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Designer Magnets Containing Cyanides and Nitriles

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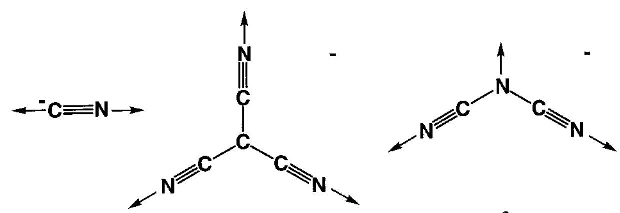
ABSTRACT

Magnets synthesized from molecules have contributed to the renaissance in the study of magnetic materials. Three-dimensional network solids exhibiting magnetic ordering have been made from several first-row metal ions and bridging unsaturated cyanide, tricyanomethanide, and/or dicyanamide ligands. These materials possess several different structural motifs, and the shorter the bridge, the stronger the interaction (i.e., −C≡N− > −N≡C−N− ≫ N≡C−N−C≡N− = N≡C−C−C≡N−). Cyanide additionally has the ability to discriminate between C- and N-bonding to form ordered heterobimetallic magnets, and the strong coupling can lead to ferro- or ferrimagnetic ordering substantially above room temperature. Tricoordination of tricyanomethanide results in spin-frustrated systems, which possess interpenetrating rutile-like networks. In contrast, single rutile-like frameworks are formed by μ_3-bonded dicyanamide, which leads to ferromagnetics and weak ferromagnetics.

Introduction

The renaissance in the study of the magnetism of transition metal (M) complexes is fueled in part by the discovery of magnetic ordering in chains, layers, and 3-D network structures. Key is the magnetic coupling between nearest-neighbor M-based spin sites that is provided by an intermediary ligand. Except for ligands possessing unpaired electron spins, the strongest coupling, in general, arises from ligands with the fewest atoms and the greatest conjugation. Cyanide (**1**), tricyanomethanide (**2**), and dicyanamide (**3**) are small ligands that can bridge two (**1**) or three (**2**, **3**) M's and, due to their highly conjugated nature, can provide strong spin coupling between the M's.



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The ability of these ligands to form homoleptic compounds[1] as well as to bridge, but not chelate, to two or more M's can lead to extended 3-D network structures that are essential for the stabilization of magnetic ordering. Additionally, the asymmetry of cyanide enables the discrimination between C- and N-bound M's and formation of ordered heterobimetallic compounds.

In this Account we focus on the directed synthesis of 3-D network structures based on these ligands that has occurred in our laboratory. Clearly, other groups worldwide have made and continue to make important contributions in the development of magnets based on these ligands; however, due to the nature of this journal, we dwell primarily on work from our laboratory.

Cyanide-Based Magnets

Prussian blue, $Fe_3^{III}[Fe^{II}(CN)_6]_3 \cdot xH_2O$, is the prototype for a growing family of designer magnets. The ideal Prussian blue structure consists of →M←C≡N→M′←N≡C→M← linkages along all three Cartesian directions (Figure 1), and with relative ease the metal ions, their charges, and consequently the number of spins per site can be varied, leading to a variety of magnetic behaviors. Ferromagnetic coupling, which may lead to ferromagnetic ordering, occurs when spins on nearest-neighbor metal ion sites reside in orthogonal orbitals. This occurs for d^8 ($t_{2g}^6e_g^2$) and d^3 (t_{2g}^3) metal ions such as that found in $CsNi^{II}[Cr^{III}(CN)_6] \cdot 2H_2O$, which is a ferromagnet below its critical temperature, T_c, of 90 K.[2] In contrast, when the spin-containing orbitals are not orthogonal (i.e., both sites contain spins in the t_{2g} or e_g orbitals), the unpaired spins couple antiferromagnetically, which can lead to a ferrimagnet. This is observed for d^5 ($t_{2g}^3e_g^2$) and d^3 (t_{2g}^3) $CsMn^{II}[Cr^{III}(CN)_6] \cdot H_2O$ (T_c = 90 K).[5] Many magnets complying with this paradigm have been reported by the Verdaguer[2,4] and Girolami[5] groups.

Room-Temperature Magnet. In 1995, Verdaguer's group reported that the mixed-valent nonstoichiometric $V^{II/III}[Cr^{III}(CN)_6]_{0.86} \cdot 2.8H_2O$ ordered as a ferrimagnet above

Joel S. Miller received a Ph.D. from UCLA (1971). After a postdoctoral fellowship at Stanford University and several positions in industry including the Central Research & Development Department at Du Pont, he joined the faculty at the University of Utah (1983), where he is currently a Distinguished Professor. He has been a Visiting Scientist at the Weizmann Institute and a Visiting Professor of Chemistry at the University of Pennsylvania as well as the University of California, Irvine. He is on the advisory boards of *Advanced Materials, Chemistry—a European Journal, CrystEngComm, Inorganic Chemistry,* and *Journal of Materials Chemistry,* and is a member of the Inorganic Synthesis Corporation. His research interests focus on the solid-state magnetic, electrical, and optical properties of molecular (organic, organometallic, and inorganic coordination) compounds and electron-transfer complexes as well as the surface modification of solids. Currently he is actively involved in synthesis and characterization of molecular/organic-based ferromagnets. He has edited 11 monographs and published over 350 papers in these and other areas and was the recipient of the 1996 Pinguin Foundation's Wilhelm Manchot Research Professorship at the Technische Universität München, Wayne State University's 1998 Distinguished Alumni Award, and the 2000 American Chemical Society Award for *Chemistry of Materials*.

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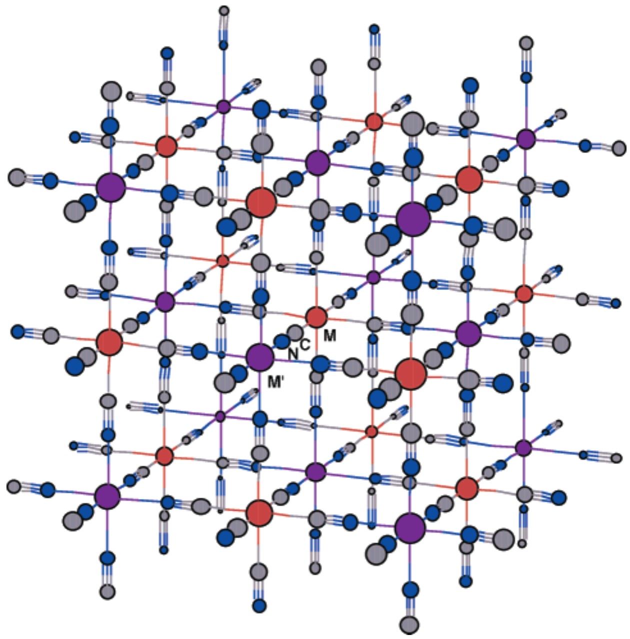


FIGURE 1. Idealized structure of Prussian blue →M←C≡N→M′←C≡N→M← linkages (N is blue, C is gray, M is brown, M′ is purple) along all three Cartesian directions.

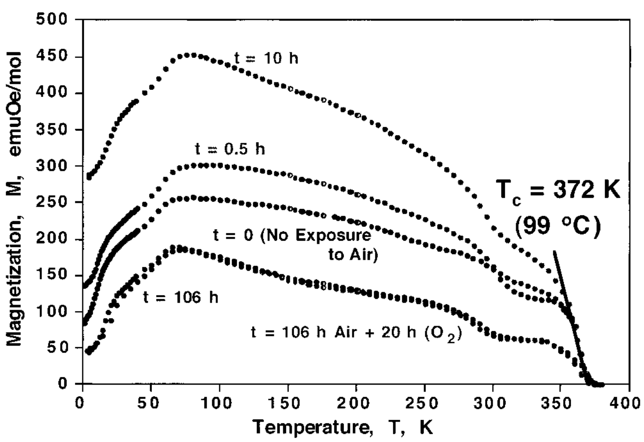


FIGURE 2. Temperature dependence of the magnetization of $K_{0.058}V^{II/III}[Cr^{III}(CN)_6]_{0.79}\cdot(SO_4)_{0.058}\cdot 0.93H_2O$ upon exposure to air and pure oxygen up to 106 h for air and and additional 20 h of O_2. Note that the 372 K T_c is not altered.

room temperature at 315 K.[6] Although Michel Verdaguer kindly provided us with the procedure to make this complex magnet, we had our share of trials and tribulations. Ultimately, we prepared a material with a nominal composition of $K_{0.058}V^{II/III}[Cr^{III}(CN)_6]_{0.79}\cdot(SO_4)_{0.058}\cdot xH_2O$, which orders as a ferrimagnet at 372 K (99 °C).[7] This material is far more complex than Verdaguer's but appears to have enhanced air stability, as samples maintain a T_c at 372 K even upon exposure to air for 108 h and to oxygen for an additional 20 h (Figure 2). Almost simultaneously, Girolami reported a related stoichiometric magnet of $KV^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$ composition, which orders at 376 K.[8] Although the material formally contains only V^{II} ($S = {}^3/_2$), the magnetic ordering is attributed to the presence of V^{III} ($S = 1$) impurities.

Thin-Film Magnets. The deposition of magnetic thin films is technologically important. Taking advantage of

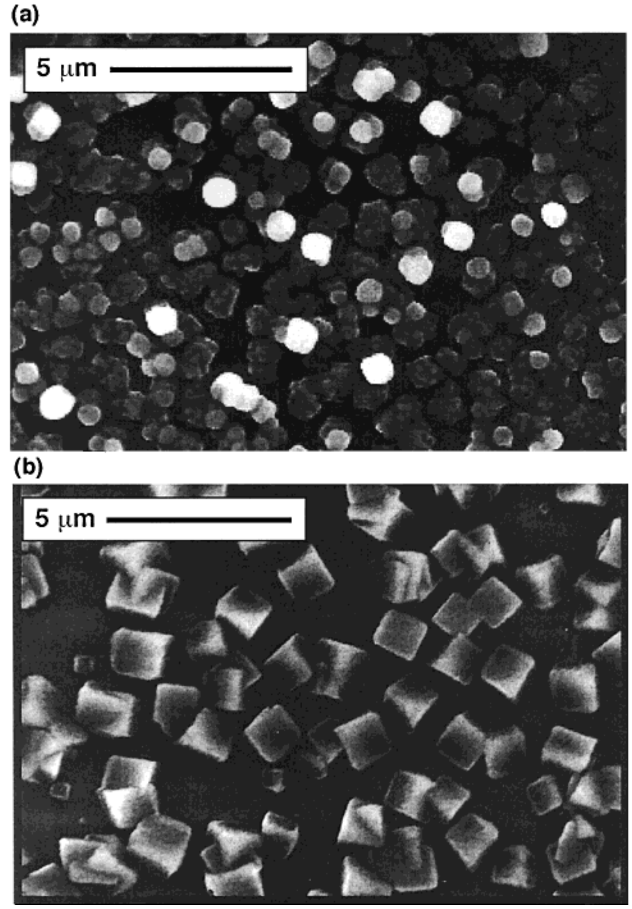


FIGURE 3. Scanning electron microscopic (SEM) images of (a) an amorphous film and (b) a crystalline film of $K_{2.0}Cr^{II}[Cr^{II}(CN)_6]$ composition.

earlier work[4b,9] as well as the knowledge that the substitutionally inert $[Cr^{III}(H_2O)_6]^{3+}$ can be electrochemically reduced to labile Cr^{II}, amorphous or crystalline 1.0 ± 0.5 μm films were formed (Figure 3). Typically, oxidized films were of $Cr^{III}\{[Cr^{III}(CN)_6]_{0.98}[Cr^{II}(CN)_6]_{0.02}\}$ composition, while the reduced films were of $K_{2.0}Cr^{II}[Cr^{II}(CN)_6]$ composition, as determined from an analysis of the υ_{CN} IR data $\{[Cr^{II}(CN)_6]^{4-}$, $\upsilon_{CN} = 2072$ (s) cm^{-1}; $[Cr^{III}(CN)_6]^{3-}$, $\upsilon_{CN} =$ 2185 (m) $cm^{-1}\}$ and X-ray photoelectron spectra. The T_c, which varies with the oxidation state of chromium, ranges between 135 K for the reduced films and 260 K (−13 °C) for the oxidized films of either type. Hence, the T_c values are independent of crystallinity, suggesting that the magnetic domains are smaller than the short-range structural order for both types of films. Hysteresis was observed for both films, with coercive fields as high as 830 Oe at 20 K for the amorphous material, but substantially less for the crystalline material. This is attributed to the larger number of defects in the amorphous films. In another research thrust, not dwelled upon in this Account, thin films of the $V[TCNE]_x$ room-temperature magnet have recently been reported.[10]

$[Mn^{IV}(CN)_6]^{2-}$-Based Magnets. The quest to identify new ferromagnets led us to prepare $Ni^{II}[Mn^{IV}(CN)_6]$. Like $CsNi^{II}[Cr^{III}(CN)_6]\cdot 2H_2O$,[2] it should possess spins in orthogonal orbitals on nearest-neighbor spin sites and order ferromagnetically. This targeted material required a source

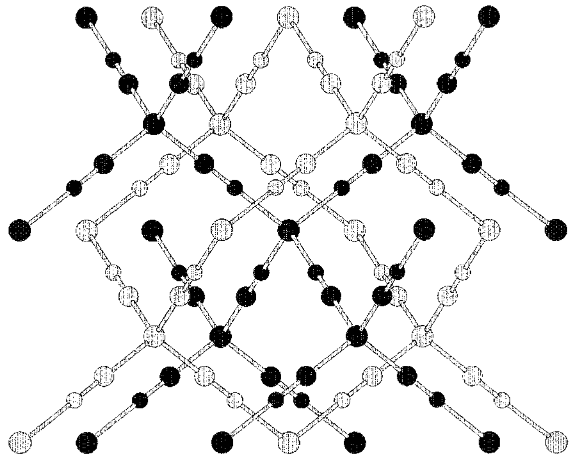


FIGURE 4. Proposed interpenetrating diamond-like (sphalerite) lattices for $Mn^{II}[Mn^{II}(CN)_4]$.

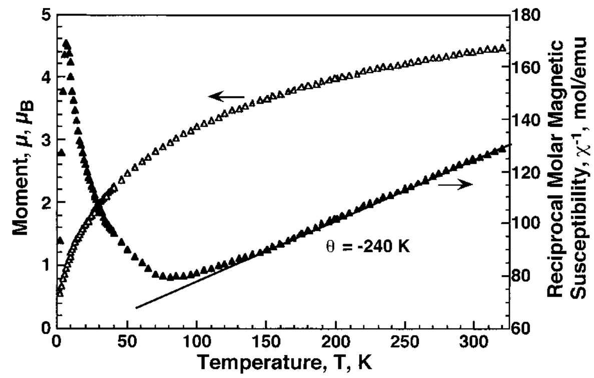
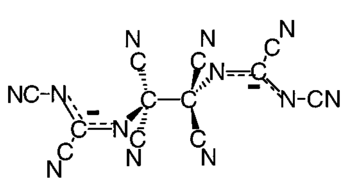


FIGURE 5. Corrected reciprocal molar magnetic susceptibility and moment as a function of temperature for $Mn^{II}[Mn^{II}(CN)_4]$. Above 140 K, $\chi^{-1}(T)$ is linear and fits the Curie–Weiss expression with $\theta = -240$ K.

of hydrolytically unstable $[Mn^{IV}(CN)_6]^{2-}$, which was prepared as the $[(Ph_3P)_2N]^+$ salt from aprotic media.[11] Valance-ambiguous materials of $M'[Mn(CN)_6]$ (M = V, Cr, Mn, Fe, Co, Ni) {i.e., $M^{II}[Mn^{IV}(CN)_6]$ or $M^{III}[Mn^{III}(CN)_6]$} composition were prepared. Analyses of the data revealed that the former description occurred for M = Co, Ni, while the latter occurred for M = V, Cr, Mn.[11b] In contrast, $Mn^{II}[Mn^{IV}(CN)_6]{\cdot}0.57H_2O$ (T_c = 48.7 K) has been prepared from aqueous solution.[12] More complex behavior, including linkage isomerization, occurred for M = Fe.[11c]

$[(Ph_3P)_2N]_2[Mn^{IV}(CN)_6]$ exhibited unexpected photochemistry in CH_2Cl_2 with the formation of $[(Ph_3P)_2N]_2[C_{12}N_{12}]$.[15] $[C_{12}N_{12}]^{2-}$ (**4**) is planar except for nitriles on the central, albeit long (1.577 Å), CC bond. This remarkable compound is the largest $(CN)_x^z$ oligomer and undoubtedly forms via a complex 10-electron-transfer reaction that involves the formation of CN^- and $CN^{\bullet}$ from the photoinduced decomposition of $[Mn^{IV}(CN)_6]^{2-}$ in CH_2Cl_2, but not in MeCN.

Nonetheless, what is the fate of the manganese?



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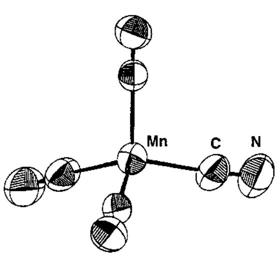

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$[Mn^{IV}(CN)_4]^{2-}$—High or Low Spin? Comparable to the improbability of isolating $[C_{12}N_{12}]^{2-}$ was the improbability of isolating $[(Ph_3P)_2N]_2[Mn^{II}(CN)_4]$. $[Mn^{II}(CN)_4]^{2-}$ (**5**) is an electron-poor 13-e^- tetrahedral complex[13b,14] and is the first tetrahedral percyano complex of a transition metal, as the large stability constants with cyano ligands strongly favor octahedral complexes. A key question arising from ligand field theory is that of the spin state of $[Mn^{II}(CN)_4]^{2-}$. Is it high spin ($S = {}^5/_2$) or low spin ($S = {}^1/_2$), as observed for octahedral $[Mn^{II}(CN)_6]^{2-}$?[15] While by far the predominate number of tetrahedral complexes are high spin,[16] all known percyano complexes, due to the strong ligand field imposed by the cyanide ligand, are low spin.[17] Although the prediction of the spin state is difficult, the observed temperature-independent moment of 5.99 μ_B clearly indicated that $[Mn^{II}(CN)_4]^{2-}$ was high spin.[14] The structure has long Mn^{II}–CN distances of 2.16 Å, 0.11 Å longer than that observed for low-spin $Na_4[Mn^{II}(CN)_6]{\cdot}10H_2O$,[18] and hence consistent with the high-spin ground state.

$[Mn^{II}(CN)_4]^{2-}$ can be used as a synthon, akin to $[M(CN)_6]^{z-}$ being a synthon for Prussian blue structured materials, to develop a new structural class of materials. Except, of course, the resulting 3-D network structure has tetrahedral, not octahedral, sites and is overall diamond-like (or sphalerite). With this motif targeted, the reaction of $[(Ph_3P)_2N]_2[Mn^{II}(CN)_4]$ and $[M^{II}(NCMe)_6][B[C_6H_3(CF_3)_2]_4]_2$ led to the formation of $Mn^{II}[Mn^{II}(CN)_4]$.[19] $Mn^{II}[Mn^{II}(CN)_4]$ exhibits an υ_{CN} absorption at 2170 cm^{-1} which is shifted 32 cm^{-1} to lower energy with respect to $[(Ph_3P)_2N]_2[Mn^{II}(CN)_4]$, suggesting lengthening of the CN bond upon N-coordination to high-spin Mn^{II}. The powder pattern was assigned to the cubic $P\bar{4}3m$ space group with a = 6.123 Å. This lattice spacing is inconsistent with a diamond-like motif, but is in accord with a motif of two interpenetrating diamond-like lattices (Figure 4). Each independent lattice comprises tetrahedral Mn^{II} sites with a $Mn^{II}{\cdots}Mn^{II}$ separation of 5.303 Å, 0.20 Å shorter than that found for $Zn(CN)_2$[20] and 0.23 Å longer than that in $K_2Mn^{II}[Mn^{II}(CN)_6]$.[5b] The observed density of 1.68 g/cm^3 is additionally consistent with an interpenetrating structure.

The room-temperature magnetic moment of 4.40 μ_B/Mn is substantially reduced from the predicted value (5.92 μ_B/Mn) for uncoupled $S = {}^5/_2$ Mn^{II} ions, but is consistent with very strong antiferromagnetic coupling. The magnetic susceptibility, χ, gradually increases with decreasing temperature, reaching a broad maximum, and then decreases rapidly upon further cooling to 2 K. The broad maximum is consistent with antiferromagnetic ordering, while the upturn at low temperature is assigned to the presence of Mn^{II} $S = {}^5/_2$ impurities. Mn^{II} spin impurities are believed to arise as a result of simultaneous formation of an insoluble oligomeric species as the solid precipitates from solution. Subtraction of a spin impurity leads to the

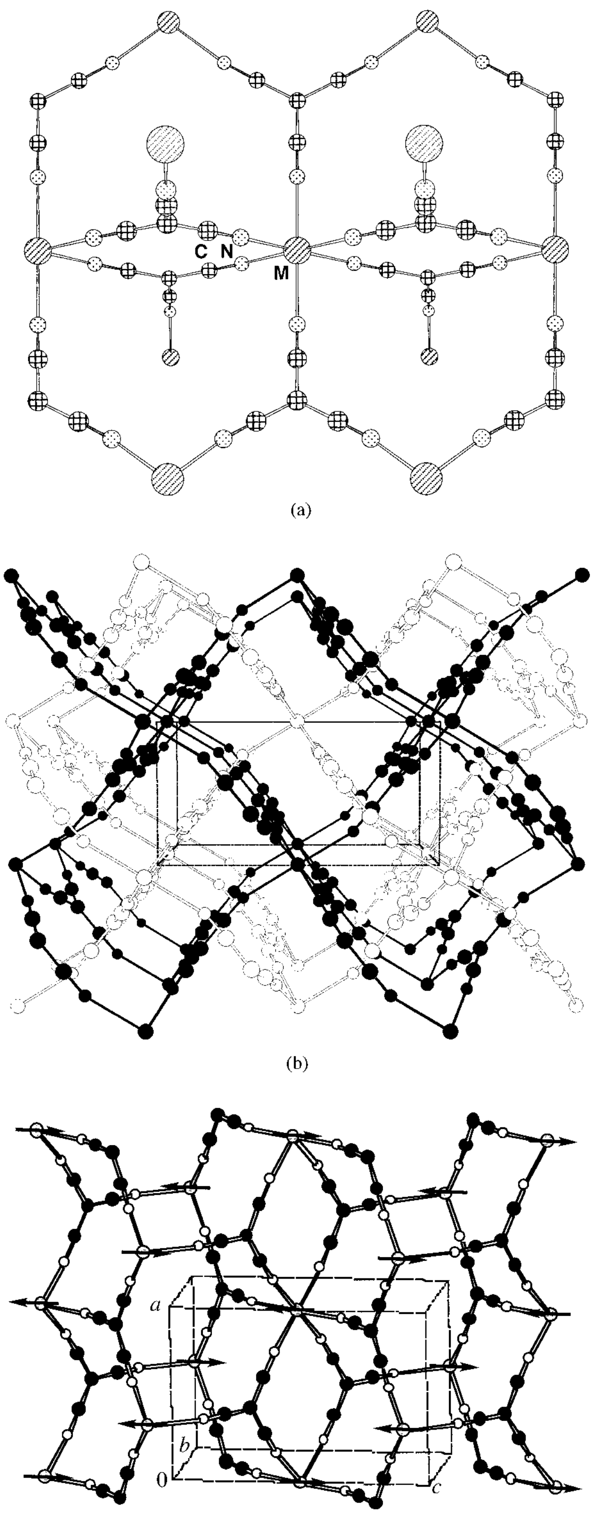

FIGURE 6. Segment of a chain of $M[C(CN)_3]_2$ with each M being hexacoordinate and bridged by μ_3-$[C(CN)_3]^-$ (a), segment of interpenetrating $M[C(CN)_3]_2$ networks (b), and segment of a chain of $Cr^{II}[C(CN)_3]_2$, showing the magnetic structure at 2 K (c). The arrows denote the spin orientation of the Cr(II) ordered magnetic moment in (c). These representative illustrations were based on $Cr^{II}[C(CN)_3]_2$.[22a]

corrected susceptibility with a broad maximum at 80 K (Figure 5), due to 3-D antiferromagnetic ordering, as expected. Above 140 K, χ can be fit to the Curie−Weiss expression, $\chi \propto (T - \theta)^{-1}$, with a strongly antiferromagnetic θ value of −240 K (Figure 5). The Neèl ordering temperature, T_N, is ~65 K.

Tricyanomethanide-Based Magnets

The new and enhanced magnetic behavior observed for percyano complexes, as well as the magnetic ordering observed for a plethora of metal complexes containing $S = {}^1/_2$ $[C_2(CN)_4]^{\bullet -}$,[23] led us to revisit the homoleptic complexes of $[C(CN)_3]^-$ (**2**) and study $M[C(CN)_3]_2$ (M = V, Cr, Mn, Fe, Co, Ni). As each M prefers to be hexacoordinate, each **2** can bind to three M's, but due to bonding constraints it cannot chelate. Each M forms chains (illustrated in Figure 6a), which are further connected to form a 3-D lattice similar to that of rutile, TiO_2. The crystal structure, however, is more complex, as it is comprised of two independent interpenetrating $M[C(CN)_3]_2$ networks (Figure 6b).[22] As a consequence of the interpenetrating networks, the intranetwork M···M distance (e.g., 7.68 Å for M = Mn) exceeds the internetwork M···M distance (e.g., 5.38 Å for M = Mn) and contributes to some enhancement of the antiferromagnetic coupling for Mn^{II}-$[C(CN)_3]_2$; i.e., θ obtained from a fit of the susceptibility to the Curie−Weiss expression is −5.1 K and not ca. −2 K.[22b]

The rare three-fold symmetry of **2** should lead to geometrical spin frustration akin to a Kagomé lattice.[23] Although expected, the weak spin coupling via the 5-atom −NCCCN− bridge, albeit conjugated, is ineffective, as observed for $Mn^{II}[C(CN)_3]_2$.[22b] In contrast, stronger antiferromagnetic coupling of $\theta = -46$ K is observed for Cr^{II}-$[C(CN)_3]_2$.[22a] In addition, $Cr^{II}[C(CN)_3]_2$ undergoes a Jahn−Teller distortion (Cr−N distances of 2.08 and 2.45 Å), which leads to the stabilization of antiferromagnetic ordering at 6.12 K. This is confirmed from neutron diffraction studies that reveal additional Bragg reflections as a result of antiferromagnetic ordering with a 4.7 μ_B moment on each Cr^{II} aligned parallel to *c* (Figure 6c). This is consistent with 2-D Ising behavior.[22a]

Dicyanamide-Based Magnets

Related to tricyanomethanide (**2**) is the smaller dicyanamide (**3**) ligand, which in addition to the five-atom −NCNCN− conjugated spin-coupling bridge can provide a shorter three-atom −NCN− conjugated spin-coupling pathway. This, however, requires the weaker amide central N to bond to an M. This led to the exploration of homoleptic complexes of $[N(CN)_2]^-$ (**3**)[24] and characterization of $M[N(CN)_2]_2$ (M = V, Cr, Mn, Fe, Co, Ni, Cu).[25]

Similar to **2**, each M prefers to be hexacoordinate, and each **3** can bind to three M's, but it also cannot chelate, and a rutile structure forms (Figure 7).[26] However, unlike $M^{II}[C(CN)_3]_2$, the shorter $M-N(CN)_2$ linkage prohibits the interpenetration of a second lattice.

Unexpectedly, $M^{II}[N(CN)_2]_2$ (M = V, Cr, Mn, Fe, Co, Ni) complexes all magnetically order with T_c values as high as 47 K (M = Cr).[27] Detailed studies show that $M^{II}[N(CN)_2]_2$ (M = Co, Ni) complexes order as ferromagnets,[26] while

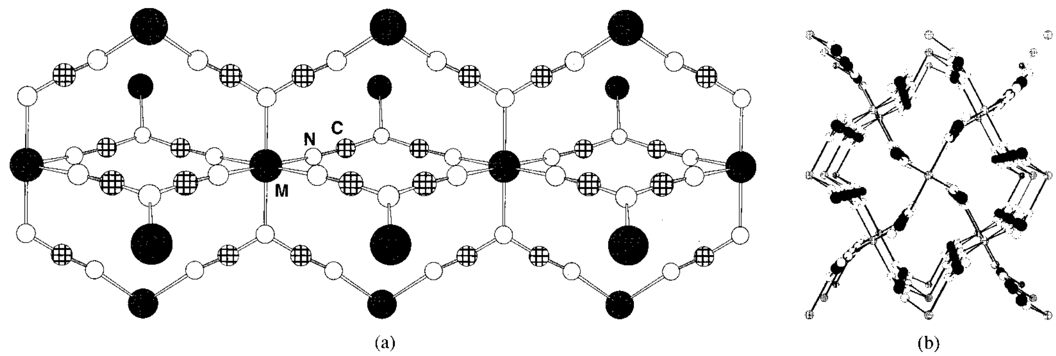

FIGURE 7. Segment of a chain of $M[N(CN)_2]_2$ with each M being hexacoordinate and bridged by μ_3-$[N(CN)_2]^-$ (a); view perpendicular to the chain (b). These representative illustrations were based on $Co^{II}[C(CN)_3]_2$.[26]

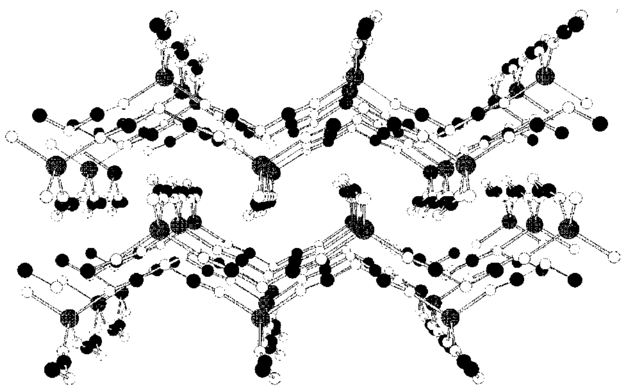

FIGURE 8. Corrugated structure of $Zn[N(CN)_2]_2$ with adjacent tightly packed $Zn[N(CN)_2]_2$ 2-D layers offset by *a*/2 with respect to alternating sheets. The closest interlayer Zn···Zn separations are 6.335 and 6.673 Å between pairs and 4.492 Å between staggered pairs.

$M^{II}[N(CN)_2]_2$ (M = V, Cr, Mn, Fe) complexes order as weak ferromagnets[27,28] (or canted antiferromagnets). $Co^{II}[N(CN)_2]_2$ is unusual, as two phases, pink (α-phase) and deep blue (β-phase), were isolated.[26] The structure and electronic absorption spectra of the pink phase are those of an octahedral complex, while the electronic absorption spectra of the deep blue phase is typical of a tetrahedral Co(II) complex. α-$Co^{II}[N(CN)_2]_2$ is a ferromagnet that orders at 8.7 K, while β-$Co^{II}[N(CN)_2]_2$ is a weak ferromagnet ordering at 8.9 K (and has a second magnetic transition at 2.7 K).[26] It is interesting to note that ferromagnetic $Ni^{II}[N(CN)_2]_2$ orders at 19.7 K, twice the temperature of isostructural α-$Co^{II}[N(CN)_2]_2$. Furthermore, the coercive field for α-Co^{II}-$[N(CN)_2]_2$ is ~800 Oe vs ~7000 Oe for $Ni^{II}[N(CN)_2]_2$. Typically, Co-based magnets have higher T_c values as well as greater coercive fields with respect to Ni-based magnets due to single-ion anisotropy; thus, this anomalous result bears further study. The structure of β-$Co^{II}[N(CN)_2]_2$ has been elusive; however, the structure of diamagnetic Zn-$[N(CN)_2]_2$ has been determined to be comprised of μ-$[N(CN)_2]^-$ bridging tetrahedral Zn^{II}, which is comprised of layers of corrugated sheets (Figure 8).[29]

Dicyanamide has two distinct bonding sites with different affinities for metal ions. As a result, there is the potential to form ordered heterobimetallic materials; however, the second nitrile, being more basic than the amide N, severely limits this possibility. Thus, dicyan-

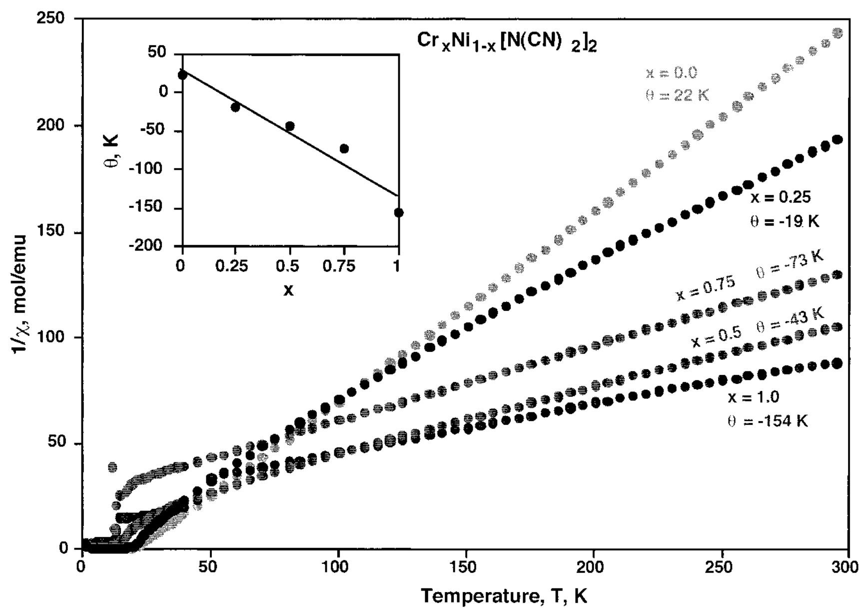

FIGURE 9. Solid solutions of $Cr^{II}_xNi^{II}_{1-x}[N(CN)_2]_2$, showing ferromagnetic coupling for Ni ($x = 0$) and strong antiferromagnetic coupling for Cr ($x = 1$) and variation in between for solid solutions. Inset shows the dependence of θ on x.

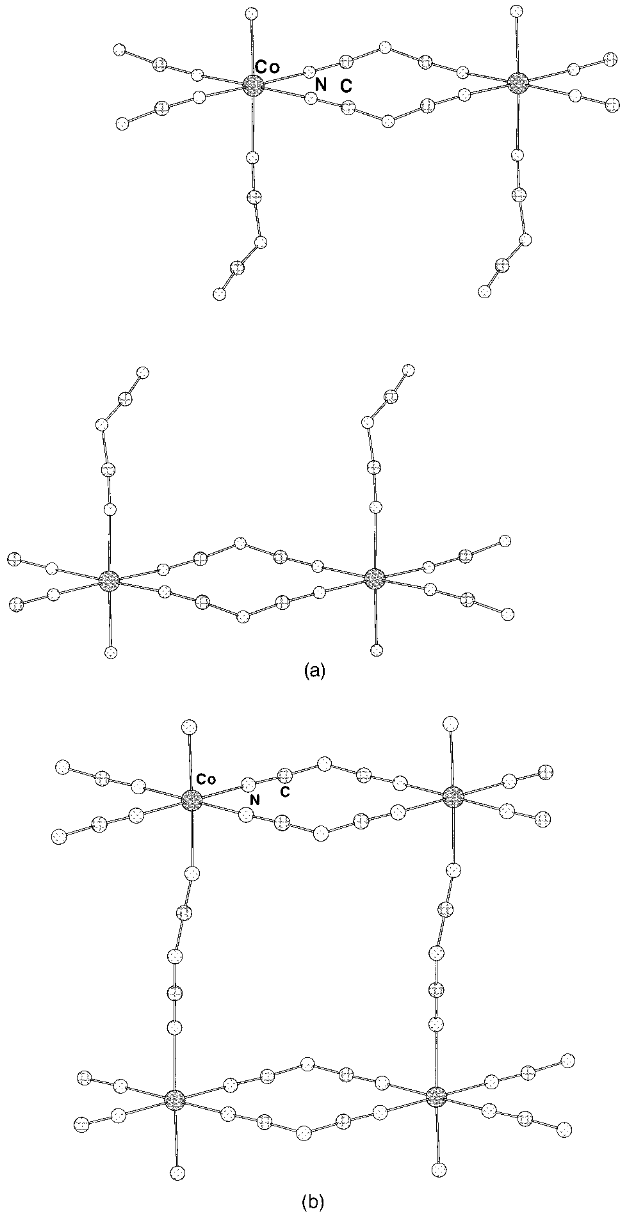

FIGURE 10. Linear structure (1-D) for $\{Co^{II}[N(CN)_2]_4\}^{2-}$ (a) and layered (2-D) structure of $\{Co^{II}[N(CN)_2]_3\}^{-}$ (b), each showing the two different types of μ-$[N(CN)_2]^-$ bonding.

amide is like tricyanomethanide in that clever synthetic methodologies have not emerged to enable the formation of ordered heterobimetallic materials. Nonetheless, solid solutions (random, nonstoichiometric bimetallic materials) can be made to modulate the magnetic properties. For example, solid solutions of the ferromagnet $Ni^{II}[N(CN)_2]_2$ ($\theta = 22$ K) and the canted antiferromagnet $Cr^{II}[N(CN)_2]_2$ ($\theta = -154$ K) can form $Ni^{II}{}_{1-x}Cr^{II}{}_x[N(CN)_2]_2$ ($0 \leq x \leq 1$). The magnetic behavior varies between ferromagnetic coupling and antiferromagnetic coupling, depending on x[30] (Figure 9).

Six-coordinate homoleptic $[PPh_4]\{M^{II}[N(CN)_2]_3\}$ (M = Mn, Co) and $[PPh_4]_2\{M^{II}[N(CN)_2]_4\}$ (M = Co) also have been characterized.[31] $\{M^{II}[N(CN)_2]_4\}^{2-}$ forms a 1-D chain with two μ-$[N(CN)_2]^-$ groups bridging two M's and two terminal ligands (Figure 10a). In contrast, $\{M^{II}[N(CN)_2]_3\}^-$ forms a 2-D layered network structure with each dicyanamide bridging two M sites (Figure 10b). In the latter structure, two μ-$[N(CN)_2]^-$ groups bridge two M's, forming chains that are connected via the third μ-$[N(CN)_2]^-$. In both cases, the $[PPh_4]^+$ cations occupy sites between the layers. Unlike $M[N(CN)_2]_2$ (M = V, Cr, Mn, Fe, Co, Ni), $[PPh_4]_n\{M^{II}[N(CN)_2]_{2+n}\}$ ($n = 1, 2$) exhibits weak magnetic coupling and does not exhibit magnetic ordering above 2 K.[31] The lack of magnetic ordering arises from a combination of weak five-atom intra- and interlayer exchange interactions.

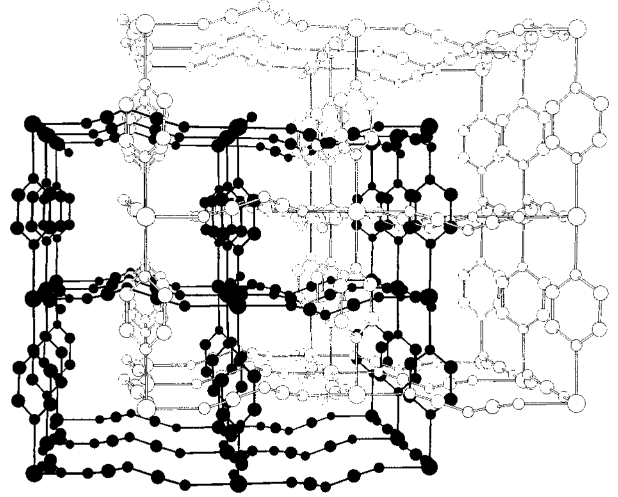

FIGURE 11. Structure of interpenetrating ReO_3-like $Mn^{II}[N(CN)_2]_2$-(pyz). The two lattices are depicted individually in black and gray.

In addition to homoleptic dicyanamide complexes, we,[32−36] and others[37] have been studying heteroleptic dicyanamide complexes, e.g., $M[N(CN)_2]_2L$, with L being Lewis bases such as pyridine (py),[32] 2,2′-bipyridine (2,2′-bipy),[32,34] 4,4′-bipyridine (4,4′-bipy),[32,34] or pyrazine (pyz).[33] These complexes have μ-bonded $[N(CN)_2]^-$ ligands, and to date there are no examples where the amide-N coordinates to an M other than for $M[N(CN)_2]_2$. One-dimensional (1-D) linear and zigzag chains are formed for the py- and 2,2′-bipy-containing complexes, respectively. In contrast, for L = 4,4′-bipy, an unusual 1-D tubular structure was observed where the tube walls are formed by the dicyanamide ligands and the 4,4′-bipy ligand is monodentate.[32,34] Most interesting are the structure and magnetic properties for L = pyz, $Mn[N(CN)_2]_2(pyz)$.[33] This structure consists of 3-D interpenetrating ReO_3-like networks (Figure 11) and exhibits long-range antiferromagnetic ordering below 2.53 K.[33] As noted for $[PPh_4]_n\{M^{II}[N(CN)_2]_{n+2}\}$ ($n = 1, 2$), where only the nitrile nitrogens coordinate, magnetic ordering does not occur. This effect is not surprising, as μ-bonding produces a five-atom −N≡C−N−C≡N− pathway, whereas the homoleptic $M[N(CN)_2]_2$ solids additionally have the shorter three-atom −N−C≡N− linkages that support stronger exchange. In addition to the spatial aspects of the structures, it is also clear that the orbital energies and symmetries are equally important and must be considered. We are currently developing a theoretical description to correlate the crystal structure and magnetic properties of these materials.

Conclusion and Future

Several classes of magnets possessing divalent or trivalent first-row metal ions and π-conjugated μ-cyanide, μ_3-tricyanomethanide, and/or μ_3-dicyanamide ligands have been prepared. Although these materials possess several different structural motifs, the exchange via the π-conjugated bridging ligand decreases with increasing bridge length as −C≡N− > −N≡C−N− ≫ N≡C−N−C≡N−. Additionally, due to less screening, the coupling is qualitatively enhanced for the early transition metals with respect to those to their right on the periodic table. Hence, higher ordering temperatures are observed for systems comprised of early transition metals. While the μ_3-tricyanomethanide and -dicyanamide ligands have similar bonding to M via all donor atoms, cyanide has the ability to discriminate via C- and N-bonding and forms structurally ordered heterobimetallic magnets, and the strong coupling can lead to magnetic ordering substantially above room temperature.

The diversity of magnetic behavior observed for homoleptic cyanides, tricyanomethanides, and dicyanamides suggests a bright future. Homoleptic dicyanophosphide complexes, $M^{II}[P(CN)_2]_2$, as well as complexes of trivalent metal ions, e.g., $M^{III}[P(CN)_2]_3$ (M = Fe, Gd), are unexplored areas under study. Likewise, heteroleptic cyanides, tricyanomethanides, and dicyanamides offer a broad array of structural as well as magnetic diversity that will lead to interesting new chemistry in the future.

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