Pentanuclear cyanide-bridged clusters of the general formula \([\text{[M(tmphen)2]}_3\text{[M'}(\text{CN})_6]\text{]}_2\) (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) have been under investigation in our laboratories for a number of years. These related molecules are conveniently prepared by a building block approach that involves the reaction of mononuclear \([\text{M}(\text{tmphen})_2\text{X}_2]^{0/2+}\) species (M = Cr, Mn, Fe, Co, Ni, Zn; \(\text{X} = \text{anion, solvent}\)) with \([\text{M'}(\text{CN})_6]^{3-}\) anions (M' = Cr, Mn, Fe, Co, Os). The resulting trigonal-bipyramidal (TBP) clusters, consisting of M and M' centers in the equatorial and axial positions, respectively, exhibit diverse properties including those that had previously been observed only for Prussian blue extended phases; these properties include single-molecule magnetism, spin crossover, charge-transfer-induced spin transitions, cyanide linkage isomerism, and magnetic coupling through diamagnetic metal ions. Given that a series of clusters with identical axial cyanometallate units can be prepared, we have been able to establish trends in magnetic coupling for families of clusters with different equatorial metal ions. The crystal packing of the clusters, which involves supramolecular \(\pi\)-stacking interactions, reveals the origin of the observed differences in the coordination environments and, in several cases, the physical properties of the metal ions in the equatorial sites. Recent work has focused on the use of these molecules as building blocks for magnetic chains and the incorporation of highly anisotropic 5d metal ions such as OsIII into the TBP core. Such comprehensive studies of small clusters are valuable for understanding and modeling the magnetic behavior of more complicated cyanide materials.

1. Introduction

Two significant developments occurred in the late 1990s that contributed to the current renaissance in the field of cyanide magnetism. First, it was discovered that early-transition-metal analogues of Prussian blue (PB) exhibit long-range magnetic ordering at moderately high temperatures,\(^1,2\) a finding that ultimately led to the synthesis of derivatives with ordering temperatures as high as 376 K.\(^3\) Second, it was recognized that paramagnetic molecules with relatively high ground-state spin values and negative Ising anisotropy can exhibit magnetic bistability.\(^4,5\) This behavior in discrete molecules, akin to superparamagnetism in nanoparticles, is now commonly referred to as single-molecule magnetism (SMM).\(^6\)
For a full decade after the initial discovery of SMM behavior, the phenomenon was known solely for select oxo- and carboxylato-bridged clusters of Mn, Fe, or Co. Given that the cyanide (CN\(^{-}\)) bridge generates moderate and predictable exchange interactions between metal centers,\(^7\) the development of synthetic strategies for generating poly-nuclear cyanide-based SMMs was a logical direction for research in this area. This approach has proven to be fruitful, as SMM behavior has now been observed in a number of cyanide-bridged clusters.\(^8\)–\(^10\)\(^,\)\(^32\)

The design of cyanide complexes with specific geometries is conveniently accomplished by a building block approach,\(^11\)\(^,\)\(^33\)\(^,\)\(^34\) in which multidentate ligands are used to block coordination sites on transition-metal ions, hence restricting the growth of the structure to finite dimensions rather than extended PB phases. By capitalizing on the high degree of synthetic control, researchers have prepared SMMs with a variety of shapes,\(^34\) ranging from linear trinuclear\(^12\)\(^,\)\(^20\) and square-planar tetranuclear species\(^16\) to octanuclear cubic\(^13\)\(^,\)\(^32\) and pentadecanuclear face-and-body-centered cubic complexes.\(^17\)\(^,\)\(^22\)\(^,\)\(^23\)

In addition to contributing new insight to the understanding of factors that play a role in SMM behavior, research in cyanide chemistry is also helping to shed light on other interesting magnetic phenomena, such as photomagnetism\(^35\)–\(^39\) and spin crossover.\(^40\)\(^,\)\(^41\) The collective data from the past several decades serve to demonstrate that cyanide complexes are versatile platforms for advancing our fundamental understanding of the behavior of molecule-based magnets. Of specific importance to the topic of this Forum Article is the fact that the pentanuclear trigonal bipiramid (TBP) is a particularly stable molecular geometry that is well suited for a variety of molecular magnetism applications.

The TBP cyanide cluster type was first documented in 1997 by Murray et al.,\(^42\) who reported a crystal structure of the ferromagnetically coupled cluster \(\{[\text{Ni}^{II}(\text{bpm})_2][\text{Fe}^{III}(\text{CN})_6]_2\}\) (bpm = bis(1-pyrazolyl)methane) with a ground-state spin value of \(S = 4\). Verdaguer et al. followed up on this theme with an interesting variation, viz., the isolation of \(\text{Ni}^{II}\text{Fe}^{III}_2\) TBP clusters with ground-state spin values of \(S = 7\) achieved by outfitting the Ni centers with paramagnetic \(S = \frac{1}{2}\) radical ligands (e.g., IM2-py = 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy).\(^43\) Other metal combinations for the TBP core were reported in the same time frame by our group (i.e., \(\{[\text{Co}(\text{bpy})_2][\text{Fe}(\text{CN})_6]_2\}\)Cl, bpy = 2,2'-bipyridine\(^44\)) and Mallah et al. (i.e., \(\{[\text{Ni}(\text{IM}2-\text{py})_2][\text{Cr}(\text{CN})_6]_2\}\)\(^45\). Over the next few years, a variety of similar clusters were isolated with various equatorial metal ions and hexacyanometallate anions (e.g., \(\{[\text{Cu}(\text{bpy})_2][\text{Fe}(\text{CN})_6]_2\}\)\(^46\) and \(\{[\text{Ni}(\text{bpm})_2][\text{Co}(\text{CN})_6]_2\}\)\(^47\). Recently, Zuo et al. reported a new family of TBP clusters in which both equatorial and axial metal centers are capped by chelating ligands (e.g., \(\{[\text{Cu}(\text{Me}-3)}\)
A number of related compounds have since been reported, including \([\text{Fe(Tp)(CN)}_3]\)\(\cdot\)\([\text{M(TpmMe)(CN)}_3]_2\)·\(\text{ClO}_4\) (TpmMe\(^{3+}\) = tris(3,5-dimethyl-1-pyrazoyl)methane, M = Ni, Co, Fe),\(^{48}\) \([\text{Ni(cyclen)}]\)\(\cdot\)\([\text{Fe(Tp)(CN)}_3]_2\)\(\cdot\)\(\text{BF}_4\)\(\cdot\)\(x\text{Me}_2\text{acn}\)clononate\(^{19}\)). A number of related compounds have since been reported, including \([\text{Fe(Tp)(CN)}_3]\)\(\cdot\)\([\text{M(TpmMe)(CN)}_3]_2\)·\(\text{ClO}_4\) (TpmMe\(^{3+}\) = tris(3,5-dimethyl-1-pyrazoyl)methane, M = Ni, Co, Fe),\(^{48}\) \([\text{Ni(cyclen)}]\)\(\cdot\)\([\text{Fe(Tp)(CN)}_3]_2\)\(\cdot\)\(\text{BF}_4\)\(\cdot\)\(x\text{Me}_2\text{acn}\)clononate\(^{19}\)).

Although there are many reports of paramagnetic cyanide cluster compounds, there is, in general, a lack of systematic data for a wide range of possible metal ion combinations within the same molecular geometry. A longstanding goal of this group is to develop general synthetic methodologies for the synthesis of structurally related molecules in order to systematically assess how the cyanide ligand affects exchange interactions and magnetic properties for different metal ion combinations in the \(\text{M}^3\text{M}^2\) pair. Our studies of TBP clusters of the general formula \([\text{M(tmphen)}_2]_3\)·\([\text{M}^{III}(\text{CN})_3]_2\) (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline), hereafter denoted as \(\text{M}^3\text{M}^2\), have been especially rewarding in this regard. In contrast to many other bidentate polypyridyl ligands that have been attempted in this research, tmphen leads to the formation of good yields of crystalline samples for many combinations of metal ions. This protocol has provided us with an opportunity to deliberately introduce various metal centers into specific sites of a cyanide-bridged cluster, efforts that have led to molecules with an exceptionally broad range of physical properties. Highlights of these studies include experimental confirmation of the SMM behavior for the \(\text{Mn}_3\text{Mn}_2\) combination, a charge-transfer-induced spin transition (CTIST) for the \(\text{Co}_3\text{Fe}_2\) analogue, a temperature-induced low-spin (LS) to high-spin (HS) transition for the \(\text{Fe}_3\text{Fe}_2\) and \(\text{Fe}_3\text{Co}_2\) molecules, and cyanide linkage isomerism for the \(\text{Fe}_3\text{Cr}_2\) and \(\text{Co}_3\text{Cr}_2\) compounds. Many of these properties have been documented for PB-type extended phases containing analogous combinations of transition-metal ions, while others are specific only for the molecular compounds. As part of our ongoing investigations, we are studying how intermolecular packing interactions affect the spin-transition behavior in these clusters, incorporating 4d and 5d metal ions into the TBP core, and developing strategies for using the \(\text{M}_3\text{M'}_2\) cluster as a building block to form molecular chains. In this Forum Article, we highlight notable magnetic phenomena of TBP compounds that we have previously described in the literature and report on several new developments in the research.

2. Synthetic Methods

The pentanuclear \(\text{M}_3\text{M'}_2\) complexes featured in this Forum Article are prepared by combining a divergent hexacyanometallate anion \(\text{M}^{III}(\text{CN})_6^{3–}\) with a convergent mononuclear precursor of an octahedral divalent metal ion \(\text{M}^{II}\), in which four coordination sites are capped by two bis-chelating tmphen ligands (Scheme 1). These reactions result in the formation of crystalline samples of clusters corresponding to the general formula \([\text{M(tmphen)}_2]_3\)·\([\text{M}^{III}(\text{CN})_3]_2\)·\(x\text{solvent}\). The preparation translates well to many \(\text{M}^{III}(\text{CN})_3^{2–}\) and \(\text{M}(\text{tmphen})_2\)^{2+} precursors to form \(\text{M}_3\text{M'}_2\) clusters of various metal combinations, which are summarized in Table 1. The clusters are generally air-stable in the solid state and contain a variable amount of interstitial solvent, the exact nature and amount of which have a profound effect on the physical properties in key instances. The interstitial solvent is readily removed by heating to ca. 120°C, and the desolvated materials remain stable up to ca. 250°C in an inert atmosphere.

The tmphen ligand is critical for ease of isolation of the \(\text{M}_3\text{M'}_2\) clusters. While a number of derivatives of bpy and phen have been tried using the reaction conditions specified in Scheme 1, they are typically unreliable with respect to reproducibility and isolation of crystals of isomorphous phases. The four peripheral methyl substituents serve to enhance the solubility of the intermediates and products to discourage the formation of extended phases and render the thermodynamic product crystalline. This solubility is evidenced by the fact that a clear reaction solution is retained after mixing of the reagents and that crystal growth occurs slowly from the mother liquor. Another important parameter in these reactions is the solvent. The reactions are carried out in nonaqueous media, although rigorously dry solvents are usually not required unless the metal ion is particularly sensitive. While these conditions can pose a problem because the common hexacyanometallate salts (alkali-metal-based) are insoluble in organic solvents, the introduction of organic
cations allows for the use of a range of solvents. Finally, the fact that the cluster is neutral undoubtedly facilitates crystallization of the compounds from a polar medium. Indeed, with the exception of the Co3Fe2, Fe3Cr2, Fe3Fe2, and Fe3Co2 analogues, which exhibit reasonable solubility in methanol, methanol/acetonitrile (1:1 v/v), or propylene carbonate, the TBP molecules are essentially insoluble in all common solvents.

The aforementioned synthesis has proven to be an efficient method for introducing numerous metal ions into the TBP core. Clusters with Cr, Fe, and Co in the axial sites were readily isolated with a variety of first-row transition metals in the equatorial positions. Only one cluster based on the [MnII(CN)6]3- unit has been isolated, namely, the Mn3Mn2 analogue with MnII ions in the equatorial sites. There are two reasons for this: the [MnII(CN)6]3- anion is relatively unstable in the absence of free CN\(^-\) even in organic media, and redox chemistry occurs when MnIII is combined with most divalent metal ions. A similar situation arises with CrIII incorporation into equatorial positions of the TBP unit because the only stable combination is with [CrIII(CN)6]3-. The preparation of clusters with CuII ions in the equatorial positions has not yet been investigated, mainly because it has only one unpaired electron and will not lend any special properties to the molecules such as anisotropy or spin-transition behavior.

The use of the \(\pi\)-accepting tmphen ligands to protect the equatorial positions of the TBP cluster also serves to stabilize oxidation states that are not possible in the extended structures of the PB type. For instance, it had been long considered that Turnbull blue, or ferrous ferricyanide, “FeII[FeII(CN)6]2”\(^-\), was different from PB, or ferric ferrocyanide, “FeIII[FeII(CN)6]3”, until, in 1962, Robin provided incontrovertible evidence that the compounds are identical and correspond to the latter formula.\(^{49}\) The instability of “Turnbull blue” is a consequence of an instantaneous electron transfer that takes place between FeII and [FeIII(CN)6]3- ions in an aqueous solution. In contrast, the FeII–CN–FeIII pair persists in the TBP cluster ([FeII(tmphen)3][FeIII(CN)6]2) because of the fact that the electron transfer is no longer favorable when the FeII ion is coordinated to tmphen; hence, the [FeII(CN)6]3- unit is retained.\(^{50}\)

Table 1. Characterization of the TBP Complexes ([M(tmphen)3][M'[CN]6]2) based on their Magnetic Properties

<table>
<thead>
<tr>
<th>M</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Os</th>
</tr>
</thead>
<tbody>
<tr>
<td>J</td>
<td>(-21,\text{cm}^{-1}) &amp; (-3.8,\text{cm}^{-1}) &amp; (&lt;0) &amp; para(^{a}) &amp; (+2.3,\text{cm}^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>(-4.7,\text{cm}^{-1}) &amp; (-) &amp; (&gt;0) &amp; para(^{a}) &amp; (+4.3,\text{cm}^{-1})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>(+0.65,\text{cm}^{-1}) &amp; (-) &amp; () &amp; (-) &amp; ()</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>(+8.5,\text{cm}^{-1}) &amp; () &amp; () &amp; (-) &amp; ()</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

\(^{a}\) \(J\) values are from a fit to the Hamiltonian in eq 1. \(^{b}\) Not isolated. \(^{c}\) SMM = single-molecule magnet (see section 4a). \(^{d}\) \(\chi T\) cannot be modeled because a more complex Hamiltonian is required. \(^{e}\) para = paramagnetic cluster; dia = diamagnetic cluster. \(^{f}\) Coupling of axial CrIII ions is mediated by diamagnetic FeII ions (see section 4d). \(^{g}\) SCO = spin-crossover behavior (see section 4c). \(^{h}\) \(\chi T\) could not be modeled successfully because of partial cyanide linkage isomerism (see section 4d). \(^{i}\) CTIST = charge-transfer-induced spin transition (see section 4b).

\(\text{Figure 1.}\) (a) Top and (b) side (with respect to the axial pseudo 3-fold axis of rotation) views of the molecular structure of \([\text{M}^{\text{II}}(\text{tmp-phen})_{3}][\text{M}'^{\text{III}}(\text{CN})_{6}]_{2}\). The cyanide-bridged core is highlighted with a polyhedron. H atoms are omitted for the sake of clarity. Color scheme: red, M; green, M'; blue, N; gray, C.

3. Single-Crystal X-ray Structures

The \(\text{M}_{3}\text{M}_{2}\) clusters featured in this Forum Article consist of two \([\text{M}^{\text{III}}(\text{CN})_{6}]_{2}^{2-}\) anions in the axial positions and three \([\text{M}^{\text{II}}(\text{tmpphen})_{3}]^{2+}\) fragments in the equatorial positions of a TBP (Figure 1). For each hexacyanometallate unit, three CN\(^-\) ligands are bridged to the equatorial M centers, whereas the remaining three are directed away from the cluster. The three equatorial M centers are in distorted octahedral environments consisting of the N atoms of two bidentate tmphen capping ligands and two bridging CN\(^-\) units spanning the edges of the TBP. Each pentanuclear cluster contains three equatorial metal centers of the same \(\Delta\) or \(\Lambda\) chirality, but the unit cell contains equal numbers of \(\Delta\Delta\Delta\) and \(\Lambda\Lambda\Lambda\) molecules, which leads to the centrosymmetric space group \(\text{P2}_{1}/c\). A notable exception is the Fe3Cr2 structure, the unit cell of which contains clusters of the same chirality, resulting in the enantiomorphic space group \(\text{P3}_{2}1\).\(^{50}\)

A careful examination of the X-ray structures reveals the presence of different secondary interactions for the M(1), M(2), and M(3) equatorial sites. Specifically, both tmphen
ligands coordinated to M(2) engage in intramolecular $\pi-\pi$ interactions with a tmphen ligand belonging to each M(1) and M(3) center (Figure 1a). The large separation between the planes of noninteracting tmphen ligands of one pentanuclear molecule creates sufficient space for two clusters to form a dimer held in close proximity via $\pi-\pi$ stacking of four tmphen ligands (Figure 2a). In this arrangement, one of the tmphen ligands on each M(1) center is engaged in two intermolecular $\pi-\pi$ contacts, whereas the ligands coordinated to the M(3) center exhibit only one such contact. Although these intermolecular interactions are rather weak, we have discovered that they play an important role in dictating the magnetic behavior of certain members of the TBP family of complexes (vide infra).

4. Magnetic Properties

The title $M_3M'_2$ clusters offer a convenient platform for probing magnetic exchange interactions between metal centers in a systematic fashion. The coordination sphere about each metal site and the inter- and intramolecular $\pi-\pi$ interactions are retained for the entire family of complexes, and the clusters are isostructural, with the exception of the Fe$_3$Cr$_2$ structure. Furthermore, the study of magnetic exchange interactions between the metal centers is simplified by the pseudotrigonal symmetry of the cluster. The six superexchange pathways can be reduced to a single exchange constant, $J$, and thus the exchange Hamiltonian can be expressed simply as:

$$\hat{H} = -2J(S_{M1} + S_{M2})(S_{M1} + S_{M2} + S_{M3}) + \beta H [g_M(S_{M1} + S_{M2}) + g_M(S_{M1} + S_{M2} + S_{M3})]$$

(1)

The fact that one can use a single $J$ value in this simple model avoids the problem of overparametrization and increases the accuracy and reliability of the extracted parameters.

All of the factors outlined above serve to provide us with a powerful platform for studying exchange interactions. An early example of this approach is illustrated by the fitting of the Ni$_3$Fe$_2$ cluster that we reported in 2003.\textsuperscript{51} The magnetic susceptibility data were modeled using the Hamiltonian (1) with the addition of a zero-field-splitting component, $3D(S_{Ni}^2 - S_{Ni}(S_{Ni} + 1)/3$) (where $D$ represents the axial zero-field-splitting term per one Ni$^{II}$ ion), accurately reproducing the $\chi T$ product over the entire temperature range. The ferromagnetic interactions between the Fe$^{III}$ ($S = 3/2$) and Ni$^{II}$ ($S = 1$) ions lead to a $S = 4$ ground state, as reported earlier by Murray et al. for $\text{[(Ni$^{II}$(bpm)$_2$)$_3$(Fe$^{III}$(CN)$_6$)$_2$]}^2$.\textsuperscript{42} Continuing in the vein of this general method, we set out to introduce highly anisotropic ions into the TBP framework, efforts that resulted in the isolation of the antiferromagnetically

coupled MnII3MnIII2 cluster, an early example of a cyanide-based SMM.

While the majority of subsequently isolated M3M′2 clusters do not exhibit SMM behavior, other magnetic phenomena emerged that proved to be equally or perhaps even more fascinating; highlights of these findings are outlined in the following sections. Of equal importance is the fact that the preparation and characterization of TBP complexes with many different combinations of metal have led to the recognition of patterns that are useful for the future design of systems with predictable properties (Figure 3).

For example, an examination of magnetic properties in the M3Cr2 series (M = Cr, Mn, Co, Ni) reveals a gradual change in the nature and strength of magnetic coupling. In general, when there are pathways for both ferromagnetic and antiferromagnetic coupling between unpaired spins, the resulting magnetic exchange is determined by a sum of both contributions.9 The change in the sign of the coupling in going from Cr3Cr2 to Ni3Cr2 stems from progressively increasing ferromagnetic contributions due to the population of eg orbitals with unpaired electrons and decreasing antiferromagnetic contributions due to the pairing of spins in t2g orbitals (Scheme 2).

a. Single Molecule Magnétism. In the MnII3MnIII2 cluster, the three equatorial MnII ions are coordinated to six N atoms and thus exist in the HS S = 5/2 state, while the two axial MnIII ions are each surrounded by six C-bound cyanide ligands and adopt the LS S = 1 configuration. Magnetic susceptibility measurements indicate that antiferromagnetic superexchange interactions occur between the MnII and MnIII ions, and examination of the out-of-phase susceptibility component measured under an alternating current (ac) magnetic field revealed a frequency-dependent signal below 3.5 K, indicating that MnII3MnIII2 is a possible SMM.11

In order to confirm this SMM behavior, hysteresis loops were collected on oriented single crystals of MnII3MnIII2 using a micro-SQUID apparatus. Temperature-dependent scans revealed hysteretic behavior, with the coercivity increasing at lower temperatures and higher field sweep rates (Figure 4). (Note that the prominent step observed at zero field is due to magnetization relaxation by quantum tunneling.) These results confirm that the MnII3MnIII2 cluster is, indeed, a SMM.

In the MnII3MnIII2 cluster, each MnII ion is in the orbitally nondegenerate 6A1 state, but each MnIII ion is described by the orbital triplet 3T1 and thus has an unquenched orbital angular momentum due to the nearly octahedral symmetry of its coordination environment. Not unexpectedly, attempts to simulate the magnetic behavior of this compound using a spin-only Hamiltonian (1) were unsuccessful. Consequently, a more elaborate theoretical model was developed (Figure 5)15 that takes into account the effects of spin–orbit coupling.
and trigonal crystal-field splitting ($\Delta$) operating at each of the axial MnII centers, as well as isotropic magnetic superexchange ($J_{ex}$) between MnII and MnIII ions mediated by the cyanide bridges:

$$\mathcal{H} = -\kappa \lambda \{(S_{Mn1}^{\prime} L_{Mn1}^{\prime}) + (S_{Mn2}^{\prime} L_{Mn2}^{\prime}) - 2 J_{ex} (S_{Mn1}^{\prime} + S_{Mn2}^{\prime}) - \Delta (L_{Mn1}^{\prime^{2}} + L_{Mn2}^{\prime^{2}} - 4/3) + \beta H \left[ -(L_{Mn1}^{\prime} + L_{Mn2}^{\prime}) + g_{ex} (S_{Mn1}^{\prime} + S_{Mn2}^{\prime}) + g (S_{Mn1} + S_{Mn2} + S_{Mn3}) \right] \}$$

(2)

where variable parameters were $\lambda, \Delta, J_{ex}$, the orbital reduction factor $\kappa$, and the $g$ factor of the equatorial MnIII ions. In the framework of this model, the total angular momentum of the TBP cluster is given by

$$J_{tot} = S_{Mn1}^{\prime} + L_{Mn1}^{\prime} + S_{Mn2}^{\prime} + L_{Mn2}^{\prime} + S_{Mn1} + S_{Mn2} + S_{Mn3}$$

(3)

with the ground-state value shown to be $J = 15/2$. It is important to note that, in this case, only the negative sign of the crystal-field-splitting parameter $\Delta$ creates a scenario where the ground state is sufficiently isolated, a prerequisite for SMM behavior (Figure 4a). If the value of $\Delta$ were positive, the ground state would have the lowest $M_j = 15/2$ (Figure 4b) and SMM behavior would not be observed. This is reminiscent of the situation in “classical” SMMs (i.e., adequately described by the spin-only model) that requires the zero-field-splitting parameter $B$ to be negative.52

A number of cyanide-based SMMs have been subsequently reported, all of them incorporating ions with appreciable spin-orbit coupling.34 The detailed theoretical treatment of the MnIII$_3$MnII$_2$ cluster is, however, the first attempt to unveil the origin of SMM properties in a multinuclear complex with unquenched orbital angular momenta for individual ions. In light of this reasoning, it is clear that the spin-only formalism used to explain the magnetic properties of other cyanide-based SMMs is an oversimplification and that further development of advanced theoretical models is crucial if we are to thoroughly understand the origins and ramifications of magnetic anisotropy in these systems for which the quantum number $S$ is not longer a valid parameter.

**Figure 5.** Calculated energy level diagrams for the MnIII$_3$MnII$_2$ cluster in the case of positive (a) and negative (b) trigonal crystal-field-splitting parameters ($J_{ex} = -3.8$ cm$^{-1}$; $\Delta = \pm 250$ cm$^{-1}$; $\kappa = 0.8$).

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**b. Charge-Transfer-Induced Spin-Transition.** One of our attempts to introduce anisotropy into the equatorial sites of the TBP cluster was to use CoII ions to form the neutral Co$_3$Fe$_2$ complex.53 Red crystalline samples formulated as CoIII$_2$FeIII$_2$ were isolated from a wet acetonitrile solution following the treatment of [18-C-6-K]$_3$[Fe(CN)$_6$] with [Co(tmphen)$_2$]$^{3+}$. While electron transfer between the FeIII and CoII ions to form the product was not unexpected (it had been observed by us44 and others54,55 in other assemblies), the facile reversibility of this process was not anticipated. As established by a combination of X-ray crystallography, Mössbauer spectroscopy, and magnetometry, the variation of the temperature and/or interstitial water content dramatically influences the metal-to-metal charge-transfer (MMCT) process in this cluster. Because this MMCT process governs the spin states of the metal ions, the magnetic properties of the cluster could, in principle, be manipulated by external stimuli.

The cluster can exist in three different electronic forms (i.e., CoIII$_2$CoIIFeII$_2$, CoIII$^2$CoII$^2$FeIII$^2$II$_2$, and CoII$_3$FeII$_2$), and transitions between these redox isomers are accompanied by dramatic color changes (Figure 6a). The red crystalline phase obtained in acetonitrile corresponds to [CoIII(tmphen)$_2$]$_3$-[FeIII(CN)$_6$)$_3$·xH$_2$O ($x \sim 6–13$ for different crystals based on the single-crystal X-ray diffraction and thermogravimetric analysis (TGA) data), where the equatorial CoII ions are in the LS $S = 1/2$ state and the axial FeIII ions are in the LS $S = 3/2$ state. As the temperature is lowered, the solvated crystals acquire a deep blue color, which is accompanied by a diminishing of the $\chi_T$ value down to $\sim 130$ K (Figure 6b). This behavior is a consequence of an intramolecular MMCT (CoII $\rightarrow$ FeIII) process to produce the CoIII$^2$CoII$^2$FeII$^2$ redox isomer at lower temperatures with the diamagnetic LS FeII and CoIII ions.56 Because this MMCT process drives the spin transition at the Co sites (i.e., HS CoII is converted to LS CoIII), it is classified as a CTIST. Although this transformation had been observed in the extended PB-type phase $K_0.2Co_{1.4}[Fe(CN)_6]$,57 this is the first example of a molecule that exhibits such behavior.

Further examination of these samples revealed that the filtration of the red crystalline material in a humid atmosphere leads to a second form of the compound, viz., a blue solid. This behavior is a consequence of an intramolecular MMCT (CoII $\rightarrow$ FeIII) process to produce the CoIII$^2$CoII$^2$FeII$^2$ redox isomer at lower temperatures with the diamagnetic LS FeII and CoIII ions.56 Because this MMCT process drives the spin transition at the Co sites (i.e., HS CoII is converted to LS CoIII), it is classified as a CTIST. Although this transformation had been observed in the extended PB-type phase $K_0.2Co_{1.4}[Fe(CN)_6]$,57 this is the first example of a molecule that exhibits such behavior.

56 Note that these data may also correspond to a mixture of clusters with [CoII$^2$FeII$_2$] and [CoII$^2$CoIII$^2$FeII$_2$] cores.
for a single HS CoII ion, an indication of the onset of a CTIST to the CoII2FeIII2 redox isomer. This conclusion is in accordance with the results of temperature-dependent Mössbauer studies. A sharp increase in $\chi T$ observed above 280 K is due to dehydration of the blue solid phase.

Dehydration of the blue solid phase, or filtration of red crystals in a dry, inert atmosphere, produces a third form of the complex, a red solid formulated as $[\text{Co}(tmphen)_2]_3[\text{Fe(CN)}_6]_2 \cdot 2\text{H}_2\text{O}$ (from elemental analysis). Mössbauer spectroscopy and magnetic data established that the core of this form of the cluster corresponds to CoII3FeIII2 over the entire 2–300 K temperature range. The red solid can be reversibly converted to the blue solid upon exposure to a humid environment.

An important feature of the CTIST in this TBP arrangement is that a single Co site remains paramagnetic over the entire temperature range. While it would be reasonable to predict that the spin transition would occur indiscriminately at any one of the three Co sites, temperature-dependent crystallographic studies indicate that the phenomenon occurs only at the Co(1) and Co(3) sites (Figure 1). The Co(2) site is unique in that it does not participate in the CTIST process and remains paramagnetic at all temperatures. This observation highlights how the influence of long-range interactions cannot be neglected when assessing the magnetic behavior in discrete molecules (recall, as mentioned earlier, that the tmphen ligands bound to the Co(2) site do not participate in intermolecular $\pi-\pi$ contacts).

The complex behavior of the Co3Fe2 molecule indicates that the family of TBP complexes can serve as molecular prototypes of extended PB-type phases. Indeed, similar CTIST behavior was observed for the PB analogue, $K_{0.2}\text{Co}_{1.4}[\text{Fe(CN)}_6]_2$.57 that contains a mixture of the paramagnetic FeIII LS and diamagnetic FeII LS electronic isomers. Irradiation with red light at 5 K triggers an electron transfer from FeII to CoIII centers and an increase in the population of the paramagnetic FeIII/CoII pairs. As a result, the material exhibits higher values for the magnetic ordering temperature, remnant magnetization, and coercivity. The original phase can be restored by irradiating the material with blue light or by applying heat.

The CTIST phenomenon was not thought to be possible for discrete molecules prior this study, but since our first report, other examples of Co/Fe cyanide clusters have been found to exhibit similar behavior. Given the photomagnetic properties of the extended $K_{0.2}\text{Co}_{1.4}[\text{Fe(CN)}_6]_2$ phase, we are currently investigating photoinduced magnetic-state switching for the Co3Fe2 cluster. The results of these studies will be reported in due course. Such switching has recently also been reported for a cubic cyanide bridged complex $[\{\text{pzTpFe(CN)}_3\}]_4[\text{Co}(\text{pz})_3\text{CH}_2\text{OH}]_4\text{(ClO}_4)_4$, that exhibits CTIST initiated by a temperature change or irradiation.39

c. Spin Crossover. Spin-crossover complexes provide an alternative mechanism to SMM or photoinduced magnetism for realizing magnetic bistability. Although the phenomenon has been extensively studied for the past half a century,58 molecular spin-crossover research is dominated by mononuclear complexes.59–61 Very few examples of clusters with three or more spin-crossover centers have been reported to date.41,62

Given that the coordination environment of equatorial metal ions in the TBP structure is similar to that in the well-known mononuclear spin-crossover complex Fe(phen)$_2^{2+}$ (NCS)$_2$63 (Figure 7), a logical question to pose was whether the introduction of FeII ions into the equatorial positions of the TBP would result in a multinuclear spin-crossover.

compound. Indeed, the TBP clusters $\text{Fe}^{\text{II}}_3\text{M}^{\text{III}}_i$ ($\text{M} = \text{Fe}, \text{Co}$) exhibit a gradual temperature-induced spin transition, with the onset occurring at $\sim 150$ K (Figure 8).

A combination of variable-temperature Mössbauer spectroscopy, magnetic data, and crystallographic studies conclusively was used to quantify the nature of the spin-transition behavior. Below 150 K, the $\text{Fe}^{\text{II}}_3\text{Fe}^{\text{III}}_2$ complex contains only LS $\text{Fe}^{\text{II}}$ centers, whereas the $\text{Fe}^{\text{II}}_3\text{Co}^{\text{III}}_2$ complex contains a small fraction ($\sim 10\%$) of HS $\text{Fe}^{\text{II}}$ ions. The fraction of the HS $\text{Fe}^{\text{II}}$ ions increases with temperature and, at 300 K, corresponds to an occupancy of $1/3$ and $2/3$ equatorial $\text{Fe}^{\text{II}}$ centers for the $\text{Fe}_3\text{Fe}_2$ and $\text{Fe}_3\text{Co}_2$ clusters, respectively.

As expected, the spin-transition event at the $\text{Fe}^{\text{II}}$ centers significantly affects the metal–ligand bond lengths and leads to pronounced changes in the octahedral coordination geometry. The average Fe–N distances in LS and HS complexes of the $[\text{FeN}_6]$ type are $1.92–2.00$ Å and $2.16–2.21$ Å, respectively. The deformation of the octahedral surroundings is quantified by changes in the parameter $\Sigma$, which is defined as the sum of deviations from $90^\circ$ for the 12 cis N–Fe–N angles. While $\Sigma = 0$ for an ideal octahedron, this parameter is $\sim 30–50^\circ$ and $\sim 70–90^\circ$, respectively, for LS and HS $[\text{FeN}_6]$ complexes with three bidentate ligands. The crystal structure determination of the $\text{Fe}^{\text{II}}_3\text{Co}^{\text{III}}_2$ species confirmed that at 110 K one $\text{Fe}^{\text{II}}$ center is partially HS (Table 2), while the other two $\text{Fe}^{\text{II}}$ ions are in the LS state. At 298 K, both the $\text{Fe}^{\text{II}}$ bond lengths and $\Sigma$ for $\text{Fe}(1)$ and $\text{Fe}(3)$ are typical of HS $\text{Fe}^{\text{II}}$, with $\text{Fe}(2)$ essentially remaining in the LS state. These results are in excellent agreement with the results of the Mössbauer experiments.

The change in the Fe–N bond distances for the equatorial $\text{Fe}^{\text{II}}$ atoms (Table 2) supports a stepwise nature for the spin transition. The $\text{Fe}(1)$ centers are the first sites to be converted to the HS state with increasing temperature, followed by the $\text{LS} \rightarrow \text{HS}$ transition at the $\text{Fe}(3)$ centers. The $\text{Fe}(2)$ sites remain LS up to 298 K but eventually undergo the $\text{LS} \rightarrow \text{HS}$ transition at higher temperatures, as evidenced by a further increase in $\chi^T$ above 300 K. As in the earlier example of a CTIST for the $\text{Co}_3\text{Fe}_2$ TBP, the behavior is rationalized by considering the intra- and intermolecular $\pi–\pi$ interactions between the tmphen ligands (Figure 2). Recall that one of the tmphen ligands coordinated to the $\text{Fe}(1)$ center engages in two intermolecular $\pi–\pi$ contacts, while the other ligand participates in only one intramolecular $\pi–\pi$ contact. In the case of the $\text{Fe}(3)$ site, one of the tmphen ligands is involved in an intramolecular $\pi–\pi$ interaction whereas the other one participates in one intermolecular $\pi$-stacking interaction. There are two intramolecular and no intermolecular $\pi–\pi$ contacts for the tmphen ligands on the $\text{Fe}(2)$ center.

It can therefore be inferred that the ligand field of each $\text{Fe}^{\text{II}}$ ion is affected by the type and number of $\pi–\pi$ interactions exhibited by tmphen ligands coordinated to that ion (Table 2). The results indicate that $\pi–\pi$ interactions weaken the ligand

![Figure 7](image7.png)

**Figure 7.** Crystal structure of a $\text{Fe}_3\text{M}^{\text{II}}_2$ TBP with emphasis on the similarity of the equatorial sites to the $\text{Fe}(\text{phen})_2(\text{NCS})_2$ molecule.

![Figure 8](image8.png)

**Figure 8.** Temperature dependence of $\chi^T$ for the $\text{Fe}^{\text{II}}_3\text{M}^{\text{III}}_i$ clusters ($\text{M} = \text{Fe}, \text{Co}$).

<table>
<thead>
<tr>
<th>temperature</th>
<th>$\Sigma$</th>
<th>$\chi^T (\text{em} \cdot \text{emu mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 K</td>
<td>72.2</td>
<td>2.11</td>
</tr>
<tr>
<td>110 K</td>
<td>71.8</td>
<td>2.15</td>
</tr>
<tr>
<td>220 K</td>
<td>77.1</td>
<td>2.17</td>
</tr>
<tr>
<td>300 K</td>
<td>81.5</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Table 2. Average Fe–N Bond Distances (Å), Parameter $\Sigma$ (deg), and the Number of $\pi–\pi$ Interactions As Determined from the Crystal Structure of $[[\text{Fe}^{\text{II}}(\text{tmphen})_2][\text{Co}^{\text{III}}(\text{CN})_6]]_2^+$ at Different Temperatures

<table>
<thead>
<tr>
<th>temperature</th>
<th>$\Sigma$</th>
<th>$\chi^T (\text{em} \cdot \text{emu mol}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 K</td>
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</tr>
<tr>
<td>300 K</td>
<td>81.5</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Trigonal-Bipyramidal Metal Cyanide Complexes

Table 3. $\nu$(C≡N) Stretching Frequencies for Fe$^{II}$,M$^{III}$ (M$^{IV}$ = Co, Fe, Cr) Clusters, Corresponding PB Analogues, and Free Hexacyanometallate Anions$^{66}$

<table>
<thead>
<tr>
<th>complex</th>
<th>bridging</th>
<th>terminal</th>
<th>PB analogue</th>
<th>free [M'(CN)$_6$]$^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{II}$,Co$^{III}$</td>
<td>2167, 2156, 2147</td>
<td>2127</td>
<td>2165</td>
<td>2126</td>
</tr>
<tr>
<td>Fe$^{II}$,Fe$^{III}$</td>
<td>2131</td>
<td>2109</td>
<td>does not exist$^v$</td>
<td>2101</td>
</tr>
<tr>
<td>Fe$^{II}$,Cr$^{III}$</td>
<td>2103</td>
<td>2117</td>
<td>2162 or 2098</td>
<td>2114</td>
</tr>
</tbody>
</table>

$^v$ See the discussion in section 2.

field and stabilize the HS state, with the intermolecular contacts exerting a more pronounced effect than the intramolecular ones. Thus, the HS state is more favorable for the Fe(1) center whose tmphen ligands exhibit three $\pi-\pi$ contacts (two of them intermolecular), as compared to the Fe(2) site with only two $\pi-\pi$ interactions (both intramolecular). The Fe(3) site represents an intermediate situation.

d. Cyanide Linkage Isomerism. Unlike Fe$^{II}$,M$^{III}$,2 clusters (M$^{IV}$ = Fe or Co), which exhibit temperature-induced LS–HS transitions at the equatorial Fe$^{II}$ centers (vide supra), the Fe$^{II}$,Cr$^{III}$2 cluster was found to contain LS diamagnetic Fe$^{II}$ ions over the entire temperature range of 1.8–300 K.$^{50}$ The Mössbauer data indicate the reversal of the CN$^-$ bridges upon formation of the Fe$^{III}$Cr$^{II}$ complex, a claim that was corroborated by IR spectroscopic data.

The spin-crossover complex Fe$^{II}$Co$^{II}$2 exhibits two $\nu$(C≡N) stretching modes (Table 3): the lower-frequency mode corresponds to terminal CN$^-$ groups, while the higher-frequency feature corresponds to the cyanide ligands in the Fe$^{II}$–N≡C–Co$^{III}$ bridging mode. This assignment is consistent with the $\nu$(C≡N) stretching modes observed for the free [Co(CN)$_6$]$^{3-}$ anion and the PB analogue Fe$^{II}$3[Co$^{III}$(CN)$_6$].$^{65}$ A similar situation is observed for the Fe$^{II}$Fe$^{III}$2 complex that exhibits $\nu$(C≡N) at 2131 and 2109 cm$^{-1}$ assigned to the bridging and terminal cyanides, respectively. The Fe$^{II}$Cr$^{III}$2 cluster, on the other hand, exhibits one stretch at 2117 cm$^{-1}$, which is similar to the $\nu$(C≡N) = 2114 cm$^{-1}$ of the free [Cr$^{III}$(CN)$_6$]$^{3-}$ anion and is assigned to the terminal cyanides, and a second absorption band that is shifted to lower frequency (2103 cm$^{-1}$). The latter is attributed to the Fe$^{II}$–C≡N–Cr$^{III}$ bridging arrangement, which is in accordance with more efficient d–π back-bonding when the CN$^-$ ligand is carbon-bound to the Fe$^{II}$ ion. The IR data, in combination with the results of Mössbauer, magnetic, and crystallographic studies, support the conclusion that the cyanide bridges in the Fe$^{II}$Cr$^{III}$2 cluster have undergone complete reversal from the [Cr$^{III}$(CN)$_6$]$^{3-}$ reactant to the TBP product. Analogous cyanide linkage isomerism has been documented for Fe$^{II}$–C$^{III}$$^-$ analogues of PB, for which the higher- and lower-frequency $\nu$(C≡N) stretches were assigned to Fe$^{II}$–N≡C–C$^{III}$ and Fe$^{II}$–C≡N–Cr$^{III}$ bridging modes, respectively.$^{66,67}$


Figure 9. Cyanide stretches in the IR spectra of [Co$^{II}$,(tmphen)$_3$][Cr$^{III}$(CN)$_6$]$_2$ prepared in acetonitrile and methanol.

A cyanide “flip” was also observed for the Co$^{III}$Cr$^{II}$2 complex,$^{68}$ although, in this case, the isomerization did not go to completion. When the Co$^{III}$Cr$^{II}$2 complex is formed in acetonitrile, two sets of bands with shoulders are observed in the IR spectrum, one with a maximum at 2155 cm$^{-1}$ (sh, 2147 cm$^{-1}$) and the other with a maximum at 2126 cm$^{-1}$ (sh, 2136 cm$^{-1}$) (Figure 9). These absorptions are assigned to the bridging and terminal CN$^-$ ligands, respectively, with the bridging ligands being C-bound to the axial Cr$^{III}$ ions. An additional weak feature at 2103 cm$^{-1}$ is attributed to partial isomerization of the CN$^-$ ligands with the formation of the Co$^{III}$–C≡N–Cr$^{III}$ bridging mode. This conclusion is supported by the magnetic data. When the reaction was carried out in methanol, instantaneous precipitation of a solid ensued, in contrast to the slow appearance of a crystalline material from acetonitrile. Although the IR spectrum of the sample isolated from methanol did not show a discernible feature at ~2103 cm$^{-1}$, the magnetic behavior indicates the presence of a small amount of the Co$^{II}$–C≡N–Cr$^{III}$-bridged isomer in the sample.

Although, at first glance, the reversal of cyanide bridges upon formation of the M$^{III}$Cr$^{II}$ complexes may seem surprising given the usually inert nature of the C-bound CN$^-$ ligands in the [Cr$^{III}$(CN)$_6$]$^{3-}$ anion, it appears that the stability of the complex is substantially diminished in the presence of certain Lewis acids. Specifically, in an unrelated study, we encountered an interesting case of cyanide linkage isomerism for the product of the reaction between [Cr$^{III}$(CN)$_6$]$^{3-}$ and the Lewis acid BPh$_3$ in acetonitrile.$^{69}$ The resulting anion is [Cr$^{III}$(NCBPh$_3$)$_6$]$^{3-}$, which contains six nitrile ligands derived from CN$^-$ and BPh$_3$. The mechanism whereby all six cyanide ligands manage to “flip” in this remarkable sterically crowded molecule is unknown.


e. Superexchange through Intervening Diamagnetic $-\text{NC} \cdot \text{M} \cdot \text{CN}-$ Linkages. The Fe$_3$Cr$_2$ cluster exists only in the LS form after complete conversion of the bridging CN$^-$ ligands to the form in which the strong-field carbon end is bound to the equatorial Fe$^{II}$ centers. In this case, the equatorial metal ions are always in a diamagnetic LS d$^6$ electronic configuration, and paramagnetism of the cluster must be dictated by the axially disposed $S = \frac{3}{2}$ Cr$^{III}$ ions. This scenario resembles the situation in the classical PB structure, Fe$^{III}$(Fe$^{III}$(CN)$_6$)$_2$.xH$_2$O, in which paramagnetic $S = \frac{5}{2}$ Fe$^{III}$ ions are separated by intervening diamagnetic [Fe$^{II}$(CN)$_6$]$^{4-}$ units. In spite of the long distance between the paramagnetic sites, ferromagnetic ordering of this material is, nonetheless, observed ($T_C = 5.5$ K). Mayoh and Day$^{70}$ proposed that ferromagnetic superexchange between the HS Fe$^{III}$ ions is mediated by the diamagnetic LS Fe$^{II}$ centers along the Fe$^{III}$-$\text{N} \equiv \text{C}$-$\text{Fe}^{III}$ pathway. This superexchange is accomplished by a mixed-valence delocalization, or “hopping”, of electrons between Fe$^{II}$ and Fe$^{III}$ sites.

Interestingly, in the Fe$_2$Cr$_2$ cluster, we also observe ferromagnetic coupling between the axial Cr$^{III}$ ions mediated by the diamagnetic LS Fe$^{II}$ sites (Figure 10a).$^{50}$ A theoretical simulation of the magnetic data using the Heisenberg–Dirac–Van Vleck exchange Hamiltonian $\hat{H} = -2J_{\text{ex}}S_{\text{Cr1}}S_{\text{Cr2}} + \beta g_\text{Cr}S_{\text{Cr1}}H + \beta g_\text{Cr}S_{\text{Cr2}}H$ produced a small exchange parameter of $J_{\text{ex}} = +0.65$ cm$^{-1}$. Most important, however, is the fact that $^{57}$Fe Mössbauer data at 4.2 K in an 8 T applied field revealed the presence of a small internal field of 0.6 T at the Fe$^{II}$ nucleus, which is antiparallel to the applied field (Figure 10b). With increasing temperature, the internal field at the Fe$^{II}$ nucleus exhibited a decay similar to that of the magnetic susceptibility measured for the cluster (Figure 10a).

These unprecedented experimental findings explain how magnetic coupling between the axial Cr$^{III}$ ions in the Fe$^{II}_2$Cr$^{III}_2$ cluster is mediated by the diamagnetic Fe$^{II}$ ions. Indeed, if we assume partial delocalization of the spin density from the t$_{2g}$ orbitals of Fe$^{II}$ to the t$_{2g}$ orbitals of Cr$^{III}$, then such delocalization can take place only for the minority spins on the Cr$^{III}$ centers (Scheme 3). This generates uncompensated electronic spin density at the equatorial Fe$^{II}$ ions (estimated to be approximately 0.05 unpaired electrons per Fe$^{II}$ ion in the 3d shell), which is parallel to the majority spin density on the Cr$^{III}$ ions. Consequently, the Fermi contact field at the Fe$^{II}$ nuclei aligns antiparallel to the applied magnetic field.

While this long-range exchange mechanism has been cited to account for the magnetic properties of several other cyanide-bridged complexes,$^{71-74}$ our results provide the first direct experimental evidence for magnetic superexchange interactions through the long N=Fe$^{III}$-C≡N bridge incorporating the diamagnetic LS Fe$^{II}$ ion. The success of our experimental approach rests on the application of a high magnetic field, which allows for the accurate measurement of the internal field on the Fe$^{II}$ nucleus. At lower applied fields, the internal field induced at the Fe$^{II}$ nucleus would be too small to be measured. Given this newly recognized fact, it would be interesting to examine the high-field Mössbauer properties of other compounds in which LS Fe$^{II}$ sites are present in bridges between paramagnetic metal ions.

References:


expected for three continuous series of hexacyanometallate anions from species that is isoelectronic with \([\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}\). The use to look beyond the first transition series to examine hexacyanometallate anions of heavier transition elements. The use of 3d and 5d metal ions, characterized by strong magnetic anisotropy due to significant spin–orbit coupling, is now an established strategy for isolating cyanide-based SMMs.10,17,21 Whereas 3d metal ions form the continuous series of hexacyanometallate anions from \([\text{Ti}(\text{CN})_6]^3-\) to \([\text{Co}(\text{CN})_6]^{3-}\), analogous series with heavier transition metals are lacking. With a limited number of compounds from which to choose, our initial foray into this chemistry focused on the \([\text{Os}^{\text{III}}(\text{CN})_6]^{3-}\) building block, a species that is isoelectronic with \([\text{Fe}^{\text{III}}(\text{CN})]^{3-}\). In order to be able to perform reactions with \([\text{Os}(\text{CN})_6]^{3-}\) in nonaqueous media, the \(K^+\) cation was exchanged with PPN\(^+\) [PPN = bis(triphenylphosphine)iminium],75 and this salt was used to prepare the \([\text{Ni}^{\text{II}}\text{Os}^{\text{III}}]^{2-}\) TBP complex by following the protocol established for the 3d cyanometallate precursors.76

This cluster exhibits a room temperature \(\gamma T\) value of 4.73 emu·K·mol\(^{-1}\) at 300 K, which is slightly higher than that expected for three \(S = 1\) and two \(S = \frac{1}{2}\) centers in the absence of magnetic coupling (3.75 emu·K·mol\(^{-1}\)). The \(\gamma T\) value exhibits a slight increase as the temperature is lowered, reaching a maximum of 5.29 emu·K·mol\(^{-1}\) at 21.6 K. This behavior is indicative of weak ferromagnetic coupling between the \(\text{Ni}^{\text{II}}\) and \(\text{Os}^{\text{III}}\) ions. The decrease in \(\gamma T\) at lower temperatures is due to zero-field splitting as well as anisotropy of the \(\text{Os}^{\text{III}}\) ions (Figure 11).77

The magnetic behavior of the \(\text{Ni}_3\text{Os}_2\) cluster was modeled by taking into account the effects of both magnetic superexchange and zero-field splitting:

\[
\hat{\mathbf{H}} = -2J_{\text{Ni-Os}}(\hat{S}_{\text{Os}} + \hat{S}_{\text{Ni}})(\hat{S}_{\text{Os}} + \hat{S}_{\text{Ni}} + \hat{S}_{\text{Os}}) + 3D(S_{\text{Ni}}^2 - S_{\text{Os}}(S_{\text{Os}} + 1)/3) + \beta H(g_{\text{exp}}(\hat{S}_{\text{Os}} + \hat{S}_{\text{Ni}})(\hat{S}_{\text{Os}} + \hat{S}_{\text{Ni}} + \hat{S}_{\text{Os}}))
\]

Ferromagnetic coupling between the \(\text{Ni}^{\text{II}}\) and \(\text{Os}^{\text{III}}\) ions with a resulting \(S = 4\) ground state was confirmed by fitting this Hamiltonian to the experimental data using MAGPACK,78 which produced best-fit values of \(g_{\text{Os}} = 2.03\), \(g_{\text{Ni}} = 2.13\), \(J_{\text{Os}} = +2.3\) cm\(^{-1}\), and \(D_{\text{Ni}} = 19.5\) cm\(^{-1}\). Although the calculated \(D\) parameter is unreasonably high for a \(\text{Ni}^{\text{II}}\) ion, it must be emphasized that the proposed model does not take into account the effects of anisotropic superexchange interactions and spin–orbit coupling at the \(\text{Os}^{\text{III}}\) centers, both of which are expected to be significant issues. A more accurate description of the magnetic behavior for this cluster requires a rigorous theoretical treatment similar to the one developed by us for the \(\text{Mn}_3\text{Mn}_2\) cluster (vide supra) in collaboration with Tsukerblat, Klokiñsher, and co-workers. These efforts are currently underway.

Although the \(\text{Ni}_3\text{Os}_2\) cluster contains the highly anisotropic \(\text{Os}^{\text{III}}\) ion and exhibits a rather high ground-state spin value of \(S = 4\), an examination of the ac magnetic susceptibility data did not reveal any features in the out-of-phase susceptibility component. Interestingly, and of relevance to the current discussion, Mironov recently published a paper in which he reports the results of theoretical predictions of the magnetic properties of hypothetical TBP clusters \(\text{Mn}_3\text{Os}_2\), \(\text{Cr}_3\text{Os}_2\), and \(\text{Ni}_3\text{Os}_2\), with the \([\text{Os}^{\text{III}}(\text{CN})_6]^{3-}\) moiety in the axial positions.79 His calculations indicate that the compounds containing equatorial \(\text{Mn}^{\text{II}}\) and \(\text{Cr}^{\text{II}}\) ions could potentially exhibit SMM behavior with significant blocking temperatures but that the \(\text{Ni}_3\text{Os}_2\) complex would be unlikely to behave as a SMM. The latter prediction has now been corroborated by our experimental results. In light of this study, we are currently pursuing the \(\text{Mn}_3\text{Os}_2\) complex in order to verify the prediction of SMM behavior.

As an extension to the TBP study, we also prepared the PB analogue \(\text{Ni}_3[\text{Os}(\text{CN})_6]_2\cdot8\text{H}_2\text{O}\), which exhibits ferromagnetic ordering at 6.2 K. To the best of our knowledge, this PB analogue and the TBP cluster represent the first documented cases of cyanide-bridged structures incorporating the paramagnetic \([\text{Os}^{\text{III}}(\text{CN})_6]^{3-}\) fragment.

5. TBP Clusters as Building Blocks

An attractive structural feature of this class of TBP complexes is the presence of six terminal \(\text{CN}^-\) ligands that can be used to attach additional metal ions to the molecular scaffold. This situation provides a convenient means to access higher-nuclearity clusters as well as extended structures. Although most of the TBP clusters are insoluble, four clusters are sufficiently soluble in organic media and are potential candidates for this strategy; these are the \(\text{Co}_3\text{Fe}_2\), \(\text{Fe}_3\text{Fe}_2\), \(\text{Fe}_3\text{Co}_2\), and \(\text{Fe}_3\text{Cr}_2\) molecules, with \(\text{Co}_3\text{Fe}_2\) exhibiting the highest solubility (approximately 1 mM in methanol).

of the neutral Co$_3$Fe$_2$ cluster (Co$_{III}$$_2$Co$_{II}$Fe$_{II}$$_2$) reacts with our efforts to prepare extended structures that incorporate excellent “proof-of-concept” for the building block approach with a polyhedron. H atoms are omitted for clarity. Color scheme: red, Co; green, Fe; yellow, Ni; brown, O; blue, N; gray, C.

Figure 12. Molecular structure of the [[Co(tmpphen)$_2$]$_2$][Fe-(CN)$_6$][Ni(H$_2$O)$_6$]$_2$ cluster. The cyanide-bridged TBP core is highlighted with a polyhedron. H atoms are omitted for clarity. Color scheme: red, Co; green, Fe; yellow, Ni; brown, O; blue, N; gray, C.

a. Higher-Nuclearity Clusters. The building block strategy was applied successfully in chemistry that involved reactions of the oxidized form of the Co$_{III}$Co$_{II}$Fe$_{II}$ CTIST cluster (see section 4b), viz., the cation form [[Co$_{III}$tmpphen)$_2$][Fe$_{II}$](CN)$_6$]$_2$ with an excess of [Ni(H$_2$O)$_6$]$_2$$. The resulting product is the unusual heterometallic undecanuclear molecule [[Co$_{III}$tmpphen)$_2$][Fe$_{II}$](CN)$_6$$_2$$][Ni$_{II}$H$_2$O)$_6$]$]_{13}$ (Figure 12).80 The molecular structure of this complex revealed that all of the terminal CN$^-$ ligands of the TBP complex are used to bridge the hydrated Ni$_{II}$ ions. This stepwise assembly provides an excellent “proof-of-concept” for the building block approach to preparing high-nuclearity cyanide-bridged complexes.

b. One-Dimensional Arrays of TBP Clusters. As part of our efforts to prepare extended structures that incorporate the TBP building block, we discovered that the blue form of the neutral Co$_3$Fe$_2$ cluster (Co$_{III}$Co$_{II}$Fe$_{II}$) reacts with [Mn(H$_2$O)$_6$]$_2$ to form two different one-dimensional materials in which Mn$_{II}$ centers bridge the oxidized clusters (Figure 13). In the first structure, [[Co$_{III}$tmpphen$_2$][Fe$_{II}$](CN)$_6$$_2$$][Mn$_{II}$H$_2$O)$_6$]$]_{2}$[ClO$_4$)$_{13}$ (Figure 12).80 The molecular structure of this complex revealed that all of the terminal CN$^-$ ligands of the TBP complex are used to bridge the hydrated Ni$_{II}$ ions. This stepwise assembly provides an excellent “proof-of-concept” for the building block approach to preparing high-nuclearity cyanide-bridged complexes.

4.30 emu$\cdot$mol$^{-1}$). Given that photomagnetism is exhibited by both Co$-$Fe PB analogues57 as well as discrete Co$-$Fe cyanide-bridged clusters,83 we plan to investigate the photomagnetic behavior of this and related chain compounds.

6. Concluding Remarks

The cyanide-bridged TBP complexes described in this Forum Article constitute a unique family of molecular cyanide compounds whose ease of preparation allows for the deliberate introduction of metal ions into the two different positions of the pentanuclear cluster. Numerous isostructural complexes have been isolated that display an exceptionally broad range of physical properties, including SMM, spin crossover, CTIST, and magnetic coupling through extended diamagnetic bridges. The small size of a TBP cluster, with its symmetry-related pairwise interactions, has rendered possible the development of advanced theoretical models of the magnetic behavior of compounds with significant spin–orbit coupling. Ultimately, these studies will aid in the understanding of more complex cyanide-bridged solids.

Our earlier foray into the magnetoochemistry of heavy transition-metal ions that began with Re$_{II}$ has been extended to the highly magnetically anisotropic Os$_{III}$ ion as described herein. We are also looking to increase the magnetic anisotropy of these clusters by introducing early 3d metal ions, specifically Ti$_{III}$ and V$_{III}$, that have not been exploited to any great extent in the chemistry of discrete cyanide complexes.83,84 It must be emphasized, however, that the instability of [Ti(CN)$_6$]$^3-$ and, to a lesser degree, [V(CN)$_6$]$^3-$ may hinder the use of these building blocks even in nonaqueous media.

The use of TBP clusters as secondary building blocks is a high priority in our current work, with most of the efforts being directed at the connection of these magnetic molecules with metal ions that are known to engender strong Ising anisotropy. For example, chain architectures could exhibit interesting magnetic phenomena such as single-chain magnetism, photoinduced magnetism, and abrupt spin crossover accompanied by a thermal hysteresis. Clearly, many exciting prospects remain for the chemistry of these TBP molecules as well as other cyanide-bridged compounds being prepared in laboratories around the world.

7. Experimental Section

Syntheses. Starting Materials. Commercially available 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen; Alfa Aesar), bis(triphenylphosphine)iminium chloride (PPNCI, Aldrich), 18-crown-6 (Acros), K3[Fe(CN)6] (Fisher), Mn(ClO4)·6H2O (Alfa Aesar), Co(NO3)2·6H2O (Strem), and Ni(BF4)2·6H2O (Aldrich) were used as received. Acetonitrile and methanol were of ACS reagent grade and were always handled in a humid atmosphere. In this work, perchlorate salts are potentially explosive and should always be used with care. In this work, the starting materials and products were hydrate compounds and should always be handled in a humid atmosphere.

![Image](image_url)

**Figure 13.** Fragments of infinite chains of MnII-bridged TBP clusters in the crystal structures of \{[Co(tmphen)2]3[Fe(CN)6]2·(ClO4)3 \}∞, \{[Ni(tmphen)2]3[Os(CN)6]2·(ClO4)3 \}∞, \{[Ni(tmphen)2]3[Os(CN)6]2·(ClO4)3 \}∞, and \{[Ni(tmphen)2]3[Os(CN)6]2·(ClO4)3 \}∞. H atoms are omitted for the sake of clarity. Color scheme: red, Co; green, Fe; pink, Mn; brown, O; blue, N; gray, C.


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**Caution:** Although we have experienced no safety problems with either of these products, perchlorate salts are potentially explosive and should always be used with care. In this work, the starting materials and products were hydrate compounds and were always handled in a humid atmosphere.
Physical Measurements. The TGAs were performed on a Shimadzu TGA-50 or an Instrument Specialists Inc. TGA 1000 thermogravimetric analyzer in the 298–573 K temperature range at a heating rate of 5 K·min⁻¹, under a N₂ gas flow of 20 L·min⁻¹. IR spectra were measured on a Nicolet 740 FTIR spectrometer as Nujol mulls placed between KBr plates.

Magnetic measurements were performed on a Quantum Design SQUID MPMS-XL magnetometer. Magnetic susceptibility measurements in the direct current mode were carried out in an applied field of 0.1 T in the 2–300 K range. Magnetization data were acquired at 1.8 K, with the magnetic field varying from 0 to 7 T. Whenever appropriate, the fitting of magnetic behavior was carried out with MAGPACK. Magnetic data obtained for samples were corrected for diamagnetic contributions by the use of Pascal constants. Because of the high content of disordered solvent in the crystals, each sample was also subjected to TGA. The molecular weight of each compound was adjusted according to the interstitial solvent content determined from the TGA. Micro-SQUID measurements were collected on samples of aligned single crystals at the temperatures indicated.

Single-Crystal X-ray Diffraction Studies. The crystal selected for study was suspended in polybutene oil (Aldrich), mounted on a cryoloop, and placed in a N₂ cold stream. Single-crystal X-ray data were collected on a Bruker APEX II or Bruker SMART 1000 diffractometer equipped with a CCD detector. The data sets were recorded as three ω scans of 606 frames each, at 0.3° step width, and integrated with the Bruker SAINT software package. The absorption correction was based on the fitting of a function to the empirical transmission surface as sampled by multiple equivalent measurements. Solution and refinement of the crystal structures were carried out using the SHELX suite of programs and the graphical interface X-SEED. Preliminary indexing of the data sets established monoclinic unit cells for [[Co(tmphen)₂]₃[Fe(CN)₆]₂[Mn(CH₃OH)₄]₀.5[Mn(CH₃OH)₃(CH₃O)]₆(ClO₄)₃] and triclinic for [[Co(tmphen)₂]₃[Fe(CN)₆]₂[Mn(CH₃OH)₄][Mn(CH₃OH)₃(CH₃O)]₆(ClO₄)₃]. Systematic extinctions indicated that the compounds crystallized in the space groups C2/c (No. 15) and P1 (No. 2), respectively. The structures were solved by direct methods, which resolved the positions of all metal atoms and most of the C and N atoms. The remaining non-H atoms were located by alternating cycles of least-squares refinements and difference Fourier maps. All H atoms were placed in calculated positions. A large number of disordered interstitial solvent molecules are present in the crystals. The final refinement was carried out with anisotropic thermal parameters for all non-H atoms. Summaries of pertinent information relating to unit cell parameters, data collection, and refinement statistics as well as complete listings of positional and thermal parameters, bond distances, bond angles, and thermal ellipsoid plots of the asymmetric units are provided in the Supporting Information.

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Supporting Information Available: Crystal data, additional magnetic plots, thermal ellipsoid plots, and crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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