(BDC)}\textsubscript{1.5}(bipy) is orthorhombic and the space group is \textit{Pbca}.\textsuperscript{26} In is eight coordinated by six oxygens from three carboxylate groups and two nitrogens from one bipy (Figure 3.6b). In the framework, InO\textsubscript{6}N\textsubscript{2} clusters do not connect with each other directly, but through BDC linkers. The structure of the framework is shown in Figure 3.6a.
Figure 3.6 Framework (a) and coordination of In (b) in In(BDC)$_{1.5}$(bipy).

The crystal symmetry of In(BTC)(H$_2$O)(phen) is monoclinic. The space group is $P2_1/n$. In is six coordinated by three oxygens from three carboxylate groups, one oxygen from H$_2$O and two nitrogens from bipy (shown in Figure 3.7b). In the framework, InO$_6$N$_2$ clusters extend to infinite framework through BTC linkers. The structure of the framework is shown in Figure 3.7a.

Figure 3.7 Framework (a) and coordination of In (b) in In(BTC)(H$_2$O)(phen).

In static SSNMR spectra, the pattern is influenced by both quadrupolar interaction and chemical shift anisotropy (CSA) broadening. As discussed in Chapter 1, quadrupolar interaction is decided by the electric field gradient (EFG) of local environment. Chemical shielding results from the interaction between nuclear spins and creates a local secondary magnetic field. It represents the response of electronic cloud around the nucleus to an
applied magnetic field. When we obtain a spectrum, we can extract the EFG and CSA tensors, which are the key to understand the local chemical environment. However, since there are many parameters, more than one combination may exist. The parameters we obtained may not be accurate.

To improve the reliability of NMR parameters, two magnetic fields are employed to acquire $^{115}$In NMR spectra. The magnitude of quadrupolar broadening is inversely proportional to $B_0$, while the magnitude of the CSA broadening is proportional to it. So at different magnetic fields, the quadrupolar interaction and the CSA will have opposite effects, which helps extract the true parameters.

$^{115}$In static NMR spectra are acquired at two magnetic fields, 9.4 T and 21.1 T. Figure 3.8 displays the spectra of In(BDC)$_{1.5}$(bipy). Figure 3.9 displays the spectra of In(BTC)(H$_2$O)(phen). Table 3.4 displays the parameters extracted by fitting the spectra at both fields.

**Table 3.4 $^{115}$In NMR parameters of In(BDC)$_{1.5}$(bipy) and In(BTC)(H$_2$O)(phen)**

|                      | $|C_Q|$/MHz | $\eta_Q$ | $\delta_{iso}$/ppm | $\Omega$/ppm | $\kappa$ | $\alpha$ | $\beta$ | $\gamma$ |
|----------------------|------------|----------|---------------------|--------------|----------|----------|---------|---------|
| **Experimental results** |            |          |                     |              |          |          |         |         |
| In(BDC)$_{1.5}$(bipy) | 79.5(20)   | 0.57(5)  | -110(20)            | 130(5)       | 1.0(1)   | 0        | 50(5)   | 0       |
| In(BTC)(H$_2$O)(phen)| 145.0(20)  | 0.18(5)  | -10(20)             | 500(10)      | 1.0(1)   | 0        | 60(5)   | 0       |
| **Gaussian calculation results** |            |          |                     |              |          |          |         |         |
| In(BDC)$_{1.5}$(bipy) | 5.0        | 0.53     | 117                 | 16.0         | -0.19    | 167      | 71      | 41      |
| In(BTC)(H$_2$O)(phen)| 9.2        | 0.72     | 72                  | 35           | 0.44     | 88       | 84      | 252     |

Comparing with previous literature work on indium coordination complexes, the $C_Q$ values of In(BDC)$_{1.5}$(bipy) and In(BTC)(H$_2$O)(phen) are within the range$^{18, 21}$, but smaller than many indium coordination complexes. The smaller bond length distributions
make the spherical symmetry around $\text{In}^{3+}$ higher than most indium coordination complexes, resulting in lower $C_Q$ values.

Figure 3.8 $^{115}\text{In}$ static spectra of $\text{In(BDC)}_{1.5}(\text{bipy})$ at 21.1 T and 9.4 T.
Figure 3.9 $^{115}$In static spectra of In(BTC)(H$_2$O)(phen) at 21.1 T and 9.4 T. The peak marked as # may be due to impurity in the MOF.
Figure 3.10 The CSA and quadrupolar interaction contribution in the spectra of $\text{In(BDC)}_{1.5}(\text{bipy})$. 
Figure 3.10 and 3.11 show the broadening due to CSA and quadrupolar interaction in the spectra of the two In-MOFs. It is noticed that the broadening due to quadrupolar interaction is the dominant component.

Comparing the parameters of In(BDC)$_{1.5}$(bipy) and In(BTC)(H$_2$O)(phen), we find that the $C_Q$ value of In(BTC)(H$_2$O)(phen) is much higher than that of In(BDC)$_{1.5}$(bipy). Since $C_Q$ reflects the deviation from spherical symmetry of the local environment of In nucleus, the difference indicates that the local environment of In in In(BTC)(H$_2$O)(phen) is less spherically symmetric. To better understand the difference, the bond lengths around In are measured.
Figure 3.12 Bond lengths of $\text{InO}_6\text{N}_2^{15}$- and $\text{InO}_5\text{N}_2^{13}$- clusters (In, O and N are in blue, red and dark yellow).

Figure 3.12 displays the bond lengths of In-O and In-N bonds (unit: Å). For In(BTC)(H$_2$O)(phen) there is an approximate C$_5$ axis. The O(N)-In-O(N) angles on the C$_5$ plane are 72.2, 83.5, 74.1, 50.2 and 81.5 degree. In perfect C$_5$ symmetry, the angle should be 72 degree. The angles in the MOF are around the desired angle, but a bit deviated. As a result, the $\eta_Q$ is 0.18, which is lower than In(BDC)$_{1.5}$(bipy) and more close to zero.

The bond lengths in In(BDC)$_{1.5}$(bipy) range from 2.22 to 2.55 Å. In bond length range of In(BTC)(H$_2$O)(phen), however, is from 2.12 to 2.82 Å, which is much higher. The larger range lowers the spherical symmetry, resulting in a larger $C_Q$ as a consequence. Such relationship between structure and $C_Q$ is also confirmed by Gaussian calculation (Table 3.4). Calculation is based on the clusters displayed in Figure 3.12. Clusters with organic ligands are too large for Gaussian calculation using the computational facility available to us.

In(BDC)$_{1.5}$(bipy), which exhibits higher spherical symmetry around In atom, has a lower $C_Q$ value compared with In(BTC)(H$_2$O)(phen). As a result, the calculated $C_Q$ is
much smaller than experimental one. But the relationship between the spherical symmetry and $C_Q$ value has been confirmed.

**MIL-68(In)**

The crystal symmetry of MIL-68(In) is orthorhombic. The space group is $Cmcm$.\textsuperscript{24} In is six coordinated with four oxygens from four carboxylate groups and two hydroxyl oxygens (shown in Figure 3.13b). In the framework, InO\textsubscript{6} clusters extend to infinite framework through BDC linkers. The structure of the framework is shown in Figure 3.13a. As is shown, two In sites appear alternatively in the structure. The site symmetry of In1 and In2 are $i$ and $C_{2h}$. The ratio between In1 and In2 is 2. The In-OH and In-O (-COO\textsuperscript{-}) bond lengths are displayed in Figure 3.13c (units: Å). Two types of tunnels are present in the framework along $c$ axis (Figure 3.13a). The diameters of the tunnels are about 16 and 6 Å.\textsuperscript{27} In as-synthesized phase, there are DMF molecules in the small tunnel, which can be removed upon desolvation.

![Figure 3.13 Framework (a) and In coordination environment (b, c) of MIL-68(In).](image)
Figure 3.14 $^{115}$In static spectra of as-synthesized MIL-68(In).

Figure 3.14 displays the $^{115}$In static spectra of as-synthesized MIL-68(In). Two signals are observed in the spectra. Table 3.5 lists their NMR parameters. Signal 1 and 2 are assigned to In1 and In2 for two reasons. First, the intensity of signal 1 is stronger than that of signal 2, consistent with the larger population of In1. Second, the signal 2 has a larger $C_Q$ than signal 1. Since the InO$_6$ octahedron of In2 is more deviated from perfect octahedron (Figure 3.13c), the signal due to In2 should have a larger $C_Q$. 
Gaussian calculations were also used to predict the theoretical NMR parameters. Clusters are built based on one In atom, two hydroxyl groups and four BDC linkers (Figure 3.15). Calculation results (Table 3.5) confirm the assignment. The $C_Q$ of In1 is smaller than that of In2. So signal 1 is assigned to In1 and signal 2 is assigned to In2.

**Table 3.5** $^{115}$In EFG and CSA parameters of MIL-68(In)

|                     | $|C_Q|$/MHz | $\eta_Q$ | $\delta_{iso}$/ppm | $\Omega$/ppm | $\kappa$ |
|---------------------|------------|----------|---------------------|--------------|----------|
| **Experimental results (as-synthesized)** |            |          |                     |              |          |
| Signal 1            | 248(5)     | 0.075(5) | -100(50)            | 600(20)      | 1.0(1)   |
| Signal 2            | 300(5)     | 0.14(1)  | 0(50)               | 700(20)      | 0.7(1)   |
| **Gaussian calculation results (as-synthesized)** |          |          |                     |              |          |
| In 1                | 235        | 0.39     | 4596                | 651          | 0.55     |
| In 2                | 295        | 0.02     | 4520                | 711          | 0.17     |
| **Experimental results (activated)** |            |          |                     |              |          |
| Signal 1            | 184(5)     | 0.07(2)  | -40(50)             | 500(20)      | 0        |
| Signal 2            | 300(5)     | 0.67(5)  | 350(50)             | 400(20)      | 0        |

* $\alpha$, $\beta$ and $\gamma$ are 0
Figure 3.16 shows the $^{115}$In static spectra of activated MIL-68(In). The NMR parameters are displayed in Table 3.5. Two signals are observed in the spectra. Signal 2 has similar $C_Q$ to In2 of as-synthesized MIL-68(In). And the intensity of signal 2 is also lower than signal 1. So signal 1 is assigned In1 and signal 2 is assigned to In2, respectively. It is noticed that the $C_Q$ of In1 in activated phase is much smaller than that in as-synthesized phase, but $C_Q$ of In2 does not change. It is assumed that the DMF molecules have strong interaction with In1. When they are removed upon calcination, the chemical environment of In1 becomes more symmetric. The interaction between DMF and In2 must be weak, so the removal of DMF does not affect the environment of In2 much.

![Experimental, stepwise Offset=500kHz](image)

![Experimental, co-added](image)

![Signal 1 + Signal 2](image)

![Signal 2](image)

![Signal 1](image)

Figure 3.16 $^{115}$In static spectra of activated MIL-68(In).
3.3.3 \(^{139}\text{La}\) SSNMR study of La-MOFs

The crystal symmetry of \(\text{La}_2(\text{BDC})_3(\text{H}_2\text{O})_4\) is triclinic. The space group is \(P-1.\)\(^{30}\) There is only one La site, which is eight coordinated by six oxygens from six carboxylate groups and two oxygens from water (Figure 3.17b). The site symmetry of the La is \(C_1.\) In the framework, LaO\(_8\) clusters do not connect with each other directly, but through BDC linkers. The structure of the framework is shown in Figure 3.17a.

La\(_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}\) belongs to monoclinic system. The space group is \(C2/c.\)\(^{33}\) There is also only one La site, which is nine coordinated by eight carboxylate oxygens from six BDC ligands and one oxygen from water (Figure 3.18b). The site symmetry of La is \(C_1.\) LaO\(_9\) clusters do not connect with each other directly, but through BDC linkers. The structure of the framework is shown in Figure 3.18a.
To measure the NMR parameters of \( \text{La}_2(\text{BDC})_3(\text{H}_2\text{O})_4 \), the MAS spectrum at 21.1 T is first acquired. The EFG parameters including \( C_Q, \eta_Q \) and \( \delta_{\text{iso}} \) are extracted from it. Then static spectra are acquired to determine the CSA parameters. As is discussed in the previous section, NMR study at different magnetic fields helps determine the NMR parameters accurately. \(^{139}\) \( \text{La} \) static NMR spectra are acquired at two magnetic fields, 14.1 T and 21.1 T. The Larmor frequencies are 84.7 MHz and 127.1 MHz, respectively. Figure 3.19 displays the spectra of \( \text{La}_2(\text{BDC})_3(\text{H}_2\text{O})_4 \). For \( \text{La}_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O} \), only static spectra are acquired, because the resonance is too broad for MAS. Figure 3.20 displays the spectra of \( \text{La}_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O} \). Table 3.6 shows the NMR parameters extracted via fitting the spectra at both fields.

Comparing with previous literature work on \( \text{La} \) compounds\(^{36, 38}\), the \( C_Q \) values of \( \text{La}_2(\text{BDC})_3(\text{H}_2\text{O})_4 \) and \( \text{La}_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O} \), are within the range.
Figure 3.19 $^{139}$La spectra of La$_2$(BDC)$_3$(H$_2$O)$_4$ at 21.1 T and 14.1 T. *: spinning sidebands.
Figure 3.20 $^{139}$La static spectra of $\text{La}_2(\text{C}_4\text{H}_4\text{O}_4)_3(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}$ at 21.1 T and 14.1 T.
Table 3.6 $^{139}$La EFG and CSA parameters of La-MOFs

| $|Q|$/MHz | $\eta_Q$ | $\delta$iso/ppm | $\Omega$ppm | $\kappa$ | $\alpha$ | $\beta$ | $\gamma$ | 
|---|---|---|---|---|---|---|---|
| Experimental results | | | | | | | |
| La$_2$(BDC)$_3$(H$_2$O)$_4$ | 18.1 | 0.10 | 18 | 370 | -1 | 50 | 65 | 0 |
| La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O | 28.0 | 0.43 | 125 | 100 | 0.2 | 30 | 45 | 30 |
| Gaussian calculation results | | | | | | | |
| La$_2$(BDC)$_3$(H$_2$O)$_4$ | 4.7 | 0.16 | 15 | 102 | 0.30 | 231 | 16 | 166 |
| La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O | 3.4 | 0.16 | 40 | 112 | -0.88 | 265 | 68 | 178 |

Figure 3.21 CSA and quadrupolar interaction contribution in the spectra of La$_2$(BDC)$_3$(H$_2$O)$_4$. 
Figure 3.22 Quadrupolar interaction and CSA contribution in the spectra of La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O.

Figure 3.21 shows the broadening due to the CSA and the quadrupolar interaction in the spectra of La$_2$(BDC)$_3$(H$_2$O)$_4$. The broadening due to the CSA has similar magnitude with that due to quadrupolar interaction. Figure 3.22 shows the broadening due to the CSA and quadrupolar interaction in the spectra of La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O. Here the broadening due to quadrupolar interaction is the dominant component.

Figure 3.23 shows the La-O bond length distribution around the La in the two MOFs. The bond length distribution of La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O (mostly between 2.50 ~ 2.60 Å) is much smaller than that of La$_2$(BDC)$_3$(H$_2$O)$_4$ (2.28 ~ 2.53 Å). The $C_Q$ of La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$·H$_2$O, however, is much larger than that of La$_2$(BDC)$_3$(H$_2$O)$_4$. This may be due to the geometry environment of La in La$_2$(BDC)$_3$(H$_2$O)$_4$ can be viewed as deviated quadratic antiprism (Figure 3.24a). As is known, a metal cation in the center of a perfect tetrahedron, octahedron, cubic and quadratic antiprism (Figure 3.24b) has a $C_Q$ of
0.78 La in the center of a distorted quadratic antiprism should have reduced $C_Q$. Gaussian calculation results based on the structure in Figure 3.23 ((LaO$_8$)$_{13}^-$ and (LaO$_9$)$_{15}^-$) also confirm the assumption (Table 3.6). The two effects that affect $C_Q$ for La$_2$(BDC)$_3$(H$_2$O)$_4$ are bond length distribution which increases $C_Q$, and geometry which decreases $C_Q$. In this case, the geometric effect partially negates the effect of the large bond length distribution.

![La-O bond length distribution in La-MOFs (unit: Å). Blue: La. Red: O.](image1)

![La environment of La$_2$(BDC)$_3$(H$_2$O)$_4$ (a) and standard quadratic antiprism (b) (Copyright 2012 ELSEVIER).](image2)
3.3.4 $^{47/49}$Ti SSNMR study of MIL-125(Ti)

The crystal symmetry of MIL-125(Ti) is orthorhombic. The space group is $Pbca$. There is only one Ti site, and its symmetry is $C_i$. Ti is six coordinated by three oxygens from three carboxylate groups, two $\mu_2$-$O^2$ and one $\mu_2$-$OH$ (Figure 3.25c) to form TiO$_6$ SBUs. $\mu_2$-$O^2$ and $\mu_2$-$OH$ cannot be distinguished by XRD since it is not sensitive to hydrogen atoms. Eight TiO$_6$ SBUs form a ring (Figure 3.25b), which extends through BDC linkers. Rings on the same layer are connected through BDC linkers on the vertex of the ring, and those of adjacent layers are linked through BDC linkers on the edge (Figure 3.25b). The structure of the framework is shown in Figure 3.25a. The framework displays rings constructed by TiO$_6$ octahedra. Some DMF remains in the framework, which can be removed upon activation process. Both as-made phase and activated phase are studied by $^{47/49}$Ti static NMR.

![Figure 3.25 Framework (a, b) and coordination of Ti (c) in MIL-125(Ti).](image)

Figure 3.26 and Figure 3.27 show the experimental and simulated spectra of as-made and activated MIL-125(Ti). The lineshapes of MIL-125(Ti) spectra are not typical quadrupolar patterns due to the local disorder of Ti sites. Thus they are simulated using disorder model. The resonances of both Ti-47 and Ti-49 are added to get the simulated spectra. It is noticed that the pattern of Ti-47 is wide and its intensity is very low compared with that of Ti-49, due to the larger quadrupole moment of Ti-47.
Figure 3.26 $^{47/49}$Ti spectra of as-made MIL-125(Ti).

Figure 3.27 $^{47/49}$Ti spectra of activated MIL-125(Ti).
<table>
<thead>
<tr>
<th></th>
<th>$C_Q$/MHz</th>
<th>$\eta_Q$</th>
<th>$\delta_{iso}$/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-made, Ti-47</td>
<td>20.1 ± 1.0</td>
<td>0.68 ± 0.10</td>
<td>-590 (20)</td>
</tr>
<tr>
<td>As-made, Ti-49</td>
<td>16.4 ± 0.8</td>
<td>0.68 ± 0.10</td>
<td>-590 (20)</td>
</tr>
<tr>
<td>Activated, Ti-47</td>
<td>16.4 ± 1.0</td>
<td>0.50 ± 0.10</td>
<td>-658(20)</td>
</tr>
<tr>
<td>Activated, Ti-49</td>
<td>13.4 ± 0.8</td>
<td>0.50 ± 0.10</td>
<td>-658(20)</td>
</tr>
</tbody>
</table>

Table 3.7 shows the NMR parameters extracted from experimental spectra. Upon activation, the $C_Q$ values of activated phase decrease along with the shrink of the width of NMR peaks. Such phenomenon is similar to the observation on MIL-68(In). After calcination process, powder X-ray pattern remains identical (Figure 3.1) but the NMR resonance of the metal cations gets narrower. Such observation indicates that the framework of the MOF remains intact upon activation, but the local environment of metal cations has changed.

Generally, a lower $C_Q$ value means higher spherical symmetry around the nucleus. The absence of DMF lowers the $C_Q$ value, which indicates the spherical symmetry around Ti$^{4+}$ cations is higher after DMF is removed. In the framework, DMF molecules probably present inside the ring. DMF, which is a polar molecule, may have strong dipolar interaction with oxo and hydroxyl, which are close to the inner side of the ring. The dipolar interaction between DMF molecules and the framework may lower the spherical symmetry around Ti$^{4+}$ cations, leading to a higher $C_Q$ value when DMF is present.

In the structure of MIL-125(Ti), the coordination of titanium, oxygen and carbon atoms was determined by powder X-ray diffraction. As is mentioned, the six oxygens coordinated to Ti$^{4+}$ are from 3 –COO⁻ oxygens, 2 $\mu_2$-OH and 1 $\mu_2$-O²⁻. The location of hydrogen cannot be directly determined. As a result, it is not possible to discriminate oxygen atoms from oxo and hydroxo moieties, while IR spectroscopy confirms the presence of $\mu_2$-OH groups. In order to distinguish the oxo and hydroxo around Ti$^{4+}$,
Gaussian calculations were performed. Calculation is based on the structure displayed in Figure 3.25b. Figure 3.28 shows three possible ways to locate hydrogen. In structure a, four $\mu_2$-OH groups are on the inner side of the ring. In structures b and c, the inner side of the ring is occupied by four $\mu_2$-O$^2$-groups. In structure c, the four $\mu_2$-OH groups are on the same side of the ring (all pointing up). In structure b, the four $\mu_2$-OH groups appear on different sides of the ring alternatively.

![Figure 3.28 Three possible structures of MIL-125(Ti) for calculation.](image)

Table 3.8 shows the Gaussian calculation results based on the three structures. It is noticed that the calculations with the 3F(4333/43/4) basis set give the best predictions of $^{47/49}$Ti $C_Q$, which is consistent with the literature. Comparing with the simulation results of activated MIL-125(Ti) in Table 3.7, the $|C_Q|$ values of structure b and c are more close to the experimental values (13.4 MHz for Ti-49). The arrangement of oxo and hydroxyl groups may be close to structures b and c.

The Gaussian calculation results also reveal a possible reason for the local disorder. As is shown, the location of $\mu_2$-OH groups have a profound effect on the $C_Q$ of $^{47/49}$Ti. Structures a, b and c may coexist in the structure of MIL-125(Ti). The coexistence may be the reason for the distribution of NMR parameters of $^{47/49}$Ti.
Table 3.8 Gaussian calculation results of MIL-125(Ti)

| Structure | Basic sets         | $^{47}$Ti $|C_Q|$ (MHz) | $^{49}$Ti $|C_Q|$ (MHz) | $\eta_Q$ |
|-----------|--------------------|-------------------|-------------------|---------|
| a         | 3F(4333/43/4)      | 23.97             | 19.61             | 0.777   |
|           | 3F(5333/53/5)      | 23.74             | 29.02             | 0.657   |
|           | 5F(4333/43/4)      | 25.98             | 21.25             | 0.667   |
|           | 5F(5333/53/5)      | 30.18             | 24.68             | 0.613   |
| b         | 3F(4333/43/4)      | 19.58             | 16.01             | 0.671   |
|           | 3F(5333/53/5)      | 19.82             | 24.23             | 0.460   |
|           | 5F(4333/43/4)      | 22.60             | 18.48             | 0.433   |
|           | 5F(5333/53/5)      | 26.68             | 21.82             | 0.305   |
| c         | 3F(4333/43/4)      | 20.37             | 16.66             | 0.662   |
|           | 3F(5333/53/5)      | 20.52             | 25.10             | 0.452   |
|           | 5F(4333/43/4)      | 23.37             | 19.11             | 0.422   |
|           | 5F(5333/53/5)      | 27.48             | 22.48             | 0.288   |

3.3.5 $^{67}$Zn SSNMR study of Zn-MOFs

TIF-1

TIF-1$^{62}$ displays zeolite-like structure. TIF stands for tetrahedral imidazolate framework. TIF-1 crystallizes in a space group $P4_2/mnm$. There are four Zn sites with a ratio of Zn1: Zn2: Zn3: Zn4= 4: 4: 4: 1. Each Zn atom is coordinated by four N atoms from four different 5,6-dimethylbenzimidazolate (DMBIM) linkers. The site symmetries of Zn1, Zn2, Zn3 and Zn4 are $C_I$, $C_I$, $C_I$ and $C_{4h}$. Figure 3.29 shows the structure
information of TIF-1.\textsuperscript{52} In Figure 3.29a and 3.29b, organic linkers are not displayed to simplify the illustration. Figure 3.29a displays the topology of TIF-1. It is denoted zeatopology. The diameter of the tunnel is about 17 Å. The positions of four Zn sites are shown in Figure 3.29b. Four Zn1 atoms form a square and four Zn2 atoms occupy the centers of the edges. Zn4 locates at the center of the square. Squares on adjacent layers are connected via Zn3 tetrahedra. Figure 3.29c shows the Zn coordination.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.29.png}
\caption{Topology (a), four Zn sites (b) and Zn coordination in TIF-1(Zn). DMBIM is not displayed in a and b.}
\end{figure}
Figure 3.30 $^{67}$Zn spectra of TIF-1.

Figure 3.30 shows the $^{67}$Zn NMR spectra of TIF-1. The signal/noise ratio of static echo spectra is low though the experiment time is very long (24 h). This is due to the unfavorable NMR properties of $^{67}$Zn. WURST-QCPMG is used to get better spectra. Two Zn sites are observed. Their NMR parameters are displayed in Table 3.9. Signal 1 is narrower and has a smaller $C_Q$.

In the framework of TIF-1, there are four crystallographically non-equivalent Zn sites. To assign the NMR peaks, Gaussian calculation is carried out. Gaussian calculation is performed based on the cluster [Zn(DMBIM)$_4$]$^{2-}$ (Figure 3.29c). Calculation results are displayed in Table 3.9. Zn1, Zn2 and Zn4 have similar $C_Q$, while Zn 3 has the largest one. Based on the calculation results, Signal 1 is assigned to the mixture of Zn1, Zn2 and Zn4, and Signal 2 in the spectra is assigned to Zn3.
Table 3.9 $^{67}$Zn EFG parameters of different Zn sites

| MOF     | Zn signal/site | $|C_Q|$/MHz | $\eta_Q$ | $\delta_{iso}$/ppm |
|---------|----------------|------------|----------|-------------------|
|         |                | Experimental results |          |                   |
| TIF-1   | Signal 1       | 6.8 (10)   | 0.90 (10)| 350 (25)          |
|         | Signal 2       | 4.2 (10)   | 0        | 300 (25)          |
| Zn-zni  | Signal 1       | 5.9 (5)    | 0.90 (10)| 315 (10)          |
|         | Signal 2       | 4.3 (5)    | 0.35 (10)| 305 (10)          |
|         |                | Gaussian calculation results |          |                   |
| TIF-1   | Zn1            | 7.2        | 0.94     | -61               |
|         | Zn2            | 6.0        | 0.68     | -90               |
|         | Zn3            | 14.6       | 0.66     | -113              |
|         | Zn4            | 6.6        | 0        | 3                 |
| Zn-zni  | Zn1            | 12.1       | 0.15     | -76               |
|         | Zn2            | 7.2        | 0.95     | -60               |

*TIF-5*

TIF-$5^{63}$ crystallizes in a space group $I4_1/a$. There is only one Zn site (Figure 3.31c), which is coordinated by four N atoms from two DMBIM and two imidazolate (IM). Four Zn atoms occupy the vertexes of the rectangular SBU (Figure 3.31b). Figure 3.31a displays the topology of TIF-5, which is denoted gis. The diameter of the tunnel is about 12 Å.
Figure 3.31 Framework (a), SBU (b) and Zn environment of TIF-5(Zn).

Figure 3.32 displays the MAS and static spectra of TIF-5(Zn). Only one Zn resonance is observed. It is consistent with the fact that there is only one Zn site in the framework of TIF-5.\textsuperscript{63} The patterns, however, are not typical quadrupolar patterns due to the local disorder of Zn, which may be induced by the unremoved ethanol in the framework. The EFG and CSA parameters are extracted via fitting MAS and static spectra using disorder model. The parameters are listed in Table 3.10. The NMR parameters are comparable with those reported for other ZIFs in the literature.\textsuperscript{79, 80} Gaussian calculation is applied based on the cluster $[\text{Zn(DMBIM)}_2\text{IM}_2]^2^-$ (Figure 3.31c). The results are in Table 3.10, which are in good agreement with experimental results.
Figure 3.32 MAS and static spectra of TIF-5 at 21.1 T.

Table 3.10 $^{67}$Zn EFG and CSA parameters of TIF-5

<table>
<thead>
<tr>
<th></th>
<th>$C_Q$/MHz</th>
<th>$\eta_Q$</th>
<th>$\delta_{iso}$</th>
<th>$\Omega$/ppm</th>
<th>$\kappa$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td>4.0(3)±1.2(2)</td>
<td>0.60(5)±0.10(5)</td>
<td>303(10)</td>
<td>150(10)</td>
<td>1.0(0.1)</td>
<td>45(5)</td>
<td>45(5)</td>
<td>0</td>
</tr>
<tr>
<td>Calculated</td>
<td>4.6</td>
<td>0.51</td>
<td>-55</td>
<td>37</td>
<td>0.31</td>
<td>347</td>
<td>75</td>
<td>157</td>
</tr>
</tbody>
</table>

Zn-zni crystallizes in a space group $I4_{1}cd$. It is also denoted Zn-zni for its zni topology. There are two Zn sites, both of which are coordinated by four N atoms from four IM linkers (Figure 3.33c). Four Zn atoms occupy the vertexes of the square SBU (Figure 3.33b), in which Zn1 and Zn2 appear alternatively. Such square SBUs extend to
three dimensions to form infinite framework. Figure 3.33a displays the framework of Zn-zni. The edge length of the tunnel is about 6 Å.

Figure 3.33 Framework (a), SBU (b) and Zn environment of Zn-zni.

Figure 3.34 displays the static and MAS spectra of Zn-zni. Two signals are observed in the spectra, corresponding to the two crystallographically non-equivalent Zn sites in the framework of Zn-zni. The width of signal 2 is larger than the magnitude of spinning rate (5 kHz). As a result, the spinning sidebands overlap with the peak. Table 3.9 shows the NMR parameters. Gaussian calculation is applied based on the cluster (ZnIM₄)²⁻ (Figure 3.33c). The $C_Q$ of Zn1 (12.1 MHz) is significantly larger than that of Zn2 (7.2 MHz). As a result, the resonance of Zn1 is much broader than that of Zn2. Thus signal 1 should be assigned to Zn2.
Figure 3.34 $^{67}$Zn spectra of Zn-zni. *: spinning sidebands.

Zn-dia\textsuperscript{65}

Zn-dia crystallizes in a monoclinic space group $P2_1/c$. It is also denoted Zn-dia for its dia topology.\textsuperscript{81} There are two Zn sites, both of which are coordinated by four N atoms from four 2-methylimidazolate (MIM) linkers (Figure 3.35c). Figure 3.35b shows the construction of SBUs. There are six Zn atoms in each SBU. Three Zn atoms on the left side are equivalent and the rest occupy the other Zn site. Such square SBUs extend to
three dimensions to form infinite framework. Figure 3.35a displays the framework of Zn-dia.

Figure 3.35 Framework (a), SBU (b) and Zn environment of Zn-dia.

Figure 3.36 $^{67}$Zn QCPMG spectra of Zn-dia.
Table 3.11 $^{67}$Zn EFG parameters of Zn-dia

| MOF          | Zn signal/site | $|C_Q|$/MHz | $\eta_Q$       | $\delta_{\text{iso}}$/ppm |
|--------------|----------------|----------|---------------|--------------------------|
| **Experimental results** |                |          |               |                          |
| Zn-dia       | Signal 1       | 8.8 (5)  | 0.21 (5)      | 280 (10)                 |
|              | Signal 2       | 10.1 (5) | 0.56 (5)      | 268 (10)                 |
| **Gaussian calculation results** |                |          |               |                          |
| (ZnMIM₄)²⁻   | Zn1            | 10.2     | 0.16          | -83                      |
|              | Zn2            | 10.2     | 0.73          | -92                      |
| (Zn₅MIM₄)⁶⁺  | Zn1            | 10.2     | 0.22          | -96                      |
|              | Zn2            | 10.7     | 0.83          | -109                     |
| (Zn₅MIM₁₆)⁶⁻  | Zn1            | 10.6     | 0.30          | -82                      |
|              | Zn2            | 10.3     | 0.70          | -91                      |

Figure 3.36 shows the static spectrum of Zn-dia. As is shown, the reasonance is very broad comparing with those of the previous three Zn-MOFs. QCPMG spectrum is also acquired to get better $^{67}$Zn signal. Two signals are observed in the spectra, corresponding to the two crystallographically non-equivalent Zn sites in the framework of Zn-dia. The NMR parameters are shown in Table 3.11. Gaussian calculation based on the cluster (ZnMIM₄)²⁻ (Figure 3.37a) is employed to differentiate the Zn sites. Table 3.11 displays the calculation results. Zn1 has smaller $\eta_Q$ and larger $\delta_{\text{iso}}$, corresponding to signal 1. But the calculated $C_Q$ of Zn1 and Zn2 are identical. To confirm the differentiation of the Zn sites, the clusters are expanded by adding four adjacent Zn²⁺ cations (Zn₅MIM₄²⁺, Figure 3.37b). The calculation results are displayed in Table 3.11. Then the clusters further expanded by adding the MIM linkers to all the Zn²⁺ cations (Zn₅MIM₁₆⁶⁻, Figure 3.27c). The calculation results are also in Table 3.11. The calculations using three clusters
consistently predict that the $\eta_Q$ of Zn1 is smaller than that of Zn2. $\delta_{iso}$ of Zn1 is more shielded than Zn2. We tentatively assign signal 1 to Zn1 and signal 2 to Zn2. But the $C_Q$ of Zn1 and Zn2 are very close, indicating that the signals cannot be assigned unambiguously based on Gaussian calculation.

![Figure 3.37 Gaussian calculation clusters of Zn-dia.](image)

### 3.4 Summary

In this chapter, several MOFs with different metal cations are synthesized. SSNMR studies of the metal cations in this chapter convey that SSNMR is a powerful technique for characterization of MOFs. It is complementary to diffraction method and can be used to study local structure. $^{91}$Zr SSNMR shows that the proposed structure of MIL-140A may be inaccurate. The CASTEP calculation provides a more accurate structure. $^{115}$In spectra of In(BDC)$_{1.5}$(bipy), In(BTC)(H$_2$O)(phen) and MIL-68(In), $^{139}$La spectra of La$_2$(BDC)$_3$(H$_2$O)$_4$ and La$_2$(C$_4$H$_4$O$_4$)$_3$(H$_2$O)$_2$.H$_2$O, $^{47/49}$Ti spectra of MIL-125(Ti) and $^{67}$Zn spectra of TIF-1, TIF-5, Zn-zni and Zn-dia are sensitive to the local structure of metal cations. It is demonstrated that in combination with computational modeling, SSNMR can be used as an effective tool for directly probing the local environment of the metal cations in the framework. Both the bond length distribution and the geometry around metal centers have profound effect on their NMR parameters. SSNMR spectra are also sensitive to the local disorder of metal centers.
The spectra are primarily acquired at an ultrahigh magnetic field of 21.1 T as static spectra. In some cases, the patterns are relatively narrow. MAS spectra are also acquired, which determine the EFG parameters more accurately. Static spectra at lower magnetic fields of 9.4 and 14.1 T are also acquired to determine CSA parameters more accurately. Since NMR instruments operating at very high magnetic fields are becoming increasingly accessible, it is hoped that this work will encourage other researchers to use SSNMR for MOF materials characterization.

3.5 References


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Chapter 4

4 Conclusions and Future Work

4.1 Conclusions

The studies in this thesis are focused on the SSNMR studies of MOFs. Our studies have shown that SSNMR spectra of $^{17}$O and metal ions are sensitive to the environment of nuclei of interest. As a result, SSNMR is a useful tool to probe the structure of MOFs.

In Chapter 2, $^{17}$O-enriched MOFs are synthesized. $^{17}$O SSNMR spectra are acquired at an ultrahigh magnetic field of 21.1 T using these MOFs. The CASTEP and Gaussian calculations are also performed to assign the $^{17}$O signals. It is demonstrated that $^{17}$O SSNMR spectroscopy can be used to differentiate chemically and, under favorite circumstances, crystallographically nonequivalent oxygens and to follow the phase transitions. The degrees of $^{17}$O-enrichment of MOFs are evaluated. Estimation results show that the $^{17}$O-enrichment in this chapter is cost-effective.

Chapter 3 explores the SSNMR studies of metal cations in MOFs in combination with CASTEP and Gaussian calculations. The NMR spectra of several challenging quadrupolar nuclei are acquired at several magnetic fields of 21.1, 14.1 and 9.4 T. It is demonstrated that SSNMR spectra of cations are sensitive to the local structure of MOFs and can be used to refine the crystal structure obtained from powder XRD.

4.2 Future work

Gaussian calculations of In-MOF, La-MOFs, Ti-MOFs and Zn-MOFs have been performed in Chapter 3. The calculation results are sometimes deviated from experimental results. CASTEP calculations should provide more accurate results. The calculation results of the two Zn sites in Zn-dia are very close. CASTEP calculation may help differentiate them more accurately.
Many MOFs exhibit excellent adsorption capability of carbon dioxide. The further work should focus on understanding the CO$_2$ adsorption in MOFs. To this end, preliminary $^{13}$C SSNMR study of CO$_2$ adsorption in MOFs was carried out (results not included in the thesis). The $^{13}$C spectra of CO$_2$ loaded in MIL-68(In) at different temperatures were acquired. Three signals are observed, corresponding to three possible CO$_2$ adsorption sites. But theoretical calculation needs to be done in order to predict the CO$_2$ adsorption sites in MIL-68(In).

Besides MIL-68(In), a series of MOF with good CO2 adsorption capacity, including Zn$_2$(Atz)$_2$(ox), ZIF-95 and ZIF-100, have been synthesized. $^{13}$C spectra of CO$_2$ adsorbed in such MOFs should help detect the CO$_2$ adsorption mechanism.
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Poster Presentation: