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SYNTHESES, STRUCTURES AND MAGNETIC CHARACTERIZATION OF DI- AND TRIVALENT HYDRIDOTRIS(3,5-DIMETHYLPYRAZOL-1-YL)BORATE CYANOMANGANANATES

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SYNTHESSES, STRUCTURES AND MAGNETIC CHARACTERIZATION OF DI- AND TRIVALENT HYDRIDOTRIS(3,5-DIMETHYLPYRAZOL-1-YL)BORATE CYANOMANGANATES

The syntheses, structures, and magnetic properties of a series of di/trivalent hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*) cyanomanganates were investigated. Treatment of manganese(II)acetylacetonate with KTp* followed by tetra(ethyl)ammonium cyanide affords \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\text{acac})(\text{CN})]\) (1). Attempts to oxidize 1 with iodine affords \{[\text{Tp}^*]\text{Mn}^{\text{II}}(\kappa_2\text{O-acac-CN})\}_n (7); a minor complex \{[\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa_2\text{O-acac-3-CN})]\}_2(\mu-\text{CN}) (8) was also isolated.

The manganese(II) complex \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2\text{O-acac-3-CN})(\kappa_1^f\text{N-3-NC-acac})]\) (2) was obtained via treatment of \(\text{Mn}(3\text{-acacCN})_3\) with KTp* and \([\text{NEt}_4]\text{CN}\). \([\text{NEt}_4][\text{Mn}^{\text{II}}(\text{CN})_6]\) (3) was prepared via treatment of \(\text{Mn}^{\text{II}}(\text{OTf})_2\) with excess \([\text{NEt}_4]\text{CN}\). \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3]\) (4), is prepared via treatment of 4 with \(\text{Mn}(3\text{-acacCN})_3\), KTp* and excess \([\text{NEt}_4]\text{CN}\). \([\text{PPN}][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3]\) (5) is obtained via treatment of \([\text{PPN}][\text{Mn}^{\text{II}}(\text{CN})_6]\) with \((\text{Tp}^*)\text{SnBu}_2\text{Cl}\).

Combination of 4 with \([\text{Mn}^{\text{II}}(\text{bipy})_2(\text{OH}_2)_2][\text{OTf}]_2\) afforded a tetranuclear rectangular cluster \{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2\} (9). At low temperature, \{\text{Mn}^{\text{III}}_2\text{Ni}^{\text{II}}_2\} (10) was prepared via treatment of 4 and \([\text{Ni}(\text{II})(\text{bipy})_2(\text{H}_2\text{O})_2][\text{OTf}]_2\). Treatment of 4 with \([\text{Co}^{\text{II}}(\text{bipy})_2(\text{OH}_2)_2][\text{OTf}]_2\) at low temperature failed to give the desired \{\text{Mn}^{\text{III}}_2\text{Co}^{\text{II}}_2\} complex.

Magnetic measurements indicate that 1, 2, and 7 contain high-spin isotropic Mn^{II} with no long-range magnetic order observed for 7 \((T > 2 \text{ K})\); 4 contains low-spin Mn^{III} that likely adopt an isotropic \(^3\text{A}_2\) spin ground state. Surprisingly 9 and 10 do not exhibit slow relaxation of the magnetization \((T > 1.8 \text{ K})\) despite the presence of significant molecular anisotropy.

KEYWORDS: Single Molecule Magnet, Anisotropy, Cyanomanganates, Tetranuclears Rectangle Cluster, Magnetic Materials

Minao Tang
June 20, 2008
SYNTHESES, STRUCTURES AND MAGNETIC CHARACTERIZATION OF DI- AND TRIVALENT HYDRIDOTRIS(3,5-DIMETHYLPYRAZOL-1-YL)BORATE CYANOMANGANATES

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June 20th, 2008
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THESIS

Minao Tang

The Graduate School
University of Kentucky
2008
SYNTHESES, STRUCTURES AND MAGNETIC CHARACTERIZATION OF DI- AND TRIVALENT HYDRODITRIS(3,5-DIMETHYLPIRAZOL-1-YL)BORATE CYANOMANGANATES

THESIS

A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in the college of Art and Sciences at the University of Kentucky

By

Minao Tang

Lexington, Kentucky

Director: Dr. Stephen M. Holmes, Assistant Professor of Chemistry

Lexington, Kentucky

2008

Copyright © Minao Tang 2008
This thesis is dedicated to my family: my wife, Dongtao Cui, my daughter, Yining Tang, my parents, and brother.
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# TABLE OF CONTENTS

Acknowledgments .................................................................................................................. iii  
List of Tables .......................................................................................................................... v  
List of Figures .......................................................................................................................... vi  
List of Schemes ........................................................................................................................ ix  

Chapter One: Requirements for Observing Slow Relaxation of the Magnetization  
Introduction ............................................................................................................................ 1  
Strategies ................................................................................................................................ 4  
Outlook and Future Directions .............................................................................................. 9  

Chapter Two: Synthesis, Structural and Magnetic Characterization of Di- and Trivalent  
Hydridotris(3,5-dimethylpyrazol-1-yl)borate Cyanomanganates  
Introduction ............................................................................................................................ 14  
Experimental Section ............................................................................................................. 18  
Results and Discussion ............................................................................................................ 22  
  Synthesis and spectroscopic characterization ....................................................................... 22  
  Crystallographic studies ........................................................................................................ 27  
  Magnetic studies .................................................................................................................... 39  
Conclusions .............................................................................................................................. 48  

Chapter Three: Syntheses, Structures, and Magnetic Characterization of a  
Cyanomangante Network and Polynuclear Complexes  
Introduction ............................................................................................................................ 49  
Experimental Section ............................................................................................................. 51  
Results and Discussion .......................................................................................................... 53  
  Synthesis and spectroscopic characterization ....................................................................... 54  
  Crystallographic studies ........................................................................................................ 57  
  Magnetic studies .................................................................................................................... 59  
Conclusions .............................................................................................................................. 72  

References ............................................................................................................................... 84  
Vita ......................................................................................................................................... 89
LIST OF TABLES

Table 2.1. Crystallographic Data for $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac})(\text{CN})]\text{]}\text{ }\text{(1)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})(\kappa^1N\text{-3-NC-acac})]\text{]}\text{ }\text{(2)}$, $\text{[NEt}_4\text{][}\text{Mn}^{\text{II}}(\text{CN})_4]\text{]}\text{ }\text{(3)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{III}}(\text{CN})_3]\text{]}\text{ }\text{(4)}$, $\text{[PPN][}\text{(Tp*)Mn}^{\text{III}}(\text{CN})_3]\text{]}\text{ }\text{(5)}$, and $\text{[Cp}_2\text{Co}^{\text{III}}\text{]}\text{ }\text{[Mn}^{\text{II}}(\text{CN})_6]\text{]}\text{ }\text{(6)}$........................................................................30

Table 2.2. Selected Bond Distances (Å) for $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-2-acac})\text{-}(\text{CN})]\text{]}\text{ }\text{(1)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-2-acac-3-CN})(\kappa^1N\text{-1-3-NC-acac})]\text{]}\text{ }\text{(2)}$, $\text{[NEt}_4\text{][}\text{Mn}^{\text{II}}(\text{CN})_4]\text{]}\text{ }\text{(3)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{III}}(\text{CN})_3]\text{]}\text{ }\text{(4)}$, $\text{[PPN][}\text{(Tp*)Mn}^{\text{III}}(\text{CN})_3]\text{]}\text{ }\text{(5)}$, and $\text{[Cp}_2\text{Co}^{\text{III}}\text{]}\text{ }\text{[Mn}^{\text{II}}(\text{CN})_6]\text{]}\text{ }\text{(6)}$........................................................................31

Table 2.3. Selected Bond Angles (deg) for $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac})(\text{CN})]\text{]}\text{ }\text{(1)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})(\kappa^1N\text{-3-NC-acac})]\text{]}\text{ }\text{(2)}$, $\text{[NEt}_4\text{][}\text{Mn}^{\text{II}}(\text{CN})_4]\text{]}\text{ }\text{(3)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{III}}(\text{CN})_3]\text{]}\text{ }\text{(4)}$, $\text{[PPN][}\text{(Tp*)Mn}^{\text{III}}(\text{CN})_3]\text{]}\text{ }\text{(5)}$, and $\text{[Cp}_2\text{Co}^{\text{III}}\text{]}\text{ }\text{[Mn}^{\text{II}}(\text{CN})_6]\text{]}\text{ }\text{(6)}$........................................................................32

Table 3.1. Crystallographic Data for $\{(\text{Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})\}_n\text{ }\text{(7)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-2-acac-3-CN})(\mu\text{-CN})\text{]}\text{ }\text{(8)}$, $\{(\text{Tp*)Mn}^{\text{III}}(\text{CN})_3\}_2\text{ }\text{[Mn}^{\text{II}}(\text{bipy})_2\text{]}\text{ [OTf]}_2\text{]}\text{ }\text{(9)}$, and $\{\text{cis-Co}^{\text{III}}(\text{CN})_2(\text{bipy})_2\text{]}\text{ [OTf]}\text{]}\text{ }\text{(11)}$ ........................................................................................................61

Table 3.2. Selected Bond Distances (Å) for $\{(\text{Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})\}_n\text{ }\text{(7)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})(\mu\text{-CN})\text{]}\text{ }\text{(8)}$, $\{(\text{Tp*)Mn}^{\text{III}}(\text{CN})_3\}_2\text{ }\text{[Mn}^{\text{II}}(\text{bipy})_2\text{]}\text{ [OTf]}_2\text{]}\text{ }\text{(9)}$, and $\{\text{cis-Co}^{\text{III}}(\text{CN})_2(\text{bipy})_2\text{]}\text{ [OTf]}\text{]}\text{ }\text{(11)}$ ........................................................................62

Table 3.3. Selected Bond angles (deg) for $\{(\text{Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})\}_n\text{ }\text{(7)}$, $\text{[NEt}_4\text{][}\text{(Tp*)Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})(\mu\text{-CN})\text{]}\text{ }\text{(8)}$, $\{(\text{Tp*)Mn}^{\text{III}}(\text{CN})_3\}_2\text{ }\text{[Mn}^{\text{II}}(\text{bipy})_2\text{]}\text{ [OTf]}_2\text{]}\text{ }\text{(9)}$, and $\{\text{cis-Co}^{\text{III}}(\text{CN})_2(\text{bipy})_2\text{]}\text{ [OTf]}\text{]}\text{ }\text{(11)}$ ........................................................................63
LIST OF FIGURES

Figure 1.1. Energy level diagram for an $S = 10$ ground state with an axial zero-field splitting of $D < 0$, showing the spin-reversal barrier $\Delta E = |DS_z^2| = 100|D|$ ................................................................. 10

Figure 1.2 Illustration of the origin of slow relaxation of the magnetization ................. 11

Figure 1.3. Structure of ligands: (a) tris(pyrazolyl)borate (Tp), (b) tris(3, 5-dimethylpyrazolyl)borate (Tp*), (c) tetra(pyrazolyl)borate (pzTp) ......................................................... 12

Figure 1.4. Simplified molecular orbital diagram for predicting sign of superexchange interaction in M($\mu$-CN)M$^-$ units ............................................ 13

Figure 2.1. Truncated X-ray structure of 1. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity ......................................................... 33

Figure 2.2. Truncated X-ray structure of 2. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity ......................................................... 34

Figure 2.3. Truncated X-ray structure of 3. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity ......................................................... 35

Figure 2.4. Truncated X-ray structure of 4. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity ......................................................... 36

Figure 2.5. Truncated X-ray structure of 5. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity ......................................................... 37

Figure 2.6. Truncated X-ray structure of 6. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity ......................................................... 38

Figure 2.7. Temperature dependence of the $\chi T$ product of 1 between 1.85 and 300 K for $H_{dc} = 1$ kG ................................................................. 40

Figure 2.8. Field dependence of the magnetization of 1 at 1.85 K between 0 and 7 T ................................................................. 41
Figure 2.9. Temperature dependence of the $\chi T$ product of 2 between 1.85 and 300 K for $H_{dc} = 1$ kG .................................................................42

Figure 2.10. Field dependence of the magnetization of 2 at various temperatures ($0 \leq H_{dc} \leq 7$ T) ...........................................................................43

Figure 2.11. Field dependence of the reduced magnetization of 2 ($1.8 \leq T \leq 8$ K) ..................44

Figure 2.12. Temperature dependence of the $\chi T$ product of 4 between 1.85 and 300 K for $H_{dc} = 1$ kG .................................................................45

Figure 2.13. Field dependence of the magnetization of 4 at 1.85 K between 0 and 7 T .................................................................46

Figure 3.1. Truncated X-ray structure of asymmetric unit of 7. Thermal ellipsoids are at the 50% level and all hydrogen atoms and lattice solvent are removed for clarity .........................................................64

Figure 3.2. Truncated X-ray structure of zig-zag chain of 7. Thermal ellipsoids are at the 50% level and all hydrogen atoms and lattice solvent are removed for clarity .........................................................65

Figure 3.3. Truncated X-ray structure of 8. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity .........................................................66

Figure 3.4. Truncated X-ray structure of 9. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity .........................................................67

Figure 3.5. Truncated X-ray structure of 11. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity .........................................................68

Figure 3.6. Temperature dependence of the $\chi T$ product of 7 between 1.85 and 300 K for $H_{dc} = 1$ kG .................................................................74

Figure 3.7. Field dependence of the magnetization of 7 at 1.85 K between 0 and 7 T .................................................................75

Figure 3.8. Temperature dependence of the $\chi T$ product of 9 between 1.85 and 300 K at $H_{dc} = 1$ (•) and 10 (•) kG .................................................................76

Figure 3.9. MAGPACK simulation of $\chi T$ vs $T$ data (—) for 9 at $H_{dc} = 1$ kG ..........77

Figure 3.10. Field dependence of the magnetization for 9 at 1.85 K ($0 \leq H_{dc} \leq 7$ T) ..........78
Figure 3.11. Temperature dependence of the $\chi T$ product of 10 between 1.85 and 300 K at $H_{dc} = 1$ (•) and 10 (•) kG .................................................................79

Figure 3.12. Fit of the $\chi T$ vs $T$ data (—) for 10 at 1 kG between 1.8 and 300 K.................80

Figure 3.13. Fit of the $\chi T$ vs $T$ data (—) for 10 at 1 kG between 30 and 300 K.................81

Figure 3.14. Field dependence of the magnetization for 10 at various temperatures ($0 \leq H_{dc} \leq 7$ T)..........................................................82

Figure 3.15. $M$ vs $HT^{-1}$ for 10 at various temperatures ($0 \leq H_{dc} \leq 7$ T).........................83
LIST OF SCHEMES

Scheme 1.1.  The synthesis route for preparing \([\text{NEt}_4]_{(m-n+1)}[(L)\text{M}^n(\text{CN})_m]\)
building blocks \((L = \text{Tp}^*, \text{Tp}, \text{pzTp}; n = 2, 3)\) ........................................6

Scheme 2.1.  The initial synthesis route for \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3]\) .........................22

Scheme 2.2.  Synthesis of \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2\text{O}\text{-acac})(\text{CN})](1)\) ........................................23

Scheme 2.3.  Synthesis of compound \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2\text{O}\text{-acac-3-CN})
-\{(\kappa^2\text{N}\text{-3-NC}\text{-acac})\}^{1/2}\text{Et}_2\text{O}\) (2) ..................................................24

Scheme 2.4.  Synthesis of \([\text{NEt}_4]_2[\text{Mn}^{\text{II}}(\text{CN})_4]\) (3) .......................................................25

Scheme 2.5.  Synthesis of \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3]\) (4) and \([\text{PPN}][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3]\) ........................................26

Scheme 3.1.  Synthesis of \([][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2\text{O}\text{-acac}-3-CN)]_n\) (7) and \([\text{NEt}_4][(\text{Tp}^*)
-\text{Mn}^{\text{II}}(\text{acac-CN})-(\mu\text{-CN})(\text{Tp}^*)\text{Mn}^{\text{II}}(\text{acac-CN})]\cdot\text{MeCN}^{1/2}\text{Et}_2\text{O}\) (8) ...............54

Scheme 3.2.  Syntheses of rectangular tetranuclear cyanometalate clusters ..................56

Scheme 3.3.  Syntheses of \([\text{cis-Co}^{\text{III}}(\text{CN})_2(\text{bipy})_2][\text{OTf}]\) ..................................................57
Chapter One: Requirements for Observing Slow Relaxation of the Magnetization.

Introduction.

Single-Molecule Magnets. Magnetic materials are technologically important materials that find use 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, thus limiting 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) concomitantly decreases, eventually becoming comparable to available thermal energy. While these smaller magnetic particles offer the prospect of decreasing device size and as a function of 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.

Despite these limitations, nanoscale magnets remain attractive as potential switchable components in devices applications. A particularly attractive class of magnetic materials is those known collectively as single-molecule magnets (SMMs). These nanoscale magnets are soluble, single domain superparamagnetic molecules that often exhibit high spin ground states, large and negative axial (uniaxial Ising-like) magnetic anisotropy ($D < 0$), low-symmetry molecular shapes (e.g. disk-shaped, butterfly), and high spin reversal barriers (Figure 1.1), on the order of $\frac{S^2 |D|}{k_B} < 50 \text{ cm}^{-1}$.$^{1-14}$ While the magnetic hysteresis and bistability exhibited by these clusters are proposed to be useful for molecule-based memory applications engineering and predicting cluster properties remain a formidable synthetic and theoretical challenge. Furthermore, thermal magnetization reversal in these clusters becomes energetically favorable at extremely low temperatures ($ca. T < 4 \text{ K}$) and increasing this “blocking temperature” is of fundamental interest and technological
importance.\textsuperscript{1-14}

A popular strategy that is often utilized in an attempt to increase apparent blocking temperatures of SMMs is to insert transition metal centers that possess even greater single-ion anisotropy, either via spin state (large zero-field splitting parameters, $D$) or orbital anisotropy (large spin-orbit coupling parameters, $\lambda$) into the cluster framework.\textsuperscript{15-25} However, the majority of SMM clusters contain first-row transition metals linked by oxo- and carboxylate bridges that exhibit relatively small zero-field splitting and spin-orbit coupling constant values, despite the presence of efficient superexchange interactions ($J$).

The first described single-molecule magnet is \{Mn$_{12}$O$_{12}$(O$_2$CMe)$_{16}$(OH)$_4$\}, which exhibits superparamagnetic-like behavior owing to the large spin ground state ($S = 10$) and uniaxial anisotropy ($D < 0$ and small $E$) derived from the low-symmetry transition metal centers present (Figure 1.1).\textsuperscript{1-14} Because the orbital contributions to the cluster anisotropy are essentially quenched, the molecules behave like spin systems where the barrier to magnetization reversal ($U$ or $\Delta$) is proportional to the first term in the Hamiltonian $DS_z^2$ ($D \approx -0.5$ cm$^{-1}$), where $D$ is the zero-field splitting value.\textsuperscript{4, 5, 7, 14} The Mn$_{12}$ cluster belongs to a class of inorganic clusters known as oxo-carboxylates, in which the paramagnetic metal centers are bridged by both -oxo and -carboxylato ligands. The $\mu^3$-oxo bridged ligands provide for the most efficient superexchange pathway ($J \sim 200$ cm$^{-1}$) in these clusters with Mn$_{12}$ exhibiting the highest reported blocking temperature (ca. 4 K) to date.

In single-molecule magnets an energy barrier ($U$) exists separating between two thermodynamically equivalent $m_S = \pm S$ configurations. Below $T_B$, the so-called “blocking temperature”, the available thermal energy is insufficient to overcome $\Delta$ and the spin is trapped in one of two possible configurations (Figure 1.2). Application of large magnetic fields ($H$) saturate the magnetization ($M$) of the sample, and upon removal of this field ($H = 0$), a slow decay of $M$ towards zero with a characteristic relaxation time ($\tau$) is observed. The relaxation time usually exhibits thermally activated behavior, and can be measured via magnetization ($M$) vs time or frequency ($\nu$) dependence of the ac susceptibility, respectively; at very low temperatures quantum tunneling of the magnetization ($QTM$) often relaxes the magnetization faster than thermally activated pathways.\textsuperscript{4, 5} However,
systematic substitution of the transition metal centers present in these clusters remains a difficult synthetic challenge and consequently, significant enhancement of their blocking temperatures has not been realized, limiting their use in consumer products.\textsuperscript{4, 5, 7, 14}

Because the blocking temperature is closely related to the magnitude of the spin reversal barrier, which is also related to the global magnetic anisotropy, increasing this energy barrier could lead to progressively higher blocking temperatures. Since the global cluster anisotropy mainly arises from the single-ion anisotropy of the constituent transition metal centers present, introducing metal centers that exhibit greater anisotropy into the cluster framework, either via spin state (large zero-field splitting parameters, $D$) or orbital anisotropy (large spin-orbit coupling parameters, $\lambda$), is a potentially useful strategy to enhance the blocking temperatures of these compounds.\textsuperscript{15-19}

However, systematically tuning the magnetic behavior of oxo-carboxylate SMMs is synthetically difficult for a variety of reasons. First, the oxygen atom can bridge between two to six metal centers resulting in a range of M-O-M′ bond angles and structural archetypes. Second, the M-O-M′ angles and cluster geometry strongly influence the pair-wise magnetic exchange interactions making predictions of cluster magnetic properties rather difficult.\textsuperscript{5} Third, low-symmetry coordination environment and asymmetric crystal fields partially or fully quench the orbital angular momentum present at the paramagnetic centers consequently removing single-ion anisotropy and orbital degeneracy; weak single-ion and second-order anisotropy on metal centers is often the result of the highly distorted coordination spheres. Fourth, although the energy barrier to thermally activated magnetization reversal ($DS^2_z$) is proportional to the square of the ground state spin and negative zero-field splitting parameter ($D$), the large ground state spin ($S$) cannot significantly increase the energy barrier because the $DS^2_z$ term represents a second-order correction to the Hamiltonian involving spin-orbit coupling, and consequently $D$ usually adopts a small value;\textsuperscript{22} Furthermore, recent calculations suggest that $D$ scales as a function of $S^0$ rather than $S^2$, with $D(Mn_{12}) \sim -0.5$ cm$^{-1}$.\textsuperscript{6-9} Consequently we have sought to develop a systematic route for engineering molecular clusters that exhibit slow relaxation of the magnetization, by maximizing $D$ rather than the multiplicity of the spin ground state $S$. In the next section we will describe recent efforts in pursuit of these goals.
Strategies.

**Cyanometalate-based Magnetic Materials.** 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.$^{15-25}$ The cyanometalate clusters are constructed from $\text{M(} \mu$-$\text{CN)M'}$ units and contain a variety of transition metal centers that exhibit significant orbital anisotropy suggesting that this is a critical factor for constructing these materials. Cyanometalates are excellent building blocks for constructing molecule-based clusters because cyanides generally form linear $\mu$-$\text{CN}$ linkages between two metal centers, stabilize a variety of transition metal centers and oxidation states, and efficiently communicate spin density information. Furthermore, the sign and magnitude of the local exchange interactions can be controlled via substitution and often predicted using simple orbital symmetry arguments.$^{26-33}$

To prepare robust molecular clusters with predictable and tunable properties it is crucial to control the self-assembly of precursors during synthesis. To address these issues, we propose to synthesize several well-defined cyanometalate precursors (building blocks) that will self-assemble with structures intact, into a common structural archetype. Through this “building block approach,” the magnetic, optical, and electronic properties of resulting clusters can be altered in a systematic fashion, allowing for accurate magneto-structural correlations to be described.$^{34-44}$

Given the robust nature of most transition metal cyanide linkages and the relative ease in which they assemble into well-defined structures, we prepared a series of facially-capped tris- and tetra(pyrazolyl)borate di- and tricyanide complexes (building blocks) for use in magnetic cluster synthesis. The low-spin $\{(\text{Tp}^{R,H}_{R,H})\text{Fe}^{III}(\text{CN})_{3}\}$ ($R = \text{H, Me}; S = 1/2$) building blocks exhibit significant orbital contributions to the magnetic moment ($g = 2.9$), and upon treatment with a variety of divalent trifluoromethane-sulfonate salts, afford isostructural clusters; rectangular and “V-shaped” clusters exhibit slow magnetic relaxation behavior characteristic of SMMs.$^{16-19}$ To date, few tris(pyrazolyl)borate cyanometalate complexes are known and only a single systematic effort to prepare anisotropic cyanometalate clusters has been reported. Furthermore the importance of spin-orbit coupling in these clusters have only recently been investigated.$^{22,23}$
Recent studies indicate that cyanometalate clusters that contain paramagnetic centers with first-order spin-orbit coupling exhibit fundamentally different behavior than oxide-bridged clusters, in which the spin-orbit interaction is nearly quenched by the low-symmetry ligand environment.\textsuperscript{22,23} For these cyanide-based SMMs, the total angular momentum projection ($|M_J|$) is very important in establishing negative cluster anisotropy and an activation energy barrier ($U$) to thermal magnetization reversal. In contrast, oxide-bridged clusters are considered as spin systems where orbitally nondegenerate metal centers exhibit weak single-ion and second-order anisotropy, whose barrier heights ($U \sim S^2|D|$) are proportional to the spin ground state ($S$) and negative zero-field splitting parameter ($D$).\textsuperscript{22,23} Furthermore, fundamental questions concerning how paramagnetic and magnetically anisotropic spin centers interact and contribute to the magnetic ground state, impact magnetic exchange, effective barrier heights, and quantum tunneling of the magnetization have yet to be described for a series of structurally related cyano-metalate clusters, further limiting our understanding magnetic relaxation and quantum tunneling behavior in these materials.

In chapters two and three we will describe recent efforts to probe relationships between molecular shape and orbital anisotropy, $\pi$ backbonding, and superexchange efficiency in a series of rectangular magnetic clusters derived from $\pi$ backbonding, and superexchange efficiency in a series of rectangular magnetic clusters derived from tris(pyrazolyl)borate di- and tri-cyanides to determine how inserted transition metal centers impact magnetic and photomagnetic behavior in a given structural archetype. These studies have greatly assisted our understanding of how molecular symmetry, single-ion anisotropy, and superexchange efficiency translate into and impact overall cluster properties. In our synthetic building block approach we have investigated relationships between molecular shape and orbital anisotropy, $\pi$ backbonding, and superexchange efficiency in a series of rectangular clusters derived from tris(pyrazolyl)borate di- and tricyanides. Via systematic insertion of anisotropic transition metal centers into the framework, critical factors for constructing cyano-metalate clusters that exhibit tunable magnetic (possibly blocking temperatures), effective barrier heights, and optical properties were probed. Poly(pyrazolyl)borate building blocks are versatile reagents for constructing well-defined cyanometalate clusters:
(1) **Tris(pyrazolyl)borate ligands are easily prepared and modified at each of their ten substitutable positions.** This allows for facile tuning of solubility, dimensionality, and coordination preferences. The electronic properties of the metal centers can be tuned via substitution of the ligand backbone (Figure 1.3); most other tricyanide complexes contain ligands that are difficult to systematically alter (L = tacn, Me₃tacn, triphos).

![Diagram](image)

Scheme 1.

(2) **Tris(pyrazolyl)borate ligands stabilize multiple oxidation states for most transition metal centers.** Systematic variation of the transition metal centers and oxidation states affords several structurally related building blocks with similar coordination preferences. (Scheme 1.1) These complexes differ by the number of unpaired electrons, overall charge, symmetries, and energies of their molecular orbitals. *A variety of tris- and tetra(pyrazolyl)borate cyanometalate complexes and clusters containing a series of transition metal centers have been prepared (preliminary results).* Many contain low-valent early metals.

(3) **Few paramagnetic [fac-LM⁺⁺(CN)₂] and [fac-LM⁺⁺⁺(CN)₃] cyanometalate complexes are known and no low-valent early derivatives have been described.** Few complexes and clusters containing 1,4,7-trimethyl-1,4,7-triazacyclononane (Me₃tacn), 1,4,7-triazacyclononane (tacn), 1,3,5-triaminocyclohexane (tach), or triphos (1,1,1-tris(diphenylphosphanyl)methyl)ethane ligands are known and none contain low-valent
early metal ions; we recently reported the syntheses and characterization of several low-valent di- and tricyanometalates pzTp and Tp* analogues.\textsuperscript{15-19}

(4) Most cyanometalate clusters contain diamagnetic centers due to linkage isomerism or building block choice. Clusters containing tacn or Me\textsubscript{3}tacn building blocks often contain both paramagnetic and diamagnetic centers due to linkage isomerism and hydrolysis;\textsuperscript{5,20,55,58} those prepared from Cp and Cp* ligands only contain diamagnetic centers.\textsuperscript{65-69} However, [NEt\textsubscript{4}]{(m-n+1)}[LM\textsubscript{n}(CN)\textsubscript{m}] building blocks (L = Tp*-(hydridotris(3,5-dimethylpyrazol-1-yl)borate), Tp’(hydridotris(pyrazol-1-yl)borate), pzTp’(tetra(pyrazol-1-yl)borate); n = 2, 3) are versatile reagents for constructing robust clusters and networks which do not suffer from either linkage isomerism or hydrolysis, as the building blocks self-assemble within anhydrous solvents at room temperature;\textsuperscript{15-19} linkage isomerism is not seen in our clusters.

The primary objectives of these studies are to prepare and characterize a series of manganese cyanometalates and their cluster and network derivatives. In chapter two several di- and trivalent manganese building blocks are described while in chapter three the controlled aggregation of these complexes into a series of magnetic rectangular clusters and a network are described. Questions concerning how these spin centers interact and contribute to the magnetic ground state, impact magnetic exchange, effective barrier heights, and quantum tunneling of the magnetization are also described.

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. Furthermore the sign and magnitude of the local exchange interactions can be controlled via substitution and predicted by using simple orbital symmetry arguments.\textsuperscript{19,20} (Figure 1.4) Interestingly recent studies indicate there is a significant difference between the physical mechanism of the SMM behavior of cyanometalate-clusters, like [Mn\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{2-} [Mn\textsuperscript{II}(tmphen)\textsubscript{2}]\textsubscript{3} (tmphen = 3, 4, 7, 8-tetramethyl-1,10-phenanthroline), and the commonly accepted explanation that is valid for Mn\textsubscript{12} and other oxide-bridged spin
systems. In cyanometalate clusters such as \{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_3\} the \([\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}\) centers exhibit first-order orbital angular momentum contributions arising from spin-orbit interactions that cannot be described by the Hamiltonian term \(S_z^2\). For these cyanide-based SMMs, the total angular momentum projection (\(|M_J|\)) is very important in establishing negative cluster anisotropy and an activation energy barrier \((U)\) to thermal magnetization reversal. Calculations suggest that in \{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_3\}, assuming for simplicity that it adopts idealized \(C_3\) symmetry, the 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. Since the trigonal field in the \{\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_3\} 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 Mn\(^{\text{III}}\) centers. Related studies have been performed by Holmes and coworkers for \(C_3\) symmetric \([\text{(L)}\text{Fe}^{\text{III}}(\text{CN})_3]^-\) anions and \{\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}_2\} and \{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_2\} cluster derivatives (L = pyrazolylborate).

If spin-orbit interactions act to increase the magnitude of 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 act to enhance orbital contributions (via alteration of symmetry). Second, via insertion of second- and third row transition metal ions into cluster frameworks, single-ion anisotropy is expected to be enhanced due to greater spin-orbit coupling often found for these late transition metal centers (a relativistic effect).

Using a series of well-defined facially-capped tris- and tetra(pyrazolyl)borate di- and tricyanide complexes a series of structurally related magnetic clusters have been previously described by Holmes for use in magnetic cluster synthesis. The studies have focused primarily on the synthesis of clusters containing low-spin \([(\text{Tp}^{\text{R,R}})\text{-Fe}^{\text{III}}(\text{CN})_3]^-\)\((\text{R} = \text{H, Me}; S = \frac{1}{2})\) spin centers and a series of structurally related cluster derivatives. These tetraneuclear \{\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}_2\} and trinuclear \{\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}_2\} clusters exhibit slow magnetic relaxation behavior characteristic of many SMMs.

In addition to low-spin iron(III), Jahn-Teller distorted octahedral Mn\(^{\text{III}}\) ions are also promising for constructing additional SMM analogues, due to their expected single-ion anisotropy (via spin-orbit coupling). This thesis project was primarily focused on the
synthesizes, spectroscopic, crystallographic, and magnetic investigations of a variety of di- and trivalent hydridotris(3,5-dimethylpyrazol-1-yl)borate cyanomanganese building blocks, and their aggregation into well-defined cyanometalate clusters derivatives. These studies complement and significantly enhance our understanding of the factors necessary for engineering cyanometalate clusters that exhibit slow relaxation of the magnetization.

**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 in this class of magnetic materials, thus precluding their use as data storage bits in memory devices. Nevertheless such materials offer the prospect of probing the basic mechanism 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.
Figure 1.1 Energy level diagram for an Mn$_{12}$ cluster exhibiting an $S = 10$ ground state, a negative zero-field splitting value ($D$), and a thermal barrier to spin reversal ($U$) is proportional to $S_z^2|D|$. 

$m_s = -10$ 

$m_s = 0$ 

$m_s = 10$ 

"Up" Spin 

"Down" Spin 

Energy 

Magnetization Direction
Figure 1.2. Illustration of the origin of slow relaxation of the magnetization.
Figure 1.3. Idealized structures of (a) hydridotris(pyrazol-1-yl)borate (Tp), (b) hydridotris(3,5-dimethylpyrazol-1-yl)borate (Tp*), (c) tetra(pyrazol-1-yl)borate (pzTp), and (d) a poly(pyrazol-1-yl)borate tricyanometalate anion
Figure 1.4. Simplified molecular orbital diagram for predicting sign of superexchange interaction within M(μ-CN)M units.
Chapter 2: Syntheses, Structures, and Magnetic Characterization of Di- and Trivalent Hydridotris(3,5-dimethylpyrazol-1-yl)borate Cyanometalates.

Introduction.

Molecule-based materials that exhibit tunable magnetic and photomagnetic behavior is currently an active area of intense study due to their potential use in information storage technologies. Of molecule-based materials those derived from cyanometalate building blocks are especially attractive for constructing molecule-based networks and clusters that exhibit tunable magnetic and optical behavior. Via a building block synthetic approach, well-defined cyanometalate precursors (building blocks) are allowed to self-assemble with structures intact into a common structural archetype. Cyanometalates are especially attractive building blocks in that cyanide ligands generally stabilize a variety of transition metal centers and oxidation states, can efficiently communicate spin density information, and the products often contain linear M(μ-CN)M linkages. Moreover the sign and magnitude of the local magnetic exchange interactions can be controlled via substitution and often predicted by using simple orbital symmetry arguments. Through this synthetic approach the magnetic, optical, and electronic properties of the resulting products can be altered in a systematic fashion, allowing for accurate magneto-structural correlations to be described.

Recent studies indicate that polynuclear cyanometalate complexes that contain paramagnetic centers with first-order spin-orbit coupling exhibit fundamentally different behavior than oxide-bridged clusters, in which the spin-orbit interaction is nearly quenched by the low-symmetry ligand environment. For cyanide-based complexes that exhibit slow relaxation of the magnetization, the total angular momentum projection (|M_J|) appears to be critical for establishing negative cluster anisotropy and an activation energy barrier (Δ) to thermal magnetization reversal. In contrast, oxide-bridged clusters are considered as spin systems where orbitally non-degenerate metal centers exhibit weak single-ion and second-order anisotropy, whose barrier heights (Δ ∝ S^2|D|) are proportional to the square of the spin ground state (S) and negative zero-field splitting parameter (D).
The dominant building blocks for constructing polynuclear cyanometalate complexes are those of \([\text{fac-LM(CN)}_2]^{n^-}\) and \([\text{fac-LM(CN)}_3]^{n^-}\) general stoichiometry, where L is a facially coordinate tridentate ligand.\(^{20,23,24,25}\) These tridentate ligands limit the number and directionality of cyanide linkages formed often affording soluble polynuclear complexes (clusters). Via judicious choice of cyanometalate building blocks, namely those with orbital contributions to their magnetic moment (e.g. Fe\(^{III}\), Mn\(^{III}\), Mo\(^{III}\), Re\(^{II}\)), literature reports show that magnetic chains and polynuclear complexes that exhibit slow relaxation of the magnetization can be engineered. For example, we recently prepared several structurally related tricyano ferrate(III)-based clusters, that despite their low spin ground states \((1 \leq S \leq 6)\), exhibit rather large and negative zero-field splitting values \((\text{ca.} -5 \text{ cm}^{-1})\) and slow relaxation of the magnetization.\(^{15-19}\) While tuning the single-ion anisotropy can in principle be accomplished via alterations of the spin state (large zero-field splitting parameters, \(D\)) and/or orbital anisotropy (large spin-orbit coupling parameters, \(\lambda\)) via the use of various building blocks,\(^{22-25}\) predicting how these single-ion properties translate into the overall molecular magnetic anisotropy of a polynuclear complex still remains a formidable synthetic and theoretical challenge.

In order for cyanometalate-based polynuclear complexes to exhibit slow relaxation of the magnetization, anisotropic paramagnetic transition metal centers are clearly required, but surprisingly few pyrazolylborate cyanometalate-based analogues have been described, being solely limited iron and vanadium derivatives.\(^{22-29,31,32,35,36}\) Two years ago we initiated a concerted effort to prepare a series of anisotropic and structurally related cyanometalate building blocks that self-assemble into a common structural archetype.\(^{15-19}\) At the time, few \([\text{fac-}(L^x)\text{M}^n\text{(CN)}_m]^{(n-m-x)}\) complexes were known with only a single example containing tris(pyrazolyl)borate ligands.\(^{123}\) Tetra(pyrazolyl)borate (pzTp) and tris(3,5-dimethylpyrazolyl)borate (Tp\(^*\)) ligands were initially chosen for their solubility, number of known complexes, and ability to stabilize a variety of transition metal centers and oxidation states;\(^{15-19}\) most known paramagnetic di- and tricyano \([\text{(L}^x)\text{M}^n\text{(CN)}_m]^{(n-m-x)}\) complexes contain ligands that are often difficult to systematically alter.\(^{5,20-25,37}\)

Recent efforts have sought to expand the number of cyanometalate complexes that exhibit slow relaxation of the magnetization, by incorporating paramagnetic ions other than low-spin Fe\(^{III}\). Dunbar has reported that trigonal bipyramidal \([[\text{Mn}^{III}(\text{CN})_6]]^2-\)
Complexes of the form \([\text{Mn}^{II}L]_3\) exhibit magnetic relaxation that is characteristic of single-molecule magnets. However, rather low blocking temperatures are found for this neutral \({\text{Mn}^{III}_2\text{Mn}^{II}_3}\) complex and we reasoned that intercluster interactions may play a role in this fast relaxation of the magnetization or quantum tunneling of the magnetization (QTM) behavior. Given that tetranuclear cationic \({\text{Fe}^{III}_2\text{M}^{II}_2}\) (\(\text{M}^{II} = \text{Ni}, \text{Cu}\)) complexes exhibit comparable and in some cases higher blocking temperatures, in comparison to those containing low-spin \(\text{Mn}^{III}\) centers, we strived to prepare tricyanomanganate(III) analogues to probe whether (1) tricyanomanganate(III) clusters exhibit comparable magnetic behavior, (2) if more efficient superexchange interactions translate into higher blocking temperatures, and (3) investigate how changes in molecular symmetry impact QTM rates relative to \({\text{Fe}^{III}_2\text{M}^{II}_2}\) analogues.

A survey of the literature reveals that surprisingly few paramagnetic cyanomanganate complexes are known in comparison to reported diamagnetic analogues. For example, the dinuclear yellow dinitroso salt \(\text{K}_4[\text{Mn(CN)}_2(\text{NO})_2]_2\) is prepared via treatment of \(\text{Mn(NO)}_3\text{CO}\) with KCN in liquid ammonia,\(^71\) and subsequent reduction of this complex with potassium affords \(\text{K}_3[\text{Mn(CN)}_2(\text{NO})_2]\) as an air-sensitive diamagnetic complex.\(^71\) A mononitroso complex \(\text{K}_3[\text{Mn(CN)}_5\text{NO}]\)\(^74-79\) in addition to several air-sensitive carbonyl complexes of \(\text{Mn(CO)}_5\text{CN}, \text{K}[\text{Mn(CO)}_4(\text{CN})_2], \text{K}_2[\text{Mn(CO)}_3(\text{CN})_3],\) and \(\text{K}_3[\text{Mn(CO)}_2(\text{CN})_4]\) stoichiometry are also known;\(^80-83\) \(\text{Na}_5[\text{Mn}^{I}(\text{CN})_6]\)\(^85-88, 89-92\) is the only example of a diamagnetic homoleptic cyanomanganate complex.

However there are comparatively few well-defined paramagnetic cyanomanganates, being limited to only four examples: \(\text{K}_4[\text{Mn(CN)}_6]\cdot 3\text{H}_2\text{O} (2037; S = \frac{1}{2}, g = 2.5)\)\(^39,90,93,94\), and \(\text{K}_3[\text{Mn}^{III}(\text{CN})_6]\cdot \text{H}_2\text{O} (S = 1, g = 2.47)\)\(^95,96,97,98,99,100\). \([\text{PPN}]_3[\text{Mn}^{III}(\text{CN})_6]\)\(^101\), and \([\text{PPN}]_2[\text{Mn}^{IV}(\text{CN})_6]\)\(^102\) and \([\text{PPN}]_2[\text{Mn}^{II}(\text{CN})_4]\). Homoleptic di- and trivalent hexacyanomanganates are known to exhibit low-spin \(t_{2g}^5 (S = \frac{1}{2})\) and \(t_{2g}^4 (S = 1)\) electron configurations, respectively, with significant orbital contributions to their magnetic moments. In comparison to low-spin \(\text{Fe}^{III}\) analogues, paramagnetic low-spin \(\text{Mn}^{II}\) and possibly \(\text{Mn}^{III}\) ions are expected to engage in more efficient \(\pi\) backbonding and cyanide-mediated superexchange interactions, in addition to substantial orbital contributions to their magnetic moments.
Despite the widespread use of poly(pyrazolyl)borates as ancillary ligands in inorganic chemistry we were among the first groups to investigate their coordination chemistry and magnetic properties. We reasoned that these soluble tricyano building blocks would be useful for constructing structurally related analogues of \{Mn^{II}_2Mn^{III}_3\} clusters that contain [Mn^{III}(CN)_6]^{3-} ions. Insertion [(Tp^{R,R})Mn^{III}(CN)_3]^− units into the trivalent sites of rectangular \{Fe^{III}_2M^{II}_2\} complexes should be possible allowing for a direct comparison of their structures, magnetic, and optical properties; incorporating low-spin Mn^{II} cyanometalates should also afford clusters that exhibit greater π-backbonding and more efficient cyanide-mediated superexchange interactions than isoelectronic analogues containing [Fe^{III}(CN)_6]^{3-}, [(Tp*)Fe^{III}(CN)_3], and [(pzTp)Fe^{III}(CN)_3]− centers. Lastly, alteration of the steric demand of the poly(pyrazolyl)borates may also allow for systematic tuning of the orbital anisotropy (λ) of the cyanometalate ions and their cluster derivatives, providing a better understanding of the physical origins of magnetic relaxation behavior, in a series of structurally related cyanometalate complexes.

As a first approximation we initially reasoned that tris(pyrazolyl)borate tricyanomanganates would exhibit magnetic ground states comparable to those seen for octahedral [Mn^{II}(CN)_6]^{4+} (t_2g^5; 2T_2) and [Mn^{III}(CN)_6]^{3-} (t_2g^4; 3T_1) anions. However these [(Tp^{R,R})Mn^{n}(CN)_3]^n− anions (n = 2, 3, 4) are C_{3v}-symmetric and the d orbitals should transform from e_g and t_2g into a singly- (A_1, z^2) and doubly-degenerate (E) [(xz, yz) and (xy, x^2−y^2)] sets of orbitals, respectively. Further assuming that the A_1 symmetric orbital (z^2) is lowest in energy, the degenerate (xz, yz) and (xy, x^2−y^2) orbital sets will be found at comparatively higher energies, respectively. We predict that the C_{3v}-symmetric [(Tp*)Mn^{III}(CN)_3]− anions will exhibit magnetically isotropic 3A_2 ground states (S = 1) in comparison to anisotropic octahedral [Mn^{III}(CN)_6]^{3−} anions [^3T_2g; S = 1]. If this is the case, then the electronic configurations in order of increasing energy, of the C_{3v}-symmetric anions will be (z^2)^2(xz, yz)^3 for Mn^{II}, (z^2)^2(xz, yz)^2 for Mn^{III}, and (z^2)^2(xz, yz) for Mn^{IV}, affording magnetic ground states of S = ½, 1, and ½, respectively. Herein we describe an improved preparation of [cat]_2[Mn^{II}(CN)_4] salts and the syntheses, structures, and magnetic properties of the first mono- and tricyanomanganate complexes.
Experimental Section.

Materials. All operations were conducted under an argon atmosphere using standard Schlenk 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), sodium-benzophenone (diethyl ether), or magnesium turnings (methanol) and sparged with argon prior to use. Solvents were distilled under dinitrogen from CaH$_2$ (acetonitrile), sodium-benzophenone (diethyl ether), or magnesium turnings (methanol) and sparged with argon prior to use. The preparation of KTp*, [NEt$_4$]CN, 3-cyano-2,4-pentanediione, tris(dipivaloylmethanato)manganese(III), tris(3-cyano-2,4-pentanedionato)manganese(III), [PPN]$_3$[Mn$^{III}$(CN)$_6$], and (Tp*)SnBu$_2$Cl are described elsewhere. Iodine (Baker) and cobaltacene (Aldrich) were used as received.

Physical Measurements. The IR spectra were recorded as Nujol mulls between KBr plates on a Mattson Galaxy 5200 FTIR instrument. Magnetic measurements were conducted on a Johnson-Matthey magnetic susceptibility balance and a Quantum Design MPMSXL SQUID magnetometer. Diamagnetic corrections were estimated using Pascal’s constants. Microanalyses were performed by Robertson Microlit Laboratories.

Synthesis of [NEt$_4$][(Tp*)Mn$^{II}$(κ$^2$O-acac)(CN)] (1). Treatment of Mn(acac)$_3$ (3.68 g, 10.5 mmol) in CH$_2$Cl$_2$ (20 mL) with solid KTp* (3.68 g, 11.2 mmol) rapidly afforded a brown mixture that was allowed to stir overnight. The mixture was filtered and the brown filtrate was evacuated to dryness at room temperature. Addition of MeCN (20 mL), followed by [NEt$_4$]CN (3.94 g, 22.4 mmol) in MeCN (20 mL), afforded a brown solution that was allowed to stir for 2 h. The solution was filtered and concentrated under vacuum (ca. 15 mL) at room temperature; addition of Et$_2$O (100 mL) with stirring precipitated a pale brown residue and rapid filtration, afforded yellow crystals upon standing. The crystals were isolated via filtration, washed with Et$_2$O (3 × 10 mL), and dried under vacuum at room temperature for 2 h. Yield: 3.52 g (55.2%). Anal. Calcd for C$_{29}$H$_{47}$B-MnN$_8$O$_2$: C, 57.3; H, 7.80; N, 18.4. Found: C, 57.4; H, 7.88; N, = 18.62. IR (Nujol, cm$^{-1}$): 3113 (s), 3067 (s), 2735 (m), 2508 (s), 2099 (m), 2076 (w), 1604 (s), 1539 (s),
Synthesis of [NEt₄][(Tp*)MnⅡ(κ²O-acac-3-CN)(κ¹N-3-NC-acac)]·MeCN·½Et₂O (2).

Method A. Treatment of tris(3-cyano-2,4-pentanedionato)manganese(III) [ν_{CN} = 2213 cm⁻¹; ν_{CO} = 1599 cm⁻¹] (0.330 g, 0.767 mmol) in MeOH (20 mL) with KTp* (0.250 g, 0.758 mmol) afforded a red-brown mixture that was allowed to stir overnight. Addition on [NEt₄]CN (0.360 g, 2.31 mmol) in MeOH (20 mL) and stirring for 1 h afforded a yellow suspension that was evacuated to dryness under vacuum at room temperature. The yellow residue was extracted with MeCN (15 mL), filtered, and Et₂O (100 mL) was added to the brown filtrate. The yellow crystals were isolated via filtration, washed with Et₂O (3 × 5 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.150 g (25.3%). Anal. Calcd for C_{37}H_{59}B_{10}MnN_{9}O_{4.5}: C, 57.89; H, 7.75; N, 16.42. Found: C, 57.89; H, 7.56; N, 16.67. IR (Nujol, cm⁻¹): 3118 (m), 2737 (m), 2528 (m), 2449 (w), 2418 (w), 2256 (w), 2188 (vs), 2140 (m), 1619 (vs), 1585 (vs), 1540 (vs), 1506 (s), 1486 (vs), 1446 (vs), 1416 (vs), 1378 (vs), 1328 (vs), 1291 (s), 1199 (vs), 1124 (s), 1069 (s), 1043 (vs), 997 (s), 958 (m), 925 (s), 913 (m), 843 (m), 808 (s), 780 (s), 700 (s), 697 (m), 651 (s), 611 (m).

Synthesis of [NEt₄][(Tp*)MnⅡ(κ²O-acac-3-CN)(κ¹N-3-NC-acac)]·MeCN·½Et₂O (2).

Method B. Treatment of tris(3-cyano-2,4-pentanedionato)manganese(III) (0.500 g, 1.16 mmol) in CH₂Cl₂ (20 mL) with KTp* (0.380 g, 1.15 mmol) in CH₂Cl₂ (20 mL) afforded a red-brown mixture that was allowed to stir overnight. The mixture was evacuated to dryness at room temperature and dried under vacuum an additional 2 h. (0.40 g crude yield). The solid was dissolved into MeCN (20 mL) and was treated with [NEt₄]CN (0.180 g, 1.16 mmol) in MeCN (10 mL); stirring for 1 h afforded a brown solution and a white precipitate. The mixture was filtered, the filtrate was concentrated under vacuum at room temperature to ca. 10 mL, layered with Et₂O (40 mL), and allowed to stand 16 h. The yellow crystals were isolated via filtration and were dried under vacuum for 1 h. A second crop can be obtained via Et₂O addition to the mother liquor.
Yield: 0.268 g (30.0%).

\([\text{NEt}_4]_2[\text{Mn}^{III}(\text{CN})_4]\) (3). Addition of a \(\text{MeCN} (10 \text{ mL})\) solution of \(\text{Mn(OTf)}_2\) (0.200 g, 0.566 mmol) to \([\text{NEt}_4]CN\) (0.400 g, 2.56 mmol) in \(\text{MeCN} (10 \text{ mL})\) rapidly afforded a pale yellow mixture that was allowed to stir for 30 min. The mixture was concentrated to \(ca. 10 \text{ mL}\) under vacuum at room temperature, \(\text{Et}_2\text{O} (50 \text{ mL})\) was layered onto the yellow solution, and allowed to stand for 16 h. The pink crystals were isolated via filtration, washed with \(\text{Et}_2\text{O} (2 \times 5 \text{ mL})\), and dried under vacuum at room temperature for 5 min. Yield: 0.176 g (56.3%).

Anal Calcd for \(\text{C}_{20}\text{H}_{40}\text{BMnN}_6\): C, 57.26; H, 9.61; N, 20.03. Found: C, 56.92; H, 9.89; N, 20.02. IR (Nujol, cm\(^{-1}\)): 2957 (vs), 2923 (vs), 2855 (vs), 2578 (s), 2455 (s), 2357 (s), 2311 (s), 2120 (s), 2078 (s), 1804 (m), 1678 (m), 1581 (m), 1451 (vs), 1401 (vs), 1376 (vs), 1264 (s), 1175 (vs), 1059 (s), 1010 (vs), 908 (m), 799 (vs), 723 (m), 604 (w).

\([\text{NEt}_4][(\text{Tp}^\ast)\text{Mn}^{III}(\text{CN})_3]\) (4). Treatment of tris(3-cyano-2,4-pentanedionato)-manganese(III) (0.33 g, 0.767 mmol) in \(\text{MeOH} (20 \text{ mL})\) with \(\text{KTP}^\ast (0.25 \text{ g}, 0.758 \text{ mmol})\) afforded a brown mixture, that was allowed to stir for 20 min. Addition of \([\text{NEt}_4]CN\) (0.479 g, 3.07 mmol) in \(\text{MeOH} (15 \text{ mL})\) rapidly afforded a yellow mixture that was stirred for 1 h, filtered, and concentrated to \(ca. 10 \text{ mL}\) under vacuum at room temperature. Addition of \(\text{Et}_2\text{O} (200 \text{ mL})\) with stirring precipitated a yellow solid that was isolated via filtration. The yellow precipitate was dissolved into \(\text{MeCN} (10 \text{ mL})\) and subsequent \(\text{Et}_2\text{O}\) addition (20 mL), afforded yellow crystals after 24 h. The crystals were isolated via filtration, washed with \(\text{Et}_2\text{O} (3 \times 10 \text{ mL})\), and dried under vacuum for 2 h at room temperature. Yield: 0.213 g (49.6%).

Anal Calcd for \(\text{C}_{26}\text{H}_{42}\text{BMnN}_{10}\): C, 55.72; H, 7.55; N, 24.99. Found: C, 55.49; H, 7.37; N, 24.86. IR (Nujol, cm\(^{-1}\)): 2552 (s), 2113 (m), 1539 (s), 1484 (s), 1448 (s), 1415 (s), 1392 (s), 1369 (s), 1262 (m), 1200 (s), 1172 (s), 1062 (s), 1049 (s), 998 (m), 879 (w), 861 (m), 813 (m), 789 (s), 780 (s), 721 (w), 695 (m), 648 (s).

**Synthesis of \([\text{PPN}][(\text{Tp}^\ast)\text{Mn}^{III}(\text{CN})_3]\) (5).** Treatment of a \(\text{CH}_2\text{Cl}_2 (5 \text{ mL})\) solution of \([\text{PPN}]_3[\text{Mn}^{III}(\text{CN})_6]\) (0.020 g, 0.11 mmol) with \((\text{Tp}^\ast)\text{SnBu}_2\text{Cl}\) (0.061 g, 0.11 mmol) in \(\text{CH}_2\text{Cl}_2 (5 \text{ mL})\) with stirring afforded a yellow solution that was allowed to magnetically...
stir for 15 min at room temperature. The yellow mixture was layered with Et<sub>2</sub>O (30 mL) and rapidly precipitated a white solid; the mixture was filtered and allowed to stand for 7 d. The yellow crystals were isolated via filtration, washed with Et<sub>2</sub>O (2 × 5 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.037 g (35.0 %). IR (Nujol, cm<sup>-1</sup>): 2547(s), 2108(m), 1538(s), 1482(s), 1436(s), 1415(s), 1376(s), 1285(s), 1260(m), 1200(s), 1172(s), 1114(s), 1026(s), 997(m), 930(w), 863(m), 795(m), 761(s), 749(s), 721(w), 695(m), 648(s).

**Synthesis of [Cp<sub>2</sub>Co<sup>III</sup>]<sub>4</sub>[Mn<sup>II</sup>(CN)<sub>6</sub>] (6).** Treatment of a MeCN (15 mL) solution of complexe(4) (0.050 g, 0.089 mmol) with Cp<sub>2</sub>Co<sup>II</sup> (0.017 g, 0.090 mmol) in MeCN (5 mL) with stirring afforded a yellow solution that was allowed to magnetically stir for 30 min at room temperature. 40 mL Et<sub>2</sub>O was slowly added to this yellow solution. Yellow crystals appeared after 24 hours. The yellow crystals were isolated via filtration, washed with Et<sub>2</sub>O (2 × 5 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.0072g (8.2%). IR (Nujol, cm<sup>-1</sup>): 3111(m), 3072(m), 2923(s), 2854(s), 2099(m), 1624(m), 1581(m), 1443(s), 1416(s), 1378(s), 1346(m), 1310(w), 1261(s), 1224(s), 1197(s), 1157(s), 1090(s), 1067(s), 1027(s), 867(s), 840(m), 803(s), 757(s), 695(m).

**Structure Determinations and Refinements.** X-ray diffraction data were collected at 90.0(2) K for 1 was collected on a Bruker X8 Proteum rotating anode diffractometer using graphite-monochromated Cu Kα radiation while data for 2-5 were obtained on a Nonius kappaCCD diffractometer using Mo Kα radiation. Crystals were mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained (DENZO)<sup>110</sup> from ten 1º frames (SCALEPACK)<sup>110</sup> Lorentz/polarization corrections were applied during data reduction. The structures were solved by direct methods (SHELXL97)<sup>111</sup> and completed by difference Fourier methods (SHELXL97).<sup>111</sup> Refinement was performed against R<sup>2</sup> by weighted full-matrix least-squares (SHELXL97)<sup>111</sup> and empirical absorption corrections (either SCALEPACK<sup>110</sup> or SADABS<sup>112</sup>) 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.*\(^{113}\) Crystal data, relevant details of the structure determinations, and selected geometrical parameters are provided in Tables 2.1-2.3.

**Results and Discussion.**

**Synthesis and Spectroscopic Characterization.** In the first row transition metal series octahedral Jahn-Teller distorted high-spin Mn\(^{III}\)\((t_{2g}^3e_g^1, S = 2)\) is an ideal metal ion for constructing SMMs due to its anisotropic single-ion magnetic properties. However, many trivalent manganese complexes are strongly oxidizing in aqueous solution and easily disproportionate into Mn\(^{IV}\) and Mn\(^{II}\) ions, respectively. Complicating matters further, few substitutionally labile Mn\(^{II}\) and Mn\(^{IV}\) complexes suitable for our synthetic methods are currently known. Therefore Mn(acac)\(_3\) (acac\(^-\) = acetylacetonate or 2,4-pentandionate) was chosen as an initial starting material because it is stable to air, water, and common organic solvents in both solution and solid states. Furthermore a variety of substituted pentanedionate ligands can be prepared allowing for tuning of the redox potentials of the Mn(acac-R)\(_3\) complexes. Cyanide as a strong-field ligand, generally affords low-spin complexes and the target complex, [NEt\(_4\)]([Tp\(^*\)]Mn\(^{III}\)(CN)\(_3\)], is expected to exhibit an \(S = 1\) magnetic ground state \((t_{2g}^4\), Scheme 2.1).

\[
\text{Mn}^{III}(acac)_3 \xrightarrow{1) \text{KTP}^*} \xrightarrow{2) 3[\text{NEt}_4]\text{CN}} \text{Scheme 2.1}
\]

Upon treatment of Mn(acac)\(_3\) with potassium hydridotris(3,5-dimethylpyrazolyl)borate [KTP\(^*\)] in dichloromethane a mixture of red-brown precipitate and supernatant was obtained. The infrared spectra of the soluble and insoluble material suggests that the Tp\(^*\)
anion has coordinated to the manganese centers, as judged via a shift of the $\nu_{\text{BH}}$ stretching absorption to higher energy [2512 and 2522 cm$^{-1}$] relative to KTp* [2436 cm$^{-1}$] for the soluble and insoluble material, respectively. If the energy of the $\nu_{\text{BH}}$ stretch scales as a function of charge, assuming that the metal center oxidation state remains constant, the dichloromethane-insoluble materials may be a cationic complex, as the greater likely positive charge on the Mn$^{\text{III}}$ ion will act to increase the strength of the B-H bond. Therefore we tentatively propose that the soluble fraction contains a neutral complex while the insoluble portion is a salt; likely formulations are [(Tp*)Mn$^{\text{III}}$(acac)$_2$] and [(Tp*)Mn$^{\text{III}}$(acac)](acac) for the soluble and insoluble compounds, respectively.

Treatment of manganese(III)acetylacetonate with potassium hydridotris-(3,5-dimethylpyrazol-1-yl)borate (KTp*), followed by excess tetraethylammonium cyanide, affords [NEt$_4$][(Tp*)Mn$^{\text{II}}$(κ$^2$O-acac)(CN)] (1) as a yellow crystalline solid (Scheme 2.2). Attempts to isolate and structurally characterize the putative divalent cyanide-free complexes, [(Tp*)Mn(κ$^2$O-acac)(κ$^1$O-acac)] and [(Tp*)Mn(κ$^2$O-acac)][acac], have consistently met with failure and the mixture was used in-situ. Attempted oxidation of 1 with molecular iodine yields \{[(Tp*)Mn$^{\text{II}}$(κ$^2$O-acac-CN)]\}_n (7) and \{[NEt$_4$][(Tp*)Mn$^{\text{II}}$(κ$^2$O-acac-CN)]$_2$(μ-CN)\} (8) as the major and minor products, respectively (see Chapter 3); air exposure of 1 affords intractable mixtures. We presume that electrophillic iodination of 1, followed by cyanide substitution, affords 7 and 8 (Chapter 3) rather than the desired trivalent complex [(Tp*)Mn$^{\text{III}}$(κ$^2$O-acac)(CN)].

Scheme 2.2
Consequently, a different tris(acetylacetonate) manganese(III) precursor was chosen in the hope that more labile (Tp*)Mn^{III}(acac-R)_n complexes may be prepared. The ultimate goal of these synthetic efforts is the preparation of substitutionally labile manganese(III) acetylacetonate complexes and investigate their substitution reactions with cyanide. Treatment of Mn^{III}(L)_3 (L = 3-cyano-2,4-pentanedionato; 3-NC-acac) with KTp*, followed by [NEt_4]CN in methanol affords a new six-coordinate complex of [NEt_4][(Tp*)Mn^{II}(κ²O-acac-3-CN)(κ¹N-NC-acac)] (2) stoichiometry (Scheme 2.3). Given that no cyano complexes have been found to date under these synthetic conditions, we propose that cyanide oxidation and concomitant reduction of the Mn^{III} centers occur, affording 2 in modest yield as yellow crystals. We propose that 2 may be structurally related to the dichloromethane-insoluble material found when treating Mn(acac)_3 with KTp*.

![Scheme 2.3](image)

The infrared spectra of 1 and 2 exhibit intense cyanide stretching absorptions that are shifted to higher energies relative to tetra(ethyl)ammonium cyanide (2056 cm⁻¹) and most cyanomanganate(II) compounds. The ν_{CN} absorptions seen for 1 [2099(m) and 2076(w) cm⁻¹] are found at lower energies than those in K_4[Mn^{II}(CN)_6]·3H_2O (2060 cm⁻¹), [Mn^{II}(CN)_2(bipy)_2]·3H_2O [2114 cm⁻¹], and [NEt_4]_2[Mn^{II}(CN)_4] (3) [2120 and 2078 cm⁻¹] suggesting that efficient π backbonding is present in 1. For 2, the ν_{CN} stretches are found at higher energies [2247, 2202, and 2146 cm⁻¹] than those seen for [PPN]_2[Mn^{IV}(CN)_6] (2132 cm⁻¹), [PPN]_3[Mn^{III}(CN)_6] (2092 and 2098 cm⁻¹), K_3[Mn^{III}(CN)_6] (2112 and 2121 cm⁻¹), K_2[Mn^{IV}(CN)_6] (2240, 2150 cm⁻¹), K_2Mn^{II}.
[MnII(CN)₆] (2055 cm⁻¹), suggesting that these absorptions are due to nitriles rather than terminal cyanides. The infrared spectrum of 2 also exhibits intense νCO stretches that are shifted to higher energies relative to those in 1. The νCN stretches are also found at higher energies suggesting that the cyanide groups are due to coordinated 3-cyano-2,4-pentanedionato rather than anionic cyano ligands.

In our pursuit of other cyanomanganates via methathesis of homoleptic cyanomanganates, we have also discovered an improved and direct route for the preparation of tetracyanomanganate(II) salts. Treatment of Mn(OTf)₂ with four equivalents of [NEt₄]CN in acetonitrile cleanly affords [NEt₄]₂[MnII(CN)₄] (3) as pale yellow crystals (Scheme 2.4). The infrared spectrum of 3 exhibits two νCN stretching absorptions [2120 cm⁻¹] that are considerably lower in energy than those reported for [PPN]₂[MnII(CN)₄] [2209 cm⁻¹], [PPN]₃[MnIII(CN)₆] [2092 and 2098 cm⁻¹], and [PPN]₂[MnIV(CN)₆] (2132 cm⁻¹), and is comparable to the cyano stretch exhibited by [MnII(CN)₂(bipy)]·3H₂O [2114 cm⁻¹]. Given that the reported νCN stretches for [PPN]₂[MnII(CN)₄] are uncharacteristically high in energy, in comparison to [MnII(CN)₂(bipy)]·3H₂O and 3, we propose that the published νCN absorption is most likely due to an organic nitrile (probably MeCN) rather than coordinated cyanide.

Subsequent treatment of 2 with excess [NEt₄]CN affords [NEt₄][(Tp*)MnIII(CN)₃] (4) as the first example of a tricyanomanganate(III) complex. Alternatively, a bis(triphenylphosphine)iminium derivative, [PPN][(Tp*)MnIII(CN)₃] (5), can be prepared via treatment of [PPN]₃[MnIII(CN)₆] with (Tp*)SnBu₂Cl (Scheme 2.5). Curiously, use of methanol as a reaction solvent appears to afford trivalent cyano complexes rather than
divalent ones when using 2 or Mn\textsuperscript{III}(L)\textsubscript{3} as starting materials. The infrared spectra of 4 and 5 exhibit intense $\nu_{BH}$ and $\nu_{CN}$ stretches [2552 and 2113 cm\textsuperscript{-1}] that are shifted to higher energies than those seen in 1-3, suggesting that oxidized manganese centers are present. The cyano stretching absorption energies in 4 and 5 are comparable to those observed for [PPN]$_3$[Mn\textsuperscript{III}(CN)$_6$] [2092 and 2098 cm\textsuperscript{-1}] and K$_3$[Mn\textsuperscript{III}(CN)$_6$] [2112 and 2121 cm\textsuperscript{-1}], but are far from those seen for [PPN]$_2$[Mn\textsuperscript{IV}(CN)$_6$] (2132 cm\textsuperscript{-1}) and K$_2$[Mn\textsuperscript{IV}(CN)$_6$] (2240, 2150 cm\textsuperscript{-1}). From the infrared data we tentatively propose that Mn\textsuperscript{III} centers are present in 4 and 5.

Literature precedent suggests that tin reagents containing Tp* groups can effectively substitute chloro ligands (from [Nb\textsuperscript{IV}Cl$_4$(THF)$_2$]) to afford complexes of (Tp*)Nb\textsuperscript{IV}Cl$_3$ stoichiometry.\textsuperscript{45} Given that cyanides are a member of the pseudohalides family and can undergo displacement reactions in a manner that is mechanistically similar to halides, we reasoned that treatment of [Mn\textsuperscript{III}(CN)$_6$]\textsuperscript{3-} anions with (Tp*)SnBu$_2$Cl may transfer Tp*\textsuperscript{-} anions to the Mn\textsuperscript{III} metal center with concomitant extrusion of SnBu$_2$Cl(CN) rather than SnBu$_2$Cl$_2$. Indeed in dichlormethane solution (Tp*)SnBu$_2$Cl in the presence of [PPN]$_3$[Mn\textsuperscript{III}(CN)$_6$] affords the first tricyanomanganate complex as a salt of [PPN][(Tp*)Mn\textsuperscript{III}(CN)$_3$] (5) stoichiometry.

\begin{verbatim}
1) Mn\textsuperscript{III}(L)$_3$
2) KTp*, MeOH
3) 3[NEt$_4$]CN, MeCN
\end{verbatim}

L = 3-cyano-2,4-pentanedione

\begin{verbatim}
2 + 3[NEt$_4$]CN
MeCN
\end{verbatim}

1) [PPN]$_3$[Mn\textsuperscript{III}(CN)$_6$]
2) (Tp*)SnBu$_2$Cl, CH$_2$Cl$_2$

[cat]$^{+}$

[cat]$^{+}$ = NEt$_4$, 4; PPN, 5

\[\text{Scheme 2.5}\]
Attempts to prepare additional pyrazolylborate cyanomanganates using a variety of reagents have consistently met with failure. For example treatment of 4 with cobaltacene in acetonitrile or dichloromethane affords a mixture of (Tp*)$_2$Mn$^{II}$ and [Cp$_2$Co$^{III}$]$_4$. [Mn$^{II}$((CN)$_6$)] (6) with the energy of the $\nu_{CN}$ [2098 cm$^{-1}$] in the range expected for divalent hexacyanometalates. Treatment of 4 with cis-Co$^{II}$([bipy]$_2$(OH)$_2$)$_2$[OTf]$_2$ cleanly affords [cis-Co$^{III}$((CN)$_2$)(bipy)]$_2$[OTf] (9, $\nu_{CN} = 2142$ cm$^{-1}$) as the sole cyanide-containing complex, while Na/Hg amalgam or air exposure affords intractable mixtures (Chapter 3).

Similarly treatment of [PPN]$_2$[Mn$^{II}$((CN)$_4$)] with either KTp* or (Tp*)Sn$^{II}$Bu$_2$Cl in acetonitrile forms (Tp*)$_2$Mn$^{II}$ [$\nu_{BH} = 2523$ cm$^{-1}$] as the exclusive manganese containing product.

**Crystallographic Studies: Divalent Complexes.** Compound 1 crystallizes as yellow crystals in the monoclinic $P2_1/n$ space group (Table 2.1 and Figure 2.1). The pseudo $C_5$-symmetric anions exhibit Mn-C and Mn-O bond distances of 2.261(6) [Mn1-C16] and 2.165(3) [Mn1-O1] and 2.220(4) [Mn1-O2], while the Mn-N distances range from 2.267(4) to 2.291(4) Å (Table 2.2). The acetylacetonate (acac) ligand C-O bond lengths are identical [1.261(6) Å], while the C18-C19 [1.398(8) Å] and C19-C20 [1.412(8) Å] distances are nearly equivalent (Table 2.2). The O1-Mn1-O2, Mn-O1-C18, and Mn1-O2-C20 bond angles are 83.3(2), 126.7(3), and 125.4(4)$^\circ$, while the Mn-C16-N7 and C16-Mn1-N1 angles nearly linear, being 177.5(5) and 171.2(3)$^\circ$, respectively (Table 2.3). The manganese, O1, and O2 centers are ca. -0.167(4), +0.171(4), and +0.145 Å above the mean O1-C18-C19-C20-O2 plane, suggesting that torsional twisting (ca. 22$^\circ$) of the acac ligand may be induced by steric interactions with the Tp* ligand methyl group (C1), directed towards the Mn($\eta^2$-acac) unit; the closest contact between the acac ligands and Tp* pyrazolate methyl group is 3.382(1) Å [C1···O1].

Compound 2 crystallizes in the monoclinic $P2_1/n$ space group as a six-coordinate complex that is structurally related to 2 (Table 1 and Figure 2.2). Charge balance considerations suggest that 2 contains two anionic 3-cyanoacetylacetonate ligands in addition to a facially coordinate Tp* ion. In 2 the anionic 3-cyanoacetylacetonate ligands adopt $\kappa^1O$- and $\kappa^2O$- configurations, respectively (Figure 2.2), and the C-O and C-C distances for the $\kappa^2O$-(3-cyano)-2,4-pentanedionato ligand are comparable to those found in [(Tp*)Mn$^{II}$($\kappa^2O$-acac-3-CN)]$_2$(µ-CN) (7, Chapter 3). The C-O and C-C bond distances
are identical for the $\kappa^2O$-3-CNacac fragment, being 1.253(2) [C17-O1] and 1.427(3) Å [C17-C18], respectively; the terminal nitrile C-N bond is 1.148(3) Å [C21-N7] long. The Mn-O1 and Mn1-O2 distances are also comparable [2.159(1) and 2.178(2) Å] (Table 2.2).

In comparison the C-O distances in the $\kappa^1O$-3-CNacac fragment are slightly shorter, suggesting that greater localization of negative charge occurs in this ligand. The O3-C23 and O4-C25 bonds are 1.226(3) and 1.241(3) Å while the C23-C24 and C24-C25 bonds are nearly equivalent at 1.445(3) and 1.442(3) Å, respectively (Table 2.2). The $\eta^1$-nitrile in 2 has C27-N8 and Mn1-N8 bonds [1.092(3) and 2.256(2) Å] are slightly shorter than those found 7 [1.150(3) and 2.315(2) Å]. Based upon structural and infrared spectroscopic studies of 2 we tentatively propose that greater $\pi$-back bonding occurs between the Mn$^{II}$ and nitrile group in comparison to those present in 7.

Compounds 3 and 6 are a rare examples of homoleptic cyanomanganate(II) complexes and crystallize in the monoclinic and tetragonal $C2/c$ and $I-4$ space groups, respectively (Table 2.1). In Figure 2.3 the X-ray structure of 3 clearly shows that the anion adopts a nearly tetrahedral geometry and consists of a 1:4 ratio of Mn$^{II}$ and cyanides, respectively. The Mn-C distances are slightly different, 2.137(2) Å [Mn1-C1] and 2.151(2) Å [Mn1-C2], and are comparable to those reported by Miller and coworkers [2.151(6) Å] for the structurally related complex [PPN]$\_2$[Mn$^{II}$(CN)$_4$]; the C-N bond distances range from 1.152(3) to 1.144(3) Å, while the C1-Mn-C2 bond angle is 111.47(7)$^\circ$ in 3. Complex 6 crystallizes in the tetragonal $I-4$ space group (Table 2.1 and Figure 2.6) and represents the first crystallographically characterized hexacyanomanganate(II) complex that is free of alkali metal cations. The Mn-C distances are nearly equivalent and range from 1.960(7) Å [Mn1-C2] to 1.98(1) Å [Mn1-C1] while the C-N bonds range from 1.18(1) to 1.14(2) Å. The C1-Mn1-C1C and C1-Mn1-C2 bond angles are 90.0(1) and 179.6(6)$^\circ$ indicating that 6 adopts a nearly perfect octahedral geometry.

**Crystallographic Studies: Trivalent Complexes.** X-ray data collected for 4 and 5 suggests they crystallize as a $C_{3v}$ symmetric, six-coordinate complexes in the trigonal $P3_2$ (4) and triclinic P-1 space groups, respectively (Table 2.1, Figures 2.4 and 2.5). Assuming that the Mn-C distances scale as a function of metal center oxidation state, Mn$^{III}$ centers
are expected to engage in stronger electrostatic interactions with cyanides present, with the shortest Mn-C distances anticipated for 4 and 5; efficient π backbonding should be more likely for cyanomanagates(II) complexes and the shortest Mn-C distances should be found for 1. However in 4 and 5 the Mn-C<sub>CN</sub> bond distances range from 1.976(3) to 1.985(3) Å and are considerably shorter than the Mn1-C16 bond length [2.261(6) Å] seen in 1 (Table 2.2). As judged from structural and infrared spectroscopy studies of 1 and 5 we propose that little π-back bonding occurs in 4 and 5.

Complexes containing trivalent manganese centers are expected to exhibit markedly different Mn-C and Mn-N bond lengths in addition to more acute N-Mn-N bond angles, in comparison to divalent analogues. The Mn-N bonds range between 2.018(2) and 2.036(2) Å in 4 and 5, being considerably shorter than those found for 1-3, further indicating that 4 and 5 contain trivalent centers. The N-Mn-N bond angles are also more acute in 4 and 5, ranging from 89.4(1) to 90.3(1)°, while the C-Mn-C angles are between 85.8(1) and 91.7(1)°, suggesting that the Tp* ligand exerts modest steric pressure and/or electrostatic influence on the coordination sphere of the Mn<sup>III</sup> centers (Table 2.3). The ionic radii of trivalent ions should be smaller than the divalent ones and should allow for tighter binding of Mn<sup>III</sup> ions within the [N]<sub>3</sub> pocket of the facially coordinate Tp* ligand. The distance between the mean plane of the three coordinated Tp* nitrogen atoms and manganese centers appear to support this assumption: the Mn"-[N]<sub>3</sub> distances are 1.476(7), 1.377(3), 1.193(3), and 1.193(3) Å for 1, 2, 4, 5, respectively, with the smallest value being found for 5 (Table 2). Consistent with expected period trends the average Mn-C distances in 4 and 5 [1.985(3) and 1.982(3) Å] are shorter than those seen for early transition metal [(Tp*)M<sup>III</sup>(CN)₃]⁻ analogues [e.g. Ti<sup>III</sup>, 2.171(3) Å; V<sup>III</sup>, 2.090(3) Å], and are longer than those containing Co<sup>III</sup> ions [1.875(3) Å] (Table 4) as expected.
Table 2.1. Crystallographic Data for $\text{[NEt}_4\text{][}(\text{Tp}^\ast\text{)Mn}^{\text{II}}(\kappa^2\text{O-}\text{acac})(\text{CN})] (1)$, $\text{[NEt}_4\text{]}[(\text{Tp}^\ast\text{)Mn}^{\text{II}}(\kappa^2\text{O-}\text{acac}-\text{3-CN})(\kappa^1\text{N-3-NC-}\text{acac})] (2)$, $\text{[NEt}_4\text{]}[\text{Mn}^{\text{II}}(\text{CN})^4] (3)$, $\text{[NEt}_4\text{]}[(\text{Tp}^\ast\text{)Mn}^{\text{III}}(\text{CN})_3] (4)$, $\text{[PPN]}[(\text{Tp}^\ast\text{)Mn}^{\text{III}}(\text{CN})_3] (5)$, and $\text{[Cp}_2\text{Co}^{\text{III}}[\text{Mn}^{\text{II}}(\text{CN})_6] (6)$.

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* $I > 2\sigma(I)$, $R = \sum|F_o| - |F_o|\sum|F_o|$. $R_w = [(\sum w(F_o| - |F_o|)^2/\sum wF_o^2)]^{1/2}$
Table 2.2. Selected Bond Distances (Å) for [NEt$_4$][(Tp*)Mn$^{II}$($\kappa^2$O-acac)(CN)] (1), [NEt$_4$][(Tp*)Mn$^{II}$($\kappa^2$O-acac-3-CN)-(\kappa^2$N-3-NC-acac)] (2), [NEt$_4$]$_2$[Mn$^{II}$($\kappa^2$CN)$_4$] (3), [NEt$_4$][(Tp*)Mn$^{III}$($\kappa^3$CN)$_3$] (4), [PPN][(Tp*)Mn$^{III}$($\kappa^3$CN)$_3$] (5), and [Cp$_2$Co$^{III}$]$_4$[Mn$^{II}$($\kappa^3$CN)$_6$] (6).

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Table 2.3. Selected Bond Angles (deg) for \([\text{NET}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2O\text{-acac})(\text{CN})] (1), [\text{NET}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2O\text{-acac-3-CN})(\kappa^2N\text{-3-NC-acac})] (2), [\text{NET}_4][\text{Mn}^{\text{II}}(\text{CN})_4] (3), [\text{NET}_4][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3] (4), [\text{PPN}][(\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3] (5), and [\text{Cp}_2\text{Co}^{\text{III}}][\text{Mn}^{\text{II}}(\text{CN})_6] (6).\

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Figure 2.1. X-ray structure of anionic portion of 1. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
Figure 2.2. X-ray structure of anionic portion of 2. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
Figure 2.3. X-ray structure of anionic portion of 3. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
**Figure 2.4.** Truncated X-ray structure of anionic portion of 4. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
Figure 2.5. Truncated X-ray structure of anionic portion of 5. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
Figure 2.6. X-ray structure of anionic portion of 6. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
**Magnetic Studies: Divalent Complexes.** The temperature dependence of the $\chi T$ product suggests that the Mn$^{II}$ centers present in 1 are magnetically isolated between 1.8 and 300 K. As judged from the $\chi T$ vs $T$ data using crushed single crystals, the $\chi T$ product of 1 remains nearly constant ($\sim 4.1$ cm$^3$ K mol$^{-1}$), as the temperature is lowered from 300 to ca. 50 K (Figure 2.7). Below 50 K, the $\chi T$ product decreases slightly, approaching a minimum value of 3.13 cm$^3$ K mol$^{-1}$ at 1.8 K. Fitting of the susceptibility data to the Curie-Weiss expression affords Curie and Weiss constants of 4.093 cm$^3$ K mol$^{-1}$ and -0.17 K, respectively. Lastly, fitting the field dependence of the magnetization data, collected between 1 and 7 T at 1.85 K, with an $S = 5/2$ Brillouin function suggests that 1 contains isotropic ($g = 1.93$) Mn$^{II}$ spin centers that are magnetically isolated (Figure 2.8).

Compound 2 exhibits magnetic behavior that is consistent with the presence of magnetically isolated Mn$^{II}$ centers. The temperature dependence of the $\chi T$ product gradually decreases from 4.26 to 4.11 cm$^3$ K mol$^{-1}$ between 300 and 12 K, increasing slightly at lower temperatures, reaching a maximum value of 4.21 cm$^3$ K mol$^{-1}$ at 1.8 K. Fitting of the $\chi T$ vs $T$ data via the Curie-Weiss expression affords a Curie, and Weiss constant values of 1.97, 4.2 cm$^3$ K mol$^{-1}$ and -0.02 K, respectively, suggesting that 2 contains isotropic $S = 5/2$ Mn$^{II}$ centers with very weak interactions present at low temperatures. Further support for the presence of Mn$^{II}$ centers can be found in the field dependence of the magnetization and fitting of the data with an $S = 5/2$ Brillouin function; plots of $M$ vs. $HT^{-1}$ between 1.8 and 8 K are superimposable confirming that the Mn$^{II}$ centers in 2 are isotropic (Figure 2.11).
Figure 2.7. Temperature dependence of the $\chi T$ product of 1 between 1.85 and 300 K for $H_{dc} = 1$ kG.
Figure 2.8. Field dependence of the magnetization of 1 at 1.85 K between 0 and 7 T.
Figure 2.9. Temperature dependence of the $\chi T$ product of 2 between 1.85 and 300 K for $H_{dc} = 1$ kG.
Figure 2.10. Field dependence of the magnetization of 2 at various temperatures ($0 \leq H_{dc} \leq 7$ T).
**Figure 2.11.** Field dependence of the reduced magnetization of $2$ ($1.8 \leq T \leq 8$ K).
Figure 2.12. Temperature dependence of the $\chi T$ product of 4 between 1.85 and 300 K for $H_{dc} = 1$ kG.
Figure 2.13. Field dependence of the magnetization of 4 at 1.85 K between 0 and 7 T.
Magnetic Studies: Trivalent Complexes. For 4, the room temperature value of the \( \chi T \) product is much smaller, suggesting that the manganese centers are low-spin (\( S = 1 \)) and in the trivalent state. Octahedral complexes such as \( \text{K}_3[\text{Mn}^{III}(\text{CN})_6] \cdot \text{H}_2\text{O} \) low-spin \( \text{Mn}^{III} \) centers are expected to exhibit significant orbital contributions to the magnetic \( ^3A_{2g} \) ground state and often have \( g \) values that deviate significantly from 2.0.\(^{97-99}\) Fitting of the \( \chi T \) vs \( T \) data between 1.8 and 300 K indicates that 4 is paramagnetic but it does not follow Curie-Weiss law behavior (Figure 2.12). The room temperature value of \( \chi T \) is 1.08 cm\(^3\) K mol\(^{-1}\) and is close to that expected for an \( S = 1 \) low-spin \( \text{Mn}^{III} \) complex (\( C = 1.0 \) cm\(^3\) K mol\(^{-1}\), \( g = 2 \) assumed). Fitting the \( \chi T \) vs \( T \) data using an anisotropic Heisenberg Hamiltonian (\( H = DS^2 \)) affords calculated values for \( g \) and \( D/k_B \) of 2.09 and 9.4 K, respectively (Figure 2.12). For the low temperature data, the experimental curve deviates significantly from predicted behavior and qualitatively explains the unexpectedly large value of \( D \) deduced from the Heisenberg treatment of the \( \chi T \) vs \( T \) data. Furthermore, fitting the \( M \) vs \( H \) data of 4 (for \( T = 1.85 \) K) failed to corroborate the \( D \) values estimated via modeling the \( \chi T \) vs \( T \) data (Figures 2.12 and 2.13). We tentatively propose that weak antiferromagnetic interactions and/or the presence of paramagnetic impurities, likely due to the reactive nature of 4, conspire to give physically unrealistic values of \( D \).

For complex 4, \( [(\text{Tp}^*)\text{Mn}^{III}(\text{CN})_3]^- \) ion is \( C_{3v} \)-symmetric and the \( d \) orbitals should transform from \( e_g \) and \( t_{2g} \) symmetry orbitals into a singly- \( (A_1, \ z^2) \) and two doubly-degenerate \( (E) \ [(xz, yz) \ and \ (xy, x^2-y^2)] \) sets of orbitals. According to this orbital distribution, the \( A_1 \) symmetric orbital \( (z^2) \) is lowest in energy, and the \( E \ [(xz, yz) \ and \ (xy, x^2-y^2)] \) orbital sets will be found at comparatively higher energies. Therefore, the \( [(\text{Tp}^*)\text{Mn}^{III}(\text{CN})_3]^- \) ion is expected to exhibit a different spin ground state than the corresponding octahedral symmetry cyanomanganates for a given oxidation state. The room temperature value of the \( \chi T \) product (1.08 cm\(^3\)K/mol) indicates that the manganese centers in complex 4 are low-spin (\( S = 1 \)) and in the trivalent state. Consequently the electronic configuration of that \( \text{Mn}^{III} \) center should be \( (z^2)^2(xz, yz)^2 \) for \( \text{Mn}^{III} \). Since the two unpaired electrons occupy the doubly degenerate \( E \)-symmetry \( xz \) and \( yz \) orbitals, an isotropic magnetic ground state is reasonable. Additional evidence in support of this hypothesis is supported by the isotropic experimental \( g \) value [2.09] found for 4. The
above data suggest that 4 adopts an \(^3A_2\) magnetic ground state with no orbital contributions to the magnetic moment (via spin-orbit interactions).

**Conclusions.** A variety of magnetically isotropic di- and trivalent cyanomanganate complexes have been prepared and structurally and magnetically characterized. Orbital contributions via spin-orbit interactions appear to be necessary for designing anisotropic cyanometalate complexes and appear to follow our general model: low-spin Fe\(^{\text{III}}\) (one unpaired electron, \(^2T_2\) state) building blocks are anisotropic while Mn\(^{\text{III}}\) (two unpaired electrons, \(^2A_2\) state) complexes appear to be isotropic under idealized \(C_{3v}\) symmetry. Chapter three we will describe recent efforts to incorporate these building blocks into magnetic networks and polynuclear complexes that are isostructural to those containing low-spin Fe\(^{\text{III}}\) centers. Efforts towards describing the basic mechanism of slow relaxation of the magnetization and quantum tunneling in well-defined and structurally related discrete magnetic complexes will also be described.
Chapter 3: Syntheses, Structures, and Magnetic Characterization of Polynuclear Cyanomanganate Complexes and a One-Dimensional Network.

Introduction.

Dunbar and coworkers have reported that trigonal bipyramidal \([\text{Mn}^{III}(\text{CN})_6]^{2-}\cdot[\text{Mn}^{III}L_3]\) \((L = 3,4,7,8\text{-tetramethyl-1,10-phenanthroline})\) complexes exhibit magnetic relaxation that is characteristic of single-molecule magnets. In this polynuclear complex the \(\text{Mn}^{III}\) ions exhibit first-order orbital contributions to the magnetic ground state via spin-orbit interactions and is purported to be the origin of slow relaxation of the magnetization in the \([\text{Mn}^{III}_2\text{M}^{II}_3]\) clusters. These studies indicate that polynuclear cyanometalate complexes that contain paramagnetic centers with substantial spin-orbit coupling interactions exhibit fundamentally different behavior than oxide-bridged clusters, in which these interactions are nearly quenched by the low-symmetry ligand environment. For cyanide-based complexes that exhibit slow relaxation of the magnetization, the total angular momentum projection (\(|M_J|\)) appears to be very important in establishing negative cluster anisotropy and an activation energy barrier \((U)\) to thermal magnetization reversal.

To our knowledge only two homoleptic di- and trivalent hexacyanomanganates are known, and each appears to exhibit orbital angular momentum contributions to their magnetic ground states. These complexes, \(K_4[\text{Mn(CN)}_6]3\text{H}_2\text{O} (S = \frac{1}{2}, g = 2.5)^{90,93,94}\) and \(K_3[\text{Mn}^{III}(\text{CN})_6]\cdot\text{H}_2\text{O} (S = 1, g = 2.47)^{95,96,97,98,99,100}\) exhibit low-spin \(t_{2g}^5 (S = \frac{1}{2})\) and \(t_{2g}^4 (S = 1)\) electron configurations, respectively, with significant orbital contributions to their magnetic moments. Unfortunately only the former complex is stable under the synthetic conditions commonly used to construct well-defined polynuclear cyanomanganates.

Consequently we began a concerted effort to expand the number of known cyanomanganate complexes, in an attempt to expand the number of cyanometalate complexes that exhibit slow relaxation of the magnetization. Previous efforts have focused primarily on the systematic preparation of polynuclear cyanide-bridged complexes containing low-spin \(S = \frac{1}{2}\) \([(\text{Tp}^R)^3\text{Fe}^{III}(\text{CN})_3](\text{Tp}^{R,R} = \text{poly(pyrazolyl)borate})\) anions. In comparison to these \(\text{Fe}^{III}\) analogues, paramagnetic low-spin \(\text{Mn}^{II}\) and \(\text{Mn}^{III}\) ions are
anticipated to engage in even more efficient $\pi$ backbonding and cyanide-mediated superexchange interactions, in addition to being magnetically anisotropic.

To our knowledge no other paramagnetic cyanomanganate complexes are known and none contain poly(pyrazolyl)borates as ancillary ligands. We reasoned that these soluble tricyano building blocks would be useful for constructing structurally related analogues of $\{\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\}_3$ clusters derived from $[\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}$ ions. Insertion of Mn$^{\text{III}}$ centers into the trivalent sites of rectangular $\{\text{Fe}^{\text{III}}\text{M}^{\text{II}}\}_2$ complexes that exhibit slow relaxation of the magnetization should also be possible, allowing for a direct comparison of their structures, magnetic, and optical properties. Furthermore, low-spin Mn$^{\text{II}}$ cyanometalates should exhibit greater $\pi$-backbonding and more efficient cyanide-mediated superexchange interactions than isoelectronic Fe$^{\text{III}}$ analogues containing $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, $[(\text{Tp}^*)\text{Fe}^{\text{III}}(\text{CN})_3]^-$, and $[(\text{pzTp})\text{Fe}^{\text{III}}(\text{CN})_3]^-$ centers. Incorporating tricyanomanganate(III) complexes into tetranuclear cluster frameworks should also allow for direct comparisons to be made to those containing $[\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}$ ions. Lastly, alteration of the steric demand of the poly(pyrazolyl)borates may also allow for systematic tuning of the orbital anisotropy ($\lambda$) of the cyanometalate ions and their cluster derivatives, providing a better understanding of the physical origins of magnetic relaxation behavior, in a series of structurally related cyanometalate complexes.

As judged from previous studies, we initially limited our synthetic investigations to rectangular tetranuclear complexes as these $\{\text{Fe}^{\text{III}}\text{M}^{\text{II}}\}_2$ clusters are known to exhibit slow relaxation of the magnetization. We reasoned that insertion of anisotropic Mn$^{\text{III}}$ centers into the trivalent sites would afford $\{\text{Mn}^{\text{III}}\text{M}^{\text{II}}\}_2$ ($\text{M}^{\text{II}} = \text{Mn}, \text{Ni}, \text{Co}$) complexes that may exhibit high blocking temperatures than their structurally related $\{\text{Fe}^{\text{III}}\text{M}^{\text{II}}\}_2$ analogues. In chapter two we described the preparation of a series of di- and trivalent cyanomanganate complexes with $[\text{cat}]((\text{Tp}^*)\text{Mn}^{\text{III}}(\text{CN})_3)$ [cat = NEt$_4$, PPN] being the most useful building block for constructing polynuclear complexes. Herein we describe the syntheses, crystallographic and magnetic characterization of several new network and polynuclear complexes containing Mn$^{\text{II}}$ and Mn$^{\text{III}}$ ions.
Experimental Section.

Materials. All operations were conducted under an argon atmosphere by using standard Schlenk 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), sodium-benzophenone (diethyl ether), or magnesium turnings (methanol) and sparged with argon prior to use. The preparation of KTp*,[34-39] [NEt$_4$]CN, Mn(OTf)$_2$, [cis-Co$^{II}$(bipy)$_2$(OH)$_2$][OTf]$_2$, and [cis-Ni$^{II}$(bipy)$_2$(OH)$_2$][OTf]$_2$ are described elsewhere. Iodine (Baker), and 2,2'-bipyridine (Aldrich) were used as received.

Physical Measurements. The IR spectra were recorded as Nujol mulls between KBr plates on a Mattson Galaxy 5200 FTIR instrument. Magnetic measurements were conducted on a Johnson-Matthey magnetic susceptibility balance and a Quantum Design MPMSXL SQUID magnetometer. Diamagnetic corrections were estimated using Pascal’s constants.$^{107-109}$ Microanalyses were performed by Robertson Microlit Laboratories.

Synthesis of {(Tp*)Mn$^{II}$($\kappa^2$O-acac-3-CN)}$_n$ (7). Treatment of [NEt$_4$][(Tp*)Mn$^{II}$($\kappa^2$O-acac)(CN)] (1.00 g, 1.65 mmol) in MeCN (5 mL) with I$_2$ (0.21 g, 0.82 mmol) rapidly afforded a brown solution that was allowed to stand for 12 h. The yellow crystals that formed were isolated via filtration, washed with Et$_2$O (2 $\times$ 3 mL), and dried under vacuum for 2 h at room temperature. Yield: 0.172 g (20.1%). Anal. Calcd for C$_{23}$H$_{31}$BMnN$_8$O$_2$: C, 53.40; H, 6.04; N, 21.66. Found: C, 53.12; H, 6.08; N, 21.44. IR (Nujol, cm$^{-1}$): 3468 (s), 3376 (s), 3251 (s), 3124 (s), 2733 (m), 2516 (s), 2452 (m), 2247 (m), 2202 (s), 2146 (m), 1634 (s), 1541 (s), 1522 (s), 1456 (s), 1417 (s), 1377 (s), 1348 (s), 1273 (m), 1196 (s), 1181 (s), 1148 (m), 1126 (m), 1067 (s), 1044 (s), 983 (m), 912 (m), 843 (m), 805 (s), 776 (m), 723 (w), 694 (m), 648 (s), 608 (w), 523 (w), 460 (m).

Synthesis of {[NEt$_4$][(Tp*)Mn$^{II}$($\kappa^2$O-acac-CN)]$_2$(μ-CN)}·MeCN$^{-1}$/Et$_2$O (8). Addition of a MeCN (3 mL) solution of I$_2$ (0.080 g, 0.31 mmol) to 1 (0.40 g, 0.66 mmol) in MeCN (3 mL) afforded a yellow solution that slowly deposited a white solid after 12
The mixture was concentrated under vacuum to a volume of 3 mL and was filtered. The yellow filtrate was layered with Et₂O (50 mL) and a small quantity of yellow crystals (2) formed after 24 h. The crystals were isolated via filtration, washed with Et₂O (2 × 5 mL), and dried under vacuum for 2 h at room temperature. IR (Nujol, cm⁻¹): 3363 (s), 3243 (s), 3113 (s), 2731 (m), 2517 (s), 2448 (m), 2189 (s), 2124 (m), 1624 (s), 1537 (s), 1510 (s), 1446 (s), 1378 (s), 1261 (s), 1196 (s), 1181 (s), 1068 (s), 1033 (s), 912 (m), 847 (m), 801 (s), 698 (m), 644 (s), 605 (m), 522 (m).

**Synthesis of [(Tp*)Mn³⁺(CN)₃]₂[Mn²⁺(bipy)₂]₂[OTf]₂ (9).** Treatment of [NEt₄][(Tp*)-Mn³⁺(CN)₃] (0.215 g, 0.384 mmol) in MeCN (3 mL) with a MeCN (3 mL) solution of Mn(OTf)₂ (0.135 g, 0.382 mmol) and bipy (0.120 g, 0.768 mmol) rapidly afforded an orange solution that became red-brown after several min. Et₂O (40 mL) was layered onto the mixture and was allowed to stand for 2 d. The yellow crystals that deposited were isolated via filtration, washed with Et₂O (10 mL), and dried under vacuum at room temperature for 16 h. Yield: 0.280 g (77.1%). Anal. Calcd for C₇₈H₇₆B₂F₆Mn₄N₂₆O₆S₂: C, 49.49; H, 4.05; N, 19.24. Found: C, 49.29; H, 3.77; N, 19.35. IR (Nujol, cm⁻¹): 2551 (w), 2142 (m), 1594 (s), 1565 (m), 1547 (s), 1488 (m), 1448 (vs), 1377 (s), 1365 (s), 1331 (m), 1263 (vs), 1224 (s), 1201 (s), 1153 (s), 1099 (m), 1064 (s), 1049 (s), 1031 (vs), 1016 (s), 863 (m), 811 (s), 770 (vs), 739 (s), 693 (m), 647 (s), 638 (vs).

**Synthesis of [{[(Tp*)Mn³⁺(CN)₃]₂[Ni²⁺(bipy)₂]₂[OTf]₂} (10).** Treatment of a MeCN (3 mL) solution of [Ni(bipy)₂(OH)₂]₂[OTf]₂ (0.135 g, 0.382 mmol) with [NEt₄][(Tp*)Mn³⁺(CN)₃] (0.215 g, 0.384 mmol) in MeCN (3 mL) at -40 °C rapidly afforded a brown solution. Chilled Et₂O (30 mL, 0°C) was layered onto the solution (-40 °C) and was allowed to stand for 2 d at -40 °C. The yellow solid was isolated via filtration, washed with Et₂O (2 × 10 mL, -40 °C), and dried under vacuum at room temperature for 1 h. Yield: 0.170 g (40.8%). Anal. Calcd for C₇₈H₇₇B₂F₆Mn₂Ni₂N₂₆O₆.5S₂: C, 49.06; H, 4.06; N, 19.07. Found: C, 49.02; H, 3.75; N, 18.90. IR (Nujol, cm⁻¹): 2547 (w), 2155(m), 1598 (s), 1566 (w), 1542 (s), 1489 (m), 1446 (vs), 1377 (s), 1366 (s), 1310 (m), 1273 (vs), 1202 (s), 1153 (s), 1103 (m), 1062 (vs), 1049 (m), 1030 (vs), 864 (w), 807 (m), 775 (vs), 738 (m), 693 (m), 651 (m), 637 (s).
**Synthesis of [Co(II)(bipy)₂(CN)₂][OTf]₁₁.** Treatment of a MeCN (4 mL) solution of [Co(bipy)₂(OH)₂][OTf]₂₁₂₄,₁₂₅ (0.063 g, 0.089 mmol) with [NEt₄][(Tp*)Mn(III)(CN)₃] (0.05 g, 0.089 mmol) in MeCN (4 mL) at -40 °C rapidly afforded a brown solution. Chilled Et₂O (30 mL, 0°C) was layered onto the solution (-40 °C) and was allowed to stand for 2 d at -40 °C. The yellow solid was isolated via filtration, washed with Et₂O (2 × 10 mL, -40 °C), and dried under vacuum at room temperature for 1 h. Yield: 0.035 g (30.5%). IR (Nujol, cm⁻¹): 2954 (s), 2922(s), 2852(s), 2141(m), 1605(m), 1598 (s), 1566 (w), 1467 (m), 1446 (s), 1376 (m), 1314 (m), 1263 (s), 1223 (m), 1150 (m), 1108 (m), 1068 (m), 1026 (s), 895 (w), 802 (m), 771 (s), 754 (m), 730(m), 695 (w).

**Structure Determinations and Refinements.** X-ray diffraction data were collected at 90.0(2) K for 7 and 9 was collected on a Bruker X8 Proteum rotating anode diffractometer using graphite-monochromated Cu Kα radiation while data for 8 and 11 were obtained on a Nonius kappaCCD diffractometer using Mo Kα radiation. Crystals were mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained (DENZO)¹¹⁰ from ten 1° frames (SCALEPACK).¹¹⁰ Lorentz/polarization corrections were applied during data reduction. The structures were solved by direct methods (SHELXL97)¹¹¹ and completed by difference Fourier methods (SHELXL97).¹¹¹ Refinement was performed against F² by weighted full-matrix least-squares (SHELXL97),¹¹¹ and empirical absorption corrections (either SCALEPACK¹¹⁰ or SADABSB¹¹²) 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.*¹¹³ Crystal data, relevant details of the structure determinations, and selected geometrical parameters are provided in Tables 3.1-3.3

**Results and Discussion**
**Syntheses and Spectroscopic Characterization: Divalent Cyanomanganates.** In chapter two we described that treatment of manganese(III)acetylacetonate with potassium hydridotris(3,5-dimethylpyrazol-1-yl)borate (KTP*), followed by excess tetraethylammonium cyanide, affords \([\text{NEt}_4][(\text{Tp}^\ast)\text{Mn}^{\text{II}}(\kappa^2\text{O-acac})(\text{CN})]\) as a yellow crystalline solid. Attempts to isolate a trivalent analogue consistently met with failure, while the putative divalent cyanide-free complexes, \([(\text{Tp}^\ast)\text{Mn}(\kappa^2\text{O-acac})(\kappa^1\text{O-acac})]\) and \([(\text{Tp}^\ast)\text{Mn}(\kappa^2\text{O-acac})][\text{acac}]\), were generated and used in-situ; the former is dichloromethane soluble while the latter salt is not appreciably so. Attempted oxidation of \([\text{NEt}_4][(\text{Tp}^\ast)\text{Mn}^{\text{II}}(\kappa^2\text{O-acac})(\text{CN})]\) with molecular iodine yields \(\{[(\text{Tp}^\ast)\text{Mn}^{\text{II}}(\kappa^2\text{O-acac-CN})]\}_n\) (7) and \(\{[\text{NEt}_4][(\text{Tp}^\ast)\text{Mn}^{\text{II}}(\kappa^2\text{O-acac-CN})]\}_2(\mu-CN)\) (8) as the major and minor products, respectively; We presume that electrophillic iodination of 1, followed by rapid cyanide substitution, affords 7 and 8 rather than the desired trivalent complex \([(\text{Tp}^\ast)\text{Mn}^{\text{III}}(\kappa^2\text{O-acac})(\text{CN})]\) (Scheme 3.1).

\[
\begin{align*}
\text{Complex 1} & \quad \text{Et}_2\text{O} \quad \text{I}_2/\text{MeCN} \\
[\text{NEt}_4][(\text{Tp}^\ast)\text{Mn}^{\text{II}}(\text{acac})(\text{CN})] & \quad \rightarrow \\
\text{Complex 8} & \quad \text{Complex 7}
\end{align*}
\]

**Scheme 3.1**
The infrared spectra of 7 and 8 exhibit intense cyanide stretching absorptions that are shifted to higher energies relative to tetra(ethyl)ammonium cyanide (2056 cm\(^{-1}\))\(^{103}\) and most cyanomanganate(II) compounds. The \(v_{CN}\) absorptions seen for \([\text{Tp}^*]\text{Mn}^{II}\)\((\kappa^2O\text{-acac})(\text{CN})]\), 2099(m) and 2076(w) cm\(^{-1}\), are found at lower energies than those in \(K_4[\text{Mn}^{II}(\text{CN})_6] \cdot 3\text{H}_2\text{O}\) (2060 cm\(^{-1}\)), \([\text{Mn}^{II}(\text{CN})_2(\text{bipy})_2] \cdot 3\text{H}_2\text{O}\) [2114 cm\(^{-1}\)], and \([\text{NEt}_4]_2[\text{Mn}^{II}(\text{CN})_4]\) (3) [2120 cm\(^{-1}\)] suggesting that efficient \(\pi\) backbonding is present.

For 7, the \(v_{CN}\) stretches are found at higher energies [2247, 2202, and 2146 cm\(^{-1}\)] than those seen for \([\text{PPN}]_2[\text{Mn}^{IV}(\text{CN})_6]\) (2132 cm\(^{-1}\)), \([\text{PPN}]_3[\text{Mn}^{III}(\text{CN})_6]\) (2092 and 2098 cm\(^{-1}\)), \(K_3[\text{Mn}^{III}(\text{CN})_6]\) (2112 and 2121 cm\(^{-1}\)), \(K_2[\text{Mn}^{IV}(\text{CN})_6]\) (2240, 2150 cm\(^{-1}\)), \(K_2\text{Mn}^{II}[\text{Mn}^{II}(\text{CN})_6]\) (2055 cm\(^{-1}\)), suggesting that these absorptions are due to nitriles rather than terminal cyanides.

For 7 and 8 the \(v_{CN}\) absorptions are found at higher energies than those in \([\text{Tp}^*]\text{Mn}^{III}(\kappa^2O\text{-acac})(\text{CN})]\) and many mixed-valent cyanomanganate Prussian blue analogues. For 7, the former absorption [2202 and 2146 cm\(^{-1}\)] is attributed to the 3-cyano-2,4-pentanedionato nitrile group spanning the Mn\(^{II}\) centers while the latter is tentatively assigned as the terminal cyano group. The \(v_{CN}\) stretches for 8 are found at higher energies than those in \(K_2\text{Mn}^{II}[\text{Mn}^{II}(\text{CN})_6]\) (2055 cm\(^{-1}\)), \(Mn^{II}_3[Mn^{III}(\text{CN})_6] \cdot 12\text{H}_2\text{O}\) (2148 cm\(^{-1}\)) and \(Cs\text{Mn}^{II}[Mn^{III}(\text{CN})_6] \cdot 1/2\text{H}_2\text{O}\) (2148 and 2071 cm\(^{-1}\)), suggesting that inefficient charge delocalization via \(\pi\) back bonding occurs in 2, and/or that efficient depopulation of the weakly antibonding cyanide 5\(\sigma\) orbitals of the bridging cyanides is operative.\(^{116}\) The \(v_{CN}\) absorptions exhibited by \(\text{Mn}^{III}(3\text{-NCacac})_3\) and 3-cyanoacetylacetone are 2211 and 2217 cm\(^{-1}\), respectively.

**Syntheses and Spectroscopic Characterization: Polynuclear Trivalent Cyanomanganates.** Subsequent treatment of \([\text{NEt}_4]_2[\text{Tp}^*]\text{Mn}^{III}(\text{CN})_3]\) with divalent 3\(d\) trifluoromethanesulfonates in the presence of 2,2\(^{\prime}\)-bipyridine quickly affords tetranuclear complexes in moderate yield.\(^{(\text{Scheme 3.2})}\) Treatment of \([\text{NEt}_4]_2[\text{Tp}^*]\text{Mn}^{III}(\text{CN})_3]\) with \(\text{M}(\text{OTf})_2\) (\(\text{M}^{II} = \text{Mn}, 9; \text{Ni}, 10\)) followed by 2,2\(^{\prime}\)-bipyridine affords tetranuclear complexes of \{\{[(\text{Tp}^*)\text{Mn}^{III}(\text{CN})_3]_2[M(\text{bipy})_2]_2[\text{OTf}]_2\}\} stoichiometry. The infrared spectra exhibit high energy \(v_{BH}\) and \(v_{CN}\) stretching absorptions at 2551 and 2142 cm\(^{-1}\) for 9, and 2547 and 2155 cm\(^{-1}\) for 10, respectively, with \(v_{CN}\) absorptions shifted to higher energies.
relative to those in \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{III}(\text{CN})_3]\) [2552 and 2113 cm\(^{-1}\)], suggesting that bridging cyanides \([\text{Mn}^{III}(\mu-\text{CN})\text{Mn}^{II}]\) are present. The energy of the \(\nu_{\text{CN}}\) stretch in 9 is comparable to those seen for \(\text{CsMn}^{II}[\text{Mn}^{III}(\text{CN})_6]^{1/2}\text{H}_2\text{O} [2148 (\text{Mn}^{III}(\mu-\text{CN})\text{Mn}^{II})\) and 2071 (\(\text{Mn}^{II}(\mu-\text{CN})\text{Mn}^{II}\) cm\(^{-1}\)), \(\text{Mn}^{II}_3[\text{Mn}^{III}(\text{CN})_6]_2\cdot12\text{H}_2\text{O} [2148 \text{ cm}^{-1}]\), and \{\([\text{Mn}^{III}(\text{CN})_6]_2[\text{Mn}^{II}(\text{tmphen})]_3\} [2138, 2131, 2113, 2068 \text{ cm}^{-1}; \text{tmphen} = 3,4,7,8\text{-tetramethyl-1,10-phenanthroline}\}, and is higher than the stretch seen in \(\text{K}_2\text{Mn}^{II}[\text{Mn}^{II}(\text{CN})_6]_2\cdot12\text{H}_2\text{O} [2148 \text{ cm}^{-1}]\). For 10, the \(\nu_{\text{CN}}\) stretch energy compares favorably to those in \(\text{Ni}^{II}_3[\text{Mn}^{III}(\text{CN})_6]_2\cdot12\text{H}_2\text{O} [2164 \text{ cm}^{-1}]\), \(\text{CsNi}^{II}[\text{Mn}^{III}(\text{CN})_6] [2154 \text{ cm}^{-1}]\), and \([\text{Ni}(\text{cyclam})]_3[\text{Mn}^{III}(\text{CN})_6]_2\cdot16\text{H}_2\text{O} [2116 \text{ and } 2139 \text{ cm}^{-1}; \text{cyclam} = 1,4,7,10\text{-tetraazadodecanec}]\). As judged from the infrared data we conclude that 3 and 4 likely contain \(\text{Mn}^{III}(\mu-\text{CN})\text{Mn}^{II}\) linkages.

![Scheme 3.2](image)

However, both 9 and 10 require cold reaction temperatures (-40°C) as cyanide redistribution and redox reactions appear dominate at higher temperatures. For example combination of \([\text{Ni}^{II}(\text{bipy})_2(\text{H}_2\text{O})_2][\text{OTf}]_2\) with the \([\text{NEt}_4][(\text{Tp}^*)\text{Mn}^{III}(\text{CN})_3]\) at room temperature rapidly precipitates a white solid that exhibits a \(\nu_{\text{BH}}\) stretch at 2521 cm\(^{-1}\), in addition to intense \(\nu_{\text{CN}}\) absorptions at 2139 and 2150 cm\(^{-1}\), that are likely due to \(\text{Ni}^{II}(\mu-\text{CN})\text{M}^{II}\) linkages, containing \([\text{Ni}^{II}(\text{CN})_4]^{2-}\) ions. An additional intense \(\nu_{\text{BH}}\) stretch is also found at 2524 cm\(^{-1}\) and is tentatively ascribed to \((\text{Tp}^*)_2\text{Mn}^{II}\); colorless crystals of product were isolated and crystallographic characterization confirms that this compound is indeed \((\text{Tp}^*)_2\text{Mn}^{II}\). However, for reactions preformed at -40°C \{\text{Mn}^{III}_2\text{M}^{II}_2\} complexes eventually are obtained, and their infrared spectra contain \(\nu_{\text{BH}}\) and \(\nu_{\text{CN}}\)
stretching absorptions, 2551 and 2142 (for 10) and 2547 and 2155 cm\(^{-1}\) (for 10), that resemble those observed for \{Fe\(_{\text{III}}\)\(_2\)M\(_{\text{II}}\)\(_2\}\) complexes.

Surprisingly despite performed reactions at low temperatures, we have been unable to prepare polynuclear cyanomanganate(III) complexes containing divalent cobalt ions. Treatment of \([\text{NEt}_4][(T\*p*)\text{Mn}^{\text{III}}(\text{CN})_3]\) with \([\text{cis-Co}^{\text{II}}(\text{bipy})_2(\text{OH}_2)_2][\text{OTf}]_2\) cleanly affords \([\text{cis-Co}^{\text{II}}(\text{CN})_2(\text{bipy})_2][\text{OTf}]\) (11; \(\nu_{\text{CN}} = 2142\) cm\(^{-1}\)) as the sole cyanide-containing complex, suggesting that the trivalent manganese complex readily oxidizes \([\text{cis-Co}^{\text{II}}(\text{bipy})_2(\text{OH}_2)_2][\text{OTf}]_2\); \((T\*p*)_2\text{Mn}^{\text{II}}\) was again isolated as the only identified manganese complex (Scheme 3.3).

![Scheme 3.3](image)

Crystallographic Studies: Divalent Complexes. Compound 7 crystallizes in the monoclinic \(P2_1/c\) space group as a zigzag one-dimensional chain that propagates along the crystallographic \(c\) direction (Table 3.1). The Mn1-O distances [2.156(2) and 2.195(2) Å] are slightly shorter than those found in \([\text{NEt}_4][(T\*p*)\text{Mn}^{\text{II}}(\kappa^2-O\text{-acac})(\text{CN})]\), while the Mn-N7 bond of the bridging nitrile ligand is 2.315(2) Å. The O1-Mn1-O2 bond angle is 80.93(5)\(^{\circ}\) while the Mn1-O1-C17 and Mn1-O2-C19 angles are comparable, at 130.7(2) and 129.5(2)\(^{\circ}\), respectively; the bridging nitrile Mn1-N7-C21 and 3-CNacac C17-C18-C19 angles are 155.0(2) and 124.8(2)\(^{\circ}\), respectively (Tables 3.2 and 3.3). As in \([\text{NEt}_4][(T\*p*)\text{Mn}^{\text{II}}(\kappa^2-O\text{-acac})(\text{CN})]\) the 3-CNacac ligand is twisted (\(ca.\ 21^{\circ}\)) relative to the mean plane defined by the manganese and substituted acetylacetonate ligand. The Mn\(^{\text{II}}\) and oxygen atoms deviate from this O1-C17-C18-C19-O2 plane by distances that are comparable to 1 [3.382(1) Å]. Likewise, the 3-cyanoacetylacetonate ligand is bent away from the Tp\(^*\) methyl group projecting above the Mn(\(\kappa^2-O\text{-acac}\)) unit, where the closest O\(\cdots\)C contacts are \(ca.\ 3.328(1)\) Å.
Complex 7 crystallizes as a zigzag one-dimensional chain (Figure 3.2) in the monoclinic \( \text{P}_2_1/c \) space group. Figure 3.1 shows the unit of this chain. The Mn1-O distances [2.156(2) and 2.195(2) Å] are slightly shorter than those found in \([\text{NET}_4][(\text{Tp}^*-)\text{Mn}^{\text{II}}(\kappa^2O\text{-acac})(\text{CN})]\), while the Mn-N7 bond of the bridging nitrile ligand is 2.315(2) Å. The O1-Mn1-O2 bond angle is 80.93(5)° while the Mn1-O1-C17 and Mn1-O2-C19 angles are comparable, at 130.7(2) and 129.5(2)°, respectively; the bridging nitrile Mn1-N7-C21 and 3-CN-acac C17-C18-C19 angles are 155.0(2) and 124.87(2)°, respectively. As seen for \([\text{NET}_4][(\text{Tp}^*)\text{Mn}^{\text{II}}(\kappa^2O\text{-acac})(\text{CN})]\) the 3-CN-acac ligand is also twisted (ca. 21°) relative to the mean plane defined by the Mn1, O1, C17, C18, C19 and O2 atoms.

Crystals of 8 are in the triclinic \( P\bar{1} \) space group and the structure consists of two neutral \([\text{(Tp}^*)\text{Mn}^{\text{II}}(3\text{-CNacac})]\) fragments linked via a single \( \mu\text{-CN} \) bridge (Table 3.3). The bridging cyanide carbon and nitrogen atom sites are disordered along the Mn1---Mn2 vector and nearly identical Mn1-C43(N14) and Mn2-N14(C43) bond distances [2.249(3) and 2.241(3) Å] are found (Table 3.2). The Mn-C distances in 8 are longer than those found in \( \text{Na}_4[\text{Mn}^{\text{II}}(\text{CN})_6]\cdot 10\text{H}_2\text{O} \) [1.95(1) Å] \textsuperscript{118} and the Mn-NMeCN bond lengths in \([\text{Mn}^{\text{II}}(\text{bptz})(\text{NCMe})_2][\text{BF}_4]_2 \) [2.143(4) and 2.166(4) Å] \textsuperscript{119} as expected.

The bond distances and angles present within the 3-cyanoacetylacetonate fragments of 8 are nearly identical and are representative of those generally seen in trivalent acetylacetonate complexes. The O-C bonds are nearly identical ranging from 1.250(4) [O2-C17] to 1.261(5) [O3-C40] Å while the C17-C18-C19 and C38-C39-C40 bond angles are 125.7(4) and 125.5(4)°, respectively (Table 2.3 and Figure 3.3). In 8 the 3-CNacac fragments are canted towards each other and relative to the Mn1-C43-N14-Mn2 axis the cyano groups are rotated by ca. 14.5 degrees. The close 3-CNacac ligand contacts [3.605(5) Å] are likely the result of significant steric interactions between the Tp* methyl groups [ca. 3.620(5) Å] present in 8.

**Crystallographic Studies: Trivalent Complexes.** Compound 9 is a tetranuclear cationic polynuclear complex that crystallizes in the triclinic \( P\bar{1} \) space group (Table 3.1). The Mn\textsuperscript{III} and Mn\textsuperscript{II} centers reside in alternate corners of the distorted rectangular complex and are linked via bridging cyanides, forming Mn\textsuperscript{III}(\( \mu\text{-CN} \))Mn\textsuperscript{II} units (Figure
3.4). A terminal cyanide per [(Tp*)Mn$^{III}$(CN)$_3$] anion remains and adopts an anti orientation via an inversion center relative to the symmetry equivalent terminal cyanide, above the mean {Mn$^{III}$Mn$^{II}$} plane [3.0887(2) Å]. The structure of 9 is related to {Fe$^{III}$Mn$^{II}$}$_2$ and {[V$^{IV}$O]Mn$^{II}$}$_2$ analogues, in which a Tp* methyl group protects the rectangular face opposite the terminal cyanide [ca. 2.908(7) Å] below the {Mn$^{III}$Mn$^{II}$}$_2$ plane; additional rectangular clusters have also been reported and this appears to be a general structural archetype in this class of cyanometlate materials.$^{18,21,22,60}$

The {Mn$^{III}$Mn$^{II}$}$_2$ complex is remarkably planar and is slightly larger than structurally related clusters containing trivalent iron centers. The bridging cyanide Mn1-C16 distance is 1.967(6) Å and is identical to that found in the [NEt$_4$][(Tp*)Mn$^{III}$(CN)$_3$] building block, while the Mn2-N10 bond is slightly longer at 2.253(4) Å; the average Mn-N$_{bipy}$ distance is 2.253. In complex 9, the Mn1A are Mn$^{III}$ centers with ligand Tp* and CN$^-$ (Mn1-N1 2.005(5) Å, Mn1-C18 1.978(7) Å), while Mn2 and Mn2A are Mn$^{II}$ centers with ligands bipys (Mn2-N10 2.253(4) Å). There are bridging CN$^-$ between Mn$^{III}$ and Mn$^{II}$ centers. The bond distances of Mn1-C16 and Mn2-N7 are 1.967(6) Å and 2.147(5) Å, respectively. We also found the bond angles of C16-Mn1-C17, C16-Mn1-C18 and N7-Mn2-N8A are 85.4(2)$^\circ$, 86.7(2)$^\circ$ and 99.25(17)$^\circ$. The Mn$^{III}$ centers form the linear bonds with the terminal CN$^-$ and bridging CN$^-$ respectively. The bond angles of Mn1-C16-N7, Mn1-C17-N8 and Mn1-C18-N9 are 175.9(5), 177.5(5) and 178.4(5)$^\circ$.

Complex 11 crystallizes in the monoclinic C2/c space group and adopts a structure that is qualitatively similar to that seen for [Mn$^{II}$(bipy)$_2$(CN)$_2$][OTf]$_2$. For 11, the Co-N$_{bpy}$ distances range from 1.936(5) to 1.964(5) Å being shorter than the Mn-N bond lengths reported by Dunbar [2.2844(16) to 2.3503(17) Å]. The Co1-C11 bond [1.876(6) Å] is in the range expected for trivalent cobalt centers while the C11-Co1-C11A angle is 89.0(4)$^\circ$ (Figure 3.5); the C-Mn-C bond angle in Dunbar’s complex is 96.92(8)$^\circ$. The observed bond distances and angles seen in 11 are consistent with the higher positive charge of trivalent cobalt centers, in comparison to Mn$^{II}$ analogues.

**Magnetic Studies.** In chapter two, we previously described that the temperature dependence of the $\chi T$ product suggests that the Mn$^{II}$ centers present in are magnetically
isolated between 1.8 and 300 K. As judged from the $\chi T$ vs $T$ data using crushed single crystals, the $\chi T$ product of [NEt$_4$][(Tp*)Mn$^{\text{II}}$(acac)(CN)] remains nearly constant (~ 4.1 cm$^3$ K mol$^{-1}$), as the temperature is lowered from 300 to ca. 50 K (Figure 2.7). Below 50 K, the $\chi T$ product decreases slightly, approaching a minimum value of 3.13 cm$^3$ K mol$^{-1}$ at 1.8 K. Fitting of the susceptibility data to the Curie-Weiss expression affords Curie and Weiss constants of 4.093 cm$^3$ K mol$^{-1}$ and -0.17 K, respectively. Lastly, fitting the field dependence of the magnetization data, collected between 1 and 7 T at 1.85 K, with an $S = \frac{5}{2}$ Brillouin function suggests that it contains isotropic ($g = 1.93$) Mn$^{\text{II}}$ spin centers that are magnetically isolated (Figure 2.8).
Table 3.1. Crystallographic Data for \{(Tp*)Mn^{II}(\kappa^2O-acac-3-CN)\}_n (7), [NEt_4][(Tp*)Mn^{II}(\kappa^2O-acac-3-CN)](\mu-CN) (8), \{[(Tp*)Mn^{III}(CN)]_2[Mn^{II}(bipy)]_2[OTf]_2\} (9), and [cis-Co^{III}(CN)(bipy)]_2[OTf] (11).

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* I > 2σ(I), R = Σ||F₀| - |F₀||Σ|F₀|, \ R_w = [(Σw(|F₀| - |F₀|²)²/Σw)²]¹/₂²
Table 3.2. Selected Bond Distances (Å) for \{((Tp^*)\text{Mn}^\text{II}(\kappa^2O\text{-acac-3-CN}))_n\} (7), [NEt_4][(Tp^*)\text{Mn}^\text{II}(\kappa^2O\text{-acac-3-CN})](\mu-CN) (8), \{((Tp^*)\text{Mn}^\text{III}(CN))_2[\text{Mn}^\text{II}(\text{bipy})_2][\text{OTf}]_2\} (9), and [\text{cis-Co}^\text{III}(CN)(\text{bipy})_2][\text{OTf}] (11).

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Table 3.3. Selected Bond angles (deg) for \{([Tp^*]Mn^{II}(\kappa^2O\text{-acac-3-CN}))_n\} \text{ (7)}, [NEt_4][([Tp^*]Mn^{II}(\kappa^2O\text{-acac-3-CN}))(\mu-CN)] \text{ (8)}, \{([Tp^*]Mn^{III}(CN)_3)_2[Mn^{II}(\text{bipy})_2][OTf]_2\} \text{ (9)}, \text{ and } [\text{cis-Co}^{III}(CN)(\text{bipy})_2][OTf] \text{ (11)}.

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Figure 3.1. Truncated X-ray structure of asymmetric unit of 7. Thermal ellipsoids are at the 50% level and all hydrogen atoms and lattice solvent are removed for clarity.
Figure 3.2. Truncated X-ray structure of zigzag chain of 7. Thermal ellipsoids are at the 50% level and all hydrogen atoms and lattice solvent are removed for clarity.
Figure 3.3. Truncated X-ray structure of 8. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
Figure 3.4. Truncated X-ray structure of 9. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
Figure 3.5. Truncated X-ray structure of 11. Thermal ellipsoids are at the 50% level and all hydrogen atoms, cations, and lattice solvent are removed for clarity.
The $\chi T$ vs $T$ data of 7 is qualitatively similar to that seen for [NEt$_4$][(Tp*)Mn$^{\text{II}}$(acac)-(CN)] between 300 and 50 K and low temperature data suggests that the Mn$^{\text{II}}$ centers are weakly interacting. The magnetic behavior of 7 was modeled using a modified version of a classical Heisenberg chain (eq 1)

$$\chi_M = \frac{2Ng^2\beta^2S(S+1)1-u}{3kT(1+u)}$$

(1)

Where $u = -\coth K$, $K = JS(S+1)/kT$, $S = \frac{5}{2}$, and an exchange Hamiltonian of $H = -2J \sum S_iS_{i+1}$. The values calculated for $J_{\text{Mn-Mn}}/k_B$ and $g$ are -0.062 K and 2.04, respectively. (Figure 3.6) ac susceptibility measurements indicate that $\chi'$ remains independent of changing frequency, suggesting that 7 may undergo spin canting, as reported by Coronado for Mn$^{\text{II}}$(EDTA).H$_2$O.$^{121,122}$ Finally, the field dependence of the magnetization at 1.83 K rapidly approaches a saturation value of 5.4 $\mu_B$ confirming that isotropic $S = \frac{5}{2}$ Mn$^{\text{II}}$ centers are present (Figure 3.7).

**Magnetic Studies: Trivalent Complexes.** In chapter two we described that in [NEt$_4$][(Tp*)Mn$^{\text{III}}$(CN)$_3$] the room temperature value of the $\chi T$ product is much smaller than that found for complexes containing high-spin Mn$^{\text{II}}$ centers (such as compound 1) suggesting that the manganese centers are low-spin ($S = 1$) and in the trivalent state in this tricyano complex. Octahedral low-spin Mn$^{\text{III}}$ centers are expected to have significant orbital contributions to the magnetic $^3A_g$ ground state in octahedral ions and have $g$ values that deviate significantly from 2.0. Fitting of the $\chi T$ vs $T$ data between 1.8 and 300 K indicates that [NEt$_4$][(Tp*)Mn$^{\text{III}}$(CN)$_3$] is paramagnetic but it does not follow Curie-Weiss law behavior. The room temperature value of $\chi T$ is 1.08 cm$^3$ K mol$^{-1}$ and is close to that expected for an $S = 1$ low-spin Mn$^{\text{III}}$ complex ($C = 1.0$ cm$^3$ K mol$^{-1}$, $g = 2$ assumed). Fitting the $\chi T$ vs $T$ data using an anisotropic Heisenberg Hamiltonian ($H = D S^2$) affords calculated values for $g$ and $D/k_B$ of 2.09 and 9.4 K, respectively. For the low temperature data, the experimental curve deviates significantly from predicted behavior and qualitatively explains the unexpectedly large value of $D$ deduced from the
Heisenberg treatment of the $\chi T$ vs $T$ data. Furthermore, fitting the $M$ vs $H$ data (for $T = 1.85$ K) failed to corroborate the $D$ values estimated via modeling the $\chi T$ vs $T$ data. We tentatively propose that weak antiferromagnetic interactions and/or the presence of paramagnetic impurities, likely due to the reactive nature of [NEt$_4$][(tp*)Mn$^{III}$]($CN$)$_3$] conspire to give physically unrealistic values of $D$.

Nevertheless, [NEt$_4$][(tp*)Mn$^{III}$]($CN$)$_3$] can be utilized as a building block to construct magnetically anisotropic rectangular $\{Mn^{III}_2M^{II}_2\}$ complexes that structurally related to those containing Fe$^{III}$ centers. Compound 9 is a tetranuclear complex that exhibits antiferromagnetic exchange interactions between nearest neighbor Mn$^{III}$ (S = 1) and Mn$^{II}$ h.s. (S = ½) spin centers. At room temperature, value of the $\chi T$ product (10.7 cm$^3$ K mol$^{-1}$) is close to that expected (10.75 cm$^3$ K mol$^{-1}$) for a polynuclear complex containing two non-interacting Mn$^{III}$ (S = 1; C = 1.0 cm$^3$ K mol$^{-1}$) and Mn$^{II}$ (S = 5/2; C = 4.375 cm$^3$ K mol$^{-1}$) centers, assuming that $g = 2$. Below this temperature the $\chi T$ product slowly decreases, reaching a minimum value of (6.5 cm$^3$ K mol$^{-1}$) at 14 K. Lowering the temperature further the $\chi T$ values gradually increase, passing through a maximum (6.9 cm$^3$ K mol$^{-1}$) at 6 K, and decreasing again to another minimum (5.3 cm$^3$ K mol$^{-1}$) at 1.85 K. (Figure 3.8) As a rough estimate of the magnetic exchange interactions present in 9, an isotropic spin Hamiltonian:

$$H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1)$$

(2)

where $J$ is the exchange coupling interaction between the Mn$^{III}$ and Mn$^{II}$ spin spin sites and $S_i$ are the spin operators for the respective metal ions ($S_1 = S_3 = Mn^{III}$ and $S_2 = S_4 = Mn^{II}$).

MAGPACK simulation of the $\chi T$ vs $T$ data for temperatures above 25 K was attempted to phenomenologically reproduce the magnetic data. (Figure 3.9) Simulation of the $\chi T$ vs $T$ data above ca. 25 K should minimize the impact of possible anisotropy effects and/or weak intercluster interactions that may be present in 9. Above 25 K the MAGPACK simulation only qualitatively reproduces the experimental $\chi T$ vs $T$ data and suggests that additional parameters may be required to simulate the data properly;
inclusion of anisotropy Hamiltonian terms and intercluster interactions did not improve the appearance of the MAGPACK simulation of the $\chi T$ vs $T$ data. However, the simulations suggest that a magnetic $S = 3$ ground state for 9, suggesting that the Mn$^{II}$ and Mn$^{III}$ centers engage in antiferromagnetic exchange interactions [$J/k_B = -4.0(1)$ K; $g = 2.06$], as predicted by Goodenough-Kanamori and symmetry arguments; the difference in energy between ground ($S = 3$) and first excited state estimated to be ca. 16 K.

Additional magnetic measurements were obtained to probe the anisotropy of the magnetic ground state in addition to frequency- and magnetic field-dependent relaxation behavior. Unlike the \{Mn$^{III}_2$Mn$^{II}_3$\} complex described by Dunbar and co-workers, ac susceptibility experiments suggest that 3 does not exhibit frequency-dependent behavior above 1.8 K, consistent with our hypothesis that the Mn$^{III}$ centers are isotropic ($^3A_2$ ground state). Confirmation of the magnetic ground state was obtained via field dependence of the magnetization measurements because the saturation magnetization value approaches 6 $\mu_B$ ($H_{dc} = 7$ T) at 1.8 K (Figure 3.10).

The magnetic data suggests that 10 is a tetranuclear \{Mn$^{III}_4$Ni$^{II}_4$\} complex that exhibits ferromagnetic exchange interactions. As judged via the $\chi T$ vs $T$ data at 300 K, the $\chi T$ value (5.4 cm$^3$ K mol$^{-1}$) is slightly greater than the value expected (4.4 cm$^3$ K mol$^{-1}$; $g = 2.1$ assumed) for a complex containing Mn$^{III}$ ($S = 1$) and Ni$^{II}$ ($S = 1$) in a 2:2 ratio (Figure 3.11). The $\chi T$ product increases with decreasing temperature and approach a maximum value of 9.2 cm$^3$ K mol$^{-1}$ at 14 K; below this temperature the $\chi T$ values decrease towards a minimum of 7.4 cm$^3$ K mol$^{-1}$ at 1.85 K.

Based on the tetranuclear structure of 10 the $\chi T$ vs $T$ data was modeled via an equation derived using application of the van Vleck equation to the Kambe vector coupling method (Eqn. 2). The magnetic data was initially modeled using the spin Hamiltonian described in equation 2, where $J_1$ is the magnetic exchange interaction between the Mn$^{III}$ and Ni$^{II}$ sites and $S_i$ are the spin operators for each metal ion ($S_1 = S_3$ for Mn$^{III}$ and $S_2 = S_4$ for Ni$^{II}$); MAGPACK simulations of the data have been unsuccessful to date and additional efforts became necessary to fit the magnetic data phenomenologically. (Figure 3.12)

By taking into account the possibility of dipolar interactions between the \{Mn$^{III}_2$Ni$^{II}_2$\} cores in 10 below ca. 20 K, modification of the of the expression described in Eqn. 2 and
considering inter-complex interactions in the context of the mean field approximation were considered (Eqn. 3):

$$\chi = \frac{\chi_{N_{i}M_{n_{i}}}^{N_{i}M_{n_{i}}}}{1-\frac{2zJ'}{N_{i}^{2}\mu_{B}^{2}}\chi_{N_{i}M_{n_{i}}}}$$

(3)

where $J'$ is the inter-complex interaction and $z$ is the number of neighboring $\{\text{Mn}^{III}_{2}\text{Ni}^{II}_{2}\}$ complexes. However these modifications to the magnetic model did not accurately reproduce the experimental $\chi T$ vs $T$ data, suggesting that magnetic anisotropy effects are manifested at low temperatures. Fitting of the $\chi T$ vs $T$ data above 30 K to avoid anisotropy effects that are presumed to be present in 10 afforded a reasonable fit with $J/k_{B}$, $g$, and $zJ'/k_{B}$ values of +8.8(2) K, 2.28(5), and 0.32(5) K, respectively (Figure 3.13).

Further evidence in support of this hypothesis can be found in the field dependence of the magnetization data for 10. The $M$ vs $H$ data below 8 K confirms that the magnetic exchange interaction are ferromagnetic and that an $S = 4$ ground state is present in 10. At 1.8 K and 7 T the magnetization value (7.1 $\mu_{B}$) for 10 is close to the value expected for an $S_{T} = 4$ spin ground state (8 $\mu_{B}$). (Figure 3.14) Plots of $M$ vs $H/T$ confirm that the magnetic ground state present in 10 is anisotropic, as the isofield lines are nonsuperimposable. (Fiugre 3.15) Consistent with this assumption, attempted fitting of the $M$ vs $H$ data to an $S = 4$ Brillouin function was also met with failure. Moreover for samples of 10 at 1.8 K, the magnetization data indicates that slow saturation of the magnetization occurs above 2 T, adding further support for significant magnetic anisotropy in 10 (from Ni$^{II}$).

However despite the presence of slow saturation of the magnetization and significant magnetic anisotropy in 10, ac susceptibility measurements indicate that no frequency-dependent relaxation is evident in 9 or 10 above 1.8 K, indicating that fast quantum tunneling of the magnetization is likely operative, and that little angular momentum is contributed by the isotropic Mn$^{III}$ centers.

**Conclusions.** In order to prepare polynuclear cyanometalate complexes that exhibit slow relaxation of the magnetization transition metal centers that have significant orbital
contributions to the magnetic moment are apparently required, primarily and the low-spin tricyano sites. For the first time we have probed this hypothesis and have found that this is indeed the case. A variety of new cyanomanganate complexes has been prepared during the course of our studies and while useful for constructing networks and cluster derivatives, di and trivalent cyanomanganates are magnetically isotropic. The low apparent thermal barriers to magnetization reversal likely result from insufficient orbital contributions (by low-spin Mn$^{\text{III}}$ ions) and/or efficient quantum tunneling in $\{\text{Mn}^{\text{III}}_2\text{M}^{\text{II}}_2\}$ complexes. We propose that tricyanomanganate(II) complexes, if they can be synthesized, should be isoelectronic to low-spin ($S = \frac{1}{2}$) tricyanoferrate(III) building blocks, and afford additional SMM analogues.
Figure 3.6. Temperature dependence of the $\chi T$ product of 7 between 1.85 and 300 K for $H_{dc} = 1$ kG.
Figure 3.7. Field dependence of the magnetization of 7 at 1.85 K between 0 and 7 T.
Figure 3.8. Temperature dependence of the $\chi T$ product of 9 between 1.85 and 300 K at $H_{dc} = 1$ (•) and 10 (•) kG.
Figure 3.9. MAGPACK simulation of $\chi T$ vs $T$ data (—) for 9 at $H_{dc} = 1$ kG.
Figure 3.10. Field dependence of the magnetization for 9 at 1.85 K ($0 \leq H_{dc} \leq 7$ T).
Figure 3.11. Temperature dependence of the $\chi T$ product of 10 between 1.85 and 300 K at $H_{dc} = 1$ (•) and 10 (•) kG.
Figure 3.12. Fit of the $\chi T$ vs $T$ data (—) for 10 at 1 kG between 1.8 and 300 K.
Figure 3.13. Fit of the $\chi T$ vs $T$ data (—) for 10 at 1 kG between 30 and 300 K.
Figure 3.14. Field dependence of the magnetization of 10 at various temperatures ($0 \leq H_{dc} \leq 7 \, \text{T}$).
Figure 3.15. $M$ vs $H T^{-1}$ for 10 at various temperatures ($0 \leq H_{dc} \leq 7$ T).
References:
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