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New Three-Dimensional Ferrimagnetic Materials: $K_2Mn[Mn(CN)_6]$, $Mn_3[Mn(CN)_6]_2{\cdot}12H_2O$, and $CsMn[Mn(CN)_6]{\cdot}{}^1/_2H_2O$

William R. Entley 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

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Recently, there has been much interest in the synthesis of magnetic materials from inorganic coordination complexes.$^{1-3}$ By using extended organic bridging groups such as various oxalate derivatives$^{2-5}$ to form extended lattices in which metal centers of differing spins alternate, magnetic ordering temperatures up to 30 K have been achieved.[4] Much higher magnetic ordering temperatures should be possible, however, if the organic bridging group is a better communicator of spin information between adjacent spin centers, and one attractive candidate is the cyanide ion. It has long been known that cyanide-bridged solids can be prepared by treating anionic cyanometalates with transition metal cations; the best known example of such a reaction is the synthesis of Prussian blue from $[Fe(CN)_6]^{4-}$ and Fe^{3+}. Because half of the metal centers in Prussian blue are diamagnetic, the paramagnetic centers (which are separated by over 10 Å) order magnetically only below 5.6 K.[6] By synthesizing analogues of Prussian blue in which metals with different nonzero spins occupy alternate lattice sites, Bozorth et al. showed in 1956 that magnetic ordering temperatures above 30 K can be achieved.[7] Other workers have also investigated the magnetic properties of solids related to Prussian blue;$^{3,8-11}$ 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 structures with linear M−NC−M′ bridges.[12,13]

We now describe the synthesis of three new ferrimagnetic materials based on hexacyanomanganate "building blocks" that have magnetic ordering temperatures near 40 K.

Three manganese-based Prussian blue analogues have been prepared and studied: $K_2Mn^{II}[Mn^{II}(CN)_6]$ (**1**) was prepared by addition of KCN to aqueous solutions of $MnCl_2$,[14,15] while $Mn^{II}_3[Mn^{III}(CN)_6]_2{\cdot}12H_2O$ (**2**) and $CsMn^{II}[Mn^{III}(CN)_6]{\cdot}{}^1/_2H_2O$ (**3**) were prepared by addition of $Mn(O_3SCF_3)_2(MeCN)_2$ to aqueous solutions of $K_3Mn(CN)_6$ in the absence and in the presence of $Cs(O_3SCF_3)$, respectively.[16] The structures of all of these species are based on the face-centered cubic structure discussed above, with **2** having vacancies in the M′ sites.[13] The lattice constants of **1**−**3**, as determined by X-ray powder diffraction, are given in Table 1. If the structures are ordered, then the sites with MnC_6 coordination spheres will be low-spin, while the sites with MnN_6 coordination spheres will be high-spin.[17]

Table 1. Structural and Magnetic Data for the New Cyanomanganates

compd	a/Å	T_N/K	C^a	Θ/K	$M_{sat}{}^b$
$K_2Mn^{II}[Mn^{II}(CN)_6]$ (**1**)	10.15	41	4.9	−19	2.4×10^4
$Mn^{III}_3[Mn^{II}(CN)_6]_2{\cdot}12H_2O$ (**2**)	10.62	37	16	−39	5.5×10^4
$CsMn^{II}[Mn^{III}(CN)_6]{\cdot}{}^1/_2H_2O$ (**3**)	10.69	31	6.2	−32	2.08×10^4

^{a} cm^3 K mol^{-1}. ^{b} G cm^3 mol^{-1}.

The infrared spectra of **1** ($\nu_{C\equiv N}$ = 2055 cm^{-1}) and **2** ($\nu_{C\equiv N}$ = 2148 cm^{-1}) each contain a single $\nu_{C\equiv N}$ stretching vibration due to cyanide groups C-bound to low-spin Mn^{II} and low-spin Mn^{III} centers, respectively.[13,14] These observations strongly suggest that the low-spin and high-spin centers do indeed occupy alternate lattice sites and that the cyanide ligands are ordered. In contrast, the infrared spectrum of $CsMn^{II}[Mn^{III}(CN)_6]{\cdot}{}^1/_2H_2O$ exhibits two sharp $\nu_{C\equiv N}$ stretching vibrations at 2148 and 2071 cm^{-1}. The two distinct IR stretches for **3** suggests that there is some disorder in the structure; it is possible that both Mn^{II} ions and Mn^{III} ions are present in the M′ (low-spin) sites.[11] The X-ray diffraction pattern of **3** is sharp and readily indexible to a cubic unit cell.

Variable temperature studies show that **1**−**3** become ferrimagnetic at temperatures near 40 K. For $K_2Mn^{II}[Mn^{II}(CN)_6]$ at 290 K, the magnetic moment per formula unit (μ_{eff}) of 6.32 μ_B is very close to the value of 6.31 μ_B expected for an equal population of $S = {}^5/_2$ Mn^{II} and $S = {}^1/_2$ Mn^{II} spin centers.[18] When the solid is cooled, μ_{eff} gradually decreases to a shallow minimum at ca. 105 K (not readily apparent in Figure 1) and then becomes field dependent below ca. 40 K. Upon further cooling, the magnetic moment rapidly increases to a maximum of 103 μ_B near 24 K in an applied field of 100 G. Plots of $1/\chi_m$ vs T are linear between 100 and 290 K; the Weiss constant of ca. −19 K, determined from the equation $\chi_m = C/(T - \Theta)$, is negative as expected for an antiferromagnetic interaction between the adjacent high and low spin Mn^{II} centers. Further support for the antiferromagnetic interaction comes from the field dependence of the magnetization at 4.5 K: the saturation

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(16) For **2**: Anal. Calcd for $C_{12}H_{24}Mn_5N_{12}O_{12}$: C, 18.0; H, 3.01; Mn, 34.2; N, 20.9. Found: C, 18.4; H, 2.62; Mn, 33.7; N, 21.1. For **3**: Anal. Calcd for $C_6H_1CsMn_2N_6O_{0.5}$: C, 17.7; H, 0.25; Cs, 32.6; Mn, 26.9; N, 20.6. Found: C, 17.7; H, 0.74; Cs, 32.6; Mn, 29.3; N, 20.1.

(17) For **2**, the average coordination environment of the high-spin sites is actually MnN_4O_2.[13]

(18) Chester, A. W.; Schweizer, A. E. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 451−454. We assumed that the magnetic moments of the low-spin Mn^{II} centers (which should be affected by spin−orbit coupling) are 2.18 μ_B.

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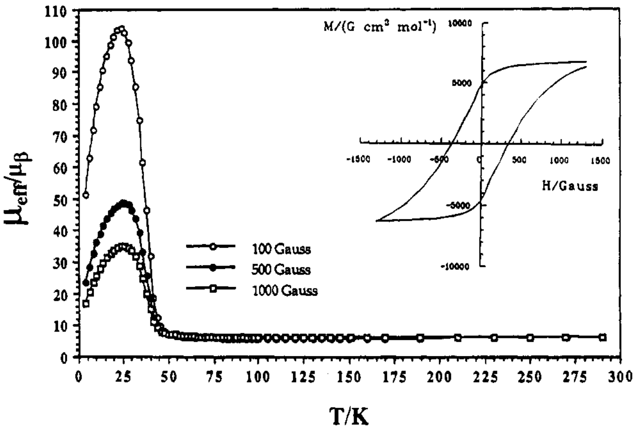

Figure 1. Temperature dependence of the magnetic moment per formula unit of $K_2Mn[Mn(CN)_6]$ (**1**) in applied magnetic fields of 100, 500, and 1000 G. The experimentally observed hysteresis loop at 24 K is shown in the inset.

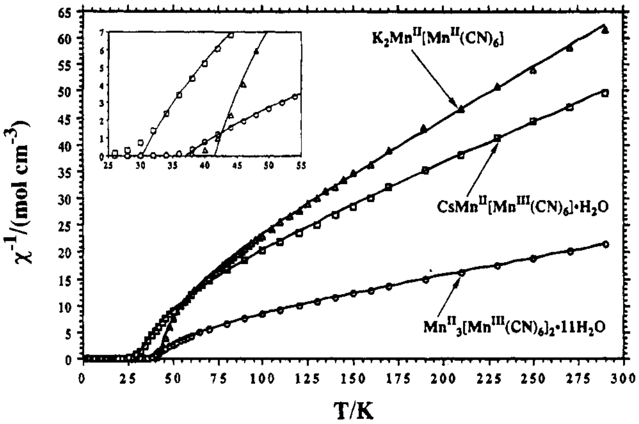

Figure 2. Least squares fit of the reciprocal susceptibility of $K_2Mn[Mn(CN)_6]$ (△), $Mn^{II}_3[Mn^{III}(CN)_6]_2\cdot 12H_2O$ (○), and $CsMn^{II}[Mn^{III}(CN)_6]\cdot {}^1/_2H_2O$ (□), to the hyperbolic equation $1/\chi_m = C^{-1}(T - \Theta) - \zeta(T - \Theta')^{-1}$. The magnetic ordering temperatures are highlighted in the inset.

magnetization at 7 T of $2.4(2) \times 10^4$ G cm³ mol⁻¹ agrees with the value of 2.23×10^4 Gauss cm³ mol⁻¹ calculated by assuming that $g = 2$ for both metal sites. The reciprocal susceptibility in the high-temperature region can be fit to a hyperbolic equation[19] based on Néel's theory (Figure 2); this fit yields a magnetic ordering temperature T_N of 41 K that agrees with the value estimated from the onset of strongly field-dependent behavior in the susceptibility measurements.

The magnetic properties of both **2** and **3** are qualitatively similar to those of **1**. The presence of antiferromagnetic interactions between adjacent spin carriers in both compounds is suggested by the appearance of shallow minima in the μ_{eff} vs T curves, by the negative Weiss constants, and by the saturation magnetization measurements[20] which indicate ferrimagnetic ground states (Table 1). From the temperatures at which the susceptibilities become strongly field dependent and from the fits of susceptibilities in the high-temperature region to Néel hyperbolas[19] (Figure 2), magnetic ordering temperatures of 37 and 31 K can be deduced for **2** and **3**, respectively.

These compounds exhibit magnetic hysteresis below their magnetic ordering temperatures. The hysteresis loops for **1** (inset of Figure 1) and **3** were determined at 24 at 4.5 K, respectively. **1** has a remnant magnetization of 4.9×10^3 G cm³ mol⁻¹ and a coercive field of ca. 370 G, while **3** has a remnant magnetization of 8.3×10^3 G cm³ mol⁻¹ and a coercive field of 1100 G. The coercive fields of both compounds are relatively large compared with those of Fe, Fe_3O_4, and CrO_2 (traditional inorganic magnetic materials), which are 1, 213, and 650 G, respectively.[1]

For **1**, the low-spin ($t_{2g}^5e_g^0$) Mn^{II} centers have only one t_{2g} magnetic orbital, while for **3** (neglecting for the moment the disorder), the low-spin ($t_{2g}^4e_g^0$) Mn^{III} centers have two t_{2g} magnetic orbitals; accordingly, there should be more antiferromagnetic contributions to the superexchange in **3**.[8,11] Because the antiferromagnetic term is generally regarded to be dominant in cyanide-bridged magnetic materials,[9,11] the magnetic ordering temperature should be higher in **3** than in **1**; this is opposite to what is observed. Presumably, the disorder in the structure of **3** (as shown by the IR spectrum) is responsible for its lower T_N. Solely on the basis of an enumeration of the antiferromagnetic contributions to the superexchange, the net exchange coupling should also be stronger in **2** than in **1**; again, this is opposite to what is observed. For **2**, the interruption of the superexchange network by the vacancies in the M′ sites probably is responsible for the lower T_N.

An alternative explanation[8] of the low Néel temperatures of **2** and **3** is that the low-spin Mn^{III} centers in these two solids back-bond less strongly into the cyanide π^* orbitals than the low-spin Mn^{II} centers in **1** and thus weaken the antiferromagnetic exchange coupling. This explanation, however, is ruled out by the observation that $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$[9] has a magnetic ordering temperature of 49 K that is *higher* than those of **1**–**3**, despite having Mn^{IV} centers that should be essentially incapable of back-bonding into the cyanide π^* orbitals. Instead, the higher Néel temperature of $Mn^{II}[Mn^{IV}(CN)_6]\cdot xH_2O$ reflects the fact that the Mn^{IV} compound has *three* t_{2g} magnetic orbitals and thus will have the best superexchange conditions. We conclude that, for these manganese-based Prussian blue analogues, the principal factors that lead to higher magnetic ordering temperatures are an ordered vacancy-free structure and a larger number of antiferromagnetic contributions to the superexchange.

Recently, Verdaguer has shown that significantly higher magnetic ordering temperatures are exhibited by certain chromium-based Prussian blue analogues.[11] We believe that, through judicious choice of the metal centers, ordering temperatures above 300 K are possible and work in this direction is underway.

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Supplementary Material Available: Figures showing the magnetization of **1** as a function of field strength and the X-ray powder diffraction pattern of **3** (2 pages). Ordering information is given on any current masthead page.

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