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William R. Entley [a], Christopher R. Treadway [a] & Gregory S. Girolami [a]

[a] School of Chemical Sciences and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 505, South Mathews Avenue, Urbana, Illinois, 61801

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MOLECULAR MAGNETS CONSTRUCTED FROM CYANOMETALATE BUILDING BLOCKS

WILLIAM R. ENTLEY, CHRISTOPHER R. TREADWAY, AND GREGORY S. GIROLAMI*
School of Chemical Sciences and Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois, 61801

Abstract. The properties of magnetic solids constructed from cyanometalate building blocks are reviewed. Most of these solids adopt face-centered cubic lattices in which adjacent metal centers are linked by CN bridges; they are analogues of the long-known inorganic coordination polymer Prussian blue. Ferromagnets, ferrimagnets, and metamagnets can be obtained depending on the building blocks used. The effects of linkage disorder, site vacancies, and the inclusion of metal ions with orbitally degenerate ground states on the magnetic ordering temperature and hysteretic behavior are discussed. Substitution of low-valent early transition metals such as vanadium(II) into the lattice leads to remarkably high magnetic ordering temperatures, in some cases above 200 K. The large exchange couplings in these vanadium-based molecular magnets are attributed to strong π-backbonding interactions with the cyanide π* orbitals.

1. INTRODUCTION.

The development of molecular magnets with high magnetic ordering temperatures depends crucially on establishing good magnetic communication between adjacent metal centers in three dimensions. Many molecular magnets currently rely on "through space" interactions to order spins in one or more dimensions; as a consequence, such solids invariably exhibit spontaneous bulk magnetization only at very low temperatures (often well below 30 K).[1-3] In order to obtain higher bulk ordering temperatures, the magnetic centers must be linked covalently in all three dimensions. For many inorganic solids that can be classified as three-dimensional polymers, however, it is not possible to design molecular building

blocks that can be polymerized under mild conditions to yield the desired lattice. An ideal building block must be capable of forming at least three covalent bridges to other metal centers, and the bridging ligands themselves should be compact and capable of supporting significant spin density.

One family of molecular building blocks, the cyanometalates,[4,5] has long been known to serve as excellent starting materials for inorganic polymers with interesting magnetic properties.[6,7] The archetypal example of a polymer formed from cyanometalate building blocks is the well-known solid Prussian blue, which was discovered by Diesbach in 1704 (although not described in the literature until 1710).[8] Prussian blue can be prepared by the addition of Fe^{3+} to the $[Fe(CN)_6^{4-}]$ anion and has the stoichiometry $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$; it has long been used as a pigment in printing inks, paints, etc.[9]

In 1936, Keggin and Miles carried out the first structural investigations of Prussian blue and related compounds.[10] These solids have the general stoichiometry $A_nM[M'(CN)_6]_m \cdot xH_2O$, where A is an alkali metal cation, and adopt face-centered cubic (*fcc*) lattices (Figure 1). For an ordered structure with m = 1, there are two types of octahedral metal sites in the *fcc* lattice: strong ligand-field sites ($M'C_6$ coordination environments) and weak ligand-field sites (MN_6 coordination environments). Only when m = 1 are both the M and M′ sites completely filled, in which case the lattice forms an uninterrupted three-dimensional framework. For m < 1, the M′ sites are fractionally occupied; there are vacancies in the lattice and the M centers surrounding the vacant sites have one (or more) water molecules in their coordination spheres. Zeolitic water molecules and/or charge balancing cations generally occupy the cube interiors in the face-centered cubic unit cell.[5]

Solids based on the Prussian blue structure are especially attractive as candidates for new molecular magnetic materials for several reasons: the linear M′-CN-M bridges

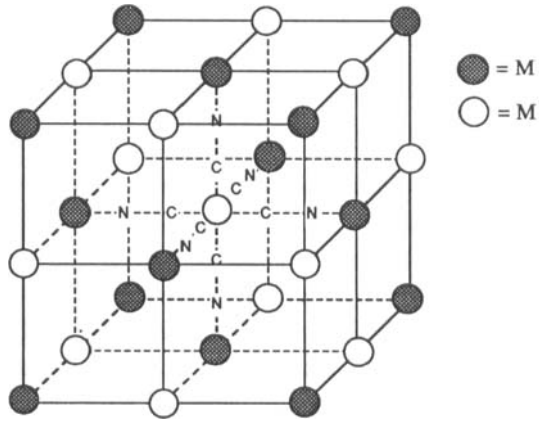

FIGURE 1. The face-centered cubic cyanometalate lattice.

promote the formation of strong magnetic interactions between adjacent spin centers,[11] the solids can be easily prepared at room temperature from well-characterized cyanometalate building blocks, and a wide range of metals with different spin states and oxidation states can be substituted into the lattice.[5] These features allow considerable control over the nature and magnitude of the local magnetic exchange interactions. It is the purpose of this brief review to summarize the magnetic and structural properties of those Prussian blue analogues which have been reported to date.

2. MAGNETIC STUDIES OF PRUSSIAN BLUE ANALOGUES.

Bozorth et. al. carried out the first low-temperature investigations of the magnetic properties of Prussian blue and related compounds in 1956 and showed that Prussian blue is ferromagnetic at low temperature.[6,7] The rather low magnetic ordering temperature (5.6 K)[12] is a consequence of the diamagnetism of half of the metal centers (the low-spin Fe^{2+} centers). Bozorth et al. also showed that analogues of Prussian blue in which all of the metal centers are paramagnetic exhibit significantly higher magnetic ordering temperatures, in some cases as high as 50 K. Unfortunately, these workers did not establish the chemical formulas of the mixed-metal Prussian blue analogues they prepared, and their own evidence suggested that the samples studied were impure.

Despite these promising results, no further investigations of the magnetic properties of Prussian blue analogues were carried out until 1980,[13] when Klenze et. al. prepared and characterized $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$.[14] This solid orders magnetically at 49 K, and the authors concluded that the magnetic coupling could be explained neither by dipole-dipole interactions nor by direct exchange via overlapping magnetic orbitals; instead, a superexchange mechanism involving ligand orbitals was invoked in order to describe the coupling. Klenze et al. suggested that there are both ferromagnetic contributions (involving orthogonal magnetic orbitals) and antiferromagnetic contributions (involving overlapping magnetic orbitals) to the superexchange in $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$, and that the latter dominate. Due to the unavailability of isoelectronic and isostructural compounds at the time, it was not possible to establish whether the antiferromagnetic exchange propagated principally via the filled π or empty π^* orbitals of the bridging cyano ligands.

In 1982, Babel prepared a compound that was isostructural and isoelectronic with $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$. This compound, $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$ (T_N = 90 K), differs from $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$ only in the relative energies of the t_{2g} orbitals in the strong ligand-field sites: chromium(III) having higher energy t_{2g} orbitals than manganese(IV).[15] Babel concluded that the higher magnetic ordering temperature, T_N, of $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$ demonstrates that one important contribution to the antiferromagnetic superexchange is π-backbonding into the empty π^* orbitals of the bridging cyano ligands.

TABLE I. Structural and magnetic data for polynuclear cyanometalates. Compounds are ordered top to bottom by the identity of the metal in the high ligand field site.[a]

Compound	a/Å	T_N/K	C[b]	θ/K[c]	Coupling[d]	Ref
$(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$	NC[d]	230			AF	11
$Cs_2Mn^{II}[V^{II}(CN)_6]$	10.71	125	11.5	-250	AF	11
$Cr^{II}_3[Cr^{III}(CN)_6]_2\cdot 10H_2O$	10.34	240	8.1	-306	AF	18
$Cs_{0.75}Cr_{1.125}[Cr(CN)_6]\cdot 5H_2O$	10.38	190	4.9	-440	AF	18
$CsMn^{II}[Cr^{III}(CN)_6]\cdot 1H_2O$	10.84	90	4.07	-207	AF	15
$CsNi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$	10.57	90			F	17
$Ni^{II}_3[Cr^{III}(CN)_6]_2\cdot 9H_2O$[e]	10.45	60	6.0	62	F	17,25
$NMe_4Mn^{II}[Cr^{III}(CN)_6]\cdot 4H_2O$	NC[d]	59			AF	22
$K_2Mn^{II}[Mn^{II}(CN)_6]$	10.15	41	4.9	-19	AF	19
$CsNi^{II}[Mn^{III}(CN)_6]\cdot 1H_2O$	10.42	42	2.96	54	F	25
$Ni^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$	10.29	30	8.01	42	F	25
$CsMn^{II}[Mn^{III}(CN)_6]\cdot {}^1/_2H_2O$	10.69	31	6.2	-32	AF	19
$Mn^{II}_3[Mn^{III}(CN)_6]_2\cdot 11H_2O$	10.62	37	16	-39	AF	19
$NMe_4Mn^{II}[Mn^{III}(CN)_6]\cdot 8H_2O$	NC[d]	29			AF	22,23,31
$Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$	10.73	49	5.96	-51.5	AF	14
$Fe^{III}_4[Fe^{II}(CN)_6]_3\cdot xH_2O$	10.13	5.6	17.92	6.74	F	12
$Ni^{II}_3[Fe^{III}(CN)_6]_2\cdot xH_2O$		23	3.7	42.2	F	16
$Cu^{II}_3[Fe^{III}(CN)_6]_2\cdot xH_2O$		20	2.7	13.0	F	16,32
$Co^{II}_3[Fe^{III}(CN)_6]_2\cdot xH_2O$		14	9.1	-15.5	AF	16
$NMe_4Mn^{II}[Fe^{III}(CN)_6]\cdot 8H_2O$	NC[d]	9.3			M	22,23,31
$Mn^{II}_3[Fe^{III}(CN)_6]_2\cdot xH_2O$		9	13.3	-28.7	AF	16

[a] Lack of an entry means that the data were not reported. [b] $cm^3\ K\ mol^{-1}$. [c] Negative Weiss constants are characteristic of local antiferromagnetic interactions while positive Weiss constants are characteristic of local ferromagnetic interactions; θ is defined from the equation $\chi = C/(T-\theta)$. [d] Abbreviations used: F = ferromagnetic, AF = antiferromagnetic, M = metamagnetic, NC = non-cubic. [e] The T_N's of $M^{II}_3[Cr^{III}(CN)_6]_2\cdot xH_2O$, where M = Mn^{II}, Co^{II} or Cu^{II}, are in the 55-65 K range.[17]

In the last three years, our knowledge of the structural and magnetic properties of various Prussian blue analogues has expanded considerably, and solids with magnetic ordering temperatures approaching room temperature have been synthesized.[11,16-19] Structural and magnetic data for the currently known polynuclear cyanometalates are reported in Table I, which is organized from top to bottom according to the metal present in the high ligand-field site. Before we summarize the conclusions drawn from the trends observed in Table I, it is appropriate to review the nature of the local exchange interactions present in Prussian blue analogues.

3. EXCHANGE INTERACTIONS IN PRUSSIAN BLUE ANALOGUES.

The nature of the superexchange interactions in Prussian blue analogues is easily understood in terms of the symmetries of the magnetic orbitals present on adjacent metal centers.[20] As discussed by Klenze et al., if two adjacent spin carriers in a cubic Prussian blue structure both have unpaired electrons only in their e_g orbitals, these unpaired electrons will prefer to spin pair; a similar situation pertains if the two adjacent spin carriers both have unpaired electrons only in their t_{2g} orbitals.[14] In these cases, the magnetic orbitals on the adjacent metal centers are of the same symmetry and the unpaired electrons will couple antiferromagnetically as a result of the Pauli principle. If there are unequal numbers of unpaired electrons on the adjacent metal centers, the spins will not cancel completely and the bulk solid can exhibit ferrimagnetic behavior below its magnetic ordering temperature, T_N. In contrast, if one metal center has unpaired electrons only in its e_g orbitals and its neighbor has unpaired electrons only in its t_{2g} orbitals, the magnetic orbitals are mutually orthogonal and the unpaired electrons will couple ferromagnetically according to Hund's rule. Such solids can exhibit bulk ferromagnetism below their magnetic ordering temperatures.

Local views of the orbital interactions responsible for superexchange in Prussian blue analogues are shown in Figure 2.[18] For the ferromagnetic interaction (left), the orthogonality of the magnetic orbitals results in stabilization of the spin state of highest spin multiplicity. For the antiferromagnetic interaction (right), the symmetry-allowed overlap of the two magnetic orbitals via the cyanide π^* system stabilizes the spin state of lowest multiplicity.

A metal center in a Prussian blue lattice that contains unpaired electrons in both its e_g and t_{2g} orbitals will interact with a paramagnetic neighbor to generate both ferromagnetic and antiferromagnetic exchange contributions to the superexchange. The net interaction is simply the sum of the ferromagnetic and antiferromagnetic contributions, and for polynuclear cyanometalates the antiferromagnetic contributions dominate.[11,14,18] The antiferromagnetic and ferromagnetic contributions are in competition, however, and in such cases the spins on adjacent metal centers are schizophrenic in the sense that

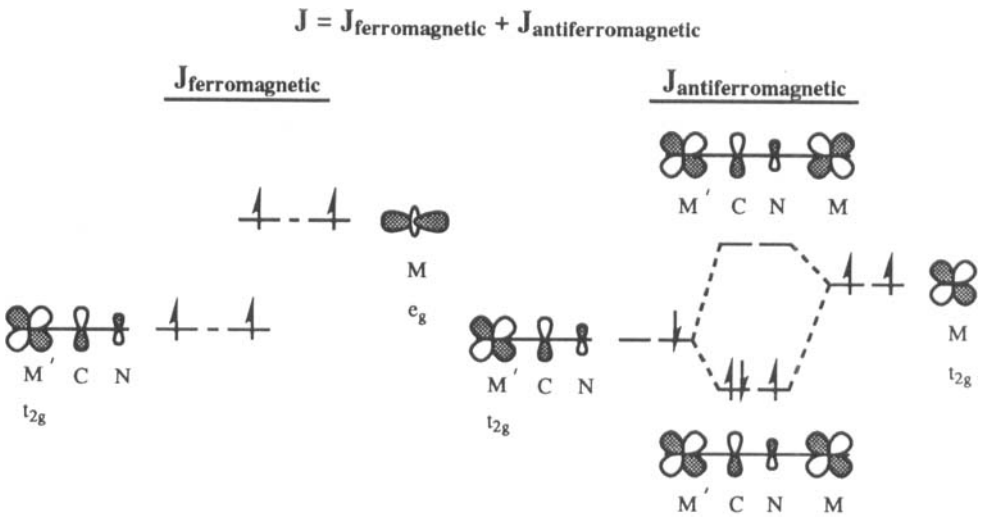

FIGURE 2. Local view of the superexchange interactions in Prussian blue analogues.

they want to spin align *and* to spin pair with each other simultaneously. These competing effects reduce the magnitude of the exchange coupling, and, other things being equal, lower the magnetic ordering temperature.

With this picture of the superexchange mechanism in mind, we can identify certain electronic conditions that should favor higher magnetic ordering temperatures. The most favorable *ferromagnetic* superexchange conditions should occur for those systems in which metal centers with $t_{2g}^6e_g^2$ and $t_{2g}^3e_g^0$ electronic configurations occupy alternate positions in the cubic lattice. This gives rise to the maximum possible number of ferromagnetic contributions to the superexchange with no competing antiferromagnetic contributions.

In contrast, the most favorable *antiferromagnetic* superexchange conditions should occur for those systems in which metal centers with $t_{2g}^3e_g^0$ and $t_{2g}^3e_g^0$ electronic configurations occupy alternate positions in the cubic lattice. For a 1:1 compound of stoichiometry $A_nM[M'(CN)_6]\cdot xH_2O$, this configuration unfortunately leads to complete cancellation of the spins and gives rise to a completely compensated antiferromagnetic system; the solid becomes diamagnetic when cooled. A bulk ferrimagnet can result, however, for solids in which all the metals have $t_{2g}^3e_g^0$ electronic configurations, *provided* that the stoichiometry is $A_nM[M'(CN)_6]_m\cdot xH_2O$ where $m < 1$: the ordered vacancies in one of the magnetic sublattices guarantees that the system will be uncompensated and that there will be a net spin per formula unit. Alternatively, choosing adjacent spin centers with electronic configurations of $t_{2g}^3e_g^1$ and $t_{2g}^3e_g^0$ would provide a net spin per formula unit in

the magnetic ground state even for a 1:1 compound, at the cost of introducing some competing ferromagnetic contributions to the superexchange.

4. IN SEARCH OF A ROOM TEMPERATURE MAGNET.

Néel's theory states that the magnetic phase transition temperature of ferrimagnetic compounds is directly proportional to the magnitude of the exchange interaction between adjacent spin centers:

$$T_N = z|J|\sqrt{\frac{C_A C_B}{N_A g^2 \mu_B{}^2}} \qquad (1)$$

where z is the number of nearest neighbors, J is the exchange integral, C_A and C_B are the Curie constants of the metal centers in the two different magnetic sublattices, N_A is Avogadro's number, g is the Landé g factor, and μ_B is the Bohr magneton.[21] There are at least two possible strategies for increasing the exchange interaction and thus the magnetic ordering temperature in polynuclear transition metal cyanides. The first involves decreasing or eliminating the ferromagnetic contributions to the superexchange while maximizing the antiferromagnetic contributions as described above;[18] the second involves increasing the intrinsic strength of the antiferromagnetic coupling.[11]

The second approach towards enhancing the magnetic phase transition temperature can be implemented as follows. Since the antiferromagnetic exchange interactions in Prussian blue analogues propagate principally through the empty π^* orbitals of the cyanide ligands,[11,15,18,22,23] it should be possible to increase the magnetic phase transition temperature by increasing the extent of π-backbonding into the cyanide π^* orbitals. This can be accomplished by substituting into the structure metals that have high-energy (and more radially expanded) t_{2g} orbitals, viz., early transition metals in lower oxidation states.

This approach has been successfully exploited in our research group by substituting low-valent vanadium centers into the strong ligand-field sites.[11] We have prepared several Prussian blue analogues by adding paramagnetic transition metal cations to solutions of the hexacyanovanadate(II) ion $[V(CN)_6^{4-}]$. One such compound, $Cs_2Mn^{II}[V^{II}(CN)_6]$, is particularly interesting; it is isostructural and isoelectronic with the chromium(III) and manganese(IV) species $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$ and $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$. All three compounds have d^5 Mn^{II} centers in the weak ligand-field sites (N_6 coordination environments) and d^3 metal centers in the strong ligand-field sites (C_6 coordination environments); the principal difference is that the energies of the t_{2g} orbitals in the latter sites decrease as the metal changes from V^{II} to Cr^{III} to Mn^{IV}. The relative magnetic ordering temperatures of 125, 90, and 49 K for $Cs_2Mn^{II}[V^{II}(CN)_6]$, $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$,[15] and $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$,[14] respectively, clearly show that incorporation of

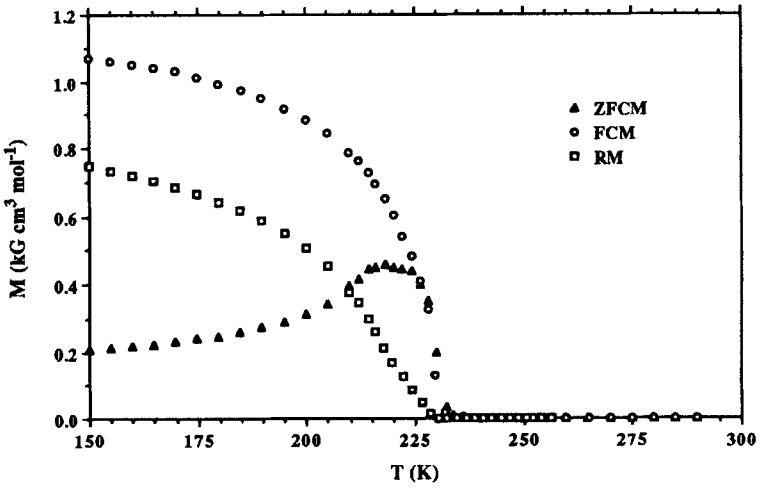

FIGURE 3. Magnetization of $(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$ as a function of temperature in an applied field of 3 Gauss: ZFCM = zero-field-cooled magnetization; FCM = field-cooled-magnetization; RM = remnant magnetization.

transition metals with higher energy t_{2g} orbitals into the strong ligand-field sites leads to higher magnetic phase transition temperatures. As the back-bonding with the cyanide π^* orbitals becomes more effective, the coupling between the adjacent spin centers increases.

A second example of a vanadium-based polynuclear cyanometalate is the compound $(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$, which is prepared by treatment of $(NEt_4)_4[V(CN)_6]$ with $Mn(OSO_2CF_3)_2(CH_3CN)_2$.[11] The ferrimagnetic phase transition temperature of 230 K, as shown in Figure 3, is among the highest reported for any molecular-based magnetic material. Only two other molecular magnets exhibit higher magnetic ordering temperatures: Miller's $V(tcne)_2\cdot xCH_2Cl_2$ compound (T_N estimated to be ~400 K),[24] and Verdaguer's cyanochromate $[Cr_5(CN)_{12}]\cdot 10H_2O$ (T_N = 240 K).[18]

The powder X-ray diffraction pattern of $(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$ clearly shows that the sample is polycrystalline but that it does not adopt a *fcc* lattice. The non-cubic powder diffraction pattern and the 5:1 cyanide-to-vanadium ratio both suggest that the structure of $(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$ is more complex than that of its *fcc* analogue $Cs_2Mn^{II}[V^{II}(CN)_6]$. Attempts to substitute cations larger than Cs^+ into the Prussian blue lattice usually give rise instead to lower-dimensional structures with substantially decreased magnetic phase transition temperatures: the relative magnetic ordering temperatures of $CsMn^{II}[Cr^{III}(CN)_6]\cdot H_2O$ (*fcc* lattice), $(NMe_4)Mn^{II}[Cr^{III}(CN)_6]\cdot 4H_2O$ (two-dimensional layer structure), and $(NMe_4)Mn^{II}[Mn^{III}(CN)_6]\cdot 8H_2O$ (one-dimensional linear chain) are 90, 59, and 29 K, respectively.[22] Even though the large NEt_4^+ cations

evidently prevent the adoption of the cubic Prussian blue structure, the high value of T_N for $(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$ suggests that its structure still consists of a three-dimensional array of interacting spin carriers.[2]

5. FERROMAGNETIC PRUSSIAN BLUE ANALOGUES.

The orbital model invoked to explain the superexchange interactions (Figure 2) affords insights that allow us to prepare magnetically ordered solids with specifically tailored magnetic exchange interactions. For example, ferromagnets can be prepared by addition of nickel(II) salts ($t_{2g}^6e_g^2$) to low-spin cyanometalates with fewer than six d-electrons.[16,17,25] The compound $Ni^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$, prepared by addition of Ni^{2+} to $[Mn(CN)_6^{3-}]$ ($t_{2g}^4e_g^0$), is such a ferromagnet and has an ordering temperature of 30 K. The stoichiometry of this material requires that vacancies be present in the lattice: only 2/3 of the M′ sites are occupied.

Figure 4 shows the temperature dependence of the magnetic moment per $Ni^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$ formula unit in applied field of 500 Gauss. As the temperature is lowered from 300 K, the magnetic moment per formula unit gradually increases (inset of Figure 4), as expected for a local ferromagnetic interaction between adjacent spins. Below ca. 50 K, μ_{eff} increases sharply and becomes strongly field dependent. Plots of χ^{-1} vs. T are linear between 100 and 290 K, and the Weiss constant of θ = 42 K, determined from

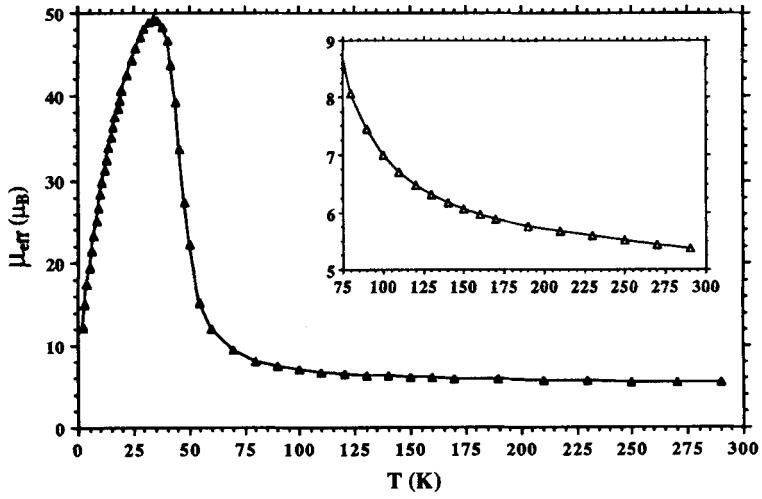

FIGURE 4. Temperature dependence of the magnetic moment per $Ni^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$ formula unit in an applied field of 500 Gauss.

the equation $\chi = C/(T-\theta)$, is positive and provides additional evidence that the Ni^{II} and Mn^{III} centers are coupled ferromagnetically. Low field magnetization measurements show that the magnetic ordering temperature is 30 K.

Since the magnetic phase transition temperature is proportional to the number of nearest neighbors, it should be possible to increase the magnetic phase transition temperature in $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$ by filling the vacancies in the three-dimensional bridging framework.[26] By carrying out the reaction of Ni^{II} and $Mn^{III}(CN)_6^{3-}$ in the presence of a cesium salt, the 1:1 product $CsNi^{II}[Mn^{III}(CN)_6] \cdot H_2O$ is obtained; in this material, all the metal lattice sites are occupied.[5] Variable temperature magnetic measurements reveal that $CsNi^{II}[Mn^{III}(CN)_6] \cdot H_2O$ orders magnetically at 42K, a 12 K increase relative to $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$. This increase illustrates the benefits of a vacancy-free framework in these polynuclear cyanometalates.

An important trend in Table I is that compounds with larger numbers of singly occupied t_{2g} orbitals in the strong ligand-field sites have higher magnetic phase transition temperatures. For example, consider the three isostructural molecular-based ferromagnets $Ni^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$,[16] $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$,[25] and $Ni^{II}_3[Cr^{III}(CN)_6]_2 \cdot 9H_2O$,[17] each of which contains a Ni^{II} center in the weak ligand-field site. The magnetic ordering temperatures of 23, 40, and 60 K for $Ni^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$, $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$, and $Ni^{II}_3[Cr^{III}(CN)_6]_2 \cdot 9H_2O$, respectively, reflect the fact that $Ni^{II}_3[Fe^{III}(CN)_6]_2 \cdot xH_2O$ has only one, $Ni^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$ two, and $Ni^{II}_3[Cr^{III}(CN)_6]_2 \cdot 9H_2O$ three unpaired electrons in the t_{2g} orbitals of the metal in the strong ligand-field site; more favorable ferromagnetic superexchange conditions lead to higher magnetic phase transition temperatures. The observed trend is also consistent with the fact that higher magnetic phase transition temperatures are favored by substituting earlier transition metals into the lattice.

6. THE EFFECT OF SITE VACANCIES AND LINKAGE ISOMERISM ON ORDERING TEMPERATURE.

One important process which has been found to occur in some polynuclear cyanometalates is linkage isomerism of the cyano ligands. Shriver first observed this phenomenon in a non-magnetically ordered analogue of Prussian blue, $KFe^{II}[Cr^{III}(CN)_6] \cdot xH_2O$.[27] When freshly prepared, this compound exhibits a sharp ν_{CN} stretch at 2162 cm^{-1}. After a few days, however, the brick red precipitate changes to a brown powder that exhibits two ν_{CN} stretches at 2162 and 2099 cm^{-1}. Heating the sample to 100 °C (or alternatively allowing the sample to stand at room temperature for several months) yields a green product with a strong ν_{CN} band at 2095 cm^{-1}. These observations have been attributed to a flip of the cyano ligand from its initial coordination mode of Fe^{II}-NC-Cr^{III} in the brick red product to Fe^{II}-CN-Cr^{III} in the green compound.[28]

In magnetically ordered Prussian blue analogues, linkage isomerism of the cyano ligands can lower the magnetic ordering temperature. For example, $Mn^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$ and $CsMn^{II}[Mn^{III}(CN)_6] \cdot {}^1/_2H_2O$, have magnetic ordering temperatures of 37 and 31 K, respectively.[19] These relative ordering temperatures are the opposite of what one would expect at first glance: the former material should have the *lower* magnetic ordering temperature because it has vacancies in the strong ligand-field (M′) sites whereas the latter compound does not.[5] These vacancies should interrupt the superexchange pathway and reduce T_N.

The infrared spectra of these two compounds allow us to understand this unexpected behavior. The infrared spectrum of $Mn^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$ shows a single sharp ν_{CN} band at 2146 cm^{-1} (Figure 5) that is consistent with an ordered array of bridging cyano ligands C-coordinated to Mn^{III} and N-coordinated to Mn^{II}. The infrared spectrum of $CsMn^{II}[Mn^{III}(CN)_6] \cdot {}^1/_2H_2O$, however, displays two sharp ν_{CN} stretches at 2148 and 2071 cm^{-1} (Figure 5). The ν_{CN} band at 2148 cm^{-1} is again consistent with bridging cyano ligands C-coordinated to Mn^{III} and N-coordinated to Mn^{II}, while the band at 2071 cm^{-1} suggests that there are bridging cyano ligands C-coordinated to Mn^{II} and N-coordinated to Mn^{III}.[18,19,27,28] The disorder in the structure interrupts the superexchange pathway and reduces the magnetic ordering temperature of $CsMn^{II}[Mn^{III}(CN)_6] \cdot {}^1/_2H_2O$. Both linkage isomerism and vacancies in the strong ligand-field sites interrupt the superexchange network; in certain cases the former has the larger effect on T_N.

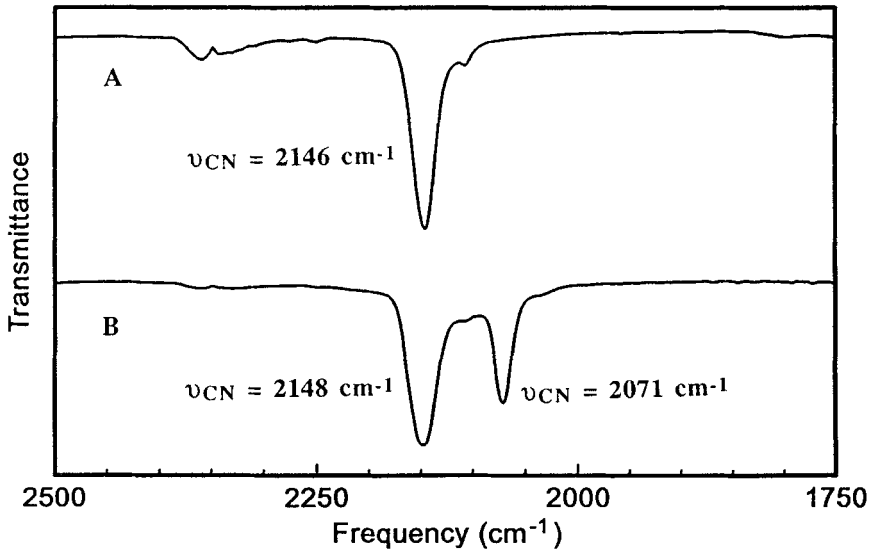

FIGURE 5. Infrared spectra of $Mn^{II}_3[Mn^{III}(CN)_6]_2 \cdot 12H_2O$ (**A**) and $CsMn^{II}[Mn^{III}(CN)_6] \cdot {}^1/_2H_2O$ (**B**) as Nujol mulls.

7. HYSTERESIS IN PRUSSIAN BLUE ANALOGUES.

With one exception, all of the completely characterized molecular-based magnetic materials in Table 1 exhibit hysteresis below their magnetic ordering temperature.[29] For example, the ferrimagnet $(NEt_4)_{0.5}Mn^{II}_{1.25}[V^{II}(CN)_5]\cdot 2H_2O$ exhibits hysteretic behavior characteristic of a soft magnet below its magnetic phase transition temperature. At 50 K, the coercive field is ca. 24 G and the remnant magnetization is 1.39×10^3 G cm^3 mol^{-1}.[11] The very small coercive field reflects the fact that all of the spin carriers are magnetically isotropic: high-spin Mn^{II} ($t_{2g}^3e_g^2$) and V^{II} ($t_{2g}^3e_g^0$) centers.[30]

The value of the coercive field depends on several factors such as the grain size of the sample and the point at which the applied field is reversed; it is not an intrinsic property of the material.[17,30] Nevertheless, the value of the coercive field can be affected chemically: substitution of spin carriers with orbitally degenerate electronic configurations into the Prussian blue framework leads to magnetic materials that often have substantially larger coercive fields. For example, the coercive field of $CsMn^{II}[Mn^{III}(CN)_6]\cdot {}^1/_2H_2O$ is 1140 G at 4.5 K (Figure 6); this large value reflects the presence of magnetically anisotropic low-spin Mn^{III} centers ($t_{2g}^4e_g^0$). The coercive field is large compared to most molecular-based magnetic materials.[1,30] In comparison, the coercive fields of Fe, Fe_3O_4, and CrO_2 (traditional inorganic magnetic materials) are 1, 213, and 650 G, respectively.[1]

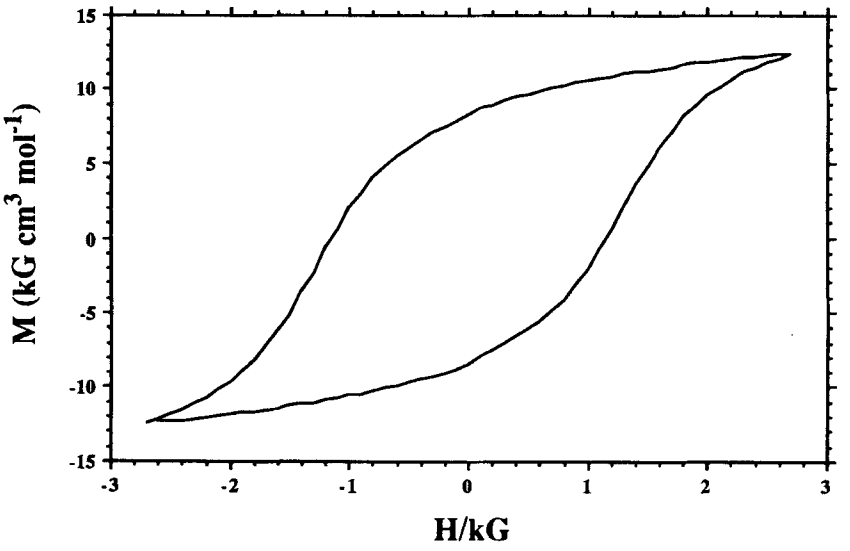

FIGURE 6. Hysteresis loop for $CsMn^{II}[Mn^{III}(CN)_6]\cdot {}^1/_2H_2O$ at 4.5 K.

8. CONCLUSIONS.

The preparation of inorganic solids from hexacyanometalate molecular building blocks has led to a general route for the preparation of materials with high magnetic ordering temperatures. Through the appropriate choice of molecular building blocks (i.e., by considering the symmetry properties of the magnetic orbitals on the adjacent spin carriers), solids that exhibit ferromagnetic or ferrimagnetic behavior can be prepared. The coercive fields in these compounds can also be tailored through the appropriate choice of molecular building blocks, magnetic materials with large coercive fields resulting from the use of magnetically anisotropic cyanometalate building blocks. While linkage isomerism and site vacancies lead to reductions in the magnetic ordering temperature, large increases in T_N can be achieved by substituting into the lattice metals that backbond strongly into the cyanide π^* orbitals. An understanding of the electronic and structural factors that favor strong coupling between adjacent spin carriers has led to the preparation of molecular based magnetic materials with magnetic phase transition temperatures over 200 K. Clearly, remarkable progress is being made toward the preparation of room temperature molecular-based magnetic materials and further improvements in T_N can be expected in the near future.

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