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A Prussian-Blue Type Ferrimagnet Na[MnCr(CN)$_6$]: Single Crystal Structure and Magnetic Properties

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A novel Prussian-blue type ferrimagnet Na[MnCr(CN)$_6$] has been prepared and characterized by single crystal X-ray analysis and magnetic measurements. The complex has a face-centered cubic lattice and shows ferrimagnetic ordering below 60 K.

In the pursuit of new molecule-based magnets, cyanide-bridged complexes are good candidates and have been extensively investigated.[1] A number of cyanide-bridged complexes with different dimensionalities have been synthesized and structurally and magnetically characterized.[2] Cyanide-bridged complexes in the Prussian blue family of general composition $C_mM_x[M'(CN)_6]_y \cdot nH_2O$ are especially attractive and promising. Nearly all members of this family show spontaneous magnetization, and some exhibit long-range magnetic ordering with T_c above room temperature, such as $V[Cr(CN)_6]_{0.86} \cdot 2.8H_2O$ (T_c = 315 K), $K_{0.058}V[Cr(CN)_6]_{0.79} \cdot (SO_4)_{0.058} \cdot 0.93H_2O$ (T_c = 372 K), and $KV[Cr(CN)_6] \cdot 2H_2O$ (T_c = 376 K).[1c,3] It is generally thought that complexes in the Prussian blue family have a face-centered cubic structure, but this is based on the analysis of powder diffraction methods and the statistical distribution of metal ions in the cubic lattice. In fact, detailed structural studies for the Prussian blue family are limited, and the origin of the high T_c remains unclear.[4] A technique for the synthesis of high quality single crystals of the Prussian blue family, which is important for a detailed study of magneto-structural relationships, has not yet been developed.[5] Herein, we report the synthesis, crystal structure, and magnetic properties of a novel three-dimensional Prussian blue analogue Na[MnCr(CN)$_6$] (**1**). The complex has a face-centered cubic lattice and shows a ferrimagnetic ordering below 60 K. To our knowledge, this is the first time that a $C_mM_x[M'(CN)_6]_y \cdot nH_2O$ Prussian blue analogue with a strictly face-centered cubic lattice structure has been characterized by single crystal X-ray analysis.

Light yellow-green crystals were obtained by slow diffusion of $K_3[Cr(CN)_6]$ dissolved in H_2O into $Mn(ClO_4)_2 \cdot 6H_2O$ and $NaClO_4 \cdot 6H_2O$ dissolved in a mixed solvent of $H_2O-CH_3CHOHCH_3$ (5:1). X-ray crystallography shows that **1** belongs to the cubic space group $Fm\bar{3}m$, $a = b = c =$

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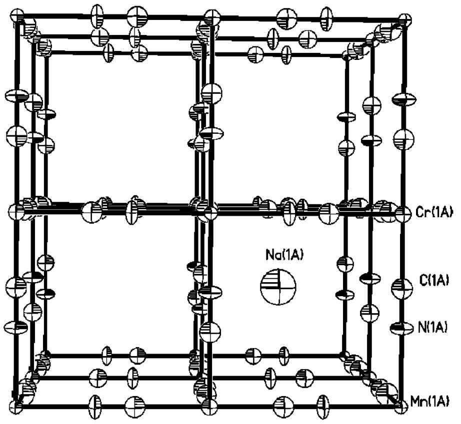

Figure 1. ORTEP of the cubic network of **1** (thermal ellipsoids set at the 30% probability level).

10.8159(12) Å, α = 90°, $V = 1265.3(2)$ Å^3, $Z = 4$, and $\rho = 1.502$ g·cm^{-3}.[6] Figure 1 shows an ORTEP of the cubic network of **1**. Each unit cell contains four Na[MnCr(CN)$_6$] molecules. Each [Cr(CN)$_6$]$^{3-}$ connects to six Mn atoms through CN$^-$ bridges, and each Mn atom connects to the six nitrogen atoms of the six cyanide bridges. A face-centered cubic framework forms from the Cr←C≡N→Mn linkages. Both Mn and Cr atoms are six-coordinated with octahedral geometry. The shortest Cr···Cr and Mn···Mn distances are both 7.648 Å, and the shortest Mn···Cr distance is 5.408 Å. The bond lengths are Cr−C = 2.088(11) Å, Mn−N = 2.207(9) Å, and C−N = 1.113(9) Å. The bond distances of Cr−C and Mn−N are consistent with those reported by H. U. Gudel and D. Bable etc.[4b−d] The bond angles are *cis* N−Mn−N = 90.0°, *cis* C−Cr−C = 90.0°, *trans* N−Mn−N = 180.0°, and *trans* C−Cr−C = 180.0°. Na atoms occupy the vacancies in the unit cell. The vacancy volume of the unit cell is 497.6 Å^3, which occupies 33.3% of the volume of the unit cell. Na atoms occupy 0.69% of the vacancy volume. The distances between Na and the adjacent Cr and Mn atoms are equal (Na···Cr = Na···Mn = 4.683 Å). The Na···Na distance is 5.408 Å.

The magnetic measurements of **1** on single crystals were carried out in an applied field of 1 T using a SQUID magnetometer in the temperature range 2−300 K. Figure 2 shows the temperature dependence of the magnetic susceptibility. The $\chi_M T$ value is 6.09 cm^3 K mol^{-1} (6.98 μ_B) at 300 K and decreases with decreasing temperature to a minimum value of 5.19 cm^3 K mol^{-1} (6.44 μ_B) at 126 K (a mole of **1** is a mole of the asymmetric unit Na[MnCr(CN)$_6$]). Upon further cooling, the $\chi_M T$ increases to a maximum value of 56.90 cm^3 K mol^{-1} (21.33 μ_B) at 43 K and then decreases below this temperature. The χ_M^{-1} versus T plot in the range from 300 to 126 K obeys the Curie−Weiss law ($\chi = C/(T - \theta)$) with a Weiss constant θ of −46.65 K (Figure 2, insert). The negative Weiss constant indicates an intramolecular antiferromagnetic interaction between adjacent Cr(III) and Mn(II) ions through the cyanide bridge. The abrupt increase of the $\chi_M T$ around 66 K suggests the onset of three-dimensional magnetic ordering. The decrease of the $\chi_M T$ below 43 K results from a saturation of the χ_M value.

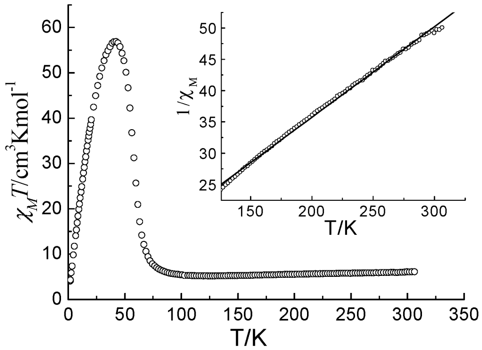

Figure 2. Temperature dependence of $\chi_M T$ for **1** in the magnetic field of 1 T. Insert: plot of χ_M^{-1} versus T in the range from 300 to 126 K.

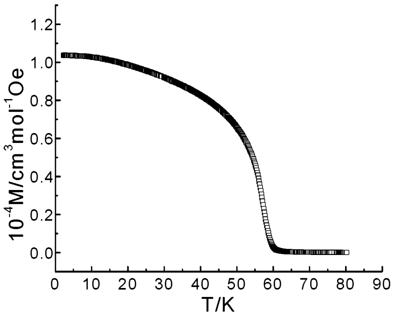

Figure 3. Thermal dependence of the field-cooled magnetization (FCM).

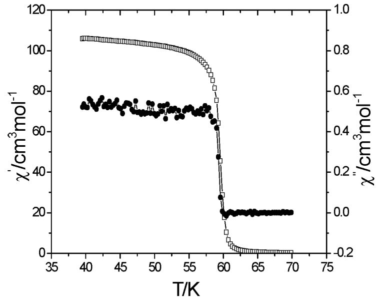

Figure 4. Frequency dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibility at 199 Hz of **1**.

The field-cooled magnetization (FCM) measurement on the sample at 200 Oe shows a sharp increase in the magnetization at 60 K, which also indicates the occurrence of spontaneous magnetization (Figure 3). Alternating current susceptibility measurements in a 199 Hz magnetic field were performed with a zero applied dc field. The observed in-phase, χ', and out-of-phase, χ'', ac responses are plotted in Figure 4. The presence of both χ' and χ'' also indicates the three−dimensional magnetic ordering of **1**. The sharp increases of the magnetization values of χ' at 60 K and χ'' at 59 K confirm the T_c value of 60 K.

The field dependence of the magnetization, M, measured on the sample at 2.0 K shows a sharp increase and rapid

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(6) (a) Characterization of **1**: IR: νCN 2156 cm^{-1}. $\mu_{eff} = 5.95$ μB at 300 K. (b) Crystal data for **1**: C$_6$CrMnN$_6$Na, MW = 286.05, T = 293 K, cubic, space group $Fm\bar{3}m$, $a = b = c = 10.8159(12)$ Å, α = 90°, $V = 1265.3(2)$ Å^3, $Z = 4$, $\rho = 1.502$ g·cm^{-3}, μ(Mo Kα) = 1.866 mm^{-1}, $F(000) = 552$, and GOF =1.360. A total of 1691 reflections were collected, and 87 reflections were unique ($R_{int} = 0.0272$). The final R1 and wR2 are 0.0520 and 0.1379, respectively, for 11 parameters and 87 reflections ($I > 2\sigma(I)$). The data were collected on a Bruker SMART CCD area detector with Mo Kα radiation (λ = 0.71073) at 293 K. The structures were solved by direction method and refined by a full-matrix least-squares technique based on F^2 using SHELXL 97 program.

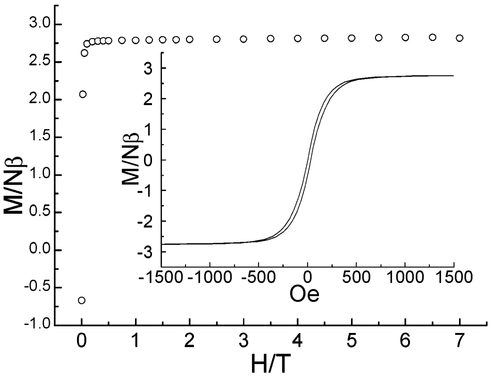

Figure 5. Field dependence of magnetization $M/N\beta$ at 2 K. Insert: hysteresis loop ($M/N\beta$ versus H) at 2 K.

saturation with applied field (0−7 T) (Figure 5). The magnetization $M_s = 2.79\ \mu_B$ is much higher than the expected value of 2.00 μ_B that would result from antiferromagnetic coupling between adjacent Mn(II) and Cr(III) ions. The reason for the much higher M_s is unclear. A higher M_s value was also observed for the homologue $K_{0.058}V[Cr(CN)_6]_{0.79}\cdot(SO_4)_{0.058}\cdot 0.93H_2O$ and was attributed to disorder of the paramagnetic ions.[3a] In other cases this magnetic behavior has been attributed to Zeeman interactions.[7] However, for the present complex, there is insufficient evidence to support either explanation. For example, if this is due to Zeeman interactions because of a small magnetic exchange integral (J), why does the M_s value of **1** saturate so quickly? It also seems unreasonable to explain the higher saturation magnetization of **1** using the disorder of the paramagnetic ions because of the 3D cubic structure of **1**. The origin for this magnetic behavior remains to be studied in the future.

The magnetic hysteresis loop at 2 K is typical behavior for soft magnets (Figure 5, insert). It shows a remnant magnetization of 880 $cm^3\ Oe\ mol^{-1}$ and a weak coercive field $H_c = 15$ G. The small coercive field is consistent with the presence of magnetically isotropic ions such as Mn(II) and Cr(III) in a highly symmetrical cubic environment.[8]

In order to estimate the magnetic exchange integral (J) between Mn(II) and Cr(III), we used the expression derived by Verdaguer et al. based on Neel's molecular field theory as given here: $kT_c = (Z|J|N\beta^2g^2)(C_{Mn}C_{Cr})^{1/2}$ where k is Boltzmann's constant, Z the number of magnetic neighbors, N Avogadro constant, g the mean Landé factor, β the Bohr magneton, and C_{Mn} and C_{Cr} the Curie constants of Mn(II) and Cr(III), respectively. The average Z value is 6, T_c is 60 K, and $|J|$ is estimated to be 3.64 cm^{-1}.[9]

In summery, we have successfully synthesized and characterized a novel Prussian blue ferrimagnet $Na[MnCr(CN)_6]$ with magnetic ordering below 60 K. To our knowledge, it is the first time that a $C_mM_x[M'(CN)_6]_y\cdot nH_2O$ Prussian blue analogue with a strictly face-centered cubic lattice structure has been characterized by single crystal X-ray analysis. The complex provides a good example for the study of magneto-structural correlation. The magnetic transition temperature ($T_c = 60$ K) is relatively high in all cyanide-bridged complexes characterized by single crystal X-ray analysis.[2g,2n,2o,10]

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Supporting Information Available: X-ray crystallographic files in CIF format and the detailed Experimental Section for $Na[MnCr(CN)_6]$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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