Syntheses, Structures and Magnetic Properties of Cyano-bridged Transition Metal Compounds

Uma Prasad Mallik

University of Missouri St. Louis, umty8@mail.umsl.edu

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Syntheses, Structures and Magnetic Properties of
Cyano-bridged Transition Metal Compounds

Uma Prasad Mallik
B.Sc. Chemistry (Hons) Calcutta University, 1999
M.Sc. in Organic Chemistry, Indian Institute of Technology Bombay, 2001
M.S. University of Kentucky, 2008

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Advisory Committee

Stephen M. Holmes, Ph.D.
Chairperson

Eike Bauer, Ph.D.

Alicia M. Beatty, Ph.D.

Janet Braddock-Wilking, Ph.D.

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SYNTHESES, STRUCTURES AND MAGNETIC PROPERTIES OF CYANO-BRIDGED TRANSITION METAL COMPOUNDS

Abstract

To investigate the hypotheses, that systematically changing the electronic and relative sizes of tricyanido building blocks will tune magnetic properties of their cluster derivatives, we prepared two new tricyanido pyrazolylborate complexes, [NEt₄][(Tp*Me)Fe(CN)₃]·H₂O and [NEt₄][(Tp*Bn)FeIII(CN)₃]·H₂O·MeOH, and investigated their self-assembly. The new building blocks were prepared, structurally characterized, and their coordination chemistry explored to prepare small molecule-based magnetic materials.

Three bent trinuclear ferromagnetic cluster derivatives of {[(Tp*Me)FeIII(CN)₃]²[NiII(L)₂]}·n(solvent) [L = 2,2′-bipyridine or bpy, diethylenetriamine or DETA and tris(2-aminoethyl)amine or tren] stoichiometry were prepared and their properties compared to other magnetic analogues. Another building block, [NEt₄][(Tp*Bn)-FeIII(CN)₃]·H₂O·MeOH, was also used to prepare two linear trinuclear derivatives of {[(Tp*Bn)Fe(CN)₃]²MII(DMF)₄]}·2DMF (MII = Mn, Ni) stoichiometry.

Under similar synthetic conditions two tetranuclear derivatives, {[(Tp*Me)-FeIII(CN)₃]²[NiII(DMF)₄]²[OTf]₂}·2DMF and {[(Tp*Me)FeIII(CN)₃]²[NiII(bpy)₂]²[ClO₄]₂}·3MeCN·2H₂O·MeOH were obtained. Systematic alteration of the reaction conditions also allowed for the isolation of a new hexanuclear analogue, {[(Tp*Me)FeIII(CN)₃]⁴[NiII(DMF)₃]²}·4DMF·H₂O, and octa- and nonanuclear ones, {[(Tp*Me)FeIII(CN)₃]⁴[NiII(tren)]₂[ClO₄]₄}·7H₂O·4MeCN and {[(Tp*Me)FeIII(CN)₃]⁶-[NiII(MeOH)₃]²[NiII(MeOH)₂]}·3H₂O·8MeOH, respectively. Each of these clusters
display ferromagnetic coupling of their paramagnetic nickel ($S = 1$) and iron ($S = \frac{1}{2}$) spin centers.

Overall, we find that magnetic interactions may be predicted using molecular orbital symmetry arguments and that the electronic and magnetic properties of cluster derivatives (ten total) are directly related to those of the chosen building blocks. Slow magnetic relaxation is generally seen for polynuclear analogues when the magnetic anisotropy axes (B···Fe) are parallel.
This thesis is dedicated to my family: my wife, Ganna Lyubartseva; my daughter, Geeta Mallik; my son, Ogni Mallik; my parents, brothers and sisters.
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Chapter One: Basics of Molecule-Based Magnetism

1.1 Introduction. Magnetic materials are technologically important materials which could have potential applications in a variety of devices ranging from magnetic transformer cores, electric motors, information storage, and electrical switching devices. The increasing demands for better performance characteristics in these consumer products have driven the need for increasingly smaller, faster, and more energy efficient devices in addition to higher bit densities for magnetic hard drive applications. However as the size of these magnetic materials decrease there is a gradual shift from bulk or classical magnetic behavior towards the superparamagnetic regime, where long range magnetic order and magnetic domain sizes are comparatively smaller, which limits the usefulness of these magnetic materials. As the magnetic particles approach the length scales of magnetic domains, the energy required for magnetization direction reversal (magnetic alignment of the particles) also decreases, eventually becoming comparable to available thermal energy. While these smaller magnetic particles offer the prospect of decreasing device size and higher information storage densities, the ability to engineer such materials and prevent facile erasure of stored information remains a difficult synthetic and technological challenge at best.

Single-molecule magnets (SMMs) are metal-organic compounds which show slow relaxation of magnetization\textsuperscript{1-15}. Typically, it consists of a central large spin metal core, which stays surrounded by organic ligands to form a discrete molecular species. By virtue of its characteristic property, the molecule retains its spin
orientation even in the absence of any external magnetic field. As a result, single molecule magnets can be understood as tiny classical magnets. Single-molecule magnets exhibit magnetic hysteresis and multiple electronic states. As a result, they have potential to be useful for molecule-based memory applications. However because of their complex nature, engineering and predicting cluster properties remain a difficult challenge. Also, thermal magnetization reversal in these clusters generally becomes energetically favorable at extremely low temperatures (ca. $T < 4\, \text{K}$). To make them useful for practical purposes, we must increase this “blocking temperature” first. As a result, this field of study gains considerable interest among researchers over past decades.\textsuperscript{1-15}

The first single-molecule magnet (SMM) was reported by Gatteschi, Sessoli,\textsuperscript{1,2} and Christou\textsuperscript{5,6} is a mixed-valence $\{\text{Mn}^{\text{III}6}\text{Mn}^{\text{IV}4}\}$ polynuclear cluster originally

![Figure 1.1.](image)

*Figure 1.1.* (left) Molecular structure of $\{\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{OH}_2)_4\}$ viewed along the $S_4$ axis. Hydrogen atoms are eliminated and only $\text{Mn}^{\text{III}}$ (green), $\text{Mn}^{\text{IV}}$ (orange), oxygen (red), and carbon (black) are shown for clarity. (right) Perpendicular view of $\{\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{OH}_2)_4\}$ highlighting relative orientations of Jahn-Teller axes (dashed lines, green). Thermal ellipsoids are at the 50% level.\textsuperscript{3}
described by Lis\textsuperscript{3} (Figure 1.1). The complex shows superparamagnetic behavior and very slow relaxation of the magnetization at $T = 2$ K ($\tau \sim 2$ months). The complex $\{\text{Mn}_{12}\text{O}_{12}(\text{OAc})_{16}(\text{OH})_{4}\}$ consists of 12 mixed-valence Mn\textsuperscript{III}/Mn\textsuperscript{IV} ions in a 2:1 ratio that are bound to one another through bridging oxygen and carboxylate units. In the central distorted $\{\text{Mn}^{\text{IV}}_{4}\text{O}_{4}\}$ cubane core the Mn\textsuperscript{IV} (3$d^3$, $S = \frac{3}{2}$) ions are ferromagnetically coupled to one another to give a total spin of $S = 6$. The remaining eight Mn\textsuperscript{III}HS (3$d^4$, $S = 2$) centers circle the $\{\text{Mn}^{\text{IV}}_{4}\text{O}_{4}\}$ core and are linked by oxo- and acetate bridges to give a disk-shaped and $S_4$-symmetric (snowflake-shaped) cluster. The Mn\textsuperscript{III} centers are also ferromagnetically coupled to each other giving a total spin of $S = 16$ for these sites. Overall the Mn\textsuperscript{III} and Mn\textsuperscript{IV} centers undergo antiferromagnetic coupling ($J \sim 200$ cm$^{-1}$) to give a total spin of $S_T = 16 - 6 = 10$ for the cluster. The molecule also has a roughly parallel orientation of the Jahn-Teller axes (at the Mn\textsuperscript{III} sites) that are along the principal rotation axis direction.

The energies associated with creation of a thermal barrier to spin reversal may be quantified in the following:

$$H = -S_i DS_i + [DS_x^2 + E(S_x - S_y)^2] + \mu_B S g H \tag{1}$$

where $S_x$, $S_y$, and $S_z$ are projections of overall cluster spin ($S$) along the Cartesian axes, $D$ represents the axial (z-direction) zero-field splitting tensor component, and $E$ is the transverse component (xy) of $D$; $\mu_B$, $g$, and $H$ are the Bohr magneton, magnetogyric ratio, and the applied magnetic field. Equation (1) can be simplified and used to appreciate (and ultimately quantify) parameters that are important in creating a thermal energy barrier to spin reversal (Eqn. 2):
\[ H_0 = D[S_z^2 - S(S + 1)/3] + g\mu_B H_z S_z \]  

(2)

where \( D \) is the zero-field splitting, \( S_z \) is the spin orientated along the \( z \)-direction (along magnetic field), and \( S \) is the total spin ground state for the cluster. The zero-field splitting breaks the degeneracy of the total spin ground state to give sublevels \( (M_S) \) whose energies can be estimated using the following equation (3):

\[ E(M_S) = D[M_S - 110/3] + g\mu_B M_S H_z \]  

(3)

A simplified and more useful version of Eqn. 1 neglecting magnetic anisotropy in the \( xy \)-plane (Eqn. 4):

\[ H_0 = -2JS_i S_j + S_i D S_j + \mu_B (S_i g_i + S_j g_j)H \]  

(4)

where the first term describes the magnetic coupling of the paramagnetic ions \( (S_i \) and \( S_j) \), the second defines the effect of zero-field splitting on their state degeneracies, and the third defines the Zeeman or impact of an applied magnetic field on the state energies. In a practical sense to a first approximation, to achieve the highest possible energetic barrier for magnetic spin reversal, one needs to primarily maximize the first two terms in Eqn. 4- that is have efficient spin-spin coupling and large zero-field splitting of the spin states (Figure 1.2).

Under ideal circumstances slow magnetic relaxation is seen by optimizing these parameters. The superparamagnetic-like behavior is related to its large spin ground state \( (S = 10) \) and uniaxial magnetic anisotropy \( (D < 0) \) resulting from its low-symmetry transition metal centers (Figure 1.2). When \( D > 0 \), the lowest energy spin ground state is the one where no net cluster magnetization is
found \(m_S = 0\) and the remaining states are found at higher energies. However when \(D < 0\), the double potential well inverts and the lowest energy \(m_S\) states are the ±10 ones, creating an energy barrier between the ± \(m_S\) levels (Figure 1.2). Further assisting creation of this energy barrier, is the fact that intermolecular contacts are minimized due to the insulating acetates surrounding the complexes, which minimize magnetic interactions that lead to low-energy excited states. Since the molecule possesses a large spin ground state \(S\) as well as an Ising-type magnetic anisotropy \(D < 0\) this gives rise to an energy barrier that separates the 'spin-up' and 'spin down' configurations as shown in Figure 1.2. This is the result

**Figure 1.2.** (left) Energy level diagram for Mn\(_{12}\)(OAc) \((S = 10)\), a negative zero-field splitting value \((D)\), and a barrier to spin reversal \((U)\) proportional to \(S^2|D|\). Green arrow represents energy separation between spin states that are dependent on the magnetic field. Red arrow represents thermal barrier to spin reversal and blue arrow represents energy separation between ground \((m_S = 10)\) and first excited state \((m_S = 9)\). (right) Various relaxation processes over and through the thermal barrier to magnetic relaxation for Mn\(_{12}\)(OAc) cluster.⁶
of zero-field splitting (ZFS) is caused by spin-orbit coupling of the ground and excited states which splits the \( M_s \) levels in the absence of a magnetic field.

In single-molecule magnets two thermodynamically equivalent \( m_S = \pm S \) configurations are separated by an energy barrier \( (U) \) whose z-projection of cluster spin is represented by \( m_s \), which ranges between \(-S\) and \( +S \) in integer values. At the blocking temperature \( (T_B) \), the available thermal energy is just enough to overcome this energy barrier. However, below \( T_B \), the available thermal energy is insufficient to overcome this barrier and the spin gets trapped in one of two possible configurations (Figure 1.2). If large magnetic fields \( (H) \) are applied to saturate the magnetization \( (M) \) of the sample, and then removed so that \( H \) becomes zero, a slow decay of magnetization towards zero with certain relaxation time \( (\tau) \) is found. This relaxation usually exhibits thermally activated behavior, and could be measured by the change in its magnetization \( (M) \) vs time or frequency \( (\nu) \) dependence of the maximum point in its ac susceptibility data (i.e. \( \chi'' \) vs \( \nu \) plots).

At very low temperatures quantum tunneling of the magnetization \( (QTM) \) is observed by many researchers\(^7,8\). QTM is defined as the situation where electron from one side of the energy well never cross the energy barrier but end up on the other side of the well of comparable energy. QTM is often responsible for relaxing the magnetization faster than predicted thermally activated pathways.\(^7,8\)

However, the majority of these manganese-based SMMs exhibit relatively small zero-field splitting and spin-orbit coupling constant values despite the presence of efficient superexchange interactions \( (J) \). Because the orbital contributions to the cluster anisotropy are essentially quenched, due to the low symmetry of the ligand
electrostatic field, the molecules behave like spin systems where the barrier to magnetization reversal \( (U) \) is proportional to the first term in the Hamiltonian \( DS^2 \) \((D \approx -0.5 \text{ cm}^{-1})\), where \( D \) is the zero-field splitting value. Since we know that the blocking temperature is closely related to the magnitude of the spin reversal barrier\(^\text{15}\), which is also related to the global magnetic anisotropy, by increasing this energy barrier one could achieve progressively higher blocking temperatures. Since cluster anisotropy mainly results from additive single-ion anisotropy of the transition metal centers present, introducing appropriate metal centers which possess greater anisotropy into the cluster framework, either by taking advantage of spin state (large zero-field splitting parameters, \( D \)) or orbital anisotropy (large spin-orbit coupling parameters, \( \lambda \)), it is theoretically possible to further enhance the blocking temperatures of these compounds.\(^\text{16-26}\) Alternatively, an ever more popular approach investigates insertion of lanthanide ions into cluster frameworks, which also possess strong spin-orbit interactions.\(^\text{27,28}\)

Even if we know that systematically tuning the magnetic behavior of oxo-carboxylate SMMs is the correct approach for achieving higher blocking temperature, it is synthetically not that easy for a few reasons. One difficulty arises due to coordination nature of oxygen atom which could potentially bridge between two to six metal centers resulting in a range of M-O-M’ bond angles and complex structural archetypes. Since the M-O-M’ bond angles and cluster geometry the magnetic exchange interactions [i.e. ranges between antiferromagnetic (180°) to ferromagnetic (90°)] are drastically influenced and predicting cluster magnetism can become difficult. Also in case of oxo-carboxylates, the low-symmetry
coordination environment and asymmetric crystal fields generally quench the orbital angular momentum present and eliminate much of the desired single-ion anisotropy and orbital degeneracy. Under ideal circumstances the energy barrier to thermally-activated magnetization reversal ($DS_z^2$) is generally proportional to the square of the ground state spin and negative zero-field splitting parameter ($D$). However, many groups have discovered that larger clusters (maximizing $S$) often have smaller spin reversal energy barriers. This is because the energy separation between the spin states becomes smaller, this encourages population of low-lying excited states that effectively lower the barrier to spin reversal while simultaneously decreasing the value of $D$.

For example in several systems, recent calculations suggest that $D$ scales as a function of $S^0$ rather than $S^2$, with $D(\text{Mn}_{12}) \sim -0.5 \text{ cm}^{-1}$. These leads us to the conclusion that if we desire to design materials that exhibit slow magnetic relaxation at even higher temperatures, we should focus on maximizing the zero-field splitting, rather than spin state. In an effort to capitalize on this effect several groups have sought to insert transition metal centers into cluster frameworks with greater magnetic anisotropy (e.g. larger $D$ values) by taking advantage of spin-orbit coupling and/or low-lying excited states. These transition metal centers generally possess even greater single-ion anisotropy that can be generated by spin state (large zero-field splitting parameters, $D$) or orbital anisotropy (large spin-orbit coupling parameters, $\lambda$).

1.2 Cyanide-Based Magnetism. A fundamentally unique class of clusters that exhibit slow relaxation of the magnetization (so-called SMMs) contain transition metal centers that are linked by cyanides. Even if cyanide itself is highly toxic,
its use as a ligand in the synthesis of coordination compounds has led to a wide area of research, from dyes to electron transfer and in magnetic materials. From the spectrochemical series:

\[
\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{bipy} < \text{NO}_2^- < \text{CN}^- \sim \text{CO}
\]

where the carbon-bonded cyanide is located at the strong field limit whereas the field strength of the nitrogen-bonded cyanide is below that of ammonia. The chemistry of cyanide compounds is of contemporary relevance; the ditopic character of cyanide as a ligand raises the possibility of it being used either as a monodentate ligand in the synthesis of the mononuclear complexes $\text{M-CN}$ ($\text{M} = \text{metal ion}$) or as a bridging ligand. The cyanometalate clusters are constructed from $\text{M(\mu-CN)M'}$ units and contain a variety of transition metal centers that exhibit significant orbital anisotropy suggesting this is critical factor for constructing these magnetic materials.

While cyanide-bridged metal centers often exhibit inefficient superexchange in comparison to oxo bridges, cyanometalate building blocks generally form linear $\mu$-cyano linkages that allow for a high degree of predictability in product formation. In fact, in most cases, the sign and magnitude of the local exchange interactions can be controlled via substitution and predicted by using orbital symmetry as a guide (Figure 1.3). In polynuclear complexes one or more cyanides generally form linear $\mu$-CN linkages between two adjacent metal centers and are known to stabilize a variety of transition metal centers and different oxidation states. When linked by cyanides, metal centers can efficiently communicate spin density information by taking advantage of $\pi$-backbonding interactions between the metal...
centers and the shared cyanide bridge. All these advantageous features imply that cyanometalates could be excellent building blocks for constructing molecule-based clusters.

Predicting magnetic coupling in cyanide-based materials follows simple rules that concern orbital overlap and symmetry (Figure 1.3)\textsuperscript{29-33}. In octahedral systems containing three or fewer electrons one may safely assume that the electrons

![Antiferromagnetic Case](image)

![Ferromagnetic Case](image)

**Figure 1.3.** Simplified molecular orbital diagram for predicting the sign of superexchange interactions within M(\(\mu\)-CN)M\(^-\) units. (top) Local antiferromagnetic and (bottom) ferromagnetic interactions of unpaired electrons.\textsuperscript{33}
reside in the $t_{2g}$ orbitals. For greater numbers of electrons high and low spin states are possible and these can be predicted depending on which atom, that is carbon vs nitrogen, is coordinated to the metal center. For metal ions linked to the carbon end of cyanide a low spin electronic configuration is expected while the nitrogen end gives a high spin state under most situations. For cyanide-bridged V$^\text{III}$ and Cr$^\text{III}$ only the $t_{2g}$ orbitals are filled, and because of the symmetry of these occupied orbitals are the same, the overlap between the magnetic orbitals is expected to be antiferromagnetic.$^{34}$ In the case of Ni$^\text{II}$ and Cu$^\text{II}$ the unpaired electrons are located in their $e_g$ orbitals and a ferromagnetic interaction is seen when a common cyanide is also linked to Fe$^\text{III}_{\text{LS}}$ ($t_{2g}^5$), because of the orthogonality of their magnetic orbitals.

Interestingly, recent studies indicate there are significant differences between the magnetic behavior of cyanometalate- and oxo/carboxylate-based single-molecule magnets.$^{23-24}$ It is important to note that many 3$d$ cyanometalate clusters contain paramagnetic centers with significant first-order spin-orbit coupling while oxide-bridged clusters have nearly quenched orbital contributions, because of the low-symmetry ligand environment.$^{23,24}$ In cyanide-based SMMs the total angular momentum projection ($|M_J|$) is closely related to establishing negative cluster anisotropy and an activation energy barrier ($U$) to thermal magnetization reversal.$^{17}$ On the contrary, oxide-bridged clusters behave more like a spin systems where orbitally nondegenerate metal centers exhibit weak single-ion and second-order anisotropy.

To get a better understanding of fundamental questions like how paramagnetic and magnetically anisotropic spin centers interact and contribute to the magnetic
ground state, impact of magnetic exchange, effective barrier heights, and quantum tunneling of the magnetization, we need a series of structurally related cyanometalate clusters. In cyanometalate clusters, the [(L)Fe\textsuperscript{III}(CN)\textsubscript{3}]\textsuperscript{3-} centers exhibit first-order orbital angular momentum contributions arising from spin-orbit interactions that cannot be described by $S_z^2|D\rangle$. Calculations suggest that idealized $C_{3v}$ symmetry present in these tricyanoferrates gives first-order orbital angular momentum contributions are sensitive to the local crystal fields and are largely responsible for the observed slow relaxation of the magnetization behavior in polynuclear derivatives. Since the trigonal field in the cluster plays an important role in forming the energy barrier, the SMM properties can in theory be controlled via changes in the local crystal fields present at the Fe\textsuperscript{III} centers. If spin-orbit interactions act to increase orbital angular momentum contributions to the magnetic ground state there are two conceivable ways to accomplish this. First, systematic variation of the crystal field via alteration of the ancillary ligands present may enhance orbital contributions (via changing symmetry). Second, insertion of 4$d$ and 5$d$ transition metal ions into cluster frameworks may also enhance single-ion anisotropy due to greater spin-orbit coupling, an effect often seen for late transition metal centers (a relativistic effect).

A careful look at the literature reveals three main approaches commonly used to raise the blocking temperatures of SMMs: (i) the preparation of large clusters with many paramagnetic metal ions to get a large ground spin state spin value, (ii) the use of highly magnetically anisotropic metal ions to increase the negative zero-field splitting and, (iii) combination of (i) and (ii) which will synergistically help to
increase the barrier height. In the next section we are going to describe some representative earlier example of transition metal cyanide complexes which belongs to one of those above categories.

1.3 Overview of Cyanide-Based Magnets. The Long group has been focused on developing cyano-bridged cluster systems where $S$ and $D$ parameters may be readily adjusted via substitution of various metal ions. They previously demonstrated that replacing Cr$^{III}$ with Mo$^{III}$ in the linear cluster $[(\text{Me}_3\text{tacn})_2(\text{cyclam})\text{NiCr}_2(\text{CN})_6]^{2+}$, where Me$_3$tacn and cyclam are $N,N'$,$N''$-trimethyl-1,4,7-triazacyclononane and 1,4,8,11-tetraazacyclotetradecane, respectively. Insertion of Mo$^{III}$ centers in place of the Cr$^{III}$ ones contributes greater magnetic anisotropy and results a substantial increase in the magnitude of $D$ associated with the $S = 4$ ground state.49

Later work followed this methodology and investigated substitution of Cr$^{III}$ in favor of Mo$^{III}$, which has a larger spin-orbit coupling constant, within trigonal prismatic $[(\text{Me}_3\text{tacn})_6\text{MnCr}_6(\text{CN})_{18}]^{2+}$, gives a higher spin ground state ($S = \frac{13}{2}$) and the first well-documented example of a cyano-bridged single-molecule magnet.50 X-ray analysis of the heptanuclear complex, K$[(\text{Me}_3\text{tacn})_6\text{Mn-Mo}_6(\text{CN})_{18}](\text{ClO}_4)_2$, shows that six $[(\text{Me}_3\text{tacn})\text{Mo(CN)}_3]$ units surround a central Mn$^{II}$ ion, which has a trigonal prismatic MnN$_6$ coordination environment. Magnetic susceptibility measurements at 295 K show the complex contains a 6:1 ratio of magnetically non-interacting Mo$^{III}$ ($S = 3/2$) and Mn$^{II}$ ($S = 5/2$) ions. Curiously, the experimental $\chi_M T$ value (11.8 cm$^3$ K mol$^{-1}$) is lower than the expected spin-only one (15.625 cm$^3$ K mol$^{-1}$). However, with decreasing temperature, the $\chi_M T$ values
become smaller reaching a minimum at approximately 115 K, before rising sharply to a maximum of 21.4 cm$^3$ K mol$^{-1}$ at 12 K. This behavior can be explained if we assume the presence of a weak antiferromagnetic coupling between the Mn$^{II}$ and Mo$^{III}$ ions in the $S = \frac{13}{2}$ cluster.$^{34}$

Dunbar’s group research program in cyanide chemistry also involves introduction of magnetically anisotropic metal ions into clusters.$^{22-26}$ The first example is a pentanuclear cluster, [Mn$^{II}$](tmphen)$_2$][Mn$^{III}$(CN)$_6$], where tmphen is 3,4,7,8-tetramethyl-1,10-phenanthroline, a cluster that contains a $C_3$ axis on which the Mn$^{III}$ ions reside.$^{26}$ This pentanuclear cluster adopts a trigonal bipyramidal molecular geometry in which two low-spin Mn$^{III}$ ($S = 1$) ions occupy the axial positions and three high-spin Mn$^{II}$ ($S = \frac{5}{2}$) ions reside in the equatorial plane. In the cluster, each Mn$^{III}$ ion is linked by three nearly linear cyanide bridges to Mn$^{II}$ centers and is capped by three terminal cyanide ligands. Single crystal X-ray structural data shows that the Mn$^{II}$ ions are coordinated to cis-tmphen ligands as well as to the nitrile ends of two cyanide bridges. Although the Mn$^{II}$ centers in each molecule have homochiral coordination geometry, the crystal is racemic, and the cluster crystallizes in a centrosymmetric space group ($P2_1/c$). The methylated phenanthroline ligands give well-separated intermolecular Mn-Mn contacts (8.77 Å). Magnetic measurements show a room temperature $\chi_M T$ value of $\sim 13.70$ emu K mol$^{-1}$, which is lower than the expected spin only value of 15.125 emu K mol$^{-1}$. When temperature is lowered, the $\chi_M T$ product decreases 10.41 emu K mol$^{-1}$ at 45 K, after which $\chi_M T$ increases to a maximum of 15.69 emu K mol$^{-1}$ at 4.0 K. The magnetic behavior below 45 K indicates a strong antiferromagnetic interaction
between the paramagnetic Mn$^{\mathrm{II}}$ and Mn$^{\mathrm{III}}$ centers that leads to an $S = \frac{11}{2}$ magnetic ground state for the pentanuclear cluster.

Later work involved the preparation of SMMs containing 5$d$ ions.$^{51}$ The reaction of MnCl$_2$ with [Et$_4$N][Re(triphos)(CN)$_3$],$^{53,54}$ where triphos is 1,1,1-tris(diphenylphosphanylmethyl)ethane, leads to the formation of the distorted molecular cube [MnCl]$_4$[Re(triphos)(CN)$_3$]$_4$. Inside the cluster, the local geometry around Mn$^{\mathrm{II}}$ site is a distorted tetrahedron, composed of three nitrogen-bound bridging cyanide ligands and one terminal chloride. Pronounced distortions of the cluster allows for the formation of the pseudo-cubic structure from octahedral and tetrahedral corners. Careful examination of the diagonals of this distorted cube reveals a slight compression along one of the $C_3$ axes, which results lowering of the overall symmetry for the cluster.

The complex contains a 4:4 ratio cyanide-bridged Re$^{\mathrm{II}}$LS ($S = \frac{1}{2}$) and Mn$^{\mathrm{II}}$HS ($S = \frac{5}{2}$) metal ions that reside in alternate corners of a distorted cubic tetranuclear cluster. The plot of $\chi M T$ vs $T$ indicates antiferromagnetic interactions are operative between the Re$^{\mathrm{II}}$ and Mn$^{\mathrm{II}}$ metal centers. At 300 K, the value of the $\chi M T$ product is 17.90 emu K mol$^{-1}$ and is in accordance with the presence of four magnetically uncoupled Re$^{\mathrm{II}}$ (0.63 emu K mol$^{-1}$ each) and four Mn$^{\mathrm{II}}$ ions (3.85 emu K mol$^{-1}$ each). With decreasing temperature, $\chi M T$ values decrease towards a minimum at 55 K, dramatically increases again, reaching a maximum of 21.01 emu K mol$^{-1}$ at 5 K. This maximum value for $\chi M T$ (21.01 emu K mol$^{-1}$) is lower than the expected spin-only value for an $S = 8$ (36 emu K mol$^{-1}$) ground state and demonstrates the nature
the strongly antiferromagnetic interaction has significant orbital contributions at low temperature.\textsuperscript{53,54}

The Zuo program focuses on the synthesis of high-nuclearity metal-cyanide clusters using multidentate capping ligands. Using a building block synthetic approach, several well-defined clusters have been described to date. Among these are the face-centered cubic clusters, \([\text{(Me}_3\text{tacn)}_8\text{Cr}^{\text{III}}_8\text{Ni}^{\text{II}}_6\text{(CN)}_{24}]^{12+}\) and \({(\text{tach})_8(\text{H}_2\text{O})_6\text{Cu}^{\text{II}}_6\text{Co}^{\text{III}}_8\text{(CN)}_{24}^\cdot\text{THF}]^{12+}\), where Me\text{tacn} and tach are \(N,N',N''\)-trimethyl-1,4,7-triazacyclononane and 1,3,5-triaminocyclohexane, respectively.\textsuperscript{55,56}

More recent work focuses on cyanide-bridged SMMs containing pyrazolylborate

![Figure 1.4. Idealized structures of hydridotris(pyrazol-1-yl)borates](image)

\textsuperscript{57,58}
ligands, as these sterically demanding and polydentate ligands inhibit growth of extended solids by limiting the numbers of cyanide bridges formed during self-assembly. Their workhorse building block is \([(Tp)Fe^{III}\text{LS}(CN)_3]^\text{-}\), a complex that contains a six coordinate and low spin Fe^{III}\text{LS} \((S = ½)\) center, whose coordination environment contains tridentate Tp (hydrotris(pyrazolyl)borate\textsuperscript{57} and three cis cyanide anions (Figure 1.4). The monoanionic complex was originally reported by Verdaguer and has been used by Julve and co-workers as the tetraphenyl phosphonium salt.

The Tp\textsuperscript{-} ligand is a classical scorpionate ligand that enforces three-fold symmetry when coordinated to a transition metal center. In comparison to neutral capping ligands, such as Me\textsubscript{3}tacn and tach, the negatively charged ligand assists in the build-up of excessive positive charge in polynuclear clusters.

Using a modified Julve method, they synthesized \([(Tp)\text{8}(H_2O)\text{6}Cu^{II}\text{6-}Fe^{III}\text{8}(CN)\text{24}]^{4+}\), as the first face-centered- cubic cluster exhibiting SMM-type behavior.\textsuperscript{56} The \([(Tp)\text{8}(H_2O)\text{6}Cu\text{6}Fe\text{8}(CN)\text{24}](\text{ClO}_4)\text{4-}12\text{H}_2\text{O}\cdot2\text{Et}_2\text{O}\) complex crystallizes in the \textit{Immm} space group and contains well isolated \([(Tp)\text{8}(H_2O)\text{6}Cu^{II}\text{6-}Fe^{III}\text{8}(CN)\text{24}]^{4+}\) cations that resides on crystallographic special positions of \textit{mmm} site symmetry. The face-centered-cubic clusters consist of eight Tp\textsuperscript{-} capped Fe\textsuperscript{III} ions that are found at the corners of an idealized molecular cube. The \([(Tp)\text{Fe}^{III}(CN)_3]^\text{-}\) cyanides bridge to six adjacent Cu\textsuperscript{II} ions that lie just above the center of each cubic face. Completing the coordination sphere of the five coordinate and square pyramidal \([\text{Cu}^{II}(\mu\text{-NC})_4(\text{OH}_2)]^{2+}\) building unit is a single aqua ligand.
Magnetic measurements of the Cu$^{II}_{6}$Fe$^{III}_{8}$ cluster over the 1.8 – 300 K temperature range show that ferromagnetic magnetic interactions are operative as expected due to orbital symmetry. The $\chi_M T$ vs $T$ data shows that the Fe$^{II}_{LS}$ and Cu$^{II}$ ions ($S = \frac{1}{2}$) are magnetically isolated at 300 K (5.77 emu K mol$^{-1}$) and the $\chi_M T$ values slowly rise with decreasing temperature, reaching a maximum of 27.94 emu K mol$^{-1}$ at ca. 5 K. At lower temperatures smaller values are seen approaching a minimum of 23.57 emu K mol$^{-1}$ at 1.8 K. The sharp decrease of $\chi_M T$ values below 5 K were attributed to the presence of zero-field splitting. This type of magnetic behavior is indicative of the expected ferromagnetic interactions between orthogonal spin orbitals of the eight Fe$^{III}$ ($t_{2g}$) and six Cu$^{II}$ ($e_g$) ions that leads to an $S = 7$ ground state.$^{56}$ An additional class of compounds using this precursor gave the first reported example of a pyrazolylborate-based single-chain magnet of [(Tp)Fe$^{III}$(CN)$_3$][Cu$^{II}$(MeOH)]:2MeOH]$_n$ in 2004.$^{55}$ This complex was reported to display magnetic hysteresis below its blocking temperature of ca. 6 K.$^{55}$ However, subsequent work by Holmes found this is an easily desolvated material that gives aggregated and poorly-defined solids-solvated crystals are not SCMs as reported.

Other groups have investigated the use of later transition metal centers in the construction of high spin ground state cyanide-containing clusters. These include work by Decurtins,$^{60}$ Sieklucka,$^{61}$ and Song.$^{62}$ The most recent concerns Song’s octacyanometalate efforts and his report of two structurally related high spin SMMs are described. Their approach takes advantage of a high cluster spin ground state as well as use of magnetically anisotropic Co$^{II}_{HS}$ ($S = \frac{3}{2}$) ions. The use of cobalt(II) ions is advantageous as efficient spin-orbital coupling is found for these ions. Using
this strategy they successfully synthesized two novel octacyanometallate-based pentadecanuclear clusters of \{\text{Co}^{II}_9\text{W}^V(CN)_6\text{(MeOH)}_{24}\}\cdot19\text{H}_2\text{O} \text{ and } \{\text{Co}^{II}_9\text{M}^V(CN)_6\text{(MeOH)}_{24}\}\cdot4\text{MeOH}\cdot16\text{H}_2\text{O} \text{ stoichiometry.}^{62} \text{ X-ray analysis shows that the } \text{Co}^{II}_9\text{M}^V_6 \text{ clusters contain eight } \text{fac-Co}^{II}(\text{MeOH})_3^{2+} \text{ cations that reside of the corners of an idealized cube. These ions are linked to a single cyanide per adjacent } \text{M}^V(CN)_6^{3-} \text{ at each adjacent corner (M}^V = \text{Mo, W) to cap the square faces, giving } \text{fac-Co}^{II}(\text{MeOH})_3(\mu_3^-\text{CN})_3 \text{ fragments. A fifth cyanide per M}^V(CN)_6^{3-} \text{ ion links to a central Co}^{II} \text{ ion completing the body-centered (CoN}_6 \text{ environment) and facially-capped structure. The clusters are encapsulated in lattice solvent and overall the structures can be described as adopting a general } \{\text{Co}^{II}\text{[fac-Co}^{II}(\text{MeOH})_3\text{][M}^V(\mu_3^-\text{CN})_3\text{]}_6\}\cdot n\text{solvent stoichiometry.}^{62}

\text{Magnetic susceptibility measurement collected for the Co}^{II}_9\text{W}^V_6 \text{ cluster shows the Co}^{II}\text{HS (S }= 3/2) \text{ and Mo}^V \text{ (S }= 1/2) \text{ centers are uncoupled at 300 K and undergo antiferromagnetic exchange at lower temperatures. At 300 K the experimental } \chi_M T \text{ value (20.2 emu K mol}^{-1}) \text{ is slightly higher than the expected spin-only value (19.13 emu K mol}^{-1}) \text{ assuming a 9:1 ratio of paramagnetic Co}^{II} \text{ and M}^V \text{ (Mo, W) centers (assuming } g = 2). \text{ Below 50 K, the } \chi_M T \text{ product rapidly increases and reaches a maximum of 85.2 emu K mol}^{-1} \text{ at 8 K, which then sharply decreases as the temperature is further lowered. This maximum } \chi_M T \text{ value is higher than the 60.4 emu K mol}^{-1} \text{ value predicted for an } S = ^{21}/2 \text{ spin ground state, assuming antiferromagnetic coupling between the nine Co}^{II} \text{ and six W}^V \text{ ions, but is much less than the 144.4 emu K mol}^{-1} \text{ value expected for a ferromagnetically coupled } S = ^{33}/2 \text{ state. Considering the strong orbital contribution (and depopulation thermally}}
accessible excited states) often seen for Co$^{II}$ ions, it was suggested that antiferromagnetic exchange between Co$^{II}$ and W$^V$ is most likely in this system.$^{62}$ Likewise magnetic susceptibility measurement of the Co$^{II}_9$Mo$^V_6$ cluster shows magnetic behaviors very similar to those seen for Co$^{II}_9$W$^V_6$ cluster.$^{36,37}$ At the room temperature, the $\chi_M T$ value (18.6 emu K mol$^{-1}$) is slightly less than the theoretical value of 19.13 emu K mol$^{-1}$, assuming a magnetically isolated 9:6 ratio of Co$^{II}$ and Mo$^V$ ($S = \frac{1}{2}$) ions. The $\chi_M T$ value reaches the maximum of 84.6 emu K mol$^{-1}$ at 9 K and supports the assumption that antiferromagnetic interactions are operative, giving an $S = \frac{21}{2}$ spin ground state for the Co$^{II}_9$Mo$^V_6$ cluster.

In the Holmes group we are primarily interested in understanding how the magnetic, optical, and electronic properties of a clusters can be altered in a systematic fashion. For this purpose, we choose tris(pyrazolyl)borates (Figure 1.4), a tridentate anionic ligand and synthesize several well-defined cyanometalate precursors (Scheme 1.1) that self-assemble with structures intact, towards a common structural archetype.$^{16-20}$ Subsequent chapters will describe how we have

![Scheme 1.1 General synthesis of tunable tricyanometalate building blocks where X, Y, and Z are various alkyl and aryl functional groups.$^{46}$](image)
tried to accomplish this task using a building block synthetic approach, primarily focusing on low-spin [(Tp$^{R,R}$)Fe$^{III}$(CN)$_3$] ($R$ = H, Me; $R'$ = Me, Bn; $S$ = $\frac{1}{2}$) building blocks. These show significant orbital contributions to their magnetic moments ($g$ ~ 2.7 to 2.9) and have been used to construct a variety of polynuclear single-molecule magnets.$^{16-20}$ We believe that this systematic study will ultimately allow us to better understand and describe complicated design and tuning of magnetic behavior in polynuclear cyanide-based magnetic materials.

1.4 Outlook and Future Directions. A possible limitation of this approach is utilizing spin-orbit coupling as a means to introduce orbital anisotropy into the magnetic ground state. Given that spin-orbit interactions can also introduce low-lying excited state relaxation pathways, the use of anisotropic metal ions in the construction of polynuclear cyanometalate complexes may fundamentally limit the maximum blocking temperatures achievable in this class of magnetic materials. Nevertheless such materials offer the prospect of probing the basic mechanisms of slow relaxation of the magnetization and quantum tunneling in a series of well-defined and structurally related magnetic complexes as a function of paramagnetic ions present.

1.5 References.


Chapter Two: Cyanometalate Building Blocks

2.1 Introduction. In this chapter we will primarily talk about building block synthetic approach we have developed and constantly working to improve it, in our research group. Our building blocks are well-defined cyanometalate precursors. During reaction, they self-assemble with structures intact into common structural archetype. Reason we choose cyanometalates because of the presence of cyanide ligands in it. As we know, cyanide ligands typically stabilize a variety of transition metal centers and oxidation states.$^{1-5}$ They can also efficiently communicate spin density information between metal centers. Also very often, the products contain linear metal-cyanide-metal linkages.$^{1-5}$ The building blocks we will be discussing for constructing polynuclear cyanometalate complexes have the general stoichiometry $[\text{fac-LM(CN)}_2]^{n-}$ and $[\text{fac-LM(CN)}_3]^{m-}$. Ligand L is a facially coordinate tridentate ligand which is responsible for limiting the number and directionality of cyanide linkages.

One big advantage of this synthetic approach is that the magnetic, optical, and electronic properties of the resulting products can be modified in a systematic fashion. This will allow us to gain valuable understanding for accurate magneto-structural correlations, which is our primary objective. Our goal is to control the sign and magnitude of the local magnetic exchange interactions by substitution. Our findings show that often these can be predicted by using simple orbital symmetry arguments. In the next section we will briefly talk about di- and
tricyanometalate building blocks, which have been developed in our research
group.

2.2 Overview of Pyrazolylborate Cyanometalates. Over the past twenty
years several mono-,\textsuperscript{6} di-,\textsuperscript{7,8} and tricyanometalate complexes\textsuperscript{9-15} have been
described containing pyrazolylborate ligands. These are prepared by two general
synthetic routes, with the most common involving halide metathesis by excess
tetra(alkyl)ammonium cyanide and known pyrazolylborate complexes.\textsuperscript{9,11,16-19} A
second approach uses peroxide to oxidize (Tp\textsuperscript{R})\textsubscript{2}Fe\textsuperscript{II} complexes followed by
cyanide addition to give [cat][(Tp\textsuperscript{R})Fe\textsuperscript{III}(CN)\textsubscript{3}] complexes, where [cat] = NEt\textsubscript{4}+,
NBu\textsubscript{4}+, and PPh\textsubscript{4}+. As less common route involves combination of a
pyrazolylborate salt with iron(III) chloride or [Fe\textsuperscript{III}OC\textsubscript{16}]\textsuperscript{2-}, followed by addition of
excess cyanide to afford a series of tricyano complexes.\textsuperscript{19} Representative
structures of several mononuclear cyanometalates, and their magnetic properties
are found in Figures 2.1 and 2.2 and Table 2.1.

Figure 2.1. X-ray structures of representative 3\textit{d} mono- and dicyanometalates:
(a) [NEt\textsubscript{4}][(Tp\textsuperscript{*})Mn\textsuperscript{II}(acac)(CN)]\textsuperscript{6,20} (b) [NEt\textsubscript{4}][(Tp\textsuperscript{*})M\textsuperscript{IV}O(CN)\textsubscript{2}] (M\textsuperscript{IV} = Ti, V),\textsuperscript{7,11}
and (c) [NEt\textsubscript{4}][(Tp\textsuperscript{*})M\textsuperscript{II}(CN)\textsubscript{2}] (M\textsuperscript{II} = Cr, Co, Ni).\textsuperscript{8} Thermal ellipsoids are at the
50\% level and all cations and hydrogen atoms are eliminated for clarity.
Only a few mono- and dicyanometalate complexes are currently known. Among these are the monocyano \([\text{NET}_4][\text{Tp}^*]\text{Mn}^{II}(\text{acac})\text{CN}\) complex \((S = \frac{5}{2})\) which was prepared via treatment of manganese(III) acetylacetonate with KTp* followed by \([\text{NET}_4]\text{CN}\) (Figure 2.1, left).\(^6\)\(^{20}\) Two dicyano derivatives, \([\text{NET}_4][\text{Tp}^*]\text{M}^{III}(\text{CN})_2\) (M III = Cr;\(^11\) Mn;\(^6\)\(^{20}\) Co;\(^11\) Fe;\(^10\)\(^{12}\)), and \([\text{NET}_4][(\text{pzTp})\text{Fe}^{III}(\text{CN})_3]\) complex. Thermal ellipsoids are at the 50% level and all cations and hydrogen atoms are eliminated for clarity.

![Figure 2.2. X-ray structures of representative first row transition metal tricyanometalates: (a) \([\text{NET}_4]_2[(\text{Tp}^*)\text{V}^{III}(\text{CN})_3]\),\(^7\) (b-e) \([\text{NET}_4][(\text{Tp}^*)\text{M}^{III}(\text{CN})_3]\) (M III = Cr;\(^11\) Mn;\(^6\)\(^{20}\) Co;\(^11\) Fe;\(^10\)\(^{12}\)), and (f) \([\text{NET}_4][(\text{pzTp})\text{Fe}^{III}(\text{CN})_3]\) complex. Thermal ellipsoids are at the 50% level and all cations and hydrogen atoms are eliminated for clarity.](image-url)
respectively, and other paramagnetic five-coordinate square pyramidal complexes of [NEt₄][[(Tp*)MII(CN)₂] (MII = Cr, Co, Ni) stoichiometry, spin ground states of S = 2, ½, and zero, respectively (Figure 2.1, right). The magnetic data indicates that their orbital contributions are nearly quenched. In analogous 5-coordinate square pyramidal complexes Murugesu proposed that changing the CoII ion distance relative to the basal plane dramatically changes the estimated values of g and D.21 In their work they demonstrated that small CoII···plane distances give small zero-field values and g ~ 2, indicating orbital contributions are largely absent, while for longer distances, D rapidly becomes large and negative, with slow magnetic relaxation becoming visible in their AC susceptibility data. The authors postulate changes in spin-orbit coupling associated with ligand-induced distortions of the crystal field are responsible for these effects. By analogy, the small CoII···basal plane distance in [(Tp*)CoII(CN)₂]⁻, defined by two pyrazole nitrogen and cyanide carbon atoms, may minimize orbital contributions to its S = ½ spin ground state.8

The first reported tricyanoferrate(III) complex, [(Tp)FeIII(CN)₃]⁻ appeared in 2002.16 Since then several di- and trivalent [cat]₄⁻[(TpR)Mn(CN)₃] six-coordinate complexes have been reported, where MII = V,7 MIII = Ti,11 V,7 Cr,14,15 Mn,6,20 Fe,7,9,10,12,16,17,19,22-24 and Co11 (Figure 2.2). The expected spin ground states under octahedral symmetry should mirror those seen for [Mn(CN)₆]ₙ⁻ ones. If this assumption is valid then magnetically isotropic ⁴A₂ (S = 3/2) spin ground states should be seen for VII and CrIII, while potentially anisotropic S = ½ (⁴T₂g; TiIII and FeIII_LS) and S = 1 (⁴T₂g; VIII and MnIIILS) ones are expected for the others; low spin CoIII analogues are diamagnetic (S = 0).8,11 However, the actual symmetry of the
[(Tp*R)Mn(CN)₃]ⁿ⁻⁴ complexes is $C_{3v}$ symmetric and their magnetic properties are often vastly different than those of the hexacyanometalates (Figure 2.3). Comparing the magnetism of $[(Tp*)Mn^{III}(CN)_3]^-$ ($C_{3v}$ symmetry) to $[Mn^{III}(CN)_6]^{3-} (O_h)$ the former complex is isotropic ($^3A_2$ state, $g = 2.09$) while the latter is anisotropic ($^3T_1$ state, $g = 2.39$), due to in-state orbital contributions arising from its degenerate spin ground state (Figure 2.3).⁶,²⁰,²⁵,²⁶

The electronic configuration and spin ground state of the tricyanomanganate(III) complex was studied by Extended Hückel tight binding (EHTB) methods.⁶,²⁰ Calculations confirm that nearly degenerate $d(xz)$ and $d(yz)$ orbitals are found at slightly higher energies than the corresponding $d(z^2)$ orbital (225 and 267 meV above, respectively). Substantial spin density was also found to be delocalized into the $\pi$ framework of the Tp* and cyanide ligands.⁶,²⁰ Considering the cyano-manganate(III) complexes have different symmetries their electronic configurations should also reflect these changes. The $C_{3v}$-symmetric $[(Tp*)Mn^{III}(CN)_3]^-$ complex has an $(z^2)^2(xz,xy)^2$ electronic configuration while the $[Mn^{III}(CN)_6]^{3-}$ one is $(t_{2g})^4$, as expected for a low spin octahedral complex (Figure 2.3). The tricyano complex adopts an isotropic ($^3A_2$) spin state and does not favor orbital

![Figure 2.3. Qualitative molecular orbital diagrams for (a) $[Mn^{III}(CN)_6]^{3-}$, (b) $[(Tp*)Mn^{III}(CN)_3]^-$, (c) $[Fe^{III}(CN)_6]^{3-}$, and (d) $[(Tp*R)Fe^{III}(CN)_3]^-$ anions.](image)
contributions to its moment. In contrast the octahedral \([\text{Mn}^{III}(\text{CN})_6]^{3-}\) complex is magnetically anisotropic owing to the presence of a degenerate \(^3T_1\) spin ground state \((g = 2.09 \text{ vs } 2.39)\). Following this trend low spin \(C_{3v}\)-symmetric \([(\text{Tp}^R)\text{Fe}^{III}(\text{CN})_3]^-\) complexes should have \(z^2(xz,xy)^3\) electronic configurations and lead to a doubly degenerate \(^2E\) state \((S = \frac{1}{2})\) with unquenched orbital angular momentum. Likewise, the octahedral \([\text{Fe}^{III}(\text{CN})_6]^{3-}\) anion has an \(t_{2g}\) electronic configuration and a \(^2T_{2g}\) spin ground state \((g = 2.9)\) (Figure 2.3). These data suggest that orbital degeneracy is necessary for creating magnetic anisotropy in this cyanometalate system.

Recent high-field EPR, magnetic, and structural studies show that within a family of \([(\text{Tp}^R)\text{Fe}^{III}(\text{CN})_3]^-\) complexes significant \(g\) anisotropy may be tuned with

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apparently, the \( g \) parameter and \( \text{Tp}^R \)-induced distortions of the \([\text{fac-Fe}^{\text{III}}(\text{CN})_3]\) appear to be related, with larger pyrazolylborates compressing the \( \text{Fe}^{\text{III}}(\text{CN})_3 \) unit, giving larger \( g \) values that indicate orbital contributions are enhanced. In other words, as the C-Fe-C angle becomes more acute the \( g \) parameter generally increases and may be related to mixing of the ground with excited states within the 3d orbital manifold. The magnetic properties of several di- and tricyanometalate complexes are summarized in Table 2.1.

### 2.4 Synthesis of New Tricyanoferrate Complexes

Several new and structurally related tricyanoferrate(II,III) complexes may be prepared via modifications to previously described procedures for \([\text{NEt}_4][\text{(Tp}^R\text{)}\text{Fe}^{\text{III}}(\text{CN})_3]\) (\( \text{Tp}^R = \text{Tp, Tp}^* \)) syntheses. We previously focused on the chemistry of trivalent cyanoferrate building blocks containing tris-3,5-dimethylpyrazolyl borate. As an extension of this work we started work on other substituted derivatives to explore how their reaction chemistry, structures, and magnetism changes within the pyrazolylborate series (Figure 2.4).

![Figure 2.4](image.png)

**Figure 2.4.** (left to right) Selected pyrazolylborate ligands showing relationships between substitution, steric demand, and donor strengths.
For example, treatment of \((\text{Tp}^\text{R})\text{Fe}^\text{II}(\text{OAc})\), where \(\text{Tp}^\text{R} = \text{tris}(3,4,5\text{-trimethyl-}
\text{pyrazolyl})\text{borate (Tp}^\text{Me}^\text{*})\) and \(\text{tris}(3,5\text{-dime}
\text{thyl-4-benzyl)pyrazolylborate (Tp}^\text{Bn}^\text{*})\), with cyanide readily afforded a new tricyano complex of \([\text{NET}_4]_2[(\text{Tp}^\text{R})\text{Fe}^\text{II}(\text{CN})_3]\) stoichiometry (\(\text{Tp}^\text{Me}^\text{*}, 6\)) and subsequent peroxide oxidation gives the trivalent \([\text{NET}_4][(\text{Tp}^\text{R})\text{Fe}^\text{III}(\text{CN})_3]\) analogues (\(\text{Tp}^\text{R} = \text{Tp}^\text{Me}^\text{*}, 7; \text{Tp}^\text{Bn}^\text{*}, 12\)) as crystalline materials (Scheme 2.1). The isolation of the divalent \(\text{Tp}^\text{Bn}^\text{*}\) analogue was unsuccessful. Alternatively reaction of (pzT\(\text{p})_2\text{Fe}^\text{II}\) with excess cyanide affords divalent \([\text{NET}_4]_2[(\text{pzTp})\text{Fe}^\text{II}(\text{CN})_3]\cdot\text{H}_2\text{O}\) (8) and peroxide addition gave \([\text{NET}_4][(\text{pzTp})\text{Fe}^\text{III}(\text{CN})_3]\) (9) as a trivalent analogue. A third method, particularly useful for hydrolytically sensitive \(\text{Tp}^\text{R}\) ligands, involved treatment of \([\text{NET}_4]_2[\text{Fe}^\text{III}(\text{OCi})_6]\) with K\(\text{Tp}^\text{R}\) (\(\text{Tp}^\text{R} = \text{Tp}^\text{Me}^\text{*}, \text{pz}^\text{oTp}^\text{Me}\)), followed by cyanide and peroxide addition to yield the corresponding trivalent salts (10 and 11).

The infrared spectra of the complexes are indicators of the degree of electronic delocalization into the cyanide and pyrazolylborate ligands. When the \(\text{Tp}^\text{R}\) ligand

\[\text{Scheme 2.1. General syntheses of di- and trivalent tricyanoferrate complexes.}\]
coordinates to Lewis acidic iron centers, the $\nu_{BH}$ stretch moves to higher energy in comparison to the potassium salts. For example KTp* exhibits a low-energy $\nu_{BH}$ stretch at 2436 cm$^{-1}$ in comparison to (Tp*)Fe$^{II}$(OAc) (2517 cm$^{-1}$) which is consistent with less electronic delocalization into the Tp* ligand. In the solid state divalent and trivalent cyanometalate salts may also be differentiated by their stretching absorption energies. Divalent complexes generally give lower energy $\nu_{BH}$ and $\nu_{CN}$ stretches as more electron density is delocalized onto the ligands in comparison to their trivalent analogues. In comparison to (Tp*)Fe$^{II}$(OAc) the $\nu_{BH}$ is found at even lower energy for [NEt$_4$]$_2$[(Tp*)Fe$^{II}$(CN)$_3$]·H$_2$O because cyanide is a better sigma donor that acetate (2517 vs. 2507 cm$^{-1}$) and that the complex is an anion (Figure 2.5). Both of these factors favor additional electron density delocalization into both B-H and C-N bonds of the pyrazolylborate and cyanide. As expected low energy $\nu_{CN}$ stretches are also found for [(Tp*)Fe$^{II}$(CN)$_3$]$^{2-}$ (2060 and 2043 cm$^{-1}$) in comparison to aqueous KCN ($\nu_{BH} = 2080$ cm$^{-1}$), further indicating that the complex is electron rich. The $\nu_{CN}$ for [NEt$_4$]$_2$[(Tp*)Fe$^{II}$(CN)$_3$]·H$_2$O are also comparable to other iron(II) cyanometalates such as K$_4$[Fe$^{II}$(CN)$_6$] (2044 cm$^{-1}$), Na[(tach)Fe$^{II}$(CN)$_3$]·MeOH, where tach = 1,3,5-triaminocyclohexane (2052 and 2014 cm$^{-1}$), and [L$_2$Fe$^{II}$(CN)$_2$], where L = phen (2079 and 2065 cm$^{-1}$) and bpy (2070 and 2078 cm$^{-1}$).$^{41-45}$ Other tricyano complexes such as 6 (2044 cm$^{-1}$) and 8 (2069 and 2050 cm$^{-1}$) also display low-energy $\nu_{CN}$ absorptions that also indicate extensive electron density delocalization (Figure 2.5). Note that there are ligand-
Figure 2.5. Truncated X-ray structures of $[\text{NET}_4]_2[(\text{Tp}^\text{Me})\text{Fe}^{\text{II}}(\text{CN})_3]\cdot\text{MeCN}$ (6), $[\text{NET}_4][(\text{Tp}^\text{Me})\text{Fe}^{\text{III}}(\text{CN})_3]\cdot\text{H}_2\text{O}$ (7), $[\text{NET}_4]_2[(\text{pzTp})\text{Fe}^{\text{II}}(\text{CN})_3]\cdot2\text{H}_2\text{O}$ (8), and $[\text{NET}_4][(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]$ (9). Ellipsoids are at the 50% level and all cations, lattice solvents, and hydrogen atoms are eliminated for clarity.\textsuperscript{19,70,90}
Figure 2.6. X-ray structures of [NEt₄][(pz²Tp²⁻Me)Fe³⁺(CN)₃]·H₂O (10), [NEt₄]-
[(Tp²Me)Fe³⁺(CN)₃]·4H₂O (11), and [NEt₄][(Tp²*Bn)Fe³⁺(CN)₃]·2MeOH·H₂O (12)
anions. All cations, lattice solvents, and hydrogen atoms are eliminated for
clarity. Ellipsoids are shown at the 50% level for 10 and 11.¹¹,³²,⁵¹,⁹⁰
dependent changes that show inductive effects are important in the relative energies of their $\nu_{CN}$ absorptions.

In comparison, tricyanoferrate(III) complexes display higher energy $\nu_{BH}$ and $\nu_{CN}$ absorption energies in comparison to their divalent analogues. For example, the infrared spectrum of $[\text{NEt}_4][(\text{Tp}^*)(\text{Fe}^{III})(\text{CN})_3]\cdot\text{H}_2\text{O}$ exhibits $\nu_{CN}$ and $\nu_{BH}$ absorptions at 2119 and 2528 cm$^{-1}$, that are shifted to higher energies relative to $[\text{NEt}_4][(\text{Tp}^*)(\text{Fe}^{II})(\text{CN})_3]\cdot\text{H}_2\text{O}$.$^{10,35}$ This behavior can be explained assuming that oxidation of the iron center decreases charge delocalization (via $\pi$ back bonding) into the cyanide ligands as well as that into the B-H $\sigma$ bond. The cyano stretching absorption is comparable to those observed for $\text{K}_3[\text{Fe}^{III}(\text{CN})_6]$ (2135 cm$^{-1}$) and $[\text{PPh}_4][\text{LFe}^{III}(\text{CN})_4]$, where $\text{L} = \text{phen, bpy}$ (2120 and 2118 cm$^{-1}$), $[(\text{tach})\text{Fe}^{III}(\text{CN})_3]\cdot\text{H}_2\text{O}$ (2121 cm$^{-1}$), $[\text{PPN}][(\text{Tp})\text{Fe}^{III}(\text{CN})_3]$ ($\nu_{BH} = 2527$ cm$^{-1}$; $\nu_{CN} = 2117$ cm$^{-1}$), and

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure27.png}
\caption{X-ray structure of $[\text{NEt}_4][(\text{Tp}^*\text{Me})\text{Fe}^{III}(\text{CN})_3]\cdot\text{MeCN}$ (6) highlighting hydrogen bonding along the crystallographic (left) $a$- and (right) $c$-directions. Ellipsoids are at the 50% level and all cations and hydrogen atoms are eliminated for clarity.$^{19}$}
\end{figure}
[cat][[(Tp)Fe$^{III}$(CN)$_3$]-2H$_2$O (cat = PPh$_4^+$, K$^+$; 2123 cm$^{-1}$).$^{46-50}$ Following this trend we found that in the solid state compounds 7, 9 and 10 – 12 give high energy $\nu_{\text{BH}}$ (2544, none, none, 2481, 2521 cm$^{-1}$) and $\nu_{\text{CN}}$ (2119, 2120, 2124, 2121, 2119 cm$^{-1}$) stretches that appear to generally scale with Tp$^R$ donor strength.$^{35,51}$ Interestingly, in acetonitrile solution this trend is more easily observed and clearly shows that the energies of $\nu_{\text{BH}}$ stretches increase while the $\nu_{\text{CN}}$ ones decrease, suggesting there is a push-pull effect operative within the [cat][[(Tp$^R$)Fe$^{III}$(CN)$_3$] complexes, that is related to pyrazolylborate donor strengths (Figure 2.4).$^{35,51}$

2.5 X-ray Structural Studies. The six-coordinate tricyanometalate complexes adopt idealized $C_3V$ or $C_3$-symmetric structures, depending on the functionalities appended to the pyrazolylborate ligands (Figures 2.5 and 2.6). Divalent complexes 6 and 8 crystalize in the orthorhombic ($Pca2_1$ and $P2_12_12_1$) space group while the trivalent ones, are found in the monoclinic $P2_1/n$ (7, 9, and 10), $P2_1/c$ (11), and $C2/c$ (12) groups (Table 2.1).$^{11,19,32,51,70,90}$ The average Fe-C bonds in 6 and 8 are identical [1.903(2) Å] and do not reflect differences in their pyrazolylborate $\sigma$ donor abilities (pzTp vs. Tp$^{*\text{Me}}$). Likewise, the Fe-C bonds in [NEt$_4$]$_2$[(Tp$^{*\text{Me}}$)Fe$^{II}$(CN)$_3$]-H$_2$O [1.899(2) - 1.908(2) Å] are also similar to those in 6 and 8, with average Fe-N bond lengths also comparable for the three complexes (Tables 2.2-2.3). An interesting aspect of the structure of 6 is that the lattice water participates in hydrogen-bonded with the terminal cyanides to form anionic one-dimensional helical chains (Figure 2.7).
Table 2.2. Crystallographic Data for [NEt₄]₂[(Tp*Me)Fe²⁺(CN)₃]·MeCN (6), [NEt₄][(Tp*Me)Fe³⁺(CN)₃]·H₂O (7), [NEt₄]₂-[(pzTp)Fe²⁺(CN)₃]·2H₂O (8), and [NEt₄][(pzTp)Fe³⁺(CN)₃] (9).

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[a] I ≥ 2σ(I): R₁ = Σ||F₀|- |F₂||Σ|F₀|, wR₂={Σ[w(F₀²-F₂²)²]/ Σ[w(F₀²)]}¹/²

40
Table 2.3. Crystallographic Data for [NEt₄][(pz°Tp²Me)Fe^{III}(CN)₃] (10), [NEt₄][(Tp²Me)Fe^{III}(CN)₃]·4H₂O (11), and [NEt₄]-[(Tp²*Bn)Fe^{III}(CN)₃]·2MeOH·H₂O (12).

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[^a] I ≥ 2σ(I): R₁ = Σ||F₀| - |Fₑ||/Σ|F₀|, wR₂=Σ[w(F₀²-Fₑ²)²]/Σ[w(F₀²)²]^{1/2}
Table 2.4. Selected Bond Distances (Å) and Angles (°) for \([\text{NET}_4]_2[(\text{Tp}^{*}\text{Me})\text{Fe}^{III}(\text{CN})_3]\cdot\text{MeCN} \ (6), [\text{NET}_4][(\text{Tp}^{*}\text{Me})\text{Fe}^{III}(\text{CN})_3]\cdot\text{H}_2\text{O} \ (7), [\text{NET}_4]_2[(\text{pzTp})\text{Fe}^{III}(\text{CN})_3]\cdot2\text{H}_2\text{O} \ (8), \text{and} [\text{NET}_4][(\text{pzTp})\text{Fe}^{III}(\text{CN})_3] \ (9).\\

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Table 2.5. Selected Bond Distances (Å) and Angles (°) for [NEt₄]((pz°TpMe)Fe³⁺(CN)₃) (10) and [NEt₄]((TpMe)Fe³⁺(CN)₃)-·4H₂O (11), and [NEt₄]((Tp*Bn)Fe³⁺(CN)₃)·2MeOH·H₂O (12).

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As a counterintuitive trend, Fe-C bonds are often longer for trivalent complexes in comparison to those of divalent analogues. This can be explained through the competing effects of \( \pi \) back bonding and \( \sigma \) donation as relative to iron oxidation state. For example, \([\text{NET}_4]_2[(\text{Tp}^*)\text{Fe}^{\text{II}}(\text{CN})_3] \cdot \text{H}_2\text{O}\) has shorter Fe-C bonds [1.899(2) - 1.908(2) \(\text{\AA}\)] while those in \([\text{NET}_4][(\text{Tp}^*)\text{Fe}^{\text{III}}(\text{CN})_3] \cdot \text{H}_2\text{O}\) are longer, ranging between 1.929(2) and 1.935(2) \(\text{\AA}\), suggesting electrostatic interactions alone cannot explain this behavior. If electrostatic interactions are the primary factor in determining Fe-C bond lengths, then the shortest Fe-C bonds should be seen for trivalent complexes (a better Lewis acid) assuming that \( \pi \) back bonding is minimal.

However, the opposite trend is observed, indicating that \( \text{Fe}^{\text{II}} \) has enhanced \( \pi \) back-bonding relative to \( \text{Fe}^{\text{III}} \). Consistent with this hypothesis, the average Fe-C bond lengths in 6 and 7 [1.903(2) vs 1.921(2) \(\text{\AA}\)] show comparable differences to the structures of 8 and 9 [1.903(5) vs. 1.924(2) \(\text{\AA}\)].\(^{11,19,32,51,70,90}\) Compounds 10 – 11 also have longer Fe-C bonds than those seen for divalent complexes (i.e. 6 and 8). The data indicates that enhanced \( \pi \) back bonding is seen for \( \text{Fe}^{\text{II}} \) in comparison to \( \text{Fe}^{\text{III}} \) analogues. Given that the Fe-N bond distances are comparable for the series we propose they are not useful indicators for the extent \( \pi \) back bonding operative in the tricyano complexes. This reflects the relative insensitivity of X-ray as a method for estimating the extent of \( \pi \) back bonding within the tricyano series.

The majority of work presented in this thesis project concerns tris(3,4,5-trimethylpyrazolyl)borate tricyanoferrates(III) and we will describe its structural properties in more detail than the other analogues. Compound 7 crystallized in the
monoclinic $P2_1/n$ space group. The Fe-C bond distances lie between 1.920(2) and 1.923(2) Å and are comparable to those of other trivalent complexes, such as [NEt$_4$][(Tp*)Fe$^{	ext{III}}$(CN)$_3$]·H$_2$O [1.929(2) to 1.935(2) Å]. The Fe-N bond distances are also similar and range from 2.002(1) to 2.007(1) Å. The C-Fe-C and N-Fe-N angles range between 86.90(7) and 89.34(7)$^\circ$ and 89.20(5)$^\circ$ and 89.82(5)$^\circ$ (Table 2.2). Overall, 7 exhibits longer Fe-C and Fe-N bonds and smaller C-Fe-C bond angles, when compared to those in [cat][(Tp)Fe$^{	ext{III}}$(CN)$_3$]·2H$_2$O (cat = PPh$_4^+$ or PPN$^+$), indicating that Tp*Me is a better donor ligand than Tp*.$^{52-56}$

For the tricyanometalate family of complexes the C-Fe-C bond angles vary slightly with pyrazolylborate steric demand which is primarily dependent on functional groups present at the 3-position of the pyrazoles. In the divalent complexes, the C-Fe-C angles range between 89.86(7) and 92.34(7)$^\circ$ for 6 and 88.2(2) and 90.5(2)$^\circ$ for 8 with average angles of 91.13(7) and 89.1(2)$^\circ$, respectively. In comparison, the iron(III) derivatives generally have smaller C-Fe-C angles, ranging between 86.90(7) and 89.34(7)$^\circ$ for 7, 86.46(9) and 90.07(9)$^\circ$ for 9, 83.47(9) and 91.83(9)$^\circ$ for 10, 86.9(2) and 89.3(2)$^\circ$ for 11, and 85.9(1) and 87.2(1)$^\circ$ for 12. The average C-Fe-C angles are 87.90(7), 88.75(9), 88.00(9), 87.9(2), and 86.4(1)$^\circ$ for 7 and 9-12 and are slightly smaller than those found for their iron(II) derivatives. This might be due to greater electron donation and steric demand of the larger pyrazolylborates ligand relative to Tp.

2.6 Magnetic Measurements. The tricyanide complexes are either diamagnetic or paramagnetic depending on their oxidation numbers and spin states. All of the tricyano complexes contain low spin iron ions with the Fe$^{	ext{III}}$_LS ones (7 and 9-12)
giving paramagnetic salts \((S = \frac{1}{2})\). The Fe\(\text{II}\) salts, for example 6 and 8, are diamagnetic \((S = 0)\). These data are presented in Figures 2.8-2.10. As a typical example, the room temperature value of \(\chi T\) for 7 is \(0.66\) cm\(^3\) K mol\(^{-1}\) and is consistent with an \(S = \frac{1}{2}\) spin ground state with a \(g\) factor of 2.65 (Figure 2.8). Like other \([(Tp^R)Fe\text{III}(CN)_3]^-\) building blocks spin-orbit coupling gives \(g\) values that are greater than 2.002. As the sample temperature is lowered the \(\chi T\) values decrease towards a minimum at 1.8 K. The magnetic susceptibility is described by magnetization vs applied magnetic field or \(M/H\). The field dependence of the magnetization below 10 K confirms the \(S = \frac{1}{2}\) spin states and fitting of the data to a Brillouin function allows \(g\) to also be estimated.\(^{25,26}\) These results are summarized in Table 2.1. The minor differences between the \(\chi T\) values are related to how much spin-orbit coupling is present in each complex. The possible reasons for this behavior are presented in the next section.\(^{35}\)
Figure 2.9. (top) $\chi T$ vs $T$ data for (left) 9, (middle) 11, and (right) 12 (with $\chi$ defined as the magnetic susceptibility and equal to $M/H$) at 1000 Oe. (bottom) $M$ vs $H$ data for (left) 9, (middle) 11, and (right) 12 at various temperatures. Note: Red line (bottom, left) is fit of the data collected for 9 to an $S = \frac{1}{2}$ Brillouin function at 1.8 K.25,26
2.7 Structure-Property Trends. Over the past decade the Holmes group has explored several tricyanide complexes, their self-assembly reactions, and how they form robust transition metal cyanide linkages. These observations lead us to prepare a series of facially-capped tris(pyrazolyl) borate tricyanide complexes (building blocks) for use in magnetic cluster syntheses. These low spin \([\text{[(Tp}^R\text{R})\text{Fe}^{III}\text{LS(CN)}_3]^\text{-}}\) \((R = \text{H, Me} ; R' = \text{Me, Bn} ; S = \text{1/2})\) building blocks show significant orbital contributions to the magnetic moment \((g > 2.002)\).\(^{11,19,32,51,70,90}\)

Previous to this work very few tris(pyrazolyl)borate cyanometalate complexes were known and only a single systematic effort to prepare anisotropic cyanometalate clusters has been reported in the literature.

There are several interesting and complex relationships between the UV-visible spectra \((\lambda_{\text{max}})\), electrochemical, and structural data collected for the \([\text{[NEt}_4][(\text{Tp}^R)\text{Fe}^{III}\text{(CN)}_3]]\) complexes and seem to be related to the pyrazolylborate...
ligands present. For the (Tp*Me → pZTp) series, the ligand-to-metal charge transfer (LMCT) absorptions with lowest energy are found for electron-rich ligands like Tp*Me (Figure 2.10) These complexes are more easily oxidized than others in the series as they have the most negative FeIII/FeII couples (E₁/₂) and this is also seen in their infrared spectra, where the lowest energy νCN absorptions are also seen.

Figure 2.11. (top) Electronic absorption maxima (λmax) vs. infrared cyanide (νCN) stretching absorption energies for various [NEt₄][(TpR)FeIII(CN)₃] salts (in MeCN solution). (bottom) Electronic absorption maxima (λmax) vs. infrared borohydride (νBH) stretching absorption energies for various [NEt₄][(TpR)-FeIII(CN)₃] salts (in MeCN solution).³⁵
(Figure 2.11). Interestingly the energies of the $\nu_{CN}$ and $\nu_{BH}$ stretches appear to have an inverse relationship, where low energy $\nu_{BH}$ values give high energy $\nu_{CN}$ ones. Comparing the $\lambda_{max}$ LMCT absorption energies to the average cyanide C-Fe-C angles the highest energy LMCT absorptions are observed for electron-deficient and smaller pyrazolylborates such as Tp. These sterically less demanding ligands give larger average C-Fe-C angles in $[\text{NEt}_4][(\text{Tp}^\text{R})\text{Fe}^{\text{III}}(\text{CN})_3]$ complexes and the smallest iron distances from the mean plane defined by the three cyanide carbon atoms distances (Figure 2.12).

![Figure 2.12](image)

**Figure 2.12.** Absorption maxima ($\lambda_{max}$) vs. average cyanide C-Fe-C angle for structurally characterized $[\text{NEt}_4][(\text{Tp}^\text{R})\text{Fe}^{\text{III}}(\text{CN})_3]$ salts. Electronic absorption spectra were collected as MeCN solutions.$^{35}$

In all of the $[(\text{Tp}^\text{R})\text{Fe}^{\text{III}}\text{LS}(\text{CN})_3]^-$ complexes there is significant magnetic anisotropy that originates from first-order orbital contributions (spin-orbit interactions) to their paramagnetic $S = \frac{1}{2}$ spin ground states. Under $C_{3v}$ symmetry the low spin Fe$^{\text{III}}$LS ions adopt $(z^2)^2(xz, yz)^3$ electronic configurations which gives
a doubly degenerate $^2E$ states. In comparison hexacyanoferrate(III) complexes have octahedral geometry and triply degenerate ($xz$, $yz$, $xy$) or $^2T_{2g}$ states.\textsuperscript{36,42-50,53,54,57-60} The relative energies of the tricyanometalate orbitals was estimated by performing density-functional theory calculations on several $[(T_p^R)M^{III}(CN)_3]^{-}$ anions ($M^{III} = Fe$, Mn). Initial calculations on $[(T_p^*)M^{III}(CN)_3]^{-}$ showed that the metal-based orbitals order in decreasing energy as $z^2 < (xz, yz) < (x^2-y^2, xy)$.\textsuperscript{30,61} The tricyanomanganate(III) ions adopt an isotropic $^3A_2$ state rather than a magnetically anisotropic $^3T_{2g}$, because of symmetry differences (Figure 2.3).\textsuperscript{30,35,36,42-50,53-61}

Density-functional theory calculations were performed by Theoretical calculations were done by Dr. Benjamin J. Bythell from University of Missouri St. Louis, at the B3LYP/DGDZVP level for a variety of $[NEt_4][(T_p^R)Fe^{III}L_5(CN)_3]$ complexes (Figures 2.13-2.18).\textsuperscript{35} The calculations show that the iron(III) orbitals are arranged in increasing energy, $z^2 < (xz, yz) < (x^2-y^2, xy)$, and very small differences are encountered between the $xz$ and $yz$ orbitals (ca. 27-82 eV) for the tris(pyrazolyl)borate-containing complexes. We were surprised to learn that the tetra(pyrazolyl)borates give singly degenerate $3d$ orbitals (Figures 2.17 and 2.18) and this may reflect the more significant distortions found in their structures. Efficient spin delocalization and orbital mixing of the iron $xz$ and $yz$ orbitals with the cyanide $\pi^*$ ones is found and the most extensive one is found for the electron-rich $T_p^*Me$ derivative. Overall the DFT data roughly mirrors the ligand-dependent trends seen in the spectroscopic data already described.\textsuperscript{35}
Figure 2.13. (left) Qualitative molecular orbital diagram for gas phase [(Tp)Fe$^{III}$(CN)$_3$]$^-$ anions. (right) Molecular orbitals deduced for [(Tp)Fe$^{III}$(CN)$_3$]$^-$ anions highlighting 3$d$ orbital interactions.$^{35}$
Figure 2.14. (left) Qualitative molecular orbital diagram for gas phase [(TpMe)Fe^{III}(CN)_{3}]^{-} anions (in 11). (right) Molecular orbitals deduced for [(TpMe)-Fe^{III}(CN)_{3}]^{-} anions (in 11) highlighting 3d orbital interactions.⁵³
Figure 2.15. (left) Qualitative molecular orbital diagram for gas phase \([\text{(Tp}^*\text{)Fe}^{III}(\text{CN})_3]^-\) anions. (right) Molecular orbitals deduced for \([\text{(Tp}^*\text{-Fe}^{III}(\text{CN})_3]^-\) anions highlighting 3\(d\) orbital interactions.\(^{35}\)
Figure 2.16. (left) Qualitative molecular orbital diagram for gas phase [(Tp*Me)Fe^{III}(CN)_3]^− anions (in 7). (right) Molecular orbitals deduced for [(Tp*Me)-Fe^{III}(CN)_3]^− anions (in 7) highlighting 3d orbital interactions.35
Figure 2.17. (left) Qualitative molecular orbital diagram for gas phase [(pzTp)Fe$^{III}$(CN)$_3$]$^-$ anions (in 8). (right) Molecular orbitals deduced for [(pzTp)-Fe$^{III}$(CN)$_3$]$^-$ anions (in 8) highlighting 3$d$ orbital interactions.\textsuperscript{35}
Figure 2.18. (left) Qualitative molecular orbital diagram for gas phase \( [(pz^0Tp^{Me})Fe^{III}(CN)_3]^- \) anions. (right) Molecular orbitals deduced for \( [(pz^0Tp^{Me})-Fe^{III}(CN)_3]^- \) anions highlighting 3d orbital interactions.35
In the [NEt$_4$][(Tp$^R$)Fe$^{III}$](CN)$_3$ complexes, the $g$ values obtained from the magnetic data apparently scale with the steric demand of the poly(pyrazolyl)borate (Tp$^R$) ligand (Table 2.6). The value of $g_{iso}$ decreases from 2.92 to 2.35 as the C-Fe-C angle becomes more acute [87.7(1) to 88.2(1)$^\circ$], for the Tp$^*$ → Tp$^{*Bn}$ series (Figure 2.21). However, for smaller ligands such pzTp and Tp, slightly larger $g_{iso}$ values are seen for when the average C-Fe-C angles become greater (>88.5$^\circ$) suggesting that this simple trend has additional and more complicated contributions that are subtly dependent on metal-ligand bonding interactions and orbital mixing, perhaps excited states (Figure 2.19).$^{35,59}$ There also appears to be additional links between the tricyanometalate structures and magnetic anisotropy.

The $g$ terms generally become smaller as both the C-Fe-C angles and distance of the Fe$^{III}$ center from the Fe⋯[C$_{3}$N]$_3$ mean plane containing the three cyanide carbons decrease (Figure 2.20, bottom) going from Tp$^*$ to pzTp. We also find that
smaller $g_{iso}$ values are found as $\lambda_{max}$ increases, while $E_{1/2}$ shifts to the positive direction (more oxidizing), suggesting that orbital contributions to the spin ground state are related to efficiency of metal-ligand bonding interactions (Figure 2.20, top; Figure 2.19). A general summary of the ligand-dependent spectroscopic data trends are depicted in Scheme 2.2.

Four general factors are known to dramatically reduce spin-orbit coupling in complexes. These are related to metal-ligand orbital mixing (bonding covalency), availability of excited states (structural distortions and other mixing interactions), ligand spin-orbit coupling (ligand orbital contributions), and changes in the nephelauxetic properties of the complex (electronic delocalization).12,13,17,37-40,63-69 We find electron deficient complexes give the highest energy infrared $\nu_{CN}$ stretches and LMCT ($\lambda_{max}$) absorptions which indicate that the FeII/III redox couples are the most positive for the series (Figure 2.20, top and Table 2.6). As there is little electron density to delocalize into the cyanide ligands the $\nu_{CN}$ should also be seen at the highest energies for the series as well. In the structures of these electron-poor complexes we also find they have the smallest Fe···[C$_3$N]$_3$ contacts and $g_{iso}$
values suggesting that removal of electron density from the Fe$^{III}$ site also leads to lower magnetic anisotropy (Figure 2.20, bottom).$^{18,19,22,31,32,35,40,70-77}$ This is reminiscent of Murugesu descriptions of for square pyramidal \{bis(imino)pyridine\}-Co$^{II}$(NCS)$_2$ complexes. In these structurally related complexes increasing the Co$^{II}$
distance from the mean $[N_4]$ plane of the ligand nitrogen atoms leads to larger zero-field splitting resulting from larger orbital contributions to their $S = \frac{3}{2}$ spin ground states.\textsuperscript{47}
### Table 2.6. Summary of Structural, Spectroscopic, Electrochemical, and Magnetic Data for [NEt₄][(Tp°FeIII(CN)₃].

<table>
<thead>
<tr>
<th>cmpd.</th>
<th>avg. N-Fe-N (°)</th>
<th>avg. C-Fe-C (°)</th>
<th>$E_{1/2}$[a] (mV)</th>
<th>$\lambda_{max}$[b] (nm)</th>
<th>vCN[b] (cm⁻¹)</th>
<th>vBH[b] (cm⁻¹)</th>
<th>vCN[c] (cm⁻¹)</th>
<th>vBH[c] (cm⁻¹)</th>
<th>giso</th>
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<tr>
<td>[NEt₄][(pzTp)FeIII(CN)₃]</td>
<td>87.9</td>
<td>89.9</td>
<td>-758</td>
<td>412</td>
<td>2122</td>
<td>2120</td>
<td>2.41</td>
<td></td>
<td></td>
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<tr>
<td>[NEt₄][(Tp)FeIII(CN)₃]</td>
<td>88.1</td>
<td>89.5</td>
<td>-790</td>
<td>410</td>
<td>2117</td>
<td>2491</td>
<td>2117</td>
<td>2491</td>
<td>2.41</td>
</tr>
<tr>
<td>[NEt₄][(TpMe)FeIII(CN)₃]·3H₂O</td>
<td>88.4(3)</td>
<td>88.1(5)</td>
<td>-911</td>
<td>415</td>
<td>2120</td>
<td>2502</td>
<td>2115</td>
<td>2528</td>
<td>2.70</td>
</tr>
<tr>
<td>[NEt₄][(Tp*)FeIII(CN)₃]·H₂O</td>
<td>89.9</td>
<td>87.7</td>
<td>-944</td>
<td>425</td>
<td>2118</td>
<td>2523</td>
<td>2116</td>
<td>2554</td>
<td>2.92</td>
</tr>
<tr>
<td>[NEt₄][(Tp*Me)FeIII(CN)₃]·H₂O</td>
<td>89.42(5)</td>
<td>87.90(7)</td>
<td>-1060</td>
<td>445</td>
<td>2118</td>
<td>2540</td>
<td>2119</td>
<td>2521</td>
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<tr>
<td>[NEt₄][(pz°TpMe)FeIII(CN)₃]</td>
<td>89.06(7)</td>
<td>88.00(9)</td>
<td>-849</td>
<td>460</td>
<td>2123</td>
<td>2123</td>
<td>2.58</td>
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<td></td>
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<tr>
<td>[NEt₄][(Tp*Br)FeIII(CN)₃]</td>
<td>89.31(9)</td>
<td>88.2(1)</td>
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<td></td>
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<td>2.35</td>
</tr>
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</table>

[a] Data collected as MeCN solutions at room temperature. Electrochemical potentials are referenced to the [Cp₂Fe]⁺/0 couple. 
[b] Data collected as MeCN solutions at room temperature. 
[c] Infrared data collected as Nujol mulls between KBr plates.

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2.8 Conclusions. The magnetic properties of several structurally related tricyanoferroate(III) complexes are described as a function of ligand substitution. For the series, there is significant magnetic ($g$ anisotropy) is present in the $[\text{NEt}_4][(\text{TpR})\text{Fe}^{III}(\text{CN})_3]$ salts, particularly those where tetragonal distortions are more pronounced, namely those that exhibit the smallest C-Fe-C angles (Figures 2.19 and 2.21). The ligand-induced steric distortions due to the pyrazolylborates lead to the structure-dependent changes that heavily influence the extent of ground and excited state mixing of their electronic excited states and is verified via density-functional theory. These combined effects ultimately lead to changes in experimentally observed single-ion magnetic anisotropy for the tricyanoferroate(III) family of complexes.

General Considerations. All operations were conducted under an argon atmosphere using standard Schlenk line and dry box techniques. Transfers of solutions containing cyanide were carried out through stainless steel cannulas. Solvents were distilled under dinitrogen from CaH$_2$ (acetonitrile, dichloromethane), sodium-benzophenone (diethyl ether), or magnesium turnings (methanol) and sparged with argon prior to use. DMF (Baker) was dried using activated alumina columns (VAC Atmospheres). K$_2$CO$_3$ (Acros), 2-propanol (Fisher), ethyl acetate (Fisher), petroleum ether (Fisher), 2,4-pentanedione (Acros), hydrazine hydrate (Acros), acetic acid (Fisher), NEt$_4$Cl·H$_2$O (TCI), KBH$_4$ (Aldrich), MgSO$_4$ (Acros), [NBu$_4$]PF$_6$ (TCI), CoCl$_2$·6H$_2$O (Acros), Co(ClO$_4$)$_2$·6H$_2$O (Aldrich), 2,2′-bipyridine (Acros), Celite (Aldrich), Na[BPh$_4$] (Acros), and deionized water were used as
received. The preparation of potassium hydridotris(3-methylpyrazol-1-yl)borate K[TpMe]$_7$, [NEt$_4$]CN, and [NEt$_4$]$_2$[Fe$_2$OCl$_6$] are described elsewhere.

**Physical Methods.** The IR spectra were recorded as Nujol mulls between KBr plates on a Thermo-Fisher Nicolet 6700 FTIR instrument in the 400-4000 cm$^{-1}$ range. Solution spectra for 1 were obtained as MeCN solutions on a Varian Cary Bio UV-vis spectrometer. Electrochemistry experiments employed a three electrode system consisting of platinum disk working, Pt wire counter, and Ag/Ag$^+$ reference electrodes. [NBu$_4$]PF$_6$ (0.1 M) was used as a supporting electrolyte in MeCN solution. All potentials are reported relative to the ferrocene/ferrocenium [Cp$_2$Fe/Cp$_2$Fe$^+$] redox couple. Magnetic measurements were conducted on a Quantum Design MPMS XL magnetometer Quantum Design SQUID MPMS-XL magnetometer and PPMS-9 susceptometer that operate between 1.8 and 400 K for dc applied fields ranging from –7 to 7 T (MPMS-XL). ac susceptibility measurements were obtained with an oscillating ac field of 1 Oe at frequencies between 10 to 10000 Hz (PPMS) and with an oscillating ac field of 3 Oe at frequencies between 1 to 1500 Hz (MPMS). Measurements were performed on polycrystalline samples dried in air for ca. 2 minutes after filtration and introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm). The magnetic data were corrected for the sample holder and the diamagnetic contributions. Diamagnetic corrections were estimated using Pascal’s constants.$^{26}$ Microanalyses were performed by Robertson Microlit Laboratories. These syntheses of 1, 2, 4, and 5 were prepared via modified literature procedures.$^{86-88}$ Structures determinations were done by Dr. Yuanzhu Zhang and Dr. Nigam P. Rath from University of
Structure Determinations and Refinements. Crystallographic data for 6, 7, 10, and 12 were collected at 90.00(2) K on a Bruker Apex II diffractometer using graphite-monochromated MoKα radiation while 8, 9, and 11 were collected at 100(2) K (8 and 9) and 293(2) K (11) on a Nonius Kappa CCD diffractometer equipped with a graphite-monochrometer (MoKα radiation). Crystals were mounted in Paratone-N oil on glass fibers and data were collected at 100 K. Structure was solved by direct methods and refined against all data using SHELX-97. Refinement was performed against $F^2$ by weighted full-matrix least-squares (SHELXL-97), and empirical absorption corrections (either SCALEPACK or SADABS) were applied. Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography Vol. C.

Synthesis of 3-methylpentane-2,4-dione (1). Under an argon atmosphere 2,4-pentanedione (20.02 g, 200.1 mmol) was dissolved into anhydrous acetone (100 mL) and pre-dried anhydrous K₂CO₃ (27.64 g, 200.3 mmol) was added in four equal portions every 15 min. The mixture was allowed to stir for 30 min. and an acetone (20 mL) solution of MeI (29.10 g, 205.1 mmol) was added drop wise.
via cannulation over 15 min. The mixture was allowed to stir overnight under reflux. Reaction progress was monitored by gas chromatography using periodic reaction aliquots. Once the acetylacetone peaks disappeared the reaction mixture was filtered using a Buchner funnel and washed with Et₂O (50 mL). Organic solvents were evaporated at room temperature using a rotary evaporator. Pure products were obtained via silica gel chromatography, using a 20:1 (v/v) petroleum ether/ethyl acetate eluant, followed by removal of solvents via rotary evaporation. Yield: 19.95 g (87.4%). ¹H NMR (CDCl₃): δ 1.25 (d), 1.83 (s), 2.02 (s), 2.10 (s), 2.18 (s), 3.82 (9), 16.50 (s). Based on NMR analysis the enol form comprises ca. 20% of the mixture.

**Synthesis of 3,4,5-Trimethylpyrazole (2).**⁸⁷ Compound 1 (26.2 g, 0.23 mol) was added drop wise over 1 h to a stirred solution of hydrazine hydrate (80% solution, 15 mL, 0.24 mol), water (1 mL), and acetic acid (1 mL) at 10 °C. The mixture was stirred an additional 20 h at 10 °C for 20 h and the crude precipitated 3,4,5-trimethylpyrazole was collected via suction filtration. The isolated white solid was washed with petroleum ether (100 mL), filtered, and dried under vacuum for 2 min. at room temperature. Yield: 20.1 g (79.0%): ¹H NMR (CDCl₃): δ 1.85 (s, 3H), 2.15 (s, 6H), 7.10 (br, s, 1H).

**Synthesis of KTp*Me (3).** Under an argon atmosphere solid samples of 2 (11.6 g, 105 mmol) and KBH₄ (1.6 g, 30 mmol) were combined and slowly heated to 120 °C and kept at this temperature for 1 h. After that, the temperature was raised to 210 °C and kept at this temperature for an additional 3 h. After cooling, the solid was taken inside glove box, converted to powder using a mortar and pestle, and
sublimed under reduced pressure to remove excess 2. Yield: 9.81 g (86.3 %). IR (Nujol, cm\(^{-1}\)): \(v_{BH} = 2438\) cm\(^{-1}\). Anal. Calcd for C\(_{18}\)H\(_{38}\)N\(_6\)BK: C, 57.14; H, 7.56; N, 22.21. Found: C, 57.17; H, 7.43; N, 22.24.

**Synthesis of (Tp*Me)Fe(OAc) (4).**\(^{88}\) Drop wise addition of a 1:1 DMF/MeCN (v/v, 40 mL) solution of 3 (2.10 g, 6.25 mmol) into Fe(OAc)\(_2\) (1.20 g, 6.90 mmol) in DMF (25 mL) over 30 min. afforded a gray suspension. After 2 h., the mixture was evacuated to dryness at 50 °C and the gray residue was dissolved into MeCN (20 mL), filtered, and Et\(_2\)O (30 mL) was added. The precipitated solid was isolated by filtration and dried under vacuum (27 °C) for 2 h. Yield: 2.12 g (70.3%). IR (Nujol, cm\(^{-1}\)): 2517 (s), 1679 (vs), 1623 (vs), 1593 (vs), 1543 (vs), 1415 (vs), 1380 (vs), 1351 (vs), 1335 (vs), 1259 (s), 1200 (vs), 1089 (s), 1066 (vs), 1041 (vs), 1022 (s), 981 (s), 936 (m), 864 (m), 847 (s), 807 (vs), 773 (s), 698 (s), 664 (vs), 651 (vs), 617(m), 462 (m).

**Synthesis of [NEt\(_4\)]CN (5).**\(^{89}\) To a solution of NEt\(_4\)Cl·H\(_2\)O (40.0 g, 218 mmol) in MeOH (400 mL) pulverized KCN solid (28.8 g, 436 mmol) was added. The suspension was stirred for 36 h. and filtered under argon. The filtrate was evacuated to dryness under vacuum at 40 °C, the white residue was extracted with MeCN (3 × 100 mL), and all extracts were combined and filtered again. The mixture was concentrated under vacuum at room temperature to ca. 75 mL and allowed to stand at -20 °C for 24 h. The white crystals were isolated by filtration, washed with Et\(_2\)O (3 × 25 mL), and dried under vacuum at room temperature overnight. Yield: 21.7 g (63.8 %). Anal. Calcd for C\(_9\)H\(_{20}\)N\(_2\): C, 69.1; H, 12.9; N, 17.9. Found: C, 68.6; H, 12.0; N, 18.1. IR (Nujol, cm\(^{-1}\)): \(v_{CN} = 2051\) cm\(^{-1}\).
Synthesis of \([\text{NEt}_4]_2[(\text{Tp}^{\text{Me}})\text{Fe}^{\text{II}}(\text{CN})_3] \cdot \text{H}_2\text{O}\) (6). Drop wise addition of a 1:1 DMF/MeCN (v/v; 40 mL) solution of 3 (2.40 g, 6.36 mmol) in a DMF solution (20 mL) of Fe(OAc)_2 (2.20 g, 12.6 mmol) over 30 min. afforded a gray mixture that was evacuated to dryness after 3 h at 50 °C. The gray residue was extracted with MeCN (2 × 20 mL), filtered, and was added drop wise to a MeCN (30 mL) solution of 5 (2.98 g, 19.1 mmol). The brown suspension was stirred for 4 h and filtered to remove a brown precipitate. The filtrate was concentrated to ca. 20 mL and Et_2O (90 mL) was added to afford a red precipitate. The solid was isolated via suction filtration, washed with Et_2O (2 × 5 mL), and dried under vacuum for 20 min. Yield: 3.05 g (63.8%). Crystals are obtained from slow diffusion of Et_2O into a MeCN solutions of 6. IR (Nujol, cm\(^{-1}\)): \(\nu_{\text{BH}} = 2507, \nu_{\text{CN}} = 2044\). \(\mu_{\text{eff}} (\mu_\text{B}) = 0\).

Synthesis of \([\text{NEt}_4][(\text{Tp}^{\text{Me}})\text{Fe}^{\text{III}}(\text{CN})_3] \cdot \text{H}_2\text{O}\) (7). Drop wise addition of aqueous 30% H_2O_2 (20 mL) into a 4:1 ratio of CH_2Cl_2/iPrOH (v/v, 50 mL) containing 6 (3.05 g, 4.06 mmol) over 30 min. afforded a red mixture. That was allowed to stir an additional 3 h at room temperature. The aqueous phase was decanted and the organic phase dried over anhydrous MgSO_4. Filtration of the red-brown mixture gave a red filtrate that was concentrated under vacuum to ca. 10 mL. Et_2O (60 mL) addition afforded a red powder. Yield: 1.75 g (69.3%). Red tablets are obtained via slow evaporation of 2:1 MeOH/H_2O (v/v) solutions of 7. Anal. Calcd for C_{29}H_{50}BFeN_{10}O: C, 56.05; H, 8.11; N, 22.54%. Found: C, 56.05; H, 7.90; N, 22.46%. IR (Nujol, cm\(^{-1}\)): \(\nu_{\text{BH}} = 2544, \nu_{\text{CN}} = 2119\). UV-vis (MeCN): \(\lambda_{\text{max}}/\text{nm} (\varepsilon_{\text{M}}/\text{M}^{-1} \text{cm}^{-1}) 317 \text{ nm} (162), 445 \text{ nm} (453)\). CV (MeCN, \(c = 2.0 \times 10^{-3} \text{ M}\), scan rate = 10 mV s\(^{-1}\)): \(E_c = -1135 \text{ mV} (i_c = 3.57 \mu\text{A}), E_a = -1042 \text{ mV} (i_a = 3.20 \mu\text{A}), E_{1/2} = -1060 \text{ mV}\).
Synthesis of [NEt₄][pzTp]Fe[II](CN)₃ (8). Treatment of [(pzTp)₂Fe[II]] (1.228 g, 2.00 mmol) with 5 (0.967 g, 6.20 mmol) in MeCN (40 ml) for 1 h at 50 °C afforded an orange solution that was evacuated to dryness. The orange residue was dissolved into MeCN (15 mL), filtered, and the filtrate was layered with Et₂O (40 mL). Orange blocks were obtained after 3 d and were isolated via filtration, washed with Et₂O (2 x 5 mL), and dried under vacuum for 2 h. Yield: 1.22 g (86.0 %). Anal Calcd. For C₃₁H₅₂N₁₃BFe: C, 55.23; H, 7.80; N, 27.02 . Found: C, 56.14; H, 8.41; N, 28.49. IR (Nujol, cm⁻¹): 3658 (w), 3351 (vs, br), 3240 (vs, br) 3089 (s), 2954 (vs), 2924 (vs), 2855 (vs), 2069 (vs), 2050 (vs), 1499 (vs), 1481 (vs), 1461 (vs), 1411 (vs), 1390 (vs), 1293 (vs), 1213 (vs), 1189 (s), 1174 (s), 1091 (vs), 1056 (s), 1047 (s), 1004 (s), 920 (m), 871 (m), 842 (s), 814 (s), 795 (vs), 780 (vs), 759 (vs), 669 (s), 623 (s). μeff (μB) = 0.

Synthesis of [NEt₄][(pzTp)Fe[III](CN)₃] (9). Treatment of (pzTp)₂Fe[II] (1.228 g, 2.00 mmol) with 5 (0.967 g, 6.20 mmol) in MeCN (40 ml) for 1 h at 50 °C afforded an orange solution that was evacuated to dryness. The orange residue was dissolved into 30% H₂O₂ (30 mL) and allowed to stir for 20 h at room temperature. The yellow precipitate was collected via suction filtration, washed with cold water (2 x 5 ml), and dried under vacuum for 5 h at room temperature. Yield: 0.815 g (75.1%, (pzTp)₂Fe[II]-based). Yellow crystals of 9 are obtained after 3 d from dry MeCN/Et₂O mixtures. Anal. Calcd for C₂₃H₃₂BN₁₂Fe: C, 50.85; H, 5.94; N, 30.94. Found: C, 50.62; H, 6.42; N, 30.83. IR (Nujol, cm⁻¹): 3147 (m), 3139 (m), 3126 (m), 2120 (s), 1501 (s), 1485 (s), 1441 (vs), 1409 (vs), 1392 (vs), 1366 (s), 1305 (vs), 1246 (m), 1204 (vs), 1188 (s), 1172 (m), 1105 (s), 1092 (m), 1081 (s), 1059 (vs),
996 (m), 923 (m), 873 (m), 858 (s), 832 (m), 809 (s), 783 (vs), 772 (vs), 760 (s),
663 (w), 618 (m), 529 (w), 479 (w), 408 (m). \( \mu_{\text{eff}} (\mu_B) = 2.25. \) UV-vis (MeCN):
max/nm (\( \Delta M/M^1 \text{ cm}^{-1} \)) 322 nm (283), 412 nm (530). CV (MeCN, \( c = 2.0 \times 10^{-3} \text{ M}, \)
scan rate = 10 mV s\(^{-1}\)): \( E_{c} = -811 \text{ mV} \) (\( i_{c} = 5.74 \text{ \mu A} \)), \( E_{a} = -708 \text{ mV} \) (\( i_{a} = 5.0 \text{ \mu A} \)),
\( E_{1/2} = -758 \text{ mV} \).

**Synthesis of [NEt\(_4\)][(pz\(^0\)TpMe)Fe\(^{III}\)(CN)\(_3\)]\( \cdot \)H\(_2\)O (10).** Treatment of [Et\(_4\)N]\(_2\)-
[Fe\(_2\)OCl\(_6\)] (3.02 g, 6.58 mmol) with K(pz\(^0\)TpMe) (2.23 g, 6.02 mmol) in 1:1
MeOH/MeCN (v:v) for 1 h afforded a n orange-red solution. Addition of 5 (2.34 g,
15.0 mmol) in MeCN (30 mL) afforded an orange-red mixture that was allowed to
stir for 3 h at room temperature. The red mixture was suction filtered through Celite
and the filtrate was evacuated to dryness via rotary evaporation. The red residue
was dissolved into a 6:1 MeOH/H\(_2\)O (35 mL) mixture (v:v) and was filtered again
though Celite. The filtrate was concentrated under vacuum to ca. 8 mL volume with
heating (60 °C). The solution was allowed to stand at 0°C for 12 h. The orange
microcrystalline solid was isolated via suction filtration, washed with hexanes (3 ×
20 mL), and dried under vacuum for 2 min. at room temperature. Yield: 1.35 g
(45.0%). Anal. Calcd for C\(_{27}\)H\(_{40}\)BFeN\(_{12}\): C, 54.11; H, 6.73; N, 28.04; Found: C,
54.06; H, 6.69; N, 27.88. IR (Nujol, cm\(^{-1}\)): 3154 (w), 3138 (w), 3123 (w), 3111 (w),
3095 (w), 2124 (w), 2114 (m), 1534 (w), 1510 (s), 1477 (m), 1385 (m), 1354 (s),
1341 (s), 1248 (w), 1229 (w), 1215 (s), 1189 (s), 1169 (m), 1076 (s), 1058 (w),
1045 (w), 1038 (w), 1020 (w), 1008 (w), 995 (m), 901 (w), 868 (m), 853 (s), 836
(w), 806 (s), 799 (s), 773 (m), 765 (s), 734 (w), 722 (w), 686 (w), 682 (w), 526 (w),
483 (m), 419 (w). UV-vis (MeCN): \( \lambda_{\text{max}}/\text{nm} \) (\( \varepsilon_{\text{M}}/\text{M}\text{-}1 \text{ cm}^{-1} \)) 370 nm (1677), 460 nm (3988).

**Synthesis of [NEt₄][Tp^Me]Fe^{III}(CN)₃·4.5H₂O (11).** A solution of K[Tp^Me] (1.77 g, 6.02 mmol) in MeOH (30 ml) was slowly added to a solution of [NEt₄]₂[Fe₂OCl₆] (3.02 g, 5.00 mmol) in MeCN (30 ml) over 1 hour. After stirring for an additional hour, a solution of [NEt₄]CN (2.81 g, 18.0 mmol) in MeCN (30 ml) was then added to afford a red mixture, which was allowed to stir for 3 hours at room temperature. The red mixture was filtered through Celite and the filtrate was concentrated to dryness via rotary evaporation. The remaining brick red solid was dissolved into a 6:1 mixture (v:v) of MeOH/H₂O (35 ml) and filtered again through Celite. The filtrate was concentrated under vacuum (ca. 8 mL) at 35 °C and was subsequently cooled to 0 °C for 5 minutes. The orange microcrystalline solid was isolated via suction filtration, washed with H₂O (3 × 5 mL), hexane (3 × 10 mL), and dried under vacuum for 5 minutes at room temperature. Yield: 1.15 g (41.4%). Suitable crystals for X-ray studies were obtained via slow evaporation of a 3:1 MeOH/H₂O (v:v) mixture of 13 in air. Anal. Calcd for C₂₃H₄₀BFeN₁₀O₂ (13·2.5H₂O): C, 49.75; H, 7.26; N, 25.22. Found: C, 50.12; H, 7.09; N, 25.43. IR (Nujol, cm⁻¹): 3460 (m, br), 3138 (w), 3121 (m), 2481 (m), 2121 (m), 1747 (w), 1642 (w), 1632 (w), 1504 (s), 1482 (s), 1392 (s), 1348 (s), 1198 (vs), 1173 (s), 1100 (w), 1079 (w), 1050 (vs), 1001 (m), 967 (w), 877 (w), 844 (w), 820 (w), 785 (s), 738 (s), 683 (w), 646 (w), 622 (w). UV-vis (MeCN): \( \lambda_{\text{max}}/\text{nm} \) (\( \varepsilon_{\text{M}}/\text{M}\text{-}1 \text{ cm}^{-1} \)) 330 nm (1194), 415 nm (2815). CV (MeCN, \( c = 2.0 \times 10^{-3} \text{ M} \), scan rate = 10 mV s⁻¹): \( E_{\text{c}} = -960 \text{ mV} \) (\( i_{\text{c}} = 2.95 \mu\text{A} \)), \( E_{\text{a}} = -862 \text{ mV} \) (\( i_{\text{A}} = 3.21 \mu\text{A} \)), \( E_{1/2} = -911 \text{ mV} \).
**Synthesis of 3-benzylpentane-2,4-dione.** In the dark and under an argon atmosphere, benzyl chloride (26.58 g, 210 mmol) was dissolved into anhydrous acetone (60 ml) and NaI (32.23 g, 210 mmol) was added. The reaction mixture was stirred for 2 h, allowed to stand for 1 h, and filtered. In another flask, acetylacetone (20.02 g, 200 mmol) was dissolved in anhydrous acetone (100 mL), K₂CO₃ (27.64 g, 200 mmol) was added in four equal portions every 15 min., and the mixture was allowed to stir for an additional 30 min. the reaction mixture from the previous flask which was kept at dark was filtered using a cannula and added drop wise. After addition is complete, the reaction mixture was refluxed overnight. Completion of the reaction was monitored by gas chromatography analysis of reaction aliquots. Once the acetylacetone peak is gone, reaction mixture was filtered using a Büchner funnel and washed with Et₂O (50 mL). The mixture was evaporated to dryness using rotary evaporator at room temperature. Pure products were obtained via silica gel chromatography using 12:1 petroleum ether/ethyl acetate (v/v) as an eluent, followed by rotary evaporation to yield a colorless oil. Yield: 31.9 g (84.1%). ¹H NMR (CDCl₃,) δ 2.01 (s, 6H), 3.32-3.79 (m, 3H), 7.21-7.08 (m, 5H).

**Synthesis of 4-benzyl-3,5-dimethylpyrazole.** 3-benzylpentane-2,4-dione (43.8 g, 0.23 mol) was added drop wise to a stirred solution of hydrazine hydrate (80% solution, 15 mL, 0.24 mol), H₂O (1 mL), and acetic acid (1 mL) held at 10 ºC (circulating chiller). The mixture was allowed to stir for an additional 20 h at 10 ºC and the precipitated 4-benzyl-3,5-dimethylpyrazole was collected via suction filtration as white solid. The solid was washed with petroleum ether (2 x 20 mL)
and briefly dried under vacuum for 2 min. at room temperature. Yield: 30.6 g (71.4%). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.85 (s, 3H), 2.15 (s, 6H), 7.10 (br s, 1H). The product may be recrystallized from dry toluene to obtain crystals suitable for X-ray structural determinations.

**Synthesis of KTp\(^{Bn}\).** 4-benzyl-3,5-dimethylpyrazole (19.6 g, 105 mmol) was added to freshly ground KBH\(_4\) (1.6 g, 30 mmol) and the mixture was slowly heated to 120 °C and kept at this temperature for 1 h. After that, the temperature was raised to 225 °C and kept at this temperature for 3 h. After cooling, the solid was taken inside glove box, pulverized using a mortar and pestle, placed into a sublimator, and excess pyrazole was removed via sublimation under reduced pressure. Yield: 14.3 g (78.6%). IR (Nujol, cm\(^{-1}\)): \(\nu\) \(\text{BH}^{-}\) = 2438. Anal. Calcd for C\(_{36}\)H\(_{40}\)N\(_6\)BK: C, 71.27; H, 6.65; N, 13.85. Found: C, 71.33; H, 6.43; N, 13.67.

**Synthesis of [NEt\(_4\)][(Tp\(^{Bn}\)Fe\(^{III}\)(CN)\(_3\)]\(\cdot\)2MeOH\(\cdot\)H\(_2\)O (12).** Drop wise addition of a 1:1 (v/v) DMF/MeCN (40 mL) solution of KTp\(^{Bn}\) (3.82 g, 6.30 mmol) into a DMF (20 mL) solution of Fe(OAc)\(_2\) (2.20 g, 12.6 mmol) over 30 min afforded a gray mixture that was allowed to stir for 15 h at 50 °C; evacuation to dryness at 50 °C afforded a gray residue. The gray solid was extracted into MeCN (2 \(\times\) 20 mL), filtered, and was added drop wise to a MeCN (30 mL) solution of [NEt\(_4\)]CN (2.98 g, 19.1 mmol). The brown suspension was stirred for 4 h and filtered to remove a brown precipitate. The filtrate was concentrated to ca. 20 mL and addition of Et\(_2\)O (90 mL) afforded a red solid. The precipitate was isolated via suction filtration, washed with Et\(_2\)O (2 \(\times\) 5 mL), and dried under vacuum for 2 h at room temperature. Drop wise addition of aqueous 30% H\(_2\)O\(_2\) (20 mL) into a 4:1 CH\(_2\)Cl\(_2\)/iPrOH (v/v, 50
mL) solution of the red solid over 30 min afforded a red biphasic mixture. After 3 h the aqueous phase was decanted and the organic phase dried over anhydrous MgSO$_4$. The red-brown mixture was filtered and the filtrate concentrated under vacuum to ca. 10 mL at room temperature. Addition of Et$_2$O (60 mL) afforded a red powder that was crystallized via slow evaporation of a 2:1 MeOH/H$_2$O solution containing 11. Yield: 2.13 g (36.9%). Anal. Calcd for C$_{49}$H$_{70}$BFeN$_{10}$O$_3$: C, 64.54; H, 7.51; N, 15.90. Found: C, 64.40; H, 7.72; N, 15.33. IR (Nujol, cm$^{-1}$): 3387 (br), 2923 (vs), 2854 (vs), 2521 (m), 2119 (s), 1631 (w), 1602 (m), 1554 (w), 1493 (m), 1460 (vs), 1376 (s), 1238 (m), 1152 (m), 1061 (s), 1002 (w), 830 (m), 727 (s), 701 (m), 588 (w).

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Chapter Three: Synthesis and Characterization of Trinuclear Cyanide-Bridged Complexes and Single-Molecule Magnets

3.1 Introduction. In this chapter we describe our recent effort to prepare five trinuclear cyanide-bridged complexes. We are primarily interested in lower nuclearity complexes because the energy gap between $M_s$ levels can often be bigger thus favoring a higher energetic barrier to magnetization reversal. In theory this makes the relaxation of magnetization more difficult at a given temperature. In contrast the gaps between $M_s$ magnetization levels are often found to be very small for larger clusters.\textsuperscript{1-15} To synthesize lower molecularity complexes, we need proper ancillary ligands and have chosen to focus on pyrazolylborate ligands.\textsuperscript{16-33} These tridentate ligands are ideal as they stabilize a variety of metal oxidation states, can be chemically modified giving a systematic means to tune the electronic, steric demand, and solubility properties of their polynuclear complexes. Typically, combination of tricyanometalate complexes, which we refer to as building blocks (see chapter 2) with those containing labile ligands, allows us to construct polynuclear products whose numbers/spatial orientations of $M(\mu$–CN)$M^-$ units formed may be controlled during self-assembly, and their magnetic interactions predicted via orbital symmetry.\textsuperscript{34,35} Our working hypotheses is that the magnitude of the magnetic exchange between the low spin Fe$^{III}$ ($S = \frac{1}{2}$) and Ni$^{II}$ ($S = 1$) metal centers can be controlled via ancillary ligand choice and their steric demand.

The last couple of decades have witnessed an explosion of study on single molecule magnets (SMMs) because of their unique physical properties and
potential applications for information storage. These finite-size molecules possess an energy-barrier ($U$) for magnetic spin reversal, which under low temperature conditions, allows for slow relaxation in magnetization to be observed. The energy barrier to magnetic spin reversal is defined by the two necessary requirements, a large ground-state spin ($S_T$) and uniaxial Ising-like magnetic anisotropy ($D < 0$), with the equation of $U = |D| S_T^2$ or $|D| (S_T^2 - 1/4)$ for integer or half-integer total spin ($S_T$) values of the clusters.\textsuperscript{1-15} A lot of synthetic efforts have been devoted to the preparation of new magnetic molecules by choosing different anisotropic metallic ions ranging from transition metals to rare earth ones bridged by ligands such as oxo- and carboxylate, azide, cyanide, oxalate, etc.\textsuperscript{1-7} World-wide efforts have sought to better understand what is necessary to increase the barrier heights and has driven synthetic efforts towards larger molecular clusters of increasing nuclearity. However, this approach does not seem to work efficiently as expected as significantly faster relaxation is seen. In these systems the high nuclearity clusters often see the effect that $|D|$ decreases as the total spin increases, where $|D|$ becomes proportional to $S^2$, meaning that the real world/experimental energy barrier for spin reversal ($U_{\text{eff}}$) scales as a function of $S^0$ and not $S^2$ as theory would predict.\textsuperscript{25,36,37}

Another unresolved question is how single ion magnetic anisotropy and their tensors lead to overall cluster properties. Symmetry appears to play a complex role and bad anisotropy tensor alignments (partial or complete cancellation) is expected to significantly lower the energy barrier $U_{\text{eff}}$.\textsuperscript{25,26,32,38,39} Recently, more concerns are focused on realizing a better alignment of single ion anisotropies.
within a given system. Obviously, For the most well-studied Mn(III)-SMMs, where the orbital contributions to the magnetic spin moments are nearly quenched/eliminated, a clear magneto-structural correlation has been described where the relative orientations of the Jahn-Teller axes (on the Mn$^{III}_{HS}$ sites) can act as a predictor for magnetic anisotropy, with parallel alignment often giving the largest magnetic anisotropy and $U_{eff}$. Following this approach a number of new SMMs based on those metallic ions with unquenched orbital angular momentum have reported in recent years.

Single-molecule magnets (SMMs) continue to receive intense attention owing to their rich synthetic chemistry and their ability to allow for detailed structure-property relationships to be described. Cyanometalate-based analogues are relatively new and are unique in that their unquenched orbital angular momentum is often greater than the better known oxo/carboxylate clusters. While several cyanide-based SMMs have been reported the best characterized use $[(Tp^R)M(CN)_3]^-$ building blocks, where $Tp^R$ is a tridentate poly(pyrazolyl)borate and $M^{n+}$ is a trivalent (e.g. low spin Fe$^{III}$) ion. Due to the combination of a large spin ground state ($S_T$) and uniaxial Ising-like magnetic anisotropy (i.e. $D < 0$), these molecular objects exhibit appreciable energy barriers ($U$) to spin inversion. A number of SMMs have been explored with an aim to increase the barrier height. As one of the well-known bridges, the cyanide complexes have become attractive candidates for the development of SMMs and thus generated a new and fast-growing family in recent years based on a tailored building block synthetic approach. This strategy relies on self-assembly of molecular precursors that give
structurally related molecules. The most common building-blocks are those derived from \([(Tp^R)Fe^{III}(CN)_{3}]^-\) ions (with \(T^pR\) = a pyrazolylborate). The low-spin \(Fe^{III}_{LS}\) ion in a \(C_{3v}\) symmetry environment gives a quite large single-ion anisotropy due to the presence of spin-orbital coupling, which may be tuned with \(T^pR\) ligand steric demand and donor strength. These complexes are magnetically different than \(Mn^{III}_{HS}\)-based SMMs, where the orbital angular moment of \(Mn(III)\) centers are quenched due to the tetragonally elongated \(Mn^{III}\) ions. While many of the manganese-based clusters have very high molecular symmetries we were curious if lower symmetry complexes give higher magnetic anisotropy and energy barriers to magnetization reversal.

In previous work Zuo and Long suggested that the magnetization reversal barrier is enhanced upon conversion of cubic \(\{Fe^{III}_{6}Cu^{II}_{8}\}\) complexes \((S_T = 7, U_{eff} = 11.3 \text{ K})\) to trigonal bipyramidal \(\{Fe^{III}_{2}Cu^{II}_{3}\}\) \((S_T = 5/2, U_{eff} = 23.2 \text{ K})\), proposing without other evidence that lower symmetry may be a cause for this behavior. Likewise, we also reported a linear-like octanuclear \(\{Fe^{III}_{4}Ni^{II}_{4}\}\) SMMs (Chapter 4), that can be viewed as an unfolded or opened versions of the previously reported \(\{Fe^{III}_{4}Ni^{II}_{4}\}\) symmetrical cubes, also exhibits a much higher anisotropy energy \((U_{eff} = 33 \text{ K})\) than the latter. Taking into account the structural data, the reduction of symmetry in the rod-shaped \(\{Fe^{III}_{4}Ni^{II}_{4}\}\) cluster led to a parallel or nearly parallel alignment of the three-fold rotation axes \(C_3\) that lie along the \(Fe^{III}\)···B directions.

In this chapter we present a systematic study that further tests this hypothesis, within a series of trinuclear \(\{Fe^{III}_{2}Ni^{II}\}\) complexes containing a number of ancillary ligands. This work is based on reports by Holmes in 2006, where a trinuclear “V-
shaped” \{\text{Fe}^{III}\text{II}\text{Ni}^{II}\} complex, \([(\text{pzTp})\text{Fe}^{III}(\text{CN})_3\text{II}(\text{bpy})_2] \cdot 2\text{H}_2\text{O}\), was reported to be the smallest cyanide-based SMMs.\textsuperscript{25,26,32} In this complex the three-fold rotation axes are oriented in a common direction and are ca. 22° from being parallel due to the mirror symmetry at Ni site, suggesting that a favorable projection of orbital angular momentum may be engineered with proper ligand choices. As part of a continuing interest in this behavior we synthesized five more trinuclear \{\text{Fe}^{III}\text{II}\text{M}^{II}\} compounds, where \text{M}^{II} = \text{Ni} and \text{Mn} in the presence of various monodentate (dimethylformamide, DMF) and polydentate ligands (2,2’-bipyridine, bpy; tris(2-aminoethyl)amine, tren; diethylenetriamine, DETA) at the divalent sites. We now describe their structures, spectroscopic, and magnetic properties.

3.2 Synthesis and Spectroscopic Characterization. Combining a 2:1 ratio of \([\text{NEt}_4][\text{Tp}^{Me}]{\text{Fe}^{III}(\text{CN})}_3\cdot\text{H}_2\text{O}\) with various nickel(II) salts, in the presence of polydentate ammine ligands (bpy, tren, and DETA) affords three structurally related trinuclear “V-shaped” complexes of \([(\text{Tp}^{Me})\text{Fe}^{III}(\text{CN})_3\cdot2[\text{Ni}^{II}(\text{bpy})_2]\cdot3\text{H}_2\text{O}\cdot4\text{MeOH}\ (1), \ [(\text{Tp}^{Me})\text{Fe}^{III}(\text{CN})_3\cdot2[\text{Ni}^{II}(\text{tren})]\cdot2\text{H}_2\text{O}\cdot3\text{MeOH}\ (2), and \ [(\text{Tp}^{Me})\text{Fe}^{III}(\text{CN})_3\cdot2[\text{Ni}^{II}(\text{DETA})(\text{OH}_2)]\cdot6\text{H}_2\text{O}\cdot\text{MeCN}\ (3).
-4MeOH (1), \{[(Tp^{Me})Fe^{III}(CN)_3]_2[Ni^{II}(tren)]\}·2H_2O·3MeOH (2), and \{[(Tp^{Me})-Fe^{III}(CN)_3]_2[Ni^{II}(DETA)(OH_2)]\}·6H_2O·MeCN (3) stoichiometry (Scheme 3.1). The central cis-Ni^{II}(L)_x(\mu-NC)_2 unit is linked to two adjacent (Tp^{Me})Fe^{III}(CN)_3 fragments via two bridging cyanides forming Fe-CN-Ni-CN linkages. The infrared spectra of 1–3 contain two medium intensity \nu(CN) stretching absorptions for each complex, at 2156 and 2125 cm\(^{-1}\) for 1, 2153 and 2119 cm\(^{-1}\) for 2, and 2154 and 2122 cm\(^{-1}\) for 3, indicating that bridging (higher energy) and terminal (lower energy) cyanides are present. In comparison the cyano absorption in [NEt_4][(Tp^{Me})Fe^{III}(CN)_3]·H_2O is found at 2119 cm\(^{-1}\). The corresponding \nu(BH) stretches for 1-3 are found at 2533, 2536, and 2529 cm\(^{-1}\), which are found at lower energies than that seen for [NEt_4][(Tp^{Me})Fe^{III}(CN)_3]·H_2O (2544 cm\(^{-1}\)), indicating that more electron density is found in the tricyano fragment with formation of the Fe-CN-Ni bridges.

Two additional linear trinuclear complexes, \{[(Tp^{Br})Fe^{III}(CN)_3]_2[M^{II}(DMF)_4]\}·x(solvent) (M^{II} = Ni^{II}, 4; Mn, 5), may also be prepared using another building block, [NEt_4][(Tp^{Br})Fe^{III}(CN)_3]·H_2O, with either manganese(II) or nickel(II) trifluoromethanesulfonate in DMF solution (Scheme 3.2). The complexes contain a 2:1
ratio of \([\text{Tp}^*\text{Me}]\text{Fe}^{III}(\text{CN})_3\) units linked via cyanides to a central trans-\(\text{M}(\text{DMF})_4(\text{m-NC})_2\) unit. The infrared spectra show \(\nu_{\text{BH}}\) (2537 and 2541 cm\(^{-1}\)) in addition to bridging (2174 and 2149 cm\(^{-1}\)) and terminal (2118 and 2116 cm\(^{-1}\)) \(\nu_{\text{CN}}\) cyanide stretches, that are also shifted from those in the tricyano building block (2521 and 2119 cm\(^{-1}\)). It is noteworthy that the bridging cyanide in 5 is lower energy cyanide stretches than the one in 4, highlighting the effect \(\pi\) back bonding has on the \(\nu_{\text{CN}}\), with the more electropositive analogue (Mn\(^{II}\), 5) giving a lower energy stretch than the more electronegative derivative (Ni\(^{II}\), 4).\(^{38}\)

3.3 Structural Characterization. The structural data collected for 1–5 confirm that they are neutral molecular and trinuclear complexes of \(\{[(\text{Tp}^*\text{Me})\text{Fe}(\text{CN})_3]_2-\text{[Ni(L)]}_x\}\) stoichiometry, where L = bpy, 1, tren, 2, or DETA, 3.\(^{39,40}\) As shown in Figure 3.1, the crystallographically independent \(\{[(\text{Tp}^R)\text{Fe}(\text{CN})_3]\}^+\) (Fe1 and Fe2) units connect to a single Ni\(^{II}\) ion though one cyanide, leaving two terminal ones per iron site. The bridging cyanide Fe-C distances are comparable in 1-3, ranging from 1.899(6) to 1.923(3) Å [Fe2-C4 in 2 and Fe1-C1 in 3], while the terminal ones are between 1.898(9) and 1.922(9) Å in 1, 1.921(6) and 1.934(5) in 2, and 1.917(3) and 1.934(3) in 3. The Fe-N distances vary little for 1-3 being adopting values between 1.972(6) and 2.018(6) Å for 1 [Fe2-N16 and Fe1-N10]. The Fe1-C-N angles involving terminal cyanides are the most distorted in 1, and are found between 172.8(3) and 179.3(3)°, while those in structures of 2 and 3 are more linear. The angle of the bridging cyanides [Fe1-C1-N1 and Fe2-C4-N4] vary considerably and are 173.1(7) and 172.7(7)° for 1, 173.9(6) and 173.2(5)° in 2, and 178.4(3) and 173.1(3)° for 3.\(^{39,40}\)
Figure 3.1. X-ray structures for (top, left) \{[(Tp^\text{Me})Fe^{\text{III}}(CN)_3]^2Ni^{\text{II}}(bpy)_2]\}-3H_2O-4MeOH (1), (top, right) \{[(Tp^\text{Me})Fe^{\text{III}}-(CN)_3]^2[Ni^{\text{II}}(tren)]\}-2H_2O-3MeOH (2), (bottom, left) \{[(Tp^\text{Me})Fe^{\text{III}}(CN)_3]^2[Ni^{\text{II}}(DETA)(H_2O)]\}-6H_2O-MeCN (3), and (bottom, right) \{[(Tp^\text{Bn})Fe^{\text{III}}(CN)_3]^2[Ni^{\text{II}}(DMF)_4]\}-2DMF (4). Hydrogen atoms and lattice solvent are removed for clarity.38-40
Table 3.1. Crystallographic Data for \{[(Tp* Me)Fe^{III}(CN)_{3}]_{2}Ni^{II}(bpy)\}_{2} \cdot 3H_{2}O \cdot 4MeOH (1), \{[(Tp* Me)Fe^{III}(CN)_{3}]_{2}[Ni^{II}(tren)]\}_{-2}H_{2}O \cdot 3MeOH (2), \{[(Tp* Me)Fe^{III}(CN)_{3}]_{2}[Ni^{II}(DETA)(H_{2}O)]\}_{-6}H_{2}O \cdot MeCN (3), \{[(Tp* Bn)Fe^{III}(CN)_{3}]_{2}[Ni^{II}(DMF)_{4}]\}_{-2}DMF (4), and \{[(Tp* Bn)Fe^{III}(CN)_{3}]_{2}[Mn^{II}(DMF)_{4}]\}_{-2}DMF (5).^{38-40}

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[^a]: I > 2σ(I): \(R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}^{1/2}\), \(wR_2 = \frac{\sum [w(F_o^2-F_c^2)]}{\sum [w(F_o^2)]^{1/2}}\)
Table 3.2. Selected Bond Distances (Å) and Angles (°) for $\{(Tp^{*}Me)Fe^{III}\text{(CN)}_{3}\text{Ni}^{II}\text{(bpy)}_{2}\}\cdot 3\text{H}_{2}\text{O}\cdot 4\text{MeOH}$ (1) and $\{(Tp^{*}Me)Fe^{III}\text{(CN)}_{3}\text{Ni}^{II}\text{(tren)}\}\cdot 2\text{H}_{2}\text{O}\cdot 3\text{MeOH}$ (2).\(^{38}\)

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Table 3.3. Selected Bond Angles (°) for \{[(T^* Me)Fe^{III}(CN)_3]_2[Ni^{II}(DETA)(H_2O)]\}_6\text{H}_2\text{O}\cdot\text{MeCN (3), [(T^* Bn)Fe^{III}(CN)_3]_2-}[Ni^{II}(\text{DMF})_4]\}_2\text{DMF (4), and [(T^* Bn)Fe^{III}(CN)_3]_2[Mn^{II}(\text{DMF})_4]\}_2\text{DMF (5).}^{38-40}

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<td>Ni1-N1-C1 173.3(3)</td>
<td>Mn1-N1-C1 168.5(2)</td>
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In 1 and 2 the nickel atoms adopt distorted $cis$-$\text{Ni}$(\(\mu\)-NC)$_2$ geometries whose coordination spheres are completed with either four nitrogen donors (1 and 2) or three N atoms and one oxygen atom in 3.\textsuperscript{39,40} The Ni-NCN bonds vary little for the three complexes and adopt values ranging from 2.024(7) to 2.079(3) Å [Ni1-N1 in 1 and Ni1-N4 in 3] while the Ni-N bonds to the coligands (bpy, tren, DETA) are slightly longer, falling between 2.067(8) and 2.143(5) Å; the Ni1-O1 bond in 3 is also longer at 2.145(2) Å.\textsuperscript{37b} The Ni1-N-C [Ni1-N1-C1 and Ni1-N4-C4] bond angles are quite different from each other: 174.2(7) and 175.4(7) for 1, 165.9(5) and 166.0(5) for 2, and 176.3(3) and 167.6(3) for 3, respectively. These differences probably reflect steric demand of the nitrogen donor ligands and flexible nature of the bridging cyanide bonds, with the tren derivative being the most demanding of the three (in 2).

The structure of 3 differs from those of 1 and 2 given that DETA is a tridentate ligand. The central [$cis$-$\text{Ni}$$^\text{II}$(DETA)(OH$_2$)(\(\mu\)-NC)$_2$] fragment contains a tridentate mer-DETA ligand, two $cis$-cyanides, and aqua ligand to give a distorted NiN$_5$O environment.\textsuperscript{39,40} The Ni1-N$_\text{cyanide}$ distances [2.030(3) and 2.079(3) Å] are shorter than either of the Ni-N$_\text{DETA}$ [2.084(3), 2.095(3), and 2.119(3) Å] or Ni1-O1 [2.145(2) Å] distances, while the bridging cyanide C1-N1-Ni1 and C4-N4-Ni1 angles are markedly different [176.3(1) and 167.3(1)\(^\circ\)]. The $cis$-N-Ni-N(O) angles range between 82.0(1) [N20-Ni1-N21] and 99.2(1)\(^\circ\) [N1-Ni1-N19]. The DETA and aqua ligands and are involved in extensive hydrogen bonding interactions with lattice water along the crystallographic a- direction (Figure 3.2) and short intermolecular O···N$_\text{cyanide}$ [2.752(4) Å], O···N$_\text{DETA}$ [3.021(3) Å], and O···O [2.773(3) to 2.994(3) Å]
Figure 3.2. Hydrogen-bonded chains present between 5 and lattice water (purple dotted lines) along the crystallographic (top) $a$- and (bottom) $b$-directions. Hydrogen atoms are eliminated for clarity.\textsuperscript{39}
contacts are found. In comparison to 1 and 2, somewhat longer intramolecular Fe···Ni and Fe1···Fe2 [ca. 5.10(1) and 7.88(1) Å] and intermolecular Fe···Ni contacts [ca. 7.11(1) Å] are found, respectively (Table 3.3), indicating that the Tp*Me and nitrogenous ligands maintain good solid state separation of the paramagnetic ions. The trinuclear complexes are also well isolated in the solid state and are at least ca. 8.2 Å away from adjacent clusters.39,40

Structures of 4 and 5 are found in the triclinic P-1 space group. The linear \{Fe\textsuperscript{III}2M\textsuperscript{II}\} clusters contain a trans-M\textsuperscript{II}(DMF)\textsubscript{4}(\mu-NC)\textsubscript{2} (M\textsuperscript{II} = Ni, Mn) fragment that lies on a crystallographic inversion center and is linked to two adjacent [(Tp*Bn)Fe\textsuperscript{III}(CN)\textsubscript{3}] anions via bridging cyanides (Figure 3.1).38 The bridging cyanide Fe-C bonds [1.888(4) and 1.904(2) Å, Fe-C1] are, like those in 1-3, slightly shorter than the average values seen for the terminal ones [1.925(4) and 1.933(3) Å], for 4 and 5, respectively. The Fe1-C1-N1 angles in 4 and 5 [178.8(3) and 176.7(2)º] are nearly linear while the M\textsuperscript{II}-N1-C1 units are more acute [173.3(3) and 168.5(2)º] reflecting steric repulsions between the coordinated DMF and Tp*Me ligands on iron. The M1-N1 [2.007(3) and 2.169(2) Å] and average M1-O1 [2.076(3) and 2.209(2) Å] distances compare favorably with those seen in a variety of cyanide-bridged \{Fe\textsuperscript{III}xM\textsuperscript{II}y\} complexes. Of the two complexes, the manganese one (5) displays the longest bonds as it is a weaker Lewis acid than divalent nickel.

3.4 Magnetic Properties. Magnetic measurements were done by Dr. Rodolphe Clérac from Universite de Bordeaux. Variable-temperature dc magnetic susceptibility data were collected for compounds 1-4 at various applied magnetic
field strengths (Figure 3.3). At room temperature the $\chi T$ values for 1-4 (2.8, 2.7, 2.6, and 2.5 cm$^3$ K mol$^{-1}$) are near the expected one (2.5 cm$^3$ K mol$^{-1}$) for a 2:1 ratio of Fe$^{III}$S (0.7 cm$^3$ K mol$^{-1}$ for $S = \frac{1}{2}$ and Ni$^{II}$ (1.2 cm$^3$ K mol$^{-1}$, $S = 1$) ions, assuming that $g$ is ca. 2.6 for Fe$^{III}$ and 2.2 for Ni$^{II}$. Unfortunately, we have not collected magnetic data for 5 to date but anticipate that an antiferromagnetic interaction between the Fe$^{III}$ ($S = \frac{1}{2}$) and Mn$^{II}$ ($S = \frac{5}{2}$) centers will give an $S = \frac{3}{2}$

Figure 3.3. $\chi T$ vs $T$ data for 1-4 collected between 1.8 and 300 K at 1000 (●) and 10000 Oe (●), where $\chi$ is the molar magnetic susceptibility that is equal to $M/H$ per complex.$^{38,39}$
Figure 3.4. Fitting of the magnetic data collected for (top) 1 and (bottom) 2 via Eqn. 1 in the text. Red line represents fitting of the data to an isotropic Heisenberg spin Hamiltonian (Eqn. 3.1).39
Figure 3.5. Fitting of the magnetic data collected for (top) 3 and (bottom) 4 via Eqn. 1 in the text. Red line represents fitting of the data to an isotropic Heisenberg spin Hamiltonian (Eqn. 3.1).\textsuperscript{39}
ground state overall. Upon cooling, the $\chi T$ values increase towards maxima at 5.53, 5.22, 4.23, and 4.20 cm$^3$ K mol$^{-1}$ near 10 K, consistent with ferromagnetic coupling between the Fe$^{III}$ and Ni$^{II}$ centers. Based on a trinuclear model with a single $g$ factor and identical coupling constant ($J$) between the Fe$^{III}$ and Ni$^{II}$ sites, an isotropic Heisenberg exchange Hamiltonian was used to model the magnetic data:

$$H = -2J(S_{Fe1} \cdot S_{Ni1} + S_{Fe2} \cdot S_{Ni1})$$

(3.1)

and the data were fitted using a procedure developed by Song over the 10-300 K range. The best fit of the data gave the following values for $J/k_B$ and isotropic (average) $g_{iso}$ parameters: 11(1) K and 2.48(1), 9.1(1) K and 2.6(1), 11.2(1) K and 2.41(5), and 7.1(1) K and 2.3(1), for 1-4, respectively (Figures 3.4 and 3.5).

MAGPACK simulations of the $\chi T$ vs $T$ data for 5 show that a sizable energy difference exists between the $S = 2$ ground and $S = 1$ first excited state (ca. 22.4 K). The energy level diagram from this effort is illustrated in Figure 3.6. The $g_{iso}$ values fall within the range seen for several magnetic clusters with Fe-CN-Ni links (Table 3.4). Most notably, efforts to simulate the $\chi T$ vs $T$ data using two different $J_{Fe-Ni}$ and $g_{Fe(III)}$ and $g_{Ni(II)}$ terms and including intermolecular exchange (via $zJ'$), led to physically unrealistic values for 2 and 3.
This is not the case for 4 and justification for this behavior will be discussed below in greater detail.

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</tbody>
</table>

The field dependence of the magnetization data (saturation magnetization) collected between 1.8 and 10 K shows with increasing applied magnetic field the data approaches maximum values of 4.35, 4.52, 4.76, and 3.8 $\mu_B$ at 1.8 K (for $H_{dc} = 7$ T) verifying that 1-4 adopt ferromagnetic $S_T = 2$ ground states, where $g_{iso} > 2$ (Figures 3.7 and 3.8).\textsuperscript{38,39} The magnetization values of 4 are lower than the other derivatives (1-3) suggesting it possesses greater magnetic anisotropy despite exhibiting lower values of $g_{iso}$ and $J_{iso}$. The reduced magnetization data ($M$ vs $H$ $T^{-1}$) indicates that significant magnetic anisotropy is present in all of the complexes, given that the $M$ vs $H$ $T^{-1}$ curves are not superimposable up to 8 K. If the compounds were magnetically isotropic then there would be no deviation in the curves and all would be superimposable. Likewise, compound 4 also shows significant magnetic anisotropy in its $M$ vs $H$ $T^{-1}$ data, as the curves, also called reduced magnetization, are non-superimposable (Figure 3.8).\textsuperscript{38,39}
Figure 3.7. $M$ vs $H$ data and $M$ vs $HT^{-1}$ collected for (top) 1, (middle) 2, and (bottom) 3 at various temperatures ($0 \leq H_{dc} \leq 7$ T). Solid lines are guides for the eyes.\textsuperscript{39}
Closer inspection shows that the $M$ vs $H$ data collected at 1.8 K for 3 displays an inflection point that can signal intercomplex antiferromagnetic interactions are operative at low temperatures (Figure 3.7, middle). Consistent with this assumption, increasing the applied magnetic fields overcomes these intermolecular (dipolar) magnetic interactions and/or weak intermolecular exchange interactions and allows for crude estimation of the critical field energy in relation to its Zeeman interaction (Figure 3.9). Using this approach the intermolecular interaction ($zJ'$) via the $g\mu_B H^* S_T = 2zJ' S_T^2$ relationship leads to $zJ'/k_B = -0.28$ K, a small but physically realistic and observable effect.\textsuperscript{39}

Surprisingly, of the three trinuclear complexes, only 3 and 4 displayed slow magnetic relaxation in their alternating current (ac) susceptibility data. To date we
have only investigated the spectroscopic properties of 3 via high-field EPR methods. The oriented single-crystal data collected at multiple frequencies confirms easy-axis-type magnetic anisotropy in 3,\textsuperscript{34} that is oriented along the z-direction, with fits giving the spin Hamiltonian parameters:\textsuperscript{40} $S_T = 2$, $D = -2.09$ cm$^{-1}$, $E = 0.08$ cm$^{-1}$, $B_{4\alpha} = -2.3 \times 10^{-3}$ cm$^{-1}$, $g_z = 2.4$, and $g_y = g_x = 1.95$. These values are comparable to those obtained from magnetic data for other cyanide-bridged \{Fe$_2^{III}$Ni$_{III}$\} complexes (Table 3.4).\textsuperscript{20-32,34,37,39,40,55,58-62,64}

To further explore the magnetic properties of 1-4 we decided to measure the ac susceptibility to determine whether the magnetic anisotropy is proportional to the energy barrier to magnetic relaxation and whether it can be experimentally observed (Figures 3.10-3.12).\textsuperscript{1,3,4} Surprisingly, 1 and 2 do not display slow relaxation while frequency-dependent dynamics are clearly seen for 3 (Figure 3.9) above 10 kHz (for $H_{dc} = 0$ Oe), suggesting rapid quantum tunneling (QTM) of the magnetization is operative.\textsuperscript{1,3,25,26,34,37,37b,37c,55,58-62,64} Assuming QTM is efficient in 3 we applied a small direct current (dc) magnetic field assuming that the QTM rate would decrease, as the degeneracy of the $M_s$ levels would be changed. As expected, the characteristic frequency (Figure 3.9) changes, but does not significantly slow the relaxation rate at 1.85 K and up to $H_{dc} \sim 4000$ Oe.\textsuperscript{38,39}
Given that many small SMMs generally undergo spin-lattice relaxation via non-Orbach processes (i.e. direct and Raman) and our limited data, we propose that our inability to fit the ac susceptibility data to an Arrhenius law may indicate that thermally-induced magnetic relaxation (Orbach) does not dominate the relaxation dynamics in 1-3, and is consistent with the apparent rapid QTM in the trinuclear complexes.\textsuperscript{39-54} However, we are able to see some magnetic relaxation in the ac susceptibility data as shoulders near 1.8 K (Figure 3.10) for complex 3.

\textbf{Figure 3.10.} (top) Temperature dependence of the characteristic frequency for the in-phase (top, left) and out-of-phase (top, right) components of the ac susceptibility between 1.85 and 2.5 K ($H_{ac} = 3$ Oe; $H_{dc} = 0$ Oe) for 3. The solid lines are guides for the eyes. (bottom) Field dependence of the characteristic frequency for the in-phase ($\chi'$, bottom left) and out-of-phase ($\chi''$, bottom right) components of the ac susceptibility at various applied dc fields ($H_{ac} = 3$ Oe; $H_{dc} = 0$ Oe) for 3 at 1.85 K. The solid lines are guides for the eyes.\textsuperscript{39}
In complex 4 the ac data clearly show that slow magnetic relaxation may be seen above 1.8 K in the absence an applied magnetic field.\textsuperscript{38} As before we were unable to estimate the relaxation time at zero applied magnetic field because there is no maximum in the out-of-phase data ($\chi''$ vs $T$) above 1.8 K. However after application of a static magnetic field were able to see peak maxima at 1.80, 1.85, and 1.9 K (at 7.7, 8.5, and 9.5 kHz ac frequencies; Figure 3.12, right). Under the

**Figure 3.11.** (top) Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac susceptibility between 10 and 10000 Hz ($H_{ac} = 3$ Oe; $H_{dc} = 0$ Oe) for 3 below 8 K.\textsuperscript{39}
assumption that QTM is operative we reasoned that application of dc magnetic fields would (Figure 3.13) eventually slow the relaxation rate, reaching an observable minimum in the characteristic frequency of the relaxation rate. We find that the relaxation rate decreases as the magnetic field is increased from zero to the 1800-2000 Oe range as judged by a decrease in the characteristic frequency, defined by the maximum in the $\chi''$ vs $\nu$ data (Figure 3.12).38 Alternatively, plotting the characteristic frequency vs magnetic field strength (Figure 3.14) clearly shows a minimum around 1800 Oe, which is the field strength that slows the magnetic relaxation to the greatest extent. Under the assumption that this is related to QTM, the temperature dependence of the magnetization (Figure 3.15, right) can be used to estimate the relaxation time. We clearly see the characteristic migration of the

**Figure 3.12.** Frequency dependence of the in-phase (left) and out-of-phase (right) components of the ac susceptibility vs characteristic frequency ($\nu$) between 1.8 and 2.75 K ($H_{ac} = 1$ Oe; $H_{dc} = 0$ Oe) for 4.38
peak maxima in the ac data when measured between 1.8 and 8 K under an applied field of 1800 Oe (Figure 3.16).\textsuperscript{38}

Assuming this magnetic relaxation is thermally-activated, application of an Arrhenius law and linear least-squares fitting of the $\tau$ vs $T^{-1}$ data allows for the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.13.png}
\caption{Frequency dependence of the in-phase (top) and out-of-phase (bottom) components of the ac susceptibility vs characteristic frequency ($\nu$) at 1.8 K at various applied dc fields ($0 \leq H_{dc} \leq 8000$ Oe; $H_{ac} = 1$ Oe) for 4. The solid lines are guides for the eyes.\textsuperscript{38}}
\end{figure}
relaxation time to be calculated. Fitting of
the data gives a relaxation time, $\tau_0 = 2.8 \times 10^{-8}$ s, which is in the range expected for
SMMs (Figure 3.17). From linear least-
squares fitting of the Arrhenius data we also
estimate an energy barrier to magnetization
reversal, which is found to be 17 K. Further
assuming that only the $S = 2$ spin ground
state is populated at 1.8 K, the uniaxial anisotropy or zero-field splitting term can
be estimated and is ca. -4.2 K for complex 4.\textsuperscript{38}

Over the past decade we have investigated the structure-property relationships
in several families of cyanide-bridged complexes. In those derived from
[(Tp$^R$)Fe$^\text{III}$](CN)$_3^-$ anions, were have been particularly interested in learning how

![Figure 3.14. $\nu$ vs $H$ data for 4 at
1.8 K. Solid line is a guide for the
eyes.]\textsuperscript{38}

![Figure 3.15. Frequency dependence of the in-phase ($\chi'$, left) and out-of-phase
($\chi''$, right) components of the ac susceptibility between 1.8 and 2.75 K ($H_{ac} = 1$
Oe; $H_{dc} = 1800$ Oe) for 4.\textsuperscript{38}]

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single-ion anisotropy tensor alignments, relative orientations of the pseudo-$C_3$ rotation axes, intermolecular contacts, and relaxation dynamics lead to the observation (or absence) of slow magnetic relaxation in a variety of polynuclear magnetic complexes.\textsuperscript{9,11,14,15,24-27,31,34,38,58-65} In many \{Fe\textsuperscript{III}\textsubscript{n}Ni\textsuperscript{II}\textsubscript{m}\} clusters the relative orientations of the Fe···B vectors ($C_3$ axes) appear to serve as structural markers for Fe\textsuperscript{III}_{LS} anisotropy tensors, with collinear ones generally giving higher SMM energy barriers when intermolecular contacts are minimized [up to $U_{\text{eff}}/k_B = 33$ K for a \{Fe\textsuperscript{III}\textsubscript{4}Ni\textsuperscript{II}\textsubscript{4}\} complex; Chapter

\textbf{Figure 3.16.} Temperature dependence of the in-phase (top) and out-of-phase (bottom) components of the ac susceptibility between 10 and 10000 Hz ($H_{\text{ac}} = 3$ Oe; $H_{\text{dc}} = 0$ Oe) for 4 at (left) 0 Oe and (right) 1800 Oe.\textsuperscript{38}
In \{Fe^{III}_2Ni^{II}\} complexes both bent and linear complexes the symmetry of the Fe^{III}LS sites, and more importantly those related by the crystallographic inversion, often afford the highest SMM energy barriers, while those of lower symmetry generally do not display slow dynamics above 1.8 K. For example, the linear and bent trinuclear \(S = 2\) complexes, \{[(Tp^*Bn)Fe^{III}(CN)_3]_2[Ni^{II}(DMF)_4] \cdot 2DMF\} \cite{25,38} (4) and \{[(pzTp)Fe^{III}(CN)_3]_2-Ni^{II}(bpy)_2 \cdot 2H_2O\} \cite{25,26} have similar coupling constants \(J_{iso}/k_B = 7.1\) and 7.0 K) and SMM energy barriers \(U_{eff}/k_B = 17\) and 21 K) despite different connectivity and orientations of their \([(Tp^R)Fe^{III}(CN)_3]\) fragments (\textit{cis}- vs \textit{trans}-\(\mu\)-NC)\_2Fe^{III} units). In both complexes the pseudo-\(C_3\) axes (B1···Fe1) are related by crystallographic mirror and inversion symmetry, and the hypothesized anisotropy tensors adopt 180 and 71° orientations,

\[ \tau = \tau_0 \exp(\Delta_{eff}/k_B T) \]
\[ \tau_0 = 2.8 \times 10^{-8} \text{ s} \]
\[ \Delta_{eff}/k_B = 16.7 \text{ K} \]

**Figure 3.17.** Semi-logarithmic \(\tau\) vs \(1/T\) plot from the frequency dependence of the ac susceptibility at \(H_{dc} = 1800 \text{ Oe}\) for 4. Solid line represents a best fit of the \(\tau\) vs \(1/T\) data.\cite{38}
respectively. In comparison lower symmetry trinuclear \{[(pzTp)Fe^{III}(CN)_3]_2[NI^{II}(IM-2Py)_2]}\cdot2DDF\cdot H_2O\cdot \frac{1}{2} Et_2O^{25,32} \quad \text{and} \quad \{[(pzTp)Fe^{III}(CN)_3]_2[NI^{II}(L)]\} \cdot \frac{1}{2} MeOH^{25,26} \}
have significantly bent Fe(\mu-CN)Ni units and slow magnetic relaxation is not observed. In complexes 1 and 2 (Figure 3.18), the Fe\cdots B
vectors are also unrelated via crystallographic symmetry and the quasi-C_{3v}
axes [e.g. B1\cdots Fe1 and B2\cdots Fe2] adopt drastically different relative orientations (ca. 26.7 and 23.0°), while those in 3 are [ca. 3.4°] are nearly collinear.

Figure 3.18. Alignment of proposed B\cdots Fe anisotropy vectors (blue lines) in (left) \{[(Tp^{*Me})FeCN]_2[Ni(bpy)_2]}\cdot3H_2O\cdot4MeOH (1) and (right) \{[(Tp^{*Me})Fe(CN)_3]_2[Ni(tren)]\} \cdot 2H_2O\cdot 3MeOH (2).^{38}

Under the assumption that the B\cdots Fe axes are coincident with the Fe^{III}_{LS}
single-ion anisotropy tensors, to a first approximation we anticipated that large SMM energy barriers would be found in all of the complexes (1-4). However we note that close intermolecular contacts are found in all of the complexes and propose that these can act to encourage fast relaxation of
the magnetization. However, slow relaxation is found in both 3 and 4, with 4 having the slowest relaxation times of the four complexes investigated. While sizable magnetic couplings are found for 3 \([J/k_B = +11.2(1) \text{ K}]\), a nearly parallel alignment of its single-ion magnetic anisotropy tensors, and a respectable energy separation between the ground and first excited state [ca. 22.4 K], we were surprised that 3 displays faster relaxation than 4 above 1.8 K.\textsuperscript{25,37,37b} We propose that the parallel orientations of the anisotropy tensors, rigorously enforced by the symmetry of the complex, leads to a higher SMM energy barrier \([U_{\text{eff}}/k_B = 17 \text{ K}]\) in 4 suggesting that the orientations of these Fe-···B axes are critically important for designing SMMs (Figure 3.19).\textsuperscript{25,38}

3.5 Conclusions. In summary, a total of five trinuclear clusters in the presence of various coligands. Of these, three are derived from the \([\text{NEt}_4][(\text{Tp}^{+\text{Me}})-\text{Fe}^{\text{III}}(\text{CN})_3]\cdot\text{H}_2\text{O}\) building block and each contains a central cis-M\(^{\text{II}}\)((\text{NC})_2\) fragment that leads to formation of “V-shaped” trinuclear clusters in the presence of bi-, tri-, and tetradeutate co-ligands to give clusters of \([(\text{Tp}^{+\text{Me}})\text{Fe}^{\text{III}}(\text{CN})_3]_2[\text{Ni}^{\text{III}}(\text{bpy})_2]_2\cdot3\text{H}_2\text{O}-4\text{MeOH}, [(\text{Tp}^{+\text{Me}})\text{Fe}^{\text{III}}(\text{CN})_3]_2[\text{Ni}^{\text{III}}(\text{DETA}(\text{H}_2\text{O}))_2]_2\cdot6\text{H}_2\text{O}-\text{MeCN}, and [(\text{Tp}^{+\text{Me}})-\text{Fe}^{\text{III}}(\text{CN})_3]_2[\text{Ni}^{\text{III}}(\text{tren})]_2\cdot2\text{H}_2\text{O}-3\text{MeOH}\), respectively, where bpy, deta, and tren are 2,2’-bipyridine, diethylenetriamine, and tris(2-aminoethyl)amine, respectively. In comparison, trinuclear complexes of \([(\text{Tp}^{+\text{Bn}})\text{Fe}(\text{CN})_3]_2\text{Mn(DMF)}_4\cdot2\text{DMF}\) stoichiometry (M\(^{\text{II}}\) = Mn, Ni) derived from \([\text{NEt}_4][(\text{Tp}^{+\text{Bn}})\text{Fe}^{\text{III}}(\text{CN})_3]\cdot\text{H}_2\text{O}\) building blocks, give linear clusters containing trans-M\(^{\text{II}}\)(NC)_2 units owing to intercluster \(\pi-\pi\) interactions between phenyl rings on the \([(\text{Tp}^{+\text{Bn}})\text{Fe}^{\text{III}}(\text{CN})_3]\) fragments.
Figure 3.19. Alignment of proposed anisotropy vectors (green/blue lines) in (a) \([(Tp^{*}Me)Fe(CN)_3]_2[\text{Ni}^{II}(DMF)_4]\cdot2\text{DMF} \ (4)\), (b) \([(Tp^{*}Me)Fe^{III}(CN)_3]_2[\text{Ni}^{II}(bpy)_2]\cdot2\text{H}_2\text{O}\), and (d) \([(pzTp)Fe^{III}(CN)_3]_2[\text{Ni}^{III}(1,5,8,12\text{-tetraazadodecane})]\cdot\frac{1}{2}\text{MeOH}\).\textsuperscript{25,26,32,38,39}
In accordance with orbital symmetry trends, Fe/Ni complexes display ferromagnetic exchange interactions while the Fe/Mn one exhibits antiferromagnetic coupling. In these five trinuclear cluster, the metal centers are coupled ferromagnetically. The Fe$^{III}_{LS}$ ($S = \frac{1}{2}$) and Ni$^{II}$ ($S = 1$) centers are ferromagnetically coupled to give $S = 2$ magnetic ground states for the majority of complexes discussed, while the iron-Mn$^{II}$ ($S = \frac{5}{2}$) interactions give the expected $S = \frac{3}{2}$ spin ground state. Of the five clusters described only a linear trinuclear cluster of \[(Tp^*Bn)Fe^{III}(CN)_3]^2[Ni^{II}(DMF)_4]\cdot2DMF stoichiometry shows slow relaxation of magnetization that is characteristic of a single molecule magnet.\textsuperscript{25,26,32,38,39} We hypothesize that minimizing intermolecular contacts while simultaneously providing for a parallel alignment of the single-ion anisotropy tensors (Fe…B axes), lead to the creation of significant magnetic anisotropy, and an energy barrier to magnetization reversal in this complex.

3.6 Experimental: Materials. All operations were conducted under an argon atmosphere by using standard Schlenk and drybox techniques. Transfers of solutions containing cyanide were carried out through stainless steel cannulas. Solvents were distilled under dinitrogen from CaH$_2$ (acetonitrile), sodium-benzophenone (diethyl ether) and sparged with argon prior to use. Dimethylformamide (DMF) was dried using activated alumina (VAC atmospheres) and sparged with argon prior to use. The preparation of M(OTf)$_2$ (M = Mn, Ni),\textsuperscript{63} Fe(OAc)$_2$,\textsuperscript{64} [NEt$_4$][CN],\textsuperscript{63,65} KTp$^*$Bn,\textsuperscript{66} and [NEt$_4$][((Tp$^{*}$Me)Fe(CN)$_3$]$\cdot$H$_2$O\textsuperscript{19} are described elsewhere. NiCl$_2$$\cdot$6H$_2$O (Acros), and Ni(ClO$_4$)$_2$$\cdot$6H$_2$O (Acros), 2,2'-
bipyridine (bpy; Acros), diethylenetriamine (DETA; Acros) and tris(2-aminoethyl)amine (tren; Acros) were used as received from their respective manufacturers.

**Physical Methods.** Structures determinations were done by Dr. Yuanzhu Zhang and Dr. Nigam P. Rath from University of Missouri St. Louis. Electron Paramagnetic Resonance measurements were done by Dr. Stephen Hill from National High Magnetic Field laboratory at Tallahassee and Dr. Rodolphe Clérac from Universite de Bordeaux. Theoretical calculations were done by Dr. Benjamin J. Bythell from University of Missouri St. Louis. The infrared spectra were recorded as Nujol mulls between KBr plates on Thermo-Electron Nicolet 6700 FTIR instruments in the 400-4000 cm\(^{-1}\) range. Magnetic measurements on polycrystalline samples of 1 and 2 were conducted on a Quantum Design SQUID MPMS-XL and PPMS-9 magnetometers in the 1.8-300 K temperature range. Diamagnetic corrections were estimated using Pascal’s constants.\(^{67}\) Elemental analyses performed by Robertson Microlit Laboratories.

**Structure Determinations and Refinements.** X-ray diffraction data for 1-5 were collected at 100(2) K on a Bruker APEX-II using an Oxford Cryostream System. Crystals were mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained (DENZO)\(^{68}\) from ten 1° frames (SCALEPACK).\(^{68}\) Lorentz/polarization corrections were applied during data reduction and the structures were solved by direct methods (SHELXS97)\(^{69}\) and completed by difference Fourier methods (SHELXL97).\(^{69}\) Refinement was performed against \(F^2\) by weighted full-matrix least-squares (SHELXL97)\(^{69}\) and empirical absorption
corrections (either SCALEPACK\textsuperscript{68} or SADABS\textsuperscript{70}) were applied. Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the \textit{International Tables for Crystallography Vol. C}.\textsuperscript{71} Crystal data, relevant details of the structure determinations, and selected geometrical parameters are provided in Tables 3.1-3.3 for 1-5.

**Synthesis of \{[(Tp^*\text{Me})FeCN]_3\}_2[Ni(bpy)_2]\cdot3H_2O\cdot4MeOH (1).** Addition of MeOH (10 mL) to a solid mixture of NiCl\textsubscript{2}\cdot6H\textsubscript{2}O (24.2 mg, 0.102 mmol) and bpy (32.5 mg, 0.208 mmol) initially afforded a light pink solution that was stirred for 60 min. The resulting solution was quickly added to a MeOH (10 mL) solution of [NEt\textsubscript{4}]\{(Tp^*\text{Me})Fe(CN)\textsubscript{3}\}\cdotH\textsubscript{2}O (125 mg, 0.207 mmol) and rapidly afforded a dark red solution. The mixture was allowed to stir for 2 min., filtered, and allowed to stand quietly at R.T. for a few days. Dark red crystals was obtained and collected via suction filtration, washed with H\textsubscript{2}O (3 mL) and 95% MeOH (3 mL). Yield: 74.8 mg (60.1%). Anal. Calcd: C, 52.86; H, 6.32; N, 20.55; Found: C, 52.17; H, 5.93; N, 20.85. IR (Nujol, cm\textsuperscript{-1}): 2533 (m), 2156 (m, bridging cyanide), 2125 (m, terminal cyanide).

**Synthesis of \{[(Tp^*\text{Me})Fe(CN)\textsubscript{3}]_2[Ni(tren)]\cdot2H\textsubscript{2}O\cdot3MeOH (2).** Addition of tren (18.5 mg, 0.126 mmol) into a solution of 5 mL of NiCl\textsubscript{2}\cdot6H\textsubscript{2}O (23.5 mg, 0.100 mmol) in MeOH (5 mL) initially afforded a pale blue solution that was stirred for 60 min. The resulting solution was quickly added to a 10 mL MeOH solution of
[NEt₄]((Tp*Me)Fe(CN)₃] (123 mg, 0.205 mmol) and rapidly afforded a dark red solution. The mixture was allowed to stir for 2 min., filtered, and allowed to stand quietly at R.T. for a few days. Dark red crystals was obtained and collected via suction filtration, washed with H₂O (2 × 3 mL) and 95% MeOH (3 mL). Yield: 73.6 mg (57.6 %). Anal. Calcd for C₅₁H₈₄B₂Fe₂N₂₂NiO₅: C, 47.95; H, 6.63; N, 24.12. Found: C, 48.12; H, 6.24; N, 24.14. IR (Nujol, cm⁻¹): 2536 (m), 2153 (m), 2119 (m).

Synthesis of \{[(Tp*Me)Fe(CN)₃]₂[Ni(DETA)(OH₂)]\}⋅6H₂O⋅MeCN (3). Dropwise addition of DETA (10.5 mg, 0.102 mmol) in MeCN (2 mL) into a MeCN (3 mL) solution of [Ni(OH₂)₆][ClO₄]₂ (37.3 mg, 0.102 mmol) initially afforded a purple solution that was stirred for 60 min. The resulting solution was quickly added to a 5 mL MeCN/H₂O (1:1 v/v) solution of [NEt₄]((Tp*Me)Fe(CN)₃] (123 mg, 0.205 mmol) and rapidly afforded a dark red solution. The mixture was allowed to stir for 2 min., filtered, and allowed to stand quietly at R.T. for a few days. Dark red crystals was obtained and collected via suction filtration, washed with H₂O (5 mL) and MeCN (5 mL). Yield: 68.4 mg (53.6 %). Anal. Calcd for C₄₈H₈₆B₂Fe₂N₂₂NiO₇: C, 47.95; H, 6.63; N, 24.12. Found: C, 48.12; H, 6.24; N, 24.14. IR (Nujol, cm⁻¹): 2529 (m), 2154 (m), 2122 (m).

Synthesis of \{[(Tp*Bn)Fe(CN)₃]₂Ni(DMF)₄\}⋅2DMF (4). Treatment of [NEt₄]-[(Tp*Bn)FeIII(CN)₃]⋅2MeOH.H₂O (189.2 mg, 0.207 mmol) with Ni(OTf)₂ (72.5 mg, 0.203 mmol) in DMF (10 mL) afforded a dark red solution which was filtered and allowed to stand for 10 d. The red blocks were isolated via filtration, washed with a 1:5 DMF/Ether solution (12 mL, v/v), and dried under vacuum for 2 min. at room temperature. Yield: 87.3 mg (44.4 %). Anal. Calcd C₉₆H₁₂₂B₂Fe₂N₂₄NiO₆: C, 60.68;
H, 6.47; N, 17.69. Found: C, 60.71; H, 6.25; N, 17.80. IR (Nujol, cm\(^{-1}\)): 3081 (m), 3060 (m), 3023 (m), 2881 (w), 2812 (m), 2537 (m), 2174 (s), 2118 (s), 1693(w), 1671(s), 1648 (vs), 1602 (w), 1582(w), 1556 (w), 1492 (m), 1429 (w), 1385 (w), 1361 (w), 1238 (m), 1156 (m), 1111 (m), 1077 (w), 1028 (w), 1006 (w), 905 (w), 892 (w), 863 (s), 834 (s), 804 (w), 725 (s), 695 (s), 684 (s), 658 (m), 644 (w), 587 (m), 565 (w), 539 (m), 514 (w), 489 (w), 444 (m), 412 (m).

**Synthesis of \{(Tp^{*Bn})Fe(CN)_3\}_2Mn(DMF)_4\} \cdot 2DMF (5).** Treatment of [NEt\(_4\)]-[\{(Tp^{*Bn})Fe^{III}(CN)_3\}] \cdot 2MeOH.H\(_2\)O (189.2 mg, 0.207 mmol) with Mn(OTf)\(_2\) (71.6 mg, 0.203 mmol) in DMF (10 mL) afforded a dark red solution which was filtered and allowed to stand for 10 d. The red blocks were isolated via filtration, washed with a 1:5 DMF/Ether solution (12 mL, v/v), and dried under vacuum for 2 min. at room temperature. Yield: 85.5 g (45.1%). Anal. Calcd for C\(_{96}H_{122}B_2Fe_2N_{24}MnO_6\): C, 60.77; H, 6.49; N, 17.73. Found: C, 60.75; H, 6.41; N, 17.80. IR (Nujol, cm\(^{-1}\)): 3059 (m), 3023 (m), 2854 (w), 2541 (m), 2149 (s), 2116 (s), 1675 (s), 1652 (vs), 1601 (w), 1582 (w), 1558 (w), 1493 (m), 1453 (s), 1381 (m), 1239 (m), 1194 (w), 1156 (m), 1113 (m), 1062 (m), 1028 (w), 1005 (w), 892 (w), 864 (m), 835 (m), 726 (s), 696 (s), 678 (s), 658 (w), 644 (w), 587 (m), 565 (w), 589 (m), 538 (w).


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Chapter Four: Syntheses, Structures, and Magnetic Characterization of Cyanide-Bridged \{\text{Fe}^{\text{III}}{\_}_n\text{Ni}^{\text{II}}{\_}_m\} Complexes

4.1 Introduction. In this chapter we are going to talk about the syntheses, structures, and magnetic properties of several ferromagnetic \{\text{Fe}^{\text{III}}{\_}_n\text{Ni}^{\text{II}}{\_}_m\} complexes, where \(n\) is the number of iron(III) metal ions and \(m\) is the number of nickel(II) metal ions in the cluster. These were prepared using the concept of dimensional reduction,\(^{1-3}\) where capping ligands control the \(\text{M(\mu-CN)M}^-\) pairs created during self-assembly. The focus of this chapter will describe complexes made from \([\{\text{Tp*Me}\}\text{Fe}^{\text{III}}(\text{CN})_3\}^-\) and those containing other pyrazolylborates such as Tp*, where Tp* = tris(3,5-dimethylpyrazol-1-yl)borate. The addition of a single methyl group per pyrazolate gives a ligand with more steric interactions between itself and other ancillary ligands and enhances the solubility of the polynuclear complex.\(^{4-24}\) In this final chapter, the structures and magnetic properties of five polynuclear complexes will be described and compared to others containing tricyano building blocks:

\[
\begin{align*}
\{[\{\text{Tp*Me}\}\text{Fe}^{\text{III}}(\text{CN})_3\}2[\text{Ni}^{\text{II}}(\text{DMF})_4]2[\text{OTf}]2\}2\text{DMF} &\ (1) \\
\{[\{\text{Tp*Me}\}\text{Fe}^{\text{III}}(\text{CN})_3\}2[\text{Ni}^{\text{II}}(\text{DMF})_4]2[\text{ClO}_4]2\}3\text{MeCN}2\text{H}_2\text{O}\text{-MeOH} &\ (2) \\
\{[\{\text{Tp*Me}\}\text{Fe}^{\text{III}}(\text{CN})_3\}4[\text{Ni}^{\text{II}}(\text{DMF})_3]2\}4\text{DMF}2\text{H}_2\text{O} &\ (3) \\
\{[\{\text{Tp*Me}\}\text{Fe}^{\text{III}}(\text{CN})_3\}6[\text{Ni}^{\text{II}}(\text{MeOH})_3]2[\text{Ni}^{\text{II}}(\text{MeOH})_2]\}3\text{H}_2\text{O}8\text{MeOH} &\ (4) \\
\{[\{\text{Tp*Me}\}\text{Fe}^{\text{III}}(\text{CN})_3\}4[\text{Ni}^{\text{II}}(\text{tren})]4[\text{ClO}_4]4\}7\text{H}_2\text{O}4\text{MeCN} &\ (5). \\
\end{align*}
\]

Over the past ten years we have worked to prepare cyanide-bridged SMMs derived from poly(pyrazolyl)borate tricyanometalates by tuning the steric demand...
of their ancillary ligands. This approach allows for the isolation of several tri-, tetra-, hexa-, octa-, and nonanuclear single-molecule magnets.\textsuperscript{6-14} We will show that lower symmetry rod-shaped \{Fe\textsuperscript{III}\textsubscript{4}Ni\textsuperscript{II}\textsubscript{4}\} complexes have higher SMM energy barriers ($U_{\text{eff}} = 33$ K) than more symmetrical molecular boxes, which is apparently related to the nearly parallel alignment of their anisotropy tensors.\textsuperscript{4,9,10,18} Surprisingly, while several hexanuclear \{Fe\textsuperscript{III}\textsubscript{2}M\textsuperscript{II}\}\textsubscript{2} complexes derived from [(Tp)Fe(CN)\textsubscript{3}]\textsuperscript{−} anions are known (Tp = trispyrazolylborate) none are bona fide SMMs\textsuperscript{4} and higher nuclearity \{Fe\textsuperscript{III}\textsubscript{2}Ni\textsuperscript{II}\}\textsubscript{n} ($n \geq 3$) analogues remain unknown in the literature.\textsuperscript{5} We will describe a general synthetic methodology for the preparation of these polynuclear complexes and show that solvent-dependent fragmentation and aggregation can be a useful synthetic strategy for engineering materials that display tunable magnetic properties.

\section*{4.2 Synthesis and Spectroscopic Characterization: Tetranuclear Squares.}

Combining either dimethylformamide or MeCN/MeOH solutions of [NE\textsubscript{4}]\textsuperscript{−}-(Tp*Me)Fe(CN)\textsubscript{3}\cdot H\textsubscript{2}O and NiX\textsubscript{2}, gives tetranuclear complexes of \{[(Tp*Me)Fe\textsuperscript{III}(CN)\textsubscript{3}]\textsubscript{2}[Ni\textsuperscript{II}(L\textsubscript{m})\textsubscript{2}]\textsubscript{2}[X\textsubscript{2}]\cdot n(solvent) stoichiometry (Scheme 4.1) in the absence ($X = \text{OTf}^\text{−}, 1$; \textit{L\textsubscript{m}} = 4 DMF) and presence of 2,2´bipyridine ($X = \text{ClO}_4^\text{−}, 2$; \textit{L\textsubscript{m}} = 2 bpy).\textsuperscript{14}
Figure 4.1. (top) TGA data for \{[(Tp^Me)Fe^{III}(CN)]_2[Ni^{II}(DMF)_4][OTf]_2\}_2DMF (1). Lattice solvent lost before 110 °C: Found (cacld.): 6.3 (7.0)%.
(bottom) TGA data for \{[(Tp^Me)Fe^{III}(CN)]_2[Ni^{II}(bpy)_2][ClO_4]_2\}_3MeCN·2H_2O·MeOH (2).
Lattice solvent loss before 100 °C: Found (calcd.): 9.0 (9.2)%. The cluster is quite stable below 250 °C.\textsuperscript{14}
The infrared spectrum of 1 and 2 display medium intensity $\nu_{BH}$ (2549 and 2545 cm$^{-1}$) and $\nu_{CN}$ (2118 and 2166 cm$^{-1}$, 1; 2155 and 2129 cm$^{-1}$, 2) stretching absorptions that are higher in energy than those found for the starting material [NEt$_4$-][(Tp*Me)Fe$^{III}$ (CN)$_3$]$\cdot$H$_2$O (2119 and 2115 cm$^{-1}$). These cyanide stretches are in the ranges expected for bridging (higher energy) and terminal (lower energy), respectively. In addition to these absorptions there are also high energy $\nu_{CN}$ (2261 and 2250 cm$^{-1}$) that result from the presence of lattice acetonitrile. Thermal gravimetric analyses (TGA) of crystalline samples of 1 and 2 (Figure 4.1) shows that both complexes easily lose lattice solvent near ca. 110 °C for 1 and at room temperature for 2, while at higher temperatures (ca. 125 and 260° C), both start to decompose (explosively for 2).

4.3 Crystallographic Studies. Compounds 1 and 2 are found in the triclinic $P$-1 space group (Table 4.1). The tetranuclear complexes are centrosymmetric and have trivalent Fe$^{III}$ and divalent Ni$^{II}$ that reside on alternate corners of an ideal molecular square (Figure 4.2). The adjacent metal centers are lined via bridging cyanides to form Fe$^{III}$($\mu$-CN)$_2$Ni$^{II}$ units. A terminal cyanide per Fe$^{III}$ centers is also found adopting anti- or Z-orientation relative to the {Fe$^{III}$($\mu$-CN)Ni$^{II}$}$_2$ cores of the complexes. As shown in Figure 4.2, the Ni$^{II}$ ion in 1 has a cis-Ni(NC)$_2$O$_4$ coordination environment and average Ni-N and Ni-O distances of 2.032(2) and 2.067(2) Å are found, respectively (Table 4.2). In 2, the Ni$^{II}$ ion has a NiN$_6$ coordination environment resulting from two cis-cyanides and four bidentate 2,2’-bipyridine (bpy) ligands. The average Ni-N$_{CN}$ bond in 2 [2.056(2) Å] is slightly
Table 4.1. Crystallographic Data for \{(Tp*Me)Fe^{III}(CN)_{3}]_{2}[Ni^{II}(DMF)]_{4}[OTf]_{2}\}-2DMF (1), \{(Tp*Me)[Ni^{II}(bpy)]_{2}[ClO_{4}]_{2}\}-3MeCN-2H_{2}O-MeOH (2), \{(Tp*Me)Fe^{III}(CN)_{3}]_{4}[Ni^{II}(DMF)]_{3}\}-4DMF-2H_{2}O (3), Fe^{III}(CN)_{3}]_{6}[Ni^{II}(MeOH)]_{3}[Ni^{II}(MeOH)]_{2}\}-3H_{2}O-8MeOH (4), and \{(Tp*Me)Fe^{III}(CN)_{3}]_{4}[Ni^{II}(tren)]_{4}[Cl] 4MeCN (5).^{5,14}

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[a] I ≥ 2σ(I): R₁ = Σ||Fo| - |Fc||/Σ|Fo|, wR₂=[Σ[w(Fo²-Fc²)]²]/[Σ[w(Fo²)]²]^{1/2}
Table 4.2. Selected Bond Distances (Å) and Angles (°) for \([((Tp^* Me)\text{Fe}^{III}(CN)_3]_2[Ni^{II}(DMF)_4][\text{OTf}_2]\cdot 2\text{DMF} \ (1)\) and \([((Tp^* Me)\text{Fe}^{III}(CN)_3]_2[Ni^{II}(bpy)_2][\text{ClO}_4]_2\cdot 3\text{MeCN}\cdot 2\text{H}_2\text{O}\cdot \text{MeOH} \ (2).^{14}}

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Figure 4.2. Ball-and-stick structure of (top) \{[(\text{Tpo}^\text{Me})\text{Fe}^\text{III}(\text{CN})_3]_2[\text{Ni}^\text{III}(\text{DMF})_4]_2-[\text{OTf}]_2\}_2\text{DMF} (1) and (bottom) \{[(\text{Tpo}^\text{Me})\text{Fe}^\text{III}(\text{CN})_3]_2[\text{Ni}^\text{II}(\text{bpy})_2][\text{ClO}_4]_2\}_{3}\text{MeCN-2H}_2\text{O-MeOH} (2). All counteranions [\text{OTf}, 1; \text{ClO}_4^-, 2], lattice solvent, and hydrogen atoms are eliminated for clarity.\textsuperscript{14}
longer than those in 1 and typical Ni-N_{bpy} distances [2.090(2) Å] are found for 2 (Table 4.2).

The tricyanoferrate(III) anions adopt $C_{3v}$-symmetric geometries due to the presence of a facially coordinate and tridentate Tp*Me ligand and fac-cyanides (Figure 4.2). In structures of 1 and 2, the average Fe-C [1.928(2) and 1.927(3) Å] and Fe-N [1.995(2) and 1.998(2) Å] distances are nearly equivalent. Each [(Tp*Me)Fe(CN)$_3$]$^-$ anion is linked to two adjacent [Ni(L)$_n$]$^{2+}$ fragments via two cis-bridging cyanides along each square edge (i.e. Fe$^{III}$($\mu$-CN)$_2$Ni$^{II}$ linkages). The tetranuclear cores in 1 and 2 are similar and have Fe···Ni and Fe···Fe distances of 5.09 × 5.11 Å (for 1) and 5.11 × 5.13 Å (for 2).

Nearly linear Fe-C≡N-Ni linkages are found in each structure with Fe-C-N and Ni-N-C angles found to be 175.8(2) and 173.4(2)$^\circ$ and 177.4(2) and 173.9(2)$^\circ$, for 1 and 2, respectively. The cationic {Fe$^{III_2Ni^{II_2}}$}$^{2+}$ cores are well-isolated from adjacent ones and intercluster Ni···Ni contacts of 8.827(2) and 9.01(2) Å were determined. However, rather close intercomplex contacts [3.537(3) Å] are found between the Tp*Me 5-methyl group and DMF nitrogen atoms in 1, while Ni···N_{C_{term}} (N3···Ni1) contacts are more distant [ca. 7.569(1) Å]. In complex 2, close contacts are also observed between the bpy ligands [ca. 3.360(2) Å] while the Ni···N_{C_{term}} contacts (N3···Ni) are slightly longer [ca. 7.883(7) Å] than those seen in structures of 2 (Table 4.2).

**4.4 Magnetic Studies: Tetranuclear Complexes.** Magnetic measurements were done by Dr. Rodolphe Clerac from Universite de Bordeaux. Various magnetic
data were collected for 1 and 2 to determine how the paramagnetic ions are coupled and whether the complexes exhibit slow magnetic relaxation that is characteristic of single-molecule magnets. The $\chi T$ product of 1 and 2 were collected in an applied dc field of 1 kOe over various temperatures, ranging between 1.8 and 300 K (Figure 4.3). The room temperature $\chi T$ values [4.3 and 4.5 cm$^3$ mol$^{-1}$ K] for 1 and 2] are consistent with a 2:2 ratio of paramagnetic and magnetically uncoupled Fe$^{III}_{LS}$ ($S = \frac{1}{2}, g = 2.6$-$2.8$) and Ni$^{II}$ ($S = 1, g = 2.2$-$2.3$) centers, being consistent with the literature-based assumption that significant orbital contributions are present at the Fe$^{III}_{LS}$ ions.$^{17-24}$ For 1 and 2, the $\chi T$ product shows temperature-dependent changes in their values. Between 300 and ca. 50 K, the $\chi T$ product gradually increases while at lower temperatures they rapidly rise.

![Figure 4.3. $\chi T$ vs. $T$ data collected in an applied field of 1 kOe for $\{[(Tp^{Me})-Fe^{III}(CN)_3]_2[Ni^{II}(DMF)_4][OTf]_2\}_2$DMF (1) and $\{[(Tp^{Me})Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2]_2-[ClO_4]_2\}_2$3MeCN$\cdot$2H$_2$O$\cdot$MeOH (2), respectively. Solid lines represent best fits to Eqn. 2. Inset: Energy level diagram for 2 estimated via MAGPACK.$^{14,28,29}$](image-url)
towards maximum values of 9.1 and 9.4 cm³ K mol⁻¹ at 4.3 K, indicating that the Fe³⁺ and Ni²⁺ centers undergo ferromagnetic exchange.¹⁴

Considering an idealized square structure for 1 and 2 the magnetic data were modeled using an isotropic Heisenberg spin Hamiltonian (Eqn. 4.1):

\[ H = -2J \left( (S_{Ni} + S_{Ni\ A}) \cdot (S_{Fe} + S_{Fe\ A}) \right) \]  

(Eqn. 4.1)

where \( J \) represents the average magnetic exchange interaction between the Fe³⁺,LS and Ni²⁺ sites and \( S \) are the spin operators for each metal ion.¹⁴ Application of the van Vleck equation to Kambe’s vector coupling method allows for an analytical expression (Eqn. 4.2) for the magnetic susceptibility to be derived.²⁵ The low temperature data (below 5 K) were eliminated from the fitting process in an effort to minimize the effects of intermolecular interactions and/or magnetic anisotropy problems. The results of these efforts (Figure 4.4, red line) gave best fit parameters of: \( S_T = 3 \), \( J/k_B = +9.0(4) \) and +8.5(4) K, and \( g = 2.4(1) \) and 2.5(1) for 1 and 2, respectively, and are comparable to those seen for other Fe³⁺/Ni²⁺ complexes containing [(TpR)Fe³⁺(CN)₃]⁻ anions within linear Fe³⁺LS(μ-CN)Ni²⁺ linkages.¹⁴ However, these magnetic parameters are significantly higher than those found for Fe³⁺/Ni³⁺ complexes containing significantly bent bridging cyanides, where magnetic coupling is less efficient.⁶,²⁶-²⁷ Typically cyanide-bridged complexes have inefficient magnetic exchange couplings that lead to small energy separations between the spin ground and higher energy excited states. Consistent with
previous reports, MAGPACK\textsuperscript{28,29} simulations of the $\chi T$ vs $T$ data suggests that the
ground ($S_T = 3$) and first excited states ($S = 2$) are close in energy (18 K and 16.8 K) for 1 and 2, respectively (Inset: Figure 4.3).

![Figure 4.4. $M$ vs $H/T$ data for $\{[(Tp^*Me)Fe^{III}(CN)\text{$_3$}]_2[Ni^{II}(DMF)_4]_2[OTf]\}_2\text{DMF}$ (1) and $\{[(Tp^*Me)Fe^{III}(CN)\text{$_3$}]_2[Ni^{II}(bpy)_2]_2[ClO_4]_2\}_3\text{MeCN} \cdot 2\text{H}_2\text{O} \cdot \text{MeOH}$ (2) below 8 K.\textsuperscript{14}

The field dependence of the magnetization data illustrated in Figure 4.4 (also known as saturation magnetization data) collected for 1 and 2 also verify that significant magnetic anisotropy is present, of the magnitude often encountered for cyanide-based SMMs (Figure 4.4).\textsuperscript{6,14,26-27,31-45,50-52} Under an applied dc magnetic field of 7 T and at an experimental temperature of 1.8 K, the magnetization values (ca. 6.3 $\mu_B$) confirm that an $S_T = 3$ spin ground state is present in both complexes and their isotropic (average) $g$ factors are greater than 2 is found. The non-superimposable $M$ vs $H/T$ curves at various temperatures provide further evidence that substantial magnetic anisotropy is present below 8 K in both 1 and 2. In the frame of a macro-spin model, the magnetic data was evaluated for the $S_T = 3$
complexes, accounting for simple uniaxial magnetic anisotropy (with the Hamiltonian: $H = DS_{T,z}^2$). However, the experimental data was not reproducible using this model and additional magnetic measurements were initiated.\textsuperscript{14} As is typical for cyanide-based magnets containing first row transition metal centers we did not observe magnetic hysteresis above 1.8 K in the $M$ vs $H$ data.\textsuperscript{9-24,30-46,50-52}

To probe the magnetization relaxation dynamics in both complexes we initiated a series of ac susceptibility measurements at various frequencies in the absence

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure45.png}
\caption{In-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibilities in zero applied magnetic field ($H_{dc} = 0$ Oe) with an $ac$ field ($H_{ac}$) of 3 Oe at different frequencies for wet (a and b) and dried samples of $\{[(\text{Tp*Me})\text{Fe}^{III}(\text{CN})_3]_2^{-}\text{[Ni}^{II}(\text{DMF})_4]\text{[OTf]}_2\}_2\cdot\text{2DMF}$ (1) (c and d).\textsuperscript{14}}
\end{figure}
and presence of a static dc magnetic field (Figures 4.5). In the absence of an applied field, where $H_{dc} = 0$ Oe, very weak frequency-dependent signals were seen in the out-of-phase ($\chi''$) susceptibility data of 1 below ca. 1000 Hz, suggesting that slow magnetic relaxation may be operative near 1.8 K (Figures 4.5a and b). However, upon prolonged standing, and particularly for dried on purpose samples, crystalline samples of 1 were found to exhibit frequency-dependent signals in both its in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility data above 2 K (Figure 4.5, c and d). Interestingly the magnetic data (i.e. $\chi T$ vs $T$, $M$ vs $H$, and $M$ vs $H/T$ plots) collected for solvated and desolvated crystals of 1 are nearly identical, offering no real explanation of why desolvated samples show slow magnetic relaxation. Unfortunately all attempts at structural characterization of these desolvated materials have failed.

**Figure 4.6.** $\tau$ vs. $T^{-1}$ plot for 1 after drying in air for a few days in zero dc field. Solid line is the best fit to the Arrhenius law discussed in the text.
The energy gap, or barrier to magnetization reversal, for the aggregated materials were estimated via non-linear least squares fitting of the ac susceptibility data to an Arrhenius law \[\tau = \tau_0 \exp\left(\frac{U_{\text{eff}}}{k_B T}\right)\] using the data collected above 1.8 K (Figure 4.6). The data shows that a moderately sized energy gap of 20.4 K with an intrinsic time \(\tau_0 = 3.0 \times 10^{-8}\) s is found for these dried samples and fall within the range expected for many SMM and SCM materials.\(^{30-41}\) Consistent with the TGA data, we hypothesize that 1 is unstable and is easily transformed into one or more unknown magnetic phases, that show slow magnetic relaxation behavior.\(^{14}\) We

![Figure 4.7. In-phase (\(\chi'\)) and out-of-phase (\(\chi''\)) ac susceptibilities at \(H_{dc} = \text{zero}\) (a and b) and 2200 Oe (c and d) with \(H_{ac} = 3\) Oe at different frequencies for \{[(Tp^*Me)Fe^{III}(CN)_3Ni^{II}(bpy)_2][ClO_4]_2\} \cdot 3\text{MeCN} \cdot 2\text{H}_2\text{O} \cdot \text{MeOH} (2)\).\(^{14}\)
note that similar behavior has been observed for structurally related \(((T_p^-)\text{Fe}^{III}(CN)_3)_2[M^{II}(DMF)_4][\text{OTf}]_2\cdot2\text{DMF} (M^{II} = \text{Co, Ni})\). As this is probably a general feature of these complexes we propose that ligand lability and sample handling should be considered as possible routes for generating undefined magnetic materials, where single crystal structural and magnetic data do not represent the same materials.

Figure 4.8. (left) Field dependence of the characteristic frequency of the relaxation mode at 1.9 K for 2 deduced from Figure 4.7. (right) \(\tau\) vs. \(T^{-1}\) plot for 2 in 2200 Oe dc field. Solid line is the best fit to the Arrhenius law.

To potentially fix this stability problem in 1 we decided to substitute the labile coordinated DMF for bpy ligands in an effort to minimize desolvation. We hypothesized that DMF loss followed by enchainment of the \(\text{Fe}^{III}_2\text{Ni}^{II}_2\) complexes, through the formation of cyanide bridges, is responsible for the unusual behavior of dried samples of 1. Given that the magnetic data for 1 and 2 are comparable (i.e. \(\chi T\) vs \(T\), \(M\) vs \(H\), and \(M\) vs \(H/T\) plots), we decided to also study complex 2 using ac susceptibility techniques, to see if it exhibits authentic SMM behavior.
Indeed, strong frequency-dependent shoulders are observed in the out-of-phase components of the ac susceptibility data at zero dc fields. (Figures 4.7a and b). In order to confirm that 2 is a true SMM, additional ac data was collected in the presence of small dc-fields, which often lift the degeneracy of the magnetic states (Zeeman energy) and decrease the probability of quantum tunneling of the magnetization. The increase in magnetic relaxation time (e.g. characteristic frequency) can be followed as a function of increasing applied dc field, and is readily apparent in ac data collected below ca. 2200 Oe (Figure 4.8).

Figure 4.9. Frequency dependence of the out-of-phase components of the ac susceptibility at different applied dc fields between 0 and 10000 Oe (with 1 Oe of ac modulation) for \{[(Tp^Me)Fe^{III}(CN)_3]_2[Ni^{II}(bpy)_2][ClO_4]_2\}-3MeCN-2H_2O-MeOH (2) and measured at 1.9 K. The solid lines are guides for eyes.\textsuperscript{14}
Confirming that that 2 is an SMM, changing the static dc magnetic field changes the rate of magnetic relaxation, and shows that 2 probably exhibits fast quantum tunneling of the magnetization in zero applied field, and much slower relaxation times at non-zero dc fields. The ac data collected at this minimum/critical field ($H_{dc} = 2200$ Oe) at various ac field oscillation frequencies and can be found in Figure 4.7 (c and d).\textsuperscript{14} The frequency-dependent ac data clearly shows magnetic relaxation allowing for its rates to be estimated via an Arrhenius law (Figure 4.9, right). The data generally follow Arrhenius behavior (albeit with some deviation at lower temperatures) giving $\tau_0 = 1.4 \times 10^{-7}$ s and an effective energy gap of $U_{\text{eff}} = 15.7$ K (Figure 4.9). Using this data, the uniaxial anisotropy term may be estimated from the critical field and $g_{\text{iso}}$ parameter deduced earlier. Under these assumptions, additional least-squares fitting of the reduced magnetization data ($M$ vs $H/T$) affords an estimation of the experimental zero-field splitting parameter ($D/k_B$) and provides for an additional method for to calculate the magnetic spin reversal energy, assuming $U_{\text{eff}} \sim |D/k_B| S^2/k_B$. Solving for the zero-field splitting term, $D/k_B/(g_{\mu_B}) \sim 2200$ Oe (the critical field), gives $D/k_B \sim -1.8$ K.\textsuperscript{14}

Lastly further confirming that 2 exhibits a single magnetic relaxation rate, the Cole-Cole plots at several temperatures were investigated (Figure 4.10).\textsuperscript{14,53} Fitting the $\chi''$ vs $\chi'$ data at several temperatures to a Debye model gives an $\alpha$ parameter, that can be used to estimate how many relaxation processes are operative within the sample.\textsuperscript{53} Low $\alpha$ values generally indicate that a single or relatively few magnetic relaxation process are operative (Figure 4.10). Both 1 and 2 belong to well-known cyanide-bridged \{Fe$^{III}$\}_2Ni$^{II}$\}_2 complexes containing
Figure 4.10. Cole-Cole plots at various temperatures for 2 ($H_{ac} = 1$ Oe; $H_{dc} = 2.2$ kOe).\textsuperscript{14}
[(TpR)FeIII(CN)3]− building blocks. However, we have yet to find a general relationship linking spin-reversal energy barriers and their structures. These vary between 15.7 and 27.2 K for reported SMMs. In subsequent sections of this chapter we will describe additional work that aims to better establish trends in these cyanide-based magnetic materials.14

4.5 Synthesis and Spectroscopic Characterization: Hexa- and Nonanuclear Complexes. The synthesis of a new hexanuclear complex, {[(Tp*Me)FeIII(CN)3]4[NiII(DMF)3]2}·4DMF·H2O (3) where Tp*Me = tris(3,4,5-trimethylpyrazole)borate), is accomplished by combining a 2:1 ratio of [NEt4]-[(Tp*Me)Fe(CN)3]·H2O4 and NiCl2 in DMF (Scheme 4.2).5 The infrared spectrum of 3 exhibits several strong \( \nu \)CN stretches (2173, 2148, and 2115 cm\(^{-1}\)) that are shifted to higher energies relative to those found for [NEt4][(Tp*Me)Fe(CN)3]·H2O (2119 and 2115 cm\(^{-1}\)) verifying both terminal and bridging cyanides are present. Unexpectedly, when methanol is instead used as a reaction solvent or

![Scheme 4.2](image)

Scheme 4.2. Synthesis of {[(Tp*Me)FeIII(CN)3]4[[NiII(DMF)3]2]·4DMF·2H2O (3), {[(Tp*Me)FeIII(CN)3]6[[NiII(MeOH)3]2[NiII(MeOH)2]]·3H2O·8MeOH (4), and {[(Tp*Me)FeIII(CN)3]4[NiII(tren)]4[ClO4]4·7H2O·4MeOH (5).5
alternatively, crystalline samples of 3 are dissolved into MeOH, a second nonanuclear complex, \([(Tp^{*Me})Fe^{III}(CN)_3]_6[Ni^{II}(MeOH)_3]_2[Ni^{II}(MeOH)_2]\)-\(\cdot3H_2O\)-8MeOH (4) is isolated. In this new complex the \(\nu_{CN}\) stretching absorptions (2165 and 2121 cm\(^{-1}\)) are very different than those found for 3 suggesting that different cyanide electronic environments are present.\(^{4,24,26,2730-46,50-52}\)
Table 4.3. Selected Bond Distances (Å) and Angles (°) for \(([(Tp^*\text{Me})\text{Fe}^{III}(\text{CN})_3]_4-\) \([\text{Ni}^{II}(\text{DMF})_3]_2\)-4DMF-2H$_2$O (3) and \([(Tp^*\text{Me})\text{Fe}^{III}(\text{CN})_3][\text{Ni}^{II}(\text{MeOH})_3]_2-\) \([\text{Ni}^{II}(\text{MeOH})_2]]\)-3H$_2$O-8MeOH (4).\(^5\)

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Compound 3 crystallizes in the triclinic $P\overline{1}$ space group as a neutral and centrosymmetric hexanuclear \{Fe$^{III}_4$Ni$^{II}_2$\} complex (Table 4.1).\(^5\) The complex contains a central \{[(Tp*Me)Fe$^{III}$(CN)$_3$]$[\text{Ni}^{II}(\text{DMF})_3]$\}_2\} square that is connected to another \{[(Tp*Me)Fe(CN)$_3$]$^-$\} fragment via Fe$^{III}$(μ-CN)Ni$^{II}$ linkages. The structure of 3 resembles the \{Fe$^{III}_2$Ni$^{II}_n$\} repeat unit seen in several \{[Fe$^{III}$(L)(CN)$_4$]$^2-$Ni$^{II}$(H$_2$O)$_2$\}·4H$_2$O (L = bpy, phen) one dimensional chains (Figure 4.11, top).\(^44\) The Fe$^{III}$ and Ni$^{II}$ centers adopt distorted octahedral geometries in 3 and Fe-C, Fe-N and Ni-N/O bond lengths are found to range between 1.901(4) and 1.927(4) Å, 1.983 and 2.000(3), and 2.001(3) and 2.100(3) Å, respectively. Within the Fe$^{III}$(μ-CN)Ni$^{II}$ fragments the Fe$^{III}$ sites the bridging cyanides are nearly linear, with Fe-C-N angles between 172.9(3) and 178.2(4)°, while the Ni-N-C angles are between 170.2(3) and 177.1(3)°. The \{Fe$_4$Ni$_2$\} cores in 3 are also well-separated in the solid state and the closest intercomplex Fe···Ni contacts are ca. 8.71(1) Å (Table 4.3).\(^5\)

Crystals of 4 are found in the monoclinic $C\overline{2}/c$ space group as a neutral nonanuclear \{Fe$^{III}_6$Ni$^{II}_3$\} complex (Table 4.1). As seen in structures of 3 the molecular core of 4 also resembles the \{Fe$^{III}_2$Ni$^{II}_n$\} fragments of well-known \{4,2\}-connected chains (Figure 4.11, bottom).\(^23,44,45\) The central core of 4 contains two \{[(Tp*Me)Fe(CN)$_3$]$^-$\} fragments (Fe1 and Fe2) that are linked to two other and adjacent Ni$^{II}$ ions via two bridging cyanides. The two \{Fe$^{III}_2$Ni$^{II}_2$\} squares corner share a common Ni$^{II}$ center (Ni1) while the remaining terminal cyanides adopt anti orientations relative to the average \{Fe$^{III}_2$Ni$^{II}_2$\} plane. Additional symmetry-related Fe$^{III}$(μ-CN)Ni$^{II}$ units (Fe3-C8-N8-Ni2) link the remaining \{[(Tp*Me)Fe(CN)$_3$]$^-$\} anions to complete the structure of the complex. The metal ions in 4 have more distorted
coordination geometries (Figure 4.12) than those seen in 3, and average Fe-C, Fe-N, Ni-O and Ni-N bond lengths of ca. 1.919(6), 1.988(4), 2.115(5) and 2.023(5) Å are found (Table 4.3). The Fe-C-N and Ni-N-C angles are also more distorted and are between 171.6(5) and 177.4(7)° [Fe3-C7-N7 and Fe2-C6-N6] and 157.5(4) and 172.8(4)° [Ni2-N8-C8 and Ni2-N4-C4]. As in 3, the \{Fe₆Ni₃\} cores are also well-isolated from their nearest neighbors with the closest intercomplex distance between metal atoms being 9.26(1) Å [Fe···Fe] metal ions.\(^5\)

Figure 4.12. (top) View of relatively flat and truncated in 3. (bottom) View of twisted and truncated core present in 4.\(^5\)

In Figure 4.12, the twisting along the Ni···Ni axes is clearly seen and is more pronounced in 4 than in 3. The mean plane \{Fe₂Ni₂\} deviation of the squares in 3 and 4 are small [ca. 0.02 Å avg.] but the dihedral twisting [ca. 33.1(1)°] of the two \{Fe₂Ni₂\} squares about the central nickel atom (Ni1) is significant in 4. Another way
to visualize this is to look at the relative orientations of the $C_3$ axes (along the B···Fe vectors) in both structures. The B···Fe vectors in the $\{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_2\}$ square fragments of 3 are parallel while those in 4 are tilted by ca. 58.6(1)$^\circ$ with respect to each other. Likewise the Fe1···B1/B2···Fe2 and Fe1···B1/B3···Fe3 axes are also tilted by approximately 39.4(1)$^\circ$ and 23.7(1)$^\circ$ with respect to those in the square fragments (Figure 4.13).$^5$

Figure 4.13. (top) Ball and stick views of (top) perpendicular to the $\{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_2\}$ core in 3 and (bottom) along the Ni···Ni···Ni vector in 4 highlighting cluster structural distortion.
4.6 Magnetic Characterization: Hexa- and Nonanuclear Complexes. We began several magnetic measurements, to further investigate our hypothesis that the relative orientations of the pseudo-$C_3$ rotation axes (on Fe$^{IIl}$), are structural markers for single-ion magnetic anisotropy tensors. Given that they have very different orientations of these axes we were curious whether there would be dramatic differences in the magnetic properties of 3 and 4. We hypothesized that parallel orientations would give complexes with the high SMM energy barriers in comparison to those where they are improperly aligned. To further investigate this hypothesis, we began a magnetic measurements on our new structural archetypes, namely the hexa- and nonanuclear complexes, to see if 3 and 4 adhere to this this qualitative trend.\textsuperscript{4,6,9,10,18,20,21,26,46} The temperature dependence of the $\chi T$ product shows that the room temperature $\chi T$ values for 3 and 4 [4.8 and 8.8 cm$^3$ K mol$^{-1}$] are close to those expected for Fe$^{IIl}$LS ($S = \frac{1}{2}$) and Ni$^{II}$ ($S = 1$) ions are present in a 4:2 and 6:3 ratio, assuming that $g_{Fe} \sim 2.7$ and $g_{Ni} \sim 2.2$ for the metal centers present (Figure 4.14).\textsuperscript{5} As expected from their stoichiometries, compound 4 has a larger $\chi T$ value than that seen for 3, for a given temperature.

As the temperature is lowered, the $\chi T$ product increases towards maximum values of 14.4 and 31.5 cm$^3$ K mol$^{-1}$ near ca. 4 K, demonstrating that the magnetic interactions between the Fe$^{IIl}$ and Ni$^{II}$ centers are ferromagnetic. This is generally found for cyanide-bridged Fe$^{IIl}$/Ni$^{II}$ complexes owing to their orthogonal molecular orbitals involved in spin coupling.\textsuperscript{4,6,9,10,17,21,26,44,54,55} At lower temperatures the $\chi T$
products again decrease towards minimum values [14.0 and 29.5 cm$^3$ K mol$^{-1}$] at 1.8 K for 1 and 2, respectively.$^5$

As judged from the structures of 3 and 4, the magnetic exchange interactions were simulated$^{28,29}$ using the following isotropic Heisenberg spin Hamiltonians (Eqn. 4.3 and Eqn. 4.4) for 3 and 4, respectively:

$$H = -2J_1[S_{Ni1} \cdot (S_{Fe1} + S_{Fe2} + S_{Fe2A}) + S_{Ni1A} \cdot (S_{Fe1A} + S_{Fe2} + S_{Fe2A})]$$  \hspace{1cm} (Eqn. 4.3)
\[ H = -2J_2[S_{\text{Ni1}^+}(S_{\text{Fe1}} + S_{\text{Fe2}} + S_{\text{Fe1A}} + S_{\text{Fe2A}}) + S_{\text{Ni2}^+}(S_{\text{Fe1}} + S_{\text{Fe2}} + S_{\text{Fe3}}) + S_{\text{Ni2A}^+}(S_{\text{Fe1A}} + S_{\text{Fe2A}} + S_{\text{Fe3A}})] \]  
(Eqn. 4.4)

where \( J_1 \) and \( J_2 \) represent the average exchange interactions between the magnetically coupled Fe\(^{III} \) (\( S = \frac{1}{2} \)) and Ni\(^{II} \) (\( S = 1 \)) centers (Figure 4.15). Simulations of the \( \chi T \) vs \( T \) data (see Figure 4.14) between 300 and 12 K, gave the following parameters: \( J_1/k_B = +9.0(5) \) K and \( g_{\text{avg}(1)} = 2.3(1) \) for 3 and \( J_2 = +9.0(5) \) K and \( g_{\text{avg}(2)} = 2.5(1) \) for 4. These are reminiscent of those found to a variety of \( \{\text{Fe}^{III},\text{Ni}^{II}\}_{n,m} \) complexes containing \([\text{(Tp}^R\text{)Fe}^{III}(\text{CN})_3]^–\) anions. Attempts to incorporate more terms, different \( J \) or \( g \) parameters, or single-ion anisotropy (for Fe\(^{III} \) and Ni\(^{II} \)) did not improve the simulation below ca. 12 K, indicating that many or all of these factors may be important and are comparable in magnitude below ca. 12 K (Figure 4.15).

**Figure 4.15.** \( \chi T \) vs \( T \) data for 3 and 4 at 1000 Oe. Solid lines represent the best fit simulations down to 12 K.
Figure 4.16. (top) $M$ vs $H$ (left) and $M$ vs $H/T$ (right) data for 3 below 8 K. The solid lines are guides for the eyes on the left plot but are on the right plot the best fits obtained with a $S_T = 4$ macro-spin model with $D/k_B = -6.7$ K and $g = 2.65$. (bottom) $M$ vs $H$ (left) and $M$ vs $H/T$ (right) data for 4 below 8 K. Solid lines are guides for the eyes.
The magnetization versus field data ($M$ vs $H$) collected between 1.8 and 8 K show that at the lowest temperature (1.8 K) and highest attainable field strength (7 T) the magnetization values [6.9 and 14.0 μB] seen for 3 and 4 are still not fully saturated (Figure 4.16). This indicates that significant magnetic anisotropy is present in both complexes. The high field magnetization values support the assumption that $S_T = 4$ and 6 spin ground states (with $g_{av} > 2$) are present in 3 and 4, respectively, and confirms those estimated from the $\chi_T$ vs $T$ data. Attempts to fit the $M$ vs $H$ data of 3 and 4 using $S_T = 4$ and 6 macro-spin models (with $H = D S_T z^2$) or the program ANISOFIT lead to unrealistic magnetic parameters ($D/k_B < -6$ K for 3) suggesting that the magnetic ground state is not exclusively populated at the temperature and magnetic field limits (1.8 K and 7 T) of the experiment (Figure 4.16, top/bottom right). As was also the case for tetranuclear complexes 1 and 2 we did not observe any magnetic hysteresis in the $M$ vs $H$ data above 1.8 K for 3 or 4.

Additional ac susceptibility measurements were obtained for 3 and 4 to see if they are single-molecule magnets. Both complexes exhibit frequency-dependent behavior in their in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility data plots at zero applied magnetic field (Figures 4.17 and 4.18). The data initially suggest that both complexes have a single relaxation pathway and this assumption was investigated further in several additional measurements. As shown in Figure 4.19, both 3 and 4 show relaxation that is characteristic of single-molecule magnetism that progresses through a single relaxation mode. The magnetic relaxation times (Figure 4.20) follow Arrhenius behavior [$\tau = \tau_0 \exp(U_{eff}/k_B T)$] and estimations of their
Figure 4.17. Temperature dependence of the (top, left) in-phase and (top, right) out-of-phase components of the ac susceptibility between 10 and 10000 Hz ($H_{ac} = 1$ Oe; $H_{dc} = 0$ Oe) for 3. (bottom, left) In-phase and (bottom, right) out-of-phase components for 4 between 10 and 10000 Hz ($H_{ac} = 1$ Oe; $H_{dc} = 0$ Oe) for 4. Solid lines are guides for the eyes.\(^{5}\)
Figure 4.18. Frequency dependence of the (top, left) in-phase and (top, right) out-of-phase components of the ac susceptibility between 1.8 and 2.75 K for 3. (bottom, left) In-phase and (bottom, right) out-of-phase components of the ac susceptibility between 1.8 and 3 K ($H_{ac} = 1$ Oe; $H_{dc} = 0$ Oe) for 4. Solid lines are guides for the eyes.\textsuperscript{5}
Fig. 4.19 (top) Semi-logarithmic \( \tau \) vs \( 1/T \) plot from the frequency dependence of the ac susceptibility at \( H_{dc} = 0 \text{ Oe} (\circ) \) and \( H_{dc} = 1500 \text{ Oe} (\circ) \) for 1. (bottom) Semi-logarithmic \( \tau \) vs \( 1/T \) plot from the frequency dependence of the ac susceptibility at \( H_{dc} = 0 \text{ Oe} (\circ) \) and \( H_{dc} = 600 \text{ Oe} (\circ) \) for 2. Solid lines are best fits to an Arrhenius law.\(^5\)
Figure 4.20. Frequency dependence of the in-phase (left) and out-of-phase (right) components of the ac susceptibility at different applied dc fields between 0 and 3500 Oe (with $H_{ac} = 1$ Oe) for 3 at 1.8 K. Solid lines are guides for the eyes.\textsuperscript{5}
effective energy barriers \[ U_{\text{eff}} = 15.6 \text{ and } 17.7 \text{ K} \] and pre-exponential terms \[ \tau_0 = 2.4 \times 10^{-8} \text{ and } 9.6 \times 10^{-9} \text{ s} \] for 3 and 4, respectively.\(^5\) These Arrhenius parameters are comparable to several reported SMMs\(^47\) but quantum tunneling of the magnetization appears to significantly reduce the activation energy.

To further investigate magnetic relaxation in 3 and 4 additional ac susceptibility were also collected under application of small static or dc-fields, which was expected to remove the degeneracy of the magnetic states, and decrease the likelihood of quantum tunnelling.\(^6,14,26-27,31-45,50-52\) This effect should increase the characteristic relaxation times and lead to higher SMM energy barriers. Indeed application of small dc fields cause dramatic reductions in the characteristic frequency from 1213 to 30 Hz \( (H_{dc} = 1500 \text{ Oe}) \) and 1470 to 215 Hz \( (H_{dc} = 600 \text{ Oe}) \), for 3 and 4, respectively (Figures 4.21-4.23).\(^5\) As expected considerably higher SMM energy barriers [26 and 24.5 K] and smaller \( \tau_0 \) [2.4 \times 10^{-9} \text{ and } 1.9 \times 10^{-9} \text{ s} ] are found and again allows for an estimation of the anisotropy parameters in the presence of a magnetic field (Figures 4.24 and 4.25): \( D/k_B = -1.6 \) and \(-0.7 \text{ K} \) for 3 and 4, respectively. Confirming again that a single relaxation mode is operative in 3 and 4 the Cole-Cole plots show very small a parameters at 1.8 K [0.15 and 0.26] for 3 and 4, respectively (Figure 4.25).\(^5\)

Interestingly the thermally activated (Arrhenius) energy barriers are comparable for 3 and 4 despite substantial differences in nuclearity and overall spin ground states. These results strongly suggest that geometrical distortion and alignment of anisotropic ions plays an important role in tuning SMM behavior. In other words, a more parallel alignment of the \( C_3 \) axes of the tricyanoferrate units general appear
Figure 4.21. Frequency dependence of the (top, left) in-phase and (top, right) out-of-phase (top, right) components of the ac susceptibility at different applied dc fields for 4 at 1.9 K. (bottom, left) In-phase and (bottom, right) out-of-phase components (0 ≤ $H_{dc}$ ≤ 500 Oe; $H_{ac}$ = 1 Oe); bottom, between (500 ≤ $H_{dc}$ ≤ 3000 Oe; $H_{ac}$ = 1 Oe);). Solid lines are guides for the eyes.5
Figure 4.22. (top) Field dependence of the characteristic frequency of the relaxation mode at 1.8 K for 3 deduced from Figure 4.21. (bottom) Field dependence of the characteristic frequency of the relaxation mode at 1.9 K for 4 deduced from Figure S22. Solid lines are guides for the eyes.\textsuperscript{5}
Figure 4.23. Temperature dependence of the in-phase (left) and out-of-phase (right) components of the ac susceptibility between 10 and 10000 Hz (with $H_{ac} = 1$ Oe; $H_{dc} = 1500$ Oe) for (top) 3 below 6 K and (bottom) 4 below 5 K. Solid lines are guides for the eyes.\textsuperscript{5}
Figure 4.24. Frequency dependence of the (top, left) in-phase and (top, right) out-of-phase components of the ac susceptibility between 1.8 and 3.5 K ($H_{ac} = 1$ Oe; $H_{dc} = 1500$ Oe) for 3. Frequency dependence of the (bottom, left) in-phase and (bottom, right) out-of-phase components of the ac susceptibility for 4 between 1.8 and 2.75 K ($H_{ac} = 1$ Oe; $H_{dc} = 600$ Oe). Solid lines are guides for the eyes.\textsuperscript{5}
Figure 4.25. Cole-Cole plots for (top) 3 and (bottom) 4 obtained at various temperatures between 1.8 and 2.75 K ($H_{ac} = 1$ Oe and $H_{dc} = 0$ Oe). Solid lines are best fits to a generalized Debye model with $\alpha$ between 0.05 (2.6 K) and 0.15 (at 1.8 K) for 3 and 0.06 (2.7 K) and 0.26 (at 1.8 K) for 4.\textsuperscript{5}

to give higher SMM energy barriers, by increasing cluster magnetic anisotropy and zero-field splitting. Therefore spin states appear to play a secondary role in establishing SMM energy barriers in this system.\textsuperscript{5,6,14,26-27,31-45,50-52,56}
4.7 Synthesis, Spectroscopic, and Magnetic Characterization: Octanuclear Complex. In methanolic solution, treatment of $\text{[NE}_{\text{t}}{\text{4}}]\text{[(T}_{\text{p}*}{\text{Me}})\text{Fe}_{\text{III}}(\text{CN})_{\text{3}}]^{-}\cdot\text{H}_{\text{2}}\text{O}$, where $\text{T}_{\text{p}*}{\text{Me}} = \text{tris}(3,4,5-$trimethylpyrazolyl)borate (Chapter 2), with a mixture nickel(II) perchlorate and tris(2-aminomethyl)amine (tren), gives a new octanuclear complex of $\text{[(T}_{\text{p}*}{\text{Me}})\text{Fe}_{\text{III}}(\text{CN})_{\text{3}}]_{\text{4}}[\text{Ni}_{\text{II}}(\text{tren})]_{\text{4}}[\text{ClO}_{\text{4}}]_{\text{4}}\cdot\text{7H}_{\text{2}}\text{O} \cdot 4\text{MeCN}$ (5) stoichiometry (Figure 4.26). The red plates have intense $\nu_{\text{BH}}$ (2541 cm$^{-1}$) and several $\nu_{\text{CN}}$ (2156, 2141, 2130, and 2114 cm$^{-1}$) stretching absorptions that are at higher energies than those of $\text{[NE}_{\text{t}}{\text{4}}]\text{[(T}_{\text{p}*}{\text{Me}})\text{Fe}_{\text{III}}(\text{CN})_{\text{3}}]^{-}\cdot\text{H}_{\text{2}}\text{O}$ (2554 cm$^{-1}$, $\nu_{\text{BH}}$; 2119 and 2115 cm$^{-1}$, $\nu_{\text{CN}}$), indicating both bridging and terminal cyanides are present in 5.

![Figure 4.26. X-ray structure of 5. Thermal ellipsoids are at the 50% level all hydrogen atoms, anions, and lattice solvent are removed for clarity.](image)

Crystals of 5 are found in the triclinic $P-1$ space group (Table 4.4). The polynuclear complex consists of two crystallographically independent and cyanide-bridged Fe$^{\text{III}}$ (Fe1 and Fe2) and Ni$^{\text{II}}$ (Ni1 and Ni2) ions to form a central $\{\text{Fe}^{\text{III}}_{\text{2}}\text{Ni}^{\text{II}}_{\text{2}}\}$
square that is also linked via \( \mu \)-CN units to two adjacent \{Fe\textsuperscript{III}Ni\textsuperscript{III}\} fragments (Figure 4.27). The octanuclear complex contains six-coordinate metal ions that deviate from idealized octahedral coordination geometries. In structures of 5 the Fe–C and Ni-N bonds are between 1.919(4) and 1.935(4) Å and 2.038(4) and 2.132(4) Å, closely resembling those in other Fe/Ni clusters. The bridging cyanides have angles that range from approximately linear [179.4(4) for Fe1–C1–N1] to significantly bent [158.7(4) for Ni1–N3–C3] highlighting the low symmetry of the complex. Completing the structure are extensive hydrogen bonding interactions.

**Figure 4.27.** Packing diagram of 5 illustrating extensive hydrogen bonding within the \( ab \)-plane (dotted lines).
Figure 4.28. (top) Simplified packing arrangement of the \{Fe$_4$Ni$_4$\} cores present of 5 within the ac-plane. (bottom) Partial packing arrangement of cores in 5 in the bc-plane.$^4$
Table 4.4. Selected Bond Distances (Å) and Angles (°) for \{[(Tp^Me)Fe^{III}(CN)_3]_4-[Ni^{II}(tren)]_4[ClO_4]_4\}\cdot7H_2O\cdot4MeCN (5).^4

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond Angle (°)</th>
</tr>
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<tr>
<td>Fe1-C1</td>
<td>1.921(4)</td>
<td>C1-Fe1-C2 86.2(2)</td>
</tr>
<tr>
<td>Fe2-C2</td>
<td>1.919(4)</td>
<td>C1-Fe1-C3 90.8(2)</td>
</tr>
<tr>
<td>Fe1-C3</td>
<td>1.935(4)</td>
<td>C2-Fe1-C3 89.2(2)</td>
</tr>
<tr>
<td>Fe1-N8</td>
<td>2.001(4)</td>
<td>C1-Fe1-N8 92.2(2)</td>
</tr>
<tr>
<td>Fe1-N10</td>
<td>1.979(4)</td>
<td>C1-Fe1-N10 92.5(2)</td>
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<tr>
<td>Fe1-N12</td>
<td>2.021(4)</td>
<td>C1-Fe1-N12 177.3(2)</td>
</tr>
<tr>
<td>Fe2-C4</td>
<td>1.921(5)</td>
<td>N8-Fe1-N10 98.9(2)</td>
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<td>1.932(5)</td>
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<td>1.997(4)</td>
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</tr>
<tr>
<td>Fe2-N18</td>
<td>1.981(4)</td>
<td>Fe1-C3-N3 172.3(4)</td>
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<td>2.038(4)</td>
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<td>2.132(4)</td>
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</tr>
<tr>
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<td>1.157(6)</td>
<td>N2-N1-N20 94.9(2)</td>
</tr>
<tr>
<td>Fe1···Fe2</td>
<td>7.524(6)</td>
<td>N2-N1-N21 92.2(2)</td>
</tr>
<tr>
<td>Ni1···Ni2</td>
<td>7.181(5)</td>
<td>N2-N1-N22 175.2(2)</td>
</tr>
</tbody>
</table>
between the tren and lattice solvent (Figures 4.28 and 4.29). Despite the low symmetry at each of the iron and nickel sites the complex has centrosymmetric relationships between metal-metal pairs at the three metal sites, and gives a nearly parallel orientation of the pseudo-C$_3$ rotation axes (at the Fe$^{III}$ sites). In our working hypothesis this is probably related to significant steric interactions between the tren and Tp$^{*}$Me ligands and might lead to a favorable alignment of the anisotropy tensors in 5.$^{4,18,20,48,49,56}$

4.8 Magnetic Properties. Several magnetic measurements show that 5 is a ferromagnetic complex. At 300 K the $\chi T$ value suggests that a 4:4 ratio of magnetically isolated Fe$^{III}$ ($S = \frac{1}{2}, g \sim 2.7, C \sim 0.7$ cm$^3$ K mol$^{-1}$) and Ni$^{II}$ ($S = 1; g \sim 2.2, C \sim 1.1$ cm$^3$ K mol$^{-1}$) are in 5 (Figure 4.29). As the temperature is lowered the $\chi T$ values are found to increase towards a maximum of ca. 25.5 cm$^3$ K mol$^{-1}$ at 5 K, indicating that 5 undergoes ferromagnetic magnetic coupling. At lower temperatures

![Figure 4.29. $\chi T$ vs $T$ data for 5 (with $\chi$ defined as the magnetic susceptibility and equal to $M/H$) at 1000 (●) and 10000 Oe (●).]
the χT values approach 21.1 cm³ K mol⁻¹ at 1.8 K (Figure 4.30). The magnetic χT vs T data were simulated using MAGPACK²⁸-²⁹ via an isotropic Heisenberg Hamiltonian (Eqn. 4.5):

\[ H = -2J[S_{Ni2}(S_{Fe2} + S_{Fe1}) + (S_{Fe1} + S_{Fe1A}) \cdot (S_{Ni1} + S_{Ni1A})] \]

\[ + S_{Ni2A}(S_{Fe2A} + S_{Fe1A}) \]

where \( J \) represents the average magnetic interaction between the low spin Fe³⁺ (\( S = \frac{1}{2} \)) and Ni²⁺ (\( S = 1 \)) ions over the four possible Fe–CN–Ni pathways allowed by symmetry in the \{Fe³⁺₄Ni²⁺₄\} core, with the \( S_i \) term representing the spin operator of each metal ion. The data were successfully simulated between 300 and 15 K and gave the following parameters: \( J/k_B = +9.5(1) \) K and \( g_{avg.} = 2.4(1) \). These estimated values indicate that 5 has an \( S_T = 6 \) spin ground state and are comparable to others reported for other cyanide-bridged tri-, tetra-, and octanuclear \{Fe³⁺ₓNi²⁺ᵢ\} with \[(TpR)Fe³⁺(CN)₃\]⁻ building blocks present (Figure 4.30).⁶-¹⁰,¹⁸-²⁰,²⁶,⁵⁰-⁵² We note that

**Figure 4.30.** \( \chi T \) vs \( T \) data for 5 obtained at \( H_{dc} = 0.1 \) T. Inset: \( M \) vs \( H/T \) data between 1.9 and 6 K. Solid lines represent least-squares fitting of the data to an anisotropic \( S_T = 6 \) macro-spin model (Eqn. 4.5).⁴
using two or more magnetic interactions \((J)\), different \(g\) factors for the metal centers present, or single-ion magnetic anisotropy did not improve the simulation quality or provide reasonable simulations of the data below ca. 15 K.

The \(M\) vs \(H\) data collected below 6 K adds additional evidence that \(5\) has an \(S_T = 6\) spin ground state (Figure 4.31, top). The presence of significant magnetic anisotropy in \(5\) is illustrated by the incomplete saturation even at \(H_{dc} = 7\) T and \(T = 1.8\) K. The maximum value (12.6 \(\mu_B\)) indicates that the \(g_{avg.}\) is greater than 2.0, an assumption also found in the \(\chi T\) vs \(T\) data. Combined the magnetic data verify that \(5\) has an \(S_T = 6\) spin ground state (with \(g > 2\)). Assuming that uniaxial magnetic anisotropy is present in \(5\), that is spin-orbit coupling gives a negative \(D\) parameter, the \(M\) vs. \(H/T\) data below 6 K can be fitted to an isotropic Heisenberg Hamiltonian, \(H = D S_T^2(2)\) for the \(S_T = 6\) ground state (Inset: Figure 4.30). This fitting gives \(D/k_B\) and \(g\) values of \(-1.29(2)\) K and 2.60(5), respectively, which are slightly higher than those seen from simulations of the \(\chi T\) vs \(T\) data, and is quite different than those seen for the majority of cubic \({\text{Fe}^{III}_4\text{Ni}^{II}_4}\) \((S = 6)\) complexes [i.e. \(D/k_B = -0.33\) K and \(g_{avg.} = 2.2\)].\(^{19,56,57}\) The data suggests that the \(S_T = 6\) complex has larger zero-field splitting (uniaxial anisotropy) than more symmetrical \({\text{Fe}^{III}_4\text{Ni}^{II}_4}\) complexes. As is the case for other Fe/Ni complexes and those described in this chapter no magnetic hysteresis is found in the \(M\) vs. \(H\) data above 1.8 K (Figure 4.31, bottom).
To further assess the magnetic properties of 5 we also performed a variety of ac susceptibility measurements above 1.8 K (Figures 4.33-4.35). We found that frequency-dependent in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility are clearly evident in the absence of an applied magnetic field (Figure 4.33) for 5. Looking at the ac susceptibility as a function of applied ac oscillating

**Figure 4.31.** (top) $M$ vs $H$ data for 5 below 10 K. (bottom) $M$ vs $H$ hysteresis data for 5 at 1.9 K.\(^4\)
field (ac frequency) at several temperatures allowed us to follow the magnetization relaxation dynamics in a systematic manner (Figures 4.32 and 4.33). The relaxation time, deduced from the temperature- and frequency-dependence of the ac susceptibility data, follows thermally activated behavior. This allows for the energy gap ($U_{\text{eff}}$) of the relaxation time to be estimated using the Arrhenius law.

Figure 4.32. Temperature dependence of the in-phase ($\chi'$, left) and out-of-phase ($\chi''$, right) components of the ac susceptibility between 1 and 1500 Hz ($H_{\text{ac}} = 3$ Oe; $H_{\text{dc}} = 0$ Oe) for 5 below 8 K. Solid lines are guides for the eyes.\textsuperscript{4}
Using the data collected above 1.8 K (Inset: Figure 4.34), $U_{\text{eff}}$ and the intrinsic time ($\tau_0$, or characteristic time) were found to be 32.8 K and $2.5 \times 10^{-9}$ s, respectively. In other words the characteristic time, in the time period between two

Figure 4.33. Frequency dependence of the in-phase ($\chi'$, top) and out-of-phase ($\chi''$, bottom) components of the ac susceptibility at various temperatures ($1.8 \leq T \leq 3.6$ K; $H_{\text{ac}} = 3$ Oe; $H_{\text{dc}} = 0$ Oe) for 5. Solid lines are best fits obtained with a generalized Debye model. The $\alpha$ parameters were consistently lower than 0.31.$^4$
attempts of the crystal lattice, adjacent molecules, and/or surrounding medium to thermally relax the magnetization through spin reversal. Given that the magnitude of the characteristic time is between ca. 10^{-8} and 10^{-10}s, we conclude that rather weak intermolecular interactions are present in 5. Given that \( U_{\text{eff}} \) is smaller than that predicted from the \( U_{\text{eff}} \sim D S_t^2 \) relationship (46 K), we thought that quantum tunneling of the magnetization may assist in faster magnetic relaxation of 5. As before application of a magnetic field is expected to remove the degeneracy of the \( \pm m_S \) states and lead to slower magnetic relaxation.\(^{14,26-27,31-45,50-52}\) As expected application of a static dc magnetic field (up to 800 Oe) reduced the characteristic frequency at 1.9 K, from 2.4 to 1.3 Hz, confirming that quantum tunneling of the

Figure 4.34. \( \chi'' \) vs \( T \) data for 5 below 6 K at various ac frequencies (\( H_{\text{dc}} = 0 \) Oe; \( H_{\text{ac}} = 3 \) Oe). Inset: Semi-logarithmic \( \tau \) vs \( T^{-1} \) plot for 5. Solid red line represents the best data simulation using an Arrhenius law (with \( \tau_0 = 2.5 \times 10^{-9} \) s).\(^{4}\)
magnetization is operative in 5 (Figure 4.34).\textsuperscript{9,10,26,50} Cole-Cole plots (Figure 4.35) consistently give $\alpha$ parameters below ca. 0.31 further suggesting that magnetic relaxation proceeds through a common intermediate state, given that there is a narrow distribution of relaxation times (i.e. small $\alpha$ values).\textsuperscript{4,53,54}

\begin{center}
\textbf{Figure 4.35.} Cole-Cole plots at different temperature between 1.8 and 3.6 K for compound 5 measured in zero-dc field. Solid lines are the best fits obtained with a generalized Debye model with $\alpha < 0.31$ in all cases.\textsuperscript{4}
\end{center}

4.9 General Conclusions. In summary, we synthesized and characterized five ferromagnetic clusters of varying nuclearity to examine how numbers of coupled metal centers, spin ground state, \textit{and} their structures modify their magnetic properties. Incorporation of the [NEt$_4$][(Tp*Me)Fe$^{III}$(CN)$_3$]$\cdot$H$_2$O building block using a bottom up synthetic approach afforded two tetranuclear clusters, \{[(Tp*Me)Fe$^{III}$(CN)$_3$]$_2$[Ni$^{II}$(DMF)$_4$)$_2$[OTf]$_2$]·2DMF (1) and \{[(Tp*Me)Fe$^{III}$(CN)$_3$]$_2$-[Ni$^{II}$(bpy)$_2$][ClO$_4$]$_2$·3MeCN·2H$_2$O·MeOH (2), where bpy = 2,2$'$-bipyridine. In these
complexes the ferromagnetic interactions of the 2:2 ratio of Fe$^{III}$ ($S = \frac{1}{2}$) and Ni$^{II}$ ($S = 1$) ions gives an $S_T = 3$ spin ground state for the clusters.

In higher nuclearity clusters there appears to be structure-property relationships that relate the SMM energy barrier heights to the relative orientations of their putative anisotropy axes along the Fe⋯B direction.\textsuperscript{4,5,10,14,56} In a hexanuclear derivative, $\{(Tp^*Me)Fe^{III}(CN)_3\}_4[Ni^{II}(DMF)_3]_2\cdot4DMF\cdot2H_2O$ (3), ferromagnetic coupling of a 4:2 ratio of Fe$^{III}$ and Ni$^{II}$ ions gives a total cluster spin of $S_T = 4$, while a nonanuclear cluster, $\{(Tp^*Me)Fe^{III}(CN)_3\}_6[Ni^{II}(MeOH)_3]_2[Ni^{II}(MeOH)_2]\cdot3H_2O\cdot8MeOH$ (4),\textsuperscript{5,56} gives an $S_T = 6$ ground state. Both complexes show slow magnetic relaxation below ca. 4 K. Interestingly the higher nuclearity cluster gives a lower SMM energy barrier, which is ascribed to an unfavorable orientation of its anisotropy tensors and twisted structure, in comparison to the more symmetrical hexanuclear analogue (Figure 4.35). In the octanuclear case, $\{(Tp^*Me)Fe^{III}(CN)_3\}_4[Ni^{II}(tren)]_4[ClO_4]_4\cdot7H_2O\cdot4MeCN$ (5),\textsuperscript{4,10,56} the 4:4 ratio of ferromagnetically coupled Fe$^{III}$ and Ni$^{II}$ metal centers give an $S_T = 6$ spin ground state with the highest reported SMM energy barrier until ca. 2012 ($U_{eff} = \sim 33$ K) for first row cyanide-based single molecule magnets. The centrosymmetric structure of 5 likely gives the highest SMM energy barrier of the series owing to its parallel arrangement of Be⋯B axes and their magnetic anisotropy tensors. Octanuclear cluster shows slow relaxation of magnetization. This clearly strengthens our hypothesis spin and cluster anisotropy arising from structure may be systematically tuned to give tailored magnetic properties within a family of structurally related complexes.\textsuperscript{4,5,10,14,56}
4.10 General Overview: Cyanide-Based Single Molecule Magnets.

Comparing the magnetic properties of various Fe$^{III}$/Ni$^{II}$ complexes to one another suggests that those with significantly bent Ni$^{II}$ ($\mu$-NC)Fe$^{III}$ units give complexes with weak ferromagnetic couplings. Consequently they are not single-molecule magnets. In ferromagnetically coupled {Fe$^{III}$$^4$Ni$^{II}$$^4$} octanuclear complexes, identical spin ground states cannot explain the differences between the apparent magnetic anisotropy and slow magnetic relaxation seen. This suggests that structural feature as well as magnetic ones play an important role in establishing overall magnetic anisotropy.$^4,^{10,50,56}$ For example, in 5 and cubic {[(pzTp)Fe$^{III}$,(CN)$_3$]$^4$-[Ni$^{II}$(2,2,2-tris(pyrazolyl)ethanol)]$_4$[OTf]$_4$} $^{10}$DMF.Et$_2$O (6) (Figure 4.37b) identical exchange parameters were found [$J_{iso}/k_B = 9.5(5)$ vs $9.5(1)$ K] while fits of the $\chi T$ vs $T$ data indicates significantly different magnetic anisotropy is present, as reflected in their $D/k_B$ [-0.33(5) vs -1.29(2) K] and $g_{iso}$ [2.20(5) vs 2.60(5)] parameters.$^4,^{10,50}$ From an experimental standpoint, we are able to observe slow magnetic relaxation at milliKelvin temperatures for 6, owing to small energy barriers between states that allow for fast quantum tunneling.$^{10}$

In contrast, 5 has higher SMM energy barriers and we are able to follow the slower magnetic relaxation at higher energies (and temperatures). This suggests that the energy barriers to magnetization reversal [$U_{eff}/k_B = 12$ vs 33 K], for 6 and 5, respectively, are dependent on the structures of the complexes.$^4,^{10,50}$ If the SMM energy barriers are correlated with the relative orientations of their Fe···B axes (Figure 4.36), then the molecular {Fe$^{III}$$^4$Ni$^{II}$$^4$} box probably experiences nearly complete cancellation of the orbital angular momentum that from each Ni$^{III}$ and
Figure 4.36. Alignment of proposed B···Fe anisotropy vectors (blue lines) in (a) $\{[(Tp^*Me)Fe^{III}(CN)_3]_4[Ni(DMF)_3]_2\cdot4DMF\cdotH_2O \ (3), \ (b) \ \{[(pzTp)Fe^{III}(CN)_3]_4-[Ni^{III}(2,2,2-tris(pyrazolyl)ethanol)]_4[OTf]_4\cdot10DMF\cdotEt_2O, \ (c) \ \{[(Tp^*Me)Fe^{III}(CN)_3]_4-[Ni^{III}(tren)]_4[ClO_4]_4\cdot7H_2O\cdot4MeCN \ (5), \ and \ (d) \ \{[(Tp^*Me)Fe^{III}(CN)_3]_6-[Ni^{III}(MeOH)_3]_2[Ni^{II}(MeOH)_2]\} \cdot3H_2O\cdot8MeOH \ (4).^{4,5,14}$
Fe\textsuperscript{III} site, leading to a small spin reversal barrier for the complex (6). Given that 5 is a C\textsubscript{2}-symmetric \{Fe\textsuperscript{III}\textsubscript{4}Ni\textsuperscript{II}\textsubscript{4}\} complex, we propose that a preferential and parallel alignment of the putative anisotropy tensors leads to a significantly higher \( U_{\text{eff}} \) value.\textsuperscript{4,10,50} These differences in magnetic behavior underscore the importance of a building block synthetic approach for designing and tuning single-molecule magnetic materials.

**4.11 Experimental: Materials.** All operations were conducted under an argon atmosphere by using standard Schlenk and drybox techniques. Transfers of solutions containing cyanide were carried out through stainless steel cannulas. Solvents were distilled under dinitrogen from CaH\textsubscript{2} (acetonitrile), sodium-benzophenone (diethyl ether) and sparged with argon prior to use. Dimethylformamide (DMF) was dried using activated alumina (VAC atmospheres) and sparged with argon prior to use. The preparation of Ni(OTf)\textsubscript{2}\textsuperscript{55} and [NEt\textsubscript{4}][(Tp\textsuperscript{Me}*)Fe(CN)\textsubscript{3}].H\textsubscript{2}O\textsuperscript{4} are described elsewhere. NiCl\textsubscript{2}.6H\textsubscript{2}O (Acros), and Ni(ClO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O (Acros), and tris(2-aminoethyl)amine (tren; Acros) were used as received from their respective manufacturers.

**Physical Measurements.** The infrared spectra were recorded as Nujol mulls between KBr plates on Thermo-Electron Nicolet 6700 FTIR instruments in the 400-4000 cm\textsuperscript{-1} range. Magnetic measurements on polycrystalline samples of 1-5 were conducted on a Quantum Design SQUID MPMS-XL and PPMS-9 magnetometers in the 1.8-300 K temperature range. Alternating current (ac) susceptibility
measurements were conducted using an oscillating ac field of 3 Oe with frequencies ranging from 10 to 10000 Hz. The magnetic data were corrected for the sample holder and while diamagnetic contributions were estimated using Pascal's constants. Elemental analyses performed by Robertson Microlit Laboratories. Although no problems were encountered during our studies, cyanides are toxic and perchlorate salts are potentially explosive. Both should be handled with care. Structures determinations were done by Dr. Yuanzhu Zhang and Dr. Nigam P. Rath from University of Missouri St. Louis. Magnetic measurements were done by Dr. Stephen Hill from National High Magnetic Field Laboratory at Tallahassee and Dr. Rodolphe Clerac from Universite de Bordeaux. Theoretical calculations were done by Dr. Benjamin J. Bythell from University of Missouri St. Louis.

**Structure Determinations and Refinements.** X-ray structural data were collected at 90.0(2) and 100.0(2) K for 1-5, respectively, on Nonius Kappa CCD and Bruker APEX-II CCD diffractometers. Crystals were mounted in Paratone-N oil on glass fibers and the structures were solved by direct methods (SHELXS97) and completed by difference Fourier methods (SHELXL97). Refinement was performed against $F^2$ by weighted full-matrix least-squares (SHELXL97), and empirical absorption corrections (SADABS) were applied. Hydrogen atoms were found in difference maps and subsequently placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters and atomic scattering factors were taken from the *International Tables*.
Crystal data and selected details of structure determinations and geometrical parameters appear in Tables 4.1-4.4.

**Synthesis of \{[(Tp*Me)Fe^{III}(CN)_3]_2[Ni^{II}(DMF)_4]_2[OTf]_2\}·2DMF (1).** Treatment of [NEt₄][(Tp*Me)Fe(CN)_3]·H₂O (0.122 g, 0.196 mmol) with Ni(OTf)₂ (0.107 g, 0.300 mmol) in DMF (10 mL) under an argon atmosphere afforded a red solution that allowed to stir for 1 h. The filtrate was layered with Et₂O (50 ml) and allowed to stand for 7d. The dark red blocks were isolated via filtration and dried under vacuum for 2 min at room temperature. Yield: 116 mg (56.0 %). Anal. Calcd: C, 42.47; H, 6.07; N, 18.74. Found: C, 42.39; H, 5.78; N, 18.60. IR (Nujol, cm⁻¹): 2549 (m), 2166 (s), 2118 (m), 1674 (vs), 1645 (vs), 1559 (w), 1516 (w), 1495 (m), 1457 (vs), 1377 (vs), 1271 (s), 1240 (s), 1224 (m), 1172 (w), 1145 (s), 1103 (s), 1059 (m), 1031 (s), 888 (s), 872 (m), 832 (s), 752 (w), 736 (m), 720 (m), 680 (s), 658 (w), 638 (s), 569 (w), 547 (m), 517 (m).

**Synthesis of \{[(Tp*Me)Fe^{III}(CN)_3]_2[Ni^{II}(DMF)_4]_2[ClO_4]_2\}·3MeCN·2H₂O·MeOH (2).** Treatment of Ni(ClO₄)₂·6H₂O (0.073 g, 0.20 mmol) with bpy (0.063 g, 0.41 mmol) in MeCN (5 mL) afforded a purple mixture which was stirred for 10 min. Addition of [NEt₄][(Tp*Me)Fe^{III}(CN)_3]·H₂O (0.124 g, 0.200 mmol) in methanol (10 mL) afforded a dark red solution, that was filtered, and allowed to stand for 7 d. Dark red rectangular crystals were collected via filtration and dried under vacuum for 2 min at room temperature. Yield: 135 mg (64.9 %). Anal. Calcd: C, 51.43; H, 5.09; N, 19.54. Found: C, 50.91; H, 5.01; N, 18.99. IR (Nujol, cm⁻¹): 3426 (br, m), 3112 (w), 3092 (w), 3079 (w), 2555 (m), 2261 (m), 2250 (m), 2155 (vs), 2129 (m), 1644 (m), 1599 (vs), 1575 (m), 1567 (s), 1520 (s), 1490 (m), 1474 (w), 1429 (s),
1386 (m), 1360 (m), 1311 (m), 1239 (vs), 1191 (w), 1172 (m), 1154 (w), 1092 (vs),
1081 (vs), 1023 (s), 932 (w), 921 (w), 905 (w), 887 (w), 871 (m), 833
(m), 815 (w), 771 (vs), 738 (s), 688 (m), 667 (w), 652 (m), 623 (s), 544 (w).

**Synthesis of \[\{(Tp^{*}\text{Me})\text{Fe}^{\text{III}}(\text{CN})_{3}\}_{4}[\text{Ni}^{\text{II}}(\text{DMF})_{3}]_{2}\}\cdot4\text{DMF}\cdot2\text{H}_{2}\text{O} \ (3).**

Treatment of \[^{18}\text{NEt}_4\]^{[}\{(Tp^{*}\text{Me})\text{Fe}^{\text{III}}(\text{CN})_{3}\}\cdot\text{H}_{2}\text{O} (186.0 \text{ mg, } 0.299 \text{ mmol}) with NiCl$_2$·6H$_2$O (47.2 mg, 0.198 mmol) in a 2:1 ratio in DMF (10 mL) afforded a dark red solution that was stirred for 20 min. The mixture was filtered, layered with Et$_2$O (50 ml), and allowed to stand 7 days. The red rods were isolated via filtration, washed with DMF (3 ml), and dried under vacuum for 2 min at room temperature. Yield: 198 mg (48.1 %).

Anal. calcd for C$_{114}$H$_{184}$N$_{46}$O$_{11}$B$_4$Ni$_2$Fe$_4$: C 49.63; H 6.72; N 23.35. Found: C, 49.90; H, 6.81; N, 23.28. IR (Nujol, cm$^{-1}$): 2528 ($\nu$ BH, m), 2173 ($\nu$ CN, s), 2148, 2115 ($\nu$ CN, m).

**Synthesis of \[\{(Tp^{*}\text{Me})\text{Fe}^{\text{III}}(\text{CN})_{3}\}_{6}[\text{Ni}^{\text{II}}(\text{MeOH})_{3}]_{2}[\text{Ni}^{\text{II}}(\text{MeOH})_{2}]\}\cdot3\text{H}_{2}\text{O}\cdot8\text{MeOH} \ (4).**

Treatment of \[^{18}\text{NEt}_4\]^{[}\{(Tp^{*}\text{Me})\text{Fe}^{\text{III}}(\text{CN})_{3}\}\cdot\text{H}_{2}\text{O} (188.0 \text{ mg, } 0.303 \text{ mmol}) in MeOH (20 ml) with NiCl$_2$·6H$_2$O (43.5 mg, 0.183 mmol) in MeOH (20 mL) afforded a dark red solution, which was filtered and allowed to stand 7 days. The red blocks were isolated via filtration, washed with methanol (5 mL), and dried under vacuum for 2 min at room temperature. Yield: 115 mg (64.1 %). Anal. calcd for C$_{142}$H$_{238}$B$_6$Fe$_6$N$_{54}$Ni$_3$O$_{17.5}$: C 47.94; H 6.74; N 21.35. Found: C, 46.90; H, 6.50; N, 22.02. IR (Nujol, cm$^{-1}$): 2533 ($\nu_{\text{BH}}$, m), 2165 ($\nu_{\text{CN}}$, s), 2148, 2115 ($\nu_{\text{CN}}$, m). Dissolution of 1 into MeOH also affords crystals of 2 within four days.

**Synthesis of \[\{(Tp^{*}\text{Me})\text{Fe}^{\text{III}}(\text{CN})_{3}\}_{4}[\text{Ni}^{\text{II}}(\text{tren})]_{4}[\text{ClO}_4]\}\cdot7\text{H}_{2}\text{O}\cdot4\text{MeCN} \ (5).**

Under argon treatment of \[^{18}\text{Ni(OH}_2\text{)}_6\]^{[}\text{ClO}_4]$_2$ (73.0 mg, 0.200 mmol) with tren (30.5 mg,
0.209 mmol) in 1:1 (v/v) MeCN/MeOH (10 mL) gave a purple mixture that was stirred for 10 min. A methanolic (10 mL) solution of [NEt₄][(Tp*Me)Fe(CN)₃]·H₂O (124.5 mg, 0.200 mmol) was added and the resulting dark red mixture was filtered. After 1 week dark red tablets were isolated via suction filtration, washed with Et₂O (2 × 5 mL), and dried under vacuum for 2 min. at room temperature. Yield: 84.0 mg (49.4%). Anal. Calcd for C₁₁₂Cl₄H₂₀₄N₅₄O₂₃B₄Fe₄Ni₄: C, 40.31; H, 6.18; N, 22.65%. Found: C, 40.30; H, 6.35; N, 22.56%. IR (Nujol, cm⁻¹): 3383 (m), 3351 (m), 3304 (m), 2740 (w), 2541 (m), 2251 (w), 2156 (s), 2141 (m), 2130 (s), 2114 (m), 1604 (m), 1562 (w), 1516 (m), 1365 (s), 1243 (vs), 1173 (m), 1098 (vs), 1049 (s), 1027 (s), 998 (s), 979 (s), 930 (w), 883 (m), 874 (m), 834 (m), 736 (m), 690 (w), 667 (w), 651 (w), 625 (s), 606 (w), 561 (w), 540 (m).

4.12 References.


Vita

Uma Prasad Mallik received his Bachelor of Science with Chemistry Honors from Calcutta University in 1999, Masters of Science in Organic Chemistry from Indian Institute of Technology (IIT) Bombay in 2001, Masters of Science in Chemistry from University of Kentucky in 2008 and Graduate Certificate in College Teaching and Learning from Preparing Future Faculty (PFF) Program at University of Kentucky in 2009. He taught as instructor of Chemistry at Cochise College, Arizona (2010-2011) and teaches as an adjunct to Cochise College Online campus (2011-2017). He teaches as Instructor of Science at Southern Arkansas University, Arkansas (2011-2017). He is working under supervision of Professor Stephen M. Holmes towards his Ph. D. in Chemistry at University of Missouri St. Louis.

Publications from University of Missouri St. Louis (UMSL):


5. Tang, M.; Li, D.; Mallik, U. P.; Zhang, Y.-Z.; Clérac, R.; Yee, G. T.; Whangbo,


**Publications from Others:**


