Tuning of Superexchange Couplings in a Molecule-Based Ferroferrimagnet: (Ni$^{II}_x$Mn$^{II}_{1-x}$)$_{1.5}$[Cr^{III}(CN)$_6$]

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In the last few years, there has been considerable interest in the preparation of molecular magnets with high Curie temperature (T_c).[1−3] One of the advantages of molecular and metal complex-based magnets is that novel functions, for example, control of the magnetic properties via external stimuli, can be incorporated through proper design of the electronic properties. We recently reported the first examples of T_c control, via electrochemical[4] and optical stimuli,[5] using Prussian blue analogs. Another advantage of molecular or molecule-based magnets compared to conventional ones is that the magnet can be obtained through a selection of proper spin sources (e.g., transition metal ions, organic radicals) and associated structures such as coordinating ligands by chemical synthetic methods at room temperature. In this work, we have succeeded in controlling magnetic properties such as the saturation magnetization (I_s), the Weiss temperature (Θ) and the coercive field (H_c) and the direction of magnetic pole versus external magnetic field, using compounds in the series (Ni$^{II}_x$Mn$^{II}_{1-x}$)$_{1.5}$[Cr^{III}(CN)$_6$], by the strategy of choosing both ferromagnetic ($J > 0$) and antiferromagnetic ($J < 0$) exchange interactions by using the appropriate molar ratios of the transition metal ions. This type of magnetic behavior can be modeled using molecular field theory[6] with three sublattice (Ni, Mn, Cr) sites.

We have focused on Prussian blue analogs for this attempt, because high T_c values can be obtained,[4,5,7−9] various types of metal ions can be incorporated as spin centers,[10] and their fcc structure facilitates the understanding of the superexchange interactions between the metal ions.[8,9,11,12] Depending on the types of metal ions that are used, these materials can be either ferromagnets or ferrimagnets. For example, Ni$^{II}_{1.5}$[Cr^{III}(CN)$_6$]·8H$_2$O is a ferromagnet, and Mn$^{II}_{1.5}$[Cr^{III}(CN)$_6$]·7.5H$_2$O is a ferrimagnet.[13] First, let us consider the saturation magnetization for a given formula. Respectively, the I_s values of these two compounds are expected to be 6 μ_B (due to parallel alignment of the spins, $S_{Ni} = 1$ and $S_{Cr} = 3/2$) and 4.5 μ_B (due to antiparallel alignment of the spins, $S_{Mn} = 5/2$ and $S_{Cr} = 3/2$). When powders of the two compounds are physically mixed, the total I_s will

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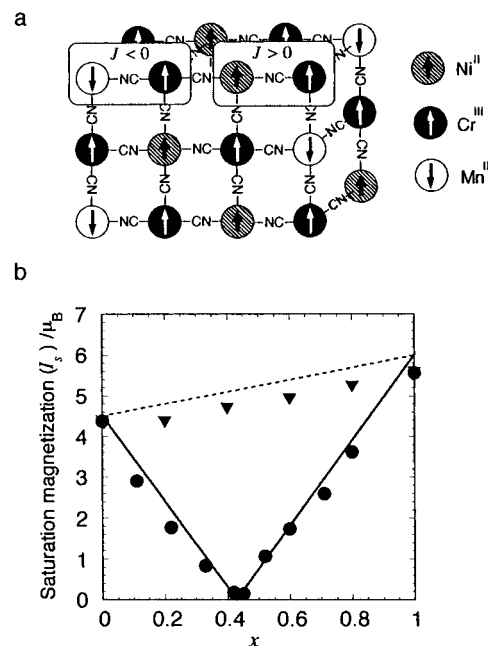

Figure 1. (a) Schematic diagram illustrating mixed ferroferrimagnetism with both ferromagnetic ($J > 0$) and antiferromagnetic ($J < 0$) interactions. Cr^{III} and either Ni^{II} or Mn^{II}, which are randomly incorporated in the lattice, are linked in an alternating fashion. (b) Calculated and experimentally observed saturation magnetizations as a function of mixing ratio x. Atomic-level mixture ((Ni$^{II}_x$Mn$^{II}_{1-x}$)$_{1.5}$[Cr^{III}(CN)$_6$]·zH$_2$O): theory (—), observed (●). Macroscopic physical mixture (xNi$^{II}_{1.5}$[Cr^{III}(CN)$_6$] + (1−x)Mn$^{II}_{1.5}$[Cr^{III}(CN)$_6$]): calculated (- - -); observed (▼).

vary between 4.5 and 6 μ_B, depending on the mixing ratio, as shown in Figure 1b (dashed line). However, when the two compounds are mixed at an atomic level, parallel spins (Cr^{III} and Ni^{II}) and antiparallel spins (Mn^{II}) can partially or even completely cancel, depending on the mixing ratio, because Cr^{III} and either Ni^{II} or Mn^{II} are linked in an alternating fashion (Figure 1a). In this manner, materials with I_s values anywhere in the range 0−6 μ_B may be prepared. Assuming $g = 2$ for Cr^{III}, Ni^{II}, and Mn^{II}, for the members of the series (Ni$^{II}_x$Mn$^{II}_{1-x}$)$_{1.5}$-[Cr^{III}(CN)$_6$], I_s is given by eq 1. The calculated dependence of

$$I_s = 2\mu_B |^3/_2 + 1.5(x - {}^5/_2(1 - x))| \tag{1}$$

I_s on x is shown in Figure 1b (solid line). As shown, I_s is predicted to vanish for $x = 3/7$ (0.428), and such a material should exhibit antiferromagnetic properties. Moreover, spin glass behavior does not occur in this series because the directions of each spin are consistent with the sign of J of nearest-neighbor spin sites. On the basis of this theoretical prediction, we synthesized members of this series and measured their magnetic properties.

These compounds were prepared by reacting mixtures of NiCl$_2$ and MnCl$_2$ aqueous solutions (with a given mole ratio x_{mix}, ranging from zero to unity, of Ni^{2+} vs the total of Ni^{2+} and Mn^{2+}) with K$_3$Cr(CN)$_6$ aqueous solution to yield green precipitates. It is important to note that the carbon ends of the cyano groups are always bonded to Cr^{III}, and the nitrogen ends

Table 1. Atomic Fraction, Lattice Constants, and Magnetic Properties of $(Ni^{II}_xMn^{II}_{1-x})_{1.5}Cr^{III}(CN)_6 \cdot zH_2O$

feed (x_{mix})	obsd (x)	a/Å	I_s/μ_B	T_c/K	Θ/K	H_c/G
0	0.00	10.787	4.38 (4.42)[a]	67 (66)[a]	−54 (−51)[a]	6 (15)[a]
0.1	0.11	10.724	2.90	67	−45	50
0.3	0.32	10.667	0.84	63	−34	340
0.4	0.42	10.642	0.18	68	−15	680
0.5	0.52	10.583	1.06	68	1	370
0.7	0.72	10.548	2.59	69	42	140
1	1.00	10.467	5.57 (5.44)[a]	72 (53)[a]	88 (75)[a]	120 (220)[a]

[a] Reference 13.

are always bonded to either Ni^{II} or Mn^{II}. Elemental analyses showed that the x values in the resulting precipitates were in good agreement with the x_{mix} values used in the syntheses and that the amounts of the other elements (Cr, C, N, and H) were essentially constant.[14] The water content (z) varied between 7.5 and 8, depending on the humidity and temperature. The X-ray powder diffraction patterns for each member of the series were consistent with fcc structure, with the lattice constant decreasing from 10.787 to 10.467 Å with increasing x (Table 1). These results indicate that the materials were not macroscopic mixtures of $Ni^{II}_{1.5}[Cr^{III}(CN)_6]$ and $Mn^{II}_{1.5}[Cr^{III}(CN)_6]$ but were ternary metal complexes in which Mn^{II} and Ni^{II} were randomly incorporated in the lattice, corresponding to the mixing ratio of $NiCl_2$ and $MnCl_2$.

The I_s values of $Ni^{II}_{1.5}[Cr^{III}(CN)_6]$ and $Mn^{II}_{1.5}[Cr^{III}(CN)_6]$ were found to be 5.57 and 4.38 μ_B for a given formula, respectively. When powders of the two compounds are physically mixed, the total I_s varied between 4.38 and 5.57 μ_B, depending on the mixing ratio, as shown in Figure 1b (triangles). On the other hand, when the two compounds are mixed at an atomic level, those for the intermediate compositions were found to vary in a systematic fashion as a function of x (Figure 1b, filled circles). Minimum values were found for x values close to $^3/_7$ (0.42 and 0.45); the molar I_s values were very close to zero, just at the point where parallel spins (Cr^{III} and Ni^{II}) and antiparallel spins (Mn^{II}) should completely cancel out. Thus the molar I_s dependence on x was found to follow eq 1 quite well. Other magnetic properties were also examined for this series (Table 1). The H_c values were found to be at a maximum for x close to $^3/_7$. On the other hand, the T_c values remained constant ($\sim$70 K). The Θ values increased monotonically from negative to positive with increasing x, indicating that the predominant interaction mode was shifting from antiferromagnetic to ferromagnetic.

One of the most interesting aspects of the magnetic behavior of this series of compounds was the temperature dependence of the magnetization. The magnetization vs temperature curves at 1000 G exhibited various types of behavior depending on x, i.e., the curves for $x = 0$ and $x = 1$ exhibited monotonic increases in magnetization with decreasing T, while the curve for $x = 0.45$ exhibited a single maximum and that for $x = 0.38$ exhibited two maxima. For example, the magnetization values for $x = 0.38$, obtained at a magnetic field larger than H_c, at various temperatures are shown in Figure 2a. These types of curves resemble those of theoretically curves predicted by Néel in 1948,[6] specifically, type R ($x = 0$), type N ($x = 0.38$), type P ($x = 0.45$), and Type Q ($x = 1$). We analyzed these temperature dependences using molecular field theory, considering only two types of superexchange couplings between nearest neighbor sites, one for Ni−Cr and the other for Mn−Cr, accord-
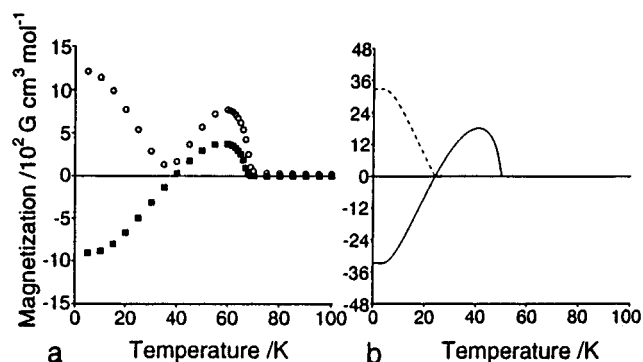
(14) Anal. Calcd for $Mn_{1.5}[Cr(CN)_6] \cdot 7.5H_2O$: Mn, 19.36; Cr, 12.22; C, 16.93; N, 19.75; H_2O, 31.74. Found: Mn, 19.13; Cr, 12.53; C, 16.68; N, 19.42; H_2O, 30.57. Calcd for $(Ni_{0.38}Mn_{0.62})_{1.5}[Cr(CN)_6] \cdot 7.5H_2O$: Ni, 7.82; Mn, 11.94; Cr, 12.16; C, 16.85; N, 19.65. Found: Ni, 7.78; Mn, 11.63; Cr, 12.52; C, 17.28; N, 19.68. $Ni_{1.5}[Cr(CN)_6] \cdot 8H_2O$: Ni, 20.00; Cr, 11.81; C, 16.37; N, 19.09; H_2O, 32.74. Found: Ni, 19.46; Cr, 11.54; C, 16.36; N, 18.60; H_2O, 32.96.

Figure 2. Magnetization vs temperature curves for $(Ni^{II}_{0.38}Mn^{II}_{0.62})_{1.5}$-$[Cr^{III}(CN)_6] \cdot zH_2O$: (a) experimental data obtained at 1000 G ($\bigcirc$) (external magnetic field larger than H_c) and those at 10 G ($\blacksquare$)(smaller than H_c); and (b) calculated temperature dependences of magnetization M_{total} (—) and $|M_{total}|$ (- - -) based on molecular field theory with three sublattice sites (Ni, Mn, Cr), with J coefficients $J_{NiCr} = 5.6$ cm^{-1} and $J_{MnCr} = -2.5$ cm^{-1}.

ing to the model shown in Figure 1a. Those between second nearest-neighbor sites (Mn−Ni and Cr−Cr) were neglected. The molecular fields H_{Ni}, H_{Mn}, and H_{Cr} acting on the three sublattice sites in $(Ni^{II}_xMn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]$ can be expressed as follows:

$$H_{Mn} = H_0 + n_{MnCr}M_{Cr} \qquad (2)$$

$$H_{Ni} = H_0 + n_{NiCr}M_{Cr} \qquad (3)$$

$$H_{Cr} = H_0 + n_{MnCr}M_{Mn} + n_{NiCr}M_{Ni} \qquad (4)$$

H_0 is the external magnetic field, the various n_{ij} are the molecular field coefficients relating to the exchange coefficients (J_{ij}), and M_{Ni}, M_{Mn}, and M_{Cr} are sublattice magnetizations per unit volume for the Ni, Mn and Cr sites, respectively. The total magnetization ($M_{total} = -M_{Mn} + M_{Ni} + M_{Cr}$) as a function of temperature can be evaluated using a Brillouin function. A J_{NiCr} value of 5.6 cm^{-1} and a J_{MnCr} value of -2.5 cm^{-1} were obtained from the experimental critical temperatures of $Ni^{II}_{1.5}[Cr^{III}(CN)_6] \cdot 8H_2O$ ($T_c = 72$ K) and $Mn^{II}_{1.5}[Cr^{III}(CN)_6] \cdot 7.5H_2O$ ($T_c = 67$ K), respectively. Using only these J values and the mixing ratio x, the temperature dependences were calculated for several different compositions. The calculated curves reproduced the experimental curves qualitatively.[15] For example, the solid line in Figure 2b is the calculated total magnetization (M_{total}) at $x = 0.38$, which exhibits negative values of magnetization at lower temperature and positive values at higher temperature, indicating that the magnetic pole can be inverted when the external magnetic field is below H_c. In fact the magnetization of this compound showed a negative value when the external magnetic field was 10 G (Figure 2a). This phenomenon is observed because the negative magnetization due to the Mn^{II} sublattice and the positive magnetizations due to the Ni^{II} and Cr^{III} sublattices have different temperature dependences.

We have shown that various types of magnets can be designed by tuning between ferromagnetic and antiferromagnetic exchange interactions. Their magnetic properties can be controlled over a wide range and rationalized with molecular field theory using three sublattices.

(15) For x close to 0 and 1, the calculated curves of $|M_{total}|$ reproduce the experimental curves at 1000 G to a good approximation in both magnetization and T_c. However, the magnitude of magnetization of experimental temperature curve for $x = 0.38$ is smaller than that of the calculated curve. One of the reasons of this is the magnetization cannot be saturated at 1000 G because the coercive field for $x = 0.38$ are larger than those for $x = 0$ and 1 (see Table 1). The difference between the calculated T_c and the observed one may be due to the superexchange interaction between second nearest neighbor sites (Mn−Ni and Cr−Cr).
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