MAGNETISM IN A NUMBER OF METAL ORGANIC FRAMEWORKS (MOFs) WITH 1D AND 3D CHARACTERISTICS: AN EXPERIMENTAL AND ANALYTICAL STUDY

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ABSTRACT

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By Youcef Hamida
Doctor of Philosophy
Temple University, 2012
Thesis Advisor: Dr. Tan Yuen

Metal Organic Frameworks (MOFs) exhibit many excellent physical properties including magnetic properties for potential applications in devices. More importantly for the subject of this thesis, MOFs are ideal for the realization of low dimensional magnetism because of the large selection of ligands connecting magnetic centers in making the framework.

The materials studied in this thesis include ten magnetic MOFs of the form $M(L_1)(L_2)$ [$M = \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}; L_1 = \text{NDC, bpdc, BDC, BODC, N}_3; L_2 = \text{DMF, H}_2\text{O, TED, bpy}$]. Polycrystalline powder samples as well as single crystal samples were synthesized. Their crystal structures were determined, and their magnetic and thermodynamic properties were measured and analyzed. Eight of these materials were characterized as 1D magnets and two as 3D magnets.
In the 1D case it is found that above $T_m$ [the temperature at which the magnetic susceptibility $\chi(T)$ has a peak] the magnetic behavior of MOFs ($S \geq 1$) can be well described with the Classical Fisher Model (CFM). Near and below $T_C$ the spins take a more definite orientation than allowed for in the CFM and hence the Ising Model (IM) was used for fitting. Both CFM and IM yield fairly consistent intrachain couplings ($J$) when applied in their appropriate temperature region. To estimate the interchain exchange ($J'$), the susceptibility for a magnetic chain in the mean field of neighboring chains is used. In all cases, as expected, the ratio of $J$ to $J'$ was less than 10%. The special case of Cu(N$_3$)$_2$bpy ($S = \frac{1}{2}$) was analyzed with the spin $\frac{1}{2}$ IM.

Although the specific heat data ($C_{total}$) for most of the 1D MOFs showed no clear phase transition, a low temperature fit to the electron-phonon specific heats yielded apparent heavy fermion-like $\gamma$ values on the order of several hundred mJ/mol K$^2$. The lattice specific heat ($C_{lattice}$) was estimated using a Debye-Einstein hybrid model. Subtracting $C_{lattice}$ from $C_{total}$, magnetic specific heat ($C_M$) with a broad peak characteristic of low dimensional magnetism was obtained. The peak in $C_M$ was at temperature near that expected from $\chi(T)$ fits. The $J$ values obtained from the magnetic specific heat fits were in good agreement with those obtained from $\chi(T)$ fits. Once the magnetic specific heat was accounted for, $\gamma$ takes values in the expected range of few mJ/mol K$^2$.

For 3D MOFs [Mn(N$_3$)$_2$bpy and Fe(N$_3$)$_2$bpy], the existence of long range canted antiferromagnetic ordering was observed in both magnetic and specific heat measurements with phase transitions at 38 K and 20 K in the case of Mn(N$_3$)$_2$bpy and
Fe(N$_3)_2$bpy, respectively. These transition temperatures are considered fairly high for molecular based materials. In both Mn(N$_3)_2$bpy and Fe(N$_3)_2$bpy, the $\chi(T)$ data fit well to the Heisenberg model for a diamond-type network. The transition can clearly be seen with an abrupt increase in the magnetization below $T_C$ and a shift to a higher temperature in the specific heat when measured under an applied magnetic field.

The systematic approach in this work led to the successful estimate of $C_{\text{lattice}}$ resulting in meaningful fitting of $\chi(T)$ and $C_{\text{magnetic}}$ to the appropriate theoretical models in magnetism. It also led the discovery of ferrimagnets or canted antiferromagnets M(N$_3)_2$bpy with large coercivity and rather high transition temperature. The results of this study have been published in three articles in the Journal of Applied physics, and two manuscripts are under preparation for submission [1-5].
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Since everyone I interacted with at Temple University has in principle made a contribution to my development as a physics graduate student, it would be virtually impossible to thank everyone in person. To an excellent approximation I will restrict myself to nearest neighbor interactions and thank those with whom I interacted with most directly.

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To all my teachers: kindergarten to graduate school.
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CHAPTER 1

INTRODUCTION

The study of magnetism is important in its own right. A changing magnetic field induces an electric field (Faraday’s law) and a changing electric field induces a magnetic field (Ampere’s law with Maxwell’s correction). Maxwell’s equations provide a not only a self-consistent theory but also a theory already in agreement with Einstein’s theory of relativity; the fact that electricity and magnetism are two faces of the same coin is a consequence of the internal agreement of Maxwell’s equations with relativity. In fact, as Edward Purcell had shown, given electrostatics, charge invariance, and relativity, the existence of magnetism is necessary; Purcell used arguments on how the charge density of a line of charge changes when viewed from the rest frame of the line of charge or the rest frame of a test charge in motion relative to the line of charge [6]. Since our first encounter with magnetism is usually with a bar magnet, it is natural to search for an explanation of why some materials are magnetic while some are not. Explaining magnetism exhibited by magnetic materials is inseparable from quantum mechanics.

After the formulation of quantum mechanics, it became possible to explain the origin of magnetism at the micro-scale level. However, this microscopic magnetism
doesn’t explain the phenomenon of spin-spin interactions and spontaneous magnetic ordering in bulk materials. To answer the question of why magnetic ordering happens one is faces the problem of solving a Hamiltonian in 3D for an Avogadro’s number of interacting spins. Such a Hamiltonian is simply too difficult to solve. A solution to the two dimensional (2D) Ising Model by Lars Onsager (1944) is considered to be “one of the outstanding achievements of twentieth century statistical physics” [7].

In this thesis, attention is devoted to magnetic Metal Organic Frameworks (MOFs). In these MOFs magnetic centers (M) are linked via a ligand L in each direction giving rise to a general structure of \(M(L_1)(L_2)(L_3)\). We denote the magnitude of the exchange parameter \((J_i, i = 1, 2, 3)\) along \(L_1\), \(L_2\), and \(L_3\), by \(J_1\), \(J_2\), and \(J_3\) respectively. If \(J_1 \gg J_2 \sim J_3\), we say that we have a 1D system; if \(J_1 \sim J_2 \gg J_3\), the system is 2D. Finally, if \(J_1 \sim J_2 \sim J_3\), the system is considered 3D. The study of magnetism in 1D and 2D systems is called low dimensional magnetism. In 1D, the system is treated as parallel chains of M–L–M. Even with this simplification the problem is tremendously difficult to solve analytically and further simplifications are needed, such as Heisenberg and Ising spin chains.

1D magnetism, the main subject of this thesis, is a microscopic approach to understanding the magnetic and thermodynamic properties of materials macroscopically. First, Wilhelm Lenz (1920) formulated what has come to be known as the Ising Model (IM) in order to have a microscopic explanation to Weiss’s macroscopic mean field theory (MFT) of magnetism [8]. Ernst Ising (student of Lenz) solved the problem in 1D in 1925 [9]. The 1D Ising Model (with the exchange interaction chosen by Ising) does
not exhibit a spontaneous phase transition, and thus falls short in explaining spontaneous magnetic ordering seen in materials like hard magnets below a certain temperature. Lars Onsager (1944) found an exact solution to the IM in a 2D square lattice which does show spontaneous long range order below a certain characteristic temperature [10]. By 1966 N. D. Mermin and H. Wagner have shown that an isotropic model in 1D and 2D can’t exhibit long range order at temperatures above absolute zero [11]. Notice that the 1D and 2D IMs are not isotropic since the spins are confined to point along a certain axis. From a mathematical perspective, a magnetic phase transition can exist even in a 1D IM with the right choice of the exchange parameter [12].

The study of low dimensional magnetism is not only of theoretical interest but it is directly applicable to explaining the magnetic behaviors of bulk materials. The discovery of high $T_C$ superconductors in the 1980s was a natural impetus to the field of magnetism in general because of the intimate relationship between superconductivity and magnetic fluctuations. Today, 1D magnetism has become a vast field on its own and materials with 1D magnetism provided a playground for testing a number of theoretical and computational techniques [13]. The theoretical methods that can and were applied in the field of 1D magnetism include

i. Many body theory (e.g. Holstein-Pimakoff transformation of the ferromagnetic Heisenberg Hamiltonian) [14]

ii. Quantum Field Theory methods (e.g. Bosonization) [15]

iii. Density matrix renormalization [16]
iv. Mapping of the Heisenberg spin ladder to a nonlinear $\sigma$ model [17], and Quantum Monte-Carlo [18].

Although the interest in magnetic MOFs (ideal for constructing low dimensional magnetic systems) was mainly theoretical for several decades, it has found way to potential applications. Researchers are always looking for novel materials with single or multiple properties such as ferromagnetism, superconductivity, and porosity for possible device applications. Studies on MOFs provide a neat junction at which both theorists and experimentalists meet. Perhaps the first MOF made can be traced back to 1965 MOF when E. Tomic published his “Thermal Stability of Coordination Polymers” [19, 20]. The subject didn’t gain much momentum until Professor O. Yaghi of UCLA and his group resurrected it with their publication of a novel $\text{Zn}_4\text{O(BDC)}_3\text{(DMF)}_8\text{(C}_6\text{H}_5\text{Cl)}$, called it MOF-5 [21]. Ever since, the subject expanded exponentially. The many excellent properties and possible device applications of Metal Organic Frameworks (MOFs) include:

i. **Interesting magnetic properties:** MOFs exhibit magnetic ordering including at relatively high temperatures [3, 22-24].

ii. **Purification:** when a gas of interest (e.g. natural gas) has traces of other impurities (e.g. tetrahydrothiophene (THT)) that need to be removed or limited to parts per million or even less [25].

iii. **Separation:** this technique is needed to separate one gas from a mixture of gases of about the same concentration. The advantage of using MOFs is due to the different of pore sizes each of them possesses [26, 27].
iv. **Gas storage:** in today’s rush for finding ‘green’ and renewable sources of energy, hydrogen gas and methane are promising. Although high pressure tanks are the most common means for storing these gases in a motor vehicle, they raise safety concerns for potential explosions and accordingly stiffer standards were introduced by the US Department of Energy (DOE) [28]. An alternative mean to provide such storage seems to be porous MOFs since the pores are accessible leaving no room for dead volume which increases their capacity for gas storage [29-32]. S. Ma and H.-C. Zhou demonstrated that over twenty porous MOFs meet and even exceed regulations made by the US DOE when it comes to the storage of hydrogen and methane gases at the cryogenic temperature of 77 K [33]. Although cryogenic temperatures are not very practical for immediate use, new materials and methods are very much underway towards practical gas storage in porous MOFs at room temperatures and reasonable pressures [34].

v. **Heterogeneous catalysis:** typically a catalyst must have uniform shape and size. Porous MOFs provide just that because of their highly ordered pores uniform channels specific to each MOF [19, 35, 36].

vi. **Relatively easy and inexpensive to make:** the synthesis of MOFs typically involves a salt (usually metal sulfates, nitrates, or acetates) as a source for the metal center (e.g. Cu, Co, Zn, etc) mixed with an organic material (typically mono-, di-, tri-, and tetra-carboxylic acids), stirred, and then baked at temperatures of about 200 °C [19].
vii. *Highest known surface areas*: until recently zeolites were thought to have the highest surface area with an upper limit of about 2030 m$^2$/g [37]. Almost every MOF has easily exceeded this record with [Zn$_4$O(bpdc)$_2$]$_n$ exhibiting a surface area of about 5640 m$^2$/g [31, 38, 39].

viii. *Control over ligand lengths*. Because ligands linking the magnetic centers can be chosen to be long or short [24].

Given the opportunities that MOFs provide for studying fundamental physics and some of their industrial applications listed above, the interest in MOFs is no longer a mystery. The number of research papers concerning MOFs grew exponentially in the past two decades, jumping from only about 200 published papers in 1986 to almost 4000 papers in the year of 2006 [40]. In the same reference the authors report that the number of newly invented MOFs has been doubling every 3.6 years since 1980.

MOFs are ideal for constructing low dimensional magnetic systems for several reasons. The large number of ligand choices available make control over the dimensionality of the system possible [24]. For example, to construct a 1D system, magnetic centers are connected via a short ligand in one direction while the connection in the other two directions is made with a long ligand (e.g. bpy). In this thesis several families of magnetic MOFs were studied. The ligands used include: azide (N$_3$), the bipyridine (bpy), TED, BDC, DMF, NDC, and BPDC.

This thesis is mainly devoted to the measurement and analysis of the magnetic and thermodynamic properties of a number of magnetic MOFs (MMOFs). The materials
presented in this work are of two types. The first is on the topic of 1D magnetism. These materials can be listed as

a. Co(NDC)(DMF)
b. [M(bpdc)(H$_2$O)$_2$].H$_2$O [Co, Zn]
c. M(N$_3$)$_2$(bpy) [M = Fe, Co, Ni, Cu]
d. Ni$_2$(BODC)$_2$(TED)
e. Ni$_2$(BDC)$_2$(TED)

The second type [M(N$_3$)$_2$(bpy) (with M = Mn, Fe)] are interesting 3D magnets that exhibit a second order phase transition at a high transition temperature. In addition to the considerably high $T_C$ temperature, they also have hysteresis and hard magnet coercivity.

Today, research in the field of magnetism and magnetic interactions continues to be live and active. MMOFs are important on both theoretical and experimental grounds. 1D MMOFs are a testing ground for the various magnetic chain models and statistical mechanics applications. Porous MOFs, in addition to their interesting magnetic properties, are the most promising when it comes to the immediate applications to gas storage. 3D MOFs, like our Mn(N$_3$)$_2$bpy, though more complicated to theoretically model their magnetic behavior, have very interesting magnetic properties including high ordering temperatures and hysteresis; these properties give them potential for industrial applications.

The subject of subsequent chapters is as follows. In CHAPTER 2, the basic definitions of quantities measured and terminology used are reviewed; a theoretical
background to the various models used is also introduced. The experimental methods
including sample synthesis, preparation, structure determination, and magnetic and
thermodynamic measurements are introduced in CHAPTER 3. Results of sample crystal
structure and analysis of magnetic and thermodynamic data are found in CHAPTER 4.
In CHAPTER 5 a summary and concluding remarks are given.
CHAPTER 2

REVIEW AND THEORETICAL BACKGROUND

2.1 UNITS AND DEFINITIONS

*Magnetic Moment* ($\vec{\mu}$): A current loop of current $I$ area $\vec{S}$ will generate a magnetic moment (Figure 2-1)

$$\vec{\mu} = I \vec{S}$$

*Figure 2-1* Magnetic moment due to a current loop.

As a result, the moment will have the SI units of Am$^2$ [or Joules/Tesla (J/T)]. In emu-ecgs the units are erg/G ($1T = 10^4 G$). The conversion factor between the two units is

$$1 \text{ erg/G} = 10^{-3} \text{ Am}^2.$$

*Magnetization* $M(H)$: at $T = 0$, the magnetization of a quantum mechanical system of volume $V$ in a uniform magnetic field $H$ is defined to be
\[ M(H) = -\frac{1}{V} \frac{\partial E_0(H)}{\partial H}. \]

\( E_0(H) \) is the ground state energy in the presence of \( H \).

\textit{Magnetic Susceptibility (\( \chi \))}: the magnetic susceptibility per unit of volume is defined as

\[ \chi = \frac{\partial M}{\partial H} = -\frac{1}{V} \frac{\partial^2 F}{\partial H^2}. \]

where \( F \) is the usual free energy as defined in thermodynamics. Magnetic susceptibility can be positive or negative depending on the atom or material. If the susceptibility is positive the material is called paramagnetic and if \( \chi \) is negative it is called diamagnetic.

Fundamental constants along with their units are listed in Table 1.
### Table 1  Fundamental constants and units.

<table>
<thead>
<tr>
<th></th>
<th>SI</th>
<th>Gaussian (cgs-emu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elementary charge (e)</td>
<td>(1.602 \times 10^{-19} \text{C} )</td>
<td>(4.803 \times 10^{-10} \text{statC(or or }} \frac{\text{erg}}{\text{cm}^{1/2}})</td>
</tr>
<tr>
<td>Planck’s Constant (h)</td>
<td>(6.626 \times 10^{-34} \text{J s} )</td>
<td>(6.626 \times 10^{-27} \text{erg s} )</td>
</tr>
<tr>
<td>Speed of Light (c)</td>
<td>(2.998 \times 10^{8} \text{ m/s} )</td>
<td>(2.998 \times 10^{10} \text{ cm/s} )</td>
</tr>
<tr>
<td>Permittivity of Free Space (\varepsilon_0)</td>
<td>(8.854 \times 10^{-12} \text{ C}^2 \text{N}^{-1} \text{m}^{-2} )</td>
<td>(1 )</td>
</tr>
<tr>
<td>Permeability of Free Space (\mu_0)</td>
<td>(4\pi \times 10^{-7} \text{ NA}^{-2} )</td>
<td>(1 )</td>
</tr>
<tr>
<td>Boltzmann Constant (k_B)</td>
<td>(1.381 \times 10^{-23} \text{ J/K} )</td>
<td>(1.381 \times 10^{-16} \text{ erg/K} )</td>
</tr>
<tr>
<td>Bohr Magneton (\mu_B)</td>
<td>(9.274 \times 10^{-24} \text{ J/T} )</td>
<td>(9.274 \times 10^{-21} \text{ erg/G (or emu)} )</td>
</tr>
<tr>
<td>Avogadro’s Number (N_A)</td>
<td>(6.022 \times 10^{23} \text{ mol}^{-1} )</td>
<td>(6.022 \times 10^{25} \text{ 1/mol} )</td>
</tr>
<tr>
<td>Fine Structure Constant (\alpha)</td>
<td>(\frac{e^2}{4\pi\varepsilon_0\eta c} \approx \frac{1}{137.036} )</td>
<td>(\frac{e^2}{\eta c} \approx \frac{1}{137.036} )</td>
</tr>
<tr>
<td>Molar Magnetic Susceptibility (\chi)</td>
<td>(\text{m}^3/\text{mol} )</td>
<td>(\text{cm}^3/\text{mol (or emu/mol)} )</td>
</tr>
<tr>
<td>(N_A\mu_B^2/\kappa_B)</td>
<td>(3.750 \text{ J K/mol T}^2 )</td>
<td>(0.375 \text{ emu K/mol} )</td>
</tr>
</tbody>
</table>
By applying the Euler-Lagrange equations, it is easy to verify that the Lagrangian for a charged particle of mass $m$ and charge $Q$ in a magnetic field $B$ is given by

$$L = \frac{m}{2} \dot{q}^2 - Q\phi + \frac{Q}{c} \dot{q} \cdot \vec{A}$$

with $\phi$ and $\vec{A}$ being the scalar and vector potentials respectively. By definition,

$$p_i = \frac{\partial L}{\partial \dot{q}_i} = m\dot{q} + \frac{Q}{c} A_i; \text{ therefore, } \vec{p} = m\vec{\dot{q}} + \frac{Q}{c} \vec{A}$$

This is the new momentum. The first term on the right is the ‘old’ momentum. Hence,

$$\vec{p}_{\text{old}} = \vec{p}_{\text{new}} - \frac{Q}{c} \vec{A}.$$  Meanwhile, the Hamiltonian is given by

$$H \equiv \vec{p} \cdot \vec{\dot{q}} - L = \frac{1}{2m} \left( \vec{p} - \frac{Q}{c} \vec{A} \right)^2 + Q\phi,$$

Where, of course, $\vec{p}'$ is $\vec{p}_{\text{new}}$.

We now look at how the presence of a magnetic field affects the Hamiltonian of an atom.

1. Before the application of a magnetic field, kinetic energy of electrons is given by

$$T_0 = \sum_i \frac{p_i^2}{2m}$$
In the presence of a magnetic field, each momentum is changed to \( P_i \rightarrow P_i + e \rho A(r_i) \)

Working in the gauge where
\[
\rho A = -\frac{1}{2} \rho \times H, \text{ both } (\hat{H} = \nabla \times \hat{A} \text{ and } \nabla \cdot \hat{A} = 0) \text{ are satisfied.}
\]

The resulting kinetic energy is then,
\[
T = T_0 + \mu_B (\hat{P} \cdot \hat{H} + \frac{e^2 \hat{H}^2}{8mc^2} \sum_i (x_i^2 + y_i^2)) + \eta \rho L = \sum_i \hat{P} \times \hat{P}_i.
\]

2. The interaction energy of the field with each electron spin \( \hat{S} \) is given by
\[
\Delta H = g_0 \mu_B H \sum_i s_z = g_0 \mu_B HS_z
\]

Where \( \mu_B = \frac{e \hbar}{2mc} = 9.274 \times 10^{-21} \text{erg/G (Bohr magneton)} \) and \( g_0 \) is the Landé g-factor.

The change in the Hamiltonian therefore is
\[
\Delta H = \mu_B (\hat{L} + g_0 \hat{S}) \cdot \hat{H} + \frac{e^2 \hat{H}^2}{8mc^2} \sum_i (x_i^2 + y_i^2)
\]

Using second order perturbation theory and only keeping terms quadratic in \( H \), we obtain
\[
\Delta E_n = \mu_B \hat{H} \cdot \langle n | \hat{L} + g_0 \hat{S} | n \rangle + \sum_{n \neq n} \frac{|n| \mu_B \hat{H} \cdot (\hat{L} + g_0 \hat{S}) |n'|^2}{E_n - E_{n'}} + \frac{e^2 \hat{H}^2}{8mc^2} \sum_i (x_i^2 + y_i^2) \langle n | n \rangle (2-1).
\]

This equation is the basis for the theory of magnetic susceptibility of atoms, ions, and molecules [41].
2.3 DIAMAGNETISM AND PARAMAGNETISM

2.3.1 Diamagnetism

Diamagnetism is the tendency of materials to create an opposing magnetic field as a response to an applied magnetic field (i.e. a negative susceptibility). Consequently, when a magnetic field is applied to a diamagnetic substance, the induced moments will have a direction opposite to that of the applied field. As a result the magnetic susceptibility contribution due to diamagnetism is (small but) negative. It is a common mistake to assume that diamagnetism is some special case of Lenz’s law; it should be stressed that diamagnetism is a quantum effect and strictly speaking classical physics cannot give rise to diamagnetism [42].

For ions with filled electronic shells, the total spin and orbital angular momentum in the ground state are zero, so that

\[ J|0\rangle = S|0\rangle = 0. \]

This leaves us with only the third term in equation (2-1):

\[ \Delta E_0 = \frac{e^2 H^2}{8mc^2}\langle 0|\sum_i (\chi_i^2 + y_i^2)|0\rangle = \frac{e^2 H^2}{12mc^2}\langle 0|\sum_i r_i^2|0\rangle \]

And so,

\[ \mu = -\frac{\partial E'}{\partial H} = -\frac{e^2 <r^2>}{6mc^2}H \Rightarrow \chi = -\frac{Ne^2 <r^2>}{6mc^2} \]
Ordinarily materials electrically neutral and so they have roughly one proton and one neutron for each electron; furthermore, the mass of the material is practically that of the protons and neutrons. It is then easy to estimate the number of electrons per gram of material:

\[
 n = \frac{\text{# of Electrons}}{\text{gram}} = \frac{1 \text{Gram of Material}}{2 \times \text{Proton Mass}} \approx 3 \times 10^{23} \text{ electrons/gram}
\]

Thus, our susceptibility will be

\[
 \chi \approx -\frac{e^2 \langle r^2 \rangle}{6m_e c^2} \times 3 \times 10^{23} \times M;
\]

with \( M \) being the molar mass of the substance. In emu-cgs units, we have:

\[
 r \sim 0.53 \times 10^{-8} \text{ cm}, \quad e^2 = (4.803 \times 10^{-10} \text{ stat coulombs})^2 = 2.307 \times 10^{-19} \text{ cm–erg}, \quad \text{and} \quad m_e c^2 = 8.2 \times 10^{-7} \text{ erg}.
\]

Roughly, the diamagnetic contribution to susceptibility for most materials is

\[
 \chi^{\text{Diamagnetic}} \approx -0.4 \times M \times 10^{-6} \text{ cm}^3 / \text{mol}.
\]

This diamagnetic contribution is negligible especially at lower temperatures. It, however, becomes important when a material has high molecular weight and only few magnetic centers.

\subsection{2.3.2 Paramagnetism}

Similar to diamagnetism, paramagnetism is a response to an applied magnetic field on a sample; it is not a spontaneous phenomenon. Without the application of a magnetic field magnetic moments are oriented randomly resulting in a total
magnetization of zero (Figure 2-2). When a magnetic field is applied, however, the magnetic moments tend to align along with the field giving a net magnetization in the direction of the field and a positive magnetic susceptibility.

![A model for a paramagnet.](image)

A model for a paramagnet.  
Left: the moments are randomly oriented before an external field is applied.  
Right: the moments line up with the external field.

**Figure 2-2** A model of a paramagnetic system.

For an atom with angular momentum $J$ and has $2J + 1$ levels, the magnetization is given in terms of the Brillouin Function $B_J$,

$$M = NgJ\mu_B B_j\left(\frac{g\mu_B JB}{kT}\right); \quad B_j(x) = \frac{2J + 1}{2J} \coth\left(\frac{(2J + 1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right).$$

For $x \ll 1$, the susceptibility reduces to
This is the Curie Law and $C$ is known as the Curie constant.

\[ \chi = \frac{M}{B} \approx \frac{NJ(J + 1)g^2 \mu_B^2}{3kT} = \frac{C}{T} \]

**Figure 2-3** Plot of the Brillouin Function for different spin states.

(Source of image: Chapter 6 Fig. 6.4 of Ref. [43]).
2.4  MAGNETIC ORDERING AND THEORETICAL MODELS

2.4.1  Magnetic Ordering

Paramagnetism and Diamagnetism are responses to some applied field. Some materials have a spontaneous magnetization even when the applied field is zero. This indicates there is some interaction that lines up the individual atomic moments into a preferred direction, giving rise to a net magnetization. Materials with such interactions are said to be ordered. The most common types of ordering are Ferromagnetic Order (FM), Ferrimagnetic Order, and Antiferromagnetic Order (AF).

![Diagram of magnetic ordering](image)

**Figure 2-4** Ferromagnetism, Antiferromagnetism, Canted Antiferromagnetism, and Ferrimagnetism.
2.4.1.1 Ferromagnetic Order: Mean Field Theory Approach

Below a certain temperature, in some materials, all the magnetic moments become oriented in the same directions. Such materials are called Ferromagnets and a simple model of this phenomenon is shown in Figure 2-4.

To proceed, an interaction called the exchange field $B_E$ is postulated. Using the mean field approximation, it is assumed that $B_E = \lambda M$. The Curie temperature, $T_C$, is the temperature above which ordering. If $T < T_C$, we have ferromagnetic order, and if $T > T_C$, ordering vanishes and we have a paramagnetic phase. Starting with the paramagnetic phase having a susceptibility of $\chi_P$, let $B_a$ be the applied field. Then,

$$M = \chi_P (B_a + B_E) = \frac{C}{T} (B_a + \lambda M) \rightarrow M = \frac{CB_a}{T - C\lambda}$$

Define $T_C = C\lambda$, then $\chi = \frac{C}{T - T_C}$ (Curie-Weiss Law).

The transition temperature for a ferromagnet can be found using the Landau theory for a ferromagnet. Landau approached the problem from the fact that there is no energetic difference from an up spin or a down spin which lead to an expression for the free energy in terms of the magnetization with no linear terms [7]

$$F = F_0 + a(T)M^2 + bM^4$$

Where $F_0$ and $b (> 0)$ are constants while $a(T)$ is assumed to be positive above transition and negative below the transition and so takes the form $a(T) = a_0(T - T_C)$. In an applied field, the term $-\mu_0 MH$ is added giving the free energy the final form
The ground state is when the free energy is a minimum and so

\[ \frac{\partial F}{\partial M} = 2a_0(T - T_C) + 4bM^3 - \mu_0H = 0 \]

Or

\[ M^2 = -\frac{2a_0(T - T_C)}{4b} + \frac{\mu_0H}{4bM} \]

A plot of \( M^2 \) vs. \( H/M \) (called an Arrott plot) will be a straight line and only goes through the origin at the transition temperature (i.e. \( T = T_C \)) [44]. Obviously, this mean field derived Arrott plot is an approximation of the ‘real’ world. Experimental data will deviate from this equation and some flexibility in the exponents is allowed. With this, the Arrott plot equation can be modified to

\[ \left( \frac{H}{M} \right)^{1/\gamma} = \frac{T - T_C}{T_i} + \left( \frac{M}{M_i} \right)^{1/\beta} \]

where \( M_i \) and \( T_i \) are constants [45]. In the ‘ideal’ case \( \gamma \) and \( \beta \) take the values 1 and 0.5, respectively. Experimentally, however, \( \gamma \) and \( \beta \) are closer to 1.30-1.33 and 0.4-0.45, respectively [45].

Why is it that an ordinary piece of iron (a ferromagnetic material) does not stick to another ordinary piece of iron? The answer is the existence of magnetic domains
throughout the body of the material. Each domain is ordered with a net magnetization. However, since there is a large number of randomly oriented domains (each domain is about \(0.1 \text{mm}^3\) to \(1 \text{mm}^3\)), the net magnetization of our ordinary piece of iron is zero, see Figure 2-5. An ordinary chunk of iron can be made into a permanent magnet by either the application of a strong magnetic field that will flip the domains into the field direction or by the expansion of one domain’s volume at the expanse of the other domains by simply applying a weaker field.

![Figure 2-5 Magnetic Domains](image)

**2.4.1.2 Ferrimagnetic Order: Mean Field Theory Approach**

Some ferromagnetic materials, the magnetization at \(T = 0 \text{K}\) does not reflect the alignment of the individual moments of the constituent ions. An example is FeO\(\cdot\)Fe\(_2\)O\(_3\). Here we have one Fe\(^{2+}\) with spin \(S = 2\) which contributes 4\(\mu_B\), and two Fe\(^{3+}\) with spin \(S = 5/2\), giving a total contribution of 10 \(\mu_B\). The effective number of Bohr magnetons is then expected to be 14 \(\mu_B\). Experimentally, however, it is found to be closer to about 4.1 \(\mu_B\).
This is explained if the moments of the two Fe$^{3+}$ are antiparallel and thus cancel out leaving only the Fe$^{2+}$ contribution [46].

We can find the magnetic susceptibility for a ferrimagnet as a function of the temperature in the region $T > T_C$. Suppose we have two ions with Curie temperatures $C_A$ and $C_B$, and assume that all the interactions are zero except for the antiparallel interaction. Now

$$B_A = -\mu M_B \text{ and } B_B = -\mu M_A (\mu > 0)$$

In the mean field approximation we have:

$$M_A T = C_A (B_a - \mu M_B) \text{ and } M_B T = C_B (B_a - \mu M_A).$$

Solving these two equations for $T$ and letting the applied field go to zero, we get

$$T = \mu (C_A C_B)^{\frac{1}{3}},$$

Now solving for $M_A$ and $M_B$, and then $\chi$ we get:

$$\chi = \frac{M_A + M_B}{B_a} = \frac{(C_A + C_B)T - 2\mu C_A C_B}{T^2 - T_C^2}$$

### 2.4.1.3 Antiferromagnetic Order: Mean Field Theory Approach

Antiferromagnetic ordering can be thought of as a special case of the ferrimagnetic order with the adjacent moments being opposite in direction but equal in magnitude. In the limit of $C_A = C_B = C$, we have the antiferromagnetic regime in which the critical temperature is called the Neel temperature ($T_N = \mu C$) with

$$\chi = \frac{2C}{T + T_N}.$$

This is for the susceptibility above the Neel temperature.
2.4.1.4 Different Magnets and their Response to the Applied Field: A Preliminary Look

Typical behavior of the different magnetic orderings can often be easily characterized by simply plotting $\chi(T)$, $\chi^{-1}(T)$ vs. $T$, and $\chi T$ vs. $T$ (See Figure 2-6, Figure 2-7, Figure 2-8). A plot of $\chi(T)$ usually shows a maximum for an antiferromagnet below a certain temperature. The effective magnetic moment in units of $\mu_B$ is $\mu_{\text{eff}} = 2.83 \sqrt{\chi T}$. Obviously then, as the temperature drops a plot of $\chi T$ vs. $T$ will show a steady increase for a ferromagnet, a steady decrease for an antiferromagnet, and a constant for a paramagnet. For ferrimagnet, the plot of $\chi T$ vs. $T$ shows a decrease in the beginning due to nearest neighbor interactions; however, as the temperature is lowered more the correlation length between the moments becomes longer which causes the magnetic moment to increase. The plot of $\chi^{-1}(T)$ is linear at higher temperatures (above the transition temperature) with an $x$–intercept being zero for a paramagnet, positive for a ferromagnet, and negative for an antiferromagnet.
Figure 2-6 General susceptibility behavior for different orders

(Source of image: Chapter 6 Fig. 6.5 of Ref. [43])

Figure 2-7 General $\chi T$ vs. $T$ behavior for different orders

(Source of image: Chapter 6 Fig. 6.6 of Ref. [43])
2.4.2 Origin of Magnetism and Magnetic Models

The most important interaction amongst atoms is the ordinary electrostatic electron-electron interaction followed by dipole-dipole and spin-orbit interactions [41]. Consider the following spin Hamiltonian:

\[ H = -2J \sum_{i=1}^{N} [aS_i^zS_{i+1}^z + bS_i^xS_{i+1}^x + cS_i^yS_{i+1}^y]. \]

For simplicity, we assume nearest neighbor interactions only. \( J \) is the exchange constant, while \( a, b, \) and \( c \) are dimensionless constants.

The Ising Model (IM) is obtained by letting \( a = 1, \) and \( b = c = 0: \)

\[ H = -2J \sum_{i=1}^{N} S_i^zS_{i+1}^z \text{ (IM)}. \]
If complete rotational symmetry in spin space is assumed, then we must set $a = b = c = 1$ and arrive at the Heisenberg Model (HM):

$$H = -2J \sum_{i=1}^{N} \vec{S}_i \cdot \vec{S}_{i+1} \text{ (HM)}.$$  

When $J > 0$ the energy is lowered with spins lined in parallel (Heisenberg ferromagnet). If $J < 0$ lower energy state is achieved when the spins are antiparallel (Heisenberg antiferromagnet). When $a = 0$ is called $XY$-Model:

$$H = -2J \sum_{i=1}^{N} [bS^x_i S^x_{i+1} + cS^y_i S^y_{i+1}] \text{ (XY-Model)}.$$  

The case of $a \neq b \neq c$ gives rise to spin anisotropy.

As an example the Heisenberg Hamiltonian is examined. Take

$$H = -\sum J_{ij} \vec{S}_i \cdot \vec{S}_j$$

where $\vec{S}_i$ is the spin of the $i^{th}$ ion, $\vec{S}_j$ is the spin of the $j^{th}$ ion, and $J_{ij}$ are known as the exchange constants or coefficients [41]. Making calculations with this already simplified Hamiltonian is still a difficult task.

If the spins in the Heisenberg model are restricted to have a value of $+1$ or $-1$, we arrive at the Ising Model. If $J_{ij} > 0$ we have a ferromagnetic interaction. If $J_{ij} < 0$ we have an antiferromagnetic interaction. When $J_{ij} = 0$, then there is not interaction. The Ising Model is by far the most important simplification of the Heisenberg Model [41].

Still further simplification of the Heisenberg Model gives the Hubbard Model in which the set of bound and continuum electron levels of each ion is reduced to a single localized orbital level [41].
2.4.3 Solutions to Linear Chain Models

A number of analytic and numeric solutions exist for the different linear chain models proposed like a chain of spin halves, a linear chain of spin 1, or a linear chain of classical spins. The solution to the latter will be detailed while the others are simply listed along with their references.

2.4.3.1 Linear Chain of Spin Half

2.4.3.1.1 Heisenberg Spin ½ Chain:

For a linear chain of spin halves, the zero field Hamiltonian for isotropic nearest neighbor interactions can be written as

\[ H = -J \sum_{i=1}^{n-1} \mathbf{S}_i \cdot \mathbf{S}_{i+1}. \]

Although there is no analytic solution to this problem with an infinite \( n \), a numerical solution for the case of \( J < 0 \) has been found by Bonner and Fisher [47]. Their approach was to make a ring of spins which becomes chain of spins when the number of spins in the ring approaches infinity. The numeric solution to the antiferromagnetic case \( (J < 0) \) is given by

\[
\chi = \frac{Ng^2\beta^2}{k_B T} \left( \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \right), \quad x \equiv |J|/k_B T.
\]

[48].

As for the ferromagnetic case \( (J > 0) \), only a high temperature series expansion solution to the problem has been found and is given by
\[
\chi = \frac{N g^2 \beta^2}{4k_B T} \left\{ \frac{N}{D} \right\}^{2/3}
\]

where

\[N = 1.0 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5\]

\[D = 1.0 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4\]

With \(x \equiv J/2k_B T\) [49].

2.4.3.1.2 Ising Chain:

In the case of the Ising chain, the spins are confined to one direction either ‘up’ or ‘down’. Choosing this ‘direction’ to be along the z-axis the Hamiltonian takes the form

\[
H = -2J \sum_{i=1}^{N} S_i^z S_{i+1}^z
\]

The magnetic susceptibility and specific heat associated with this Hamiltonian are given by [50, 51]

\[
\chi_\parallel = \frac{N_A g^2 \mu_B^2}{2J} (J / 2k_B T) \exp(J / k_B T)
\]

\[
\chi_\perp = \frac{N_A g^2 \mu_B^2}{4J} [\tanh(J / 2k_B T) + (J / 2k_B T) \sec h^2(J / 2k_B T)]
\]

\[
C_M = R (J / 2k_B T)^2 \sec h^2(J / 2k_B T)
\]

2.4.3.2 Ferromagnetic Ising Chain

For the ferromagnetic case, the solution to an Ising chain problem was obtained by Takano et al. using the transfer matrix method and it yielded the following analytic expression for susceptibility valid in the low temperature region:
\[
\chi = \frac{3}{4} \frac{N_A g^2 \mu_B^2}{k_B T} \exp \left( \frac{\Delta J}{k_B T} \right)
\]
\[
C_M = \frac{16 N_A J^2 S^2}{k_B T^2} \exp \left( -\frac{4JS}{k_B T} \right)
\]

Where \( N_A, g, \) and \( \mu_B \) are Avogadro’s number, Lande constant, Bohr magneton, with \( \Delta = 9 \) in the \( S = 3/2 \) case [52, 53].

### 2.4.3.3 Linear Chain of Spin 1

For the same Hamiltonian, \( H = -J \sum_{i=1}^{N} \vec{S}_i \cdot \vec{S}_{i+1} \), a numeric solution valid for \( J < 0 \), and spin one is given by the following equation

\[
\chi = \frac{N g^2 \beta^2}{k_B T} \frac{2.0 + 0.0194x + 0.777x^2}{3.0 + 4.346x + 3.232x^2 + 5.834x^3}, \text{ with } x = |J|/k_B T
\]

[48, 54].

### 2.4.3.4 Linear Chain of Classical Heisenberg Spins

In 1963 Michael E. Fisher obtained an analytical solution for the susceptibility of an infinite chain of classical spins [55].

M. E. Fisher started with the Hamiltonian for \( N \) in an external field \( H \):

\[
H = -\sum_{i=1}^{N} \sum_{j=1}^{N} \left[ J_{ij}^{\|} S_i^z S_j^z + J_{ij}^+ (S_i^+ S_j^+ + S_i^- S_j^-) \right] - g \beta \sum_{i} \vec{H} \cdot \vec{S}_i
\]

Where \( S_i^x, S_i^y, S_i^z \) are the components of the spin \( S \). Confining our Hamiltonian to the isotropic case \( J_{ij}^{\|} = J_{ij}^+ \) of an open linear chain of \( N + 1 \) atoms with Spin \( S \), the above Hamiltonian takes the form
\[
H = -2J_S \sum_{i=1}^{N} \vec{P}_i \cdot \vec{P}_{i-1} - g_S \beta \sum_{i=0}^{N} \vec{H} \cdot \vec{P}_i
\]

For simplicity the following parameters are introduced

\[
2J_S S^2 = \frac{1}{2} J, \quad g_S S = \frac{1}{2} g, \quad K = \frac{1}{2} J / k_B T.
\]

Furthermore, M. E. Fisher introduced the unit vectors \( s_i = S_i / S \) with the commutation relations

\[
[s_j^x, s_j^y] = (1/S) i s_j^z.
\]

In the classical limit (i.e. as \( S \to \infty \)) the two operators commute, and our Hamiltonian takes the form

\[
H = -\frac{1}{2} J \sum_{i=1}^{N} \vec{P}_i \cdot \vec{P}_{i-1} - \frac{1}{2} g \beta \sum_{i=0}^{N} \vec{H} \cdot \vec{P}_i
\]

In zero field it reduces to

\[
H = -\frac{1}{2} J \sum_{i=1}^{N} \vec{P}_i \cdot \vec{P}_{i-1}.
\]

The zero field partition function for \( N + 1 \) atoms can now be written as

\[
Z = \int \frac{d\Omega_0}{4\pi} \int \frac{d\Omega_1}{4\pi} \cdots \int \frac{d\Omega_N}{4\pi} \exp[K \sum_{i=1}^{N} \vec{P}_i \cdot \vec{P}_{i-1}],
\]

Carrying out the integration we arrive at

\[
Z = [(\sinh K) / K]^N.
\]

It should be noted that no restrictions on \( J \) were made which means that the model accommodates both ferromagnetic (\( J > 0 \)) and antiferromagnetic (\( J < 0 \)). The rest of the thermodynamic properties easily follow. In particular, the free energy is given by

\[
F = -k_B T \ln(Z) - N k_B T [\ln(\sinh K) - \ln(K)],
\]
and the internal magnetic energy is

\[ U = \frac{\partial (\alpha F)}{\partial \alpha} = \frac{1}{2} NJ [(1/K) - \coth K], \quad \alpha = 1/k_B T. \]

And finally the specific heat is given by

\[ C = \frac{\partial U}{\partial T} = \frac{\partial U}{\partial K} \frac{\partial K}{\partial T} = Nk_B \left[ 1 - \left( \frac{K}{\sinh K} \right)^2 \right]. \]

The general behavior of the CFM derived specific heat at low temperatures is plotted in Figure 2-9.
Since the specific heat does not go to zero as the temperature approaches zero, the entropy diverges to \(-\infty\), violating the third law of thermodynamics. This model is only applicable to higher temperatures. More explicitly, the entropy can be calculated to be

\[
S = \frac{\partial F}{\partial T} = \frac{\coth K - 1}{T} + \ln K - \ln(\sinh K).
\]

When plotted, indeed the entropy approaches \(-\infty\) when \(T\) approaches zero as can be seen in Figure 2-10.

![Figure 2-10 CFM entropy prediction](image)
The magnetic susceptibility was derived to be

$$
\chi = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B T} \frac{1+u}{1-u},
$$

$$
u = \coth \left( \frac{J S (S + 1)}{k_B T} \right) - \left( \frac{k_B T}{J S (S + 1)} \right).
$$

When this model is applied to quantum spins (e.g. \( S \neq \infty \)), the larger the spin the better the results would be. This model was applied to our cobalt and nickel magnetic chains (\( S = 3/2 \) and \( 2/2 \)), and the results were, as we shall see, far better than those obtained from the Mean Field Theory (MFT).

### 2.4.3.5 Heisenberg Model for Diamond-Type Network

A Heisenberg model for a diamond-type network of spin \( S \) was derived by G.S. Rushbrooke and P. J. Wood for the high temperature susceptibility \((T > T_C)\) is given by

$$
\chi(T) = \left[ N_A g^2 \mu_B^2 S(S+1)/2k_BT \right] [1 + 23.3333(J/k_BT) + 147.778(J/k_BT)^2 + 405.487(J/k_BT)^3 - 1621.13(J/k_BT)^4 - 14201(J/k_BT)^5 + 1037840(J/k_BT)^6] [56].
$$

### 2.4.3.6 Unequally Spaced Linear Chain of Spins and the Dimer Model

Magnetic chains of spins don’t have to be equally spaced. Consider the following model:
We can then write the following Hamiltonian

\[ H = -J \sum_{i=1}^{n/2} \left[ S_{A_{2i}} \cdot S_{A_{2i+1}} + \alpha S_{A_{2i}} \cdot S_{A_{2i+1}} \right] \]

So \( \alpha \) is considered the alternating parameter; when \( \alpha = 1 \) the uniform chain case is recovered and when it equals to zero a dimer chain is obtained. In the dimer case \( (\alpha = 0) \), the following solution is obtained for a ring chain of \( n = 10 \) and \( S = \frac{1}{2} \)

\[ \chi = \frac{Ng^2 \beta^2}{k_B T} \left( \frac{0.25 - 0.062935x + 0.0047778x^2}{1 + 0.053860x - 0.00071302x^2 + 0.047193x^3} \right) \]

[57, 58].

### 2.5 CHOICE OF A MODEL

Depending on the crystal structure of the MOF and the spin of its magnetic centers, a model can be selected. As will be seen, above the transition temperatures the spins can freely orient in any direction. This freedom of orientation rationalizes the use of a Heisenberg model. Combining large spin with the Heisenberg Model, the CFM can be
used. When the temperature is lowered near and below the transition temperatures, the
spins no longer have the freedom of orientation allowed for by the Heisenberg model;
rather the spins are more Ising-like. In the case of certain 3D magnets [as in Mn(N₃)₂-
bpy], it is expected from the crystal structure to behave according to the Heisenberg
diamond type magnet. The special case of Cu based compounds ($S = \frac{1}{2}$) is usually
modeled with an Ising model (IM).

2.6 SPECIFIC HEAT

Specific Heat at constant volume ($C_V$) is given by

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

where $U$ is the internal energy. The most important contributions to the specific heat are
a cubic term in temperature due to phonons called the lattice heat capacity, a linear term
due to electrons, and contributions from the magnetic degree of freedom.
2.6.1 Phonon, Electron, and Magnetic Contributions to Specific Heat

At low temperatures the phonon contribution to specific heat follows the cubic law

\[ C_i \cong \frac{12\pi^4 N k_B}{5} \left( \frac{T}{\theta} \right)^3 \cong 234 N k_B \left( \frac{T}{\theta} \right)^3 = \beta T^3 \]

[41].

The electron contribution to specific heat at low temperatures is linear

\[ C_e \cong \gamma T \] [41].

When the specific heat of a magnetic sample is measured as a function of temperature, what we actually get is combination of three terms:

\[ C(T) = C_e + C_i + C_M. \]

The last term is due to the magnetic degree of freedom. Consequently, to single out the magnetic specific heat the electron and phonon terms must be subtracted. Ideally, a nonmagnetic analog of the sample is made, its specific heat is measured, and the difference between the specific heats of the magnetic sample and its analogue would be the magnetic specific heat, \( C_M \). Unfortunately, the nonmagnetic analogues of the samples are not always possible to make experimentally. Consequently, the electron-phonon
specific heats are estimated with linear and cubic functions and subtracted from the total heat capacity. When the magnetic specific heat becomes known, or at least estimated, important quantities like entropy and effective spins can be calculated; furthermore, the theoretical specific heat curve (derived from the same partition function as susceptibility), can then be fit to the data and the internal consistency of the model can be tested.

2.7 INTERCHAIN INTERACTIONS

A strictly 1D system with no anisotropy will not order [11]. It follows that at the lower temperatures inter-chain interactions become more significant. Treating one chain in the mean field of nearest neighbor chains is used to estimate the inter-chain interaction parameter. Assuming a mean field ($H_{MF}$) on one magnetic chain due to surrounding chains to be proportional to the measured magnetization ($M_{3d}$):

$$H_{MF} = \lambda M_{3d}.$$ 

On the other hand the measured magnetization is given by

$$M_{3d} = \chi_{1d}(H_{\text{applied}} + H_{MF}) = \chi_{1d}(H_{\text{applied}} + \lambda M_{3d}).$$

Solving for $\chi_{3d}$ ($\chi_{3d} \equiv M_{3d}/H_{\text{applied}}$, and $\lambda = 2zJ/NAg^2\mu_B^2$), this approach gives
\[
\chi_{3d} = \frac{\chi_{1d}}{1 - \left( \frac{2z'J'}{N_A g^2 \mu_B^2} \right) \chi_{1d}}
\]

where \( \chi_{1d} \) is the solution to the 1D chain, \( z' \) is the number of nearest neighbor chains and \( J' \) is the inter-chain coupling constant [59]. This mean field theory approach predicts the correct magnitude sign of \( J' \) given that \( J' \) is not too small (i.e. \( J'/J > 0.01 \)). If \( J'/J \) is too small, then the mean field approach tends to further underestimate it. A more accurate estimate (that takes structure into account) using Green’s function methods was developed by T. Oguchi and A. Honma is used to estimate \( J \) [60, 61]. The results of this approach can be summarized as

\[
k_BT_c = \frac{4S(S+1)/3}{I(\eta)}
\]

where

\[
I(\eta) = \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{dq_x dq_y dq_z}{\eta(1 - \cos q_x) + \eta(1 - \cos q_y) + ((1 - \cos q_z)}
\]

and \( \eta = \left| \frac{J'}{J} \right| \), \( q_x, q_y, q_z \) are components of the wave number \( q \), and \( T_c \) is the transition temperature. This integral is solved numerically for the following cases summarized in Table 2.

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>( I(\eta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5055</td>
</tr>
<tr>
<td>0.1</td>
<td>1.9631</td>
</tr>
</tbody>
</table>

**Table 2** Numerical evaluation of the integral \( I(\eta) \).
Now if we plot log(η) vs. log[I(η)], the graph is linear (See Figure 2-12). This linear relation is used to derive the following simple, yet very useful, relation between the inter-chain and intra-chain interaction parameters:

\[
\eta = \frac{J'}{J} = 0.3150 \left( \frac{4S(S+1)J}{3k_BT_C} \right)^{-1.9117}
\]

\[
\ln(\eta) = -1.9117 \ln[I(\eta)] - 1.1551
\]

**Figure 2-12** Plot of ln(η) vs. ln[I(η)]
CHAPTER 3

EXPERIMENTAL METHODS

3.1 MATERIALS SYNTHESIS

The technique of hydrothermal synthesis of crystallizing substances from high-temperature aqueous solutions at high vapor pressures was used. Synthesis details of each material are given in the following sections\(^1\).

3.1.1 \( \text{Ni}_2(\text{BDC})_2(\text{TED}) \) and \( \text{Ni}_2(\text{BODC})_2(\text{TED}) \)

\( \text{M}(\text{II})(\text{BDC})(\text{TED})_{0.5} \) were prepared by heating a mixture of \( \text{M}(\text{II}) \) chloride hexahydrate (0.107 g), tetraphthalic acid (\( \text{H}_2\text{BDC} \), 0.060 g) and triethylenediamine (TED, 0.033 g) in DMF (20 mL) and two drops of Nitric Acid (\( \text{HNO}_3 \)) at 120 °C for 24 hours afforded light green crystalline powder (0.071 g) in the case of Ni and colorless in the case of Zn. The powder was vacuum filtered and rinsed with DMF and left to dry under

\(^1\) All materials were synthesized in collaboration with Professor Jing Li’s group at Rutgers University’s Department of Chemistry and Chemical Biology.
vacuum. The synthesis of \( \text{M}_2(\text{BODC})_2(\text{TED}) \) is identical to that of \( \text{M}_2(\text{BDC})_2(\text{TED}) \) with the exception of using \( \text{H}_2\text{BODC} \) instead of \( \text{H}_2\text{BDC} \). The synthesis is summarized in the following two reactions:

\[
2[\text{M(NO}_3)_2 . 6\text{H}_2\text{O}] + 2[\text{H}_2\text{BODC}] + \text{TED} \rightarrow \text{M}_2(\text{BODC})_2(\text{TED}) + \text{Other}
\]

\[
2[\text{M(NO}_3)_2 . 6\text{H}_2\text{O}] + 2[\text{H}_2\text{BDC}] + \text{TED} \rightarrow \text{M}_2(\text{BDC})_2(\text{TED}) + \text{Other}
\]

The empirical formula of each chemical is given:

- BODC = 4,4’-Bicyclo[2.2.2]octane dicarboxylate or \( \text{C}_{10}\text{H}_{12}\text{O}_4 \)
- BDC = Benzene-1,4-dicarboxylic acid (Terephthalic Acid) or \( \text{C}_8\text{H}_6\text{O}_2 \)
- TED = Triethylene-4,4’-diamine or \( \text{C}_6\text{H}_{12}\text{N}_2 \)
- \( \text{[Ni}_2(\text{BODC})_2(\text{TED})] \): \( \text{C}_{26}\text{H}_{36}\text{Ni}_2\text{N}_2\text{O}_8 \)
- \( \text{[Ni}_2(\text{BDC})_2(\text{TED})] \): \( \text{C}_{22}\text{H}_{24}\text{Ni}_2\text{N}_2\text{O}_4 \)

### 3.1.2 \( \text{Co}(\text{NDC})(\text{DMF}) \)

Single crystals of \([\text{Co}(\text{NDC})(\text{DMF})]\) were prepared by heating the DMF solution (10 mL) containing 0.9 mmol of NDC (NDC: 2,6-naphthalenedicarboxylate), 0.9 mmol \( \text{Co(NO}_3)_2 \) and 0.4 mmol of HMT (HMT: Hexamethylenetramine) in a Teflon-lined autoclave at 150 °C for three days; pink rod shape crystals were collected by filtration
and dried under vacuum. A yield of 82%, based on metal, was obtained.

$$[\text{Co(bpdc)}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O} \text{ and } [\text{Zn(bpdc)}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$$

### 3.1.3 $[\text{Co(bpdc)}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$

Synthesis of polycrystalline samples of $[\text{Co(bpdc)}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ was carried out by mixing an aqueous solution (10 mL) of Co(NO$_3$)$_2$ (0.2910 g, 1 mmol) with an aqueous solution (5.5 mL) of Na$_2$(bpdc) (0.143 g, 0.055 mmol) [22]. The immediately precipitated white-gray particles of $[\text{Co(bpdc)}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ were then washed by distilled water (10 mL) and collected in high yield (0.1625 g, 92%) [22]. The powder samples of isostructural $[\text{Zn(bpdc)}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ were prepared using a similar procedure [62].

### 3.1.4 $\text{M(N}_3\text{)}_2(\text{bpy})\cdot\text{1D} \ [\text{M} = \text{Cu, Ni, Co, Fe}]$

All $\text{M(N}_3\text{)}_2(\text{bpy})$ samples used were made in powder polycrystalline form. They were synthesized by adding aqueous solutions (20 mL) of $\text{MCl}_2\cdot\text{6 H}_2\text{O}$ to solution of bpy (with 1:1 M to bpy ratio) in methanol (10 mL). Then, the mixtures were stirred quickly for about five seconds before NaN$_3$ solution (20 mL with 1:2 M to N$_3$ ratio) was added. After an additional five seconds of stirring, the mixtures were then covered and left at room temperature for 20 h. Following that, the samples were centrifuged for 20 min, washed with water, treated with anhydrous ether, and then left in the oven at 70° C for 45 min for drying. The resulting $\text{Co(N}_3\text{)}_2(\text{bpy})$ samples were pale pinkish in color, pale
green for Ni(N$_3$)$_2$(bpy), and green for Cu(N$_3$)$_2$(bpy). The crystal structure of M(N$_3$)$_2$(bpy) was previously solved for a Fe(N$_3$)$_2$(bpy) single crystal. Powder X-ray diffraction pattern was then generated for the analysis of all polycrystalline samples. All samples were assured single phase.

3.1.5 $M(\text{N}_3)_2(\text{bpy})$-3D [$M = \text{Mn, Fe}$]

The synthesis of $M(\text{N}_3)_2(\text{bpy})$ [$M = \text{Mn, Fe}$] consisted of mixing aqueous solutions of $M(\text{II})$ and NaN$_3$, as well as a solution of 4,4'-bpy in methanol; slowly mixing of a solution of 4,4'-bpy in methanol, followed by drop-wise addition of an aqueous solution of NaN$_3$ to a stirred aqueous solution of an $M(\text{II})$ salt.
3.2 STRUCTURE DETERMINATION

Single crystal x-ray diffraction (XRD) is initially used to solve the structure. Once the structure is known, powder x-ray diffraction (PXRD) can be generated and is used thereafter to ensure single phase and purity of the prepared samples. Each crystal was mounted on a glass fiber in air on an Enraf-Nonius CAD4 automated diffractometer. Twenty-five reflections were centered in each case using graphite-monochromated Mo Kα radiation. All data were collected at 295(2) K with the ω-scan method within the limits $7 \leq 2\theta \leq 50^\circ$. Raw data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied in each case. The structures were solved using the SHELX-97 program [63]. The crystal structures of all samples was solved\(^2\) using SHELX-97 program [64, 65]. Rigaku Ultima, Dmax-2200T powder X-Ray diffractometer was used in the case of PXRD [65]. The crystal drawings were generated using SCHAKAL 92 [65, 66].

\(^2\) In collaboration with professor Jing Li at Rutgers University’s Chemistry Department
3.3 MAGNETIC MEASUREMENTS

The magnetic measurements were carried out using a Superconducting Quantum Interference Device (SQUID). The SQUID can supply magnetic fields from 0 G to 55 kG and varies temperatures from 1.8 K to 400 K [67]. The samples’ weights range from 10 mg to 40 mg. Samples used are usually in polycrystalline powder forms or collections of small single crystals in random orientation. The samples were weighed and wrapped in nonmagnetic weighing paper. The wrapped samples were usually cylindrical with a volume of about 20 mm$^3$. The sample is then installed into a nonmagnetic straw that gets mounted into the probe of the SQUID for measurements.

The typical quantities measured are both zero field cooled (ZFC) and field cooled (FC) magnetic susceptibility $\chi(T)$, isothermal magnetization $M(H)$, and time dependent magnetization. The ZFC $\chi(T)$ is when the sample is cooled from room temperature in zero field to the lowest temperature of 1.8 K, then the field is turned on and data is collected as the temperature is increased. The FC susceptibility is measured when the sample is cooled from room temperature in a nonzero field and then data is collected as the temperature is increased.
Figure 3-1 SQUID setup.
3.4 SPECIFIC HEAT MEASUREMENTS

3.4.1 Low Temperature Specific Heat

The low temperature heat capacity measurements were made via a 6 foot homemade probe using the quasi-adiabatic heat pulse method (Figure 3-2 and Figure 3-3).

Figure 3-2 Low temperature specific heat probe.
The samples were pressed into pellets of about 1 cm in diameter, 2 mm in height, and a mass of about 200 mg. The sample was then mounted into the probe shown in Figure 3-2. The temperature range of these measurements was 1.3 K < T < 25 K. Attached to the sample was a sample heater, a thermometer, and a shield. The functions of these components can be described as follows.

*Sample heater:* gives a heat pulse to the sample. The computer measures the temperature change of the sample (ΔT = T_f − T_i). The specific heat was computed in accordance with the usual Ohmic heating equation:

\[ I^2R \Delta t = mc\Delta T \Rightarrow C = M I^2R\Delta t / m\Delta T \]
with $I$ being the current applied through the heater, $R$ is the resistance of the heater, and $\Delta t$ is the duration of the heat pulse.

*Shield heater:* heats the shield (shielding the sample) so that it will have a temperature (ambient temperature) close to that of the sample.

*Sample thermometer V, I & Shield thermometer V, I:* these are the thermometer voltage and current which are translated (via coefficients in the case of sample or a table in the case of shield) into temperature readings.

The specific heat probe is then submerged in a liquid helium dewer, which in turn is submerged in a liquid nitrogen dewer ($T = 77$ K). The liquid nitrogen provides the ambient temperature necessary for liquid helium to condense.

The plot of temperature ($y$-axis) versus time ($x$-axis) of a sample before heat pulse is given, during heat pulse, and after the heat pulse is shown in Figure 3-4 and Figure 3-5. Shown in Figure 3-4 is the sample’s response to a heat pulse in ideal case and in Figure 3-5 is what is usually obtained in an experiment.
Figure 3-4 Ideal response to a heat pulse.

Figure 3-5 Actual response by a sample to a heat pulse.

The difference between the theoretical and experimental results is mostly due to the following two reasons. First, the sample is not a perfect heat conductor, so it takes time for the heat to permeate the sample (i.e. become homogeneous with respect to
temperature). Second, the temperature before and after is not a horizontal line as a function of time is because the shield temperature before and after is not exactly equal to the sample temperature before and after, respectively.

The parameters are usually set as follows:

1. Number of points before: take several measurements (about five points) of the temperature before the pulse is given to calculate $T_i$.

2. Number of points after: take several measurements (about five points) of the temperature after the pulse is given to calculate $T_f$.

3. Monitoring Time: this is the time we give after the pulse is given in order for the sample temperature to become homogeneous, and thus start taking its “sample temperature after”. Monitoring time is increased at higher temperatures as the sample becomes a poor thermal conductor. Monitoring time is chosen to be somewhat shorter at lower temperatures when the sample is a good conductor and because we would like to obtain as many points as we can before the temperature becomes (very quickly) higher.

4. $dT$: by how much to increase the sample temperature and hence how much heat to give. Usually: $0.1 \text{ K} < dT < 0.25 \text{ K}$.

5. Temperature Step. The next temperature to start taking data from. For example, suppose $T_i = 10 \text{ K}$, $dT = 0.2 \text{ K}$, and $T_{\text{step}} = 0.3 \text{ K}$. Then after the pulse is given, $T_f = 10.2 \text{ K}$. For the next data point, $T_i = 10.3 \text{ K}$, and after this is given a heat pulse, $T_f = 10.55 \text{ K}$, and so on.
6. **Starting specific heat:** give the expected specific heat to start measurement. This is not critical because the program will use the initial specific heat to estimate what the next will be. So, the first point will not be reliable, but the subsequent points are.

Detailed description of the probe and the program used to calculate the specific heat can be found in Professor Tan Yuen and Dr. Jason Zan’s Ph.D. dissertations [67, 68].

### 3.4.2 High Temperature Specific Heat

The High Temperature Specific Heat is measured with a high purity helium gas refrigerator. The temperature range of for this measurement is $10 \text{ K} < T < 300 \text{ K}$. The principle of measurement is the same as that detailed in section 3.4.1 “Low Temperature Specific Heat” and the previously mentioned theses [67, 68].
Figure 3-6 High temperature specific heat setup.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 ONE DIMENSIONAL SYSTEMS

4.1.1 Co(NDC)(DMF)

4.1.1.1 Crystal Structure

The network and crystal structure for Co(NDC)(DMF) are shown in Figure 4-1 and Figure 4-2.
The empirical formula of Co(NDC)(DMF) is $\text{C}_{15}\text{H}_{13}\text{CoNO}_5$ (M = 346.19 g/mol).

The crystal structure is monoclinic of space group C2/c with $\beta = 97.170(2)^\circ$ and $a = 23.406(2) \text{ Å}$, $b = 8.7191(8) \text{ Å}$, $c = 7.1688(7) \text{ Å}$. In the structure, Co$^{II}$ ions are all six
coordinated showing the octahedral coordination geometry. Each Co\textsuperscript{II} ion coordinated to four oxygen atoms belongs to the four carboxylate groups, and two oxygen atoms supplied from two DMF molecules. Co\textsuperscript{II} ions are bridged by carboxylate groups and DMF molecule to form a 1D Co\textsuperscript{II} chain extending along the c axis, in which a DMF molecule connects adjacent Co\textsuperscript{II} ions by O atom in trans mode. The Co-O bonds lengths are between 2.0185-2.0793 Å for oxygen atoms from carboxylate groups and 2.1466 Å for oxygen atoms from DMF. The intra-chain Co-Co distance is 3.5844 Å. The 1D Co\textsuperscript{II} chains are linked one to another via NDC ligands to form a 3D framework. The latest interchain Co-Co distances are 12.4887 Å in a direction and 8.7192 Å in b direction. Co(NDC)(DMF) shows nonporous structure due to the void space filled with DMF molecules coordinating to Co\textsuperscript{II} ions.

4.1.1.2 Magnetic Measurements

Susceptibility data for Co(NDC)(DMF) are shown in Figure 4-3 and Figure 4-4. $\chi^{-1}(T)$ was linear with a $\theta = 2.13$ K from the lower temperature fit to $\chi(T) = C/(T - \theta)$ (See Figure 4-5). $\mu_{\text{eff}}(T) [= 2.83\sqrt{\chi T}]$ has a value of 4.63 $\mu_B$ at room temperature (Figure 4-6). As the temperature is lowered $\mu_{\text{eff}}(T)$ stays fairly constant until 16 K then it quickly increases and reaches a maximum of 10.31 $\mu_B$ at 2.2 K. Below 2.2 K it starts decreasing.
Figure 4-3 $\chi(T)$ behavior in Co(NDC)(DMF)-1D.
Figure 4-4 Low temperature $\chi(T)$ in Co(NDC)(DMF)-1D.
Figure 4-5 $\chi^{-1}(T)$ plot for Co(NDC)(DMF)-1D.

$\theta = 2.13$ K
Figure 4-6 $\mu_{\text{eff}}(T)$ for Co(NDC)(DMF)-1D.

$\chi(T)$ data was fit to the CFM and compared to MFT's Curie-Weiss law. The expression for the CFM is given by

$$
\chi(T) = \frac{N_A g^2 \mu_B^2 S(S+1)}{3k_B T} \frac{1+u}{1-u}; \quad u = \coth \left( \frac{JS(S+1)}{k_B T} \right) - \left[ \frac{k_B T}{JS(S+1)} \right].
$$

Since this expression was derived for classical spins, the larger the quantum spin the better the description. For Co(NDC)(DMF), $S = 3/2$ was used.
The fits of $\chi(T)$ to the Classical Fisher Model (CFM) and to the Curie-Weiss law (CW) are shown in Figure 4-7 and Figure 4-8. It is very clear (Figure 4-7 and Figure 4-8) the CFM fits the data consistently much better than the MFT's Curie-Weiss law. The results of the fits are summarized in Table 3. The exchange interaction parameter $J$ (or $T_C$ for Curie-Weiss) gets progressively larger for the measurement under stronger fields. This is due to the fact that an applied field pushes the ‘transition’ temperature up which gets reflected as a higher $J$.

Figure 4-7 CFM and Curie-Weiss fits of $\chi(T)$ for Co(NDC)(DMF)-1D.
**Figure 4-8** CFM and Curie-Weiss fits to $\chi(T)$ for Co(NDC)(DMF)-1D.

**Table 3** Summary of the fitting results for Co(NDC)(DMF)-1D

<table>
<thead>
<tr>
<th>Applied Field (Oe)</th>
<th>Classical Fisher Model (CFM)</th>
<th>Curie Weiss Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Oe</td>
<td>$J/k_B = 1.78$ K; $R^2 = 0.967$</td>
<td>$T_C = 1.81$ K; $R^2 = 0.620$</td>
</tr>
<tr>
<td>50 Oe</td>
<td>$J/k_B = 1.80$ K; $R^2 = 0.999$</td>
<td>$T_C = 1.83$ K; $R^2 = 0.712$</td>
</tr>
<tr>
<td>100 Oe</td>
<td>$J/k_B = 2.02$ K; $R^2 = 0.970$</td>
<td>$T_C = 1.84$ K; $R^2 = 0.586$</td>
</tr>
<tr>
<td>500 Oe</td>
<td>$J/k_B = 2.40$ K; $R^2 = 0.998$</td>
<td>$T_C = 1.88$ K; $R^2 = 0.651$</td>
</tr>
<tr>
<td>1000 Oe</td>
<td>$J/k_B = 2.48$ K; $R^2 = 0.997$</td>
<td>$T_C = 1.88$ K; $R^2 = 0.580$</td>
</tr>
</tbody>
</table>
The interchain interactions were estimated using the expression for the 3D susceptibility ($\chi_{3d}$) defined as the susceptibility of a magnetic chain in the mean field of neighboring chains given by

$$
\chi_{3d} = \frac{\chi_{1d}}{1 - \left(\frac{2z'J'}{N_A g^2 \mu_B^2}\right)\chi_{1d}}
$$

where $\chi_{1d}$ is the solution to the 1D Ising chain, $z'$ is the number of nearest neighbor chains, and $J'$ is the inter-chain coupling constant [59]. With this 3D approximation for the susceptibility, a fit to $\chi(T)$ is shown in Figure 4-9. With $z = 2$, we obtained $J/k_B = 1.78$ K, $J'/k_B = -0.048$ K (2.7% of $J$) and $g = 2.2$. 
Figure 4-9 3D Susceptibility fit to estimate $J/k_B$ for Co(NDC)(DMF).

Shown in Figure 4-10 is the isothermal magnetization $M(H)$ at $T = 1.76$ K. When fit the paramagnetic Brillouin Function, a spin of about 1 was obtained. The data is compared to the behavior of a paramagnet of spin $S$ equal to 3/2 and 1/2. At the low fields the magnetization has values larger than that of a paramagnetic system of spin $S = 3/2$. As the applied field becomes stronger ($H > 7000$ Oe), the behavior is closer to a spin 1 paramagnet.
Figure 4-10 $M(H)$ at $T = 1.76 \text{ K}$ for Co(NDC)(DMF)-1D; curves are comparison with the Brillouin Function.

4.1.2 [Co(bpd)(H$_2$O)$_2$]H$_2$O

4.1.2.1 Crystal Structure

Room temperature powder x-ray diffraction data of polycrystalline [Co(bpd)(H$_2$O)$_2$]H$_2$O yielded a monoclinic crystal structure of space group C2/c and $a$
= 6.950(1) Å, \( b = 31.585(6) \) Å, and \( c = 6.226(1) \) Å, \( b = 95.84(3)^\circ \) [22]. The
nonmagnetic analog \([\text{Zn}(\text{bpdc})(\text{H}_2\text{O})_2]\)H$_2$O crystallizes in the same structure with very
slight variations in the lattice parameters \((a = 6.919 \) Å, \( b = 31.536 \) Å, \( c = 6.256 \) Å, and \( \beta = 96.47^\circ \)) [22]. As shown in the figure, the crystal structure of \([\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2]\)H$_2$O contains 1D chains of \([\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2]\) parallel to the \( c \) axis [22]. Each chain is formed
by connecting six-coordinated Co(II) through the four \( \mu_2\)-H$_2$O and two \( \mu_2\)-bpdc. Co is
located in slightly distorted octahedral site, with the Co-O$_3$ distances longer than the Co-
O$_1$ distance [22]. The central structure motif of the chain is an edge-sharing octahedron
of CoO$_2$O$_4$ where O is a carboxylic oxygen of \( \mu_2\)-bpdc and O$^ -$ is the oxygen from \( \mu_2\)-H$_2$O
[22]. The Co-Co distance is 3.113 Å [22]. Hydrogen bonding between the
uncoordinated carboxylate ions and aqua hydrogen from the adjacent chains are
presumably responsible for interchain interactions [22].

It is known that for the six-coordinate octahedral Co$^{2+}$ \((3d^7\), with three unpaired
electrons), the lowest electronic states are split to give a spin-doublet ground state, due to
the large spin-orbit interactions \((\lambda = -180 \text{ cm}^{-1})\) and crystalline distortions [22]. This
ground state is well separated from the next nearest state (by about 100 cm$^{-1}$, thus it is
expected that \([\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2]\)H$_2$O behaves effectively like a spin \( 1/2 \) system in the low
temperature region where \( k_B T \ll \lambda \) [22]. On the other hand, the compound should
behave as spin 3/2 system at temperatures high enough \((k_B T \gg \lambda)\) for the upper states to
be populated [22]. The empirical formula of bpdc \((4,4'$\)-biphenyldicarboxylate) is C$_{14}$H$_8$O$_4$
\((M = 240.04\text{ g/mol})\). The molar mass of \([\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2]\)H$_2$O is 353.18 g/mol
Figure 4-11 (a) Crystal Structure of $[\text{Co(bpdc)}(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$
(b) View of a chain along the $c$ direction.
See Ref. [22].
4.1.2.2 Magnetic Measurements

The susceptibility is characterized by a broad peak characteristic of low dimensional magnetism at about 5.5 K (Figure 4-13 and Figure 4-14). This indicates a possible second order phase transition as it is also seen in the specific heat data. Using these data, plots of $\chi^{-1}(T)$ and $\mu(T)$ were generated. Fitting the high temperature part of $\chi^{-1}(T)$ to the Curie-Weiss law, a $\theta = +5.6$ K was obtained (Figure 4-15). The magnetic moment increases progressively from 4.8 $\mu_B$ at room temperature (equal to that of free Co$^{2+}$ at room temperature) to 10.6 $\mu_B$ at 5.6 K. Below 5.6 K the moment decreases to a 5.4 $\mu_B$ at $T = 1.8$ K (Figure 4-16).
Figure 4-13 $\chi(T)$ for [Co(bpdc)(H$_2$O)$_2$]·H$_2$O; $H = 10$ Oe
Figure 4-14 Low temperature $\chi(T)$ for $[\text{Co(bpdc)}(\text{H}_2\text{O})_2]\text{H}_2\text{O}; H = 10 \text{ Oe}$. 
$1/\chi = 0.383 \, T^{-2.153}$

$\Rightarrow x$-intercept $= 5.62 \, K$

**Figure 4-15** $\chi^{-1}(T)$ fit to Curie-Weiss law for $[\text{Co(bpdc)(H}_2\text{O)}_2]\text{H}_2\text{O}; \, H = 10 \, \text{Oe.}$
The susceptibility data were fit to the earlier mentioned Classical Fisher model for an infinite chain with $S = 3/2$. It can be clearly seen from Figure 4-17 and Figure 4-18 that the CFM fits the data far better than the MFT’s Curie-Weiss law, especially in the low temperature range the Curie-Weiss law clearly fails to describe the data.

**Figure 4-16** $\mu_{\text{eff}}(T)$ for $[\text{Co(bpdc)(H}_2\text{O)}_2]\text{H}_2\text{O}; H = 10 \text{ Oe.}$
Figure 4-17 CFM and Curie-Weiss fits to $\chi(T); H = 10$ Oe.
Figure 4-18 CFM and Curie-Weiss fits to $\chi(T)$; $H = 1kOe$. 
The results from fitting the susceptibility data to the Fisher model and to the Curie-Weiss law are summarized in Table 4.

**Table 4** Summary of the fitting results for \([\text{Co(bpdc)(H}_2\text{O})_2]\text{H}_2\text{O}\)

<table>
<thead>
<tr>
<th>Applied Field (H) (Oe)</th>
<th>Classical Fisher Model (CFM); (S = 3/2)</th>
<th>Curie Weiss (CW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>(J/k_B = 7.40) K; (R^2 = 0.993)</td>
<td>(T_C = 5.31) K; (R^2 = 0.391)</td>
</tr>
<tr>
<td>50</td>
<td>(J/k_B = 6.78) K; (R^2 = 0.981)</td>
<td>(T_C = 5.12) K; (R^2 = 0.371)</td>
</tr>
<tr>
<td>100</td>
<td>(J/k_B = 6.55) K; (R^2 = 0.978)</td>
<td>(T_C = 5.20) K; (R^2 = 0.398)</td>
</tr>
<tr>
<td>400</td>
<td>(J/k_B = 7.37) K; (R^2 = 0.995)</td>
<td>(T_C = 5.49) K; (R^2 = 0.490)</td>
</tr>
<tr>
<td>500</td>
<td>(J/k_B = 6.77) K; (R^2 = 0.978)</td>
<td>(T_C = 4.92) K; (R^2 = 0.356)</td>
</tr>
<tr>
<td>1000</td>
<td>(J/k_B = 5.67) K; (R^2 = 0.914)</td>
<td>(T_C = 4.15) K; (R^2 = 0.177)</td>
</tr>
<tr>
<td><strong>Average:</strong></td>
<td>(J/k_B = 6.76) K</td>
<td></td>
</tr>
</tbody>
</table>

The interchain interactions were estimated using the expression for an Ising chain in the mean field of other chains given by

\[
\chi_{3d} = \frac{\chi_{1d}}{1 - \left(\frac{2z' J'}{N_A g^2 \mu_B^2} \right) \chi_{1d}}
\]

where \(\chi_{1d}\) is the solution to the 1D Ising chain, \(z'\) is the number of nearest neighbor chains, and \(J'\) is the inter-chain coupling constant [59]. With this 3D approximation for the susceptibility, a fit to \(\chi(T)\) is shown in Figure 4-19. With \(z = 6\), we obtained \(J/k_B = \ldots\)
8.40 K, $J/k_B = -0.24$ K (2.1% of $J$) and $g = 2.2$. The negative $J$ implies that the interchain interaction is antiferromagnetic. This negative interchain interaction is the cause of the second order-like transition seen in $\chi(T)$ and $C(T)$ at 5.5 K.

![Graph](image-url)

**Figure 4-19** 3D Low temperature $\chi(T)$ Susceptibility fit to estimate $J/k_B$.

The isothermal magnetization results for several temperatures ($T = 2$ K, 6 K, and 15 K) are displayed in Figure 4-20. Near and below the transition temperature, where the magnetic interactions more significant, the magnetization quickly increases with the applied field and nearly saturates at about 9000 emu/mol at the field of 5 T. On the other
hand, for $T = 15 \text{ K}$, the magnetization slowly increases with increasing field and reaches 8000 emu/mol at $H = 5 \text{ T}$. This is expected since the magnetic interactions above the transition temperature become less significant when compared to the thermal agitations. The negative interactions are clear since the magnetization at a higher temperature ($T = 6 \text{ K}$) is larger than that at lower temperatures [$M(H)$ at $T = 2 \text{ K}$]. The moment reached at high fields was about 15000 emu/mol (spin 3/2 saturates at about 16000 emu/mol). It is also noted that for $T = 2 \text{ K}$, $M(H)$ has a spin reorientation at $H = 7 \text{ kOe}$ (Figure 4-20). No hysteresis was observed for this 1D Cobalt complex.

![Graph](tan072)

**Figure 4-20** $M(H)$ at various temperatures for [Co(bpdc)(H$_2$O)$_2$]H$_2$O.
4.1.2.3 Specific Heat Measurements

The specific heat data of \([\text{Co(bpdc})(\text{H}_2\text{O})_2]\)\(\text{H}_2\text{O}\) and \([\text{Co(bpdc})(\text{H}_2\text{O})_2]\)\(\text{H}_2\text{O}\) are shown in Figure 4-21. An anomaly with a broad peak can be observed in the \(C(T)\) of \([\text{Co(bpdc})(\text{H}_2\text{O})_2]\)\(\text{H}_2\text{O}\) near \(T = 5.5\) K. The anomaly was also confirmed to be that for a ferromagnetic interaction with the peak shifting to a higher temperature when measured under the application of a 5 kOe magnetic field. This shift to a higher temperature is more obvious in the plots of \(C/T\) vs. \(T^2\) (Figure 4-22). Clearly, there is a specific heat contribution due to the magnetic interactions in addition to the electron and phonon contributions.
Figure 4-21 $C(T)$ for $[\text{Co(bpdc)}(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ and $[\text{Zn(bpdc)}(\text{H}_2\text{O})_2]\text{H}_2\text{O}$. 
At low temperatures, \( C/T \) vs. \( T^2 \) in the \([Zn(bpdc)(H_2O)_2]H_2O\) compound is linear as expected (Figure 4-23). From this plot, \( \gamma = 18.057 \text{ mJ/mol K}^2 \) and \( \beta = 2.773 \text{ mJ/mol K}^4 \) are obtained (\( C/T = \gamma + \beta T^2 \)).
Although these Co and Zn complexes are isomorphs, it is anticipated that $\beta_{\text{Co}}$ will slightly differ from that of $\beta_{\text{Zn}}$ because of the mass difference between Co and Zn. This must be accounted for in order not to ‘oversubtract’ from the total specific heat. Using $\beta \sim \theta_D^{-3}$ and $\theta_D \sim m^{-1/2}$, we obtain $\beta_{\text{Co}} = \beta_{\text{Zn}} (m_{\text{Co}} / m_{\text{Zn}})^{3/2}$ and estimate that $\beta_{\text{Co}} = 2.37$ mJ/mol K$^4$ [69]. With these parameters, the electron-phonon specific heat for [Co(bpdc)(H$_2$O)$_2$]H$_2$O are given by:

$$C_{\text{electrons}} + C_{\text{lattice}} = 18.06T + 2.37T^3.$$
Subtracting this from the total specific heat, the magnetic specific heat is shown in Figure 4-24. The magnetic specific heat was fit to the spin 3/2 IM and CFM given by

\[ C_M = \frac{16N_AJ^2S^2}{k_BT^2}\exp\left(-\frac{4JS}{k_BT}\right)\text{(IM)} \]

\[ C_M = Nk_B\left[1-\left(\frac{K}{\sinh K}\right)^2\right]\text{(CFM)} \]

As expected, CFM failed since it predicts a diverging entropy at \( T = 0 \) K. The IM reasonably fit the data giving a \( J/k_B = 6.22 \) K [from \( \chi(T) \) fit: \( J/k_B = 6.76 \) K]. This is slightly lower than that obtained from the magnetic susceptibility and the reason was traced to the fact that the intra-chain \( J \) is reduced by the negative interchain \( J' \). When this is taken into account, the \( J \) obtained from susceptibility and that obtained from specific heat are practically equal.

The reason that the IM model better fits the data at lower temperatures is due to the fact that the spins take a more rigid orientation (namely up or down). This means at lower temperatures the magnetic interactions are best described with a (ferromagnetic) Ising model. The total entropy removal was calculated from the magnetic specific heat data (\( \Delta S = \int(C/T)dT = 3800 \text{ mJ/mol K} \)) and it was only 33% of that expected for an ordered system of spin 3/2 [\( \Delta S = N_Ak_B\ln(2S+1) \)]. This is typical in the case of low dimensional magnetism.
Figure 4-24 Magnetic Specific heat of $[\text{Co(bpdc)(H}_2\text{O)}_2]\text{H}_2\text{O}$

Fits: IM(dashed green) and CFM(solid blue).
4.1.3  \( M(N_3)_2\text{bpy} \ [M = \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}] \)

4.1.3.1  **Crystal Structure**

\( M(N_3)_2(\text{bpy}) \) compounds crystallize in an orthorhombic crystal system with the space group Cmmm (No. 65). The crystal structure consists of two-dimensional \( M(N_3)_2(\text{bpy}) \) layers parallel to the crystallographic \( ac \) plane. Its three-dimensional structure is completed by stacking these layers with a shift of \([1/2]a[1/2]c\) between the adjacent layers. The \( M \) atoms are octahedrally coordinated with four \( \mu-(1, 1) \) azide ligands in equatorial plane and two bpy molecules at axial sites. The octahedral geometry around each \( M \) atom is slightly distorted through axial contraction and equatorial distortion. For each bpy ligand, two pyridyl rings are coplanar and lie in crystallographic \( ab \) plane. 1D magnetic chains of \( -(N_3)_2-M-(N_3)_2- \) are formed in a very similar manner to those formed in \( M(\text{ox})(\text{bpy}) \) and \( M(\text{Cl})_2(\text{py}) \) systems \[70, 71\]. It is anticipated that the intra-chain magnetic interactions between \( M \) moments via \( (N_3)_2 \) units are positive due to the end-on (EO) connection of the azide ligands with the \( M \) \[71\]. The inter-chain magnetic interactions are expected to be much weaker than the intra-chain interactions. The lattice constants for \( M(N_3)_2(\text{bpy}) \) are listed in Table 5. The \( M \) ion intra-chain distance is also found to decrease from Fe to Cu compound. The crystal structure is shown in Figure 4-25 and Figure 4-26.
**Table 5** Lattice constants of M(N$_3$)$_2$(4,4′-bipyridine) [M = Fe, Co, Ni, Cu]

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>$a$(Å)</th>
<th>$b$(Å)</th>
<th>$c$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(N$_3$)$_2$(4,4′-bipyridine)</td>
<td>11.443(2)</td>
<td>15.178(3)</td>
<td>3.459(5)</td>
</tr>
<tr>
<td>Co(N$_3$)$_2$(4,4′-bipyridine)</td>
<td>11.453(1)</td>
<td>15.160(2)</td>
<td>3.420(2)</td>
</tr>
<tr>
<td>Ni(N$_3$)$_2$(4,4′-bipyridine)</td>
<td>11.478(2)</td>
<td>15.145(1)</td>
<td>3.405(1)</td>
</tr>
<tr>
<td>Cu(N$_3$)$_2$(4,4′-bipyridine)</td>
<td>11.460(2)</td>
<td>15.173(3)</td>
<td>4.408(3)</td>
</tr>
</tbody>
</table>

**Figure 4-25:** the 2D layers of M(N$_3$)$_2$(bpy) stacked in a staggered fashion along the b axis. The cross-shaded circles are Fe, solid circles are C, single-shaded circles are N.

See Ref. [23].
Figure 4-26: a view showing a single layer projected along the $b$ axis.

See Ref. [23].
4.1.3.2 Cu(N$_3$)$_2$bpy

4.1.3.2.1 Magnetic Measurements

The $\chi(T)$ curve for the Cu(N$_3$)$_2$bpy is shown in Figure 4-27. No antiferromagnetic peak was observed down to the lowest temperature, 2 K. $\mu_{\text{eff}}(T)$ monotonically decreases from 1.81$\mu_B$ at room temperature (1.9$\mu_B$ for free Cu$^{2+}$) to 0.60$\mu_B$ at 2K as shown in Figure 4-28. A fit of the high temperature part of $\chi^{-1}(T)$ to the Curie-Weiss law gives a $\theta = -12.8$ K (Figure 4-29), which indicates antiferromagnetic behavior for this system.

The Ising Model for a chain of spin ½, given by

$$\chi_\parallel = \frac{N_A g_\parallel^2 \mu_B^2}{4k_B T} \exp(J / k_B T)$$

$$\chi_\perp = \frac{N_A g_\perp^2 \mu_B^2}{4J} \left[ \tanh(J / 2k_B T) + (J / 2k_B T) \sec h^2(J / 2k_B T) \right]$$

was used to fit the $\chi(T)$ data [50]. Using $\chi_{\text{powder}} = \alpha \chi_\parallel + \beta \chi_\perp$, we obtained $\alpha = 0.495$, $\beta = 0.505$, and intrachain $J/k_B = -13.14$ K, from the fit shown in Figure 4-27 [2].
Figure 4-27 $\chi(T)$ measured for Cu(N_3)_2bpy \([H = 50 \text{ Oe}].\)

IM (solid red); Curie-Weiss (dashed green).

Figure 4-28 $\mu_{\text{eff}}(T)$ for Cu(N_3)_2bpy \([H = 500 \text{ Oe}].\)
Using the expression for the susceptibility of a magnetic chain in the field of other chains given by [59]

\[
\chi_{3d} = \frac{\chi_{dd}'}{1 - \left(\frac{2z'J'}{N_A g^2 \mu_B} \right) \chi_{1d}}
\]

we obtain \(z'J'/k_B = -10.447\) K, \(J'/k_B = -14.035\) K, \(\alpha = 0.143\), \(\beta = 0.857\) and \(g = 2.055\).

From the crystal structure of Cu(N\(_3\))\(_2\)bpy it is estimated that \(z' = 8\) and hence \(J'/J = 0.093\).

It should be mentioned that the intrachain distance between the copper ions is 3.42 Å.
while the interchain distance is about 13.3 Å (the average of \(a\) and \(b\)). The value of \(J'/J = 0.093\) is reasonable because the strength varies approximately as the inverse of the square of the distance. The fit with the interchain interaction accounted for is shown in Figure 4-30.

![Graph](image)

**Figure 4-30** \(\chi(T)\) fit with interchain exchange accounted for.

The isothermal magnetization \(M(H)\) at \(T = 2\) K for \(\text{M(N}_3\text{)bpy}\) (\(\text{M} = \text{Cu, Ni, Co}\)) is shown in Figure 4-31. No hysteresis was observed in the case of Cu based compound.
Up to $H = 54$ kG no saturation was reached. The linear dependence of $M$ on $H$ is typical antiferromagnetic behavior. When saturation is reached the curve becomes horizontal with an expected value of about 5500 emu/mol in the case of $S = \frac{1}{2}$.

**Figure 4-31** $M(H)$ at 2 K for $M(N_3)_2(4,4'-bpy)$

($\square$: $M = \text{Co}$, $\Delta$: $M = \text{Ni}$, and $\circ$: $M = \text{Cu}$). Brillouin functions for $S = \frac{1}{2}$ and 1 plotted for reference.
4.1.3.2.2 Specific Heat Measurements

Although the specific heat \([C(T)]\) of Cu(N\(_3\))\(_2\)(4,4'-bpy) (See Figure 4-32) does not exhibit a typical second order transition, a significant anomaly at can be seen at low temperatures. The plot of \(C/T\) vs. \(T^2\) is clearly nonlinear at low temperatures as can be seen in Figure 4-33. If the experimental data were fit to \(\gamma T + \beta T^3\), one can obtain \(\gamma = 538\) mJ/mol K\(^2\). This large \(\gamma\) value is unexpected for this compound. Moreover, the upswing behavior at low temperatures is similar to that observed in heavy fermions. This anomalous phenomenon should be further investigated to understand whether it is due to magnetic interactions or other effects.
Figure 4-32 Specific heat for Cu(N$_3$)$_2$bpy.

The curve is an estimate of the lattice specific heat.
In order to subtract the phonon contribution from the total specific heat for Cu(N$_3$)$_2$bpy, we intended to prepare the nonmagnetic Zn isomorph of these compounds, but the synthesis was unsuccessful. We thus adapt the following method to estimate the electron-lattice specific heats [52]. The specific heat data in the temperature region far above the magnetic transition point were fit to a Debye-Einstein hybrid model:

\[
C_{\text{lattice}}(T) = (1-x)C_D(T) + xC_E(T) = (1-x)\beta T^3 + 3N_A k_B x(T_E/T)^2[1/\sinh(T_E/T)]^2
\]
The fit can be seen in Figure 4-32. Results from the fit give $x = 0.48$, $\gamma = 10.0 \text{ mJ/mol K}^2$, $\theta_D = 99.0 \text{ K}$, and $T_E = 42.9 \text{ K}$. After subtracting this calculated lattice-electron specific heat from the total specific heat, the magnetic specific heat is obtained as shown in Figure 4-34. Notice the slight shift to the left in the peak of the specific heat under an applied field, in agreement with the antiferromagnetic interpretation of $\chi(T)$ results. The magnetic specific heat is fit to that of an Ising chain of spin $\frac{1}{2}$ given by $C = R(J/2k_B T)^2 \text{sech}^2(J/2k_B T)$ [51]. The fit results (Figure 4-34) in $|J/k_B| = 13.05 \text{ K}$, in excellent agreement to the 13.14 K obtained from susceptibility. The total entropy removal ($dS_M = C/TdT$) due to the magnetic degree of freedom was calculated to be 3.51 J/mol, about 61% of that expected from $R \ln(2S+1)$. 
4.1.3.3 Ni(N₃)₂bpy

4.1.3.3.1 Magnetic Measurements

The magnetic susceptibility of Ni(N₃)₂bpy shows a maximum at $T = 3.8$ K (Figure 4-35). The high temperature fit of $\chi^{-1}(T)$ gives a positive $x$-intercept with $\theta = +10$ K (Figure 4-36). $\mu_{\text{eff}}(T)$ is shown in Figure 4-37. At room temperature the moment is $2.8 \mu_B$ (3.2 $\mu_B$ for free Ni²⁺). As the temperature is lowered the moment...
increases and reaches a peak of $3.83\mu_B$ at $T = 13$ K. Below 13 K the moment rapidly decreases and reduces to $1.8 \mu_B$ at 2 K. When $\chi(T)$ was fit to both CFM and MFT (Figure 4-35), it is found that CFM is far more descriptive of the measured susceptibility than mean field theory (MFT)'s Curie-Weiss law (CW). The CFM fit to $\chi(T)$ yielded a $J/k_B = 4.50$ K.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure4-35.png}
\caption{\(\chi(T)\) for Ni(N\textsubscript{3})\textsubscript{2}bpy \([H = 500$ Oe\)].
Curie-Weiss fit (dashed green); CFM fit (solid red).}  
\end{figure}
$\chi^{-1}(T)$ for Ni(N$_3$)$_2$bpy.

$\mu_{\text{eff}}(T)$: Ni(N$_3$)$_2$bpy (triangles); Co(N$_3$)$_2$bpy (Squares).
When the interchain interactions are accounted for at the lower temperatures, it is expected that IM of spin 1 will be more descriptive of the spin behavior than CFM because the spins have a more definite orientation at the lower temperatures. A comparison of the IM and CFM at low temperatures is shown in Figure 4-38. It is clear that the IM is more appropriate. IM yielded $J/k_B = 5.176\, \text{K}$, $z'J'/k_B = -3.661\, \text{K}$, and $g = 2.05$. Assuming eight nearest neighbors for this system, we obtain $J'/k_B = -0.458\, \text{K}$ (8.85% $J$).

The field dependent magnetization at $T = 2\, \text{K}$ is shown in Figure 4-31. As expected, at lower temperatures the negative interchain interactions become more important resulting in a smaller magnetization magnitude. The magnetization reached at 55 kOe was only about 3000 emu/mol at $H = 55\, \text{kOe}$. This is much less than the 10000 emu/mol, the saturation moment of spin 1 paramagnet, and is fairly consistent with the interpretation that significant antiferromagnetic interchain interactions at the lower temperatures.
4.1.3.3.2 Specific Heat Measurements

The specific heat $C(T)$ of Ni(N$_3$)$_2$bpy does not exhibit a typical second order phase transition as shown in Figure 4-39. The plot of $C/T$ vs. $T^2$ is nonlinear (Figure 4-40), which is similar to that of Cu(N$_3$)$_2$(bpy) discussed earlier. Since the synthesis of its nonmagnetic isomorph was not successful, we resort to the method of estimating the electron-phonon specific heats described in section 4.1.3.2.2. The fitting results were $\chi = 0.05$, $\gamma = 0.1$ mJ/mol K$^2$, $\theta_D = 91.3$ K, and $T_E = 200$ K. After subtracting this calculated lattice-electron specific heat from the total specific heat, the magnetic specific heat is
obtained as shown in Figure 4-41. The magnetic specific heat is fit to an Ising Chain of spin 1. Fit results (Figure 4-41) in $|J/k_B| = 5.65$ K, comparable to the 5.18 K obtained from $\chi(T)$ fit. The total entropy removal ($dS_M = C/TdT$) due to the magnetic degree of freedom was calculated to be 4.59 J/mol K, which about 50.4% of that expected from $R\ln(2S + 1)$. This is in qualitative agreement with low dimensional magnetism where the entropy removal is mainly achieved through short range ordering.

![Graph](image)

**Figure 4-39** $C(T)$ for Ni(N$_3$)$_2$bpy.
Figure 4-40 $C/T$ vs. $T^2$ for Ni(N$_3$)$_2$bpy.
4.1.3.4 Co(N$_3$)$_2$bpy

4.1.3.4.1 Magnetic Measurements

 Like Ni(N$_3$)$_2$bpy, Co(N$_3$)$_2$bpy does show a maximum in its susceptibility as shown in Figure 4-42. The high temperature fit of $\chi^{-1}(T)$ does give a positive $x$-intercept with $\theta = +18.8$ K (Figure 4-44). $\mu_{\text{eff}}(T)$ (Figure 4-37) has a value of 5.12 $\mu_B$ at room temperature (free Co$^{2+}$ has 4.8 $\mu_B$). The moment increases as the temperature is lowered reaching a maximum of 9.23 $\mu_B$ at 14 K. Below 14 K, the moment rapidly decreases reaching 2.06 $\mu_B$ at 2 K. This shows (like in the case of Ni) that the interchain exchange is negative and becomes important at the lower temperatures. Fitting $\chi(T)$ to CFM from
$T = 7 \text{ K to } 300 \text{ K}$, a $J/k_B = +5.54 \text{ K}$ was obtained (Figure 4-42). Fitting the low temperature susceptibility to an IM ($S = 3/2$) (Figure 4-43), it is found that $J/k_B = +5.51 \text{ K}$, $z' J'/k_B = -0.72 \text{ K}$, and $g = 2.016$. Assuming eight nearest neighbors, we obtain $J'/k_B = -0.09 \text{ K}$ (1.63% $J/k_B$). Again this confirms the assumption that spins are best modeled with an Ising behavior than CFM’s Heisenberg assumption as is clearly seen in Figure 4-43.

![Graph](image-url)  

**Figure 4-42** $\chi(T)$ for Co(N$_3$)$_2$bpy; CFM fit (solid red).
Figure 4-43 Fits of $\chi(T)$ for Co(N$_3$)$_2$bpy: IM(S=3/2) with interchain (solid red); CFM(S=3/2) with interchain (dashed green).
A hysteresis was observed for Co(N$_3$)$_2$ bpy at 2 K (Figure 4-45). The hysteresis curve is characterized by a coercive field of 2000 Oe. The magnetization is about 5000 emu/mol at 55 kOe and saturation was not reached. The saturation moment for spin 3/2 is about 16000 emu/mol. If indeed saturation is nearly reached, this indicates that a significant number of Co$^{2+}$ take the lower spin ½ since paramagnetic spin ½ have a saturation moment of 5500 emu/mol. This would be very different than in the case of the previously discussed [Co(bpdc)(H$_2$O)$_2$]H$_2$O which had a low temperature saturation moment near that of spin 3/2 system.
4.1.3.4.2 Specific Heat Measurements

As in Cu(N₃)₂(4,4'-bpy) and Ni(N₃)₂(4,4'-bpy), the specific heat of Co(N₃)₂(4,4'-bpy) does not show a typical second order phase transition as can be seen in Figure 4-46. Again no phase transition was observed. Since the synthesis of its nonmagnetic isomorph was not successful, we resort to the method of estimating the electron-phonon specific heats described in section 4.1.3.2.2. The fitting results were \( x = 0.185 \), \( \gamma = 17.74 \text{ mJ/mol} \).
K^2, \theta_D = 89.6 \text{ K}, \text{ and } T_K = 35.4 \text{ K}. \text{ After subtracting this calculated lattice-electron specific heat from the total specific heat, the magnetic specific heat is obtained as shown in Figure 4-47. The } C_M(T) \text{ is fit to that predicted for an Ising Chain of spin 3/2. Fit results (Figure 4-47) in } |J/k_B| = 8.18 \text{ K. This is higher than that obtained from the fitting of } \chi(T) \text{ data } (J/k_B = +5.54). \text{ Two possible reasons for this discrepancy. First, the lattice specific heat was only estimated. The second reason is that as the temperature is lowered, the ground state of cobalt } (S = \frac{1}{2}) \text{ is populated more and more; this is reflected in a higher } J/k_B. \text{ The total entropy removal } (dS_M = C/TdT) \text{ due to the magnetic ordering was calculated to be } 2.9 \text{ J/mol K, about 50\% of that expected from } R\ln(2S +1) \text{ with } S = \frac{1}{2}. \text{ This is in qualitative agreement with low dimensional magnetism where the entropy removal is mainly achieved through short range ordering.}
Figure 4-46 $C(T)$ vs. $T$ (□) and $C(T)/T$ vs. $T^2$ (△) for Co(N$_3$)$_2$(4,4'-bpy).

Solid line is the estimate of lattice specific heat. The Dashed line is a low temperature fit to $C(T)/T$ vs. $T^2$ to $\gamma + \beta T$. 
Figure 4-47 $C_{\text{magnetic}}(T)$ vs. $T$ for Co(N$_3$)$_2$(4,4'-bpy).

The solid line is a fit to IM for a chain of spin 3/2.
4.1.3.5  \textit{Fe(N}_3\textit{)}\textsubscript{2}bpy-1D

\subsection*{4.1.3.5.1 \textit{Magnetic Measurements}}

As in Co(N\textsubscript{3})\textsubscript{2}bpy, this Fe complex does show a maximum in the susceptibility measurement and a discrepancy between the zero field cooled (ZFC) and field cooled (FC) susceptibilities (Figure 4-48 and Figure 4-49). Curie-Weiss fit for $\chi^{-1}(T)$ reveals a positive $\theta = 49.32$ K (Figure 4-50). This is confirmed by the increasing effective moment with a lowered temperature (Figure 4-51). $\mu_{\text{eff}}(T)$ increases from 5.81 $\mu_B$ at 300 K (free Fe\textsuperscript{2+} has 5.4 $\mu_B$) to a maximum of 24.63 $\mu_B$ at 22.5 K. At lower temperatures, the moment decreases reaching 1.31 $\mu_B$ at 2K. This is similar to that we encountered with Ni and Co isomorphs. Fitting the data above the transition temperature to CFM ($S = 2$), a $J/k_B = 45.4$ K ($g = 2.1$) was obtained (Figure 4-52). This is much larger than those obtained in the case of Co and Ni. The CFM fit, however, was not excellent indicating that the spins are more represented with an IM instead because the transition happens at a high temperature and hence a rigid spin orientation at high temperatures. Using the IM (S=2), we obtained $J/k_B = 9.11$ K, $\varepsilon J'/k_B = -0.184$ K, and $g = 1.9$ (Figure 4-52). This consistent with the values obtained in the case of Co and Ni since the exchange is slightly higher reflecting a higher transition temperature.
Figure 4-48 ZFC(squares) and FC(triangles) $\chi(T)$ for Fe(N$_3$)$_2$bpy.

Figure 4-49 ZFC(squares) and FC(triangles) $\chi(T)$ for Fe(N$_3$)$_2$bpy-1D.
$\theta = 49.32\text{K}$

Figure 4-50 $\chi^{-1}(T)$ for Fe(N$_3$)$_2$bpy-1D.

Figure 4-51 $\mu_{\text{eff}}(T)$ for Fe(N$_3$)$_2$bpy-1D.
Figure 4-52 fit of $\chi(T)$ for Fe(N₃)₂bpy-1D:

CFM(solid red); IM(dashed green).
The magnetization $M(H)$ at $T = 2$ K is shown in Figure 4-53. A hysteresis curve characterized with a coercivity $H_C = 34$ kOe and a remnant magnetization $M_r = 4000$ emu/mol was observed. This is a very large coercivity and to my knowledge, no other molecular magnet has a value near this. The high field measurement of the magnetization at $T = 2$ K is shown in Figure 4-55. A meta-transition was observed at $H = 25$ kOe. The magnetization seemed to nearly saturate reaching the value of 12000 emu/mol at $H = 250$ kOe. This is still less than the saturation moment of 23000 emu/mol expected from spin 2.
Figure 4-53 $M(H)$ at $T = 2$ K for Fe(N$_3$)$_2$bpy-1D.
4.1.3.5.2 Specific Heat Measurements

The specific heat of this iron complex does not exhibit a typical second order phase transition as can be seen in Figure 4-55. The low temperature linear fit of $C/T$ vs. $T^2$ was linear with $\gamma = 72 \text{ mJ/mol K}^2$ and $\beta = 5.98 \text{ mJ/mol K}^4$ (Figure 4-56). Since the synthesis of its nonmagnetic isomorph was not successful, we resort to the method of estimating the electron-phonon specific heats described in section 4.1.3.2.2. The fitting results were $x = 0.149$, $\gamma = 0.1 \text{ mJ/mol K}^2$, $\theta_d = 6.86 \text{ K}$, and $T_E = 200 \text{ K}$ (Figure 4-55). After subtracting this calculated lattice-electron specific heat from the total specific heat,
the magnetic specific heat is obtained as shown in Figure 4-57. The magnetic specific heat is fit to that of an Ising Chain of spin 2. Fit results (Figure 4-47) in $|J/k_B| = 6.19$ K. This is lower than that derived from the susceptibility data ($J/k_B = +9.11$) since $C_M(T)$ accounts only for the overall $J$ which is a combination of the positive intrachain $J$ and the negative interchain $J'$. The total entropy removal ($dS_M = C/TdT$) due to the magnetic ordering was calculated to be 1.36 J/mol K, about 10.4% of that expected from $R \ln(2S+1)$. Again, this is in qualitative agreement with low dimensional magnetism where the entropy removal is mainly achieved through short range ordering.

![Figure 4-55](image)

**Figure 4-55** $C(T)$ of Fe(N$_3$)$_2$bpy-1D; fit to Debye-Einstein model (solid red)
Figure 4-56 $C/T$ vs. $T^2$ for Fe(N_3)$_2$bpy-1D.

Figure 4-57 $C_{\text{magnetic}}(T)$ vs. $T$ for Fe(N_3)$_2$(4,4’-bpy)-1D.

The solid line is a fit to IM for a ferromagnetic chain of spin 2.
4.1.4 Summary of the $M(N_3)_2(4,4'-bpy)$-1D [$M = \text{Cu}, \text{Ni}, \text{Co}, \text{Fe}$] System

The 1D metal organic frameworks, $M(N_3)_2(4,4'-bpy)$, forms an orthorhombic crystal system. The magnetic centers are linked via the azide $[(N_3)_2]$ ligands in an end-on (EO) 1D manner. Ordinarily EO linkage transmits positive (+) interactions. This was true for $M = \text{Ni}, \text{Co}, \text{and Fe}$. However, for $M = \text{Cu}$, negative (−) interactions were transmitted. The interaction between the chains ($J'$) was negative for all cases. No typical second order phase transition was seen in any of the specific heats. However, after subtracting the estimated specific heat from the total specific heat, a broad peaked magnetic specific heat was obtained. The magnetic specific heats were fit to the specific heat of an Ising chain. The $J$ obtained from the specific heat fits was in reasonable agreement with that obtained from $\chi(T)$ fits. A summary of the fitting results for the system are summarized in Table 6.
Table 6 Summary of the fitting results from $\chi(T)$ and $C(T)$ for the M(N$_3$)$_2$(4,4'-bpy) system.

<table>
<thead>
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<th></th>
<th>$\chi(T)$ Fits</th>
<th>$C(T)$ Fits</th>
</tr>
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<tbody>
<tr>
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<td>Classical Fisher Model (CFM)</td>
<td>Ising Model (IM)</td>
</tr>
<tr>
<td></td>
<td>$J/k_B$ (K)</td>
<td>$J/k_B$ (K)</td>
</tr>
<tr>
<td>Fe(N$_3$)$_2$(4,4'-bpy)</td>
<td>47</td>
<td>9.11</td>
</tr>
<tr>
<td>Co(N$_3$)$_2$(4,4'-bpy)</td>
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<td>5.54</td>
</tr>
<tr>
<td>Ni(N$_3$)$_2$(4,4'-bpy)</td>
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<td>5.18</td>
</tr>
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<td>Cu(N$_3$)$_2$(4,4'-bpy)</td>
<td>N/A</td>
<td>−13.14</td>
</tr>
</tbody>
</table>
4.1.5 Crystal Structure of $\text{Ni}_2(\text{BDC}_2)(\text{TED})$ and $\text{Ni}_2(\text{BODC}_2)(\text{TED})$

$\text{M}_2(\text{BDC}_2)(\text{TED})$ and $\text{M}_2(\text{BODC}_2)(\text{TED})$ are isostructural and their crystal structure is shown in Figure 4-58 and Figure 4-59. [Zn(\text{BDC})(\text{TED})\textsubscript{0.5}] crystallizes in a tetragonal crystal system (space group $P4/ncc$) with lattice constants $a = b = 14.8999(4)$ Å, $c = 19.1369(2)$ Å [72]. It features a secondary building unit (SBU) commonly known as [M2C4O8] paddle-wheel. Through these four-connected SBUs as nodes and the BDC ligands as linkers, a 2D net is formed [73]. The column-like triethylenediamine (TED) ligands coordinate to the metal centers from the axial directions of the paddle-wheels, giving rise to the typical pillared-layer 3D structure [73]. A structure change occurs upon removal of the guest molecules, and the crystal analysis indicated a different space group, $P4/mmm$ [73]. Removal of the guest molecules results in a 3D porous structure containing intersecting channels of two different sizes in which all BDC ligands become straight [73]. The structure of Ni(BODC)(TED)\textsubscript{0.5} is identical to that of M(BDC)(TED)\textsubscript{0.5} (i.e. tetragonal of space group $P4/ncc$) with $a = b = 10.7840$ Å, $c = 9.423$ Å [74].
Figure 4-58 Crystal structure for $M_2(BDC)_2(TED)$ and $N_2(BODC)_2(TED)$. 
4.1.5.1 $\text{Ni}_2(\text{BODC})_2(\text{TED})$ Magnetic Measurements

Magnetic measurements were done at different field strengths and different temperatures. The magnetic susceptibility $\chi(T)$ exhibits a discrepancy between the zero field cooled (ZFC) and the field cooled measurements (Figure 4-60).
The discrepancy between the ZFC and FC can be related in, in some materials, to the coercivity ($H_C$) of the hysteresis curve by the following simple relation:

\[
\frac{M_{ZFC}}{H_{app}} = \frac{M_{FC}}{(H_{app} + H_C)} \quad [75].
\]
Where, of course, $\chi_{ZFC} = M_{ZFC}/H_{app}$ and $\chi_{FC} = M_{FC}/H_{app}$. As a result a greater discrepancy is expected at low applied fields and small or no discrepancy is witnessed at higher fields. Rearranging the equations we can write:

$$H_C = (\chi_{FC} - \chi_{ZFC})H_{app}/\chi_{ZFC}.$$

Using the above data with $H = 2000$ Oe, we can estimate:

$$H_C = (0.27 - 0.15)(2000/0.15) \text{ Oe} = 1600 \text{ Oe}.$$

This is a very good estimate as will be seen in the $M(H)$ discussion.

A plot of the moment as a function of the temperature at a field of 2000 Oe is shown in Figure 4-61. The magnetic moment increases sharply below 40 K from 2.4 $\mu_B$ to a maximum of 3.67 $\mu_B$ at $T = 13$ K. This ferromagnetic behavior is confirmed with a positive x-intercept in the plot of $\chi^{-1}(T)$. A fit linear fit reveals a positive $\theta = +20$ K. Below 13 K the magnetic moment starts decreasing vigorously because of the negative coupling within the dimer become more relevant at lower temperatures as will be seen in the magnetization curves at different temperatures.
Figure 4-61 $\mu_{\text{eff}}(T)$ in Ni$_2$(BODC)$_2$(TED).

Figure 4-62 $\chi^{-1}(T)$ and a high temperature fit to Curie-Weiss law in Ni$_2$(BODC)$_2$(TED).
When magnetization as a function of the field was measured, a soft ferromagnetic behavior was observed via a hysteresis curve characterized by a coercivity $H_C$ of 1700 Oe and a remnant magnetization of 241 emu/mol at $T = 2$ K. At our maximum lab field of 54 kOe and $T = 2$ K, magnetization reached 3040 emu/mol and showed no saturation. The magnetization curve at $T = 1.8$ K was always lower than that at $T = 2$ K confirming that the antiferromagnetic interactions within the dimer become stronger at lower temperatures. Fitting magnetization to the Brillouin function gave an estimate of the effective spin per nickel atom to be about 0.33 at 2 K and 0.3 at 1.8 K (Figure 4-65 and Figure 4-66).

Figure 4-63 $M(H)$ at $T = 1.8$ in Ni$_2$(BODC)$_2$(TED).
Figure 4-64 $M(H)$ at $T = 2$ and $1.8$ K of Ni$_2$(BODC)$_2$(TED).
Figure 4-65 Comparison of $M(H)$ at $T = 2$ K behavior of Ni$_2$(BODC)$_2$(TED) to that of a paramagnet.
4.1.5.2 \( \text{Ni}_2(\text{BODC})_2(\text{TED}) \) Specific Heat Measurements

The heat capacity measurement did not show the typical second order magnetic transition characterized with the lambda shape. Naively fitting the low temperature part of \( C(T) \) to only phonons and electrons results in an apparent large heavy fermion-like \( \gamma = 904 \text{ mJ/mol-K}^2 \) and \( \beta = 11.1 \text{ mJ/mol-K}^4 \). However, the plot of \( C/T \) vs. \( T^2 \) (which is
expected to be linear if only electron-phonon contributions are present) is clear evidence for the magnetic degree of freedom.

\[ C(T) = \gamma T + \beta T^3 \]
\[ \gamma = 904 \text{ mJ/mol K}^2 \]
\[ \beta = 11.1 \text{ mJ/mol K}^4 \]

**Figure 4-67** $C(T)$ behavior of a Ni$_2$(BODC)$_2$(TED) sample and a fit of its low temperature part to electron-phonon specific heats
The lattice specific heat was estimated by the Debye-Einstein model discussed earlier and is shown in Figure 4-69 \[ x = 2.778 \times 10^{-4}, \beta = 11.22 \text{ mJ/mol K}^4, \text{and} T_E = 1.01 \times 10^{-4} \]. Again, after the lattice specific heat was properly estimated the high \( \gamma \) vanished \((\gamma = 13 \text{ mJ/mol K}^2)\). Subtracting the lattice specific heat from the total specific heat, the magnetic specific heat was obtained (See Figure 4-70). The total entropy removal was 11.11 J/mol K.
Figure 4.69 Estimated lattice specific heat for Ni$_2$(BODC)$_2$(TED) (solid red).
4.1.5.3 \( \text{Ni}_2(\text{BDC})_2(\text{TED}) \) Magnetic Measurements

\( \text{Ni}_2(\text{BDC})_2(\text{TED}) \) has the same crystal structure as \( \text{Ni}_2(\text{BODC})_2(\text{TED}) \) and is easier to make in the lab. Some of the few differences between them is that the ligand [BDC] is rigid unlike the flexible [BODC] one; this rigidity along with the larger lattice parameters in the \( \text{Ni}_2(\text{BDC})_2(\text{TED}) \) crystals are the reason for the different magnetic behaviors between the systems.

Shown in Figure 4-71 and Figure 4-72 are the magnetic susceptibility data for \( \text{Ni}_2(\text{BDC})_2(\text{TED}) \)-guest free and \( \text{Ni}_2(\text{BDC})_2(\text{TED}) \)-DMF.
Figure 4-71 $\chi(T)$ for Ni(BDC)(TED)-DMF

$H = 100$ Oe (squares) and $H = 1000$ Oe (Circles).
Figure 4-72 $\chi(T)$ for Ni(BDC)(TED)-Guest Free

$H = 100$ Oe (squares) and $H = 1000$ Oe (Circles).

When the guest is introduced in the pores the susceptibility shows an enhancement from 0.25 emu/mol Oe (for guest free) to 0.47 emu/mol Oe (with DMF) at $T = 2$ K. The effect for the guest (DMF) is more apparent when $\chi^{-1}(T)$ is plotted. In Figure 4-73 is a plot of $\chi^{-1}(T)$ at $H = 1000$ Oe, the Ni$_2$(BDC)$_2$(TED)-guest free is in circles and Ni$_2$(BDC)$_2$(TED)-DMF is triangles (Figure 4-73). Clearly Ni$_2$(BDC)$_2$(TED)-guest free behaves like an antiferromagnet and with a large negative $\theta$ of $-132$ K. On the other
hand Ni$_2$(BDC)$_2$(TED)-DMF behaves almost like a paramagnet with a small positive $\theta$ of + 0.5 K.

Figure 4-73 $\chi^{-1}(T)$ for Ni(BDC)(TED); Squares (Guest Free), Circles (DMF).

The magnetic moment is constant from room temperature to about 60 K for Ni$_2$(BDC)$_2$(TED)-DMF, just like a paramagnet would behave (Figure 4-74). Below 12 K, however, the magnetic moment shows a sharp increase. In contrast, Ni$_2$(BDC)$_2$(TED)-guest free shows a decrease in the magnetic moment as the temperature
is lowered from room temperature to about 120 K. Below 120 K a more complex behavior is seen which ends with a sharp decrease in the magnetic moment below 10 K. (Both magnetic moments are measured with $H = 1000$ Oe with the circles representing DMF and triangles representing guest free).

**Figure 4-74** $\mu_{\text{eff}}(T)$ for Ni(BDC)(TED) Squares (Guest Free), Circles (DMF).
$M(H)$ at $T = 1.9$ K for Ni$_2$(BDC)$_2$(TED)-guest free along with the comparison to the Brillouin Function at different spins is shown in Figure 4-75. It clearly behaves like a paramagnet with an effective spin of 0.3 at low applied fields.

![Figure 4-75](image)

**Figure 4-75** $M(H)$ at $T = 1.9$ K for Ni$_2$(BDC)$_2$(TED)-Guest Free

Compared with Brillouin Function.
Looking at the $M(H)$ at $T = 2 \text{ K}$ data of $\text{Ni}_2(\text{BDC})_2(\text{TED})\text{-DMF}$, we see a much higher effective spin of 1 at the low fields and about 0.4 at the higher fields. Further analysis needs to be done in order to compare the two cases of guest free and with DMF at the same temperatures and the same field ranges.

Figure 4-76 $M(H)$ at $T = 2 \text{ K}$ for $\text{Ni}_2(\text{BDC})_2(\text{TED})\text{-DMF}$

Compared with Brillouin Function.
4.1.5.4 Specific Heat Measurements

The specific heat data of Ni$_2$(BDC)$_2$(TED) is shown in Figure 4-77. Although no clear anomaly can be seen (except for the little bump at $T = 3$ K), a clear deviation from the linear and cubic temperature terms can be seen below $T = 4$ K.

Figure 4-77 $C(T)$ of Ni(BDC)(TED); low temperature part is fit to the electron-phonon specific heats.
The need for a third term in the function of $C(T)$ to fit the data is further manifested in the plot of $C/T$ vs. $T^2$ (Figure 4-78). The lattice specific heat was estimated by the Debye-Einstein model discussed earlier and is shown in Figure 4-79 [$\alpha = 0.652$, $\beta = 10.60$ mJ/mol K$^4$, and $T_E = 43.44$]. Again, after the lattice specific heat was properly estimated the high $\gamma$ vanished ($\gamma = 20$ mJ/mol K$^2$). Subtracting the lattice specific heat from the total specific heat, the magnetic specific heat was obtained (See Figure 4-80). The total entropy removal was 3.21 J/mol K.

Figure 4-78 $C/T$ vs. $T$ of Ni(BDC)(TED) clearly illustrates the significant presence of magnetic interactions.
Figure 4-79 Estimated lattice specific heat for Ni$_2$(BDC)$_2$(TED) (solid red).
**Figure 4-80** Estimated magnetic specific heat for Ni$_2$(BODC)$_2$(TED).
4.2 CANTED ANTIFERROMAGNETIC 3D SYSTEMS

4.2.1 Crystal Structure of $M(N_3)_2bpy$-3D [$M = Mn, Fe$]

Single crystal x-ray diffraction was used to determine the structure of the complex. Thereafter, Powder x-ray diffraction (PXRD) was used to confirm the structure of samples made later. $M(N_3)_2bpy$ has a 3D phase in the case of Fe and Mn. The crystal structure of $M(N_3)_2bpy$-3D [$M = Fe, Mn$] was tetragonal crystal system with the space group $P4_{1}2_{1}2_{1}$ (No. 92) with $a = b = 8.262\,\text{Å}$, and $c = 16.911\,\text{Å}$ in the case of Mn, $a = b = 8.132\,\text{Å}$, and $c = 16.708\,\text{Å}$ in the case of Fe.

![Image of crystal structure](image)

Figure 4-81: 3D nature of the crystal structure of $M(N_3)_2(bpy)$ [$M = Mn, Fe$] (See Ref. [23]).
Looking into the page is the *a-direction*, top to bottom is *b-direction*, and left to right is the *c-direction*. If you move from one Manganese atom to the one connected to it via the \( N_3 \)-azido, spirals you into (or out of) the page. \( \text{Mn}^{2+} \) ions are linked through \( N_3 \)-azido ions with end-to-end mode (4,4-bpy ligands represented by black sticks).

The local geometry of \( \text{M}^{2+} \) is also shown (Figure 4-82). \( \text{M}^{2+} \) ions are in a slightly distorted octahedral sites each Mn or Fe atom is bonded to four -(1,3) azido ligands and two 4,4-bpy ligands in the *trans* position. \( \text{M}−\text{M} \) distance is 5.87 Å through all EE azido bridges, and 11.50 Å when separated by 4,4-bpy ligands. It is expected that the magnetic interactions among the \( \text{M}^{2+} \) ions mainly occur in the helical chains in both *a* and *c* directions.
Figure 4-82 Local structure of $\text{M(N}_3\text{)}_2(bpy)$ [$\text{M} = \text{Mn, Fe}$] (See reference [23]).
4.2.2 \textit{Mn(N}_3\textit{)}\textsubscript{2}\textit{bpy-3D}

4.2.2.1 \textit{Magnetic Measurements}

The magnetic properties of \textit{Mn(N}_3\textit{)}\textsubscript{2}\textit{bpy-3D} captured a great deal of attention and were reported in several studies [76-79]. $\chi(T)$ was measured under different applied fields on a powder sample of \textit{Mn(N}_3\textit{)}\textsubscript{2}(bpy). Notice the splitting of the zero field cooled and the field cooled susceptibilities below a certain (transition temperature). Some of the results at the lower fields are shown (Figure 4-83).

\textbf{3D-Mn(N3)2(4,4'-bpy), DD-120, H = 3 G, 10 G, 50 G}

\textbf{Figure 4-83} Low field measurement of $\chi(T)$ for \textit{Mn(N}_3\textit{)}\textsubscript{2}\textit{bpy}: ZFC and FC split below \textit{T} = 38 K.
The derivative of $\chi(T)$ is calculated and plotted in Figure 4-84. It reveals that the transition temperature is about 38 K.

![Graph showing derivative of $\chi(T)$]{figure1}

**Figure 4-84** Derivative of $\chi(T)$ confirms $T_C = 38$ K.

The high temperature (paramagnetic) part of $\chi^{-1}(T)$ for $H = 500$ and 1000 Oe can be seen in Figure 4-85 and Figure 4-86. A fit to the Curie-Weiss law gives $\theta = -87$ K ($H = 500$ Oe), and $\theta = -99.6$ K ($H = 1000$ Oe).
Figure 4-85 $\chi^{-1}(T)$ at $H = 500$ Oe fit to Curie-Weiss law.
$\mu_{\text{eff}}(T)$ is shown in Figure 4-87. At room temperature $\mu_{\text{eff}}$ has a value of 5.1 $\mu_B$, slightly less than that of free Mn$^{3+}$ ($\mu_{\text{eff}} = 5.9 \mu_B$). The magnetic moment decreases from the high temperatures all the way to about $T = 38$ K reaching a moment of 3.3 $\mu_B$. This indicates that the Antiferromagnetic interaction is stronger at the higher temperatures. Below $T = 38$ K we see that the moment starts increasing and reaching a maximum of 9.4 $\mu_B$ and 5.5 $\mu_B$ for $H = 500$ Oe and 1000 Oe at $T = 26$ K, respectively. Therefore in this range, the ferromagnetic coupling becomes stronger.
Figure 4-87 $\mu_{\text{eff}}(T)$ for Mn(N₃)₂bpy-3D.

Modeling this Mn complex as a Heisenberg diamond-type network of spin 5/2, the high temperature susceptibility is given by

$$
\chi(T) = [N_A g^2 \mu_B^2 S(S+1)/2k_BT][1 + 23.3333(J/k_BT) + 147.778(J/k_BT)^2 + 405.487(J/k_BT)^3
- 1621.13(J/k_BT)^4 - 14201(J/k_BT)^5 + 1037840(J/k_BT)^6] \quad (\text{See [56]})
$$
Fitting $\chi(T)$ and $\mu_{\text{eff}}(T)$ to the above model, the following results are obtained: $J/k_B = -1.6K$ and $g = 1.9$. It is evident that the Rushbrooke-Wood model fits the data well above $T_C$.

![Graph showing fitting of $\chi(T)$ to Heisenberg model of a diamond-like network of $S = 5/2$.](image)

**Figure 4-88** Fit of $\chi(T)$ to Heisenberg model of a diamond-like network of $S = 5/2$. 

Below $T_C$ we resort to the spin wave theory for a ferromagnet which predicts that $\chi(T)$ should be of the form

$$\chi(T) = A - BT^\gamma; \quad \gamma = 3/2.$$ 

Allowing $\gamma$ to vary from 3/2, $\chi(T)$ is fit (Figure 4-90). An exponent of $\gamma = 2.14$ is obtained. This deviation from the Bloch $T^{3/2}$ law is expected for a 3D system where the exponent is expected to be $\gamma = 2$ for 3D and $\gamma = 3/2$ in the case of 2D half integer cases.
Our material in turn is expected to deviate from this modified spin wave theory since it is derived for the microscopic case. A deviation from this theory, as noted by the authors, is also expected since paramagnetic impurities do contribute to the magnetic signal; furthermore, magnetic measurement is made under an applied field while the theory is derived for the zero field [80]. Despite this, it is interesting to see that the exponent of this non-ideal system is in a good agreement with the prediction by an ideal theory.

\[
\chi = 0.637 - 2.01T^{2.14}
\]

**Figure 4-90** Modified Bloch law fit to $\chi(T)$ below $T_c$. 
Isothermal measurement of magnetization on Mn(N₃)₂bpy is shown in Figure 4-91 for $T = 2$ K, and a closer into the loop reveals hysteresis behavior for both $T = 1.9$ K and $T = 2$ K (Figure 4-92). Notice the slope change in $M(H)$ around $H = 25$ kOe possibly due to spin reorientation. The hysteresis has a coercivity of about 150 Oe, and a remnant magnetization of 260 emu/mol at $T = 2$ K, and, a higher, 360 emu/mol at $T = 1.9$ K.

![Graph showing $M(H)$ at $T = 2$ K](image)

**Figure 4-91** $M(H)$ at $T = 2$ K shows slope change at 25 kOe.

No sign of saturation up to 55 kOe.
Our next measurement was time dependent magnetization. We keep our temperature constant, turn on a magnetic field, then turn it off, and measure the magnetization as a function of time. We did this for several fields and at several temperatures. At $T = 2$ K, the cases for both $H = 10$ Oe, and $H = 4500$ Oe can be seen in Figure 4-93 and Figure 4-94.
Figure 4-93 Time dependent magnetization at $T = 2$ K shows decay when the applied field of $H = 10$ Oe is turned off.
What is interesting in this is the following. For the case of $H = 10$ Oe, it is what we expect. Namely, when we turn on the field the moments are more aligned; when the field is turned off, the moments relax to their previous position and hence the *decay* curve. However, for the case of $H = 4500$ Oe (and in fact all our high field measurements), when the field is turned off, the moment as a function of time *grows* back to its relaxed position.

In Figure 4-95 and Figure 4-96 I show more $M(t)$ for the case of $H = 4500$ Oe at higher temperatures ($T = 15$ K, 35 K). Again, the same growth curve is observed but shorter relaxation times.
Figure 4-95 Time dependent magnetization at $T = 15$ K shows growth when the applied field of $H = 4500$ Oe is turned off.
Figure 4-96 Time dependent magnetization at $T = 15$ K shows growth when the applied field of $H = 4500$ Oe is turned off.

### 4.2.2.2 Specific Heat Measurements

The low temperature specific heat data was fit to the electron and phonon terms as shown in Figure 4-97. The fit reveals that $\gamma = 0.395$ mJ/mol K$^2$, and $\beta = 5.12$ mJ/mol K$^4$. The linearity of the low temperature plot of $C/T$ vs. $T^2$ is shown in Figure 4-98.
Figure 4-97 Low temperature $C(T)$ and its fit to electron-phonon specific heats.

Figure 4-98 Linearity of $C/T$ vs. $T^2$.
Since the transition temperature for Mn(N$_3$)$_2$bpy is around $T = 38$ K, high temperature specific heat was measured. The result is shown in Figure 4-99. In order to calculate the magnetic contribution to the specific heat, the phonon contribution must be subtracted. The electron-phonon contribution to specific heat is estimated with curve in Figure 4-99 using the previously discussed Debye-Einstein model for specific heats given by

$$C_{\text{lattice}}(T) = (1-x)C_D(T) + xC_E(T) = (1-x)\beta T^3 + 3N_A k_B x(T_E/T)^2 [1/\sinh(T_E/T)]^2.$$ 

Results from the fit give $x = 0.00384$, $\theta_D = 462.96$ K, and $T_E = 193.63$ K.

![Figure 4-99](image_url) 

**Figure 4-99** $C(T)$ Mn(N$_3$)$_2$bpy-3D: second order transition at $T = 38$ K.

Estimate of $C_{\text{lattice}}(T)$ (solid red).
The estimated magnetic specific heat is shown in Figure 4-100. With this magnetic specific heat the total entropy removal was calculated to be 8.52 J/mol K, 57.2% of the $R \ln(2S+1)$. Ideally, for a 3D simple cubic system, the magnetic entropy below $T_C$ should be about 82% of the entropy expected from the spin degree of freedom [81]. The discrepancy in this case is mostly due to the fact that the $C_{\text{lattice}}$ was (over) estimated. For completeness, in a 2D simple quadratic system, 44% of the entropy is acquired below $T_C$; for an ideal isotropic 1D system, 0% of the entropy is acquired below $T_C$ since $T_C$ is 0 K [81].

![Figure 4-100](image)

**Figure 4-100** $C_{\text{magnetic}}$ for Mn(N$_3$)$_2$bpy-3D.
4.2.3 $\text{Fe(N}_3\text{)}_2\text{bpy-3D}$

4.2.3.1 Magnetic Measurements

This 3D phase of Fe(N$_3$)$_2$bpy exhibits a magnetic phase transition at 22 K with a discrepancy between the zero field cooled (ZFC) and field cooled (FC) susceptibilities (Figure 4-101). Curie-Weiss fit for $\chi^{-1}(T)$ reveals a positive $\theta = -24.43$ K (Figure 4-102). This is confirmed by the initially $\mu_{\text{eff}}(T)$ with a lowered temperature (Figure 4-103). Initially $\mu_{\text{eff}}(T)$ slowly decreases from 5.08 $\mu_B$ at room temperature (free Fe$^{2+}$ has 5.4 $\mu_B$), to 4.6 $\mu_B$ at 65K; below 65K it quickly increases reaching a maximum of 17.80 $\mu_B$ at 15.5 K. As the temperature is lowered further, the moment decreases reaching 6.73 $\mu_B$ at 2 K.

Modeling this Fe complex as a Heisenberg diamond-type network of spin 2, the high temperature susceptibility is given by

$$\chi(T) = [N_A g^2 \mu_B^2 S(S+1)/(2k_B T)][1 + 23.3333(J/k_B T)^2 + 147.778(J/k_B T)^3 + 405.487(J/k_B T)^4 - 1621.13(J/k_B T)^5 - 14201(J/k_B T)^6 + 1037840(J/k_B T)^7]\) (See Ref. [56]).$$

Fitting of $\chi(T)$ and $\mu_{\text{eff}}(T)$ to the above model, $J/k_B = -0.704$K and $g = 1.9$ are obtained (Figure 4-104). Clearly this Rushbrooke-Wood model fits the data well above $T_C$.

Below $T_C$ we resort to the spin wave theory for a ferromagnet which predicts that $\chi(T)$ should be of the form

$$\chi(T) = A - BT^\gamma ; \gamma = 3/2$$
Allowing $\gamma$ to vary from 3/2, $\chi(T)$ is fit (Figure 4-104). An exponent of $\gamma = 5.51$ is obtained (Figure 4-104). This deviation from the Bloch $T^{3/2}$ law is expected for a 3D system where the exponent is expected to be $\gamma = 9/2$ for 3D and $\gamma = 4/2$ in the case of 2D for an integer spin [80]. Our material in turn is expected to deviate from this modified spin wave theory since it is derived for the microscopic case (See section 4.2.2.1).

Hysteresis was observed at $T = 2$ K with $H_C = 500$ Oe. The transition temperature was confirmed to be 20 K with an Arrott plot ($M^2$ vs. $H/M$) as shown in Figure 4-106.

Figure 4-101 ZFC and FC $\chi(T)$ for Fe(N$_3$)$_2$bpy-3D.
Figure 4-102 $\chi^{-1}(T)$ for Fe(N$_3$)$_2$bpy-3D.

Figure 4-103 $\mu_{eff}(T)$ for Fe(N$_3$)$_2$bpy-3D.
Figure 4-104 $\chi(T)$ of Fe(N$_3$)$_2$bpy-3D: High temperature fit to Heisenberg diamond-type network (solid red). Low temperature to modified Bloch’s law (dashed green).
Figure 4-105 $M(H)$ at $T = 2$ K for Fe(N$_3$)$_2$bpy-3D.
4.2.3.2 Specific Heat Measurements

The heat capacity of Fe(N₃)₂bpy-3D does have a second order phase transition at $T = 20$ K (Figure 4-107). This is ferromagnetic transition observed in $\chi(T)$ is confirmed with the peak shifting to the right when $C(T)$ was measured under an applied field of 35kOe (Figure 4-107). Plotting $C/T$ vs. $T^2$ was linear with $\beta = 6.63$ mJ/mol K⁴ and a $\gamma \sim 0$ (Figure 4-108). The lattice specific heat was estimated via the same method as in
Mn(N₃)₂-bpy, described previously (Figure 4-109). After subtracting the estimated lattice specific heat, the magnetic specific heat was calculated and plotted in Figure 4-110. With this magnetic specific heat the total entropy removal was calculated to be 4.96 J/mol K (37% of the $R \ln(2S+1)$). Ideally, for a 3D simple cubic system, the magnetic entropy below $T_C$ should be about 82% of the entropy expected from the spin degree of freedom [81]. The discrepancy in this case is mostly due to the fact that the $C_{lattice}$ was (over) estimated.

![Graph showing C(T) for Fe(N₃)₂bpy-3D.](image-url)

**Figure 4-107** $C(T)$ for Fe(N₃)₂bpy-3D.
Figure 4-108 $C/T$ vs. $T^2$ for Fe(N$_3$)$_2$bpy-3D.
Figure 4-109 Estimate of $C_{lattice}$ in Fe(N$_3$)$_2$bpy-3D (Solid red).
Figure 4-110 Estimated $C_{\text{magnetic}}$ for Fe(N$_3$)$_2$bpy-3D.
SUMMARY AND CONCLUSION

The magnetic and thermodynamic properties of ten MMOFs were measured and analyzed via the appropriate models in both 1D and 3D.

For the 1D system with $S = \frac{1}{2}$, an Ising Model (IM) with spin $\frac{1}{2}$ was found to be suitable for describing the data for the entire temperature region. When $S \geq 1$ it was found that the magnetic behavior is well described with a 1D Heisenberg model of classical spins (also called Classical Fisher Model, CFM) in the temperature region $T > T_C$. In the temperature region of few degrees above and below $T_C$, it is can reasonably be assumed that the spins take a more rigid orientation along some axis (e.g. has less freedom than allowed in the Heisenberg model). This allowed for the rational use of the IM in this region and indeed it fitted the data well. The interchain exchange interactions ($J'$) were calculated by treating one magnetic chain in the mean field of nearest neighbor chains (the number neighboring chains depends on the crystal parameters of the MOF). In all cases $J'$ was negative and has a magnitude of only a few percent the value of the intrachain exchange ($J$), confirming the 1D assumption.

In Most 1D MOFs studied, no clear magnetic phase transition observed. However, if the magnetic degree of freedom is neglected, an apparent high heavy fermion-like $\gamma$ is obtained (values as high as 900 mJ/mol K$^2$). Because the synthesis of the nonmagnetic Zn isomorphs for many of these compounds was not successful, properly estimating the lattice specific heats was critical. Modeling the lattice specific
heat with a Debye-Einstein hybrid, fitting it to the high temperature region of the specific
heat where the magnetic contributions are negligible, and extending this fit to the lower
temperature region, the lattice specific heat was estimated. After subtracting the
calculated lattice specific heat and subtracting it from the total specific heat, the magnetic
specific heat was obtained.

In the case of [Co(bpdc)(H$_2$O)$_2$]H$_2$O-1D, the specific heat did have a broad
anomaly at the $T_C$ expected from $\chi(T)$ measurements. Its nonmagnetic analogue
([Zn(bpdc)(H$_2$O)$_2$]H$_2$O) was also successfully synthesized. However, the mass
difference between Co and Zn must be accounted for when subtracting the lattice specific
heat from the total specific heat. Not accounting for the mass will lead to an over
estimate of $C_{\text{lattice}}$ and, thus, an underestimate of $C_{\text{magnetic}}$. To properly account for the
mass difference effect on $\beta$, we must use $\beta_{\text{Co}} = \beta_{\text{Zn}}(m_{\text{Co}}/m_{\text{Zn}})^{3/2}$ before subtracting the Zn
specific heat from that of Co.

In porous MOFs, guest molecules can be introduced in the pores. For the porous
MOF Ni(BDC)(TED)$_{0.5}$, $\chi(T)$ measurements of the guest free were compared to the $\chi(T)$
measurements of when the DMF molecules was introduced as a guest. It was observed
that introducing DMF changed the magnetic properties from strongly antiferromagnetic
to weakly ferromagnetic: the guest free Ni(BDC)(TED)$_{0.5}$ had a $\theta = -130$ K, and + 0.5 K
when the guest was introduced into the pores. Similarly, the ratio of magnetic moments
per mol when the DMF was introduced to that of the guest free was about 3:1 (i.e.
$\mu_{\text{DMF}}/\mu_{\text{guest-free}} \approx 3$). This can have potential applications since the guest molecules can be
easily introduced or removed (by soaking the sample in guest fluid or heating the sample to release the guest).

For the MOF M(N₃)₂bpy, a 3D phase was formed for Mn and Fe. Both Mn(N₃)₂bpy-3D and Fe(N₃)₂bpy-3D had ferromagnetic transitions confirmed with a second order phase transition in the specific heat data. Above the transition temperature the susceptibility was modeled and fit to a Heisenberg model for a diamond-type network of spin 5/2 and 4/2 for Mn and Fe, respectively (derived by G.S. Rushbrooke and P. J. Wood).

The most significant results from this systematic study of MMOFs include:

1. The successful estimate of $C_{\text{lattice}}$ leading to meaningful fitting of models in both $\chi(T)$ and $C_{\text{magnetic}}$. I hope the due attention (often lacking in contemporary publications) we devoted to the measurement of $C(T)$ and estimating $C_{\text{lattice}}$ will be useful to experimentalists in the future. In particular, when the estimated $C_{\text{lattice}}$ is subtracted from $C_{\text{total}}$, it consistently produced $C_{\text{magnetic}}$ with a broad peak at a temperature consistent with that expected from $\chi(T)$ and $\mu_{\text{eff}}(T)$ measurement (See Table 7).

2. The discovery of 3D ferrimagnets or canted antiferromagnets M(N₃)₂bpy with rather high transition temperatures (39 K, and 20 K) and unmatched high coercivity of 34 kOe.

Future work will devote more time to the synthesis of other families of MOFs with an emphasis on single crystal synthesis. Synthesis of high quality single crystals will allow for the analysis of magnetic ordering using spin wave theory accounting for
the dimensionality of the system [80]. It would also be very interesting for future studies to account for the effect of pressure on the magnetic behavior of MOFs especially in the porous MOFs case under an applied stress.

**Table 7:** Summary of the temperature at which $\chi(T)$, $\mu_{\text{eff}}(T)$, and $C_{\text{magnetic}}(T)$ show a maximum.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_C$ or $T_{\text{Max}}$ in $\chi(T)$ (K)</th>
<th>Peak in $\mu_{\text{eff}}(T)$ (K)</th>
<th>Peak in $C_{\text{magnetic}}(T)$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(N$_3$)$_2$bpy-1D</td>
<td>No peak</td>
<td>No peak</td>
<td>6</td>
</tr>
<tr>
<td>Ni(N$_3$)$_2$bpy-1D</td>
<td>3.8</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Co(N$_3$)$_2$bpy-1D</td>
<td>5.5</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>Fe(N$_3$)$_2$bpy-1D</td>
<td>19</td>
<td>22.5</td>
<td>14</td>
</tr>
<tr>
<td>Ni(BODC)(TED)$_{0.5}$</td>
<td>12</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>Ni(BDC)(TED)$_{0.5}$</td>
<td>No peak</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Fe(N$_3$)$_2$bpy-3D</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Mn(N$_3$)$_2$bpy-3D</td>
<td>38</td>
<td>38</td>
<td>38</td>
</tr>
</tbody>
</table>
REFERENCES CITED


oxalate-bpy Mixed-Ligand Framework \([M(\text{ox})(\text{bpy})] (M = \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Zn(II)}; \text{ox} = \text{C}_2\text{O}_4^{2-}; \text{bpy} = 4, 4'\text{-bipyridine}). \text{Inorg. Chem.}, 38, 2695.


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