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THE SYNTHESIS OF NEW COORDINATION POLYMER USING CRYSTAL
ENGINEERING, SELF-ASSEMBLY, AND HYDROTHERMAL SYNTHESIS

by

Lei Fu, B.S.

THESIS

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by

Lei Fu

APPROVED BY

Jack Y. Lu, Ph.D , Chair

Yi Su, Ph.D, Committee Member

Rio Carlo Lirag, Ph.D, Committee Member

Jack Y. Lu, Ph.D, Committee Member

RECEIVED/APPROVED BY THE COLLEGE OF SCIENCE AND ENGINEERING:

Said Bettayeb, Ph.D. Associate Dean

Ju H. Kim, Ph.D. Dean

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ABSTRACT

THE SYNTHESIS OF NEW COORDINATION POLYMER USING CRYTAL
ENGINEERING, SELF-ASSEMBLY, AND HYDROTHERMAL SYNTHESIS

Lei Fu

University of Houston-Clear Lake, 2018

Thesis Supervisor: Jack Y. Lu, Ph.D.

The emphasis of this thesis is to design and synthesize innovative coordination polymers through crystal engineering, self-assembly, and hydrothermal synthesis. The thermal and magnetic properties of the coordination polymers are analyzed.

TABLE OF CONTENTS

List of Tables	vii
List of Figures	viii
CHAPTER I: INTRODUCTION.....	1
CHAPTER II: BACKGROUND	2
Structure.....	2
Cavities	7
Interpenetration	8
Crystal engineering	9
Self-assembly.....	10
Hydrothermal Synthesis.....	11
Thermal properties	12
Megnetic properties	14
CHAPTER III: EXPERIMENTAL.....	18
CHAPTER IV: RESULTS AND DISCUSSION	21
Reactions.....	22
Complex 1.....	39
Complex 2.....	45
FT-IR analysis.....	54
Elemental analysis	55
Thermal analysis	55
Magnetic analysis.....	56
CHAPTER V: CONCLUSION	64
REFERENCES	66
APPENDIX	69

LIST OF TABLES

Table 1. Crystal data for complex 1.....	40
Table 2. Bond length for complex 1	44
Table 3. Crystal data for complex 2.....	46
Table 4. Bond length for complex 2.	52
Table 5. Elemental Analyses for complex 2..	55
Table 6. Effective magneton numbers for iron group ions	61
Table 7. Crystal data for complex 1.....	72
Table 8. Bond length for complex 1	73
Table 9. Crystal data for complex 2.....	74
Table 10. Bond length for complex 2.	74
Table 11. Atomic coordinates for complex 2.....	75
Table 12. Bond lengths and angles for complex 2.....	76
Table 13. Anisotropic displacement parameters for complex 2..	78
Table 14. Hydrogen coordinates for complex 2.....	79
Table 15. Torsion angles for complex 2..	80

LIST OF FIGURES

Figure 1. Zero dimensional structure	3
Figure 2. Ligand of 1,3,5-triethylbenzene	3
Figure 3. One dimensional coordination polymer	4
Figure 4. Ligands for two dimensional coordination polymer	4
Figure 5. Two dimensional coordination polymer.....	4
Figure 6. Ligands for three dimensional coordination polymer	6
Figure 7. Three dimensional coordination polymer.....	7
Figure 8. Ligand of Hccdc	7
Figure 9. Coordination polymer cavities	8
Figure 10. Coordination polymer with interpenetration structure	9
Figure 11. Structure of $\text{Co}(\text{H}_2\text{O})_3(4,4\text{-bipy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	10
Figure 12. Structure of $\text{Co}(\text{DMSO})_2(4,4\text{-bipy})\text{Cl}_2$	10
Figure 13. TGA for $[\text{Fe}(\text{ox})(\text{bpy})]$	13
Figure 14. TGA for $[\text{FeCl}_2(\text{bpy})]$	14
Figure 15. Sample of complex 1	39
Figure 16. Unit cluster of complex 1	41
Figure 17. Coordination environment of complex 1.....	42
Figure 18. One dimensional structure of complex 1.....	42
Figure 19. Two dimensional structure of complex 1	43
Figure 20. Sample of complex 2	45
Figure 21. Coordination pattern for each atoms in complex 2	47
Figure 22. Complete coordination of Fe	48
Figure 23. Complete coordination of central oxide	49
Figure 24. One dimensional fragment of complex 2	50
Figure 25. Three dimensional packing arrangement of complex 2	51
Figure 26. Complete structure of three dimensional structure of complex 2.....	52
Figure 27. TGA for complex 2	54

Figure 27. IR for complex 2.....	54
Figure 28. TGA for complex 2	56
Figure 29. Temperature dependence of magnetic moment of complex 2.....	59
Figure30a. Temperature dependence of magnetic susceptibility and magnetic hardness of complex 2	59
Figure30b. χT as a function of temperature for complex 2	60
Figure 31. Temperature dependence of magnetic moment of complex 2.....	62

CHAPTER I: INTRODUCTION

The porous materials which consist of metal organic framework have been studied over decades. The design of coordination polymer is becoming the most challenging work. It is linking inorganic and organic chemistry. The coordination polymers can be used as molecular adsorbents, gas storage, drug-delivery agents, and sensors for the detection.¹ The various applications can lead to various materials and structures. The characteristic of the polymer depends on the variety of metal center and organic ligands. The chemical bond inside the coordination polymers are usually strong and more stable.³ The coordination polymer containing two-dimensional and three dimensional open-framework coordination polymers has drawn the most interest in the recent year.²⁻⁵ Since the structure and topology lead to the important properties of polymers, the design and construction of the new porous materials with specific network become an important and topical subject.²⁻⁵ There are many factors that determine the structures of the polymer, such as coordination environment of metal, types of ligands, and noncovalent interactions.²⁻⁵ The synthetic strategies include oxidation reaction, simultaneous substitution, conventional solution methods and unexpected reduction reaction.²⁻⁵ The hydrothermal synthesis is widely used in recently years.⁶⁻¹⁰ More and more coordination polymers were synthesized through hydrothermal thesis even these last two years.¹¹⁻¹⁵ The hydrothermal synthesis has been used in this thesis research. Following this thesis research, the crystal engineering, self-assembly and hydrothermal synthesis were used to design and synthesize the new coordination polymers. The successful synthesized polymer was analyzed including single crystal polymeric structural characterization, thermal stability, element consistence, and magnetic property measurements.

CHAPTER II: BACKGROUND

Structure

The structure of the inorganic crystal was first concerned by A.F. Wells. Wells has published a series of papers concerning the structure of the inorganic solids. Well has defined the crystal structure using the terms of their topology.¹⁷ Robson was the first person to use the term and expand Wells' work on the coordination polymer.¹⁷ The first generation of the coordination polymers was synthesized in 1990s.¹⁶ In mid 1990s, Dr. Zaworotko and his student Len Macgillivray studied the transition metal moieties serving as nodes then connected by organic ligands, which synthesized different structures of the coordination polymer.¹⁶ Zaworotko and his student successfully synthesized the coordination geometries of diamonded, ladder, octahedral, bilayer nets, and square grid. Then more and more coordination polymers were synthesized since 1990s.

The majority of coordination polymers usually concluded as four types of the structure. The four type of structures are zero, one, two and three dimensional structure. Zero dimensional structure is the basic structure of the coordination polymer. It is similar to the single building block of the polymer structure. The sample of this structure which is known in zeolites. The zero-dimension structure polymer can be constructed by sharing the edges of the molecular moieties and generating the one, two, three dimensional structures. The sample of one-dimensional structure can be shown in figure 1.¹⁷



Fig.1¹⁷ Zero-dimensional structure

One-dimensional structure can usually separate into three types. They are linear, zigzag line, and ladder shape polymers. Both zigzag line and ladder shape are one dimensional structure polymer. In 2004, Hiromi Ohi and his research group had successfully synthesized the one dimensional coordination polymer complexes ($[\text{Cu}^{\text{II}}(\text{L})\text{Cl}_2] \cdot \text{C}_2\text{H}_5\text{OH}$)_n, ($[\text{Co}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{CH}_2\text{Cl}_2$)_n, and ($[\text{Zn}^{\text{II}}_3(\text{L})_2\text{Cl}_6] \cdot 2\text{H}_2\text{O}$)_n with the structure zigzag line, linear chain, and ladder shape.¹⁸ The ligand L used in this research is 1,3,5-triethylbenzene. Which is shown in figure 2.

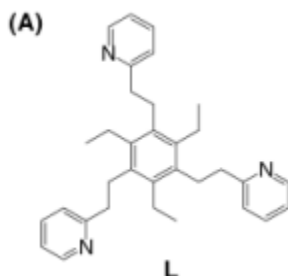


Fig.2¹⁸ Ligand of 1,3,5-triethylbenzene

The copper complex which contains the CuCl_2 and the ligand with ratio 1:1. The CuCl_2 is connected to two nitrogens of pyridine, thus constructing a zigzag chain structure polymer.¹⁸ When replacing the CuCl_2 with CoCl_2 , the ratio of metal and ligand changes to 3:2, and a linear polymer can be successfully synthesized. In the cobalt complex, the CoCl_2 is connected with all three nitrogen. The zinc complex uses ZnCl_2 as the metal center. All three nitrogens are connected with metal, thus synthesizing the ladder shape polymer. All three types of the polymer can be shown in figure 3.

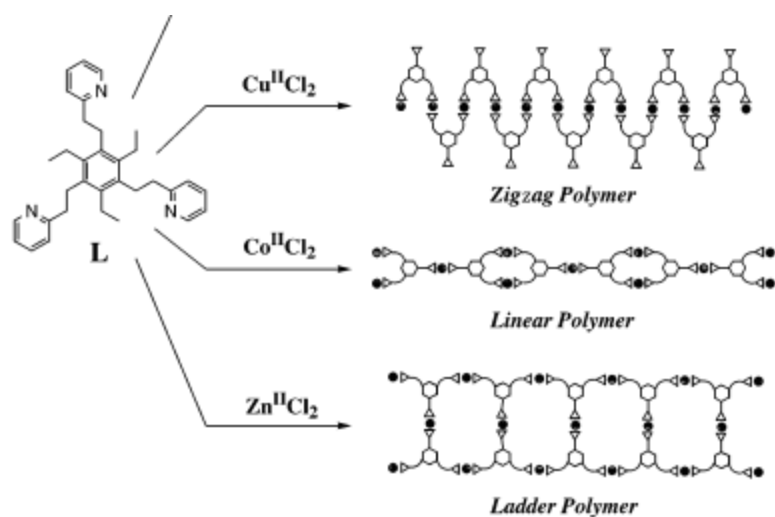


Fig 3¹⁸ One dimensional coordination polymer

A two-dimensional coordination polymer is usually constructed from a one-dimensional structure. A two-dimensional structure is similar to a sheet structure. The sample of two-dimensional coordination polymer can be copper(I) complexes which was synthesized by Hyun Jee Kim and his research group. The ligands used in this research are shown in figure 4.¹⁹

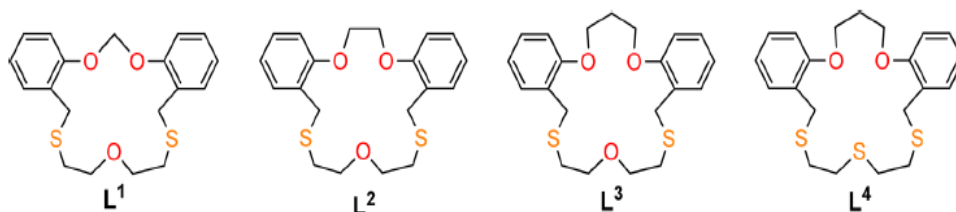


Fig 4¹⁹ Ligands for two-dimensional coordination polymer

The first polymer was synthesized through reaction O_3S_2 -macrocyclic **L¹** and CuI . The two dimensional coordination polymer $\{[(\text{Cu}_4\text{I}_4)(\text{L}^1)_2] \cdot \text{CH}_2\text{Cl}_2\}_n$ is synthesized. The layer structure was extended from Cu_4I_4 located in the center of four macrocycles.¹⁹ The second polymer was synthesized through reaction O_3S_2 -macrocycle **L²** and CuI . The one dimensional coordination polymer $\{[(\text{Cu}_4\text{I}_4)(\text{L}^2)_2] \cdot 0.8\text{CH}_2\text{Cl}_2 \cdot 0.2\text{CH}_3\text{CN}\}_n$ was synthesized. The Cu_4I_4 in this polymer which located at the node of the tubular channel.¹⁹

Third coordination polymer is the two dimensional polymer $[(\text{Cu}_2\text{I}_2)(\text{L}^3)_2]_n$. The Cu_2I_2 is connected with two sulfur tetrahedrally.¹⁹ The forth complex is also a two-dimensional structure. The formula of this complex is $[(\text{Cu}_2\text{I}_2)(\text{L}^4)_2]_n$. For the asymmetric structure in this polymer, the unit contain two L^4 ligand and one Cu_2I_2 . One of the sulfur atom remains unbonded, the other two sulfurs are connected with the ligand. Three of the coordination polymer are two dimensional structure, and one of the polymers is one dimensional structure. The structure of all four polymers in these research can be shown in figure 5.¹⁹

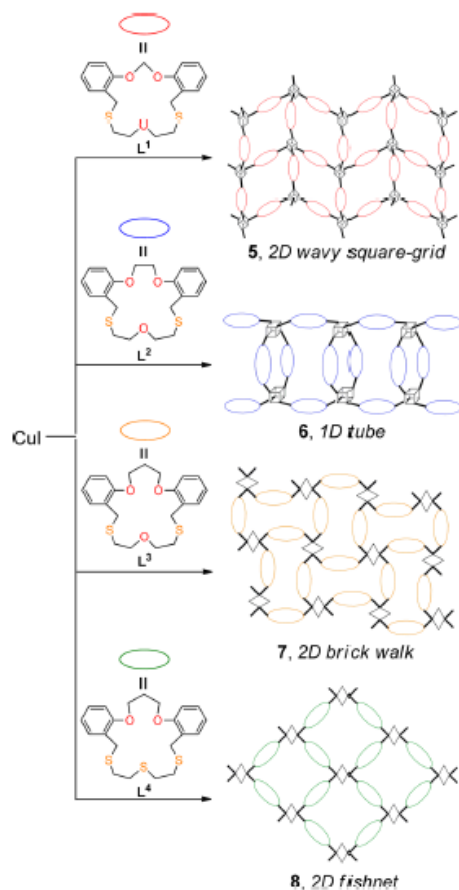


Fig.5¹⁹ Two-dimensional coordination polymer

When two-dimensional net structure is constructed together layer by layer, it becomes three-dimensional structure coordination polymer. The sample of a three-dimensional polymer can be $[K_3Co_2(L^{C4})_3(EtOH)_6]Cl$, which was synthesized by Yu-Juan Liu and her research group. The ligand involved in this research is 25,27-bis(hydroxycarbonylmethoxy)-26,28-dimethoxy-*tert*-butylcalix[4]arene (H_2L^{C4}).²⁰ The structure of the ligand can be shown in Fig.6.²⁰

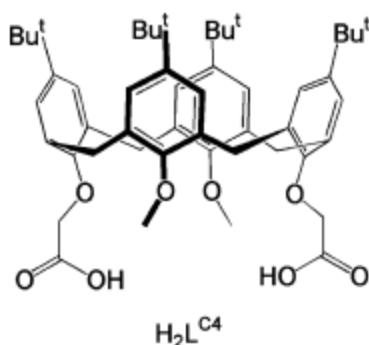


Fig.6²⁰ Ligands for three-dimensional coordination polymer

The three-dimensional polymer which was synthesized using H_2L^{C4} , K_2CO_3 and $CoCl_2 \cdot 6H_2O$. The three-dimensional structure contain three-connecting nodes and 4-fold helices which are interconnected of the same handedness. The Co^{2+} is three connection ions which are linked by $[K(L^{C4})]^-$ bridges. The Co^{2+} is six coordinate in the center of an octahedron connected by six oxygen atom. And the K^+ is connected to the oxygen atom of the hydroxycarbonylmethoxy groups. The completed three dimensional structure can be shown in figure 7.²⁰

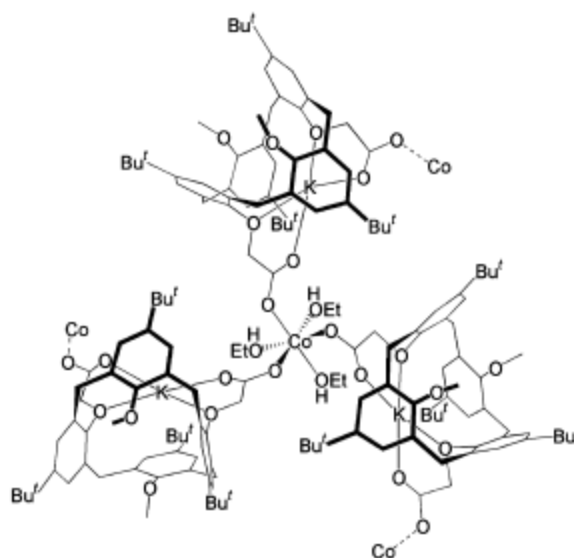


Fig.7²⁰ Three-dimensional coordination polymer

Cavities

One of the most important characteristic of coordination polymer is the large size of cavities. And the function of the polymer usually depends on which material is used to synthesize the polymer and the cavity of the polymer. The research on the cavities in porous materials is becoming more important. One of the research studies discusses the coordination polymer 1,1-dicarboxylate (ccdc). The polymer is synthesized through $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and Hccdc. The coordination form in one unit can be shown in figure 8.²¹



Fig.8²¹ Ligand of Hccdc

The crystal structure can be shown in figure 9.²¹

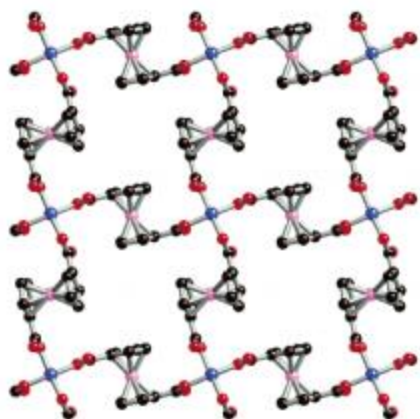


Fig.9²¹ Coordination polymer cavities

The ccdc connects with two Cu^{2+} centers give a two dimensional sheet structure polymer. The bond angle of ccdc and Cu^{2+} gives the polymer small square cavities.²¹ The cavities have $4 \times 4 \times 6 \text{ \AA}^3$ in the crystal.²¹ The cavities of these polymer can used to trap the methanol molecules, which is isolated from the outside.²¹ It is the sample of cavities affecting the structure and function of the polymer.

Interpenetration

When two independent structures interpenetrate together, it forms an interpenetration structure. The example of the interpenetration polymer was synthesized by Matthew A. Withersby and his research group. The three dimensional polymer $[\text{Cd}_2(4,4\text{-pytz})_3(\mu\text{-NO}_3)(\text{NO}_3)_3(\text{MeOH})]$ is an example of has interpenetration structure. The coordination polymer structure can be shown in figure 10.²²

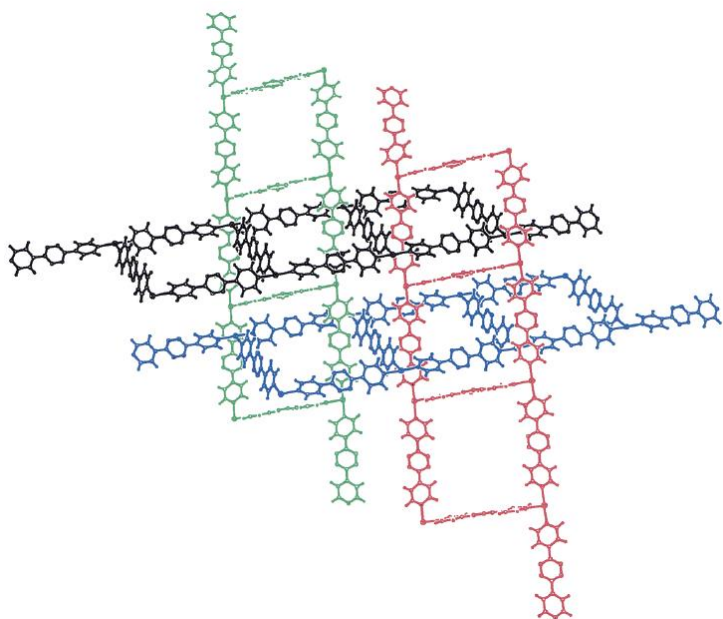


Fig.10²² Coordination polymer with interpenetration structure

In this polymer, the Cd center provides T-shaped connecting units. The units constructed ladder shape polymer. The independent ladder is interpenetrated perpendicularly by other two independent ladders. The ladder that was interpenetrated by each other extended and formed three dimensional coordination polymer which contains an interpenetration structure. This phenomenon would also affect the cavity network.

Crystal Engineering

Crystal engineering is the process of designing and performing the crystal structure synthesis. By selecting the metal and the ligand, the structure of the coordination polymer can be predicted before performing the actual synthetization process. Metal is a very important part in coordination polymer. The metal ion usually become the connection node in the polymer. Based on the oxidation state, the geometry of the connection can be determined. The ligand of the polymer usually becomes the framework of the polymer. One of the examples can be the one dimensional coordination

polymers $\text{Co}(\text{H}_2\text{O})_3(4,4\text{-bipy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (figure 11) and $\text{Co}(\text{DMSO})_2(4,4\text{-bipy})\text{Cl}_2$ (figure 12).²³

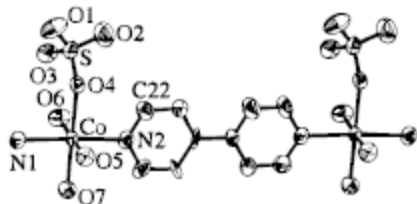


Fig.11²³ $\text{Co}(\text{H}_2\text{O})_3(4,4\text{-bipy})\text{SO}_4 \cdot 2\text{H}_2\text{O}$

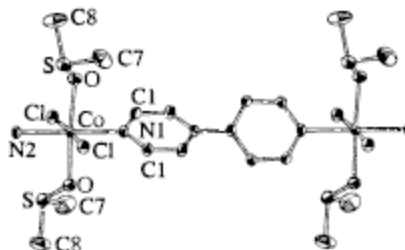


Fig.12²³ $\text{Co}(\text{DMSO})_2(4,4\text{-bipy})\text{Cl}_2$

It is easy to distinguish that Co usually constructs the octahedral structure. In both polymers, the ligand 4,4-bipy is connected to the Co center. The connection with Co center is an octahedral structure. The ligand is the base line of the framework in the structure. The N atom connect to the Co ion and extend to the whole structure becoming the one-dimensional polymer.

By selecting metal center and organic ligand, the structure of the new coordination polymer can be preselected. It is very important to consider both metal and ligand geometry before synthesizing new coordination polymer. Through crystal engineering, there were many different coordination polymers that were synthesized during these years.

Self-assembly

In coordination chemistry, self-assembly is different from other synthesis techniques. For example, organic synthesis usually involved multiple steps in the synthesize process. But in the coordination chemistry, all the starting material will be placed in one reaction vessel. With a thermodynamic drive, the polymers will assemble by themselves. The self-assembly process is only a one step reaction. The thermodynamic

drive makes the coordination polymer more thermodynamically stable. The polymers are more stable at room temperature. With higher thermodynamically drive, some polymers can be more stable at higher temperatures. Base on its simple process, self-assembly has become the most popular technique in coordination chemistry.¹⁷

Hydrothermal Synthesis

In 1862, St. Claire Deville had claimed to make a name zeolite in the laboratory.²⁴ Later in 1940s, Richard Barrer started his research and successfully reached mineral phases through hydrothermal technique. The strong salts solution was placed with high temperature (170-270°C).²⁴ In 1948, Barrer synthesized the first zeolite unknown as a natural mineral.²⁴ In the current coordination chemistry, the hydrothermal synthesis usually base on the Teflon container with water or other organic solvent. Akporiaye and co-workers were the first to report the use of Teflon containers relate to hydrothermal synthesis of zeolite.²⁴ In this research, Akporiaye had used a 10 × 10 chamber and varied cation systems at 100°C.²⁴ The hydrothermal synthesis in modern coordination chemistry is the Teflon container placed in a metal bomb. The bomb was then sealed and put into oven at certain temperatures for more than three days. During the time when the metal bomb in the oven, the pressure inside the Teflon container is increasing. The properties of the solvent inside the bomb such as viscosity, and density, become different. The properties of the starting material also changed, such as the metal ion, which might reduce from higher oxidation state to lower oxidation state. The sealed system with high temperature and pressure will trigger the reaction which will not happen in the room temperature. It allows the coordination polymer to grow by itself inside the bomb. Based on these characteristics of the Teflon bomb used in hydrothermal synthesis, more and more different structure of the coordination polymers were synthesized.

Thermal Properties

The coordination polymers are widely used in different area. Some of the coordination polymers require high temperature resistance. In order to test the thermal properties, the instrument Diamond thermogravimetric/ differential thermal analyzer (DT/TGA), is used. The DT/TGA instrument contains three components, the furnace part, scale part and computer part. The furnace part allows the TGA instrument to heat the sample to a certain temperature. At the same time, the furnace is used to provide the noble gas to prevent the sample from reacting with air and forming impurities. Second part is the scale part, with a balance inside the scale part. It provides two balance beams which extend into the furnace. The balance is used to monitor the weight changes during the temperate changes. One of the balance beam is used to place the sample. Another beam is used to place the empty sample containers. By comparing the differences of two balance beams, the changes of the sample weight can be determined. Last part is the computer part, the computer is connected to the deflection sensor. The software installed in the computer is used to control and receive the data from the DT/TGA instrument. By using this work station, the testing result can be obtained.²⁵ The example of using DT/TGA instrument can be [Fe(ox)(bpy)] which was synthesized by Jack Y. Lu.²⁶ This polymer is synthesized using hydrothermal technique. The starting materials were placed in the Teflon bomb. Under the high temperature condition, the polymer grows inside the bomb. The typical TGA graph for this polymer is shown in figure 13.²⁶

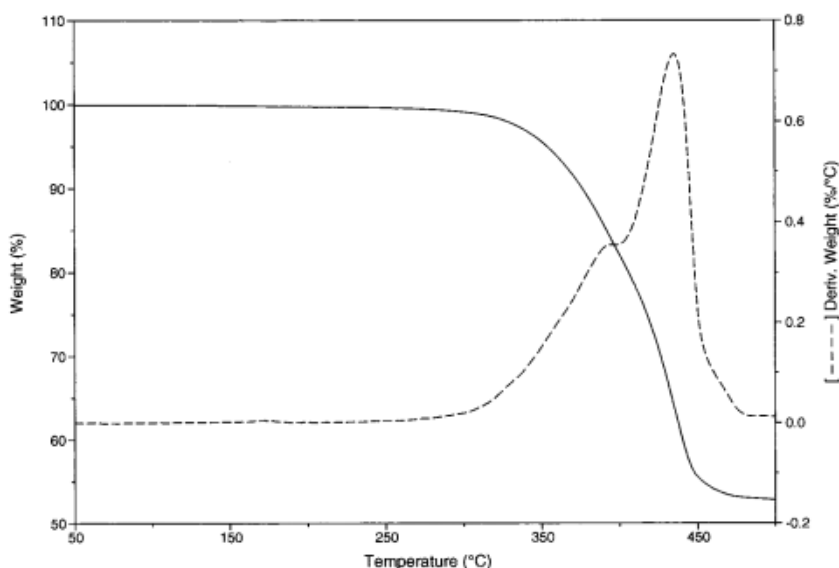


Fig.13²⁶ TGA for $[Fe(ox)(bpy)]$

In figure 13, it is the polymer analyzed using TGA instrument. It contains the temperature range from 50 to 500°C. In this graph, the solid line indicate that there is a large weight loss from 350 to 450°C. Figure 13 shows this polymer loss about 45% of its weight, which means this polymer is thermal stable until 350°C.²⁶ The dashed line is the negative of the first derivative. This polymer undergo one step decomposition process.

Coordination polymers might have more than one step decomposition process. In this case, another type of TGA graph is shown in figure 14.²⁷

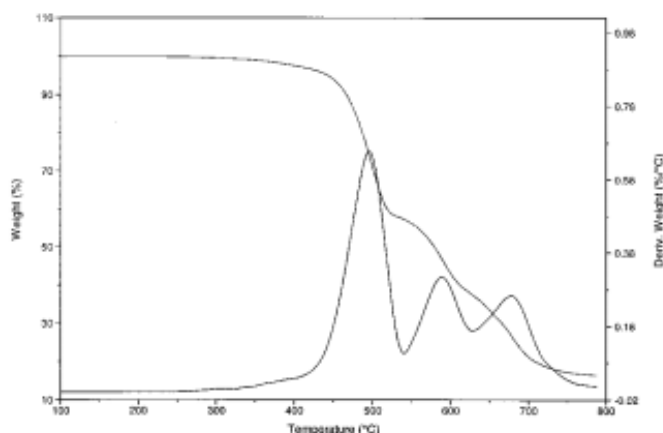


Fig.14²⁷ TGA for [FeCl₂(bpy)]

Figure 14 is the TGA graph for the coordination polymer [FeCl₂(bpy)]. Three weight loss curves can be seen in this figure.²⁷ The first derivative line has three peaks which indicate the three-step weight loss process. The reason of obtaining three step weight loss is because the functional group decomposes in different temperature. By calculating the percentage of weight loss, it can be known which functional group decomposed first and which functional group is second. For example, CuSO₄·5H₂O has molecular weight 250 g/mol. If the decomposition graph gives 36% weight loss, indicates the 5H₂O loss from the molecule. The peak of the first derivative is related to the functional group which the polymer obtains.

Magnetic Properties

The magnetic moment of each sample was measured at temperatures from 2 K to 375 K and under external magnetic fields from 0 to 7 T by a Quantum Design Magnetic Properties Measurement System (MPMS).

The MPMS is an automated system that contains a temperature control system, a sample transport system, a Superconducting Quantum Interference Device (SQUID)

amplifier system and a measurement device which consists of several superconducting components:

- a superconducting magnet to generate strong magnetic fields with maximum 7 T

- a superconducting detection coil which couples inductively

- a SQUID connected to the detection coil

- a superconducting magnetic shield surrounding the SQUID

A sample is moved through a second-derivative gradiometer. A magnetic moment is induced in the sample by the external field H created by the superconducting magnet. As the sample is moved through the coiled wire, the magnetic flux Φ through the coils due to the sample's magnetic moment changes. An electric field E and a current in the coils are created in accordance with Faraday's Law of Induction

$$\oint \vec{E} \cdot d\vec{s} = -\frac{d\Phi}{dt}$$

Where $d\vec{s}$ is an infinitesimal displacement along the boundaries of the line integral and dt is the infinitesimal time. The induced current is inductively coupled to the SQUID detector, which acts as an exceptionally sensitive current to voltage converter due to a quantum tunneling effect. The voltage is proportional to the magnetic moment of the sample, and this value is processed and recorded by a computer.

The sample is mounted in a sample holder that is attached to the end of a tough sample rod. The sample rod enters the sample space through a special type of double seal (called a lip seal) designed to allow the rod to be actuated by a drive mechanism located outside of the chamber. The component containing the lip seals is damped onto the top of the airlock with standard O-ring seals, forming the top of the sample space.

The top of the sample transport rod is attached to a stepper-motor-controlled platform which is used to drive the sample through the detection coil in a series of

discrete steps. It is possible to use discrete steps because the detection coil, SQUID input coil, and connecting wires form a complete superconducting loop. A change in the sample's position causes a change in the flux within the detection coil, thereby changing the current in the superconducting circuit. Since the loop is entirely superconducting, the current does not decay as it would in a normal conductor. During the measurement the sample is stopped at a number of positions over the specified scan length, and at each stop, several readings of the SQUID voltage are collected and averaged. The complete scans can be repeated a number of times and the signals are averaged to improve the signal-to-noise ratio.

The currents induced in the detection coil are ideally those associated with the movement of a point-source magnetic dipole through a second-order gradiometer detection coil. To get the samples being uniformly magnetized, it requires that the sample is much smaller than the detection coil. In addition to this, the shape of a sample can also require special consideration. If a sample is very long, extending well beyond the coil during a scan, its motion in the gradiometer will not be observable, since there would be no net change of the flux in the detection coil. This is the reason that a long uniform tube can be used as a sample holder since the detection coil will get little net change of flux from the contribution of the holder. In contrast to this, when the sample is short, the current in the detection coil changes with sample position. This is because different amounts of flux exist in each loop of the detection coil. So, it is important to realize that there is a limit on the length of a sample for which accurate measurements can be made.

Our samples were carefully placed into gel caps. The gel cap was then tightly attached in the straw that connected to the sample rod. The rod was then lowered into the bore of the SQUID magnetometer. The sample was cooled to 2 K without any external magnetic field, i.e. zero-field-cooled (ZFC). At 2 K, the magnetic fields of 10 Oe and

1000 Oe were applied, respectively. Magnetic moments were measured from 2 K to 350 K, and then from 350 K to 2 K (FC). M-H loops were also measured at certain fixed temperatures between -7 T and 7 T.

CHAPTER III

EXPERIMENTAL

General Techniques

In the coordination polymer synthesis, three techniques were used during these years, crystal engineering, self-assembly, and hydrothermal synthesis. Since the metal and the organic ligand determine the structure of the final product, choosing a metal is the first step of crystal engineering. The metal used in coordination polymer are usually first and second row of transition metals. The transition metal can have different oxidation states which is very important for structure design. In order to synthesize the polymer with coordination structure, the structure of the organic ligand also need to be considered. Some of the coordination polymer consists of single metal and single ligand, and some of the coordination polymer have multiple metal and multiple ligands. The weight of the starting material is decided according to the ratio of metal to ligand. Since the reaction is performed in Teflon bomb, the bomb has limited volume, the weight of each starting materials usually not over 0.24g. According to the molecular weight, the amount of the starting material generally selected is 0.001 moles. Base on the ratio and the limitation, the moles of the material can change to 0.0005 moles or 0.0015 moles. In coordination polymer synthesis, water and polar organic solvent generally are selected as solvents. Since the volume of Teflon bomb is very small, the volume of solvent is about 6 milliliters. All the materials were placed in the Teflon bomb, then the bomb was sealed and placed in the oven. By using oven, the bomb can be heated at constant temperature for certain length of time. The time spent in the reaction is generally more than three days. With the specific temperature and time, the reaction proceeded. The length of time and the temperature differences also determined the results of the reaction. After the

reaction time, the bomb was cooled to room temperature naturally. The products were washed by water and acetone. The products were placed under a microscope after dried in the air. Viewed under the microscope, crystals had formed or not can be determined.

Starting Materials

The starting materials used in this thesis research were purchased from Sigma Aldrich. The purity of the chemicals was highest purity. The di-water was used as solvent and to wash the products.

Equipment

When the crystals were found under the microscope, they need to be picked up without any impurities attached together. The pure crystals then were sent to the x-ray crystallographer. A 1K CCD area detector equipped in the x-ray diffractometer. The data collection completed on a Siemens SMART platform diffractometer.

After the crystal structures were solved and refined well, the coordination polymers were sent to Galbraith laboratories for the elemental analysis. The content of the metal, carbon, hydrogen, and nitrogen were analyzed. The percentage of each element will be reported.

The polymer then was sent to University of Houston to test thermal properties. The equipment used for TGA analysis is DT/TGA 6300. The temperature range was set from 0 to 600°C. And the temperature increasing rate was set at 10°C per minute. The gas flow used was nitrogen gas.

The polymers were then analyzed with IR spectrometer. The IR instrument used is frontier FT-IR spectrometer which was provided by the PerkinElmer Company.

The magnetic moment of each sample was measured under temperatures ranging from 2 K to 375 K and under external magnetic fields ranging from 0 to 7 T by a Quantum Design MPMS (Magnetic Properties Measurement System) SQUID (Superconducting Quantum Interference Device) magnetometer.

CHAPTER IV

RESULTS AND DISCUSSION

During this thesis research, 235 reactions were performed. Most of the reactions were repeated with different conditions. For instance, after selecting the metal and ligand, the reactions were performed with changing temperatures, mole ratio, lengths of time, and solvent. A table which listed all the reactions is included in this chapter. In these 235 reactions, most of the reactions failed to produce crystals. Some of the reactions form the crystals, but the crystals were either bad quality to analyze or identified as normal crystals instead of coordination polymers. Some of the crystals were reported by other research groups. Only two crystals were found in this thesis research. These two crystals have the same chemical formula but different structure. The chemical formula of the new coordination polymer is $\text{Fe}_3(\text{BNA})_6\text{O}$. This new coordination polymer then was then analyzed IR, DT/TGA, magnetic properties, and elemental analysis. All the results are shown in this chapter.

Reactions

trail	CoCl ₂ .6 H ₂ O (g)	BPY (g)	Trimesic acid (g)	Mole ratio	water volume (ml)	total reaction time	temperature set	crystal or not
1	0.12984	0.15618	0.21014	1:1:1	6	49 H	100	No
2	0.06492	0.07809	0.21014	1:1:2	6	49 H	100	orange crystal, very less
3	0.04328	0.05206	0.21014	1:1:3	6	49 H	100	small linear orange-red crystal
4	0.06492	0.15618	0.10507	1:2:1	6	49 H	100	a lot of orange-red crystal, linear
5	0.06492	0.15618	0.21014	1:2:2	6	49 H	100	a lot of linear orange-red crystals
6	0.04328	0.10412	0.21014	1:2:3	6	49 H	100	orange-red crystals, a lot, linear
7	0.04328	0.15618	0.07004 6667	1:3:1	6	49 H	100	orange red crystal, a lot, linear
8	0.06492	0.23427	0.21014	1:3:2	6	49 H	100	orange red crystal, a lot, linear
9	0.04328	0.15618	0.21014	1:3:3	6	49 H	100	orange red crystal, a lot, linear
10	0.12984	0.07809	0.10507	2:1:1	6	49 H	100	no
11	0.12984	0.07809	0.21014	2:1:2	6	49 H	100	no
12	0.08656	0.05206	0.21014	2:1:3	6	49 H	100	no
13	0.12984	0.15618	0.10507	2:2:1	6	72 H	100	no
14	0.12984	0.15618	0.21014	2:2:2	6	72 H	100	no
15	0.08656	0.10412	0.21014	2:2:3	6	72 H	100	no

16	0.12984	0.23427	0.10507	2:3:1	6	72 H	100	orange-red crystal, linear
17	0.12984	0.23427	0.21014	2:3:2	6	72 H	100	orange-red crystal, linear
18	0.08656	0.15618	0.21014	2:3:3	6	72 H	100	orange-red crystal, linear
19	0.19476	0.07809	0.10507	3:1:1	6	72 H	100	no
20	0.19476	0.07809	0.21014	3:1:2	6	72 H	100	no
21	0.12984	0.05206	0.21014	3:1:3	6	72 H	100	no
22	0.19476	0.15618	0.10507	3:2:1	6	72 H	100	no
23	0.19476	0.15618	0.21014	3:2:2	6	72 H	100	no
24	0.12984	0.10412	0.21014	3:2:3	6	72 H	100	no
25	0.06492	0.15618	0.10507	1:2:1	6	49 H	120	orange-red crystal, linear
26	0.06492	0.15618	0.21014	1:2:2	6	49 H	120	orange-red crystal, linear
27	0.06492	0.15618	0.10507	1:2:1	6	49 H	140	orange-red crystal, linear
28	0.06492	0.15618	0.21014	1:2:2	6	49 H	140	orange-red crystal, linear
29	0.06492	0.15618	0.10507	1:2:1	6	49 H	160	no
30	0.06492	0.15618	0.21014	1:2:2	6	49 H	160	no
31	0.06492	0.15618	0.10507	1:2:1	6	49 H	180	no
32	0.06492	0.15618	0.21014	1:2:2	6	49 H	180	no

trail	CuCl2	BPY	Trimesic acid	Mole ratio	water volume (ml)	total reaction time	temperature set	crystal or not
33	0.06722	0.15618	0.10507	1:2:1	6	49 H	180	no
34	0.06722	0.15618	0.21014	1:2:2	6	49 H	180	no
35	0.06722	0.15618	0.10507	1:2:1	6	49 H	160	no
36	0.06722	0.15618	0.21014	1:2:2	6	49 H	160	no
37	0.06722	0.15618	0.10507	1:2:1	6	49 H	140	no
38	0.06722	0.15618	0.21014	1:2:2	6	49 H	140	no
39	0.06722	0.15618	0.10507	1:2:1	6	49 H	120	no
40	0.06722	0.15618	0.21014	1:2:2	6	49 H	120	no
41	0.06722	0.15618	0.10507	1:2:1	6	49 H	100	no
42	0.06722	0.15618	0.21014	1:2:2	6	49 H	100	no
43	0.06722	0.15618	0.10507	1:2:1	6	96 H	180	no
44	0.06722	0.15618	0.21014	1:2:2	6	96 H	180	no
45	0.06722	0.15618	0.10507	1:2:1	6	96 H	160	no
46	0.06722	0.15618	0.21014	1:2:2	6	96 H	160	no
47	0.06722	0.15618	0.10507	1:2:1	6	96 H	140	no
48	0.06722	0.15618	0.21014	1:2:2	6	96 H	140	no
49	0.06722	0.15618	0.10507	1:2:1	6	96 H	120	no
50	0.06722	0.15618	0.21014	1:2:2	6	96 H	120	no
51	0.06722	0.15618	0.10507	1:2:1	6	96 H	100	no
52	0.06722	0.15618	0.21014	1:2:2	6	96 H	100	no

trail	CoCl ₂ .6 H ₂ O	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
53	0.06492	0.15618	0.10507	1:2:1	6	49 H	120	no
54	0.06492	0.15618	0.21014	1:2:2	6	49 H	120	no
55	0.06492	0.15618	0.10507	1:2:1	6	49 H	140	no
56	0.06492	0.15618	0.21014	1:2:2	6	49 H	140	no
57	0.06492	0.15618	0.10507	1:2:1	6	49 H	160	no
58	0.06492	0.15618	0.21014	1:2:2	6	49 H	160	no
59	0.06492	0.15618	0.10507	1:2:1	6	96 H	120	no
60	0.06492	0.15618	0.21014	1:2:2	6	96 H	120	no
61	0.06492	0.15618	0.10507	1:2:1	6	96 H	140	no
62	0.06492	0.15618	0.21014	1:2:2	6	96 H	140	no
63	0.06492	0.15618	0.10507	1:2:1	6	96 H	160	no
64	0.06492	0.15618	0.21014	1:2:2	6	96 H	160	no
trail	CoCl ₂ .6 H ₂ O (g)	BPY	Trimesic acid	Mole ratio	Methanol volume (ml)	total reaction time	temperature set	crystal or not
65	0.06492	0.15618	0.10507	1:2:1	6	49 H	120	no
66	0.06492	0.15618	0.21014	1:2:2	6	49 H	120	no
67	0.06492	0.15618	0.10507	1:2:1	6	49 H	140	no
68	0.06492	0.15618	0.21014	1:2:2	6	49 H	140	no
69	0.06492	0.15618	0.10507	1:2:1	6	49 H	160	no
70	0.06492	0.15618	0.21014	1:2:2	6	49 H	160	no

71	0.06492	0.15618	0.10507	1:2:1	6	96 H	120	no
72	0.06492	0.15618	0.21014	1:2:2	6	96 H	120	no
73	0.06492	0.15618	0.10507	1:2:1	6	96 H	140	no
74	0.06492	0.15618	0.21014	1:2:2	6	96 H	140	no
75	0.06492	0.15618	0.10507	1:2:1	6	96 H	160	no
76	0.06492	0.15618	0.21014	1:2:2	6	96 H	160	no
trail	CuCl2	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
77	0.06722	0.15618	0.10507	1:2:1	6	49 H	140	no
78	0.06722	0.15618	0.21014	1:2:2	6	49 H	140	no
79	0.06722	0.15618	0.10507	1:2:1	6	49 H	120	no
80	0.06722	0.15618	0.21014	1:2:2	6	49 H	120	no
81	0.06722	0.15618	0.10507	1:2:1	6	49 H	100	no
82	0.06722	0.15618	0.21014	1:2:2	6	49 H	100	no
83	0.06722	0.15618	0.10507	1:2:1	6	96 H	140	no
84	0.06722	0.15618	0.21014	1:2:2	6	96 H	140	no
85	0.06722	0.15618	0.10507	1:2:1	6	96 H	120	no
86	0.06722	0.15618	0.21014	1:2:2	6	96 H	120	no
87	0.06722	0.15618	0.10507	1:2:1	6	96 H	100	no
88	0.06722	0.15618	0.21014	1:2:2	6	96 H	100	no

trail	CuCl ₂	BPY	Trimesic acid	Mole ratio	Methanol volume (ml)	total reaction time	temperature set	crystal or not
89	0.06722	0.15618	0.10507	1:2:1	6	49 H	140	no
90	0.06722	0.15618	0.21014	1:2:2	6	49 H	140	no
91	0.06722	0.15618	0.10507	1:2:1	6	49 H	120	no
92	0.06722	0.15618	0.21014	1:2:2	6	49 H	120	no
93	0.06722	0.15618	0.10507	1:2:1	6	49 H	100	no
94	0.06722	0.15618	0.21014	1:2:2	6	49 H	100	no
95	0.06722	0.15618	0.10507	1:2:1	6	96 H	140	no
96	0.06722	0.15618	0.21014	1:2:2	6	96 H	140	no
97	0.06722	0.15618	0.10507	1:2:1	6	96 H	120	no
98	0.06722	0.15618	0.21014	1:2:2	6	96 H	120	no
99	0.06722	0.15618	0.10507	1:2:1	6	96 H	100	no
100	0.06722	0.15618	0.21014	1:2:2	6	96 H	100	no
trail	ZnCl ₂	BPY	Trimesic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
101	0.06815	0.15618	0.10507	1:2:1	6	49 H	120	no
102	0.06815	0.15618	0.21014	1:2:2	6	49 H	120	no
103	0.06815	0.15618	0.10507	1:2:1	6	49 H	140	no
104	0.06815	0.15618	0.21014	1:2:2	6	49 H	140	no
105	0.06815	0.15618	0.10507	1:2:1	6	49 H	160	no
106	0.06815	0.15618	0.21014	1:2:2	6	49 H	160	no

107	0.06815	0.15618	0.10507	1:2:1	6	96 H	120	no
108	0.06815	0.15618	0.21014	1:2:2	6	96 H	120	no
109	0.06815	0.15618	0.10507	1:2:1	6	96 H	140	no
110	0.06815	0.15618	0.21014	1:2:2	6	96 H	140	no
111	0.06815	0.15618	0.10507	1:2:1	6	96 H	160	no
112	0.06815	0.15618	0.21014	1:2:2	6	96 H	160	no
trail	ZnCl ₂	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
113	0.06815	0.15618	0.10507	1:2:1	6	49 H	120	no
114	0.06815	0.15618	0.21014	1:2:2	6	49 H	120	no
115	0.06815	0.15618	0.10507	1:2:1	6	49 H	140	no
116	0.06815	0.15618	0.21014	1:2:2	6	49 H	140	no
117	0.06815	0.15618	0.10507	1:2:1	6	49 H	160	no
118	0.06815	0.15618	0.21014	1:2:2	6	49 H	160	no
119	0.06815	0.15618	0.10507	1:2:1	6	96 H	120	no
120	0.06815	0.15618	0.21014	1:2:2	6	96 H	120	no
121	0.06815	0.15618	0.10507	1:2:1	6	96 H	140	no
122	0.06815	0.15618	0.21014	1:2:2	6	96 H	140	no
123	0.06815	0.15618	0.10507	1:2:1	6	96 H	160	no
124	0.06815	0.15618	0.21014	1:2:2	6	96 H	160	no

trail	ZnCl ₂	BPY	Trimesic acid	Mole ratio	Methanol volume (ml)	total reaction time	temperature set	crystal or not
125	0.06815	0.15618	0.10507	1:2:1	6	49 H	120	no
126	0.06815	0.15618	0.21014	1:2:2	6	49 H	120	no
127	0.06815	0.15618	0.10507	1:2:1	6	49 H	140	no
128	0.06815	0.15618	0.21014	1:2:2	6	49 H	140	no
129	0.06815	0.15618	0.10507	1:2:1	6	49 H	160	no
130	0.06815	0.15618	0.21014	1:2:2	6	49 H	160	no
trail	FeCl ₂ ·4 H ₂ O	BPY	BNA	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
131	0.0494	0.0781	0.202	1:1:2	6	49 H	120	no
132	0.1988	0.3124	0.202	1:2:1	6	49 H	120	no
133	0.0494	0.0781	0.101	1:2:2	6	49 H	120	no
134	0.1988	0.1562	0.202	1:1:1	6	49 H	120	no
135	0.0494	0.0781	0.202	1:1:2	6	72 H	120	no
136	0.1988	0.3124	0.202	1:2:1	6	72 H	120	no
137	0.0494	0.0781	0.101	1:2:2	6	72 H	120	no
138	0.1988	0.1562	0.202	1:1:1	6	72 H	120	no
139	0.0494	0.0781	0.202	1:1:2	6	96 H	120	no
140	0.1988	0.3124	0.202	1:2:1	6	96 H	120	no
141	0.0494	0.0781	0.101	1:2:2	6	96 H	120	no
142	0.1988	0.1562	0.202	1:1:1	6	96 H	120	no

143	0.0494	0.0781	0.202	1:1:2	6	49 H	140	small black crystals, a lot
144	0.1988	0.3124	0.202	1:2:1	6	49 H	140	no
145	0.0494	0.0781	0.101	1:2:2	6	49 H	140	no
146	0.1988	0.1562	0.202	1:1:1	6	49 H	140	small black crystals, a lot
147	0.0494	0.0781	0.202	1:1:2	6	72 H	140	small black crystals, a lot
148	0.1988	0.3124	0.202	1:2:1	6	72 H	140	no
149	0.0494	0.0781	0.101	1:2:2	6	72 H	140	no
150	0.1988	0.1562	0.202	1:1:1	6	72 H	140	small black crystals, a lot
151	0.0494	0.0781	0.202	1:1:2	6	96 H	140	small black crystals, a lot
152	0.1988	0.3124	0.202	1:2:1	6	96 H	140	no
153	0.0494	0.0781	0.101	1:2:2	6	96 H	140	no
154	0.1988	0.1562	0.202	1:1:1	6	96 H	140	small black crystals, a lot
155	0.0494	0.0781	0.202	1:1:2	6	49 H	160	small black crystals, less
156	0.1988	0.3124	0.202	1:2:1	6	49 H	160	no
157	0.0494	0.0781	0.101	1:2:2	6	49 H	160	no

158	0.1988	0.1562	0.202	1:1:1	6	49 H	160	small black crystals, less
159	0.0494	0.0781	0.202	1:1:2	6	72 H	160	small black crystals, less
160	0.1988	0.3124	0.202	1:2:1	6	72 H	160	no
161	0.0494	0.0781	0.101	1:2:2	6	72 H	160	no
162	0.1988	0.1562	0.202	1:1:1	6	72 H	160	small black crystals, less
163	0.0494	0.0781	0.202	1:1:2	6	96 H	160	small black crystals, less
164	0.1988	0.3124	0.202	1:2:1	6	96 H	160	no
165	0.0494	0.0781	0.101	1:2:2	6	96 H	160	no
166	0.1988	0.1562	0.202	1:1:1	6	96 H	160	small black crystals, less
165	0.0494	0.0781	0.202	1:1:2	6	168 H	140	small black crystals, a lot
166	0.1988	0.3124	0.202	1:2:1	6	168 H	140	no
167	0.0494	0.0781	0.101	1:2:2	6	168 H	140	no
168	0.1988	0.1562	0.202	1:1:1	6	168 H	140	large black crystals, a lot
trail	FeCl ₂ ·4 H ₂ O	BPY	BNA	Mole ratio	acetone volume (ml)	total reaction time	temperature set	crystal or not
169	0.0494	0.0781	0.202	1:1:2	6	72 H	140	no

170	0.1988	0.3124	0.202	1:2:1	6	72 H	140	no
171	0.0494	0.0781	0.101	1:2:2	6	72 H	140	no
172	0.1988	0.1562	0.202	1:1:1	6	72 H	140	no
173	0.0494	0.0781	0.202	1:1:2	6	96 H	140	no
174	0.1988	0.3124	0.202	1:2:1	6	96 H	140	no
175	0.0494	0.0781	0.101	1:2:2	6	96 H	140	no
176	0.1988	0.1562	0.202	1:1:1	6	96 H	140	no
trail	FeCl ₂ ·4 H ₂ O	BPY	BNA	Mole ratio	Methanol volume (ml)	total reaction time	temperature set	crystal or not
177	0.0494	0.0781	0.202	1:1:2	6	72 H	140	no
178	0.1988	0.3124	0.202	1:2:1	6	72 H	140	no
179	0.0494	0.0781	0.101	1:2:2	6	72 H	140	no
180	0.1988	0.1562	0.202	1:1:1	6	72 H	140	no
181	0.0494	0.0781	0.202	1:1:2	6	96 H	140	no
182	0.1988	0.3124	0.202	1:2:1	6	96 H	140	no
183	0.0494	0.0781	0.101	1:2:2	6	96 H	140	no
184	0.1988	0.1562	0.202	1:1:1	6	96 H	140	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Trimesic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
185	0.0494	0.078	0.105	1:2:2	6	72 H	120	no
186	0.0494	0.078	0.105	1:2:2	6	72 H	140	no

187	0.0494	0.078	0.105	1:2:2	6	96 H	120	no
188	0.0494	0.078	0.105	1:2:2	6	96 H	140	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
189	0.0494	0.078	0.105	1:2:2	6	72 H	120	no
190	0.0494	0.078	0.105	1:2:2	6	72 H	140	no
191	0.0494	0.078	0.105	1:2:2	6	96 H	120	no
192	0.0494	0.078	0.105	1:2:2	6	96 H	140	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Pyromellitic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
193	0.0494	0.078	0.254	1:2:4	6	72 H	140	no
194	0.0494	0.078	0.254	1:2:4	6	72 H	120	no
195	0.0494	0.156	0.254	1:4:4	6	72 H	140	no
196	0.0494	0.156	0.254	1:4:4	6	72 H	120	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Pyromellitic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
197	0.0494	0.078	0.254	1:2:4	6	72 H	140	no
198	0.0494	0.078	0.254	1:2:4	6	72 H	120	no
199	0.0494	0.156	0.254	1:4:4	6	72 H	140	no
200	0.0494	0.156	0.254	1:4:4	6	72 H	120	no

trail	FeCl ₂ ·4 H ₂ O	BPY	Trimesic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
201	0.1988	0.156	0.21	1:1:1	6	72 H	120	no
202	0.1988	0.156	0.21	1:1:1	6	72 H	140	no
203	0.1988	0.156	0.21	1:1:1	6	96 H	120	no
204	0.1988	0.156	0.21	1:1:1	6	96 H	140	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
205	0.1988	0.156	0.21	1:1:1	6	72 H	120	no
206	0.1988	0.156	0.21	1:1:1	6	72 H	140	no
207	0.1988	0.156	0.21	1:1:1	6	96 H	120	no
208	0.1988	0.156	0.21	1:1:1	6	96 H	140	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Pyromellitic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
209	0.0494	0.078	0.122	1:2:2	6	72 H	140	no
210	0.0494	0.078	0.122	1:2:2	6	72 H	120	no
trail	FeCl ₂ ·4 H ₂ O	BPY	Pyromellitic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
211	0.0494	0.078	0.122	1:2:2	6	72 H	140	no
212	0.0494	0.078	0.122	1:2:2	6	72 H	120	no

trail	CuCl ₂	BPY	Trimesic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
213	0.065	0.078	0.105	1:1:1	6	72 H	140	no
214	0.065	0.078	0.105	1:1:1	6	72 H	120	no
trail	CuCl ₂	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
215	0.065	0.078	0.105	1:1:1	6	72 H	140	no
216	0.065	0.078	0.105	1:1:1	6	72 H	120	no
trail	CuCl ₂	BPY	BNA	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
217	0.065	0.078	0.101	1:1:1	6	72 H	140	small green crystal, very less
218	0.065	0.078	0.101	1:1:1	6	72 H	120	small green crystal, very less
trail	CuCl ₂	BPY	BNA	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
219	0.065	0.078	0.101	1:1:1	6	72 H	140	no
220	0.065	0.078	0.101	1:1:1	6	72 H	120	no

trail	LaCl3	BPY	BNA	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
221	0.123	0.078	0.101	1:1:1	6	72 H	120	small colorless crystal, a lot
222	0.123	0.078	0.101	1:1:1	6	72 H	140	small colorless crystal, a lot
trail	LaCl3	BPY	BNA	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
223	0.123	0.078	0.101	1:1:1	6	72 H	120	no
224	0.123	0.078	0.101	1:1:1	6	72 H	140	no
trail	CoCl2	BPY	BNA	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
221	0.064	0.078	0.101	1:1:1	6	72 H	120	no
222	0.064	0.078	0.101	1:1:1	6	72 H	140	small pink crystal, a lot
trail	CoCl2	BPY	BNA	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
221	0.064	0.078	0.101	1:1:1	6	72 H	120	no
222	0.064	0.078	0.101	1:1:1	6	72 H	140	no

trail	CuCl ₂	BPY	Pyromellitic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
223	0.033	0.078	0.254	1:2:4	6	72 H	140	big colorless crystals
224	0.033	0.078	0.254	1:2:4	6	72 H	120	no
trail	CuCl ₂	BPY	Pyromellitic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
223	0.033	0.078	0.254	1:2:4	6	72 H	140	no
224	0.033	0.078	0.254	1:2:4	6	72 H	120	no
trail	CoCl ₂	BPY	Pyromellitic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
225	0.064	0.078	0.254	1:1:2	6	72 H	140	Bing pink crystal
226	0.064	0.078	0.254	1:1:2	6	72 H	120	no
trail	FeCl ₂ ·4 H ₂ O	BPY	BNA	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
227	0.0988	0.078	0.202	1:1:2	6	72 H	140	no
trail	CoCl ₂	BPY	Trimesic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not

228	0.032	0.078	0.105	1:2:2	6	72 H	140	no
229	0.032	0.078	0.105	1:2:2	6	72 H	120	no
trail	CoCl ₂	BPY	Pyromel litic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
230	0.032	0.078	0.254	1:2:4	6	72 H	140	no
231	0.032	0.078	0.254	1:2:4	6	72 H	120	no
trail	CuCl ₂	BPY	Trimesic acid	Mole ratio	Water volume (ml)	total reaction time	temperature set	crystal or not
232	0.033	0.078	0.105	1:2:2	6	72 H	140	one or two blue crystal
233	0.033	0.078	0.105	1:2:2	6	72 H	120	no
trail	CuCl ₂	BPY	Trimesic acid	Mole ratio	Acetone volume (ml)	total reaction time	temperature set	crystal or not
234	0.033	0.078	0.105	1:2:2	6	72 H	140	no
235	0.033	0.078	0.105	1:2:2	6	72 H	120	no

$\text{Fe}_3(\text{BNA})_6\text{O}$



Fig.15 Sample of complex 1

Figure 15 presents the first structure of the coordination polymer $\text{Fe}_3(\text{BNA})_6\text{O}$. It is named as complex 1. Complex 1 is the black crystals which synthesized by reacting $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 5-bromonicotinic acid (HBNA), and 4,4-bipyridine with the mole ratio 1:2:1. The materials were placed in the Teflon bomb. 6 ml of water was used as solvent. Then the bomb was put into the oven for three days. The temperature of the oven was set at 140°C . After the reaction time finished, it is allowed to cool down to room temperature naturally. The product then was washed by di water and acetone. The product is black

crystals, and the white product was the impurities (Figure 15). The x-ray crystallography shows this coordination polymer is the two dimensional coordination polymer. It constructed the 2D layer structure. The monoclinic crystal has formula weight of 1389.57. The details of this structure are listed in Table 1.

Table 1. crystal data for complex 1

Empirical formula ^a	C ₃₆ H ₁₈ Br ₆ Fe ₃ N ₆ O ₁₃
Space group	P2(1)/c
<i>a</i> (Å)	11.2904(6)
<i>b</i> (Å)	18.4960(11)
<i>c</i> (Å)	21.4349(12)
β (°)	91.029(1)
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.028
Final R indices [<i>I</i> > 4sigma(<i>I</i>)]	R1 = 0.0156, wR2 = 0.0405

$$^a R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|, wR_2 = [\Sigma (F_{0^2} - F_{c^2}) / \Sigma w(F_0)^2]^{1/2}.$$

The structure of complex 1 consists of three Fe ions. The Fe irons are six-coordinated in the octahedral coordination sphere. The equatorial plane is Fe iron connected with four oxygen atoms from different BNA ligands. One nitrogen atom from BNA and one oxygen atom occupy in the axial position. Three Fe irons have range of 3.245Å-3.343Å with no bonds connected to each other. The bond length of Fe-N is in the range of 2.202Å-2.225Å. The bond length of Fe-O is in the range of 1.833Å-2.164Å. The unit cluster of this coordination polymer is shown in figure 16.

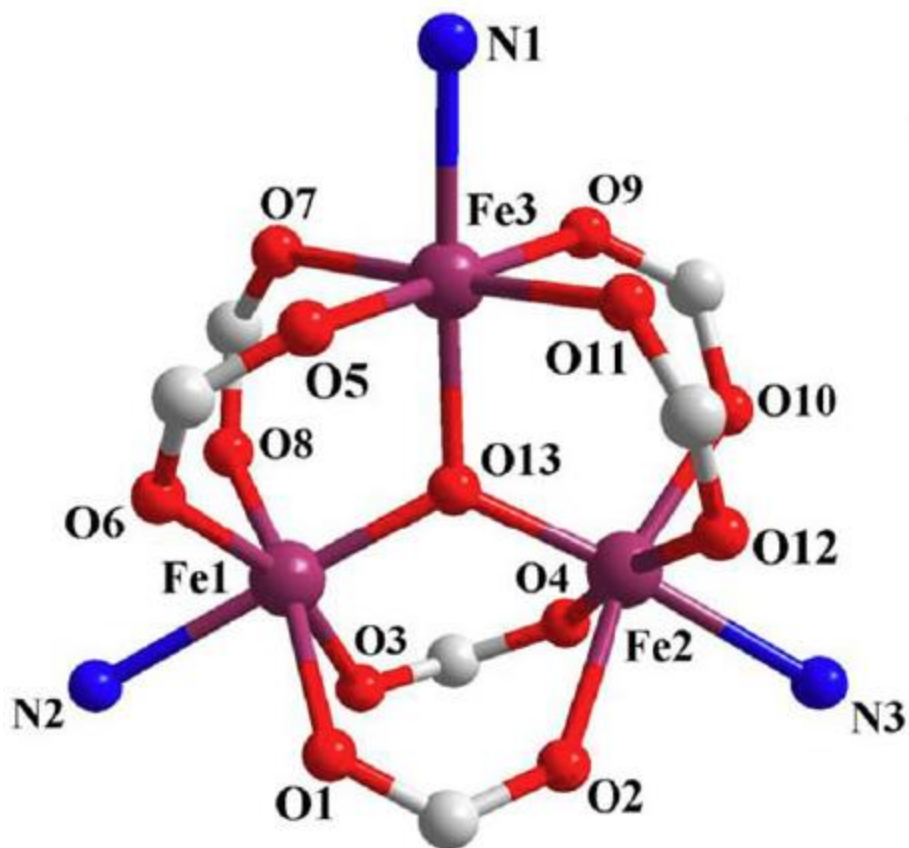


Fig.16 Unit cluster of complex 1

Figure 16 shows the unit cluster of the polymer which indicate the coordination environment of Fe ions in complex 1. Figure 17 shows the coordination modes of BNA ligands in the polymer. The white ball indicate the carbon atom and the green ball indicate the Br atom.

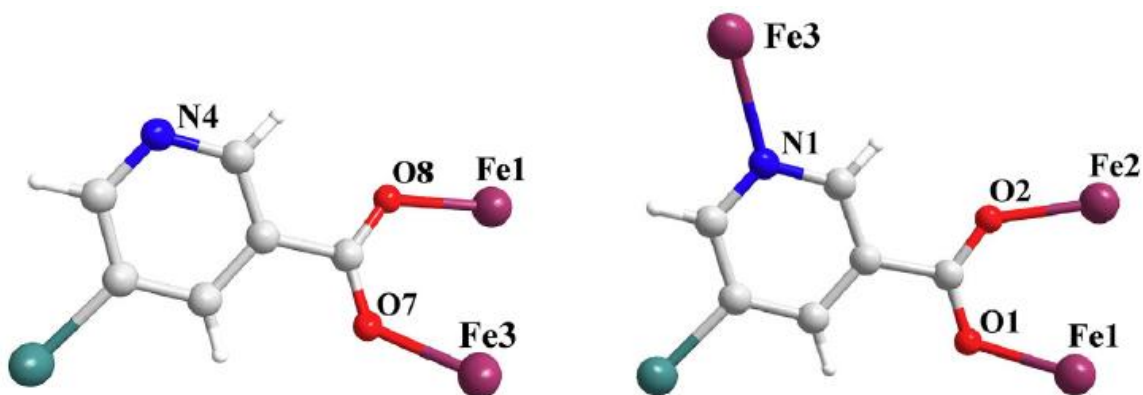


Fig.17 Coordination environment of complex 1

The nitrogen atom which shown in Figure 17 is the nitrogen in the BNA ligand. Each of the nitrogen atoms is connected to an Fe atom. And the oxygen atom is also connect to the Fe atom. The labeled Fe3 on the left is the same atom Fe3 on the right. So the coordination modes of the BNA ligand is O7-Fe3-N1 and O8-Fe1-O1. The atom N4 and Fe2 is connect to other Fe and extend to 1D and 2D structure.

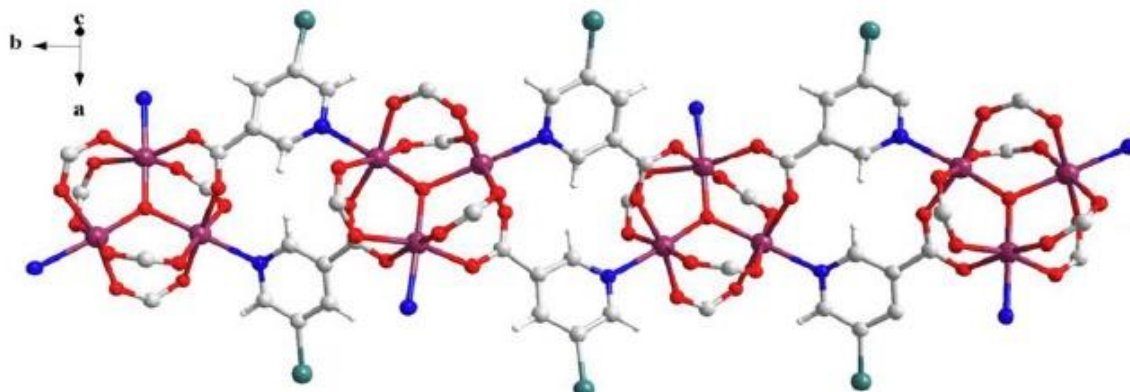


Fig.18 One dimensional structure of complex 1

Figure 18 shows the one dimensional structure of complex 1. The coordination mode is the same as shown before. When the nitrogen and oxygen are linked with different Fe ion, the 1D structure in the ab plane was formed.

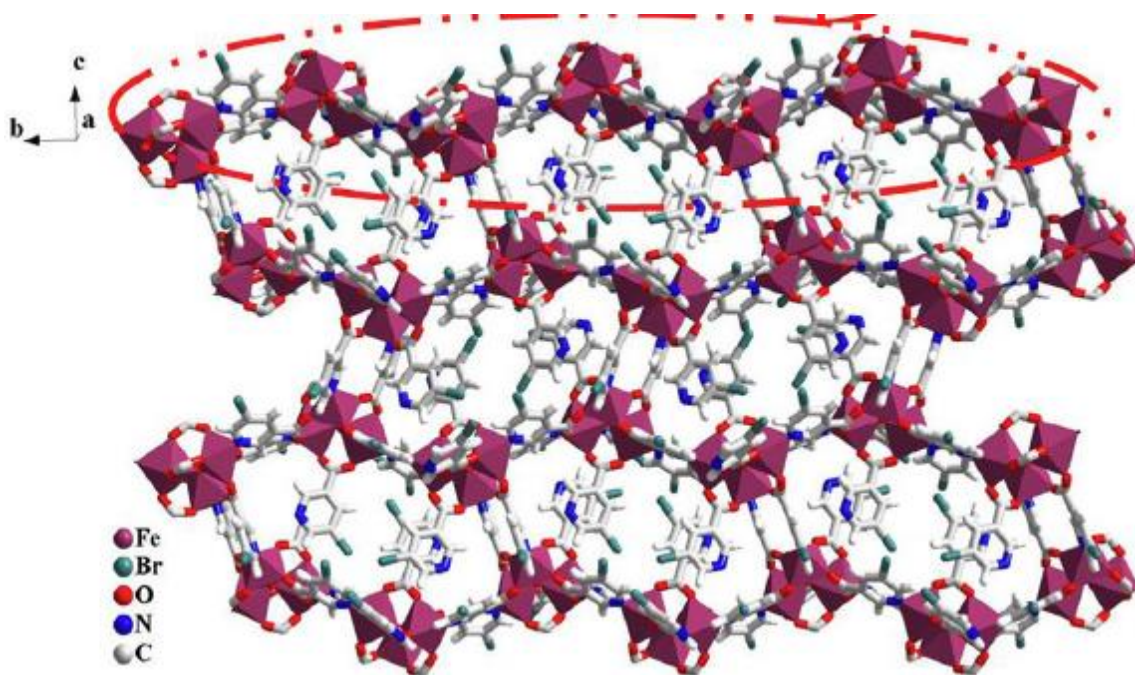


Fig.19 Two-dimensional structure of complex 1

When all the nitrogen and oxygen are connected with different Fe atom, it can extend to a two-dimensional sheet structure. The polymer structure is shown in Figure 19. The two dimensional structure is in the bc plane of the coordinate. The cycle part in Figure 19 is the one-dimensional structure fragment which shown in Figure 18. The selected bond length and angles of complex 1 is shown in Table 2.

Table 2. Selected bond length ($\text{\AA}$) and angles ($^\circ$) for complex 1

Fe(1)—O(13)	1.8348(13)	Fe(1)—O(6)	2.0099(13)
Fe(1)—O(8)	2.0303(13)	Fe(1)—O(1)	2.0490(13)
Fe(1)—O(3)	2.0554(13)	Fe(1)—N(2)#1	2.2246(16)
Fe(2)—O(13)	1.8455(12)	Fe(2)—O(10)	2.0248(13)
Fe(2)—O(12)	2.0422(13)	Fe(2)—O(2)	2.0616(13)
Fe(2)—O(4)	2.0996(13)	Fe(2)—N(3)#2	2.2221(15)
Fe(3)—O(13)	2.0294(13)	Fe(3)—O(11)	2.0764(13)
Fe(3)—O(7)	2.0771(13)	Fe(3)—O(9)	2.1323(13)
Fe(3)—O(5)	2.1639(13)	Fe(3)—N(1)#3	2.2039(16)
Br(1)—C(4)	1.8876(18)	Br(2)—C(10)	1.894(2)
N(1)—Fe(3)#2	2.2040(16)	N(2)—Fe(1)#1	2.2246(16)
N(3)—Fe(2)#3	2.2220(15)		
O(13)—Fe(1)—O(6)	102.18(5)	O(13)—Fe(1)—O(8)	93.71(5)
O(6)—Fe(1)—O(8)	95.11(5)	O(13)—Fe(1)—O(1)	97.11(5)
O(6)—Fe(1)—O(1)	91.05(5)	O(8)—Fe(1)—O(1)	166.15(5)
O(13)—Fe(1)—O(3)	93.91(5)	O(6)—Fe(1)—O(3)	163.80(5)
O(8)—Fe(1)—O(3)	85.73(5)	O(1)—Fe(1)—O(3)	84.94(5)
O(13)—Fe(1)—N(2)#1	176.55(6)	O(6)—Fe(1)—N(2)#1	80.89(5)
O(8)—Fe(1)—N(2)#1	84.39(5)	O(1)—Fe(1)—N(2)#1	84.36(6)
O(3)—Fe(1)—N(2)#1	83.10(5)	O(13)—Fe(2)—O(10)	100.72(5)
O(13)—Fe(2)—O(12)	95.57(5)	O(10)—Fe(2)—O(12)	90.47(5)
O(13)—Fe(2)—O(2)	93.85(5)	O(10)—Fe(2)—O(2)	165.42(5)
O(12)—Fe(2)—O(2)	87.72(5)	O(13)—Fe(2)—O(4)	93.72(5)
O(10)—Fe(2)—O(4)	89.71(5)	O(12)—Fe(2)—O(4)	170.51(5)
O(2)—Fe(2)—O(4)	89.72(5)	O(13)—Fe(2)—N(3)#2	175.31(6)
O(10)—Fe(2)—N(3)#2	83.96(5)	O(12)—Fe(2)—N(3)#2	84.50(5)
O(2)—Fe(2)—N(3)#2	81.46(5)	O(4)—Fe(2)—N(3)#2	86.09(5)
O(13)—Fe(3)—O(11)	89.90(5)	O(13)—Fe(3)—O(7)	93.13(5)
O(11)—Fe(3)—O(7)	175.97(5)	O(13)—Fe(3)—O(9)	92.46(5)
O(11)—Fe(3)—O(9)	90.66(5)	O(7)—Fe(3)—O(9)	91.87(5)
O(13)—Fe(3)—O(5)	89.36(5)	O(11)—Fe(3)—O(5)	84.68(5)
O(7)—Fe(3)—O(5)	92.70(5)	O(9)—Fe(3)—O(5)	174.99(5)
O(13)—Fe(3)—N(1)#3	176.71(5)	O(11)—Fe(3)—N(1)#3	86.87(5)
O(7)—Fe(3)—N(1)#3	90.06(5)	O(9)—Fe(3)—N(1)#3	88.20(5)
O(5)—Fe(3)—N(1)#3	89.73(5)	C(6)—O(1)—Fe(1)	121.08(12)
C(6)—O(2)—Fe(2)	135.13(12)	C(12)—O(3)—Fe(1)	127.87(12)
C(12)—O(4)—Fe(2)	122.02(12)	C(18)—O(5)—Fe(3)	124.75(11)
C(18)—O(6)—Fe(1)	130.04(12)	C(24)—O(7)—Fe(3)	129.45(12)
C(24)—O(8)—Fe(1)	125.65(12)	C(30)—O(9)—Fe(3)	124.80(12)
C(30)—O(10)—Fe(2)	132.33(12)	C(36)—O(11)—Fe(3)	132.34(12)
C(36)—O(12)—Fe(2)	123.81(12)	Fe(1)—O(13)—Fe(2)	123.69(7)
Fe(1)—O(13)—Fe(3)	117.12(6)	Fe(2)—O(13)—Fe(3)	119.19(6)
C(1)—N(1)—Fe(3)#2	119.07(12)	C(5)—N(1)—Fe(3)#2	121.87(12)
C(7)—N(2)—Fe(1)#1	120.07(12)	C(11)—N(2)—Fe(1)#1	121.31(13)
C(13)—N(3)—Fe(2)#3	121.60(12)	C(17)—N(3)—Fe(2)#3	119.63(12)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x + 1, y + 1/2, -z + 3/2$; #3 $-x + 1, y - 1/2, -z + 3/2$.

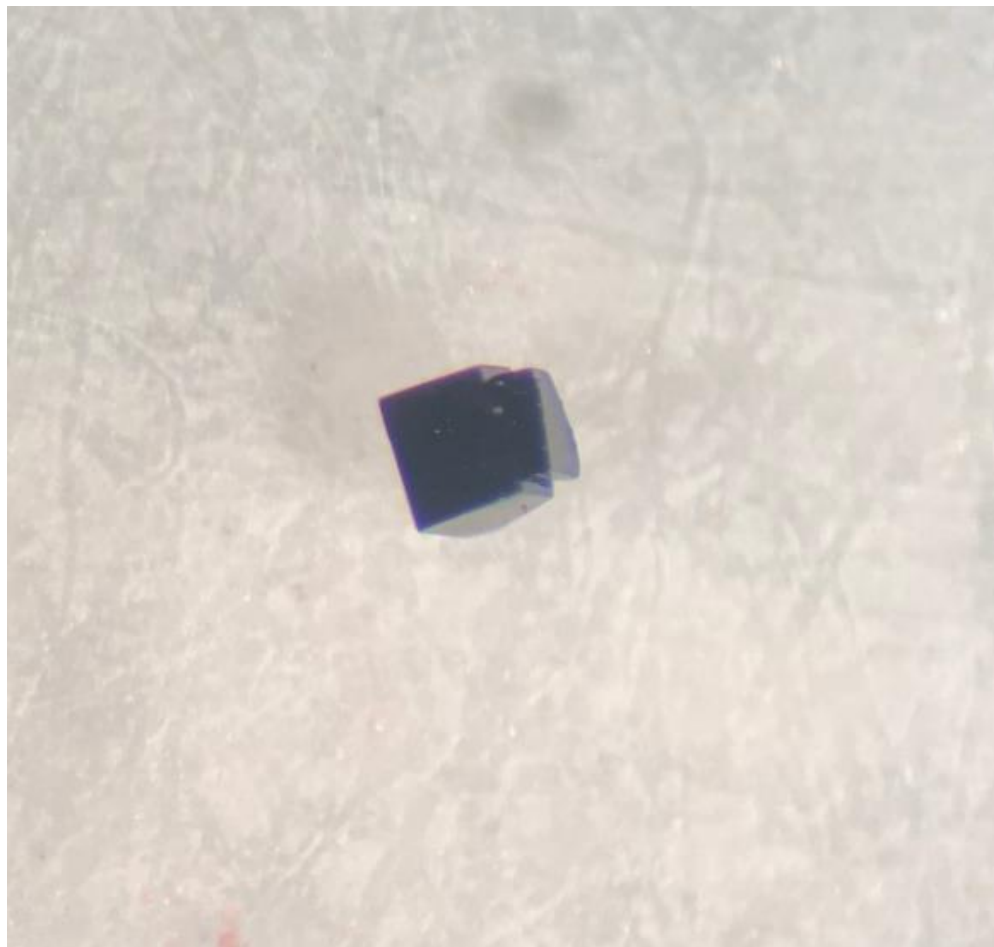


Fig.20 Sample of complex 2

Figure 20 shows the coordination polymer with same chemical formula $\text{Fe}_3(\text{BNA})_6\text{O}$ but different structure. It is named as complex 2. Complex 2 is the black crystals which is synthesized by reacting $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 5-bromonicotinic acid (HBNA), and 4,4-bipyridine with the mole ratio 1:1:1. The materials were placed in the Teflon bomb. 6 ml of water was used as solvent. Then the bomb was put into the oven for seven days. The temperature of the oven was set at 140°C . After seven days, the bomb was taken out of the oven and allowed to cool down to room temperature naturally. Then the

product is washed by di water and acetone. The product is black crystals, others are the impurities. The x-ray crystallography shows that this coordination polymer is the three dimensional coordination polymer. It constructed the three dimensional cube structure. The monoclinic crystal also has formula weight of 1389.57. The details of this structure are listed in Table 3.

The complete crystallography tables and other data for this compound is located in Appendix B.

Table 3. Crystal data and structure refinement for complex 2.

Empirical formula	C ₃₆ H ₁₈ Br ₆ Fe ₃ N ₆ O ₁₃
Crystal system, space group	Cubic, Pa-3
a (Å)	20.3708(6)
b (Å)	20.3708(6)
c (Å)	20.3708(6)
α (°)	90
β (°)	90
γ (°)	90
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.058
Final R indices [I>4σ(I)]	R1 = 0.0178, wR2 = 0.0449

The structure of complex 2 unit cell also consists of three Fe ions. The Fe ions are six-coordinated in the octahedral coordination sphere. The equatorial plane is Fe iron connected with four oxygen atoms from different BNA ligands. One nitrogen atom from BNA and one oxygen atom occupy in the axial position. Three Fe ions connect to each other. The bond length of Fe-N is in the range of 2.229Å. The bond length of Fe-O is in the range of 1.896Å-2.109Å. The 4,4-bipyridine is not presented in the structure. The asymmetric unit showing atom numbering is shown in Figure 21.

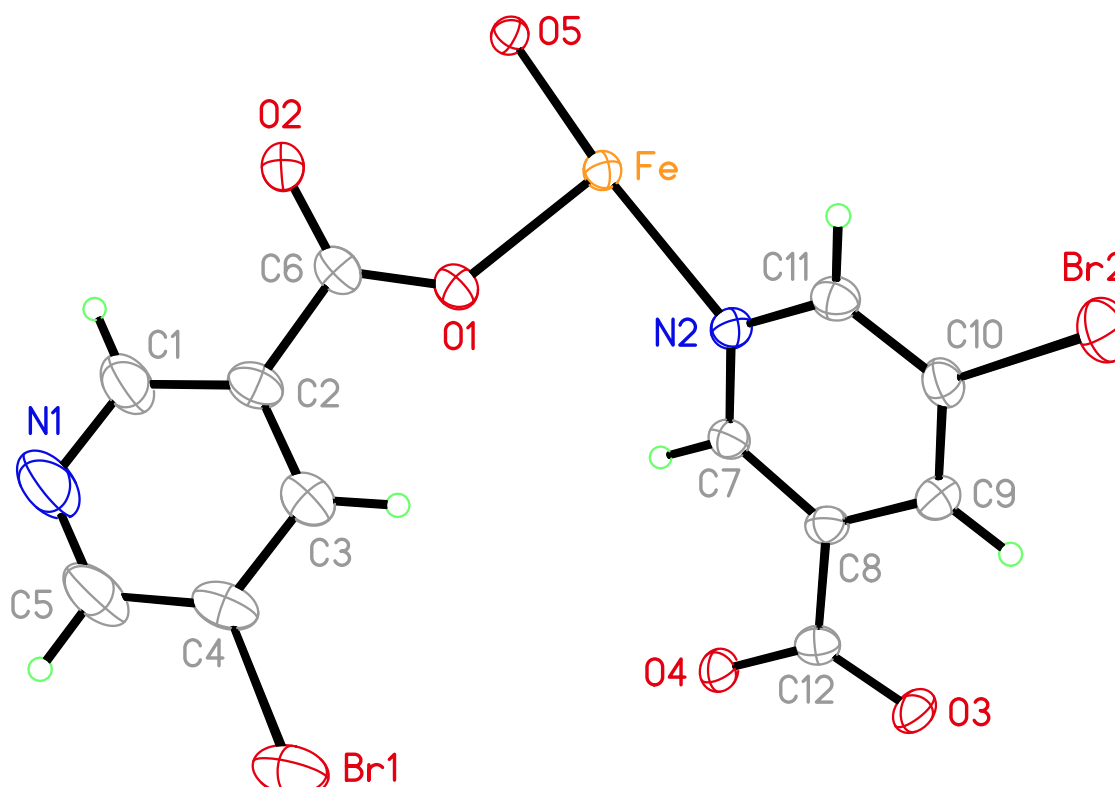


Fig.21 Coordination pattern for each atoms in complex 2

Figure 21 shows the coordination pattern for each atoms in the coordination polymer. It is the asymmetric unit. The oxygen and nitrogen atoms are coming from the BNA ligand. The small green ball is the Br atom from the BNA ligand.

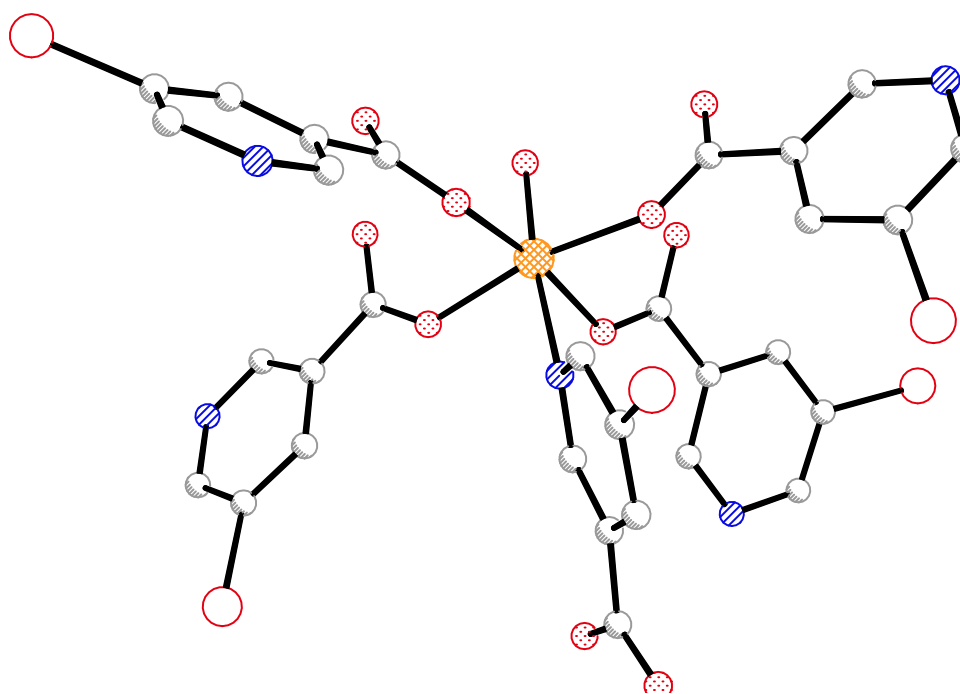


Fig.22 Complete coordination of Fe

Figure 22 shows the complete coordination about Fe. From Figure 22, it is shown that the Fe atom is six coordinated and octahedral structures. Four oxygen at equatorial position connected to the Fe. The oxygen atoms are coming from different BNA ligands. One of the axial position connected to nitrogen atom on the BNA ring.

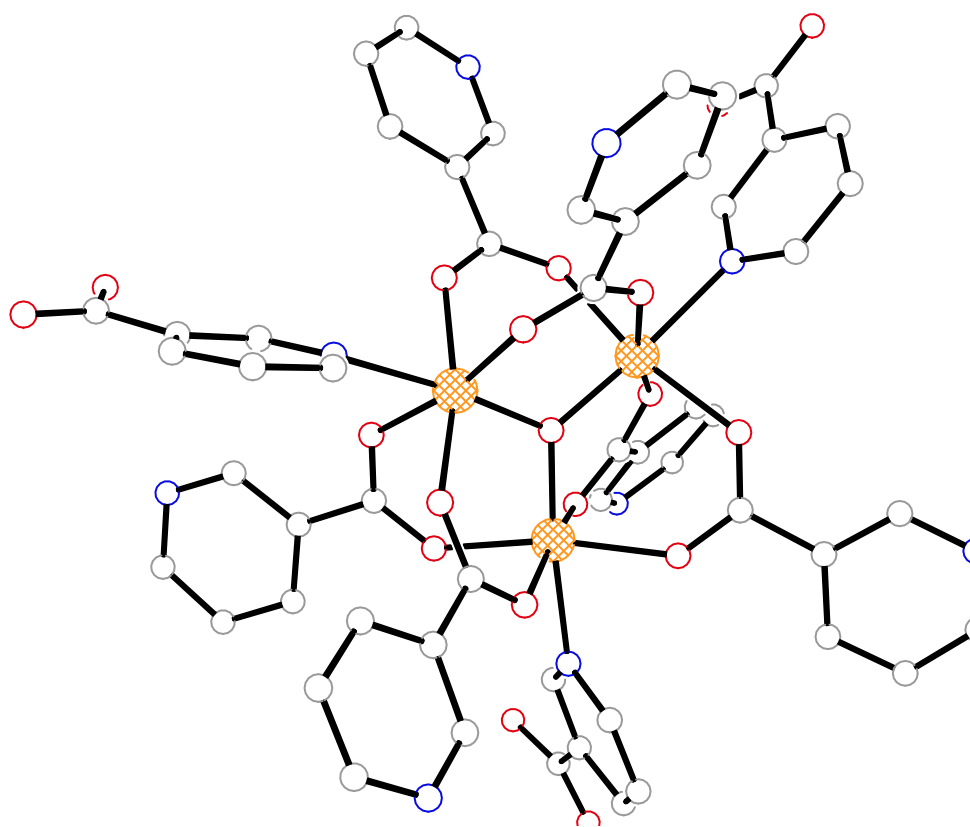


Fig.23 Complete coordination of central oxide

Figure 23 shows the complete coordination about central oxide. The Br atom is omitted. This is the unit cluster for complex 2. In this structure, each of the Fe atoms was connected to a BNA ligand through Fe-O bond. So the nitrogen of the ligand can connect to another Fe atom on the axial position.

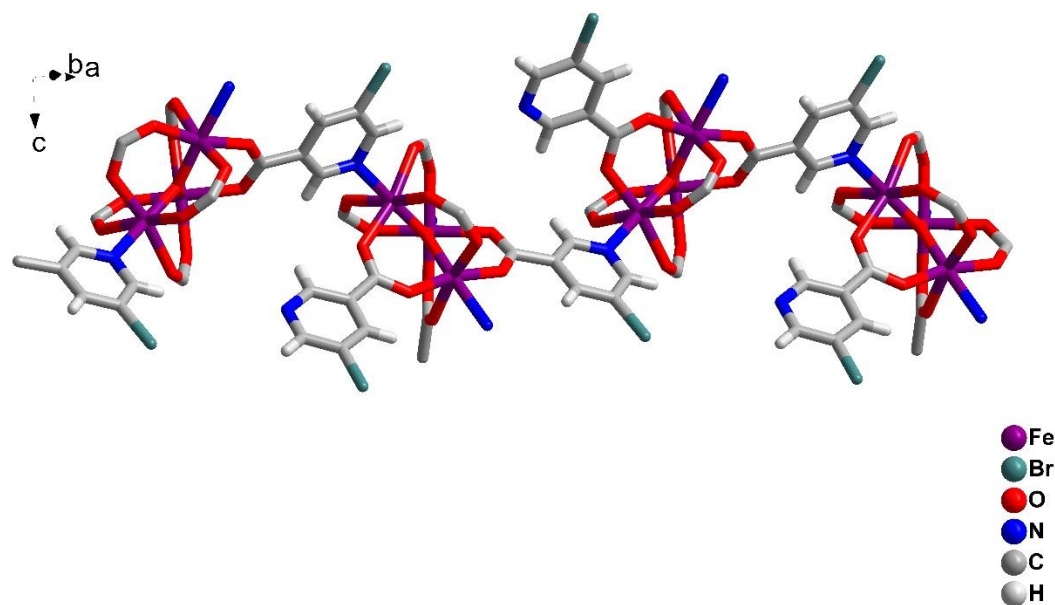


Fig.24 One-dimensional fragment of complex 2

Figure 24 shows the one-dimensional fragment of complex 2 in the bc plane of coordinate. It is similar to complex 1, but the connection pattern is different. And the bond length is different. In complex 2, the ligand is connected to the Fe in different angle. The ring of the BNA ligand can rotate in different direction when forming the Fe-N bond. When the BNA ligand with different direction connect to Fe atom, it is extender to three dimensional structure.

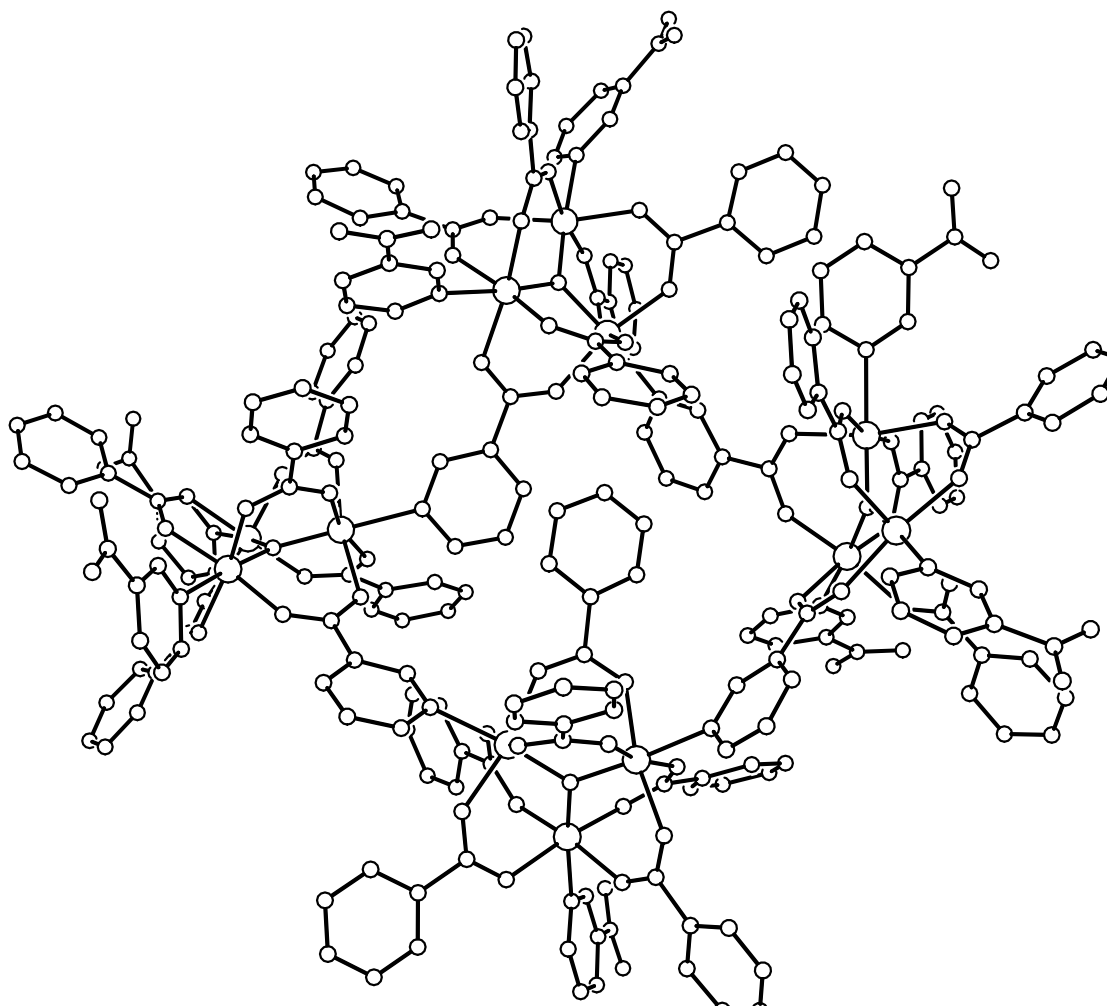


Fig.25 Three-dimensional packing arrangement of complex 2

Figure 25 is the partial section of the three dimensional packing arrangement of the complex 2. Figure 25 shows the complete fragment of the complex 2. The ring of the BNA ligand is facing different direction, so when the N-Fe-O connected, the whole structure can extend to three-dimensional structure.

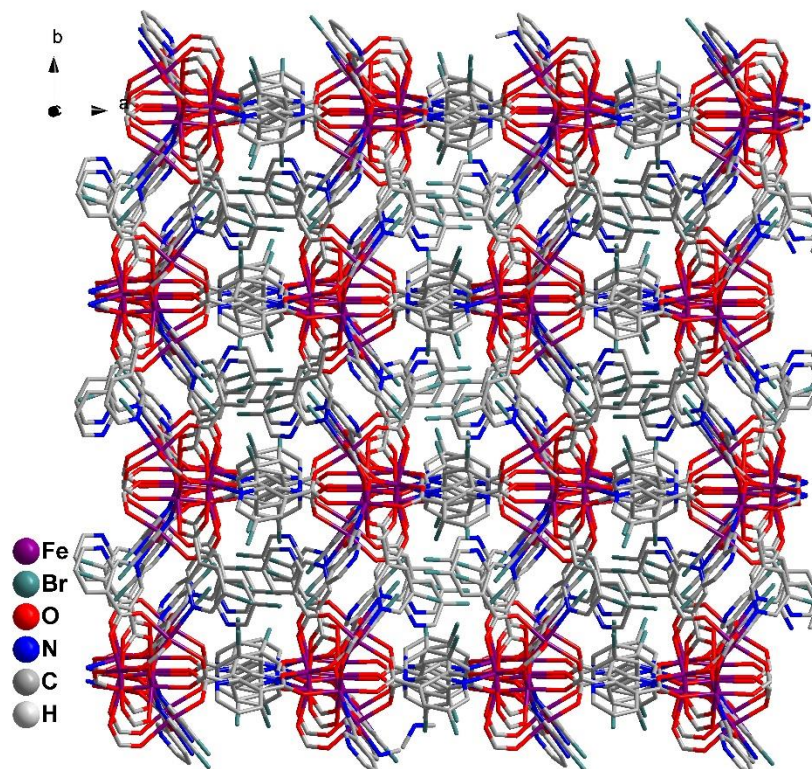


Fig.26 Complete structure of three-dimensional structure of complex 2

Figure 26 is the complete structure of the three dimensional coordination polymer. The chemical formula is $\text{Fe}_3(\text{BNA})_6\text{O}$. This three dimensional coordination polymer turn out to be a black cubic crystal when observing under the microscope. The selected bond length and bond angle is shown in table 4.

Table 4. Selected bond length ($\text{\AA}$) and angles ($^\circ$) for complex 2

Fe-O(5)	1.8962(4)	O(5)-Fe-N(2)	174.29(7)
Fe-O(1)	2.0309(19)	O(1)-Fe-N(2)	86.73(8)
Fe-O(3)#1	2.0523(19)	O(3)#1-Fe-N(2)	80.71(8)
Fe-O(2)#2	2.069(2)	O(2)#2-Fe-N(2)	82.84(8)
Fe-O(4)#3	2.1090(19)	O(4)#3-Fe-N(2)	85.75(8)
Fe-N(2)	2.229(2)	C(6)-O(1)-Fe	131.85(18)
Br(1)-C(4)	1.890(3)	C(6)-O(2)-Fe#4	129.09(18)

Br(2)-C(10)	1.887(3)	C(12)-O(3)-Fe#5	136.87(18)
O(1)-C(6)	1.261(3)	C(12)-O(4)-Fe#6	124.28(18)
O(2)-C(6)	1.263(3)	Fe#2-O(5)-Fe#4	119.903(10)
O(2)-Fe#4	2.069(2)	Fe#2-O(5)-Fe	119.903(10)
O(3)-C(12)	1.263(3)	Fe#4-O(5)-Fe	119.903(10)
O(3)-Fe#5	2.0523(19)	C(1)-N(1)-C(5)	116.9(3)
O(4)-C(12)	1.253(3)	C(7)-N(2)-C(11)	118.4(2)
O(4)-Fe#6	2.1091(19)	C(7)-N(2)-Fe	124.94(18)
O(5)-Fe#2	1.8961(4)	C(11)-N(2)-Fe	115.53(18)
O(5)-Fe#4	1.8962(4)	N(1)-C(1)-C(2)	124.0(3)
N(1)-C(1)	1.335(4)	C(1)-C(2)-C(3)	118.3(3)
N(1)-C(5)	1.337(4)	C(1)-C(2)-C(6)	122.3(3)
N(2)-C(7)	1.340(3)	C(3)-C(2)-C(6)	119.3(3)
N(2)-C(11)	1.341(4)	C(4)-C(3)-C(2)	118.0(3)
C(1)-C(2)	1.384(4)	C(3)-C(4)-C(5)	119.7(3)
C(2)-C(3)	1.391(4)	C(3)-C(4)-Br(1)	119.5(2)
C(2)-C(6)	1.496(4)	C(5)-C(4)-Br(1)	120.8(2)
C(3)-C(4)	1.377(4)	N(1)-C(5)-C(4)	122.9(3)
C(4)-C(5)	1.384(5)	O(1)-C(6)-O(2)	126.2(3)
C(7)-C(8)	1.393(4)	O(1)-C(6)-C(2)	116.5(2)
C(8)-C(9)	1.390(4)	O(2)-C(6)-C(2)	117.3(2)
C(8)-C(12)	1.508(4)	N(2)-C(7)-C(8)	122.8(3)
C(9)-C(10)	1.379(4)	C(9)-C(8)-C(7)	118.2(3)
C(10)-C(11)	1.381(4)	C(9)-C(8)-C(12)	119.8(2)
O(5)-Fe-O(1)	98.46(8)	C(7)-C(8)-C(12)	121.9(2)
O(5)-Fe-O(3)#1	94.03(8)	C(10)-C(9)-C(8)	118.7(3)
O(1)-Fe-O(3)#1	167.34(8)	C(11)-C(10)-C(9)	119.7(3)
O(5)-Fe-O(2)#2	95.00(9)	C(11)-C(10)-Br(2)	118.4(2)
O(1)-Fe-O(2)#2	86.85(8)	C(9)-C(10)-Br(2)	121.8(2)
O(3)#1-Fe-O(2)#2	90.01(8)	N(2)-C(11)-C(10)	122.1(3)
O(5)-Fe-O(4)#3	96.61(9)	O(4)-C(12)-O(3)	126.2(3)
O(1)-Fe-O(4)#3	89.62(8)	O(4)-C(12)-C(8)	118.7(2)
O(3)#1-Fe-O(4)#3	91.02(8)	O(3)-C(12)-C(8)	115.0(2)
O(2)#2-Fe-O(4)#3	168.23(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -z+3/2,x-1/2,y; #2 y+1/2,-z+1/2,-x+1

#3 -y+1,-z+1,-x+1; #4 -z+1,x-1/2,-y+1/2

FT-IR analysis

The results of the FT-IR analysis is shown in figure 27. It is corresponding to the complex 2. The peak at 1371 cm^{-1} corresponding to the C-O stretching. The peaks at 1551 cm^{-1} and 1610 cm^{-1} corresponding to the C-C stretching which is the carbon located on the BNA ring. The peak at 1287 cm^{-1} corresponding to the C-N stretching which is the C-N bond on the BNA ligand.

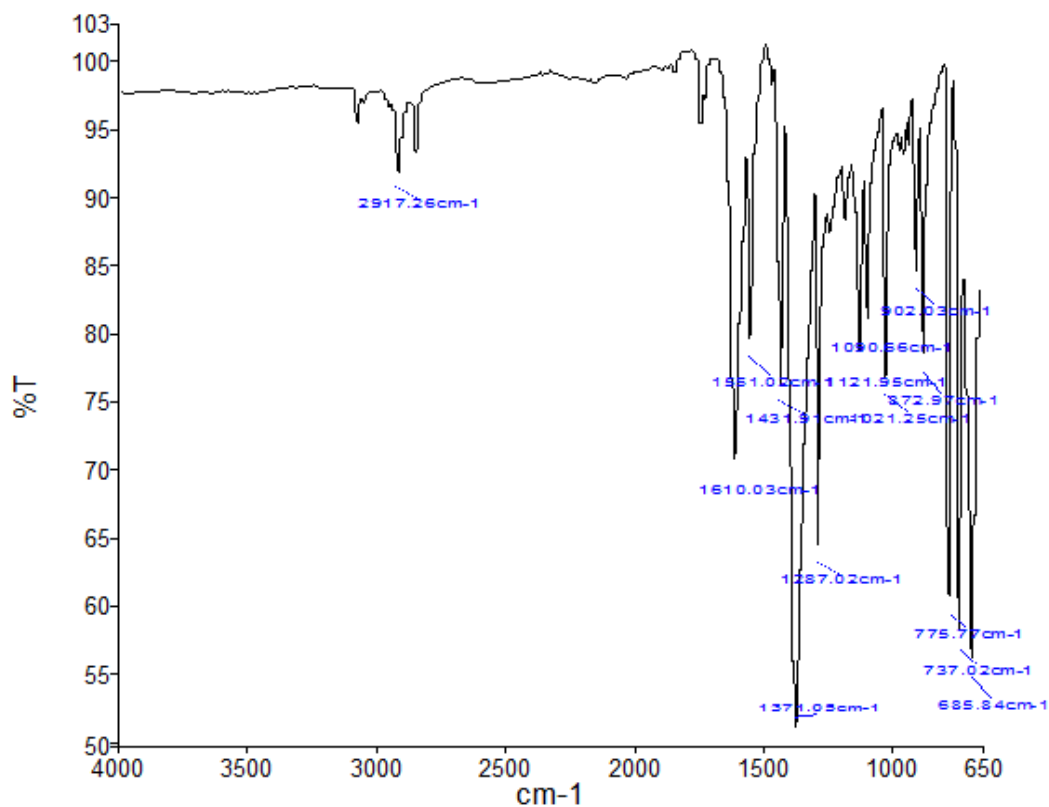


Fig.27 IR for complex 2

IR results indicate that the coordination polymer has successful synthesized.

Elemental Analysis

The results of elemental analysis shown in table 5. The calculated values will be used to compare the results. Comparing the theoretical calculations to the actual result analyzed from Galbraith Laboratories, there is only small differences. That might be due to some end groups not account for in the theoretical calculations.

Table 5. Elemental Analyses for complex 2.

Element	Found	Calculated
Carbon	30.7%	31.0%
Iron	12.0%	12.0%
Hydrogen	0.88%	1.2%
Nitrogen	5.8%	6.0%

The elemental analysis result shows that the composition of the complex 2 is same as the chemical formula shows.

Thermal Analysis

The result of thermal analysis for complex 2 is shown in figure 28. It is found that the complex 2 has one-step degradation process. Because there only one large jump from the TGA graph. The blue line which is the TG line. The TG line indicate the polymer started to decompose when temperature reach about 375°C. And finish decomposing about 550°C. I means this polymer is stable up to 375°C. During the decomposing process, 41.8% of weight was lost. And the weight remain unchanged when the temperature cools down to room temperature. The green line which is the DTA line.

There is a peak upwards in the DTA line. It indicate that the polymer is absorbing heat during the decomposing process.

Module:	TG/DTA	Temperature Program:		Comment:
Data Name:	Lei2			Operator: Administrator
Measurement Date:	11/16/2018	1*	Cal 600 10 1 0.5	Gas1: N2
Sample Name:	Lei2	2*	600 25 10 0 0.5	Pan: Pt
Sample Weight:	8.955 mg			
Reference Name:	Pt			
Reference Weight:	0.000 mg			

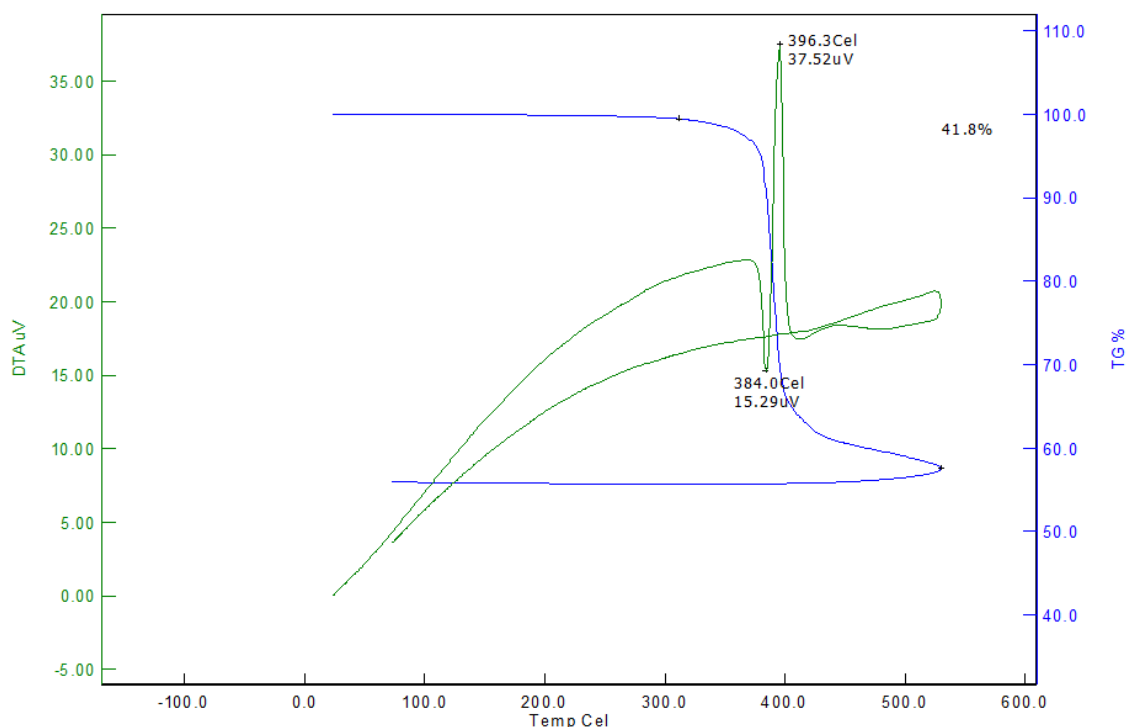


Fig.28 TGA for complex 2

Magnetic Analysis

Transition elements such as Fe, Co and Ni always introduce interesting magnetic properties in the sample due to its unpaired electrons in (n-1) d orbital. Most of transition metals themselves show paramagnetic behaviors. Structural factors leading to hybridization of orbital will change the magnetic properties and electronic structure when

the transition metals are in the form of complex ions. In this scenario, $\text{Fe}_3(\text{BNA})_6\text{O}$ is interesting from both in the magnetic property and electronic structure point of view. To explore the function of the iron ions in $\text{Fe}_3(\text{BNA})_6\text{O}$, the magnetic properties of $\text{Fe}_3(\text{BNA})_6\text{O}$ was studied in the temperature from 2 K to 375 K and under the external magnetic field from -7 T to 7 T.

Under low magnetic field (10 Oe), as shown by Fig.29, the sample behaves as a typical paramagnet without any magnetic anomaly. However, a weak split for ZFC and FC curve started from 300 K was observed, so we doubted if there is any magnetic transition over 300K that leads to the split. Figure. 30 showed the magnetic measurement under an external magnetic field of 0.1 T. The green dotted line is the fit to the Curie-Weiss law, the susceptibility starts to deviate from the Curie-Weiss law below ~ 120 K, indicating a possible enhancement of short-range magnetic correlation which have a higher Curie constant C . We suggest that it could be due to the enhancement of short-range ferromagnetic state.²⁸⁻³² Here we think the dielectric constant measurement is also

worth doing, due to the curiosity that if there will be a ferroelectric transition at 120K.

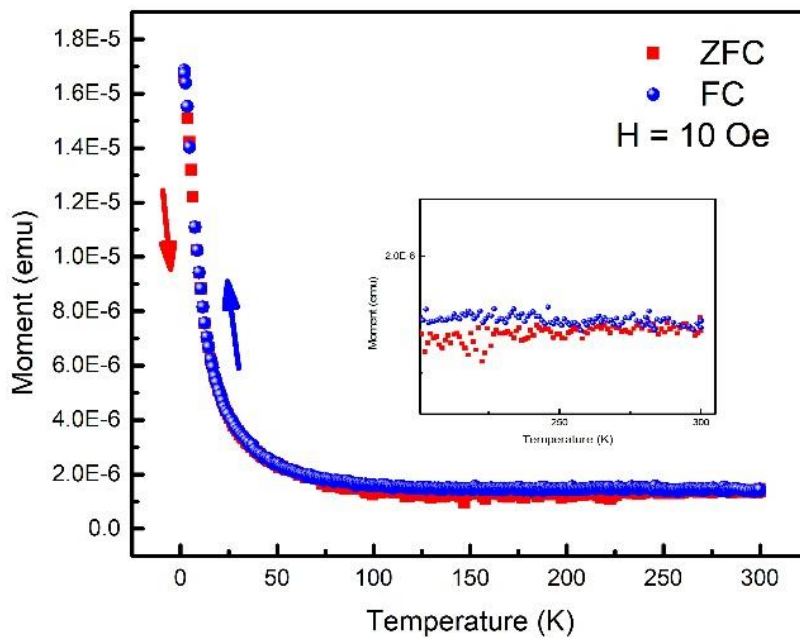


Fig.29 Temperature dependence of magnetic moment of $\text{Fe}_3(\text{BNA})_6\text{O}$ under 10 Oe

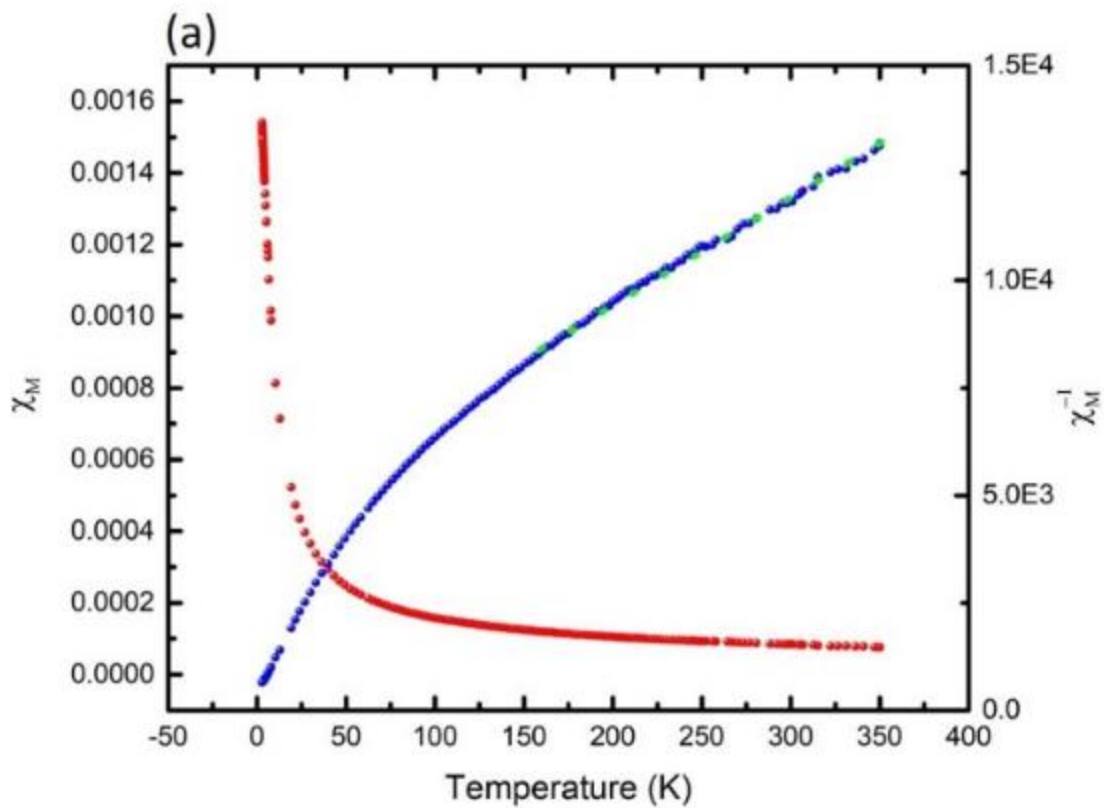


Fig.30a Temperature dependence of magnetic susceptibility and magnetic hardness (reciprocal magnetic susceptibility) of $\text{Fe}_3(\text{BNA})_6\text{O}$ under 1000 Oe., green dotted line represents the fitting according to Curies-Weiss law.

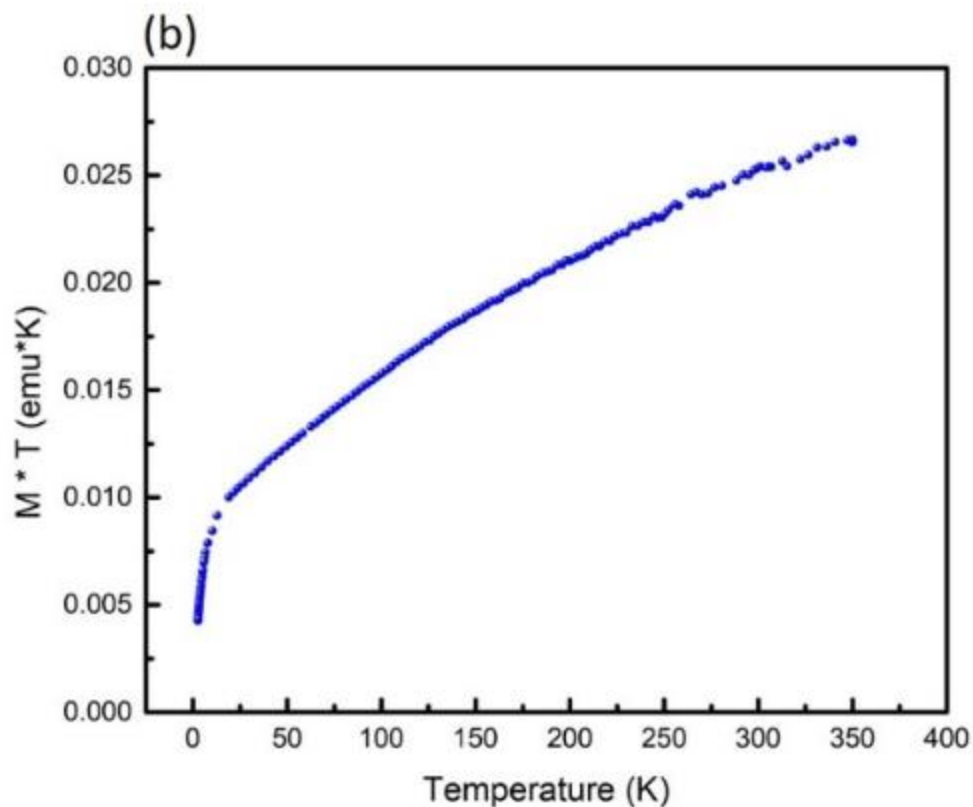


Fig.30b $\chi \cdot T$ as a function of temperature for $\text{Fe}_3(\text{BNA})_6\text{O}$

Figure 30a is the temperature dependence of magnetic susceptibility and magnetic hardness (reciprocal magnetic susceptibility) of complex 2, green dotted line represents the fitting according to Curies-Weiss law. Figure 30b χT as a function of temperature for complex 2.

From the temperature dependence of magnetic hardness χ^{-1} we can observe that the measured sample have a paramagnetic behavior from room temperature to about 120K described by a Curie-Weiss law:

$$\chi = \frac{C}{T - \theta}$$

where, $\theta = -175$ (K), the Curie Constant C is:

$$C = \frac{\Delta T}{\Delta(1/\chi)} = \frac{350 + 175}{13200} \approx 4 \times 10^{-2}$$

In statistical theory of paramagnetism, Langevin states that the thermal variation of susceptibility is:

$$\chi = \frac{M}{H} = \frac{N\mu_{eff}^2\mu_0}{3k_B T} = \frac{C}{T}$$

Where N is the ion concentration, μ_0 is the magnetic constant, k_B is the Boltzmann constant. N can be estimated from the formula weight of $\text{Fe}_3(\text{BNA})_6\text{O}$.

From this relation we know that the Curie Constant C is equal to χT and is proportional to the effective magnetic moment μ_{eff} and:

$$\mu_{eff} = \sqrt{\frac{3k_B C}{\mu_0 N}} \approx 5.6\mu_B$$

Where μ_B is Bohr magneton. The result is close to the theoretic calculation of spin state of Fe^{+3} which is 5.92, while is in the middle of Fe^{+2} (5.4) and Fe^{+3} (5.9) experimentally. See Table.6 below.³³

Table 6. Effective magneton numbers for iron group ions

Ion	Configuration	Basic level	$p^{(calc)} = g[J(J+1)]^{1/2}$	$p^{(calc)} = 2[S(S+1)]^{1/2}$	$p^{(exp)}^a$
$\text{Ti}^{3+}, \text{V}^{4+}$	$3d^1$	${}^2D_{3/2}$	1.55	1.73	1.8
V^{3+}	$3d^2$	3F_2	1.63	2.83	2.8
$\text{Cr}^{3+}, \text{V}^{2+}$	$3d^3$	${}^4F_{3/2}$	0.77	3.87	3.8
$\text{Mn}^{3+}, \text{Cr}^{2+}$	$3d^4$	5D_0	0	4.90	4.9
$\text{Fe}^{3+}, \text{Mn}^{2+}$	$3d^5$	${}^6S_{5/2}$	5.92	5.92	5.9
Fe^{2+}	$3d^6$	5D_4	6.70	4.90	5.4
Co^{2+}	$3d^7$	${}^4F_{9/2}$	6.63	3.87	4.8
Ni^{2+}	$3d^8$	3F_4	5.59	2.83	3.2
Cu^{2+}	$3d^9$	${}^2D_{5/2}$	3.55	1.73	1.9

The calculation of the Curie Constant C and effective magnetic moment suggests a mixture of spin state of 5/2 and 2 corresponding to Fe(III) and Fe(II) ions and also a

complex spin states due to the Fe ions. Applying a linear fit between 150 and 350 K, according to the Curie-Weiss law, a negative Curie-Weiss temperature of -175 K was obtained, indicating a predominant antiferromagnetic exchange interaction between spin carriers below -175 K. The regular decrease of the χT vs T plot from room temperature down to 120 K is a signature of paramagnetic order. A slope change at around 120K may corresponds to the formation of weak short-range ferromagnetic order. More measurements on the electric and thermal properties are suggested to conduct to deeply understand the magnetic and electric structure of the sample.

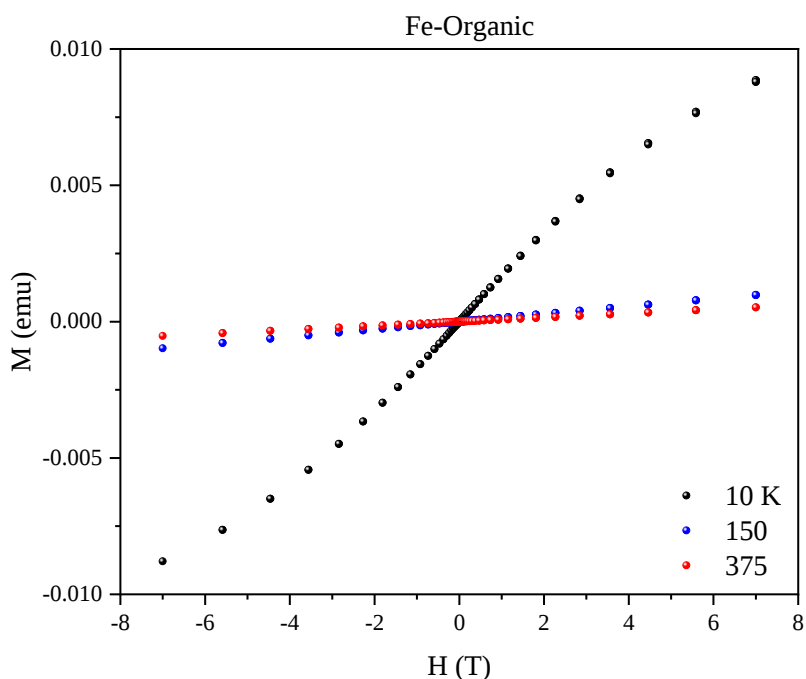


Fig.31 M-H loopos of $Fe_3(BNA)_6O$ at 10 K, 150 K, and 375K, under magnetic fields between -7 T and 7 T.

Figure 31 is Hysteresis loop, M-H curve of complex 2 at T equal to 10K, 150K, 375K, under the external magnetic field ranges from -7T to 7T. As shown by Fig. 31, the M-H curve at 10 K showed “superparamagnetic” behavior, as it has a clear deviation from the linear relation (red dash line). The observed possible superparamagnetic

phenomenon at lower temperature indicates a competition between anisotropy energy, i.e. KV where K is the anisotropy constant and V is the volume, and thermal energy, i.e. $k_B T$ where k_B is the Boltzmann constant and T is temperature of assemblies of small particles, which show magnetization behavior that is qualitatively similar to that of local moment paramagnetic materials, but with a much larger magnetic moment.

CHAPTER V

CONCLUSION

The focus of this thesis was to design and synthesize new coordination polymers using crystal engineering, hydrothermal synthesis, and self-assembly. After the single crystals were successfully obtained, a single crystal was selected for X-ray diffraction analysis. Once the crystal structure was solved successfully, the new coordination polymer were analyzed for their thermal properties using DT/TGA analyzer and FT-IR instrument. The composition of the polymer was analyzed using elemental analysis by Galbraith Laboratories. The magnetic properties were also analyzed using superconducting quantum interference device (SQUID). This thesis reports the design and synthesis of the new coordination polymer $\text{Fe}_3(\text{BNA})_6\text{O}$. This coordination polymer has one chemical formula but two different structures.

The IR analysis confirmed the structure of the ligand exists in the coordination polymer structure. The element analysis confirmed the coordination polymer chemical formula.

The thermal analysis shows that the coordination polymer $\text{Fe}_3(\text{BNA})_6\text{O}$ was stable up to about 375°C . The decomposition process of the polymer is the heat absorbing process. Compared to the copper coordination polymers, the $\text{Fe}_3(\text{BNA})_6\text{O}$ has higher stable temperature. This is likely because the coordination bonds in iron's polymer are stronger than the coordination bonds in the copper's polymer. Future research in the thermal analysis of coordination polymer should be comparing the polymer with same metal and different ligands, or same ligands and different metal.

The magnetic analysis shows the coordination polymer $\text{Fe}_3(\text{BNA})_6\text{O}$ behaves like a typical paramagnet without obvious magnetic anomaly which is sensitive to small magnetic field such as the superconductivity or to say diamagnetism.

Hydrothermal synthesis has developed more than 10 years. With hydrothermal synthesis, many of the fascinating coordination polymers were synthesized. The coordination polymer reported in this thesis research is an example of using hydrothermal synthesis. It allowed the self-assembly process to take place inside the Teflon bomb.

Crystal engineering is the basic step of the coordination polymer synthesis. The overall structure is depending on the choices of the metal and ligand. In this thesis research, iron was chosen as metal center. It provides the six coordinate octahedral structure. The ligand decided the polymer can be the shape of the coordination polymer. In $\text{Fe}_3(\text{BNA})_6\text{O}$, the oxygen and nitrogen were connected to the iron atom. The rotation of along the C-O bond gives two different structure. One of them is a two-dimensional layer structure and the other one is three dimensional cubic structure. The coordination pattern is the same as the crystal engineering predicted.

Coordination chemistry has been developing for more than 20 years. The research of coordination polymer is getting more and more popular including the uses of coordination polymer including gas absorbing, semiconductors, heat resistant, and catalysts. By using the synthesis techniques of crystal engineering, hydrothermal synthesis, and self-assembly, more and more new coordination polymers can be synthesized.

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APPENDIX A

LIST OF COMPOUNDS USED IN THE REACTIONS

List of Compounds Used in Reactions

Compound	Name	FW
CuCl_2	Copper(II)chloride	134.45
CoCl_2	Cobalt(II) chloride	129.839
LaCl_3	Lanthanum chloride	245.26
$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	Iron(II) chloride tetrahydrate	198.81
ZnCl_2	Zinc chloride	136.30
BNA	5-bromonicotinic acid	202.01
BPY	4,4' -Bipyridine	156.18
$\text{C}_6\text{H}_3(\text{CO}_2\text{H})_3$	Trimesic acid	210.14
$\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$	Pyromellitic acid	254.15
CH_3COCH_3	Acetone	58.08
CH_3OH	Methanol	32.04

APPENDIX B



Table 7. crystal data for complex 1

Empirical formula ^a	C ₃₆ H ₁₈ Br ₆ Fe ₃ N ₆ O ₁₃
Space group	P2(1)/c
<i>a</i> (Å)	11.2904(6)
<i>b</i> (Å)	18.4960(11)
<i>c</i> (Å)	21.4349(12)
β (°)	91.029(1)
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.028
Final R indices [<i>I</i> > 4sigma(<i>I</i>)]	R1 = 0.0156, wR2 = 0.0405

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$, $wR_2 = [\Sigma (F_{0^2} - F_{c^2}) / \Sigma w(F_0)^2]^{1/2}$.

Table 8. Selected bond length ($\text{\AA}$) and angles ($^{\circ}\text{C}$) for complex 1

Fe(1)—O(13)	1.8348(13)	Fe(1)—O(6)	2.0099(13)
Fe(1)—O(8)	2.0303(13)	Fe(1)—O(1)	2.0490(13)
Fe(1)—O(3)	2.0554(13)	Fe(1)—N(2)#1	2.2246(16)
Fe(2)—O(13)	1.8455(12)	Fe(2)—O(10)	2.0248(13)
Fe(2)—O(12)	2.0422(13)	Fe(2)—O(2)	2.0616(13)
Fe(2)—O(4)	2.0996(13)	Fe(2)—N(3)#2	2.2221(15)
Fe(3)—O(13)	2.0294(13)	Fe(3)—O(11)	2.0764(13)
Fe(3)—O(7)	2.0771(13)	Fe(3)—O(9)	2.1323(13)
Fe(3)—O(5)	2.1639(13)	Fe(3)—N(1)#3	2.2039(16)
Br(1)—C(4)	1.8876(18)	Br(2)—C(10)	1.894(2)
N(1)—Fe(3)#2	2.2040(16)	N(2)—Fe(1)#1	2.2246(16)
N(3)—Fe(2)#3	2.2220(15)		
O(13)—Fe(1)—O(6)	102.18(5)	O(13)—Fe(1)—O(8)	93.71(5)
O(6)—Fe(1)—O(8)	95.11(5)	O(13)—Fe(1)—O(1)	97.11(5)
O(6)—Fe(1)—O(1)	91.05(5)	O(8)—Fe(1)—O(1)	166.15(5)
O(13)—Fe(1)—O(3)	93.91(5)	O(6)—Fe(1)—O(3)	163.80(5)
O(8)—Fe(1)—O(3)	85.73(5)	O(1)—Fe(1)—O(3)	84.94(5)
O(13)—Fe(1)—N(2)#1	176.55(6)	O(6)—Fe(1)—N(2)#1	80.89(5)
O(8)—Fe(1)—N(2)#1	84.39(5)	O(1)—Fe(1)—N(2)#1	84.36(6)
O(3)—Fe(1)—N(2)#1	83.10(5)	O(13)—Fe(2)—O(10)	100.72(5)
O(13)—Fe(2)—O(12)	95.57(5)	O(10)—Fe(2)—O(12)	90.47(5)
O(13)—Fe(2)—O(2)	93.85(5)	O(10)—Fe(2)—O(2)	165.42(5)
O(12)—Fe(2)—O(2)	87.72(5)	O(13)—Fe(2)—O(4)	93.72(5)
O(10)—Fe(2)—O(4)	89.71(5)	O(12)—Fe(2)—O(4)	170.51(5)
O(2)—Fe(2)—O(4)	89.72(5)	O(13)—Fe(2)—N(3)#2	175.31(6)
O(10)—Fe(2)—N(3)#2	83.96(5)	O(12)—Fe(2)—N(3)#2	84.50(5)
O(2)—Fe(2)—N(3)#2	81.46(5)	O(4)—Fe(2)—N(3)#2	86.09(5)
O(13)—Fe(3)—O(11)	89.90(5)	O(13)—Fe(3)—O(7)	93.13(5)
O(11)—Fe(3)—O(7)	175.97(5)	O(13)—Fe(3)—O(9)	92.46(5)
O(11)—Fe(3)—O(9)	90.66(5)	O(7)—Fe(3)—O(9)	91.87(5)
O(13)—Fe(3)—O(5)	89.36(5)	O(11)—Fe(3)—O(5)	84.68(5)
O(7)—Fe(3)—O(5)	92.70(5)	O(9)—Fe(3)—O(5)	174.99(5)
O(13)—Fe(3)—N(1)#3	176.71(5)	O(11)—Fe(3)—N(1)#3	86.87(5)
O(7)—Fe(3)—N(1)#3	90.06(5)	O(9)—Fe(3)—N(1)#3	88.20(5)
O(5)—Fe(3)—N(1)#3	89.73(5)	C(6)—O(1)—Fe(1)	121.08(12)
C(6)—O(2)—Fe(2)	135.13(12)	C(12)—O(3)—Fe(1)	127.87(12)
C(12)—O(4)—Fe(2)	122.02(12)	C(18)—O(5)—Fe(3)	124.75(11)
C(18)—O(6)—Fe(1)	130.04(12)	C(24)—O(7)—Fe(3)	129.45(12)
C(24)—O(8)—Fe(1)	125.65(12)	C(30)—O(9)—Fe(3)	124.80(12)
C(30)—O(10)—Fe(2)	132.33(12)	C(36)—O(11)—Fe(3)	132.34(12)
C(36)—O(12)—Fe(2)	123.81(12)	Fe(1)—O(13)—Fe(2)	123.69(7)
Fe(1)—O(13)—Fe(3)	117.12(6)	Fe(2)—O(13)—Fe(3)	119.19(6)
C(1)—N(1)—Fe(3)#2	119.07(12)	C(5)—N(1)—Fe(3)#2	121.87(12)
C(7)—N(2)—Fe(1)#1	120.07(12)	C(11)—N(2)—Fe(1)#1	121.31(13)
C(13)—N(3)—Fe(2)#3	121.60(12)	C(17)—N(3)—Fe(2)#3	119.63(12)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 1, -z + 1$; #2 $-x + 1, y + 1/2, -z + 3/2$; #3 $-x + 1, y - 1/2, -z + 3/2$.

Table 9. Crystal data and structure refinement for complex 2.

Empirical formula	C ₃₆ H ₁₈ Br ₆ Fe ₃ N ₆ O ₁₃
Crystal system, space group	Cubic, Pa-3
a (Å)	20.3708(6)
b (Å)	20.3708(6)
c (Å)	20.3708(6)
α (°)	90
β (°)	90
γ (°)	90
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F ²	1.058
Final R indices [I>4σ(I)]	R1 = 0.0178, wR2 = 0.0449

Table 10. Selected bond length (Å) and angles (°C) for complex 2

Fe-O(5)	1.8962(4)	O(5)-Fe-N(2)	174.29(7)
Fe-O(1)	2.0309(19)	O(1)-Fe-N(2)	86.73(8)
Fe-O(3)#1	2.0523(19)	O(3)#1-Fe-N(2)	80.71(8)
Fe-O(2)#2	2.069(2)	O(2)#2-Fe-N(2)	82.84(8)
Fe-O(4)#3	2.1090(19)	O(4)#3-Fe-N(2)	85.75(8)
Fe-N(2)	2.229(2)	C(6)-O(1)-Fe	131.85(18)
Br(1)-C(4)	1.890(3)	C(6)-O(2)-Fe#4	129.09(18)
Br(2)-C(10)	1.887(3)	C(12)-O(3)-Fe#5	136.87(18)
O(1)-C(6)	1.261(3)	C(12)-O(4)-Fe#6	124.28(18)
O(2)-C(6)	1.263(3)	Fe#2-O(5)-Fe#4	119.903(10)
O(2)-Fe#4	2.069(2)	Fe#2-O(5)-Fe	119.903(10)
O(3)-C(12)	1.263(3)	Fe#4-O(5)-Fe	119.903(10)
O(3)-Fe#5	2.0523(19)	C(1)-N(1)-C(5)	116.9(3)
O(4)-C(12)	1.253(3)	C(7)-N(2)-C(11)	118.4(2)
O(4)-Fe#6	2.1091(19)	C(7)-N(2)-Fe	124.94(18)
O(5)-Fe#2	1.8961(4)	C(11)-N(2)-Fe	115.53(18)
O(5)-Fe#4	1.8962(4)	N(1)-C(1)-C(2)	124.0(3)
N(1)-C(1)	1.335(4)	C(1)-C(2)-C(3)	118.3(3)
N(1)-C(5)	1.337(4)	C(1)-C(2)-C(6)	122.3(3)
N(2)-C(7)	1.340(3)	C(3)-C(2)-C(6)	119.3(3)
N(2)-C(11)	1.341(4)	C(4)-C(3)-C(2)	118.0(3)
C(1)-C(2)	1.384(4)	C(3)-C(4)-C(5)	119.7(3)
C(2)-C(3)	1.391(4)	C(3)-C(4)-Br(1)	119.5(2)
C(2)-C(6)	1.496(4)	C(5)-C(4)-Br(1)	120.8(2)

C(3)-C(4)	1.377(4)	N(1)-C(5)-C(4)	122.9(3)
C(4)-C(5)	1.384(5)	O(1)-C(6)-O(2)	126.2(3)
C(7)-C(8)	1.393(4)	O(1)-C(6)-C(2)	116.5(2)
C(8)-C(9)	1.390(4)	O(2)-C(6)-C(2)	117.3(2)
C(8)-C(12)	1.508(4)	N(2)-C(7)-C(8)	122.8(3)
C(9)-C(10)	1.379(4)	C(9)-C(8)-C(7)	118.2(3)
C(10)-C(11)	1.381(4)	C(9)-C(8)-C(12)	119.8(2)
O(5)-Fe-O(1)	98.46(8)	C(7)-C(8)-C(12)	121.9(2)
O(5)-Fe-O(3)#1	94.03(8)	C(10)-C(9)-C(8)	118.7(3)
O(1)-Fe-O(3)#1	167.34(8)	C(11)-C(10)-C(9)	119.7(3)
O(5)-Fe-O(2)#2	95.00(9)	C(11)-C(10)-Br(2)	118.4(2)
O(1)-Fe-O(2)#2	86.85(8)	C(9)-C(10)-Br(2)	121.8(2)
O(3)#1-Fe-O(2)#2	90.01(8)	N(2)-C(11)-C(10)	122.1(3)
O(5)-Fe-O(4)#3	96.61(9)	O(4)-C(12)-O(3)	126.2(3)
O(1)-Fe-O(4)#3	89.62(8)	O(4)-C(12)-C(8)	118.7(2)
O(3)#1-Fe-O(4)#3	91.02(8)	O(3)-C(12)-C(8)	115.0(2)
O(2)#2-Fe-O(4)#3	168.23(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -z+3/2,x-1/2,y; #2 y+1/2,-z+1/2,-x+1

#3 -y+1,-z+1,-x+1; #4 -z+1,x-1/2,-y+1/2

Table 11. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Fe}_3(\text{BNA})_6\text{O}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe	7171(1)	2628(1)	3670(1)	15(1)
Br(1)	4454(1)	3813(1)	5561(1)	36(1)
Br(2)	8694(1)	4785(1)	4708(1)	31(1)
O(1)	6213(1)	2717(1)	3933(1)	22(1)
O(2)	5645(1)	2231(1)	3120(1)	25(1)
O(3)	7642(1)	3596(1)	6825(1)	23(1)
O(4)	6859(1)	2899(1)	6485(1)	20(1)
O(5)	7060(1)	2060(1)	2940(1)	14(1)
N(1)	3913(1)	2439(2)	4176(2)	46(1)
N(2)	7402(1)	3256(1)	4535(1)	17(1)

C(1)	4481(2)	2337(2)	3865(2)	35(1)
C(2)	5070(1)	2622(1)	4045(1)	22(1)
C(3)	5073(2)	3050(1)	4577(1)	24(1)
C(4)	4485(2)	3181(2)	4883(2)	27(1)
C(5)	3921(2)	2864(2)	4677(2)	40(1)
C(6)	5692(1)	2508(1)	3672(1)	18(1)
C(7)	7254(1)	3107(1)	5159(1)	17(1)
C(8)	7528(1)	3435(1)	5692(1)	17(1)
C(9)	7980(1)	3932(1)	5568(1)	19(1)
C(10)	8113(1)	4097(1)	4926(1)	19(1)
C(11)	7818(1)	3753(1)	4422(1)	18(1)
C(12)	7326(1)	3288(1)	6389(1)	17(1)

Table 12. Bond lengths [Å] and angles [deg] for Fe₃(BNA)₆O .

Fe-O(5)	1.8962(4)
Fe-O(1)	2.0309(19)
Fe-O(3)#1	2.0523(19)
Fe-O(2)#2	2.069(2)
Fe-O(4)#3	2.1090(19)
Fe-N(2)	2.229(2)
Br(1)-C(4)	1.890(3)
Br(2)-C(10)	1.887(3)
O(1)-C(6)	1.261(3)
O(2)-C(6)	1.263(3)
O(2)-Fe#4	2.069(2)
O(3)-C(12)	1.263(3)
O(3)-Fe#5	2.0523(19)
O(4)-C(12)	1.253(3)
O(4)-Fe#6	2.1091(19)
O(5)-Fe#2	1.8961(4)
O(5)-Fe#4	1.8962(4)
N(1)-C(1)	1.335(4)
N(1)-C(5)	1.337(4)
N(2)-C(7)	1.340(3)
N(2)-C(11)	1.341(4)
C(1)-C(2)	1.384(4)
C(2)-C(3)	1.391(4)
C(2)-C(6)	1.496(4)
C(3)-C(4)	1.377(4)

C(4)-C(5)	1.384(5)
C(7)-C(8)	1.393(4)
C(8)-C(9)	1.390(4)
C(8)-C(12)	1.508(4)
C(9)-C(10)	1.379(4)
C(10)-C(11)	1.381(4)
O(5)-Fe-O(1)	98.46(8)
O(5)-Fe-O(3)#1	94.03(8)
O(1)-Fe-O(3)#1	167.34(8)
O(5)-Fe-O(2)#2	95.00(9)
O(1)-Fe-O(2)#2	86.85(8)
O(3)#1-Fe-O(2)#2	90.01(8)
O(5)-Fe-O(4)#3	96.61(9)
O(1)-Fe-O(4)#3	89.62(8)
O(3)#1-Fe-O(4)#3	91.02(8)
O(2)#2-Fe-O(4)#3	168.23(8)
O(5)-Fe-N(2)	174.29(7)
O(1)-Fe-N(2)	86.73(8)
O(3)#1-Fe-N(2)	80.71(8)
O(2)#2-Fe-N(2)	82.84(8)
O(4)#3-Fe-N(2)	85.75(8)
C(6)-O(1)-Fe	131.85(18)
C(6)-O(2)-Fe#4	129.09(18)
C(12)-O(3)-Fe#5	136.87(18)
C(12)-O(4)-Fe#6	124.28(18)
Fe#2-O(5)-Fe#4	119.903(10)
Fe#2-O(5)-Fe	119.903(10)
Fe#4-O(5)-Fe	119.903(10)
C(1)-N(1)-C(5)	116.9(3)
C(7)-N(2)-C(11)	118.4(2)
C(7)-N(2)-Fe	124.94(18)
C(11)-N(2)-Fe	115.53(18)
N(1)-C(1)-C(2)	124.0(3)
C(1)-C(2)-C(3)	118.3(3)
C(1)-C(2)-C(6)	122.3(3)
C(3)-C(2)-C(6)	119.3(3)
C(4)-C(3)-C(2)	118.0(3)
C(3)-C(4)-C(5)	119.7(3)
C(3)-C(4)-Br(1)	119.5(2)
C(5)-C(4)-Br(1)	120.8(2)
N(1)-C(5)-C(4)	122.9(3)
O(1)-C(6)-O(2)	126.2(3)
O(1)-C(6)-C(2)	116.5(2)

O(2)-C(6)-C(2)	117.3(2)
N(2)-C(7)-C(8)	122.8(3)
C(9)-C(8)-C(7)	118.2(3)
C(9)-C(8)-C(12)	119.8(2)
C(7)-C(8)-C(12)	121.9(2)
C(10)-C(9)-C(8)	118.7(3)
C(11)-C(10)-C(9)	119.7(3)
C(11)-C(10)-Br(2)	118.4(2)
C(9)-C(10)-Br(2)	121.8(2)
N(2)-C(11)-C(10)	122.1(3)
O(4)-C(12)-O(3)	126.2(3)
O(4)-C(12)-C(8)	118.7(2)
O(3)-C(12)-C(8)	115.0(2)

Symmetry transformations used to generate equivalent atoms:

#1 -z+3/2, x-1/2, y #2 y+1/2, -z+1/2, -x+1

#3 -y+1, -z+1, -x+1 #4 -z+1, x-1/2, -y+1/2

#5 y+1/2, z, -x+3/2 #6 -z+1, -x+1, -y+1

*Table 13. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Fe}_3(\text{BNA})_6\text{O}$. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$*

	U11	U22	U33	U23	U13	U12
Fe	14(1)	16(1)	15(1)	-1(1)	0(1)	0(1)
Br(1)	39(1)	37(1)	31(1)	-3(1)	9(1)	13(1)
Br(2)	32(1)	28(1)	32(1)	3(1)	3(1)	-13(1)
O(1)	16(1)	27(1)	24(1)	-6(1)	2(1)	1(1)
O(2)	18(1)	34(1)	24(1)	-7(1)	-1(1)	-3(1)
O(3)	28(1)	26(1)	13(1)	-2(1)	0(1)	-11(1)
O(4)	20(1)	21(1)	18(1)	0(1)	1(1)	-7(1)

O(5)	14(1)	14(1)	14(1)	-1(1)	-1(1)	1(1)
N(1)	25(2)	52(2)	63(2)	-13(2)	13(2)	-8(1)
N(2)	16(1)	20(1)	17(1)	-4(1)	0(1)	1(1)
C(1)	21(2)	38(2)	46(2)	-11(2)	7(2)	-5(2)
C(2)	24(2)	19(2)	24(2)	2(1)	6(1)	1(1)
C(3)	22(2)	23(2)	26(2)	6(1)	3(1)	3(1)
C(4)	29(2)	24(2)	27(2)	4(1)	10(1)	8(1)
C(5)	24(2)	45(2)	52(2)	-2(2)	16(2)	0(2)
C(6)	17(2)	15(1)	23(2)	4(1)	2(1)	2(1)
C(7)	16(2)	18(2)	18(2)	-2(1)	2(1)	-1(1)
C(8)	17(2)	18(2)	15(1)	-2(1)	1(1)	2(1)
C(9)	20(2)	20(2)	18(2)	-3(1)	-1(1)	-1(1)
C(10)	16(2)	18(2)	23(2)	0(1)	2(1)	-3(1)
C(11)	19(2)	19(2)	17(2)	2(1)	1(1)	2(1)
C(12)	19(2)	15(1)	17(2)	0(1)	1(1)	4(1)

Table 14. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Fe}_3(\text{BNA})_6\text{O}$.

	x	y	z	U(eq)
H(1)	4480	2053	3501	42
H(3)	5465	3245	4723	28
H(5)	3526	2951	4898	48
H(7)	6952	2768	5239	21
H(9)	8190	4151	5916	23
H(11)	7912	3871	3985	22

Table 15. Torsion angles [deg] for Fe₃(BNA)₆O .

O(5)-Fe-O(1)-C(6)	-4.9(3)
O(3)#1-Fe-O(1)-C(6)	-175.4(3)
O(2)#2-Fe-O(1)-C(6)	-99.5(2)
O(4)#3-Fe-O(1)-C(6)	91.7(3)
N(2)-Fe-O(1)-C(6)	177.5(3)
O(1)-Fe-O(5)-Fe#2	-135.76(16)
O(3)#1-Fe-O(5)-Fe#2	42.15(18)
O(2)#2-Fe-O(5)-Fe#2	-48.21(18)
O(4)#3-Fe-O(5)-Fe#2	133.65(16)
O(1)-Fe-O(5)-Fe#4	38.04(18)
O(3)#1-Fe-O(5)-Fe#4	-144.05(17)
O(2)#2-Fe-O(5)-Fe#4	125.59(17)
O(4)#3-Fe-O(5)-Fe#4	-52.56(18)
O(1)-Fe-N(2)-C(7)	59.6(2)
O(3)#1-Fe-N(2)-C(7)	-118.8(2)
O(2)#2-Fe-N(2)-C(7)	-27.6(2)
O(4)#3-Fe-N(2)-C(7)	149.5(2)
O(1)-Fe-N(2)-C(11)	-132.6(2)
O(3)#1-Fe-N(2)-C(11)	49.03(19)
O(2)#2-Fe-N(2)-C(11)	140.2(2)
O(4)#3-Fe-N(2)-C(11)	-42.69(19)
C(5)-N(1)-C(1)-C(2)	2.5(6)
N(1)-C(1)-C(2)-C(3)	-1.1(5)
N(1)-C(1)-C(2)-C(6)	-178.3(3)
C(1)-C(2)-C(3)-C(4)	-1.7(4)
C(6)-C(2)-C(3)-C(4)	175.6(3)
C(2)-C(3)-C(4)-C(5)	2.9(4)
C(2)-C(3)-C(4)-Br(1)	-174.9(2)
C(1)-N(1)-C(5)-C(4)	-1.2(6)
C(3)-C(4)-C(5)-N(1)	-1.5(5)
Br(1)-C(4)-C(5)-N(1)	176.3(3)
Fe-O(1)-C(6)-O(2)	-7.6(4)
Fe-O(1)-C(6)-Cf(2)	174.59(18)
Fe#4-O(2)-C(6)-O(1)	-12.9(4)
Fe#4-O(2)-C(6)-C(2)	164.92(18)
C(1)-C(2)-C(6)-O(1)	-170.3(3)
C(3)-C(2)-C(6)-O(1)	12.5(4)
C(1)-C(2)-C(6)-O(2)	11.6(4)
C(3)-C(2)-C(6)-O(2)	-165.6(3)
C(11)-N(2)-C(7)-C(8)	-1.9(4)

Fe-N(2)-C(7)-C(8)	165.6(2)
N(2)-C(7)-C(8)-C(9)	-0.7(4)
N(2)-C(7)-C(8)-C(12)	176.3(2)
C(7)-C(8)-C(9)-C(10)	2.9(4)
C(12)-C(8)-C(9)-C(10)	-174.2(3)
C(8)-C(9)-C(10)-C(11)	-2.5(4)
C(8)-C(9)-C(10)-Br(2)	177.6(2)
C(7)-N(2)-C(11)-C(10)	2.4(4)
Fe-N(2)-C(11)-C(10)	-166.2(2)
C(9)-C(10)-C(11)-N(2)	-0.2(4)
Br(2)-C(10)-C(11)-N(2)	179.7(2)
Fe#6-O(4)-C(12)-O(3)	15.6(4)
Fe#6-O(4)-C(12)-C(8)	-162.03(18)
Fe#5-O(3)-C(12)-O(4)	0.2(5)
Fe#5-O(3)-C(12)-C(8)	177.88(18)
C(9)-C(8)-C(12)-O(4)	171.0(3)
C(7)-C(8)-C(12)-O(4)	-6.0(4)
C(9)-C(8)-C(12)-O(3)	-6.8(4)
C(7)-C(8)-C(12)-O(3)	176.1(3)

Symmetry transformations used to generate equivalent atoms:

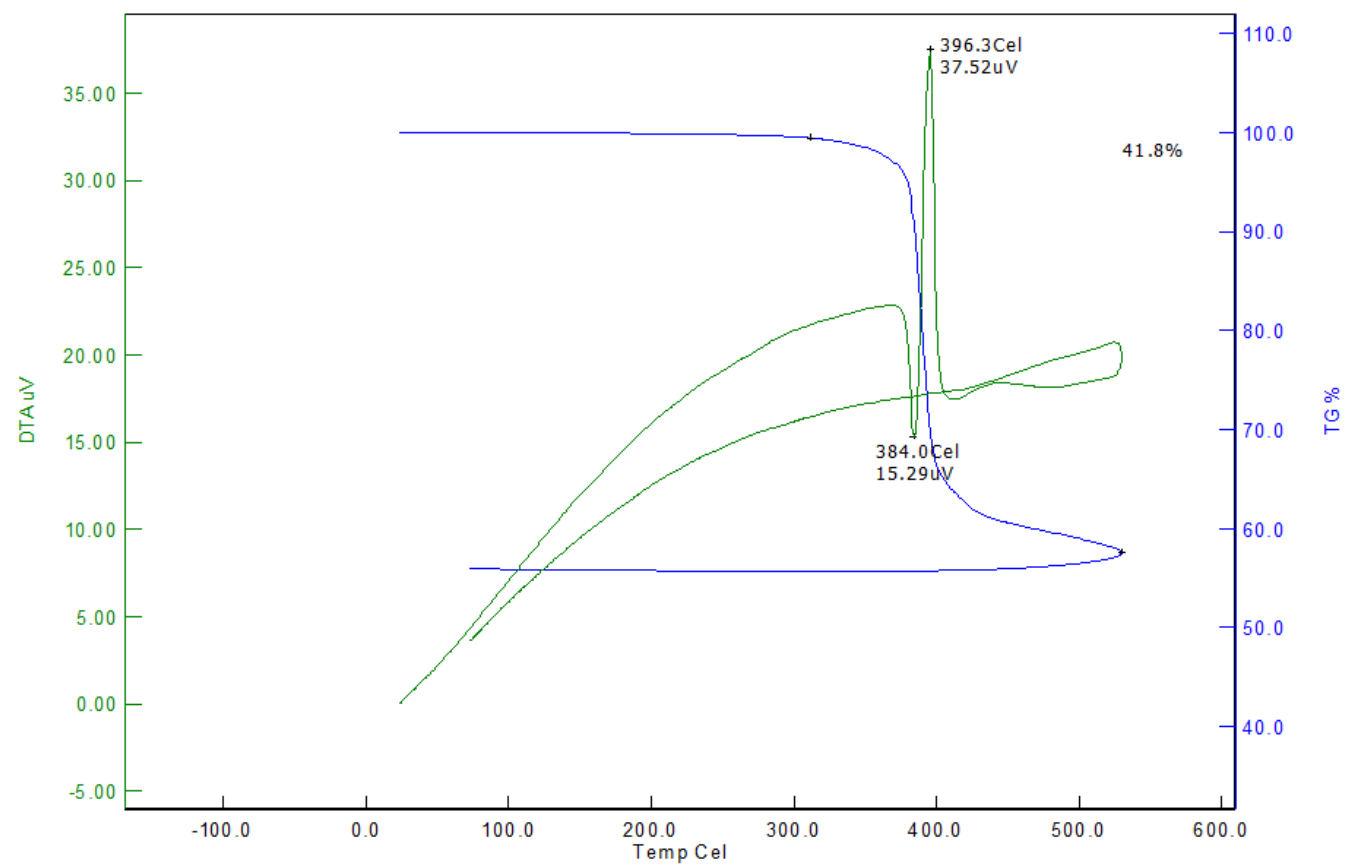
#1 $-z+3/2, x-1/2, y$ #2 $y+1/2, -z+1/2, -x+1$
 #3 $-y+1, -z+1, -x+1$ #4 $-z+1, x-1/2, -y+1/2$
 #5 $y+1/2, z, -x+3/2$ #6 $-z+1, -x+1, -y+1$

Module: TG/DTA
Data Name: Lei2
Measurement Date: 11/16/2018
Sample Name: Lei2
Sample Weight: 8.955 mg
Reference Name: Pt
Reference Weight: 0.000 mg

Temperature Program:

	Cell	Cell	Cell/min	min	s
1*	24	600	10	1	0.5
2*	600	25	10	0	0.5

Comment:
Operator: Administrator
Gas1: N2
Pan: Pt



Laboratory Report

Report prepared for:

Lei Fu
University of Houston
Clear Lake

Phone:

Email:

Report prepared by:

Mary Norris

Purchase Order:**For further assistance, contact:**

Mary Norris

Sample: Black Solid Crystals**Lab ID:** 2018-H-5649**Received:** 2018-10-30

Analysis	Method	Result	Basis	Sample Amount Used	Date (Time)
<i>C : Carbon</i>					
	GLI Procedure ME-14	30.7 %	As Received	1.057 mg	2018-11-02
<i>Fe : Iron</i>					
	GLI Procedure ME-70	12.0 %	As Received	22.27 mg	2018-11-08
<i>H : Hydrogen</i>					
	GLI Procedure ME-14	0.88 %	As Received	1.057 mg	2018-11-02
<i>N : Nitrogen</i>					
	GLI Procedure ME-14	5.8 %	As Received	1.057 mg	2018-11-02

Signatures:

Published By: Mary Norris

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Magnetic Properties Measurement

