POROUS INORGANIC-ORGANIC MATERIALS BASED ON BETA-DIKETONE LIGANDS

A Dissertation

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Abstract

Synthesis and characterization of porous inorganic-organic materials have been studied mainly on two linear β-diketone multifunctional ligands: pyridine based pyacH and isocyanide based HacphNC.

As a known ligand, the preparation of pyacH has been improved with higher yield. When pyacH reacts with Fe and Al metal salts, trigonal metal β-diketonate building blocks M(pyac)₃ are produced. When pyacH reacts with zinc acetate, both trans and cis Zn(pyac)₂ are produced, both isomers were isolated and characterized by single-crystal X-ray crystallography.

Solutions of the trigonal building block Fe(pyac)₃ generate various crystal structures on reaction with AgNO₃ in CH₃CN. When the concentration of AgNO₃ is low, porous 2D honeycomb structures (Fe:Ag 1:1) are generated. Higher concentrations of AgNO₃ result in 1D ladder structures (Fe:Ag 2:3). 1D ladder structures are generated when Fe(pyac)₃ is dissolved in 1,2-dichlorobenzene, bromobenzene, or toluene. In porous 1D ladder structure, guest solvents can be exchanged by other solvents without destruction of metal-organic framework. The guests can be exchanged from bromobenzene to 1,2-dichlorobenzene, benzene, trichloroethylene and naphthalene. The exchange between bromobenzene and 1,2-dichlorobenzene has been studied by single-crystal X-ray diffraction and GC-MS. Al(pyac)₃ can also generate a porous material with similar 1D ladder framework and guest molecules.

3-(4-isocyanophenyl)-2,4-pentanedione (HacphNC) was synthesized for the first time starting from 4-nitrobenzaldehyde. The synthesis was done by initial reduction/formylation to produce OHC-C₆H₄-NHCHO. The resulting 4-formylamino-
benzaldehyde was converted to 3-(4-formylaminophenyl)-2,4-pentanedione by reaction with the biacetyl-trimethyl phosphate adduct. The β-diketone was protected by complexation to Al$^{3+}$, Zn$^{2+}$ and Cu$^{2+}$. The metal complexes were then dehydrated by phosphorus oxychloride in the presence of diisopropylamine to generate M(acphNC)$_n$ metal complexes. The Al and Zn complexes were acidified to give the target ligand HacphNC.

Cu(I), Mn(I), and Au(I) C-bound complexes of the isocyanide-β-diketone ligand HacphNC were prepared on a small scale. NMR and IR indicate the formation of the expected products.
Chapter 1

Introduction-Supramolecular Nanoporous Materials Chemistry

There has been extensive interest in porous materials for their potential applications in separation, gas storage, molecular recognition, and catalysis due to their ability of interacting with atoms, ions, and molecules both at their surfaces and in the bulk [1.1-1.5]. Porous compounds with nanometer-sized spaces have attracted scientists because of novel phenomena that occur on the nanometer scale.

There are basically three kinds of porous materials, with frameworks that are either (a) all-inorganic, (b) all-organic, or (c) mixed (“metal-organic”). (a): Aluminosilicates and aluminophosphates are the two largest subclasses of all-inorganic microporous inorganic materials. Zeolites are 3D hydrated alkaline or alkaline-earth aluminosilicates with well-defined porous structures. The general formula is $M^{x+/n}[(AlO_2)_x(SiO_2)_y]^{x-n} \cdot wH_2O$, with frameworks built from corner-sharing tetrahedra. There are more than 100 zeolite frameworks known, usually containing cages, cavities and channels ranging from 3 to 10 Å [1.6]. The major uses of zeolites are catalysis, ion exchange and separation. Aluminophosphates are artificial materials with 3D neutral networks consisting of aluminum and phosphorus tetrahedra, which have properties different from aluminosilicate zeolites. (b): Representatives of carbon-based porous materials are activated carbons. Their structures are twisted defective carbon layer networks, connected by aliphatic bridging groups. (c): Metal-organic frameworks, constructed from metal ions and organic linkers, are examples of coordination polymers. These frameworks can be designed to have high porosity by proper choice of metal and linker.
The absorption ability of porous materials is determined by the distribution of sizes, shapes, and the void spaces. Preparing metal-organic frameworks (MOFs) involves coordination of the metal ions and organic linker moieties to yield open framework structures. MOFs are of interest because the various coordination geometries and abilities of metal ions together with different types of ligands provide many possible structures. Rational design of ligands can lead to predictable extended solid frameworks. Furthermore, modification of ligands makes it easy to functionalize the networks. Multifunctional polytopic ligands can bind with different metal ions with different binding sites to generate heterometallic frameworks. Heterometallic MOFs can provide the desired structures if we choose the ligand and metal ions carefully.

A number of MOF examples have been developed since the 1990s. There are several good reviews on this area [1.6-1.13]. Of the many examples, neutral nitrogen-donor ligands and carboxylate anionic ligands are the most common. 4,4’-Bipyridine and its derivatives have been applied to generate many types of structures, including ladders, helices, bilayers, hexagonal grids, squares and diamond nets [1.13-1.21]. Yaghi’s group has done pioneering work in carboxylate ligands to generate MOFs. With the tetrahedral Zn₄O core, Zn₄O(CO₂R)₆ is an octahedral cluster. Materials in these series are extremely stable up to 300-400 °C due to the reinforced connectivity within the octahedral units [1.3,1.4,1.7,1.8,1.21-1.28]. MOF-177 (Zn₄O(1,3,5-benzenetribenzoate)₂) has an estimated surface area of 4500 m² g⁻¹ [1.23], more than double that of activated carbon (2030 m² g⁻¹) [1.29] and five times as much as zeolite Y (904 m² g⁻¹) [1.30]. MOF–177 also show a CO₂ uptake of 33.5 mmol/g at ambient temperature (35 bar), higher than both zeolite and activated carbons [1.27]; 32 g/L of H₂ uptake [1.24] is near the 45 g/L 2010 DOE target [1.31].
In most of these metal-organic frameworks, the metal atoms are coordinatively saturated, which means the guest molecules cannot bind to the metal atoms directly. Only weak intermolecular forces play a role in the host-guest interactions, compared with the strong metal-ligand bonding in the supramolecular systems. We have been interested in metal-β-diketonate complexes for their host-guest chemistry \[1.32-1.36\] and CVD application of metal films \[1.37-1.38\] for years. In our examples metal atoms are either unsaturated or contain ligands that can easily leave under the interaction with other donors, which would make the hosts bind a variety of guest molecules efficiently. The acac-M-acac moiety not only provides rigidity for the formation of the porous framework, but it can also rotate about its principal axis without changing the shape of the host framework.

We have recently developed a “pre-constructed building block” approach \[1.39-1.40\] to build nanometer-sized porous materials from metal complexes that contain Lewis-base substituents. We have constructed inorganic-organic hybrid porous supramolecular materials whose geometries are defined by several types of nodes. The nodes are connected by rodlike metal-containing moieties. Other researchers have synthesized metal-organic supramolecular complexes by careful choice of metal atoms and organic bridging groups. However, the metal atoms in most of those systems are saturated. This means that, although those systems often exhibit host-guest chemistry, the guests cannot bind directly to the metal atoms.

In our work, we are preparing similar types of structures with a different approach. We have chosen β-diketone complexes as the “rods” because they are versatile ligands, and also because symmetrically substituted β-diketones are relatively easy to prepare. In
cases we have studied before, the bis(β-diketonato)metal units are moderately rigid and essentially linear, which can provide the regular shape we want and the rigidity to keep the porous materials stable. Most important, the unsaturated metal atoms can bind directly to guest molecules. The new porous materials may lead to applications as nanoscale sensors, catalytically active devices and gas storage materials.

The scheme for this chemistry is illustrated in Figure 1.1. Metal atoms with different coordination numbers (CN) serve as nodes N, which can combine with unsaturated bifunctional linear metal β-diketonate rods (M) to form single molecules or 1D, 2D and 3D porous network solids.

![Figure 1.1](image)

**Figure 1.1** Our approach to construction of supramolecular materials. Inorganic and organic “nodes” are joined to semi-rigid linear “rod” like metal complexes.

Pyridine and isocyanide are chosen as the soft binding sites of the bifunctional β-diketone ligands. The chosen ligands PyacH, 1.1 and HacphNC, 1.2 are shown in Figure 1.2. PyacH is a known compound, while HacphNC has never been made before. It is expected that the lone pair electrons of the pyridine and isocyanide groups will have
binding properties different from the \( \beta \)-diketone (acac) and are pointed in the opposite
direction. The resulting compounds are expected to be linear and robust enough to
provide the rigidity needed for a porous framework.

\[
\begin{align*}
\text{1.1} & \quad \text{1.2} \\
\end{align*}
\]

**Figure 1.2** Two bifunctional \( \beta \)-diketone ligands.

1.1: (PyacH); 1.2: (HacphNC).

The length of molecule 1.1 is about 6.4 Å and the length of molecule 1.2 is about
8.9 Å. The estimated pore sizes with the above ligands are shown in Figure 1.3.

\[
\begin{align*}
\text{1.3} & \quad \text{1.4} \\
\end{align*}
\]

**Figure 1.3** Approximate sizes of \( M(\text{pyac})_2 \) and \( M(\text{acphNC})_2 \) molecules.
The pore sizes are relatively large compared with zeolites and most MOF materials. This means we can build up materials of different pore sizes by choosing different ligands. These ligands with different coordination abilities, will provide more combinations with metal ions to generate the desired porous products.

In order to improve the prospects for 3D materials, we need to use building blocks based on complexes that are highly stable with monodentate ligands L. Isocyanide ligands (CNR) are very good candidates for that purpose. They are known to make very stable complexes with low oxidation state metals such as Cr, Mn, Fe and Re \[^{[1.41-1.60]}\].

There are two synthetic routes for preparing porous 3D materials (Figure 1.4), depending on which metal is bound to the ligand first.

*Figure 1.4* Schematic illustration of two routes for assembling porous 3D solids. “M'M3L6” has a ReO3-type structure; M, M': metals ions; L: bifunctional ligand.
**Route (A):** Synthesize a metal-complex building block with isocyanide substituents, and use it to construct 3D solids by reaction with the second metal ion $\text{M'}$.

**Route (B):** Synthesize a $d^6$ $\text{M'}(\text{CNR})_6$ starting material with $\beta$-diketone substituents, and use it to construct 3D materials by reaction with $\text{M}$.

The synthesis of ligand 1.2 (HacphNC) is discussed in Chapter 4, along with the preparation of its metal $\beta$-diketonate building blocks. In Chapter 5 $\text{M'}(\text{CNphacH})_6$ building blocks are discussed. Some simple mixed-metal coordination compounds are also discussed together with the preparation of 3D porous materials from two different routes. A general conclusion is given in Chapter 6 to summarize this dissertation.

1.1 References


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1.30 Chester, A.W.; Clement, P.; Han, S. US patent 6,136,291A.


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Chapter 2

Pyridine Based β-Diketone Ligands and Their Metal Complexes

2.1 Introduction

In this chapter, the chemistry of two bifunctional ligands is discussed: pyacH and pymaH. We envisioned that with each of these ligands, the O atoms would bind to one metal atom, and the pyridine N atom would bind to a second metal. The 3-(4-pyridinyl)pentane-2,4-dione (pyacH, 2.1) linear ligand has the ability to bind two different kinds of metals. After the β-diketone combines with the metals, we can use the N atom of the building block to bind other metals to generate porous materials. The rigidity of pyridine ring and acac together with the geometries of metal ions will provide the scaffold of the porous materials. The ligand synthesis is discussed first. The β-diketonate building blocks prepared from the ligand are discussed later.

![Pyridine-Based Multifunctional Ligands](image)

Figure 2.1 Two pyridine-based multifunctional ligands.

The corresponding aldehyde derivative of pyacH is pymaH. We envisioned that pymaH would have coordination properties similar to those of pyacH; also, pymaH is commercially available. The attempted application of pymaH to make linear metal complexes is also discussed in this chapter.
2.2 Results and Discussion

2.2.1 PyacH Ligand Synthesis

3-(4-Pyridinyl)pentane-2,4-dione was synthesized according to the revised procedure of Nozawa \(^2\) and Mackay et al. \(^2\) (Figure 2.2).

In the procedure described in the reference, acetyl chloride was added slowly into 4-methylpyridine in chloroform under \(-20^\circ C\). After the reaction completed, chloroform was removed and the residue was triturated with toluene. Toluene was then removed and the residue was chromatographed to purify the product \(^2\). However, my attempts to repeat that procedure gave low yield (about 20%) and not very pure product. Several side products were able to be separated and characterized.

The HCl produced in the reaction can also protonate the pyacH to form pyridinium salt (2.2) beside the major side product 4-methylpyridinium chloride. PyacH can also crystallize with HOAc generated from acetyl chloride (2.3).
[PyacH₂]Cl crystallized from the reaction mixture; see Figure 2.3. The crystal structure of 2pyacH-HOAc (2.3) is shown in Figure 2.4.

![Figure 2.3 Single-crystal X-ray structure of [pyacH₂]Cl (2.2).](image)

![Figure 2.4 Crystal structure of 2pyacH-HOAc (2.3).](image)

When the concentrated toluene solution after extraction was cooled in refrigerator, yellow lath crystals (2.4) grew from the solution. Compound 2.4 is an isomer of pyacH. Compound 2.4 is believed to be an intermediate during the reaction as shown in Figure
2.5. It is expected not to be a stable compound. Its yellow color gets darker with time at room temperature, possibly indicating decomposition. The crystal structure of compound 2.4 is shown in Figure 2.6.

Figure 2.5 Possible mechanisms during synthesis of pyacH.

Figure 2.6 Crystal structure of compound 2.4.
As shown in Figure 2.6, one acetyl group is attached on the N atom instead of carbon atom (C8) as it is in pyacH. All the nonhydrogen atoms in 2.4 are in the same plane. The bond distances show that the pyridine ring is not longer aromatic anymore, and is more like the structure on the left of the crystal structure.

PyacH decomposes under contact with water vapor in laboratory air as shown in Figure 2.7. 1-(4-Pyridinyl)-2-propanone (2.5) is generated.

![Chemical structure](2.1) \(\xrightarrow{\text{H}_2\text{O \ slowly}}\) ![Chemical structure](2.5) + CH₃COOH

**Figure 2.7** Decomposition of pyacH by H₂O.

The decomposed compound 2.5 forms complex with copper acetate in H₂O/ethanol solution (Figure 2.8).

![Chemical structure](2.5) + Cu(CH₃COO)₂ \(\xrightarrow{\text{H}_2\text{O/EtOH}}\) ![Chemical structure](2.6)

**Figure 2.8** Preparation and crystal structure of compound 2.6.
The ligand synthesis was improved by adding 4-methylpyridine into acetyl chloride solution, not the other way around reported in the reference \cite{2.2}. The toluene extract was also washed with water to get rid of any water soluble side products. After toluene solution was separated and dried, the residue was distilled under vacuum and the product collected at 115 °C. The crystal structure of ligand \textit{2.1} is shown in Figure 2.9. The yield is 37\% compared to 26\% reported in Mackay’s paper \cite{2.2}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure29.png}
\caption{Crystal structure of pyacH (2.1).}
\end{figure}

\subsection*{2.2.2 Attempted Synthesis of A Bpy-bis(\(\beta\)-diketone) Ligand}

Ru(bpy)\textsubscript{3}\textsuperscript{2+} (bpy = 2,2-bipyridine) is a very stable complex. So a compound such as \textit{2.14} (bpyacH\textsubscript{2}) should coordinate to Ru\textsuperscript{2+} to generate Ru(bpyacH\textsubscript{2})\textsubscript{3}\textsuperscript{2+} (\textit{2.15}), which contain six \(\beta\)-diketone groups in an approximate octahedral arrangement. \textit{2.15} should be able to coordinate with metal ion as Cu\textsuperscript{2+} to generate 3D networks (Figure 2.10).
The similar reaction as pyacH was applied to 4,4'-bimethyl-2,2'-bipyridine (2.13). But the attempt was not successful (Figure 2.11). One possible explanation is that the steric effect of acylation prevents the activation of methyl group.

Figure 2.10 3D network generated through bpyacH₂.

Figure 2.11 Attempted preparation of bpyacH₂.
2.2.3 Trigonal M(pyac)₃ Building Blocks

Trigonal building blocks M(pyac)₃ were synthesized with Fe and Al metals. The Fe complex (Fe(pyac)₃, 2.7) was made from Fe(NO₃)₃ and pyacH in water/methanol solution [2.4]. NaHCO₃ was used to deprotonate protons released during reaction. Excessive amount of pyacH was used to avoid the formation of Fe(OH)₃. Crystals grew directly from solution overnight (Figure 2.12 a). Al complex was prepared according to the procedure in reference [2.2]. Crystals suitable for crystallography grew from CHCl₃ solution (Figure 2.12 b).

![Crystal structures of M(pyac)₃.](image)

**Figure 2.12** Crystal structures of M(pyac)₃. **a:** Fe(pyac)₃ (2.7); **b:** Al(pyac)₃(H₂O)(CHCl₃) (2.8).

Each iron atom coordinates with six oxygen atoms from three pyac⁻ ligands. The Fe atom is approximately in the plane of one acac moiety (O1, O2, C2, C3, C4), but the others are bent away from coplanarity. The overall shape of the molecule deviates from trigonal symmetry, with N···Fe···N angles of 136.2°, 70.8° and 152.9° respectively. This distortion suggests that Fe(pyac)₃ may not function as an ideal trigonal building block. in Al(pyac)₃, which will play important role in the next step for porous materials preparation.
In the structure of Al(pyac)$_3$, the N···Al···N angles (127.7°, 86.8° and 148.2°) are closer to the ideal 120° than those in Fe(Pyac)$_3$. The water molecule forms hydrogen bonds with two nearby pyridine N atoms. The coordination geometry is closer to octahedral than that in Fe(pyac)$_3$ (adjacent O···Al···O 87.4-94.7°, vs. 83.6-94.3° of O···Fe···O in Fe(pyac)$_3$). Still the overall shape is significantly distorted from trigonal symmetry (Figure 2.12 b).

### 2.2.4 Zn(pyac)$_2$

In addition to the trigonal building blocks, I also attempted to prepare the linear building block Zn(pyac)$_2$. Cu(pyac)$_2$ was prepared by Turner et al. [2.5] first and well characterized by Chen [2.6] in our lab. Linear Cu(pyac)$_2$ reacts with Cd$^{2+}$ and generates 2D square planar porous materials [2.7]. Methanol and THF molecules bind with open sites of Cu$^{2+}$ in the compounds. Zinc(II), which has coordination properties similar to copper(II), is a good candidate to form a similar linear pyridine based β-diketone building block (Figure 2.13).

![Diagram of Zn(pyac)$_2$](image)

**Figure 2.13** Linear structure of Zn(pyac)$_2$

*a:* Expected structure; *b:* Actual crystal structure of *trans* Zn(pyac)$_2$ (2.9)
When zinc acetate aqueous solution was mixed with pyacH methanol solution, no precipitate formed. After sodium bicarbonate was added, a white precipitate of Zn(pyac)$_2$ formed. The precipitate was not soluble in common organic solvents. Crystals were grown by layering zinc acetate methanol solution on pyacH dichloromethane solution (2.9).

![Figure 2.14 Crystal structure of trans Zn(pyac)$_2$(CH$_3$OH)(H$_2$O) (2.9). Disordered solvent not shown.](image)

As shown in Figure 2.14, each zinc coordinates with two pyac$^-$ in a trans mode, leaving the other two opening sites binding with the N atom from the pyridine ring of other pyac$^-$. In Cu(pyac)$_2$ $^{[2,6]}$, 2D structure only forms when there is no polar solvents
like water and methanol. However, Zn(pyac)$_2$ (2.9) forms 2D square structure with disordered water and methanol as solvents, which is different from Cu(pyac)$_2$.

With similar reaction condition, cis-Zn(pyac)$_2$ (2.10) was able to characterized by X-ray analysis (Figure 2.15).

![Figure 2.15 Coordination environment of cis-Zn(pyac)$_2$ (2.10).](image)

Two N atoms from neighboring Zn(pyac)$_2$ units coordinate the remaining cis positions. The 3D polymerized structure explains the insolubility of the materials in common organic solvents.

![Figure 2.16 Crystal structure of cis-Zn(pyac)$_2$ (2.10).](image)

a: Two interpenetrated diamondoid structure; b: View along the a axis.
It is soluble in pyridine. The interesting feature of the structure is that two sets of distorted diamondoid network interpenetrated with each other (Figure 2.16 a), forming hexagonal channels along c axis with CH₂Cl₂ packing along the channels with double helix (Figure 2.16 b).

2.2.5 Cu(pyma)₂

PymaH 2.12 is commercially available. We thought that, due to its similarity to pyacH, it might also be able to chelate with metal ions (Figure 2.17), and the metal complexes generated can be used as building blocks.

\[
2 \text{HO-}N + \text{Cu}^{2+} \rightarrow \text{Cu}^{2+}2\text{H}^+ + \text{N} = \text{O-}N
\]

**Figure 2.17** Proposed linear Cu(pyma)₂.

The reaction is carried out starting with copper acetate. Triethylamine or ethylenediamine are used to deprotonate the H⁺ generated in the reaction. Crystals suitable for X-ray diffractions were obtained.

**Figure 2.18** Crystal structure of Cu(pyma)₂(CH₃OH)₂
The structure is not like that of Cu(pyac)$_2$, in which the two oxygen atoms chelate the copper atom. Two oxygen atoms from two different pyma$^-$ (Cu1—O1 distance: 1.98 Å, see Figure 2.18) and two nitrogen atoms from the other two pyma$^-$ (Cu1—N1 distance: 2.00 Å) form a square planar arrangement, with two other oxygen atoms on each side of the plane (Cu—O distance: 2.38 Å). Overall, Cu(pyma)$_2$ forms a 3D structure. Viewed along the a axis (see Figure 2.19), distorted square channels are generated, with disordered methanol molecules.

**Figure 2.19** View along the a axis of Cu(pyma)$_2$(CH$_3$OH)$_2$.

### 2.3 Conclusions

Linear bifunctional ligand pyacH has been synthesized according to the literature with minor revision. The reaction appears to require acylation of the pyridine ring, which is supported by the isolation of compound 2.4, an intermediate in the reaction. PyacH is not a stable compound, so it should be kept cool and under a dry atmosphere.
PyacH can react with copper, zinc, iron and aluminum salts to generate corresponding metal β-diketonate building blocks. For Zn(pyac)$_2$, both *trans* and *cis* forms were characterized by single-crystal X-ray crystallography. The Aluminum and iron compound are disordered trigonal, which shows the flexibility of the ligand.

The similar aldehyde compound of pyacH is pyridylmalonaldehyde. When it reacts with metal ions, it doesn’t chelate with the metal like β-diketone. Instead, a *cis* coordination geometry forms for copper.

2.4 Experimental

2.4.1 3-(4-Pyridinyl)pentane-2,4-dione (2.1)

A mixture of acetyl chloride (70.2 g, 0.89 mol) and CHCl$_3$ (400 mL) was cooled to −20 °C (dimethylacetamide-solid CO$_2$). Then 4-methylpyridine (104.4 g, 1.13 mol) was added in 10 minutes with stirring under N$_2$. A deep green color developed during the addition. Stirring was continued until the dry ice evaporated (4 hours). The solvent and the unreacted starting materials were removed under water aspirator vacuum at 40 °C. The dark brown residue was triturated with 700 mL toluene, and the resulting solid being separated by filtration. 50 mL H$_2$O was used to wash the filtrate for three times, and then the solution was dried by Na$_2$SO$_4$ overnight. Toluene was removed under water aspirator at 45 °C for about 6 hours. The residue was distilled under vacuum (< 1 mmHg), and the component boiling around 115 °C was collected. It crystallizes at room temperature. Yield: 29.2 g (37%). M.P.: 70-73 °C. $^1$H NMR measured in Bruker ARX-300 (300 MHz, CDCl$_3$) matches what is reported in the reference $^{[2-1]}$: δ 16.79 (1H, s), 8.66 (2H, d), 7.19 (2H, d), 1.92 (6H, s).
2.4.2 [4-(1-Acetylacetonyl)pyridinium] Chloride (2.2)

From the procedure of 2.4.1, crystals suitable for single-crystal X-ray crystallography were found from concentrated reaction mixture before it was triturated with toluene.

2.4.3 2PyacH·HOAc (2.3)

Crystals grew from the concentrated toluene solution in 2.4.1 after trituration if it was not washed with water and distillation. Crystals were found and collected data by single-crystal X-ray crystallography. M.P.: 44 °C.

2.4.4 1-Acetyl-4-(acetylmethylidene)-1,4-dihydropyridine (2.4)

The concentrated toluene solution from 2.4.3 was cooled down to around 0 °C in refrigerator and yellow lath crystals grew from the solution. M.P.: 137 °C.

2.4.5 1-(4-Pyridinyl)-2-propanone (PP, 2.5)

Solid pyacH decomposes slowly in laboratory air (probably due to water vapor) to generate 1-(4-pyridinyl)-2-propanone. \(^{1}\text{H NMR (Bruker ARX-300, CDCl}_3): \delta 8.59(2\text{H, d}), 7.19(2\text{H, d}), 3.77(2\text{H, s}), 2.24(3\text{H, s}).

2.4.6 Cu(PP)_2(OAc)_2(H_2O)_2 (2.6)

The decomposed Hpyac solution (see 2.4.5) will react with copper acetate to form deep green crystals. Cu(OAc)_2 (0.7 g, 3.8 mmol) in 10 mL H_2O is mixed with decomposed pyacH mixture (1.5 g) in 5 mL ethanol. NaHCO_3 (1.0 g, 12 mmol) was added later. Deep green crystals grew in two days. Yield: 1.38 g, 74%.

2.4.7 Fe(Pyac)_3 (2.7)

Solution of Fe(NO_3)_3·9H_2O (0.404 g, 1.00 mmol, in 10 mL H_2O) and PyacH (0.66 g, 3.7 mmol in 10 mL methanol) were mixed. To this mixture, a solution of 0.25 g
NaHCO₃ (3.0 mmol) in 4 mL H₂O was added, with stirring. The combined liquid was left to crystallize at room temperature for 24 h, and the resulting red needle-like crystals were collected and rinsed with 10 mL H₂O and air-dried. Yield: 0.555 g (95%).

2.4.8 Al(Pyac)₃(H₂O)(CHCl₃) (2.8)

The compound was prepared by the method of Sanders et al. [2.2]. Yellow needle crystals suitable for crystallography grew by evaporation of a CHCl₃ solution.

2.4.9 [Zn(Pyac)₂](CH₃OH)(H₂O) (2.9, trans)

PyacH (0.36 g, 2.0 mmol) was dissolved in 2 mL dichloromethane. 1.5 mL 1:1 methanol/dichloromethane was layered above the dichloromethane solution. Then the Zn(OAc)₂·2H₂O (0.22 g, 1 mmol) in 2.5 mL methanol was layered on the top of the test tube. Colorless crystals grew in one day. Yield: 0.048 g (10%). The crystals will lose crystallinity on exposure to air. And the crystals slowly dissolved back into solution in two weeks.

2.4.10 [Zn(Pyac)₂](CH₂Cl₂) (2.10, cis)

PyacH (0.72 g, 4 mmol) was dissolved in 5 mL dichloromethane and placed on the bottom of the test tube. 2 mL 1:1 methanol/dichloromethane was layered above. Zn(OAc)₂·2H₂O (0.44 g, 2 mmol) in 6 mL methanol was layered on the top of the test tube. Colorless crystals grew in the next day. Yield: 0.142 g (14%).

2.4.11 [Cu(pyma)₂](CH₃OH)₂ (2.11)

Cu(OAc)₂·H₂O (0.050 g, 0.25 mmol) was dissolved in 3 mL water in the test tube. 1.5 mL 1:1 water/methanol was added as buffer. PymaH (0.075 g, 0.50 mmol) and ethylenediamine (0.030 g, 0.50 mmol) was dissolved in 4 mL methanol, and the solution was layered on the top. Green crystals grew over a period of 4 days.
2.5 References


2.4 Zhang, Y.; Chen, B; Fronczek, F. R.; Maverick, A. W. Manuscript in preparation.


Chapter 3

A Nanoporous Mixed-Metal-Organic Framework Exhibiting Single-Crystal-to-Single-Crystal Transformations upon Guest Exchange

3.1 Introduction

The design of extended solids is of great interest in supramolecular chemistry because of their potential applications gas storage, host-guest chemistry, catalytic, electronic and optical properties \[^3.1-3.2]\). Rational design of ligands can lead to predictable extended solid frameworks \[^3.3-3.6]\). Metal-organic frameworks (MOFs) are of interest because the various coordination geometries and abilities of metal ions together with different types of ligands provide many possible structures \[^3.7]\). Furthermore, modification of ligands makes it easy to functionalize the network to gain desirable properties. Multifunctional polytopic ligands can bind with different metal ions with different site preferences to generate heterometallic frameworks.

In this chapter we are building nanoporous mixed-metal-organic frameworks through the pyridine based tridentate \(\beta\)-diketonate metal building blocks \(\text{Fe(pyac)}_3\) and \(\text{Al(pyac)}_3\), which we prepared in Chapter 2. Pyridine has the ability to coordinate with a variety of metal ions. The building blocks are rigid with some flexibility. Three-fold symmetric \(\text{Fe(pyac)}_3\) and \(\text{Al(pyac)}_3\) building blocks might have the ability to generate various coordination compounds, from oligomers to 1D, 2D and 3D materials. Silver ion (\(\text{Ag}^+\)) is chosen here due to the flexibility of its coordination geometry. There are abundant examples for Ag(I)-pyridine chemistry \[^3.8-3.26]\), with coordination numbers of 2, 3, and 4 and 6.
In the work described in this chapter, the tridentate building block Fe(pyac)$_3$ reacts with AgNO$_3$ under various solvents with different concentrations. Two different 2D porous honeycomb structures have been found and characterized by single-crystal X-ray diffraction. 1D porous ladder structures have been made under bromobenzene, dichlorobenzene, toluene and dichloromethane (Figure 3.1).

![Figure 3.1](image)

**Figure 3.1** Two types of porous structures observed in Fe-Ag chemistry.

Furthermore, it is found that the 1D frameworks are robust enough to allow the exchange of the solvents without destruction of the network. The solvent exchange study has been done with bromobenzene, dichlorobenzene, toluene, benzene, naphthalene and trichloroethylene. These reactions have been studied by single crystal X-ray diffraction
and GC-MS. It is also found that Al(pyac)₃ can form the same 1D ladder porous material under similar condition.

The crystalline porous materials are synthesized at room temperature by a layering technique. Silver nitrate is used as the silver source, and is usually dissolved in acetonitrile solution. The tridentate building blocks Fe(pyac)₃ and Al(pyac)₃ are dissolved in other solvents. The solution with higher density is placed in the bottom of a test tube, and then a 1:1 mixture of the two solvents is placed above the heavy solution as buffer to slow down the diffusion. Then the lighter solution is placed on the top. The crystals usually grow over a period of one day to several weeks.

For single crystal X-ray diffraction, the crystals are quickly moved out of solvent and cooled down to about 110 K, to improve data quality and prevent loss of solvent/guest molecules. For the single-crystal-to-single-crystal solvent exchange experiments, one crystal still glued on the glass fiber after the data collection is immersed in the second solvent for approximate 24 hours, and then a second data set was collected.

3.2 Results and Discussion

3.2.1 2D Porous Honeycomb Structures

We expected that Ag⁺ might crystallize in a 1:1 ratio with Fe(pyac)₃, forming a 2D honeycomb structure (M’MOF 1, Figure 3.1) with 3-coordinate Ag⁺. When we layered AgNO₃/acetonitrile solution on the Fe(pyac)₃/1,2-dichlorobenzene solution at room temperature, red crystals with hexagonal morphology grew in about two weeks. A single crystal X-ray diffraction study reveals that the composition of the compound is Fe(pyac)₃AgNO₃-(C₆H₄Cl₂)₂(CH₃CN)₂ (3.1). The compound adopts a 2D honeycomb structure as shown in Figure 3.2. In each hexagon there are two 1,2-dichlorobenzene and
two acetonitrile molecules. The edges of the hexagon range from 9.8 to 10.1 Å, with angles ranging from 99° to 141°.

![Figure 3.2](image)

**Figure 3.2** Honeycomb type I of Fe(pyac)$_3$AgNO$_3$(C$_6$H$_4$Cl$_2$)$_2$(CH$_3$CN)$_2$ (3.1). (H atoms are omitted for clarity.)

The pore sizes and angles of compound 3.1 and 3.2 are listed in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>3.1*</th>
<th>3.2 (Pore A)</th>
<th>3.2 (Pore B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (Å)</td>
<td></td>
<td>Length (Å)</td>
<td>Length (Å)</td>
</tr>
<tr>
<td>Angles(°)</td>
<td></td>
<td>Angles (°)</td>
<td>Angles (°)</td>
</tr>
<tr>
<td>10.11</td>
<td>99.4</td>
<td>9.86</td>
<td>99.3</td>
</tr>
<tr>
<td>9.85</td>
<td>141.1</td>
<td>9.95</td>
<td>127.1</td>
</tr>
<tr>
<td>9.92</td>
<td>116.8</td>
<td>9.97</td>
<td>132.0</td>
</tr>
<tr>
<td>10.11</td>
<td>99.4</td>
<td>9.99</td>
<td>100.8</td>
</tr>
<tr>
<td>9.85</td>
<td>141.1</td>
<td>9.95</td>
<td>125.3</td>
</tr>
<tr>
<td>9.92</td>
<td>116.8</td>
<td>9.90</td>
<td>134.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.97</td>
<td>132.0</td>
</tr>
</tbody>
</table>

*Lengths are measured from Ag-Fe, and angles are Fe···Ag···Fe and Ag···Fe···Ag.

When the reaction is carried out in a more dilute AgNO$_3$/acetonitrile solution, crystals with similar shape and color form, but these have a slightly different structure. Fe(pyac)$_3$AgNO$_3$(C$_6$H$_4$Cl$_2$)$_2$CH$_3$CN(H$_2$O)$_{0.5}$ (3.2) also has a 2D honeycomb-like structure. There are two different pores in compound 3.2 structure. Each Ag atom coordinates with
one acetonitrile molecule, which makes Ag atom out of 2D honeycomb plane. There are three 1,2-dichlorobenzene molecules and one nitrate anion in the bigger pore A, while only one 1,2-dichlorobenzene molecule and one water molecule were able to identified in the smaller pore B (Figure 3.3).

Figure 3.3 Honeycomb type II of Fe(pyac)₃AgNO₃(C₆H₄Cl₂)₂(CH₃CN)(H₂O)₀.₅ (3.2).

The crystal data of compound 3.1 and 3.2 are listed in Table 3.2.

Table 3.2 Selected crystal data of honeycomb structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.1 Fe(pyac)₃AgNO₃(C₆H₄Cl₂)₂(CH₃CN)₂</th>
<th>3.2 Fe(pyac)₃AgNO₃(C₆H₄Cl₂)₂(CH₃CN)(H₂O)₀.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P̄T</td>
<td>P̄T</td>
</tr>
<tr>
<td>a(Å)</td>
<td>10.474</td>
<td>11.629</td>
</tr>
<tr>
<td>b(Å)</td>
<td>15.215</td>
<td>18.219</td>
</tr>
<tr>
<td>c(Å)</td>
<td>17.051</td>
<td>24.813</td>
</tr>
<tr>
<td>α (°)</td>
<td>109.69</td>
<td>69.59</td>
</tr>
<tr>
<td>β (°)</td>
<td>98.45</td>
<td>89.30</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90.39</td>
<td>78.04</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>2526.0</td>
<td>4809.6</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>R</td>
<td>0.0729</td>
<td>0.0865</td>
</tr>
</tbody>
</table>
3.2.2 1D Porous Ladder Structures

When the concentration of the AgNO₃/acetonitrile solution is increased, a totally different type of crystal structure is obtained. Instead of the 1:1 Fe/Ag compound for the 2D honeycomb structure, a 2:3 Fe/Ag 1D ladder structure with larger pore size is generated ([Fe(pyac)₃]₂(AgNO₃)₃(C₆H₄Cl₂)₅.₅₅, \textbf{3.3}, Figure 3.4). The crystals are also red color because of the presence of iron(III).

![Diagram](image)

\textbf{Figure 3.4} 1D ladder structure of [Fe(pyac)₃]₂(AgNO₃)₃(C₆H₄Cl₂)₅.₅₅ (3.3).
(H atoms and solvent molecules are omitted for clarity.)

As is illustrated in Figure 3.4, Fe atoms lie at the interseption of uprights and rungs of ladders, with one arm of pyac⁻ connecting with another pyac⁻ arm from another Fe(pyac)₃ of the other side of upright through Ag(I) ion as the rung, and two other pyac⁻ arms connected along uprights through Ag(I) ions. The Ag(I) ions on the rungs connect
with two pyridine nitrogen atoms and one nitrate group. In addition to two pyridine nitrogen atoms, two Ag(I) ions on the upright of adjacent ladders are bridged by two nitrate groups with 3.28 Å silver-silver distance (to make 2D sheets).

There are two different size pores in the structure, each pore A holds six 1,2-dichlorobenzene solvent molecules and five molecules for pore B (Figure 3.5).

![Figure 3.5](image)

**Figure 3.5** Guest molecules in [Fe(pyac)₃]₂(AgNO₃)₃(C₆H₄Cl₂)₅.5 (3.3).

The two 1,2-dichlorobenzene guest molecules drawn as stick models in the middle of pore B are 50% occupied. H atoms are omitted for clarity.

In 1,2-dichlorobenzene system, we found that when the concentration of the AgNO₃ is high (higher than 0.075 mol/L), it tends to form 2:3 ladder structures; when the concentration of the AgNO₃ is low (lower than 0.075 mol/L), it tends to form 1:1 honeycomb structures. The possible explanation for that is that there is not enough Fe(pyac)₃ around the interface to form 1:1 three-coordinated silver compounds around the interface when the concentration is high. When AgNO₃ concentration is high, less acetonitrile is used and its concentration is low while 1,2-dichlorobenzene is in high concentration. This make it possible to have 1,2-dichlorobenzene as guest molecules.
without the participation of acetonitrile. So in the low AgNO₃ concentration case, there are more acetonitrile and less AgNO₃, 1:1 structure is preferred and acetonitrile participate in the formation of crystals. Even more than stoichiometric amount of AgNO₃, 1:1 honeycomb structure is still preferred as long as the concentration of AgNO₃ is low. When the initial concentration of AgNO₃ is lower than 0.012 mol/L, honeycomb type I structure is generated as illustrated in Figure 3.6.

<table>
<thead>
<tr>
<th>Honeycomb I</th>
<th>Honeycomb II</th>
<th>1D ladder</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.012 mol/L</td>
<td>0.075 mol/L</td>
<td>[AgNO₃]</td>
</tr>
</tbody>
</table>

**Figure 3.6** Ag-Fe reaction in 1,2-dichlorobenzene/acetonitrile solution.

When Fe(pyac)₃ in bromobenzene solution reacts with AgNO₃ in acetonitrile solution, similar 1D ladder structure is obtained (Figure 3.7).

**Figure 3.7** Framework of [Fe(pyac)₃]₂(AgNO₃)₃(C₆H₅Br)₆ (3.4). H atoms and solvent molecules are omitted for clarity.
Compound 3.4 has only one kind of pore, with six bromobenzene molecules in each pore, which is different with 3.3.

![Figure 3.8](image1.png)

**Figure 3.8** Guest molecules in [Fe(pyac)3]2(AgNO3)3(C6H5Br)6 (3.4). H atoms are omitted for clarity.

When Fe(pyac)3 in toluene solution reacts with AgNO3/acetonitrile solution, 1D ladder structure is obtained (Figure 3.9). Compound 3.5 has only one kind of pore, with five toluene molecules in each pore.

![Figure 3.9](image2.png)

**Figure 3.9** Crystal structure of [Fe(pyac)3]2(AgNO3)3(C7H8)5 (3.5). The two toluene guest molecules drawn as stick models in the middle are 50% occupied. H atoms are omitted for clarity.
When solution of Al(pyac)$_3$ in 1,2-dichlorobenzene reacts with AgNO$_3$, similar structure compound 3.9 ([Al(pyac)$_3$]$_2$(AgNO$_3$)$_3$($C_6H_4Cl_2$)$_{5.5}$) was obtained. The colorless crystals of 3.9 need more time to grow and are generally a lot smaller than the Ag-Fe compounds. Because of smaller radius of Al than that of Fe, the pore sizes of 3.9 are slightly smaller than those corresponding sizes of similar Fe compound 3.3. However, 3.9 also has two kinds of pores, with six dichlorobenzene in pore A and five in pore B. The structure of 3.9 is shown Figure 3.10.

![Figure 3.10](image)

**Figure 3.10** Guest molecules in [Al(pyac)$_3$]$_2$(AgNO$_3$)$_3$($C_6H_4Cl_2$)$_{5.5}$ (3.9). The two 1,2-dichlorobenzene guest molecules drawn as stick models in the middle of pore B are 50% occupied. H atoms are omitted for clarity.

### 3.2.3 Single-Crystal-to-Single-Crystal Guest Exchanges in 1D Ladder Structure

The most interesting property of 3.3 is that if its crystals are put in bromobenzene, they do not dissolve, but the 1,2-dichlorobenzene guest molecules are all exchanged by bromobenzene. During this process, the crystals still keep the same shape with the framework basically unchanged. This is called a single-crystal-to-single-crystal transformation. The experiment has been done for a cycle with one crystal. The exchange
experiment can be done with a variety of solvents, as shown in Figure 3.11. All the structures are characterized by single-crystal X-ray diffraction at low temperature (100 K-110 K).

As shown in Figure 3.11, one crystal of 3.3 was immersed in bromobenzene solvent after X-ray diffraction data collection; After one day, the crystal (3.4') was characterized by X-ray. 3.4' has the same structure with compound 3.4 prepared directly from Fe(pyac)₃/bromobenzene solution, which indicates all 1,2-dichlorobenzene guest molecules were exchanged out by bromobenzene. And then the same crystal was immersed back into 1,2-dichlorobenzene solvent immediately after data collection over a period of one day. The resulting crystal (3.3') was characterized by X-ray again. The structure of 3.3' is exactly the same as that of the starting material (3.3), showing that the guest exchanges in this system are reversible.

Figure 3.11 Flow chart of [Fe(pyac)₃]₂(AgNO₃)₃(guest)ₓ guest exchanges.
Starting from compound 3.4, single-crystal-to-single-crystal solvent exchange can also be done with benzene. The crystal structure after benzene exchange is in Figure 3.12.

![Diagram of crystal structure](image)

**Figure 3.12** Guest molecules in $\text{[Fe(pyac)₃]₂(AgNO₃)₃(C₆H₆)₅.₅}$ (3.6). The two benzene guest molecules drawn as stick models in the middle of pore B are 50% occupied. H atoms are omitted for clarity.

The solvent to grow crystal 3.4 were poured out, and then benzene was added in immediately. Interestingly, the crystal structure of 3.6 after exchange from benzene ($\text{[Fe(pyac)₃]₂(AgNO₃)₃(C₆H₆)₅.₅}$) shows the similar structure of compound 3.3, which has two different sizes of pores. With pore A holds six benzene molecules, pore B only holds five benzene with the one near center of pore B disordered.

Similar experiment above was also carried out with trichloroethylene and saturated naphthalene in diethyl ether solution. The mother liquor from the synthesis of 3.4 was decanted and replaced by trichloroethylene and saturated naphthalene in diethyl ether solution. Crystal data were collected at low temperature. The crystal structure is shown in Figure 3.13. $\text{[Fe(pyac)₃]₂(AgNO₃)₃(C₂HCl₃)₆(H₂O)₂}$ (3.7) has only one kind of pore.
As shown from the crystal structure (Figure 3.14), only four of the six bromobenzene molecules in 3.4 have been replaced. This may be due to the low concentration of naphthalene comparing with the pure solvent we used in the other guest exchange systems. Two bromobenzene molecules near Fe atoms of small pore angles remain in the pores. The middle naphthalene molecules are disordered like what happen in toluene guest molecules in compound 3.5.
3.2.4 GC-MS Analysis of Guest Exchanges

Another way to prove the guest exchange is using the GC-MS analysis to test the amount of the guest molecules exchanged. This experiments were done only for the bromobenzene-1,2-dichlorobenzene exchanges. Crystals grown from one solvent are collected and washed. They are weighed after air dried. The weighed crystals are then immersed into the other solvent for one day. The weighted solvent is about 150 times in weight more than the guest molecules needed to be exchanged to ensure the completion of exchange. The exchanged sample solutions are then diluted around 200 times in CH$_2$Cl$_2$ for GC-MS measurements, so as not to exceed its detector capacity. The GC-MS experiment gives a ratio of peak areas of bromobenzene and 1,2-dichlorobenzene (Figure 3.15).

![Figure 3.15 GC-MS result of bromobenzene-to-1,2-dichlorobenzene exchange.](image)

**Figure 3.15** GC-MS result of bromobenzene-to-1,2-dichlorobenzene exchange.
We also prepared standard bromobenzene/1,2-dichlorobenzene sample solutions which have concentrations in the range expected for the guest exchanged solution. These samples are also carried same experiment of GC-MS.

![Graph](image.png)

**Figure 3.16** GC-MS result of 1,2-dichlorobenzene-to-bromobenzene exchange.

For the bromobenzene-to-1,2-dichlorobenzene exchange experiment, a linear relationship is obtained when the area ratio of bromobenzene/1,2-dichlorobenzene is the Y axis, and the concentration of bromobenzene (mole ratio of bromobenzene/1,2-dichlorobenzene) is the X axis. Using the slope of the linear and the peak area ratio of bromobenzene/1,2-dichlorobenzene of the exchanged sample solution, we can calculate the bromobenzene concentration in the exchanged sample solution. Then we can calculate the mass of bromobenzene exchanged from the mass of the 1,2-dichlorobenzene
we used and the bromobenzene concentration. From that we can also calculate how much percentage of the bromobenzene is exchanged or how many molecules are exchanged out in one pore. The similar method can also be applied to 1,2-dichlorobenzene-to-bromobenzene exchange experiment.

In 1,2-dichlorobenzene-to-bromobenzene exchange experiment, 12.2 mg compound 3.3 \([\text{Fe(pyac)}_3]_2(\text{AgNO}_3)_3(C_6\text{H}_4\text{Cl}_2)_{9.5}\) was immersed in 604.7 mg bromobenzene for one day. The 1,2-dichlorobenzene and bromobenzene peak were observed in the GC-MS result, which confirms the release of 1,2-dichlorobenzene. After calculation, we found that 3.6 mg 1,2-dichlorobenzene was exchanged compared to the theoretical 3.7 mg. This is equals to 5.6 DCB molecules per pore, which matches the crystallographic data 5.5 pretty well. The detailed data are shown in Table 3.3.

Table 3.3 GC-MS data of DCB to BB exchange.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(m_{\text{BB}}) (g)</th>
<th>(m_{\text{DCB}}) (g)</th>
<th>(\text{mol}<em>{\text{BB}}/\text{mol}</em>{\text{DCB}})</th>
<th>(A_{\text{BB}})</th>
<th>(A_{\text{DCB}})</th>
<th>(A_{\text{BB}}/A_{\text{DCB}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mg/mL</td>
<td>17.2083</td>
<td>0.0340</td>
<td>0.002110</td>
<td>166000000</td>
<td>474745</td>
<td>0.00286</td>
</tr>
<tr>
<td>5 mg/mL</td>
<td>9.8914</td>
<td>0.0494</td>
<td>0.005334</td>
<td>166700000</td>
<td>1105000</td>
<td>0.00663</td>
</tr>
<tr>
<td>10 mg/mL</td>
<td>5.5680</td>
<td>0.0556</td>
<td>0.010666</td>
<td>157600000</td>
<td>2167000</td>
<td>0.01375</td>
</tr>
<tr>
<td>15 mg/mL</td>
<td>4.2793</td>
<td>0.0633</td>
<td>0.015799</td>
<td>165500000</td>
<td>3406000</td>
<td>0.02058</td>
</tr>
<tr>
<td>Exchanged*</td>
<td>0.0038</td>
<td>0.6047</td>
<td>0.006368</td>
<td>195100000</td>
<td>1609000</td>
<td>0.00825</td>
</tr>
</tbody>
</table>

*The exchange sample mass and concentration are calculated from the other data (blue).

In bromobenzene-to-1,2-dichlorobenzene exchange experiment, 16.8 mg 3.4 \([\text{Fe(pyac)}_3]_2(\text{AgNO}_3)_3(C_6\text{H}_5\text{Br})_5\) was immersed in 824.1 mg 1,2-dichlorobenzene for one day. Both bromobenzene and 1,2-dichlorobenzene peak were observed in the GC-MS result, which confirms the release of bromobenzene. We found that 4.3 mg bromobenzene was exchanged compared to the 6.0 mg theoretical amount. This is equals to 4.2 bromobenzene molecules in a pore, which is close to the crystallographic data. The detailed data are shown in Table 3.4.
Table 3.4 GC-MS data of BB to DCB exchange.

<table>
<thead>
<tr>
<th>Sample</th>
<th>m_{BB} (g)</th>
<th>m_{DCB} (g)</th>
<th>mol_{BB}/mol_{DCB}</th>
<th>A_{BB}</th>
<th>A_{DCB}</th>
<th>A_{BB}/A_{DCB}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mg/mL</td>
<td>0.0311</td>
<td>15.5954</td>
<td>0.001867</td>
<td>662608</td>
<td>270600000</td>
<td>0.002449</td>
</tr>
<tr>
<td>5 mg/mL</td>
<td>0.0547</td>
<td>10.4271</td>
<td>0.004912</td>
<td>1438000</td>
<td>243700000</td>
<td>0.005901</td>
</tr>
<tr>
<td>10 mg/mL</td>
<td>0.0610</td>
<td>6.1549</td>
<td>0.009279</td>
<td>2494000</td>
<td>237100000</td>
<td>0.010519</td>
</tr>
<tr>
<td>15 mg/mL</td>
<td>0.0543</td>
<td>3.4152</td>
<td>0.014886</td>
<td>3672000</td>
<td>233100000</td>
<td>0.015753</td>
</tr>
<tr>
<td>Exchanged*</td>
<td>0.0040</td>
<td>0.8241</td>
<td>0.007329</td>
<td>1473000</td>
<td>279200000</td>
<td>0.005276</td>
</tr>
</tbody>
</table>

*The exchange sample mass and concentration are calculated from the other data (blue).

3.2.5 Relationship of Guest Volumes and Pore Sizes of 1D Ladder Structures

The selected crystal data of 1D ladder structure with two different pores are listed in the Table 3.5.

Table 3.5 Selected crystal data of 1D ladder structure with two different pores.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.3</th>
<th>3.6</th>
<th>3.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P1̅</td>
<td>P1̅</td>
<td>P1̅</td>
</tr>
<tr>
<td>a(Å)</td>
<td>7.627</td>
<td>7.62</td>
<td>7.633</td>
</tr>
<tr>
<td>b(Å)</td>
<td>22.424</td>
<td>21.302</td>
<td>22.391</td>
</tr>
<tr>
<td>c(Å)</td>
<td>31.273</td>
<td>30.513</td>
<td>31.089</td>
</tr>
<tr>
<td>α (°)</td>
<td>83.795</td>
<td>88.355</td>
<td>83.682</td>
</tr>
<tr>
<td>β (°)</td>
<td>85.6</td>
<td>87.387</td>
<td>84.66</td>
</tr>
<tr>
<td>γ (°)</td>
<td>83.083</td>
<td>85.2</td>
<td>83.105</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>5267.5</td>
<td>4928.9</td>
<td>5225.8</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>R</td>
<td>0.1362</td>
<td>0.1673</td>
<td>0.1233</td>
</tr>
</tbody>
</table>

The cell volume of the aluminum complex (3.9) is slightly smaller than that of the iron compound (3.3), possibly due to the smaller size of aluminum atom. For compound 3.3 and 3.6, which have the same framework but different guest molecules, show more variation cell volume. The similar phenomena are also observed in the 1D ladder structures with unified pores (Table 3.6). When the volumes of guest molecules are considered, we can find that the cell volumes change mainly due to the number and size of guest molecules. This means the main framework is adjustable through the control of guest molecules.
Table 3.6 Selected crystal data of 1D ladder structure with one kind of pore.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.4</th>
<th>3.5</th>
<th>3.7</th>
<th>3.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>(P\bar{1})</td>
<td>(P\bar{1})</td>
<td>(P\bar{1})</td>
<td>(P\bar{1})</td>
</tr>
<tr>
<td>a(Å)</td>
<td>7.788</td>
<td>7.786</td>
<td>7.715</td>
<td>7.835</td>
</tr>
<tr>
<td>b(Å)</td>
<td>15.728</td>
<td>15.470</td>
<td>15.868</td>
<td>15.541</td>
</tr>
<tr>
<td>(\alpha) (°)</td>
<td>94.37</td>
<td>89.81</td>
<td>92.79</td>
<td>91.50</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>95.32</td>
<td>85.12</td>
<td>95.37</td>
<td>92.21</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>100.51</td>
<td>79.13</td>
<td>99.56</td>
<td>101.60</td>
</tr>
<tr>
<td>(V(Å^3))</td>
<td>2679.0</td>
<td>2507.4</td>
<td>2582.5</td>
<td>2519.7</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>R</td>
<td>0.139</td>
<td>0.1079</td>
<td>0.1143</td>
<td>0.0888</td>
</tr>
</tbody>
</table>

To prove the theory, we calculate the volume of guest molecules from their pure state at room temperature (Table 3.7).

Table 3.7 Calculated volume for each guest molecule from densities of pure compounds.

<table>
<thead>
<tr>
<th>Guest Molecules</th>
<th>M.W. (g/mol)</th>
<th>Density (g/cm³)</th>
<th>Volume(Å³/molecule)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromobenzene (BB)</td>
<td>157.01</td>
<td>1.500</td>
<td>173.82</td>
</tr>
<tr>
<td>Dichlorobenzene (DCB)</td>
<td>147.00</td>
<td>1.300</td>
<td>187.77</td>
</tr>
<tr>
<td>Benzene (Bz)</td>
<td>78.11</td>
<td>0.870</td>
<td>149.09</td>
</tr>
<tr>
<td>Toluene (Tol)</td>
<td>92.14</td>
<td>0.865</td>
<td>176.89</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>131.39</td>
<td>1.460</td>
<td>149.44</td>
</tr>
<tr>
<td>Naphthalene (Naph)</td>
<td>128.17</td>
<td>1.140</td>
<td>186.70</td>
</tr>
<tr>
<td>Water</td>
<td>18.00</td>
<td>1.000</td>
<td>29.89</td>
</tr>
</tbody>
</table>

These data are summarized in Table 3.8. We found that the cell volumes change as the guest molecule volumes change nearly linearly. After we subtract the guest molecule volumes from the total cell volume, we can get the volume of the framework occupy. The framework volume for each \([\text{Fe(pyac)}_3]_2\cdot(\text{AgNO}_3)_3\) unit are about the same as expected, ranging from 1601 to 1644 Å³. This indicates this framework is flexible.

Table 3.8 Calculated guest volumes for AgFe 1D ladder structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.3</th>
<th>3.6</th>
<th>3.7</th>
<th>3.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guest molecules</td>
<td>DCB</td>
<td>Bz</td>
<td>BB</td>
<td>Tol</td>
</tr>
<tr>
<td>(V_{cell}(Å^3))</td>
<td>5267</td>
<td>4929</td>
<td>2679</td>
<td>2507</td>
</tr>
<tr>
<td>(V_{guest}(Å^3))</td>
<td>2065</td>
<td>1640</td>
<td>1043</td>
<td>884</td>
</tr>
<tr>
<td>(V_{frame}(Å^3))</td>
<td>3202</td>
<td>3289</td>
<td>1636</td>
<td>1623</td>
</tr>
<tr>
<td>(V_{pore}(Å^3))</td>
<td>1601</td>
<td>1644</td>
<td>1636</td>
<td>1623</td>
</tr>
</tbody>
</table>
To understand how the framework corresponds to the change of guest molecules, the pore sizes and estimated pore areas are listed in Table 3.9 and Table 3.10. We use the Ag-Ag distances on the rungs as the width of pores, and the Ag-Ag distances on the sides as the length of pores. Each pore can be viewed as approximately rectangular, with usually straight rung sides and bent edges. In the ideal square shape, the pore will have the biggest room while the Fe(pyac)₃ group have to bend most. To estimate pore areas, we make frameworks (without nitrate group) as spacefilled models and measure the projected pore areas. It is found that in compound 3.3 and 3.9 (dichlorobenzene as guest), both pore As significantly have bigger areas than pore Bs.

**Table 3.9 Pore sizes and areas of 1D ladder structure with two different pores.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.3</th>
<th>3.6</th>
<th>3.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Big pore A length (Å)</td>
<td>22.58</td>
<td>23.10</td>
<td>22.42</td>
</tr>
<tr>
<td>Big pore A width (Å)</td>
<td>20.55</td>
<td>19.17</td>
<td>20.39</td>
</tr>
<tr>
<td>Big pore A area (Å²)</td>
<td>195</td>
<td>182</td>
<td>189</td>
</tr>
<tr>
<td>Small pore B length (Å)</td>
<td>25.05</td>
<td>24.82</td>
<td>25.02</td>
</tr>
<tr>
<td>Small pore B width (Å)</td>
<td>16.86</td>
<td>18.28</td>
<td>16.57</td>
</tr>
<tr>
<td>Small pore B area (Å²)</td>
<td>175</td>
<td>187</td>
<td>172</td>
</tr>
</tbody>
</table>

**Table 3.10 Pore sizes and areas of 1D ladder structure with one kind of pore.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>3.4</th>
<th>3.5</th>
<th>3.7</th>
<th>3.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore length (Å)</td>
<td>23.86</td>
<td>24.10</td>
<td>23.83</td>
<td>23.85</td>
</tr>
<tr>
<td>Pore width (Å)</td>
<td>18.78</td>
<td>18.58</td>
<td>18.76</td>
<td>18.76</td>
</tr>
<tr>
<td>Pore area (Å²)</td>
<td>197</td>
<td>193</td>
<td>190</td>
<td>193</td>
</tr>
</tbody>
</table>

### 3.2.6 3D Interpenetrated Spiral AgFe Structure

1D ladder porous material containing benzene as guest molecules (3.6) can be prepared through guest exchange from compound 3.4, but not directly. When similar method was applied to grow 1D ladder porous material from benzene, different kind of crystals 3.10 were obtained instead of the ladder structure. It is a 3D structure, with two sets of interpenetrated spiral structures spiraling in opposite directions along the b axis. The crystal structure is shown in Figure 3.17.
Figure 3.17 Asymmetric unit of Fe(pyac)$_3$AgNO$_3$(C$_6$H$_6$)$_2$(H$_2$O)$_{1.5}$ (3.10).

Figure 3.18 Interpenetrated structure of Fe(pyac)$_3$AgNO$_3$(C$_6$H$_6$)$_2$(H$_2$O)$_{1.5}$ (3.10).

It looks like just 2D honeycomb structures when it is viewed along the b axis (Figure 3.18). However, due to the coordination of silver (I) with two oxygen atom of nitrate, its coordination with three nitrogen atoms of pyridine group is no longer in a plane, which make it spiraling along b axis.
The crystals cracked into small piece in 30 seconds after it was put into bromobenzene solvent. It doesn’t seem to be a good candidate for solvent exchange. One possible reason is that there is no channel big enough for the solvent exchange.

3.3 Conclusions

Solutions of the trigonal building block Fe(pyac)₃ can generate various crystal structures on reaction with AgNO₃ in CH₃CN. When the Fe(pyac)₃ is dissolved in 1,2-dichlorobenzene, bromobenzene, or toluene, a high concentration of AgNO₃ in the CH₃CN phase can result in a 1D ladder structure (Fe:Ag 2:3). Furthermore, guest solvents can exchange between different solvents in single-crystal-to-single-crystal transformations. The solvent can be exchanged from bromobenzene to 1,2-dichlorobenzene, benzene, trichloroethylene and naphthalene. The exchange between bromobenzene and 1,2-dichlorobenzene has been studied on one crystal by single X-ray diffraction and GC-MS. Through the study of crystal structure, we found that the frameworks are flexible according to the guest molecules through the edges and angles adjustment. Al(pyac)₃ can also generate 1D ladder porous material in acetonitrile and 1,2-dichlorobenzene solution, which has similar framework and guest molecules as iron compound.

3.4 Experimental

3.4.1 Fe(pyac)₃(AgNO₃)(C₆H₄Cl₂)₂(CH₃CN)₂ (3.1)

Fe(pyac)₃ (5.5 mg, 0.0094 mmol) was dissolved in 5 mL 1,2-dichlorobenzene in the bottom of a 10 mL test tube. 1.5 mL 1,2-dichlorobenzene/acetonitrile solution was layered on. A solution of AgNO₃ (2.5 mg, 0.015 mmol) in 0.4 mL acetonitrile was layered on the top. Red crystals 1-2 mm grew after 2 weeks. Yield: 6.7 mg (62%).
3.4.2 Fe(pyac)$_3$(AgNO$_3$)(C$_6$H$_4$Cl$_2$)$_2$(CH$_3$CN)(H$_2$O)$_{0.5}$ (3.2)

Fe(pyac)$_3$ (17.5 mg, 0.03 mmol) was dissolved in 5 mL 1,2-dichlorobenzene in the bottom of a 10 mL test tube. 1.5 mL 1,2-dichlorobenzene/acetonitrile solution was layered on. The solution of AgNO$_3$ (10.1 mg, 0.06 mmol) in 3 mL acetonitrile was layered on the top. Crystals grew in 3 weeks. Yield: 15.1 mg (46%).

3.4.3 [Fe(pyac)$_3$]$_2$(AgNO$_3$)$_3$(C$_6$H$_4$Cl$_2$)$_{5.5}$ (3.3)

Fe(pyac)$_3$ (17.5 mg, 0.03 mmol) was dissolved in 6 mL dichlorobenzene in a 10 mL test tube. Dichlorobenzene/acetonitrile (1.5 mL 1:1) was layered above as the buffering solution. The solution of AgNO$_3$ (10.1 mg, 0.06 mmol) in 0.8 mL acetonitrile was layered on the top. 1 cm long red crystals grew after 1 week. Yield: 12.2 mg, 32.7%. Anal. calc.: C, 44.91; H, 3.32; N, 5.07. Found: C, 44.14; H, 3.03; N, 5.78.

[Fe(pyac)$_3$]$_2$(AgNO$_3$)$_3$(C$_6$H$_4$Cl$_2$)$_{5.5}$ (3.3')

The crystal of 3.4' was put into dichlorobenzene solvent overnight. The crystal morphology did not change visibly during this exchange.

3.4.4 [Fe(pyac)$_3$]$_2$(AgNO$_3$)$_3$(C$_6$H$_5$Br)$_6$ (3.4)

Fe(pyac)$_3$ (17.5 mg, 0.03 mmol) was dissolved in 5 mL bromobenzene in the bottom of a 10 mL test tube. Bromobenzene/acetonitrile solution (1 mL 1:1) was layered above as the buffering solution. A solution of AgNO$_3$ (6.8 mg, 0.04 mmol) in 0.5 mL acetonitrile was layered on the top. 1-2 cm long crystals grew after 1-2 weeks. Yield: 23.2 mg, 63%. Anal. calc.: C, 43.88; H, 3.40; N, 5.12. Found: C, 43.96; H, 3.26; N, 5.16.

[Fe(pyac)$_3$]$_2$(AgNO$_3$)$_3$(C$_6$H$_5$Br)$_6$ (3.4')

A crystal of 3.3 was put into bromobenzene solvent overnight. The crystal morphology did not change visibly during this exchange.
3.4.5 \([\text{Fe(pyac)}_3]_2(\text{AgNO}_3)_3(\text{C}_7\text{H}_8)_{5.5}(3.5)\)

\(\text{Fe(pyac)}_3\) (5.5 mg, 0.0094 mmol) was dissolved in 3 mL toluene in a 10 mL test tube. 1.5 mL toluene/acetonitrile solution was layered on. A solution of AgNO\(_3\) (2.8 mg, 0.016 mmol) in 0.2 mL acetonitrile was layered on the top. Red blade crystals grew in 2 weeks.

3.4.6 \([\text{Fe(pyac)}_3]_2(\text{AgNO}_3)_3(\text{C}_6\text{H}_6)_{5.5}(3.6)\)

The mother liquor from the synthesis of 3.4 was decanted and replaced by benzene.

3.4.7 \([\text{Fe(pyac)}_3]_2(\text{AgNO}_3)_3(\text{C}_2\text{HCl}_3)_{6}(\text{H}_2\text{O})_{2}(3.7)\)

The mother liquor from the synthesis of 3.4 was decanted and replaced by trichloroethylene.

3.4.8 \([\text{Fe(pyac)}_3]_2(\text{AgNO}_3)_3(\text{C}_6\text{H}_5\text{Br})_{2}(\text{C}_{10}\text{H}_8)_{3}(3.8)\)

The mother liquor from the synthesis of 3.4 was decanted and replaced by saturated naphthalene solution in diethyl ether.

3.4.9 \([\text{Al(pyac)}_3]_2(\text{AgNO}_3)_3(\text{C}_6\text{H}_4\text{Cl}_2)_{5.5}(3.9)\)

\(\text{Al(pyac)}_3\) (16.5 mg, 0.03 mmol) was dissolved in 7.5 mL 1,2-dichlorobenzene in a 10 mL test tube. Dichlorobenzene/acetonitrile (0.8 mL, 1:1) was layered above as the buffering solution. A solution of AgNO\(_3\) (8.5 mg, 0.05 mmol) in acetonitrile (0.3 mL) was layered on the top. 1-2 mm long needle colorless crystals grew in 4 weeks. Yield: 12.3 mg, 34%.

3.4.10 \(\text{Fe(pyac)}_3\text{AgNO}_3(\text{C}_6\text{H}_6)_{2}(\text{H}_2\text{O})_{1.5}(3.10)\)

\(\text{Fe(pyac)}_3\) (5.5 mg, 0.0094 mmol) was dissolved in 4 mL toluene in a 10 mL test tube. Benzene/acetonitrile solution (1.5 mL, 1:1) was layered on. A solution of AgNO\(_3\)
(2.8 mg, 0.016 mmol) in acetonitrile (0.2 mL) was layered on the top. Red hexagonal crystals grew in 3 weeks.

3.5 References


Chapter 4

An Isocyanide Based β-diketone Ligand and Its Metal Complexes

4.1 Introduction

Usually a coordination number of 3 or 4 does not lead to a 3D structure, so we hope to use conditions that are suitable for the assembly of six ligands around one metal. Although a few M(py)$_n^{n+}$ complexes are known, they are generally prepared in pyridine solution [4.1,4.2] or by adding an excess of pyridine [4.3]. This is difficult to do with Cu(pyac)$_2$ (Figure 4.1), because supramolecular materials usually cannot be made if a large excess of one reactant is present. The relatively weak binding ability of nitriles also makes it difficult to generate six-coordinate complexes M(NCR)$_6^{n+}$.

![Cu(pyac)$_2$](image1)

**Cu(pyac)$_2$, 4.1**

![Cu(acphCN)$_2$](image2)

**Cu(acphCN)$_2$, 4.2**

![Cu(acphNC)$_2$](image3)

**Cu(acphNC)$_2$, 4.3**

![HacphNC](image4)

**HacphNC, 4.22**

**Figure 4.1** Copper β-diketonate “rods” with pyridine, cyanide and isocyanide substituents.

Therefore, in order to improve the prospects for 3D materials, we need to use building blocks based on complexes that are highly stable with monodentate ligands L.
Cu(acphNC)_{2} (Figure 4.1), with an isocyanide group at each end, is believed to have the best chance for conversion to 3D porous materials. Isocyanide ligands (CNR) are already known to make very stable complexes with metal such as Cr, Mn, Fe and Re \cite{4.4-4.23}. For example, Barybin et al. \cite{4.4} recently prepared a chromium isocyanide complex Cr(CNR)_{6} in 93% yield, using only 8% excess of the isocyanide ligand. Sacco \cite{4.5-4.7} synthesized a series of air stable manganese(I) isocyanide complexes through anion exchanges after making [(RNC)_{6}Mn]I_{3} with 25% excess of isocyanide ligand in anhydrous ethanol.

4.2 Results and Discussion

4.2.1 Synthetic Strategy

We plan to carry out the initial steps of this chemistry, as shown in Figure 4.2.

**Figure 4.2** Two possible routes of preparing 4-formylaminophenylacac (4.6).

To synthesize the target ligand CNphacH, the most likely routes are through 4-formylaminophenylacac (4.6), because isocyanides are normally prepared by dehydration of formamides. There are two possible routes starting from 4-nitrobenzaldehyde (Figure
4.2. In route A, aldehyde group is converted into acac first; nitro group is reduced to amino group by H₂ and formylated later. In route B, nitro group is reduced to amino group and then formylated first, and then the aldehyde is converted into β-diketone.

After the aldehyde group was turned into a β-diketone, it is followed by coordination to Cu²⁺ as a “protecting group” (Figure 4.3). The copper complex was then dehydrated to isocyanide complex. We will attempt to use the isocyanide derivative Cu(acphNC)₂ to construct 3D porous materials. We will do this either by direct reaction with a M'-containing starting material (e.g. Cr(naphthalene)₂ or Fe²⁺) or by reaction with a M' compound in a higher oxidation state (e.g. Mn²⁺ or ReO₄⁻) and a suitable reducing agent. The isocyanide metal β-diketonate complex was protonated into the desired ligand.

Figure 4.3 Synthesis of isocyano-β-diketone complex Cu(acphNC)₂.
4.2.2 Synthesis of HacphNHCHO (4.6)

The attempt to prepare 4-nitrophenylacac 4.9 was tried through route A. Compound 4.8 (4-nitrobenzaldehyde) was mixed with Phospholene 4.5 in dichloromethane for one day and then reflux in anhydrous methanol for three days. No desired product was obtained. Instead, the intermediate compound 4.12 (Figure 4.4) was obtained and characterized after reaction in dichloromethane.

![Figure 4.4 Crystal structure of phospholane intermediate (4.12).](image)

![Figure 4.5 Mechanism of β-diketone formation through phospholane.](image)

As what is proposed by Ramirez [4.24] (Figure 4.5), the cleavage of trimethoxyphosphate causes the formation of carbon cation right next to benzene ring,
which lead to the 1,2 shift of acetyl group and end up with keto form of β-diketone. The β-diketone will usually turn into enol form in most cases. Therefore an electron withdrawing group R will hinder the formation of carbon cation while an electronic donating group will accelerate the process. This theory was confirmed by the fact that this reaction with 4-nitrobenzaldehyde stops at phospholane and can’t go further to β-diketone due to strong electron withdrawing property of nitro group.

When the methanol solution of the intermediate 4.12 was left in the air for several days, compound 4.13 crystallize from the reaction mixture. The crystal structure is shown in Figure 4.6. It is possibly the hydrolyzed product of phospholane with water in air.

![Figure 4.6 Hydrolysis of phospholane.](image)

Because the experiment of route A was not successful, I turned to route B to make compound 4.6. As illustrated in Figure 4.2, the nitro group in is reduced by tin metal to amino group and then immediately formylated to make OHCNHphCHO, 4.4. I tried the reaction with the method from the reference [4,25], but could not get a yield close to the reported 47% as what is claimed in the reference. In the reported procedure, toluene and formic acid are used. The starting material 4.8 is mainly in toluene solution after 3-day reaction. It might be that 4.8 has little contact with tin metal and formic acid due to the
immiscibility of formic acid and toluene. Most starting material in the toluene phase has no chance to be reduced and formylated. We replaced toluene with ethyl formate and ethyl acetate because they are miscible with formic acid. So the reaction changes from three phase (tin/formic acid/toluene) to two phase (tin/solution).

There is competition with formylation reaction after nitro group is reduced. The amino group can easily react with aldehyde group of starting material to generate 4.14, or self condense into polymer 4.15 (Figure 4.7).

\[
\begin{align*}
\text{CHO} & \quad \text{NH}_2 \\
\text{NO}_2 & \\
\text{CHO} &
\end{align*}
\]

\[\text{CHO} \quad \text{NO}_2 \quad \text{CH} \quad \text{NH}_2 \]

\[4.11\]

\[4.14\]

\[4.15\]

\[4.4\]

\[ \text{E} : \text{Z} \text{ ratio is about 39:61, while it is about 25:75 in deuterated} \]

\[ \text{CDCl}_3 \text{, the E:Z ratio is about 39:61, while it is about 25:75 in deuterated} \]
DMSO. However, only the $E$ isomer crystallized readily (Figure 4.8). In this structure, intermolecular hydrogen bonds connect molecules in a zig-zag arrangement (Figure 4.9).

![Figure 4.8 Crystal structure of 4.4, (E)-4-(formylamino)benzaldehyde.](image)

![Figure 4.9 1D zig-zag structure of 4.4 (E) connected by H-bonds.](image)

After compound 4.4 is made, it is treated with biacetyltrimethylphosphite in dichloromethane to generate β-diketone compound 4.6 (HacphNHCHO, Figure 4.2).

If the methyl groups of acac are changed to ethyl groups, the solubility of the β-diketone compounds in organic solvents usually increase. When compound 4.4 is reacted
with phospholene, the reaction stops at the phospholane 4.16 as illustrated in Figure 4.10. The heating also doesn’t work in the reaction, and it causes the decomposition of intermediate to other side products.

\[
\begin{array}{c}
\text{CHO} \\
\text{NHCHO} \\
\text{4.4}
\end{array} \xrightarrow{\text{MeOPOMe}} \begin{array}{c}
\text{CHO} \\
\text{NHCHO} \\
\text{4.16}
\end{array} \xrightarrow{\text{X}} \begin{array}{c}
\text{CHO} \\
\text{NHCHO} \\
\text{4.17}
\end{array}
\]

**Figure 4.10** Attempt to prepare 4-(4-formylaminophenyl)-3,5-heptanedione (4.17).

Compound 4.6 was purified through chromatography. Yellow product crystallizes from hexane/ethyl acetate solution. Both \( E \) and \( Z \) forms of 4.6 were characterized with X-ray (Figure 4.11) and NMR.

\[
\text{3-(4-formylaminophenyl)-pentane-2,4-dione.}
\]

**Figure 4.11** Crystal structures of HacphNHCHO (4.6) isomers.
Hydrogen-bonding geometries of the above formamides compounds are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>D—H· · ·A</th>
<th>D—H</th>
<th>H· · ·A</th>
<th>D· · ·A</th>
<th>D—H· · ·A</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCHphNHCHO (E)</td>
<td>N1—H1· · ·O2\textsuperscript{i}</td>
<td>0.88</td>
<td>2.01</td>
<td>2.88</td>
<td>170.8</td>
</tr>
<tr>
<td>4.4 (E)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HacphNHCHO (Z)</td>
<td>O2—H2· · ·O1</td>
<td>1.01</td>
<td>1.54</td>
<td>2.47</td>
<td>152.5</td>
</tr>
<tr>
<td>4.6 (Z)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HacphNHCHO (E)</td>
<td>N1—H1· · ·O3\textsuperscript{ii}</td>
<td>0.88</td>
<td>2.03</td>
<td>2.90</td>
<td>170.5</td>
</tr>
<tr>
<td>4.6 (E)</td>
<td>O2—H2· · ·O1</td>
<td>1.09</td>
<td>1.44</td>
<td>2.48</td>
<td>157.0</td>
</tr>
<tr>
<td>HacphNHCHO</td>
<td>N1—H1· · ·O3\textsuperscript{iii}</td>
<td>0.92</td>
<td>2.03</td>
<td>2.94</td>
<td>177.0</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 1 − x, y − 1/2, 1 − z; (ii) −x, 1/2 + y, −1/2 − z; (iii) −x, −y, 1 − z.

Like compound 4.4, NMR of 4.6 shows both E and Z conformation. In CDCl\textsubscript{3}, the $E$:Z ratio is about 42:58, while it is about 25:75 in the deuterated DMSO. Furthermore, enol-keto equilibrium is also observed in the NMR. In CDCl\textsubscript{3}, the ratio is approximately 94% enol : 6% keto.

For (Z)-4.6, the intermolecular hydrogen bonds connect molecules in a 1D zig-zag way like (E)-4.4 (Figure 4.12).

Figure 4.12 1D zig-zag structure of (Z)-HacphNHCHO (4.6).
On the other hand, (E)-4.6 crystalizes as dimer through intermolecular H-bond as shown in Figure 4.13.

![Figure 4.13 Dimer of (E)-HacphNHCHO (4.6) connected through H-bond.](image)

Selected geometric parameters of compound 4.4 and 4.6 are listed in Table 4.2, and selected crystal data are listed in Table 4.3.

<p>| Table 4.2 Selected geometric parameters of compound 4.4 and 4.6 (Å, °). |
|---------------------------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>OHCphNHCHO (4.4)</th>
<th>HacphNHCHO (4.6)</th>
<th>E</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1—C1</td>
<td>1.219</td>
<td>O1—C2</td>
<td>1.259</td>
</tr>
<tr>
<td>O2—C4</td>
<td>1.324</td>
<td>O2—C4</td>
<td>1.329</td>
</tr>
<tr>
<td>C2—C3</td>
<td>1.444</td>
<td>C2—C3</td>
<td>1.432</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.380</td>
<td>C3—C4</td>
<td>1.379</td>
</tr>
<tr>
<td>C1—C2</td>
<td>1.502</td>
<td>C1—C2</td>
<td>1.498</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.492</td>
<td>C4—C5</td>
<td>1.484</td>
</tr>
<tr>
<td>C8—N1—C5</td>
<td>127.36</td>
<td>C8—N1—C5</td>
<td>126.98</td>
</tr>
<tr>
<td>O2—C8—N1</td>
<td>123.16</td>
<td>O2—C8—N1</td>
<td>126.13</td>
</tr>
<tr>
<td>O1—C1—C2—C3</td>
<td>1.3</td>
<td>O1—C1—C2—C3</td>
<td>68.23</td>
</tr>
<tr>
<td>C8—N1—C5—C4</td>
<td>178.4</td>
<td>C8—N1—C5—C4</td>
<td>155.84</td>
</tr>
<tr>
<td>C5—N1—C8—O2</td>
<td>176.7</td>
<td>C5—N1—C8—O2</td>
<td>-4.88</td>
</tr>
</tbody>
</table>
Table 4.3 Selected crystal data for compounds 4.4 and 4.6.

<table>
<thead>
<tr>
<th>Compound</th>
<th>OHCphNHCHO</th>
<th>HacphNHCHO</th>
<th>HacphNHCHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.W. (g/mol)</td>
<td>149.15</td>
<td>219.23</td>
<td>219.23</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P_2_1$</td>
<td>$P_{2_1}/c$</td>
<td>$C_2/c$</td>
</tr>
<tr>
<td>a(Å)</td>
<td>4.391</td>
<td>13.289</td>
<td>14.379</td>
</tr>
<tr>
<td>b(Å)</td>
<td>6.917</td>
<td>7.518</td>
<td>10.339</td>
</tr>
<tr>
<td>c(Å)</td>
<td>11.793</td>
<td>11.561</td>
<td>14.974</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>97.808</td>
<td>111.153</td>
<td>91.296</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>354.86</td>
<td>1077.20</td>
<td>2225.53</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>R</td>
<td>0.0417</td>
<td>0.0422</td>
<td>0.0473</td>
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</tbody>
</table>

4.2.3 Syntheses of M(acphNHCHO)$_n$

After we made compound 4.6, we needed to protect the $\beta$-diketone group during the dehydration of the formylamino groups to isocyanides. Metal ions are chosen to protect the $\beta$-diketone because we can make the building blocks directly. Three metal ions, Cu$^{2+}$, Zn$^{2+}$, and Al$^{3+}$ are chosen to react with 4.6 (Figure 4.14).

Zinc complex 4.18 is made from zinc acetate and ligand 4.6. As shown on the equation above, sodium bicarbonate is used to neutralize the proton of ligand. Crystals grown during synthesis are suitable for single-crystal X-ray diffraction. In the structure of 4.18 (see Figure 4.15), the two $\beta$-diketonate groups form a stepped arrangement about
In addition to those oxygen atoms from β-diketonate groups, Zn$^{2+}$ also coordinates with two water molecules octahedrally. The compound is not very soluble in chloroform, dichloromethane, but it is easily soluble in DMSO, pyridine.

The similar reaction is also applied to copper acetate to generate complex 4.7. Copper(II) has higher affinity toward acac than Zn(II), and the bluish green product 4.7 precipitates immediately when ligand and metal salt are mixed together in water/methanol solution. Crystals suitable for X-ray analysis were grown in DMSO/water solution. Unlike zinc complex, there is no solvent molecule in crystals of 4.7 (Fig. 4.16).

The copper atoms are four coordinate with two acac ligand. In contrast with 4.18, the 4.7 is coplanar with the two acac ligands (Figure 4.16). The copper complex is
slightly soluble in DMSO, soluble in pyridine derivatives, and it is insoluble in almost all other common solvents.

In copper complex 4.7, hydrogen bonds from amino groups of one molecule to the aldehyde oxygen atoms of the other molecules connect the molecules into an infinite 2D network in a zig-zag way as is illustrated in Figure 4.17. This is different from the zinc complex 4.18, which shows mainly hydrogen bond through water molecules.

**Figure 4.17** 2D zig-zag framework of (Z)-Cu(acphNHCHO)$_2$ (4.7) through H-bonds.

In both zinc and copper complexes the formylamino groups are in Z conformations. The reason might be that Z formylamino groups are more stable in the polar solvents. The fomyamino group of copper complex 4.7 is 31.4° away from benzene ring, which is similar to compound 4.6 (Table 4.4); while it is almost in the same plane of benzene ring in zinc complex 4.18, just like 4.4. The difference might be due to hydrogen bonding of water in the crystals.
Table 4.4  Selected geometric parameters of M(acphNHCHO)$_x$ (4.7, 4.18) (Å, °).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu(acphNHCHO)$_2$ (4.7)</th>
<th>Zn(acphNHCHO)$_2$(H$_2$O)$_4$ (4.18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1—O1</td>
<td>1.917</td>
<td>Zn1—O1w</td>
</tr>
<tr>
<td>Cu1—O2</td>
<td>1.924</td>
<td>Zn1—O2</td>
</tr>
<tr>
<td>O1—C2</td>
<td>1.275</td>
<td>O1—C2</td>
</tr>
<tr>
<td>O2—C4</td>
<td>1.272</td>
<td>O2—C4</td>
</tr>
<tr>
<td>C2—C3</td>
<td>1.408</td>
<td>C3—C4</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.416</td>
<td>C1—C2</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.512</td>
<td>C4—C5</td>
</tr>
<tr>
<td>O1—C2</td>
<td>1.917</td>
<td>Zn1—O1</td>
</tr>
<tr>
<td>O2—C4</td>
<td>1.924</td>
<td>Zn1—O2</td>
</tr>
<tr>
<td>O1—C2</td>
<td>1.275</td>
<td>O1—C2</td>
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<tr>
<td>O2—C4</td>
<td>1.272</td>
<td>O2—C4</td>
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<tr>
<td>C2—C3</td>
<td>1.408</td>
<td>C3—C4</td>
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<tr>
<td>C3—C4</td>
<td>1.416</td>
<td>C1—C2</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.512</td>
<td>C4—C5</td>
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<tr>
<td>O1—C2</td>
<td>1.917</td>
<td>Zn1—O1</td>
</tr>
<tr>
<td>O2—C4</td>
<td>1.924</td>
<td>Zn1—O2</td>
</tr>
<tr>
<td>O1—C2</td>
<td>1.275</td>
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<td>O2—C4</td>
<td>1.272</td>
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<td>C2—C3</td>
<td>1.408</td>
<td>C3—C4</td>
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<td>C3—C4</td>
<td>1.416</td>
<td>C1—C2</td>
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<td>C4—C5</td>
<td>1.512</td>
<td>C4—C5</td>
</tr>
<tr>
<td>O1—C2</td>
<td>1.917</td>
<td>Zn1—O1</td>
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<tr>
<td>O2—C4</td>
<td>1.924</td>
<td>Zn1—O2</td>
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<tr>
<td>O1—C2</td>
<td>1.275</td>
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<td>O2—C4</td>
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<td>O2—C4</td>
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<td>C2—C3</td>
<td>1.408</td>
<td>C3—C4</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.416</td>
<td>C1—C2</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.512</td>
<td>C4—C5</td>
</tr>
<tr>
<td>C2—C3</td>
<td>1.408</td>
<td>C3—C4</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.416</td>
<td>C2—O1—Zn1</td>
</tr>
<tr>
<td>C4—C5</td>
<td>1.512</td>
<td>C1—C2</td>
</tr>
<tr>
<td>C3—C4</td>
<td>1.416</td>
<td>C4—O2—Zn1</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 2 − x, −y, −z; (ii) 2 − x, y − 1/2, 1/2 − z; (iii) 1 − x, 1 − y, −z; (iv) 1 − x, 1 − y, 1 − z; (v) −x, 1 − y, −z; (vi) 1/2 − x, 1/2 + y, 1/2 − z.

Table 4.5  Hydrogen-bonding geometries of compound 4.7 and 4.18 (Å, °).

<table>
<thead>
<tr>
<th>Compound</th>
<th>D—H· · ·A</th>
<th>D—H</th>
<th>H· · ·A</th>
<th>D· · ·A</th>
<th>D—H· · ·A</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1—H1· · ·O1w</td>
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<td>2.09</td>
<td>2.959</td>
<td>170.8</td>
<td></td>
</tr>
<tr>
<td>O1w—H1w· · ·O3ii</td>
<td>0.84</td>
<td>1.95</td>
<td>2.797</td>
<td>179.7</td>
<td></td>
</tr>
<tr>
<td>O1w—H2w· · ·O2wiii</td>
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<td>2.651</td>
<td>179.3</td>
<td></td>
</tr>
<tr>
<td>O2w—H3w· · ·O1iv</td>
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<td>2.844</td>
<td>179.6</td>
<td></td>
</tr>
<tr>
<td>O2w—H4w· · ·O3v</td>
<td>0.85</td>
<td>2.16</td>
<td>3.017</td>
<td>179.7</td>
<td></td>
</tr>
</tbody>
</table>

| 4.7          | N1—H1· · ·O3vi | 0.88 | 2.16 | 3.017 | 164.3 |

Symmetry codes: (i) 1 − x, y − 1/2, 1/2 − z; (ii) 1 − x, 1 − y, −z; (iii) 1 − x, 1/2 + y, 1/2 − z; (iv) 1 − x, 1 − y, 1 − z; (v) −x, 1 − y, −z; (vi) 1/2 − x, 1/2 + y, 1/2 − z.
Table 4.6 Selected crystal data of compound 4.18 and 4.7.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Zn(acphNHCHO)₂(H₂O)₄ (4.18)</th>
<th>Cu(acphNHCHO)₂ (4.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.W.</td>
<td>573.89</td>
<td>499.99</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>P2₁/n</td>
</tr>
<tr>
<td>a(Å)</td>
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<td>8.136</td>
</tr>
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<td>b(Å)</td>
<td>9.637</td>
<td>7.480</td>
</tr>
<tr>
<td>c(Å)</td>
<td>11.947</td>
<td>17.771</td>
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<tr>
<td>α (°)</td>
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<td>β (°)</td>
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<td>103.166</td>
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<tr>
<td>γ (°)</td>
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<td>90</td>
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<tr>
<td>V(Å³)</td>
<td>1302.5</td>
<td>1053.1</td>
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<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
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<tr>
<td>R</td>
<td>0.0537</td>
<td>0.0543</td>
</tr>
</tbody>
</table>

Aluminum complex 4.19 is made according to the similar way of zinc complex. Sodium bicarbonate is used to neutralize the solution. The product is soluble in DMSO, and only slightly soluble in chloroform and dichloromethane.

Due to the equilibria of E and Z conformation of formamides in the solution, it is necessary to organize the NMR data for better understanding. In compound 4.2, the chemical shift of Z aldehyde hydrogen in CDCl₃ is upfield around 7.6 comparing with 8.5 of the E CHO. When changed to polar solvent DMSO, Z CHO moves downfield at 10.6, even lower than the E CHO. ¹H NMR of formamides is listed in Table 4.7.

Table 4.7 ¹H NMR of formamides in DMSO.

<table>
<thead>
<tr>
<th>Compound</th>
<th>OHCphNHCHO 4.4</th>
<th>HacphNHCHO 4.6</th>
<th>Zn(acphNHCHO)₂ 4.18</th>
<th>Al(acphNHCHO)₃ 4.19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1*</td>
<td>10.64</td>
<td>10.26</td>
<td>10.18</td>
<td>10.23</td>
</tr>
<tr>
<td>Z2</td>
<td>8.37</td>
<td>8.29</td>
<td>8.28</td>
<td>8.28</td>
</tr>
<tr>
<td>Z3</td>
<td>7.79</td>
<td>7.62</td>
<td>7.58</td>
<td>7.61</td>
</tr>
<tr>
<td>Z4</td>
<td>7.89</td>
<td>7.20</td>
<td>7.14</td>
<td>7.14</td>
</tr>
<tr>
<td>E1</td>
<td>10.56</td>
<td>10.20</td>
<td>10.13</td>
<td>10.18</td>
</tr>
<tr>
<td>E2</td>
<td>9.03</td>
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<td>8.81</td>
<td>8.81</td>
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<tr>
<td>E3</td>
<td>7.40</td>
<td>7.16</td>
<td>7.19</td>
<td>7.22</td>
</tr>
<tr>
<td>E4</td>
<td>7.86</td>
<td>7.23</td>
<td>7.16</td>
<td>7.18</td>
</tr>
<tr>
<td>CH₃</td>
<td>N/A</td>
<td>1.85</td>
<td>1.65</td>
<td>1.77</td>
</tr>
</tbody>
</table>

*The position code is shown in Figure 4.18.
4.2.4 Syntheses of $\text{M(acphNC)}_n$

Metal formylamino $\beta$-diketonate complexes are dehydrated by $\text{POCl}_3$ in the presence of diisopropylamine (Figure 4.19).

$$\begin{align*}
\text{Zn} \left( \text{O} \right) \left( \begin{array}{c}
\text{Z} \text{Z} \text{Z} \\
\text{Z} \text{Z} \\
\text{Z} \text{Z}
\end{array} \right) \text{NHCHO}_2 + \text{POCl}_3 & \rightarrow 1. \text{iPr}_2\text{NH/CH}_2\text{Cl}_2 \\
& + 2. 10\% \text{NaHCO}_3 \\
\text{Al} \left( \text{O} \right) \left( \begin{array}{c}
\text{E} \text{E} \text{E} \\
\text{E} \text{E} \\
\text{E} \text{E}
\end{array} \right) \text{NHCHO}_2 + \text{POCl}_3 & \rightarrow 1. \text{iPr}_2\text{NH/CH}_2\text{Cl}_2 \\
& + 2. 10\% \text{NaHCO}_3 \\
\text{Cu} \left( \text{O} \right) \left( \begin{array}{c}
\text{E} \text{E} \text{E} \\
\text{E} \text{E} \\
\text{E} \text{E}
\end{array} \right) \text{NHCHO}_2 + \text{POCl}_3 & \rightarrow 1. \text{iPr}_2\text{NH/CH}_2\text{Cl}_2
\end{align*}$$

Figure 4.19 Preparation of isocyanide $\beta$-diketonate metal complexes.

Reactions are carried out in dichloromethane solution. The corresponding amount of diisopropylamine was added to neutralize the acid produced in the reaction. The starting materials are not very soluble, while products are soluble in the solution. Aluminum and zinc starting materials (4.18, 4.19) both dissolve in the solution after one hour. In contrast, most of the copper starting material (4.7) still remains insoluble even after five days. The IR absorptions ($\nu_{\text{C=N}}$) of isocyanide group are 2124 cm$^{-1}$ for the Zn complex and 2121 cm$^{-1}$ for the Al complex, which are very close to the free phNC ligands $^{[4.26-4.29]}$. For copper reactions, isocyanide frequency is 2147 cm$^{-1}$ in $\text{CH}_2\text{Cl}_2$. 

\textbf{Figure 4.18} H positions of formamides.
solution. This high frequency could indicate coordination of isocyanide with open site of copper atom. Crystals of aluminum complex were able to grow with diffusion of hexane into dichloromethane. The crystal structure of aluminum (III) isocyanide phenyl-β-diketonate complex is shown in Figure 4.20. It has the expected approximately trigonal shape, with CN···Al···NC angles of 137.7°, 81.9° and 140.3°.

**Figure 4.20** Crystal structure of Al(acphNC)₃·H₂O (4.21)

**4.2.5 Synthesis of HacphNC**

We were also interested in preparing the free HacphNC ligand (4.22). We attempted to make it directly from 4.6 by reacting with POCl₃. However, the β-diketone group was not stable under the reaction conditions. We succeeded in isolating HacphNC from Zn and Al complexes (4.20, 4.21) by reaction with dilute acid. It is noticed that only weak acid can be used in this process (Figure 4.21). Strong acids like HCl decompose the isocyanide group.
Figure 4.21 Synthesis of HacphNC by protonation of M(acphNC)$_n$ (Al, Zn).

Although the yield of HacphNC was low, it was obtained in crystalline form (Figure 4.22). IR absorption ($\nu$$_{C\equiv N}$) of isocyanide group is 2122 cm$^{-1}$.

Figure 4.22 Structure of HacphNC (4.22, 3-(4-isocyanophenyl)pentane-2,4-dione).

The experimental data of isocyanide crystals are listed in Table 4.8.

Table 4.8 Selected crystal data of isocyanides 4.21 and 4.22.

<table>
<thead>
<tr>
<th>name</th>
<th>Al(acphNC)$_3$(H$<em>2$O)$</em>{0.66}$(4.21)</th>
<th>HacphNC(4.22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.W.</td>
<td>639.59</td>
<td>201.22</td>
</tr>
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<td>Crystal system</td>
<td>Triclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>$P\overline{1}$</td>
<td>$P2_1/c$</td>
</tr>
<tr>
<td>a(Å)</td>
<td>7.433</td>
<td>7.082</td>
</tr>
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<td>b(Å)</td>
<td>13.51</td>
<td>11.606</td>
</tr>
<tr>
<td>c(Å)</td>
<td>20.657</td>
<td>12.427</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>107.653</td>
<td>120.0</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>97.532</td>
<td>93.666</td>
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<tr>
<td>$\gamma$ (°)</td>
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<td>90</td>
</tr>
<tr>
<td>V(Å$^3$)</td>
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<td>1019.3</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>R</td>
<td>0.1085</td>
<td>0.0581</td>
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</table>
The selected geometric parameters of Al isocyanide (Al(acphNC)$_3$) and free ligand HacphNC are listed in Table 4.9.

**Table 4.9 Selected geometric parameters of isocyanides 4.21 and 4.22 (Å, °).**

<table>
<thead>
<tr>
<th></th>
<th>Al(acphNC)$_3$(H$<em>2$O)$</em>{0.66}$(4.21)</th>
<th>HacphNC(4.22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al1—O1</td>
<td>1.872</td>
<td>O2—H2</td>
</tr>
<tr>
<td>Al1—O3</td>
<td>1.872</td>
<td>O1—C2</td>
</tr>
<tr>
<td>Al1—O2</td>
<td>1.873</td>
<td>O2—C4</td>
</tr>
<tr>
<td>Al1—O6</td>
<td>1.874</td>
<td>O3—C14</td>
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<td>Al1—O5</td>
<td>1.877</td>
<td>O4—C16</td>
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<td></td>
</tr>
<tr>
<td>O2—H2</td>
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<td></td>
</tr>
<tr>
<td>O1—C2</td>
<td>1.282</td>
<td></td>
</tr>
<tr>
<td>O2—C4</td>
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<td></td>
</tr>
<tr>
<td>Al1—O1</td>
<td>1.165</td>
<td></td>
</tr>
<tr>
<td>Al1—O3</td>
<td>1.408</td>
<td></td>
</tr>
<tr>
<td>Al1—O2</td>
<td>177.60</td>
<td></td>
</tr>
<tr>
<td>Al1—O6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al1—O5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al1—O4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**4.3 Conclusion**

3-(4-isocyanophenyl)-2,4-pentanedione (HacphNC) was synthesized for the first time starting from 4-nitrobenzaldehyde. Probably due to the electron withdrawing property of the nitro group, 3-(4-nitrophenyl)-2,4-pentanedione can’t be made through direct reaction of 4-nitrobenzaldehyde with the biacetyl-trimethyl phosphate adduct. An improved synthesis was developed, based on reducing the nitro group to –NH$_2$ and formylating it to OHCphNHCHO. The resulting 4-formylaminobenzaldehyde was converted to 3-(4-formylaminophenyl)-2,4-pentanedione (HacphNHCHO) successfully.

Due to the reactivity of β-diketone with phosphorus oxychloride, HacphNHCHO was protected by Al, Zn and Cu metal ions. The metal complexes were then dehydrated by
phosphorus oxychloride in the presence of diisopropylamine to generate M(acphNC)$_n$ metal complexes. Al and Zn complexes were acidified to free the target ligand HacphNC.

4.4 Experimental

4.4.1 4-Formylaminobenzaldehyde (OHCphNHCHO, 4.4)

4-nitrobenzaldehyde (6.04 g, 40 mmol) was dissolved in a mixture of formic acid (90%, 60 mL), ethyl formate (50 mL) and ethyl acetate (150 mL). The solution was refluxed under nitrogen with stirring. Tin metal (9.0 g, 76 mmol) was added separately over two days. The reaction was complete after three days, as judged by TLC. The solution was filtered when it was still hot. The filtrate was evaporated nearly to dryness with a rotary evaporator. Toluene (300 mL) was added to the residue and the mixture refluxed with a Dean-Stark trap for about 2 hours to get rid of the remaining water and formic acid. The mixture was filtered when it was still hot and the filtrate was distilled to dryness. The residue was chromatographed on silica gel with 2:1 ethyl acetate/hexane. Crystals grow easily from the eluate by evaporation. Yield: 3.91 g (66%). M. P. 134 – 136 °C. (Literature: 139 °C $^{[4.25]}$)

$^1$H NMR (250 MHz, CDCl$_3$): E: 7.24 (E3, 2H, d), 7.91 (E4, 2H, d), 8.30 (E1, 1H, d), 8.91 (NH, 1H, d), 9.95 (E5, 1H, s); Z: 7.60 (Z1, 1H, s), 7.75 (Z3, 2H, d), 7.88 (Z4, 2H, d), 8.47 (NH, 1H, s), 9.94 (Z5, 1H, s). $^1$H NMR(250 MHz, DMSO): E: 7.40 (E3, 2H, d), 7.86 (E4, 2H, d), 9.03 (NH, 1H, d), 9.89 (E5, 1H, s), 10.56 (E1, 1H, d); Z: 7.79 (Z3, 2H, d), 7.89 (Z4, 2H, d), 8.37 (NH, 1H, s), 9.89 (Z5, 1H, s), 10.64 (Z1, 1H, s).

4.4.2 3-(4-Formylaminophenyl)pentane-2,4-dione (HacphNHCHO, 4.6)

4.4 (2.56 g, 17.2 mmol) and biacetyl trimethylphosphite (4.02 g, 19.2 mmol) were mixed in 15 mL anhydrous dichloromethane under argon. Compound 4.4 dissolved in 30
minutes. The reaction completed after 3 days. After the distillation of solvent, the residue was chromatographed on silica gel with 2:1 ethyl acetate/hexane eluent. Yield: 1.95 g (52%). M.P. (E): 124 °C. Anal. calc. (E): C, 65.74; H, 5.98; N, 6.39. Found: C, 65.59; H, 6.14; N, 6.48. 1H NMR(250 MHz, CDCl₃): E: 7.12 (E3, 2H, d), 7.18 (E4, 2H, d), 8.19 (E1, 1H, d), 8.74 (E2, 1H, d); Z: 7.15 (Z4, 2H, d), 7.45 (Z1, 1H, s), 7.58(Z3, 2H, d), 8.41 (Z2, 1H, s); Enol: 1.88 (CH₃, 6H, s), 16.66 (OH, 1H, s); Keto: 2.20 (CH₃, 6H, s), 4.83 (CH, 1H, s). 1H NMR(250 MHz, DMSO): E: 7.16 (E3, 2H, d), 7.23 (E4, 2H, d), 8.84 (E2, 1H, d), 10.20 (E1, 1H, d); Z: 7.20 (Z4, 2H, d), 7.62 (Z3, 2H, d), 8.29 (Z2, 1H, s), 10.26 (Z1, 1H, s); Enol: 1.85 (CH₃, 6H, s), 16.79 (OH, 1H, s); Keto: 2.13 (CH₃, 6H, s), 5.30 (CH, 1H, s).

4.4.3 Zn(acphNHCHO)₂ (4.18)

Zn(OAc)₂·2H₂O (0.11 g, 0.50 mmol) in 5 mL H₂O was added to 3 mL methanol solution of HacphNHCHO (0.22 g, 1.00 mmol) with stirring. NaHCO₃ (0.08 g, 1.0 mmol) in 2 mL H₂O was added and yellow precipitate formed immediately. The light yellow precipitate was collected and washed with dichloromethane, H₂O and diethyl ether. Single crystals were obtained from the H₂O/methanol filtrate the next day. The raw sample were dried in oven at 70 °C. Yield: 0.11 g (38%). 1H NMR(DMSO): 1.65 (s, Me, 12H); E: 7.16 (E4, 4H, d), 7.19 (E3, 4H, d), 8.81 (E2, 2H, d), 10.13 (E1, 2H, d); Z: 7.14 (Z4, 4H, d), 7.58 (Z3, 4H, d), 8.28 (Z2, 2H, s), 10.18 (Z1, 2H, s).

4.4.4 Al(acphNHCHO)₃ (4.19)

Al(NO₃)₃·9H₂O (1.125 g, 3.00 mmol) in 15 mL H₂O was added to 15 mL of a methanol solution of HacphNHCHO (2.19 g, 10.0 mmol) under stirring. NaHCO₃ (0.756 g, 9.0 mmol) in 5 mL H₂O was added after the addition of methanol solution to neutralize
the proton released in the reaction. A light yellow precipitate formed, which was collected and triturated with H2O (2 \times 15 \text{ mL}) and methanol (10 \text{ mL}). Yield: 1.89 g (92%). Anal. calc.: C, 63.43; H, 5.32; N, 6.16. Found: C, 63.47; H, 5.33; N, 6.24. 1H NMR: 1H NMR(DMSO): 1.77 (s, Me, 18H); E: 7.18 (E4, 6H, d), 7.22 (E3, 6H, d), 8.81 (E2, 3H, d), 10.18 (E1, 3H, d); Z: 7.14 (Z4, 6H, d), 7.61 (Z3, 6H, d), 8.28 (Z2, 3H, s), 10.23 (Z1, 3H, s).

4.4.5 Cu(acphNHCHO)2 (4.7)

Cu(OAc)2 (0.363 g, 2.0 mmol) in 7 mL H2O was added to 8 mL methanol solution of HacphNHCHO (0.92 g, 4.2 mmol) with stirring. A blue green precipitate formed, which was collected and washed with H2O and methanol and air-dried. Yield: 0.90 g (90%). Anal. calc.: C, 57.64; H, 4.84; N, 5.60. Found: C, 57.49; H, 4.63; N, 5.58.

4.4.6 Zn(acphNC)2 (4.20)

Zn(acphNHCHO)2·2H2O (0.163 g, 0.30 mmol), tPr2NH (0.217 g, 2.15 mmol) were mixed into anhydrous dichloromethane (10 mL). POCl3 (0.110 g, 0.72 mmol) was added into the stirring solution slowly. The whole solution became clear in 30 minutes. The solution was washed with 10% NaHCO3 (10 mL). The organic phase was evaporated almost to dryness and the product precipitated with hexane. Yield: 0.018 g (13%). IR: 2124 cm⁻¹. 1H NMR(250 MHz, CDCl3): 1.87, 12H, s; 7.23, 4H, d; 7.42, 4H, d.

4.4.7 Al(acphNC)3 (4.21)

To a solution of Al(acphNHCHO)3 (1.023 g, 1.50 mmol) and diisopropylamine (1.50 g, 14.8 mmol) in CH2Cl2 (50 mL), POCl3 (0.690 g, 4.50 mmol) was added at room temperature under argon. After stirring for 1 hour, the whole solution became clear and was washed with 10% NaHCO3 (20 mL). The CH2Cl2 was removed with a rotary
evaporator. Hexane was added to the solution to precipitate the product. Yield: 0.710 g (75%). Anal. calc.: C, 68.89; H, 4.82; N, 6.70. Found: C, 68.69; H, 4.81; N, 6.78. IR: 2121 cm⁻¹. ¹H NMR(250 MHz, CDCl₃): 1.87, 18H, s; 7.25, 6H, d; 7.41, 6H, d. Single crystals suitable for X-ray diffraction were grown from diffusion of hexane into a dichloromethane solution of the compound.

4.4.8 Cu(acphNC)₂ (4.3)

To a solution of Cu(acphNHCHO)₂ (4.7, 0.350 g, 0.70 mmol) and diisopropylamine (0.446 g, 4.4 mmol) in CH₂Cl₂ (20 mL), POCl₃ (0.220 g, 1.44 mmol) was added at room temperature under argon. The color slowly changed from blue to green. After stirring for 5 days, the precipitate was filtered off. The organic phase was washed with water twice to get rid of diisopropylamine. When hexane was added to the dichloromethane phase, sticky brown stuff formed. IR: 2147 cm⁻¹.

4.4.9 3-(4-Isocyanophenyl)pentane-2,4-dione (HacphNC, 4.22)

The aluminum isocyanide complex Al(acphNC)₃ (0.750 g, 1.20 mmol) was dissolved in 50 mL dichloromethane. The solution above was stirred with aqueous HOAc solution (0.5%, 50 mL) for one hour. The dichloromethane phase was washed as above procedure five times. After two phase protonation, the organic phase was evaporated and the residue was chromatographed with 1:2 ethyl acetate/hexane. Yield: 0.070 g, 10%. Anal. calc.: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.44; H, 5.36; N, 7.03. ¹H NMR (250 MHz, CDCl₃): 1.89, 6H, s; 7.23, 2H, d; 7.42, 2H, d; 16.71, 1H, s. IR: 2122 cm⁻¹. Compound 4.22 decomposed at around 140 °C.

4.5 References


4.5 Sacco, A. Recueil des Travaux Chimiques des Pays-Bas et de la Belgique 1956, 75, 646.


Chapter 5

C-bound Complexes of the Isocyanide-β-diketone Ligand HacphNC

5.1 Introduction

In order to improve the prospects for 3D materials, we need to use building blocks based on complexes that are highly stable with monodentate ligands L. Cu(acphNC)$_2$, with an isocyanide group at each end, is believed to have the best chance for conversion to 3D porous materials as we stated in Chapter 4. Isocyanide ligands (CNR) are already known to make very stable complexes with metal such as Cr, Mn, Fe and Re$^{[5.1-5.16]}$. For example, Barybin et al.$^{[5.1]}$ recently prepared a chromium isocyanide complex Cr(CNR)$_6$ in 93% yield, using only 8% excess of the isocyanide ligand. Sacco$^{[5.2-5.4]}$ synthesized [(RNC)$_6$Mn]I$_3$ with 25% excess of isocyanide ligand in anhydrous ethanol. Sacco also prepared a series of air stable manganese(I) isocyanide complexes through anion exchanges after making [(RNC)$_6$Mn]I$_3$.

The preparation of metal-complex building blocks (copper, zinc, aluminum) with isocyanide substituents as illustrated in route A, Figure 1.4 is discussed in Chapter 4. We also prepared 3-(4-isocyanophenyl)-2,4-pentanedione (HacphNC, 4.22) by removal of metal ions from M(acphNC)$_n$. The preparation of metal-complex building blocks (manganese) with β-diketone substituents as route B of Figure 1.4 starting from HacphNC is discussed in this chapter. Mixed-metal complexes showing different binding abilities of multifunctional ligands are also discussed in this chapter.

5.2 Results and Discussion

Soft metals are picked to react with isocyanide. Due to the small amount of the ligand HacphNC (4.22) available, most of the reactions were carried out on a small scale
and the products analyzed by NMR and IR. Mn\(^+\), Cu\(^+\), and Au\(^+\) isocyanide compounds were prepared. In addition to free HacphNC ligand, Al(acphNC)\(_3\) was also used to react with Au\(^+\) metal ion.

Kitagawa \(^{[5.17]}\) synthesized a series of copper(I) isocyanide complexes starting from [Cu(CH\(_3\)CN)\(_4\)]ClO\(_4\) at room temperature. It is expected that [Cu(CH\(_3\)CN)\(_4\)]PF\(_6\) can also react with isocyanide easily. With tetrahedral geometry, (HacphNC)\(_4\)Cu\(^+\) would be a diamondoid building block. The following reaction was carried out in CD\(_3\)CN for one hour. NMR was taken directly. After the NMR experiment, IR experiment was performed immediately.

\[
[Cu(CH_3CN)_4]PF_6 + 4 \text{C=}\text{N} \xrightarrow{CD_3CN} \text{Cu}\left(\text{C=}\text{N}\right)_4\text{PF}_6
\]

**Figure 5.1** Preparation of [(HacphNC)\(_4\)Cu]PF\(_6\) (5.1).

When HacphNC coordinates with a metal atom, \(\nu_{\text{C}=\text{N}}\) is expected to increase. The trend is different from CO stretching, because there is usually little \(\pi\) back-bonding in the isocyanide-metal bond. IR absorption \(\nu_{\text{C}=\text{N}}\) of product increases to 2262 cm\(^{-1}\), indicating the formation of metal-ligand bond. The IR band changed in several minutes, indicating the oxidation of Cu(I) to Cu(II).

Mn reaction was also carried out in similar condition. It is believed that [(HacphNC)\(_6\)Mn]I\(_3\) (5.2) will have octahedral geometry (Figure 5.2), so it may react with metals like copper(II) to generate 3D networks.

\[
\text{MnI}_2 + 6 \text{C=}\text{N} \xrightarrow{CD_3CN} \text{Mn}\left(\text{C=}\text{N}\right)_6\text{I}_3
\]

**Figure 5.2** Preparation of [(HacphNC)\(_6\)Mn]I\(_3\) (5.2).
Mn(II) oxidizes iodide in the reaction. Excess isocyanide ligand should be used for the oxidation of isocyanide. The IR show the same band at 2262 cm\(^{-1}\) compared to 2122 cm\(^{-1}\) of free ligand. And it is stable in the air even after hours, which is different from the Cu(I) compound 5.1.

A gold(I) compound was also tried to react with the isocyanides. We chose Me\(_2\)SAuCl because it reacts cleanly with one mole of isocyanide, making RNCAuCl \([5.18]\). Also, Au(I) complexes usually crystallize relatively well.

![Figure 5.3 Preparation of HacphNCAuCl (5.3).](image)

Me\(_2\)SAuCl and HacphNC were refluxed in CDCl\(_3\) for 1.5 h. NMR shows the disappearance of the starting material and formation of desired product. IR \(\nu_{C≡N}\) at 2223 cm\(^{-1}\) confirmed the presence of product. The product is stable in the air over a period of one day as judged by IR.

In addition to free ligand HacphNC, Al(acphNC)\(_3\) was also used to react with Me\(_2\)SAuCl.

![Figure 5.4 Preparation of Al(acphNCAuCl)\(_3\) (5.4).](image)

Al(acphNC)\(_3\) and Me\(_2\)SAuCl were refluxed in dichloromethane for two hours. NMR and IR indicate the completion of reaction and formation of product Al(acphNCAuCl)\(_3\) (5.4); IR \(\nu_{C≡N}\) at 2226 cm\(^{-1}\).
The NMR and IR data of isocyanide complexes prepared in this chapter and last chapter are listed in Table 5.1.

**Table 5.1** NMR data (CDCl₃) and ν_C≡N of IR for HacphNC and its complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>OH (enol, 1H, s)</th>
<th>CH (2H, d)</th>
<th>CH (2H, d)</th>
<th>CH₃ (6H, s)</th>
<th>ν_C≡N cm⁻¹</th>
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<tbody>
<tr>
<td>Zn(acphNC)₂ (4.20)</td>
<td>7.42</td>
<td>7.23</td>
<td>1.87</td>
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<td>2124</td>
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<tr>
<td>Al(acphNC)₃ (4.21)</td>
<td>7.41</td>
<td>7.25</td>
<td>1.87</td>
<td></td>
<td>2121</td>
</tr>
<tr>
<td>HacphNC (4.22)</td>
<td>16.71</td>
<td>7.42</td>
<td>7.23</td>
<td>1.88</td>
<td>2122</td>
</tr>
<tr>
<td>[(HacphNC)₄Cu]PF₆ (5.1) *</td>
<td>16.84</td>
<td>7.57</td>
<td>7.39</td>
<td>1.85</td>
<td>2262</td>
</tr>
<tr>
<td>[(HacphNC)₆Mn]I₃ (5.2) *</td>
<td>16.80</td>
<td>7.48</td>
<td>7.33</td>
<td>1.83</td>
<td>2262</td>
</tr>
<tr>
<td>HacphNCAuCl (5.3)</td>
<td>16.75</td>
<td>7.60</td>
<td>7.37</td>
<td>1.88</td>
<td>2223</td>
</tr>
<tr>
<td>Al(acphNCAuCl)₃ (5.4)</td>
<td>7.61</td>
<td>7.36</td>
<td>1.86</td>
<td></td>
<td>2226</td>
</tr>
</tbody>
</table>

* CD₃CN is the solvent.

**5.3 Conclusion**

Cu(I), Mn(I), and Au(I) C-bound complexes of the isocyanide-β-diketone ligand HacphNC were prepared in small scales. NMR and IR indicate the formation of the expected products. When HacphNC binds to metal ions, via its −N≡C group, its ν_C≡N stretching frequency increases from 2121 cm⁻¹ to more than 2200 cm⁻¹. Al(acphNC)₃ also reacted with Me₂SAuCl just like the free ligand. More work is expected to be done in this area when large supply of HacphNC is possible.

**5.4 Experimental**

**5.4.1 [Cu(CNphacH)₄]PF₆ (5.1)**

[Cu(CH₃CN)₄]PF₆ (1.8 mg, 0.005 mmol) and HacphNC (4.0 mg, 0.02 mmol) were dissolved in CD₃CN (1 mL) under Ar. The solution took on a brown color. It was then heated to 50 °C for one hour. The solution was checked by NMR and IR immediately. ¹H NMR (250 MHz, CD₃CN): 1.85, 6H, s; 7.39, 2H, d; 7.57, 2H, d; 16.84, 1H, s. IR: 2262 cm⁻¹. The IR pattern changed in the air after five minutes, probably indicating oxidation of the product.
5.4.2 [Mn(CNphacH)₆]I₃ (5.2)

MnI₂ (1 mg, 0.003 mmol) and HacphNC (4.5 mg, 0.022 mmol) were dissolved in CD₃CN (1mL) and heated at 40 °C for one hour. The solution was checked by NMR and IR immediately. ¹H NMR (250 MHz, CD₃CN): 1.83, 6H, s; 7.33, 2H, d; 7.48, 2H, d; 16.80, 1H, s. IR: 2262 cm⁻¹.

5.4.3 HacphNCAuCl (5.3)

Me₂SAuCl (5.9 mg, 0.02 mmol) and HacphNC (4.0 mg, 0.02 mmol) were dissolved in CDCl₃ (1.5 mL) and refluxed for 1.5 hours. The solution was checked by NMR and IR immediately. ¹H NMR (250 MHz, CDCl₃): 1.88, 6H, s; 7.37, 2H, d; 7.60, 2H, d; 16.75, 1H, s. IR: 2223 cm⁻¹.

5.4.4 Al(acphNCAuCl)₃ (5.4)

HacphNC (31.4 mg, 0.050 mmol) and Me₂SAuCl (44.1 mg, 0.150 mmol) were dissolved in 10 mL CH₂Cl₂ and refluxed under nitrogen for 2 hours. The solution was then evaporated to dryness to give yellow solid. ¹H NMR (250 MHz, CDCl₃): 1.86, s, 18H; 7.34, d, 6H; 7.60, d, 6H. IR: 2222 cm⁻¹.

5.5 References


5.2 Sacco, A. Recueil des Travaux Chimiques des Pays-Bas et de la Belgique 1956, 75 646.


Chapter 6

Conclusions and Prospects

This dissertation mainly focuses on synthesis and characterization of porous inorganic-organic materials based on multifunctional β-diketone ligands. As β-diketones usually act as hard chelating ligands, pyridine and isocyanide are chosen as the soft binding sites of multifunctional ligands. All the study in this dissertation is carried out based on these two linear multifunctional ligands pyacH and HaephNC.

The linear bifunctional ligand pyacH is a known ligand. The preparation of pyacH has been improved by increasing yield and purity, and shortening reaction time. The reaction appears to proceed via acylation of the pyridine ring, which is supported by the separation of an intermediate reaction. PyacH is not a stable compound, and it slowly decomposes in air. It should be kept under inert atmosphere at low temperature.

PyacH reacts with copper, zinc, iron and aluminum metal salts to generate the corresponding metal β-diketonate building blocks. For Zn$^{2+}$, both trans and cis isomers were characterized by single-crystal X-ray analysis. Trans-Zn(pyac)$_2$ forms a 2D square structure in the presence of water and methanol, which is different from Cu(pyac)$_2$. Al(pyac)$_3$ like Fe(pyac)$_3$, has a distorted trigonal structure, which shows the flexibility of the ligand.

The β-dialdehyde that is most closely related to pyacH is pyridylmalonaldehyde. When it reacts with Cu$^{2+}$, it doesn’t chelate to the metal like a β-diketone. Instead, it forms a polymetric structure by bridging Cu$^{2+}$ ion in an approximately linear fashion.

Solutions of the trigonal building block Fe(pyac)$_3$ can generate various crystal structures on reaction with AgNO$_3$ in CH$_3$CN. Different crystals can be generated in
different solvents. When concentration of AgNO₃ is low, 2D honeycomb structures (Fe:Ag 1:1) are generated. When the Fe(pyac)₃ is dissolved in 1,2-dichlorobenzene, bromobenzene, or toluene, a high concentration of AgNO₃ in the CH₃CN phase can result in a porous 1D ladder structure (Fe:Ag 2:3). Furthermore, solvent/guest molecules in the pores of the “Fe₂Ag₃” structures can be exchanged without disrupting the crystal structure. The solvent can be exchanged from bromobenzene to 1,2-dichlorobenzene, benzene, trichloroethylene and naphthalene. The exchange between bromobenzene and 1,2-dichlorobenzene has been studied on one crystal by single X-ray diffraction and GC-MS. Through the study of crystal structure, it is found that the frameworks are flexible according to the guest molecules through the edges and angles adjustment. Al(pyac)₃ can also generate 1D ladder porous material in acetonitrile and 1,2-dichlorobenzene solution, which has a similar framework and guest molecules that are similar to those of the iron compound. Also, a 3D interpenetrated spiral structure (Fe:Ag 1:1) was generated when benzene was used as the initial solvent for Fe(pyac)₃.

3-(4-isocyanophenyl)-2,4-pentanedione (HacphNC) was synthesized for the first time starting from 4-nitrobenzaldehyde. An improved synthesis was developed for a required intermediate, OHCphNHCHO. This was converted to 3-(4-formyaminophenyl)-2,4-pentanediene (HacphNHCHO) successfully by reaction with the biacetyl-trimethyl phosphite adduct. Due to the reactivity of β-diketone with phosphorus oxychloride, HacphNHCHO was first protected by coordination to Al³⁺, Zn²⁺ and Cu²⁺ metal ions. The metal complexes were then dehydrated by phosphorus oxychloride under the presence of diisopropylamine to generate M(acphNC)ₙ metal complexes. The Al and Zn complexes were acidified to free the target ligand HacphNC.
Cu(I), Mn(I), and Au(I) C-bound complexes of the isocyanide-β-diketone ligand HacphNC were prepared on a small scale. NMR and IR indicate the formation of the expected products. IR frequencies (νC≡N) increase to more than 2200 cm⁻¹ when isocyanides bind to metal ions. This free isocyanide group of Al(acphNC)₃ also react with Me₂SAuCl to give a mixed-metal complex, Al(acphNC-AuCl)₃.

More work is expected to be done in this area when a larger supply of HacphNC is available. The reaction of HacphNC with MnI₂, producing (HacphNC)₆Mn⁺ appears to be the most promising route to preparing 3D porous materials from this ligand.
Vita

Yixun Zhang was born on May 12th, 1976 in Rongan, Guangxi, China. He received his Bachelor of Science degree in chemistry and Bachelor of Engineering degree in computer science from University of Science and Technology of China in 1998. He received his Master of Engineering degree in materials science from University of Science and Technology of China in 2001. He is currently a candidate for the Doctor of Philosophy degree in the Department of Chemistry of Louisiana State University and Agricultural and Mechanical College with Dr. Andrew W. Maverick as his supervisor.