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[15] a) This resonance is about 384 G wide, and the peak-to-peak linewidths vary from 69 through 70, 71, and 72 to 73 ± 1 G from low to high field. b) This resonance is about 414 G wide with an average hyperfine coupling constant $|A| = 71 \pm 1$ G. The peak-to-peak linewidths are 56, 68, 73, 78, 80 ± 1 G from low to high field.

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$Mn^{II}[Mn^{II}(CN)_4]$—A Magnetic Interpenetrating Three-Dimensional Diamondlike Solid[**]

Jamie L. Manson, Wayne E. Buschmann, and Joel S. Miller*

The preparation of the first paramagnetic tetrahedral tetracyanometalate[1] enables the construction new magnetic 3-D network solids, as $[Mn^{II}(CN)_4]^{2-}$ is a building block for the preparation of four-coordinate extended network structures akin to the interpenetrating diamondlike $Zn(CN)_2$.[2] Information on the magnetic properties of this new class of materials will enable a direct comparison to the six-coordinate Prussian Blue family of ordered magnets.[3]

The reaction of equimolar amounts of $[PPN]_2[Mn^{II}(CN)_4]$ (PPN = $[Ph_3P{=}N{=}PPh_3]^+$) and $[Mn^{II}(NCMe)_6]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$ leads to the immediate precipitation of a solid of composition $Mn(CN)_2$, formulated as $Mn^{II}[Mn^{II}(CN)_4]$. This red solid exhibits an $\tilde{\nu}_{CN}$ absorption at 2170 cm^{-1}, shifted relative to the corresponding band of $[Mn^{II}(CN)_4]^{2-}$ by 32 cm^{-1} to lower energy, which suggests the lengthening of the CN bond upon coordination of its N atom to high-spin Mn^{II}. Based on the 2θ values and relative intensities, the powder pattern is assigned to the cubic $P\bar{4}3m$ space group with $a = 6.1229(5)$ Å (Figure 1).[4] This is consistent with an interpenetrating diamondlike (sphalerite) lattice (Figure 2), based on tetrahedral Mn^{II} sites with an $Mn^{II}\cdots Mn^{II}$ separation of 5.303 Å, which is 0.20 Å longer than the intermetallic distance found for $Zn(CN)_2$ and 0.23 Å longer than that in $K_2Mn^{II}[Mn^{II}(CN)_6]$.[7] Solvent is not evident from either IR or thermal gravimetric analyses. The interpenetrating structure would lead to a density twice the value of 0.775 g cm^{-3} (i.e., 1.550 g cm^{-3}) calculated for a noninterpenetrating structure; indeed, 1.68 g cm^{-3} is observed for a small sample.[8] Due to the inherent lability and coordinative unsaturation of the 13 e$^-$ $[Mn(CN)_4]^{2-}$ building block in polar organic solvents, the CN ligand can dissociate or bind to other $[Mn(CN)_4]^{2-}$ ions permitting the competitive formation of by-products such as octahedral complexes. Consequently, some variability in the energy of the $\tilde{\nu}_{CN}$ band and in the magnetic properties is observed.

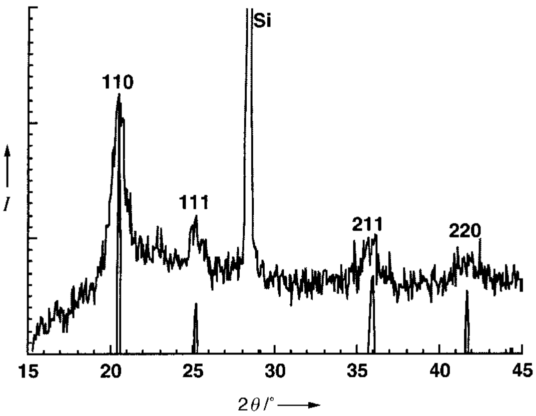

Figure 1. Observed (top) and calculated (lower) powder X-ray diffraction pattern for $Mn^{II}[Mn^{II}(CN)_4]$. The calculated pattern is for the $P\bar{4}3m$ space group with $a = 6.1229$ (5) Å. Silicon was used as an internal standard. I = intensity.

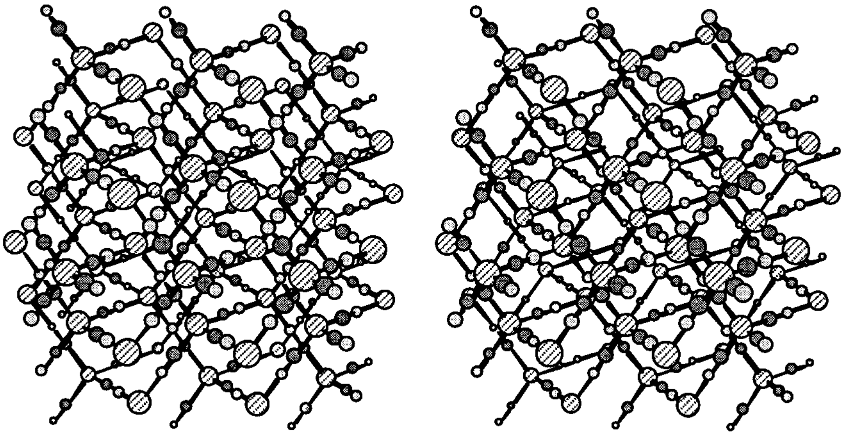

Figure 2. Stereoview of the proposed double-density interpenetrating diamondlike lattice for $Mn^{II}[Mn^{II}(CN)_4]$. The structure resembles that of sphalerite.

The room-temperature magnetic moment μ is 4.4μ_B, a value substantially lower than the predicted value (5.92μ_B) for uncoupled Mn^{II} ions with $S = 5/2$, but consistent with strong antiferromagnetic coupling. As depicted in Figure 3 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 impurities with $S = 5/2$. Mn^{II}

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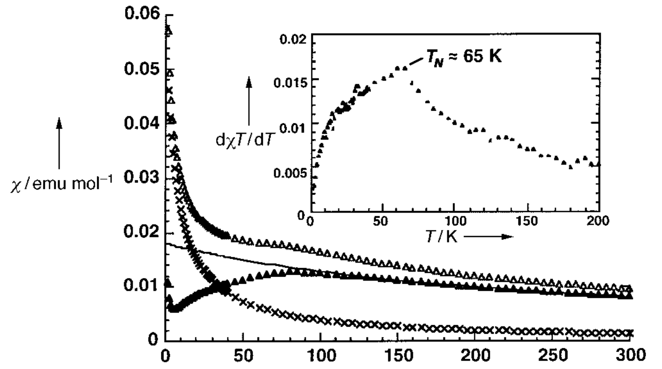

Figure 3. Uncorrected (△) and corrected (▲) molar magnetic susceptibility χ as a function of temperature T for $Mn^{II}[Mn^{II}(CN)_4]$, as well as that obtained after correction for a spin impurity (9.5%) containing Mn^{II} with $S = 5/2$ (×). The fit above 140 K to the Curie–Weiss expression is also presented (—). The inset shows the maximum at $T_N \sim 65$ K from the d$\chi T(T)$/dT (▲) data.

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[6] leads to the corrected susceptibility with a broad maximum at 80 K due to 3-D antiferromagnetic ordering (Figure 3). Above 140 K χ can be fitted by the Curie–Weiss expression, $\chi \propto (T - \theta)^{-1}$ with a strongly antiferromagnetic θ value of -240 K (Figure 4). The Neèl ordering temperature T_N is ~ 65 K, as detemined from the maximum in the dχT/dT data (Figure 3 inset). Alternating current susceptibility χ_{ac} below 75 K further substantiates antiferromagnetic ordering, as a peak in χ'' is not observed.

Although both $K_2Mn^{II}[Mn^{II}(CN)_6]$[3e] and $Mn^{II}[Mn^{II}(CN)_4]$ have $Mn^{II} \leftarrow C{\equiv}N \rightarrow Mn^{II}$ linkages (six for the former and four for the latter), the former has an uncompensated moment and is a ferrimagnet below 41 K, whereas the latter has a compensated moment and is an antiferromagnet with a higher ordering temperature. This is a consequence of the different electronic structures. Each substance has high-spin Mn^{II} ($S = 5/2$) centers bound to the N atoms. However, the six C-bound CN ligands provide a strong field and the Mn^{II} bound to them is low-spin ($S = 1/2$) and in contrast, as noted above, the tetrahedral Mn^{II} bound to C atoms of the CN ligands is high-spin ($S = 5/2$). Hence, $K_2Mn^{II}[Mn^{II}(CN)_6]$ has coupling between the high- and low-spin sites ($S = 5/2 - 1/2 = 2$) leading to an uncompensated moment, while both Mn^{II} centers have a spin $S = 5/2$ for $Mn^{II}[Mn^{II}(CN)_4]$ and lead to a compensated moment, that is, $S = 5/2 - 5/2 = 0$.

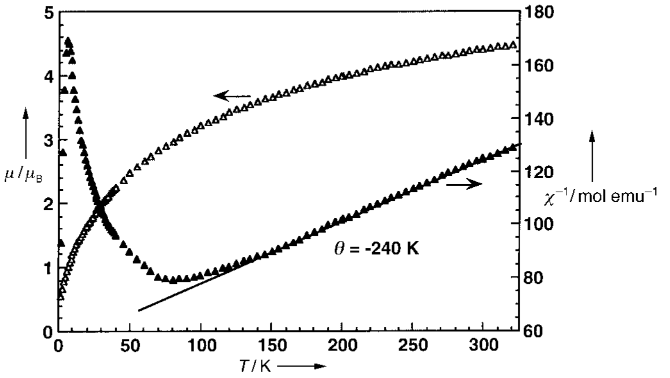

Figure 4. Corrected reciprocal molar magnetic susceptibility χ^{-1} (▲) and moment μ/μ_B (△) as a function of temperature T for $Mn^{II}[Mn^{II}(CN)_4]$. Above 140 K χ^{-1}(T) is linear and can be fitted by the Curie-Weiss expression with $\theta = -240$ K.

T_c can be estimated[3b, f] from Equation (a), where J is the nearest neighbor magnetic coupling constant, and C_{MC} and C_{MN} are the Curie constants for the C- and N-bound Mn^{II}

$$T_c \propto zJ[C_{MC}C_{MN}]^{1/2} \qquad \text{(a)}$$

centers. For systems with a Landé factor g of 2, C is proportional to $S(S+1)$, and assuming identical J values the T_c for tetrahedral $Mn^{II}[Mn^{II}(CN)_4]$ should be 2.28 times greater than the 41 K (i.e., 93.5 K), which is observed for octahedral $K_2Mn^{II}[Mn^{II}(CN)_6]$. Since only 1.58 times the 41 K is observed, J for $Mn^{II}[Mn^{II}(CN)_4]$ must be smaller. This is consistent with the substantially longer Mn^{II}–C bond (by about 0.20 Å), which reduces J. An independent estimation of J requires a model for a 3-D diamond-type Heisenberg system with $S = 5/2$, which at present does not exist.

In contrast to $Mn^{II}[Mn^{II}(CN)_4]$, $M'[Mn^{II}(CN)_4]$ ($M \neq Mn$) should have uncompensated moments and order ferrimagnetically. Studies on these materials are in progress.

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[4] Based upon the corrected (with respect to Si internal standard) *d*-spacings, a crude lattice parameter was calulated and peak indices using $Zn(CN)_2$ as a structural model.[2] Using LATPARM and assuming cubic symmetry the reflection indices along with *d*-spacings were refined. The refinement converged after only four cycles and generated a new lattice parameter with the standard deviation. The space group $P\bar{4}3m$ assumes an ordered arrangement of cyano ligands that is MnC_4 and $Mn\text{-}N_4$, which in reality may not be reasonable. Based on a random orientation of the cyano ligands, that is, $ZnCN_3$, ZnC_2N_2, ZnC_3N, ZnC_4, and ZnN_4, a lower symmetry space group, $Pn\bar{3}m$, has been proposed.[5] Altering the space group merely changes (slightly) the calculated peak intensities. A calculated X-ray diffraction pattern was generated with CRYSTALDIFFRACT[6] on using the refined lattice parameter and atomic positions of the isostructural $Zn(CN)_2$ compound. Therefore the calculated and experimental diffraction patterns are in excellent agreement.

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[7] The $Mn^{II} \cdots Mn^{II}$ separation is determined from the positions of the Mn centers (Mn Wyckoff positions: 1a Mn(1) 0,0,0; 3d Mn(2) 0,0,½ as follows: $3^{1/2}a/2$.

[8] The density of the material was determined by utilizing a CH_2I_2/CH_2Cl_2 mixture and weighing a 1.00 mL volume.

[9] The impurity (9.5%) is not a simple paramagnet, but possesses some antiferromagnetic coupling ($\theta = -9$ K). This coupling suggests nearest neighbor interactions among adjacent Mn^{II} sites.