Enhanced Structural Support of Metal Sites as Nodes in Metal-Organic Frameworks Compared to Metal Complexes

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ENHANCED STRUCTURAL SUPPORT OF METAL SITES AS NODES IN METAL-ORGANIC FRAMEWORKS COMPARED TO METAL COMPLEXES

by

Sanjit Das

A thesis submitted in partial fulfillment
of the requirements for the degree
of
MASTER OF SCIENCE
in
Chemistry

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2013
ABSTRACT

Enhanced Structural Support of Metal Sites as Nodes in Metal-Organic Frameworks Compared to Metal Complexes

by

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Utah State University, 2013

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Metal-organic frameworks are a new class of crystalline, porous solid-state materials with metal ions periodically linked by organic linkers. This gives rise to one-, two- or three-dimensional structures. Here, we compare the stability of similar metal sites toward external ligand (solvent) induced disruption of the coordination environment in metal complexes and in metal-organic frameworks. Our experimental results show that a metal site as node of a metal-organic framework retains much higher stability compared to a similar metal site in a metal complex.

(47 pages)
PUBLIC ABSTRACT

Enhanced Structural Support of Metal Sites as Nodes in Metal-Organic Frameworks Compared to Metal Complexes

Crystalline porous materials have gained long-standing interest for their application in gas storage, separation and catalysis. These materials have been useful for domestic, scientific and industrial purposes for many decades. Zeolites are a well known example of such materials.

Metal-organic frameworks are a new class of crystalline porous materials. They have many advantages over the more widely known zeolites. Though metal-organic frameworks are relatively new, their basic structure, known as the secondary building unit, very closely resembles the structure of metal complexes. Such metal complexes have been characterized in chemistry for more than a century.

Chemical catalysis is a process wherein a reaction rate becomes faster in the presence of an external agent. Metal complexes have been used for this purpose for many decades. Like other crystalline porous materials, metal-organic frameworks find applications in catalysis. Catalysis is often done in the presence of a solvent. This report deals with the stability of metal complexes and compares with that of metal-organic frameworks, with respect to their metal ions in the presence of external solvents.

Sanjit Das
I dedicate the work presented herein to my younger brother, Prosenjit Das.
ACKNOWLEDGMENTS

I would like to thank Dr. Siddhartha Das for allowing me to pursue research work in his lab. His idea and knowledge have been instrumental to achieve this work. I would like to thank all of my committee members, Dr. Lisa M. Berreau, Dr. John L. Hubbard and Dr. Robert S. Brown, for spending their valuable time for me. Their help and suggestions have been remarkable to complete my thesis. Also, Dr. Berreau and Dr. Hubbard have been great sources for my inorganic chemistry knowledge. I would also like to thank the Dept. of Chem. & Biochem., USU for the financial support.

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Finally, I would like to thank my parents, brother and Arpita for being there to motivate and inspire me. They also have been my constant companion and strength.

Sanjit Das
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LIST OF ABBREVIATIONS

Abs. Absorbance
AlO$_4^{5-}$ Aluminate
ATC Adamentanetetracarboxylate
BDC Benzenedicarboxylate
BZA Basiczincacetate
CFSE Crystal field stabilization energy
HKUST Hong Kong University of Science and Technology
HSAB Hard soft acid and base
Im Imidazolate
IRMOF Isoreticular metal-organic framework
MIL Materials Institute of Lavoisier
MOF Metal-organic framework
NbO Niobium oxide
$N$-MeIm $N$-methyl imidazole
OM Open metal
PtS Platinum sulfide
PXRD Powder x-ray diffraction
SBU Secondary building unit
SiO$_4^{4-}$ Silicate
UV-Vis Ultraviolet Visible
w.r.t. with respect to
Wt. % Weight percentage
ZIF Zeolite imidazolate framework
CHAPTER 1

INTRODUCTION

This report introduces the work on the investigation of structural support for metal sites in metal complexes and compares the same in metal-organic frameworks.

1.1 Metal complex

A coordination entity or compound is an assembly consisting of a central atom (usually metallic) to which is attached a surrounding array of other group(s) of atom(s) (ligands). Coordination compounds were known to the chemists from the beginning of eighteenth century. For example, an iron complex named ‘Prussian blue’ was discovered in 1706. Zeise’s salt, shown in Fig. 1-1, a platinum complex, was first isolated in the 1820s.

![Fig. 1-1 Structure of Zeise’s salt, a square planar platinum complex.](image-url)

During earlier days, coordination compounds seemed to be unusual as they appeared to withstand the normal rules of valence and used to be called ‘complex’ compounds. In a practical sense, a coordination compound or a coordination complex, or a metal complex, is synonymous and the term ‘metal complex’ will be used throughout this report.
Though metal complexes were known historically, their modern study began with two great men, Sophus Mads Jørgensen (1837-1914) and Alfred Werner (1866-1919) during the late nineteenth century. With the beginning of modern study, their academic and industrial importance was realized. Their presence and importance in biological processes were discovered as well.

There are plenty of examples of organic transformation reactions which are catalyzed by metal complexes. For example, alkene hydrogenation – addition of hydrogen to the double bond of an alkene is catalyzed by a rhodium complex known as “Wilkinson’s catalyst”. There are many natural processes where metal complexes are involved in a complicated manner to perform a particular task in selective and systematic way. For example, hemoglobin is an iron complex which carries oxygen in the blood. Studies of simpler model metal complexes similar to those involved in various natural processes helps us to better understand natural processes.

1.2 Ligand exchange in metal complexes

In a metal complex, a ligand can be replaced by another one and the process is known as ligand exchange or ligand substitution. Fig. 1-2 shows an example of ligand exchange on an octahedral metal complex, MA₆ where ligand A is being replaced by ligand L and ‘k’ is the rate constant for this ligand exchange reaction. There are two limiting mechanisms for ligand exchange on a metal center: dissociative and associative. A dissociative mechanism follows first-order kinetics; similar to S_N1 reaction in organic chemistry and an associative mechanism follows second-order kinetics; similar to S_N2 reaction in organic chemistry.

Depending on the rate of ligand exchange, metal complexes can be classified qualitatively as inert or labile (kinetic terms). An inert complex is characterized by slow ligand exchange whereas a labile complex undergoes fast ligand exchange. In a metal complex, generally the metal ion acts as a Lewis acid and ligands serve as Lewis bases and the stability of metal complexes conforms qualitatively to the expectation based on the HSAB concept of charge
and size. Their stability also depends on other factors like π-bonding contribution, chelate effect, CFSE (transition metal complexes), etc.

When a metal-ligand complex is dissolved in a solvent, it may undergo ligand dissociation and the empty metal sites can be coordinated by solvent molecules and the process is known as \textit{solvolysis}. Generally water is being used as solvent for reactions involving metal complexes. When water is used as solvent, the above process is called \textit{hydrolysis}. The reverse reaction of hydrolysis in which the water molecules in aquo complex of metal ions are being replaced by ligand molecules is often called \textit{anation}.

Metal complexes have been studied for a long time and their properties are well documented. In 1967, F. Basolo and R.G. Pearson compiled a book discussing metal complexes, their reaction rate, mechanism etc. Table 1-1 lists some of the first-order rate constants for water substitution on metal-aquo complexes from their report. In general, the magnitude of metal-ligand exchange rates follows the same trends as the metal-aquo complexes.

\textbf{Table 1-1} Water exchange rate constants for some metal-aquo complexes at 25\(^\circ\)C

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>Co(^{2+})</th>
<th>Mn(^{2+})</th>
<th>Fe(^{3+})</th>
<th>Cr(^{2+})</th>
<th>Ni(^{2+})</th>
<th>Zn(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constants (s(^{-1}))</td>
<td>6x10(^5)</td>
<td>3x10(^8)</td>
<td>2x10(^7)</td>
<td>1x10(^9)</td>
<td>3x10(^7)</td>
<td>2x10(^7)</td>
<td>3x10(^9)</td>
<td>2x10(^7)</td>
</tr>
</tbody>
</table>
We have studied the solvolysis of some metal-ligand complexes using UV-Vis spectroscopy to find out the minimum amount of solvent required to initiate their solvolysis and the results are discussed in this report.

1.3 Porous materials

Solid materials having pores or channels with large enough dimensions to allow access of guest molecules are known as porous materials. In terms of crystallinity, they can be broadly divided in two categories: crystalline porous materials and amorphous porous materials. With respect to the diameter of their pores, porous materials can also be classified as macro-, meso- or microporous materials (Table 1-2).\(^1\) Crystalline porous materials are advantageous over amorphous ones and have gained long-standing interest for being suitable for separation,\(^7\) molecular sensing,\(^8\) catalysis,\(^9\) as host template\(^10\) and many other applications. Silica and zeolites are well-known representative examples of crystalline porous materials. They are advantageous because (1) their structures can be characterized unambiguously by X-ray diffraction and other techniques, (2) they feature pores/channels with reproducible topologies and dimensions, and (3) they possess high mechanical and thermal stability.

<table>
<thead>
<tr>
<th>Material type</th>
<th>Pore diameter</th>
</tr>
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<tr>
<td>Macroporous material</td>
<td>&gt;50nm</td>
</tr>
<tr>
<td>Mesoporous material</td>
<td>2 to 50nm</td>
</tr>
<tr>
<td>Microporous material</td>
<td>&lt;2nm</td>
</tr>
</tbody>
</table>

Table 1-2 Classification of porous materials with respect to their pore diameter
1.4 Zeolites\textsuperscript{\textit{11, 12}}

Within the class of crystalline porous materials, zeolites are the most widely studied. Zeolites are naturally occurring inorganic porous minerals, aluminosilicates with alkali or alkaline earth metal cations. Zeolite framework structures consist of SiO\textsubscript{4}\textsuperscript{4-} and AlO\textsubscript{4}\textsuperscript{5-} tetrahedra linked by shared oxygen atoms. They are also known as molecular sieves and used commercially for applications in separation, molecular adsorption, removal, catalysis, ion-exchange, etc. For example, zeolite 4A is a porous inorganic solid with channels of 4Å diameter resulting from eight tetrahedrally coordinated silicon/aluminium atoms and eight oxygen atoms. Due to the size-selective specificity and hydrophilic nature of the channels, zeolite 4A is used as drying agent to absorb water. Once used as drying agent, it can be reactivated at elevated temperature for reuse.

Despite their widespread use, zeolites have some drawbacks. For example, their syntheses can be difficult to control. Only a limited number of synthetic and natural zeolites are known and modification to vary structures and/or topologies or properties of channel are not possible without alteration of the zeolite structure.

1.5 Metal-organic frameworks

Metal-organic frameworks are new class of porous, crystalline solid-state materials with one-, two- or three-dimensional structures. They are formed when metal ions or clusters are linked by organic molecules and/or anions (often called linkers) in a periodic manner (Fig. 1-3). Structure and properties of MOFs solely depend on the nature of the metal ion(s) and linker(s) present in MOFs. In MOFs, the coordination preference of the metal site dictates the number of linkers that can attach to the metal site and their orientation in the space.

1.5.1 Background

MOFs can be considered as successors of zeolites (natural minerals). In 1990, B. F. Hoskins and R. Robson proposed the possibility of a new class of scaffolding like material with
broader scope. They reported the structure and synthesis of such a three-dimensional material made from copper(I) as metal ion and 4, 4’, 4”, 4”’-tetracyanotetraphenylmethane as linker with tetrafluoroborate as the counter anion. They speculated about some exciting features of their newly proposed materials which are common to zeolites. They proposed that the new materials would have bigger cavities, better access of guest molecules, greater number of active sites, and more widely variable functionalization of the matrix than cross-linked polymers or zeolites.\textsuperscript{13}

Structures and syntheses of a few more such materials were reported during the next decade.\textsuperscript{14-16} Breakthroughs in this area came with the report of iconic MOF-5\textsuperscript{17} and HKUST-1,\textsuperscript{18} two of the most studied MOFs, during late twentieth century. The contributions of Mohamed Eddaoudi, Michael O’Keeffe and Omar M. Yaghi to the development of this new research area are remarkable.\textsuperscript{17,19-21}

1.5.2 Advantages over zeolites

As crystalline porous materials, MOFs are very promising as they exhibit some of the largest pore volumes and highest surface areas known in the literature. For example, MIL-101 has two types of pores, sized 29Å and 34Å, and it has surface area of 5900 m\textsuperscript{2}/g.\textsuperscript{22} Also most of the known MOFs possess permanent porosity and high thermal stability. During the last decade
MOFs have received a great deal of interest among researchers because of their exciting features and potential advantages over zeolites. In MOFs, organic linkers are present in the backbone of the framework whereas metal ions are linked by oxygen atoms in zeolites. The presence of organic linkers in MOFs offers possible modifications of dimension and properties (e.g., hydrophobicity, reactivity, exposed functionality etc.) of pores at the molecular level by means of synthetic modification of the organic linker either before or after synthesis of the MOF.\(^{19, 23}\) Accordingly, the structures and properties (physical and chemical) of MOFs can be controlled to a far greater extent relative to the zeolites. Control over the dimension and volume of the channels can selectively allow small to medium sized molecules to diffuse through the channels and functional groups present on the wall of the channels can help to bind molecules covalently inside the channels. With high accessible void volume, MOFs are suitable for hydrogen storage.\(^{24}\) Like zeolites, the use of MOFs as heterogeneous catalysts has also been explored.\(^{9, 25}\) In case of MOFs, the added advantage is that they contain organic linkers which can be tailored to accommodate a range of reactive groups which can actively or passively take part in catalysis.\(^ {25}\)

An obvious advantage of MOFs over any other solid state materials is that it is possible to design and tailor the structures and the sizes of pores within the MOF by carefully choosing the metal ions and organic linkers. Tailoring the MOFs structures and pore sizes are further advanced by (i) the wide variety of coordination preferences for transition and lanthanide metal ions, and (ii) structures and reactive functionalities of organic linkers which can be modified in a wide range by means of organic synthesis. Thus it is possible to generate a diverse range of MOF architectures.

1.5.3 Metal-organic frameworks: Terms, design and synthesis\(^ {20, 21}\)

Metal-organic frameworks are networks (abbreviated as nets) of metal ions or clusters with organic linkers. MOFs are reticular because it has the form of a net (usually periodic). This
is why sometimes MOF chemistry is referred as reticular chemistry. If a MOF has same net (with the same topology) throughout its structure it is called an isoreticular MOF. When a MOF is grown with the mutual intergrowth of two or more networks with same or different topology in a structure where the networks are physically but not chemically linked – the phenomenon is known as interpenetration. Use of longer linker to increase the space between vertices of a network is a process to replace a bond by a sequence of bonds and this process is called expansion. For example, oxalic acid and terephthalic acid both have two carboxylate moieties but as a linker, the latter one is longer in length (Fig. 1-4). The process involving replacement of a vertex with a group of vertices is named decoration. Fig. 1-5 shows an illustrative example of decoration where a metal-carboxylate cluster with a group of atoms representing the vertex in a primitive cubic network instead of a single atom. In reticular chemistry, secondary building units (SBUs) are polyatomic groups, which may be similar to molecular metal complexes known in coordination chemistry. They are connected through their points of extension to give a framework structure. For example, in Fig. 1-5, the metal-carboxylate clusters are SBUs linked by phenylene rings through their points of extension (carboxylate groups).

Fig. 1-4 Replacement of a bond by a sequence of bonds increases the length of the linker.
**Fig. 1-5** Rigid metal-carboxylate clusters are linked by benzene “struts” to form a rigid extended framework in which the M-O-C core (SBU) of each cluster acts as a large octahedron decorating a 6-connected vertex in a cube (M, purple; O, red; C, gray). “Reprinted (adapted) with permission from Ref. 20. Copyright © 2001 American Chemical Society.”

To construct a MOF, the first step is to identify a discrete di-, tri- or tetra-nuclear metal cluster as symmetrical module for polymerization involving multidentate linker. The metal clusters can act as SBUs and can be linked by linkers to give a network with a particular topology depending on the geometry of SBU and linker. For example, MOF-11 results from polymerization of paddle-wheel copper acetate (SBU) involving 1,3,5,7-adamantanetetracarboxylate (multidentate linker).

A metal cluster serves as an inorganic SBU. Its shape is defined by atoms representing its points of extension to other SBUs. Those atoms define the underlying geometry of the SBU and geometry of the SBU is important to predict the overall topology of the network. As shown in Fig. 1-6, to construct MOF-11, the carboxylate carbon atoms of paddle-wheel copper acetate define its square geometry.
A metal cluster serves as an inorganic SBU. Its shape is defined by atoms representing its points of extension to other SBUs. Those atoms define the underlying geometry of the SBU and geometry of the SBU is important to predict the overall topology of the network. As shown in Fig. 1-6, to construct MOF-11, the carboxylate carbon atoms of paddle-wheel copper acetate define its square geometry.

Now each ligand of the metal cluster can be substituted by a di-, tri- or multi-dentate linker in order to polymerize SBUs into an extended network. Geometry of the multi-dentate linker is also critical to predict the overall topology of the resulting network. As in case of MOF-11, ATC acts as the multi-dentate linker with tetrahedral geometry to polymerize square SBUs to give the extended network with PtS topology as shown in Fig. 1-7a. The final extended framework adopts the PtS topology as each square Pt atom and tetrahedral S atom in platinum sulfide are replaced by a square inorganic unit and a tetrahedral organic unit respectively in
MOF-11.

If some metal clusters are associated with terminal ligands, the terminal ligands may be removed from their coordination sites to study the reactivity of the open metal (OM) sites. During synthesis of a MOF, the terminal coordination sites are generally occupied by weak ligands like solvents and are pointed towards the pores. After synthesis, it is possible to cause those weak ligands to be susceptible to dissociation and then evacuate them from the pores to give a periodic arrangement of OM sites in the extended framework. MOF-11 is synthesized by heating a basic aqueous solution of Cu(NO$_3$)$_2$·2.5H$_2$O and 1,3,5,7-adamantetetraacarboxylic acid. When synthesized Cu sites in MOF-11 are coordinated by terminal water molecules and pores are also occupied by water molecules. Dissociation of terminal water molecules and evacuation of pores give periodic arrangement of OM sites in MOF-11 (Fig. 1-7b).

**Fig. 1-7** a) Assembly of building blocks (green square SBU and red tetrahedral linkers) resulting in the extended structure of MOF-11 with PtS topology. b) Periodic arrangement of open metal sites in MOF-11. (Cu, blue; O, red; C, grey). “Reprinted (adapted) with permission from Ref. 20. Copyright © 2001 American Chemical Society.”
1.5.4 Zeolite imidazolate frameworks (ZIFs): Special class of MOFs

Zeolite imidazolate frameworks (ZIFs) are considered as a special class of metal-organic frameworks. ZIF networks are topologically isomorphic with zeolites and are made of metal ions (like Zn$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Cu$^{2+}$) bridged by imidazolate linkers. The Si-O-Si angle in zeolites and the metal-imidazolate-metal bridging angle in ZIFs are both similar and close to 145° (Fig. 1-8). Thus ZIFs adopt the same topology as zeolites. In addition to mimicking the known zeolite structures, it is possible to make ZIFs with topologies previously unknown in zeolites.

![Fig. 1-8 M-Im-M bridging angle (in ZIFs) and Si-O-Si angle (in zeolites).](image)

Many ZIFs possess high chemical and thermal stability. For example, ZIF-8 made of Zn$^{2+}$ ions and a methyl imidazolate linker sustains its crystallinity and porosity even after boiling in water, alkaline solution or refluxing in organic solvents. ZIFs are widely used for separation and heterogeneous catalysis.

1.6 Structural similarity in metal complex and MOF

MOFs are made of inorganic SBUs and organic linkers. In many cases those inorganic SBUs resemble molecular metal complexes known in coordination chemistry. For example, HKUST-1$^{18}$ is a well known MOF where the inorganic SBU resembles the structure of paddle-
wheel copper acetate.

The structure of basic zinc acetate ($\mu^4$-oxo-hexakis($\mu$-acetato)tetrazinc, Fig. 1-9), formulated as $\text{Zn}_4\text{O}$(OOCCH$_3$)$_6$, has been known for many decades. The tetranuclear moiety, $\text{Zn}_4\text{O}(\text{COO})_6$, was also known for other zinc carboxylate clusters (benzoate, pivalate).$^{28}$

![Fig. 1-9 Supertetrahedral structure of basic zinc acetate (BZA).](image)

This tetranuclear moiety, $\text{Zn}_4\text{O}(\text{COO})_6$, represents the SBU of iconic MOF-5. Synthesis of MOF-5 (also known as IRMOF-1, Figure-10) was first achieved by Omar M. Yaghi by means of replacing the monocarboxylate ligand of basic zinc acetate with a dicarboxylate linker, terephthalate.$^{17}$ He also realized that this inorganic SBU, $\text{Zn}_4\text{O}(\text{COO})_6$, could be linked by a variety of other ditopic linkers to make a series of MOFs with the same topology and with a predetermined cavity size and functionality. Thus, he made a series (isoreticular series) of MOFs known as IRMOFs using a diverse range of dicarboxylate linkers of varying lengths and functionalities.$^{19}$
Fig. 1-10 Structure of MOF-5, four blue tetrahedra linked together by a red oxygen atom represents an SBU, Zn₄O(COO)₆ and the yellow ball represents void space inside. “Reprinted (adapted) with permission from Ref. 24. Copyright © 2003 The American Association for the Advancement of Science.”

BZA and the SBU of MOF-5 are structurally similar, their bond lengths and bond angles are also comparable. Table 1-3 compares some of the bond lengths and angles in BZA and in MOF-5.

<table>
<thead>
<tr>
<th>Bond / Bond angle</th>
<th>BZA</th>
<th>MOF-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-O⁰⁺</td>
<td>1.936(1)</td>
<td>1.9411(11)</td>
</tr>
<tr>
<td>Zn-O⁰⁻</td>
<td>1.946(4)</td>
<td>1.922(5)</td>
</tr>
<tr>
<td>Zn-O²⁻-Zn</td>
<td>109.5</td>
<td>109.467(1)</td>
</tr>
<tr>
<td>O³⁻-Zn-O⁰⁻</td>
<td>111.1(1)</td>
<td>112.55(19)</td>
</tr>
<tr>
<td>O⁰⁻-Zn-O⁰⁻</td>
<td>107.8(1)</td>
<td>106.2(2)</td>
</tr>
</tbody>
</table>

*central oxygen atom, ćarboxylate oxygen atom
Though many metal complexes have structural resemblance with the inorganic SBUs of MOF, however, the structural support for the metal sites in metal complexes and MOFs are not similar. This report discusses about the structural support for metal sites in metal complexes and compares the same in MOFs.
CHAPTER 2

MATERIALS, METHODS, RESULTS and DISCUSSION

The observation of intact crystallinity of suspended Ni-MOF-74 (with Nickel (II) as metal ion and 2,5-dihydroxyterephthalate as organic linker) in neat water caused us to wonder as the PXRD of Ni-MOF-74 after being immersed in neat water for hours was unchanged from that of the as synthesized one; which could be the consequence of maintaining crystallinity in water. In 1967, Basalo and Pearson compiled a book where they tabulated data on half-lives and water exchange rates for several metal sites with d-shell configuration ranging from d^3 to d^{10}. According to their report, the water exchange rate on a Ni^{2+} ion (for a Ni(II)-complex) is 3 x 10^{4} s^{-1}.6 A similar ligand exchange rate for the Ni(II)-center of Ni-MOF-74 in the presence of water would have rapidly produced a significantly disordered crystal of Ni-MOF-74, which is contrary to the above observation. This counterintuitive observation motivated us to investigate and compare the relative solvent stability of metal sites in several metal complexes and corresponding MOFs with similar metal nodes as presented here.

2.1 Materials

All of the commercially available chemicals and solvents were used as received from commercial suppliers (Sigma-Aldrich, Alfa Aesar, VWR, J T Baker, PHARMCO-AAPER) without further purification. Syntheses of all the molecular metal complexes (except copper acetate and nickel acetate), MOFs and activation of MOFs were done following literature procedures. Table 2-1 lists all the metal sites studied with their corresponding metal complexes and MOFs. Details of source and/or characterization for solvents and metal complexes are given below.

* Thanks to Royal Society of Chemistry for publishing this work in their esteemed journal Crystal Engineering Communication (CrystEngComm, 2012, 14, 6136-6139). I would also like to thank Daniel E. Johnston and Dr. Siddhartha Das for their significant contribution to accomplish this work.
Table 2-1 All the metal complexes and MOFs studied with their representative metal sites

<table>
<thead>
<tr>
<th>Metal sites</th>
<th>Metal complexes</th>
<th>MOFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{II}_{2}$</td>
<td>Cu$^{II}_{2}$(CH$_3$COO)$_4$</td>
<td>HKUST-1$^{18}$</td>
</tr>
<tr>
<td>Ni$^{II}$</td>
<td>Ni$^{II}$(CH$_3$COO)$_2$</td>
<td>Ni-MOF-74$^{30}$</td>
</tr>
<tr>
<td>Co$^{II}$</td>
<td>Co$^{II}$(N-MeIm)$_4$(NO$_3$)$_2$</td>
<td>Co-ZIF-9$^{27}$</td>
</tr>
<tr>
<td>($\mu^3$-O)Cr$^{III}_{3}$</td>
<td>($\mu^3$-O)Cr$^{III}_{3}$(CH$_3$COO)$_6$Cl$^{32}$</td>
<td></td>
</tr>
<tr>
<td>Ru$^{II,III}_{2}$</td>
<td>Ru$^{II,III}_{2}$(CH$_3$COO)$_4$Cl$^{33}$</td>
<td></td>
</tr>
</tbody>
</table>

**Acetone:** Acetone was purchased from PHARMCO-AAPER (Typical lot analysis-99.8%, water-0.2%). Acetone was dried over activated molecular sieve and used within a week.

**1,4-dioxane:** AR$^{\circledast}$ (ACS) grade 1,4-dioxane was purchased (Assay by GC, corrected for water-99.0% min.; Water by coulometry – 0.05% max.) from MACRON CHEMICALS.

**Ammonium hydroxide** (NH$_4$OH): 28% ammonium hydroxide solution was purchased from PHARMCO-AAPER and was diluted to 14% with deionized water for use.

**Copper acetate** (Cu$^{II}_{2}$(CH$_3$COO)$_4$): Copper acetate was purchased from Sigma-Aldrich as copper (II) acetate monohydrate (Assay-$\geq 99.0\%$ (RT), grade- puriss. p. a.).

**Nickel acetate** (Ni$^{II}$(CH$_3$COO)$_2$): Nickel acetate was purchased from Sigma-Aldrich as nickel (II) acetate tetrahydrate (Assay-$98\%$).

**Cobalt complex** (Co$^{II}$(N-MeIm)$_4$(NO$_3$)$_2$): From the UV-Vis study as described below, at maximum absorbance molar extinction coefficient ($\varepsilon$) is 97 L mol$^{-1}$ cm$^{-1}$ (Wavelength – 530 nm, Solvent- 1,4-dioxane in presence of 0.238 wt.% of water w.r.t. the wt. of cobalt complex).

**Ruthenium complex** (Ru$^{II,III}_{2}$(CH$_3$COO)$_4$Cl): From the UV-Vis study as described below, at maximum absorbance molar extinction coefficient ($\varepsilon$) is 1018 L mol$^{-1}$ cm$^{-1}$ (Wavelength – 435 nm, Solvent- acetone in presence of 125 wt.% of water w.r.t. the wt. of ruthenium complex). In EPR, we see $g_{\perp}$ peak at $\sim$4.0 and $g_{\parallel}$ peak at $\sim$2.0. The latter one shows expected isotopic contribution from $^{99}$Ru-$^{101}$Ru.$^{34}$
**Chromium complex** \((\mu^3\text{-O})\text{Cr}^{\text{III}}_3(\text{CH}_3\text{COO})_6\text{Cl})\): From the UV-Vis study as described below, at maximum absorbance molar extinction coefficient \((\varepsilon)\) is 160 L mol\(^{-1}\) cm\(^{-1}\) (Wavelength – 440 nm, Solvent- 1,4-dioxane in presence of 5 wt.% of water w.r.t. the wt. of chromium complex).

2.2 Instruments

All of the UV-Vis studies were done in a Shimadzu UV-2401 spectrophotometer and all of the powder X-ray diffractions (PXRD) were recorded in a Rigaku MiniflexII Desktop X-ray diffractometer.

2.3 Methods

All of the UV-Vis and PXRD studies were done at room temperature and ambient atmosphere unless stated otherwise.

2.3.1 General condition for UV-Vis studies with metal complexes

A weighed amount of a metal complex was suspended (except nickel complex which was dissolved in water (see below)) in measured amount of a water-miscible solvent which does not dissolve the corresponding metal complex in a screw cap test tube. Then the resulting mixture was stirred about 5 minutes and centrifuged about 30 seconds to settle down the insoluble residue. After centrifugation, the supernatant solution of the resulting mixture was used to record the UV-Vis absorbance at characteristic wavelength(s) of the corresponding metal complex in aqueous solution. Next water was added in \(\mu\)L amounts and after each addition UV-Vis absorbance was recorded of the supernatant solution of the resulting mixture following stirring and centrifugation. Following this procedure water was added till the absorbance became constant or started decreasing after reaching a maximum. The weight of metal complexes, choice and volume of solvent employed and the wavelength(s) for UV-Vis absorbance recording are discussed below and summarized in Table 2-2.
Table 2-2 Experimental details for UV-Vis studies with metal complexes

<table>
<thead>
<tr>
<th>Metal complex</th>
<th>Weight (mg)</th>
<th>Choice of solvent</th>
<th>Volume of solvent (mL)</th>
<th>Wavelength(s) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(<em>{2}^{II})(CH(</em>{3})COO)(_{4})</td>
<td>5.0</td>
<td>Acetone</td>
<td>10</td>
<td>670</td>
</tr>
<tr>
<td>Ru(<em>{2}^{II,III})(CH(</em>{3})COO)(_{4})Cl</td>
<td>3.0</td>
<td>Acetone</td>
<td>10</td>
<td>435</td>
</tr>
<tr>
<td>((\mu^{3})-O)Cr(<em>{3}^{III})(CH(</em>{3})COO)(_{6})Cl</td>
<td>5.0</td>
<td>1,4-Dioxane</td>
<td>10</td>
<td>440 &amp; 585</td>
</tr>
<tr>
<td>Co(<em>{2}^{II})(N-MeIm)(</em>{4})(NO(<em>{3}))(</em>{2})</td>
<td>8.5</td>
<td>1,4-Dioxane</td>
<td>8</td>
<td>530 &amp; 565</td>
</tr>
</tbody>
</table>

**Cu\(_{2}^{II}\)(CH\(_{3}\)COO)\(_{4}\)**: Cu\(_{2}^{II}\)(CH\(_{3}\)COO)\(_{4}\) (5mg) was suspended in 10 mL acetone and the above mentioned procedure was followed adding deionized water and the absorbance was recorded at 670 nm which is the characteristic wavelength of Cu\(_{2}^{II}\)(CH\(_{3}\)COO)\(_{4}\) in aqueous solution.

**Ru\(_{2}^{II,III}\)(CH\(_{3}\)COO)\(_{4}\)Cl**: Ru\(_{2}^{II,III}\)(CH\(_{3}\)COO)\(_{4}\)Cl (3mg) was suspended in 10 mL acetone and the above mentioned procedure was followed adding deionized water and the absorbance was recorded at 435 nm which is the characteristic wavelength of Ru\(_{2}^{II,III}\)(CH\(_{3}\)COO)\(_{4}\)Cl in aqueous solution.

**(\(\mu^{3}\)-O)Cr\(_{3}^{III}\)(CH\(_{3}\)COO)\(_{6}\)Cl**: (\(\mu^{3}\)-O)Cr\(_{3}^{III}\)(CH\(_{3}\)COO)\(_{6}\)Cl (5mg) was suspended in 10 mL 1,4-dioxane and the above mentioned procedure was followed adding deionized water and the absorbance was recorded at 440 and 585 nm which are the characteristic wavelength of (\(\mu^{3}\)-O)Cr\(_{3}^{III}\)(CH\(_{3}\)COO)\(_{6}\)Cl in aqueous solution.

**Co\(_{2}^{II}\)(N-MeIm)\(_{4}\)(NO\(_{3}\))\(_{2}\)**: Co\(_{2}^{II}\)(N-MeIm)\(_{4}\)(NO\(_{3}\))\(_{2}\) (8.5mg) was suspended in 8 mL 1,4-dioxane and the above mentioned procedure was followed adding deionized water and the absorbance was recorded at 530 and 565 nm which are the characteristic wavelength of Co\(_{2}^{II}\)(N-MeIm)\(_{4}\)(NO\(_{3}\))\(_{2}\) in aqueous solution.

**Ni\(_{2}^{II}\)(CH\(_{3}\)COO)\(_{2}\)**: NiII(CH\(_{3}\)COO)\(_{2}\) (50 mg) was dissolved in 8 mL of water and the above mentioned procedure was followed adding 14% aqueous ammonia and the absorbance was
recorded at 576 nm which is the characteristic wavelength of Ni(CH\textsubscript{3}COO\textsubscript{2}) in aqueous ammonia solution.

2.3.2 General condition for PXRD studies with MOFs

About 5-6 mg of MOF was suspended in the solvent (10mL) which was used for UV-Vis study of the corresponding metal complex in a number of tubes with varying weight % of water with respect to the weight of the MOF, also all the MOFs were suspended in neat water. The resulting suspension was kept at room temperature about 15 hours. Then PXRD of the remaining residue was recorded and compared with the PXRD of the as synthesized MOF to find out at what weight % of water MOFs start missing characteristic PXRD feature (i.e.; losing its crystallinity). As none of the above MOFs except HKUST-1 lost any PXRD features even in neat water, and then pH variation was done for those MOFs to find out the pH range they sustain their crystallinity as described below.

About 5-6 mg of MOF was suspended in different pH solutions (pH 3 to pH 10) and the resulting suspension was kept about 15 hours at room temperature. The PXRD of the remaining residue was then taken and compared with the PXRD of the as synthesized MOF. Different pH solution was made by adding dilute ammonium hydroxide or hydrochloric acid solution in deionized water.

2.4 Results and discussion

For all of the metal complexes, water or ammonia was added in µL increments to the suspension. As water or ammonia started solvation of the corresponding metal ion, the supernatant solution started showing characteristic UV-Vis absorbance. Absorbance was recorded after each addition and it was increasing gradually with each addition to reach a maximum before started decreasing. Table 2-3 represents the amount of water added to the suspension of 4.9 mg of copper acetate in 10 mL of acetone and the corresponding UV-Vis absorbance for solvated Cu\textsuperscript{2+}
ions from the supernatant solution. It was found that only 0.01 (estimated from Fig. 2-1) weight % of water (w.r.t. the weight of copper acetate) is required to start solvation of Cu$^{2+}$ ion of copper acetate.

![Fig. 2-1](image)

**Fig. 2-1** Plot of UV-Vis absorbance of solvated copper acetate from supernatant solution vs. weight % of water added. Inset shows the selected area of the plot.

<table>
<thead>
<tr>
<th>Wt. % of H$_2$O (Vol. in μL)</th>
<th>Abs.</th>
<th>Wt. % of H$_2$O (Vol. in μL)</th>
<th>Abs.</th>
<th>Wt. % of H$_2$O (Vol. in μL)</th>
<th>Abs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (0)</td>
<td>0.046</td>
<td>0.102 (5)</td>
<td>0.124</td>
<td>0.204 (10)</td>
<td>0.175</td>
</tr>
<tr>
<td>0.02 (1)</td>
<td>0.051</td>
<td>0.122 (6)</td>
<td>0.136</td>
<td>0.245 (12)</td>
<td>0.18</td>
</tr>
<tr>
<td>0.041 (2)</td>
<td>0.068</td>
<td>0.143 (7)</td>
<td>0.153</td>
<td>0.286 (14)</td>
<td>0.18</td>
</tr>
<tr>
<td>0.061 (3)</td>
<td>0.082</td>
<td>0.163 (8)</td>
<td>0.164</td>
<td>0.367 (18)</td>
<td>0.181</td>
</tr>
<tr>
<td>0.082 (4)</td>
<td>0.103</td>
<td>0.184 (9)</td>
<td>0.169</td>
<td>0.408 (20)</td>
<td>0.177</td>
</tr>
</tbody>
</table>

Similarly, minimum amount of solvent (water/NH$_3$OH) required to start solvation of
other metal ions of the corresponding metal complexes were estimated from the UV-Vis study (Fig. 2-2). Table 2-5 accumulates all those data and compares with the corresponding MOFs.

![Plots of absorbance of solvated metal complexes from supernatant solution vs. amount of solvent (water/14% NH₄OH) added.](image)

**Fig. 2-2** Plots of absorbance of solvated metal complexes from supernatant solution vs. amount of solvent (water/14% NH₄OH) added. A) (μ³-O)Cr^{III}_3(CH₃COO)_6Cl, B) Co(N-MeIm)_4(NO₃)₂, C) Ru^{II,III}_2(CH₃COO)_4Cl and D) Ni^{II}(CH₃COO)_2.

Like metal complexes, UV-Vis study was done for all the MOFs adding water or ammonia in gradual increments. As none of the MOFs showed any metal leaching even after immersing in neat water for hours, UV-Vis spectra of the supernatant solution were not
informative. Therefore, PXRD of all the activated MOFs were recorded as described above and compared with the PXRD of the as synthesized MOFs.

It needs only 0.01 weight % of water to start solvation of copper acetate. A MOF, HKUST-1, having similar node Cu$^{II}$$_2$(COO)$_4$ as of copper acetate and 1,3,5-benzenetricarboxylate linker was examined. From the PXRD study, it was found that it maintains its crystallinity in presence of ≤ 25 weight % of water as shift in the peak positions, change in peak intensities and peak broadening are obvious in presence of 25 weight % of water. In presence of < 25% water, the PXRD of the suspended MOF and the as synthesized one are similar. However, in presence of ≥ 25% water, the PXRD of the suspended MOF start missing characteristic features (Fig. 2-3).

Fig. 2-3 Comparison of PXRD of as synthesized HKUST-1 and suspended HKUST-1 in presence of various wt. % of water.
As both copper acetate and HKUST-1 have the similar node \( \text{Cu}_2(\text{COO})_4 \) (Fig. 2-7), we compare some of their bond lengths and bond angles from literature. It was found that they were pretty similar except the O(W)-Cu-Cu angle. Table 2-4 lists some of the average bond lengths and angles of copper acetate and HKUST-1 from their crystal structures.

![Node-Cu\(_2\)(COO)\(_4\)](image)

**Fig. 2-4** Node-Cu\(_2\)(COO)\(_4\) of copper acetate and HKUST-1. The black circle represents a methyl group for copper acetate and point of extension for HKUST-1. Both of them contain a water molecule on each copper center.

It took only 0.02 weight % of water to start solvation of \([\text{Co}^{II}(\text{N-MeIm})_4]^{2+}\) but Co-ZIF-9 with similar node, \(\text{Co}^{II}(\text{imidazolate})_4\) (linker: benzimidazole) was able to maintain its crystallinity even in neat water. Co-ZIF-9 was able to maintain its crystallinity between pH 4.5 and pH 9. Similarly, Ni-MOF-74 (node Ni\(^{II}\), linker: 2,5-dihydroxyterephthalate) was able to maintain its crystallinity between pH 5 and pH 9.5 whereas 0.04 weight % of ammonia was enough to start solvation of Ni\(^{II}\)(CH\(_3\)COO)\(_4\) (pH of the resulting solution was found to be 8).

\((\mu^3-O)\text{Cr}^{III}_3(\text{CH}_3\text{COO})_8\text{Cl}\) and Ru\(^{II,III}\)_2(\text{CH}_3\text{COO})_6\text{Cl}\) were found to be highly stable towards water induced disruption of their coordination environment. It took about 3 and 9 weight
Table 2-4 Bond lengths and angles of copper acetate and HKUST-1. Bond lengths are in Å and bond angles are in degree. *18, 35

<table>
<thead>
<tr>
<th>Bond lengths/Angles</th>
<th>Copper acetate</th>
<th>HKUST-1</th>
<th>Bond lengths/Angles</th>
<th>Copper acetate</th>
<th>HKUST-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-Cu</td>
<td>2.6143(17)</td>
<td>2.628(2)</td>
<td>O(C)-Cu-Cu</td>
<td>82.82(7)</td>
<td>84.11(11)</td>
</tr>
<tr>
<td>Cu-O(C)</td>
<td>1.9898(14)</td>
<td>1.952(3)</td>
<td>O(C)-Cu-O(W)</td>
<td>93.50(7)</td>
<td>95.89(11)</td>
</tr>
<tr>
<td>Cu-O(W)</td>
<td>2.16113(17)</td>
<td>2.165(8)</td>
<td>O(W)-Cu-Cu</td>
<td>174.45(7)</td>
<td>180.0(2)</td>
</tr>
<tr>
<td>C-O(C)</td>
<td>1.2593(19)</td>
<td>1.252(5)</td>
<td>C(C)-O(C)-Cu</td>
<td>124.46(11)</td>
<td>123.0(4)</td>
</tr>
<tr>
<td>O(C)-Cu-O(C) (trans)</td>
<td>168.70(7)</td>
<td>168.2(2)</td>
<td>O(C)-C(C)-C</td>
<td>118.14(11)</td>
<td>117.2(3)</td>
</tr>
<tr>
<td>O(C)-Cu-O(C) (cis)</td>
<td>89.20(7)</td>
<td>89.7(2)</td>
<td>O(C)-C(C)-O(C)</td>
<td>124.42(11)</td>
<td>125.6(7)</td>
</tr>
</tbody>
</table>

* O(C)-Carboxylate oxygen atom, O(W)-Water oxygen atom and C(C)-Carboxylate carbon atom

% of water to start solvation of (µ³-O)Cr³⁺(CH₃COO)₆Cl and Ru²⁺Ⅲ₂(CH₃COO)₄Cl, respectively. Corresponding MOFs maintain their crystallinity in broad range of pH. Table 2-5 compares relative solvent stability of molecular complexes and their corresponding MOFs.

Though HKUST-1 maintains its crystallinity in presence of ≤ 25 weight% of water, however, it was important to investigate the effect of water on crystallinity of other Cu-MOFs with similar node but different topology. The synthesis of two Cu-MOFs with Kagomé lattice and NbO net topologies were reported by Zaworotko et al. using a substituted isophthalate linker (5-NPIA) by variation of solvent conditions. Both of them have the similar node, Cu²⁺(COO)₄, as of HKUST-1. It was found that the Cu-NPIA MOF with Kagomé lattice topology was able to maintain its crystallinity in presence of ≤ 23 weight % of water which was comparable with HKUST-1 (tbo net topology).

Cr-MIL-101 (linker: terephthalate) and Cr-MIL-88D (linker: 4,4’-biphenyl dicarboxylate) have similar node like Cr-MIL-100, [(µ³-O)Cr³⁺(CH₃COO)₆]⁺, but have different pore sizes and topologies because of different length and geometry of their linker. Both Cr-MIL-101 and Cr-
Table 2-5 Relative stability of metal complexes and corresponding MOFs

<table>
<thead>
<tr>
<th>Metal complexes</th>
<th>H₂O wt. % to start solvation</th>
<th>Corresponding MOFs</th>
<th>H₂O wt.% to affect crystallinity</th>
<th>Effect of pH on crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(µ⁴-O)Zn₄(CH₃COO)₆</td>
<td>0.01³⁶</td>
<td>MOF-5</td>
<td>4³⁷</td>
<td>N/A</td>
</tr>
<tr>
<td>Cu₂⁺(CH₃COO)₄</td>
<td>0.01</td>
<td>HKUST-1</td>
<td>25</td>
<td>N/A</td>
</tr>
<tr>
<td>Co²⁺(N-MeIm)₄(NO₃)₂</td>
<td>0.02</td>
<td>Co-ZIF-9</td>
<td>Stable</td>
<td>Stable at 9 ≥ pH ≥ 4.5</td>
</tr>
<tr>
<td>Ni²⁺(CH₃COO)₂</td>
<td>0.04#</td>
<td>Ni-MOF-74</td>
<td>Stable</td>
<td>Stable at 9.5 ≥ pH ≥ 5</td>
</tr>
<tr>
<td>(µ³-O)Cr₃⁺(CH₃COO)₆Cl</td>
<td>3</td>
<td>Cr-MIL-100</td>
<td>Stable</td>
<td>Stable at 8 ≥ pH ≥ 1</td>
</tr>
<tr>
<td>Ru³⁺₂⁺(CH₃COO)₆Cl</td>
<td>9</td>
<td>Ru-BTC-MOF</td>
<td>Stable</td>
<td>Stable at 10.5 ≥ pH ≥ 1</td>
</tr>
</tbody>
</table>

*Wt. % of ammonia, pH of the resulting solution was 8

MIL-88D are highly stable like Cr-MIL-100. Comparable solvent stability of several ZIFs with similar node Zn(Im)₄ were reported by Yaghi et al.²⁷

For metal complexes, metal sites were chosen with characteristic spectroscopic (UV-Vis) feature and all together cover a broad range of ligand exchange rate. From our study, we could find the minimum amount of solvent required to start solvation of metal complexes which followed the same trend as the reported half-lives or ligand exchange rates for the corresponding metal sites. For example, half-lives of Cu²⁺, Co²⁺ and Ni²⁺ are, respectively, 10⁻⁹ s (8 x 10⁻⁹ s⁻¹), 10⁻⁶ s (1 x 10⁻⁶ s⁻¹) and 10⁻⁴ s (3 x 10⁻⁴ s⁻¹) (corresponding ligand exchange rates for water substitution are in parentheses) and minimum amount of solvent required for corresponding metal sites were found to be 0.01, 0.02 and 0.04 weight %, respectively. Though ligand exchange rates or half-lives for Cr³⁺ and Ru²⁺/Ru³⁺ are not reported, however, they are ranked among cations with slow ligand exchange rates. Accordingly it was found that a greater amount of solvent was required to start solvation of these metal sites.
All the MOFs were chosen such that they have similar metal sites as of their corresponding metal complexes and were known for various catalyses. As shown above in Table 8, all the MOFs are highly stable towards external ligand/solvent induced disruption of their coordination environment compared to their corresponding metal complexes. Though metal sites in MOFs are structurally highly stable that did not have any effect on their functionality. As a general concept in catalysis, when a metal complex becomes highly stable and resilient to ligand exchange it becomes catalytically inactive. Drawing reference from this general concept it was anticipated that a metal complex will be a better catalyst than a MOF with similar metal site for a specific catalysis. Co-ZIF-9 was known to catalyze the Knoevenegal condensation between benzaldehyde and malononitrile using Lewis acidity of Co(II) site. It was expected that the corresponding metal complex, $[\text{Co(N-MeIm)}_4]^{2+}$ with similar metal site as of Co-ZIF-9 will be a better catalyst for this reaction. However, it was found that $\text{Co(N-MeIm)}_4$ was not able to catalyze the reaction at all. Likewise, a Ru-BDC MOF (node: $[\text{Ru}^{II,III}_2(\text{COO})_4]^+$, linker: terephthalate) is known for light-driven $\text{H}_2$ production (in presence of photosensitizer and electron relayer) and corresponding metal complex $\text{Ru}_2(\text{CH}_3\text{COO})_4\text{Cl}$ shows a little or no catalytic activity for $\text{H}_2$ production.

It can be inferred that although the metal sites are highly stable towards solvent induced structural disruption in MOFs compared to metal complexes, they are functionally more active in MOFs. The reason behind these observations may be that in presence of large excess of solvent/substrate the metal site undergoes irreversible ligand exchange in case of metal complexes and reversible ligand exchange in case of MOFs (Fig. 2-5) and in case of MOFs metal site enjoys a scaffold-driven structural ballasting which prevents it from falling apart while having transient ligand exchange steps, and allows it to go through the transient steps and perform catalysis.
From this study it can be said that a metal site attains much higher structural support when incorporated into a crystalline metal-organic framework compared to a metal complex. As the research area is still in a rudimentary stage, solvent stability of metal nodes in MOFs are not well understood yet. Relative resistance of the metal node in a MOF towards solvation by coordinating solvents (H₂O, NH₃ etc.) compared to the corresponding metal complex could provide crucial information regarding their further application.
CHAPTER 3
CONCLUSION AND SUMMARY

Metal-organic frameworks are relatively new and are of great importance for heterogeneous catalysis, hydrogen storage, and separations. On the other hand metal complexes are known for centuries, have been applied for various purposes and in some cases they are very similar as SBUs of MOFs. Our objective has been to expand the understanding of MOFs for their further application in catalysis by comparing their relative solvent stabilities with metal complexes. In this regard, it is noteworthy to mention that in solid-state most of the metal complexes and MOFs contain water or other solvent as a part of their solid-state structure.

From this study we gained some knowledge about the solvent stability and functionality of a metal site in metal complex compared to its corresponding metal-organic framework. Specifically, we found:

- Structural support or stability of a metal site towards external solvent induced structural disruption is much higher when incorporated as node in a metal-organic framework than in a metal complex.
- Higher stability does not affect the functionality (ability for catalysis) of a metal site in a MOF; a MOF could be a better catalyst than the corresponding metal complex.
- Most of the MOFs were able to maintain their crystallinity even in neat water.
- For MOFs, there was no metal leaching which could be a problem for their application as catalysts for industrial and environmental purposes.

This study helped us to learn about the structural integrity of a metal site as part of an extended framework. This structural integrity has no dampening effect on the application of MOFs in catalysis and could be highly useful for further application of MOFs in catalysis as replacement of metal complexes.
REFERENCES


APPENDIX
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I, Daniel E. Johnston, do hereby grant Sanjit Das permission to reproduce the research work published in a paper I coauthored in his master’s thesis.

Paper Title: “Structural Bolstering of Metal Sites as Nodes in Metal-Organic Frameworks” (*CrystEngComm*, 2012, 14, 6136-6139)

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