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Spontaneous Magnetization in the M[N(CN)$_2$]$_2$ (M = Cr, Mn) Weak Ferromagnets

Jamie L. Manson,[†] Carmen R. Kmety,[‡] Arthur J. Epstein,[‡] and Joel S. Miller*,[†]

Department of Chemistry, University of Utah, 315 S. 1400 E. RM Dock, Salt Lake City, Utah 84112-0850, and Department of Physics and Department of Chemistry, The Ohio State University, Columbus, Ohio 43210-1106

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The occurrence of a spontaneous magnetization in a material is a characteristic typified by ferromagnets and is very important for several commercial applications. Spontaneous magnetizations can also arise as a result of the incomplete cancellation of spins, e.g., a net magnetic moment due to spin canting.[1] Even in antiferromagnets, a spontaneous moment may occur via spin canting which gives rise to weak ferromagnetic behavior. More complex behavior such as spin reorientation or a transition from one magnetically ordered state to another can also occur.

Due to stabilization of relatively strong magnetic coupling, multidimensional coordination polymers consisting of transition metal cations and the dicyanamide ligand, [N(CN)$_2$]$^-$, are currently being studied.[2−4] Homoleptic dicyanamide complexes with octahedral metal sites form 3-D rutile-type architectures (Figure 1). M[N(CN)$_2$]$_2$ (M = Co, Ni) exhibit ferromagnetic ordering[2] at 9 and 21 K, respectively, and have been further characterized by neutron diffraction[4a] and specific heat[4b] measurements. In contrast, interpenetrating M[C(CN)$_3$]$_2$ (M = Mn, Fe, Co, Ni, Cu) also have rutile-type networks, but exhibit weak antiferromagnetic coupling while M = V and Cr are strongly antiferromagnetically coupled and exhibit spin frustration.[5] Differences in the magnetic behavior lies in the shorter three-atom spin coupling pathway available for μ_3-[N(CN)$_2$]$^-$, while μ_3-[C(CN)$_3$]$^-$ only provides five-atom pathways.

Herein, we report the magnetic ordering with a relatively high T_c for the weak ferromagnets M[N(CN)$_2$]$_2$ (M = Cr, **1**; Mn, **2**). Because Cr^{II} is oxygen-sensitive, **1** was prepared in an inert atmosphere glovebox. Sky blue and colorless microcrystalline powders of **1** and **2**, respectively, are obtained by reactions of [Cr(NCMe)$_4$][BF$_4$]$_2$, and MnCl$_2$ with Na[N(CN)$_2$] in a 1:2 stoichiometry in aqueous solutions. Isostructural rutile-type frameworks have been confirmed by powder X-ray diffraction[6] and infrared spectroscopy with structurally characterized M[N(CN)$_2$]$_2$ (M = Co, Ni).[2] High-spin, octahedral Cr^{II} ion in **1** is expected to undergo a significant Jahn−Teller distortion, a characteristic of the ^5E_g ground state while the $^6A_{1g}$ ground state of **2** is expected to afford a structure only weakly distorted from octahedral coordination geometry. The observation of several $\nu_{C\equiv N}$ modes, i.e., **1**, 2197 s, 2263 s, 2322 m, 2356 m, 2408 w cm^{-1}; **2**, 2194 s, 2261 s, 2293 s, 2322 m sh, 2350 w, 2386 w cm^{-1}, is a common characteristic of many well studied dicyanamide-metal complexes, regardless of the coordination environment about the metal. Bands above approximately 2250 cm^{-1} are assigned to $(\nu_{as} + \nu_s)_{C\equiv N}$ combination modes while lower energy absorptions (<2250 cm^{-1}) are associated with individual $(\nu_{as})_{C\equiv N}$ and $(\nu_s)_{C\equiv N}$ modes.[2a,3,7]

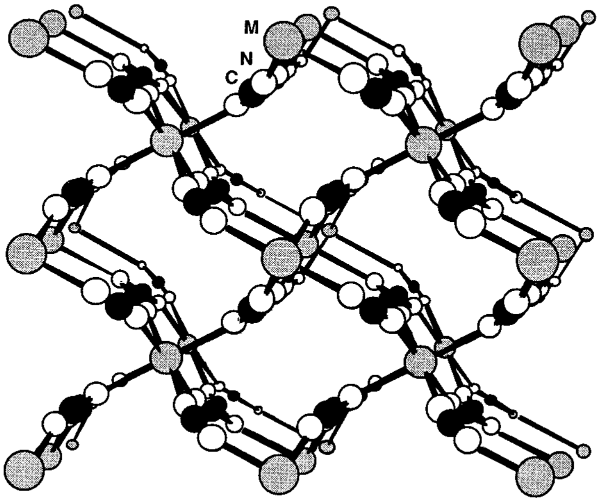

Figure 1. Noninterpenetrating rutile-type structure typical of octahedral M^{II}[N(CN)$_2$]$_2$.

The 2−300 K temperature dependencies of the magnetic susceptibility of **1** and **2** were fit by the Curie−Weiss expression, $\chi \propto (T - \theta)^{-1}$, with Landé g values of 2.39 and 2.00 and θ values of −154 and −16 K for $T > 50$ K, respectively, indicative of moderate to very strong antiferromagnetic coupling between metal sites, Figure 3. The 2.39 g value is in the range of values reported for Cr^{II}[C(CN)$_3$]$_2$[5b] and [H$_3$N(CH$_2$Ph)]$_2$CrCl$_4$.[8] The room-temperature effective moments, μ_{eff} [$\equiv(8\chi T)^{1/2}$], of **1** and **2** are 4.79, and 5.79 μ_B, respectively. These values are reduced from their

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[†] University of Utah.

[‡] The Ohio State University.

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(6) The room-temperature unit cell parameters obtained from the LATPARM fitting of the powder X-ray diffraction patterns are: M = Mn: a = 6.124(6) Å, b = 7.308(6) Å, c = 7.535 (8) Å, V = 337.2 Å^3; M = Cr: a = 5.922(2) Å, b = 7.478(3) Å, c = 7.564 (3) Å, V = 334.9 Å^3. These are isomorphous to that obtained for M = Co [a = 6.0109(3) Å, b = 7.0724(4) Å, c = 7.3936(4) Å, V = 314.32(3) Å^3],[2a] and M = Ni [a = 5.97357(25) Å, b = 7.03196(28) Å, c = 7.29424(22) Å, V = 306.40(3) Å^3].[2a]

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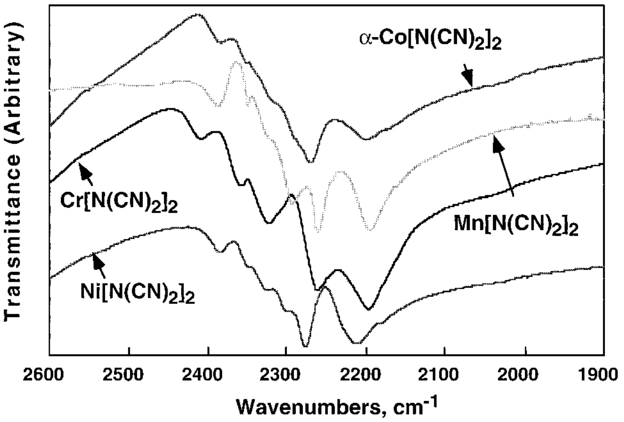

Figure 2. Infrared spectra of octahedral $M[N(CN)_2]_2$ (M = Cr, Mn, Co, Ni) in the ν_{CN} region.

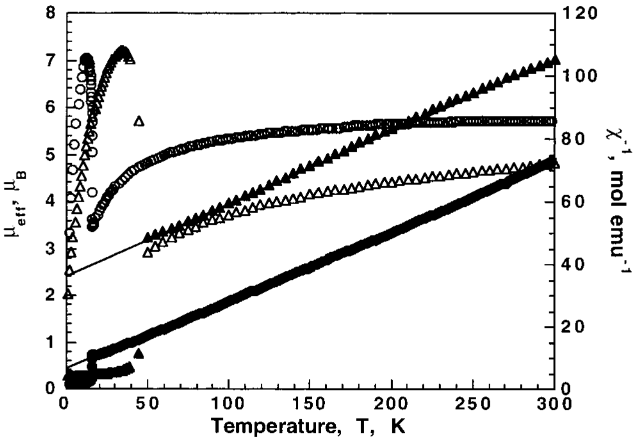

Figure 3. Temperature dependence of the effective moment (○, △) and reciprocal molar magnetic susceptibility (●, ▲) of **1** and **2**, respectively. Fits to the Curie−Weiss expression are denoted as heavy lines.

respective values of 5.64 and 5.92 μ_B for uncoupled $S = 2$ and $S = {}^{5}/_{2}$ ions due to antiferromagnetic coupling, i.e., the large negative θ values, assuming g values of 2.39 and 2.00 for **1** and **2**, respectively. Below 300 K, the moments of **1** and **2** decrease gradually, reaching minima below 50 and 16 K[13] (Figure 3), respectively, attributed to long-range magnetic ordering. This is also confirmed by zero-field-cooled and field-cooled magnetization (Figure 4) and ac susceptibility measurements above and below the transition temperature. Below the minima, a rapid increase in the effective moment occurs due to an increase of the ferromagnetic component of the weak ferromagnetic state. Maxima are observed at 35 (**1**) and 12 K (**2**) which are followed by swiftly decreasing moments until the lowest temperature of 2 K is reached due to saturation effects and/or increasing antiferromagnetic correlations. In the presence of small-applied dc magnetic fields, a spontaneous magnetization occurs in **1** and **2**.

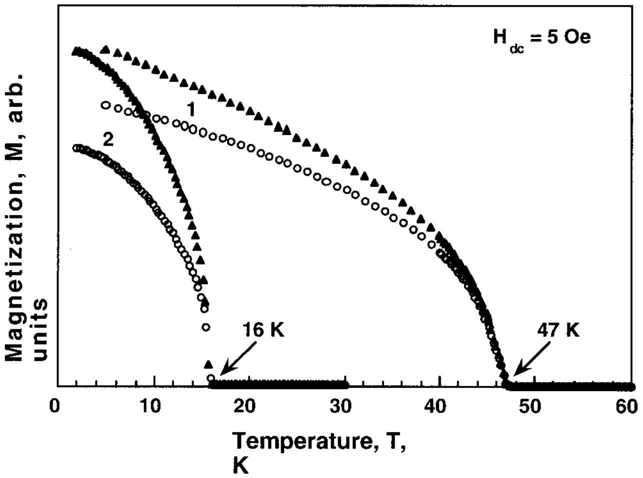

Figure 4. Temperature dependence of the zero-field-cooled (▲) and field-cooled (○) magnetization of **1** and **2**. Data were taken in a 5 Oe dc magnetic field upon warming.

Low saturation magnetization values consistent with weak ferromagnetic behavior are observed for **1** and **2**. The 2 K field-dependence of the magnetization, M(H), for **2** maintains a nearly constant slope to 5.5 T reaching a value of 5400 emuOe/mol, well below 27 925 emuOe/mol expected for an $S = {}^{5}/_{2}$ system and significantly larger than the zero value expected for an antiferromagnetic ground state. This behavior is in contrast to **1** that shows an initial sharp rise in the magnetization to approximately 300 emuOe/mol at 3500 Oe and then becomes linear to 5 T reaching a substantially reduced value of 1000 emuOe/mol. A transition to a weak ferromagnetic state could account for the observed magnetic behavior. Hysteresis with remanant magnetizations, M_r, of 220 and 63 emuOe/mol and coercive fields, H_{cr}, of 300 and 750 Oe are observed for **1** and **2**, respectively. A more detailed account including results of neutron diffraction is the subject of another paper.

Weak ferromagnetism arises when the spins are not perfectly aligned and leads to a net magnetic moment.[1] This can result from (a) single-ion anisotropy and/or (b) antisymmetric exchange. For **2**, the g value of 2.00 suggests isotropic behavior as is typical for Mn^{II} while that of **1** suggests significant anisotropy as expected for Cr^{II} ions, respectively. Hence, for **1** and **2**, the spin canting is a likely consequence of anisotropy due to crystal field effects. Small, but sufficient anisotropy is attributed to the stabilization of weak ferromagnetism ($T_c = 35.5$ K) for formally isotropic $g = 2.00$ β-4-NCC_6F_4CNSSN.[9]

Weak ferromagnets are uncommon. Typical examples include $S = {}^{5}/_{2}$ ions (Mn^{II}, Fe^{III}), e.g., NH_4MnF_3 ($T_c = 75.1$ K),[10] $Rb_2FeCl_5{\cdot}H_2O$ ($T_c = 14.06$ K),[11] and $Mn^{II}(O_3PC_{18}H_{37}){\cdot}H_2O$ ($T_c = 13.5$ K),[12a] while $Cr^{II}(O_3PMe){\cdot}H_2O$ ($\theta = -226$ K; $T_c = 35.8$ K)[12b] is the only previously reported example of a weak ferromagnet containing high-spin Cr^{II}. In all cases zero-field and field-cooled magnetization measurements were performed to confirm the presence of a spontaneous moment and establish T_c.

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