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Tuning the Magnetic Behavior via Dehydration/Hydration Treatment of a New Ferrimagnet with the Composition of $K_{0.2}Mn_{1.4}Cr(CN)_6\cdot 6H_2O$

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A new complex (**1**) of Prussian blue analogue with the composition of $K_{0.2}Mn_{1.4}Cr(CN)_6\cdot 6H_2O$ was prepared and characterized structurally as well as magnetically. The crystal structure of complex **1** was determined by X-ray diffraction analysis. The results indicate that complex **1** consists of a 3D cubic lattice similar to those of $Mn_3[Cr(CN)_6]_2\cdot xH_2O$, $Mn_3[Co(CN)_6]_2\cdot xH_2O$, $Cd_3[Cr(CN)_6]_2\cdot xH_2O$, and $Cd_3[Co(CN)_6]_2\cdot xH_2O$. Magnetic measurements show that complex **1** is a ferrimagnet with $T_c = 66$ K. It is interesting to note that the magnetic behavior of complex **1** can be substantially modulated through a dehydration/rehydration treatment. The T_c value of this ferrimagnet increases to 99 K after dehydration reaching a 23.4% weight loss, and it decreases back to 66 K after the dehydrated sample reabsorbs water molecules.

Introduction

Research on molecular magnetism has become one of the interesting and challenging fields in modern chemistry and materials science. Since 1980, various molecular magnets have been reported.[1] For instance, many cyanide-bridged paramagnetic metal complexes have been found to exhibit spontaneous magnetization.[2] Among them, the Prussian blue (PB) family of general formula $C_iA_j[B(CN)_6]\cdot nH_2O$ has received great attention.[3–5] A number of high-T_c magnets based on PB have been discovered, 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 $KV[Cr(CN)_6]\cdot 2H_2O$ ($T_c = 376$

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K).[4a,5d] Detailed crystal data are crucial for the studies of PB analogue complexes; however, high-quality crystals of these PB-based magnets are hard to obtain. Hence, structural information for these PB analogue magnets is usually extrapolated from the analysis of X-ray powder diffraction data. It is generally accepted that complexes of the form $C_iA_j[B(CN)_6]\cdot nH_2O$ have a face-centered cubic lattice structure.[6] To the best of our knowledge, only a few Prussian blue analogues have been characterized by single-crystal structural analysis.[7a−7g]

In addition to the pursuit of enhancing the T_c values of molecular magnets, external stimulations that can modulate their magnetic properties have also attracted great attention recently, because such efforts might shed light on the structure−magnetic property relationship and also bode well for potential applications of these magnets in the area of magnetic sensors. In this context, it was found that the magnetic phase transition in a chromium cyanide thin film could be modified electrochemically.[8] Photoinduced and pressure-induced switching of bulk magnetization in a cobalt−iron cyanide has also been reported.[4a,9] Coronado et al.[10] just recently described pressure tuning of magnetism and linkage isomerism in iron(II) hexacyanochromate. In addition, a thermally induced spin crossover was just described for cesium−iron(II) hexacyanochromate.[11] More interestingly, Hashimoto and co-workers[12] reported humidity-induced magnetization and magnetic pole inversion in a cyano-bridged cobalt(II)−manganese(II)−chromium(III) metal complex. It should be mentioned that the magnetic properties of several other types of molecular magnets were also found to be modified substantially upon removal of water or solvent molecules.[13−15] Herein, we report the synthesis, characterization, and crystal structure of a new PB complex with the composition of $K_{0.2}Mn_{1.4}Cr(CN)_6\cdot 6H_2O$ (**1**). Magnetic measurements show that complex **1** is a ferrimagnet with T_c = 66 K, which increases to 99 K after dehydration reaching a 23.4% weight loss. It is interesting to note that the magnetic behavior of this new ferrimagnet can be almost reversibly tuned via the dehydration/hydration treatment.

Experimental Section

General. Elemental analyses were performed with a Perkin-Elmer model 2400 CHN analyzer. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. IR spectra were measured on a Perkin-Elmer SYSTEM FT-IR 2000 spectrophotometer in the form of KBr pellets. X-ray photoelectron spectroscopy data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300-W Al Kα radiation. Magnetic measurements were performed with microcrystals of the fresh sample of complex **1**, as well as the same sample after dehydration and rehydration, on a Quantum Design MPMS-XL5 SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

Warning! Perchlorate salts are potentially explosive and should be handled only in small quantities with care.

Synthesis and Characterization of Complex 1. Single crystals suitable for X-ray diffraction were obtained by slow diffusion in a H-tube (total volume ca. 40 mL) of two aqueous solutions, $K_3Cr(CN)_6$ (0.124 g, 0.5 mmol) in one arm and $Mn(ClO_4)_2\cdot 6H_2O$ (0.182 g, 0.5 mmol) in the other arm. The light-green crystals were collected and air-dried (0.124 g, 82%). IR (KBr pellet, cm^{-1}) ν_{CN}: 2158 (w), 2127 (sh), 2112 (s). XPS (binding energies, eV): 642.2 (Mn $2p_{3/2}$), 576.95 (Cr $2p_{3/2}$), 398.30 (N 1s), 293.90 (K $2p_{3/2}$). Anal. Calcd for $K_{0.2}Mn_{1.4}Cr(CN)_6\cdot 6H_2O$: C, 17.96; H, 3.02; N, 20.96; K, 1.95; Mn, 19.18; Cr, 12.97. Found: C, 17.75; H, 3.26; N, 20.48 (by microanalysis); K, 1.22; Mn, 18.73; Cr, 12.76 (by ICP).

Preparation of an Almost Dehydrated Sample of Complex 1. Green crystals of **1** were gradually heated to 110 °C at a rate of 4.5 °C/min in a vessel under an atmosphere of N_2, and the sample was kept at 110 °C for another ca. 10 min. After the sample had been weighed, the weight loss was calculated to be 23.4%, i.e., 87% of the water molecules (by mass) were removed. Thus, the composition of the "almost dehydrated sample" was estimated to be $K_{0.2}Mn_{1.4}Cr(CN)_6\cdot H_2O$. The initial green crystals changed in color to light red.

Preparation of a Partially Dehydrated Sample of Complex 1. The partially dehydrated sample was obtained by leaving the almost dehydrated sample of complex **1** in open air (20 °C, ca.

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Table 1. Crystallographic and Refinement Data of Complex **1**

formula	$C_{17.14}H_{34.28}Cr_{2.86}K_{0.57}Mn_4N_{17.14}O_{17.14}$
fw	1145.62
temperature (K)	293(2)
crystal system	cubic
space group	$Fm\bar{3}m$
a (Å)	10.7836(12)
b (Å)	10.7836(12)
c (Å)	10.7836(12)
V (Å^3)	1254.0(2)
Z	1
ρ_{calcd} (g·cm^{-3})	1.517
reflns collctd/unique	3036/162 ($R_{int} = 0.0218$)
GOF on F^2	1.298
final R indices [$I > 2s(I)$]	R1 = 0.0416, wR2 = 0.1386
R indices (all data)	R1 = 0.0439, wR2 = 0.1418

12% humidity) for 24 h. Its composition was estimated to be $K_{0.2}Mn_{1.4}Cr(CN)_6{\cdot}4H_2O$.

Preparation of the Rehydrated Sample of Complex 1. The rehydrated sample was obtained by mixing the almost dehydrated sample of complex **1** with water for 1.0 h. Then, the sample was air-dried (20 °C, ca. 12% humidity) for 24 h. The light-red crystals changed to green in color.

X-ray Crystallographic Study. A single crystal of complex **1** was selected and mounted on a Siemens SMART CCD diffractometer equipped with graphite-monochrometed Mo Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied to the data using the SADABS program. The structure was solved with direct methods and refined by full-matrix least-squares based on F^2 using the SHELXTL-97 program package.[16] The corresponding crystallographic and refinement data are provided in Table 1.

Results and Discussion

Stoichiometry and Crystal Structure. Single crystals of complex **1** were obtained by slow diffusion of two aqueous solutions of $K_3Cr(CN)_6$ and $Mn(ClO_4)_2{\cdot}6H_2O$. XPS analysis was performed for complex **1**, and binding energies of 642.2 (Mn $2p_{3/2}$), 576.95 (Cr $2p_{3/2}$), and 293.90 (K $2p_{3/2}$) were detected, indicating the presence of K^+, Mn^{2+}, and Cr^{3+} in complex **1**. The IR spectrum of complex **1** clearly shows the presence of a CN group (2158 cm^{-1}) and H_2O (strong broad band around 3500 cm^{-1}) in complex **1**. Elemental analyses were performed with inductively coupled plasma mass spectrometry and a standard microanalytical method (see Experimental Section). These elemental analysis and spectroscopic data together with electroneutrality considerations lead to the composition of $K_{0.2}Mn_{1.4}Cr(CN)_6{\cdot}6H_2O$ for complex **1**. This stoichiometry is in agreement with the results of crystal structural analysis and magnetic studies as discussed below.

The X-ray diffraction data were collected at room temperature. The diffraction data indicate that complex **1** belongs to the cubic system in the $Fm\bar{3}m$ space group, $a = b = c = 10.7836(12)$ Å, $V = 1254.0(2)$ Å^3, which are comparable to the values for $Mn_3[Cr(CN)_6]_2{\cdot}xH_2O$, $Mn_3[Co(CN)_6]_2{\cdot}xH_2O$, $Cd_3[Cr(CN)_6]_2{\cdot}xH_2O$, and $Cd_3[Co(CN)_6]_2{\cdot}xH_2O$.[6,7a−7g] As the Mn(II)/Cr(III) ratio is approximately 3:2, the crystal structure of complex **1** was solved by adapting the model used for $Mn_3[Cr(CN)_6]_2{\cdot}xH_2O$,[7c] $Mn_3[Co(CN)_6]_2{\cdot}xH_2O$,[7d] $Cd_3[Cr(CN)_6]_2{\cdot}xH_2O$,[7e] and $Cd_3[Co(CN)_6]_2{\cdot}xH_2O$[7f] with the SHELXS-97 program.[16] The crystallographic agreement factors were R1 = 0.0416 [$I > 2\sigma(I)$] and R1 = 0.0439 (all data). The formula determined from crystal structural analysis was $C_{17.14}H_{34.28}Cr_{2.86}K_{0.57}Mn_4N_{17.14}O_{17.14}$, which is in agreement with the composition $K_{0.2}Mn_{1.4}Cr(CN)_6{\cdot}6H_2O$ based on the elemental and ICP analysis data. Figure 1 shows the asymmetric unit of complex **1**, and Figure 2 shows its cubic lattice.

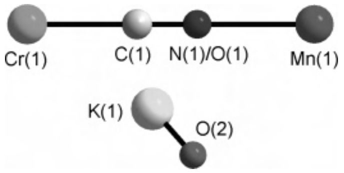

Figure 1. Asymmetric unit of complex **1**.

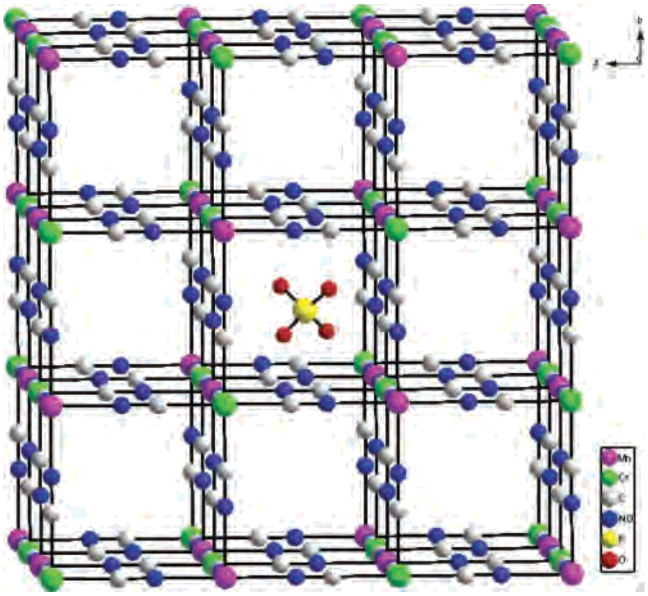

Figure 2. Cubic lattice of complex **1**.

The crystal structure of complex **1** is closely related to those of $Mn_3[Cr(CN)_6]_2{\cdot}xH_2O$,[7c] $Mn_3[Co(CN)_6]_2{\cdot}xH_2O$,[7d] $Cd_3[Cr(CN)_6]_2{\cdot}xH_2O$,[7e] and $Cd_3[Co(CN)_6]_2{\cdot}xH_2O$.[7f] The asymmetric unit contains Mn(1), Cr(1), cyanide bridge [N(1)] and C(1)], water molecules [O(1) and O(2) with occupancy factors of 0.04464], and potassium [K(1) with an occupancy factor of 0.00298]. All of the cyanide groups act as bridges between Mn(II) and Cr(III) in the 3D framework, with the carbon atom pointing toward Cr(III). Because of the incomplete occupancy of $Cr(CN)_6^{3-}$, Mn(II) ions have a mixed nitrogen [N(1)] and oxygen [O(1)] coordination of the average composition MnN_4O_2. As for $Mn_3[Cr(CN)_6]_2{\cdot}xH_2O$,[7c] the coordination of water molecules to Mn(II) is responsible for the interruptions in the 3D network, which are considered to occur at random, leading to a statistically disordered structure. The following interatomic distances were determined (Å): Cr(1)−C(1), 2.062(6); C(1)−N(1), 1.128(10); Mn(1)−N(1), 2.202(6); Mn(1)−O(1), 2.202(6). The Cr−C and Mn−N bond lengths are comparable to those of Prussian blue analogues reported previously. The water molecules

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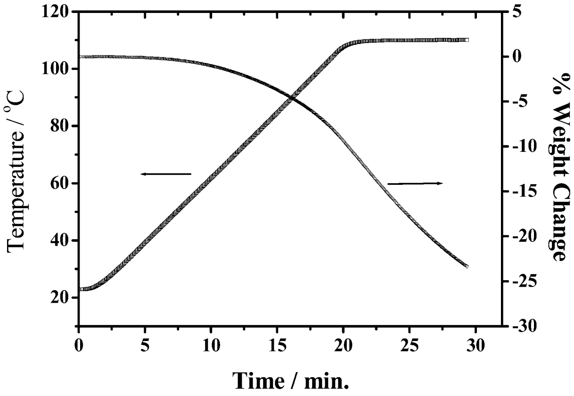

Figure 3. Overlay of plots of temperature and percentage weight loss vs time, obtained by a thermogravimetric study of complex **1**.

[O(2)] and potassium atoms [K(1)] are distributed in a disordered fashion in the cavities of the cubic lattice.

Thermogravimetric and XRD Analyses. Figure 3 shows the overlay of time versus temperature and time versus percentage change in weight for a sample of complex **1**. Initially, the temperature was increased at a rate of 4.5 °C per min, and after 21 min, the temperature of the system was kept at 110 °C for another ca. 10 min. The weight loss, which was ascribed to the dehydration of complex **1**, reached 23.4%, corresponding to removal of 87% (by mass) of the water molecules from complex **1**. Concomitantly, the sample of complex **1** gradually turned from green in the beginning to light red after dehydration. The sample after this treatment is referred to as the almost dehydrated sample. If the sample was heated at 120 °C for 30 min under N_2, complete dehydration was achieved. However, the XRD results indicated that the structure after the latter treatment changed dramatically compared to that of the fresh sample of **1**. As expected, if the sample was heated under vacuum, the dehydration process could be accelerated. For example, it took about 20 min to remove 87% of the water molecules (by mass) from complex **1** under vacuum (0.096 MPa) at 50 °C. The light-red sample after dehydration started to reabsorb water at room temperature, and the degree of hydration was dependent on the humidity of the atmosphere. For instance, it took ca. 24 h to complete the rehydration of the almost dehydrated sample of complex **1** left in open air (23 °C, 34% humidity); the IR spectrum of the rehydrated sample, particularly for the region of 3000−3600 cm^{-1}, was restored to that of the fresh sample of complex **1**, and concomitantly, the color of the sample was restored to green. However, if the almost dehydrated sample of complex **1** was placed in a closed vessel containing a beaker of water (24 °C, 70% humidity), the rehydration process could be finished within 10 h.

Figure 4 shows the XRD patterns of the fresh sample of complex **1** (Figure 4a) and the same sample after dehydration (the almost dehydrated sample) (Figure 4b), as well as that of the same sample after rehydration (Figure 4c). The main diffraction peaks remained the same after dehydration (see Figure 4b), indicating that the crystal structure of complex **1** was retained after dehydration, and the crystal lattice parameters remained unchanged. However, after dehydration, the crystal quality was reduced, to the extent that single-crystal structural analysis was not possible. Efforts to control the heating process to retain the crystal quality were unsuccessful. It was interesting to note that almost all features of the XRD pattern were restored after the dehydrated sample had been rehydrated (see Figure 4c), demonstrating that the dehydration/rehydration treatment could be repeated for complex **1**. Such a dehydration/rehydration treatment could be repeated for at least four cycles without any detectable difference in the XRD pattern, provided that the heating temperature was kept below 110 °C.

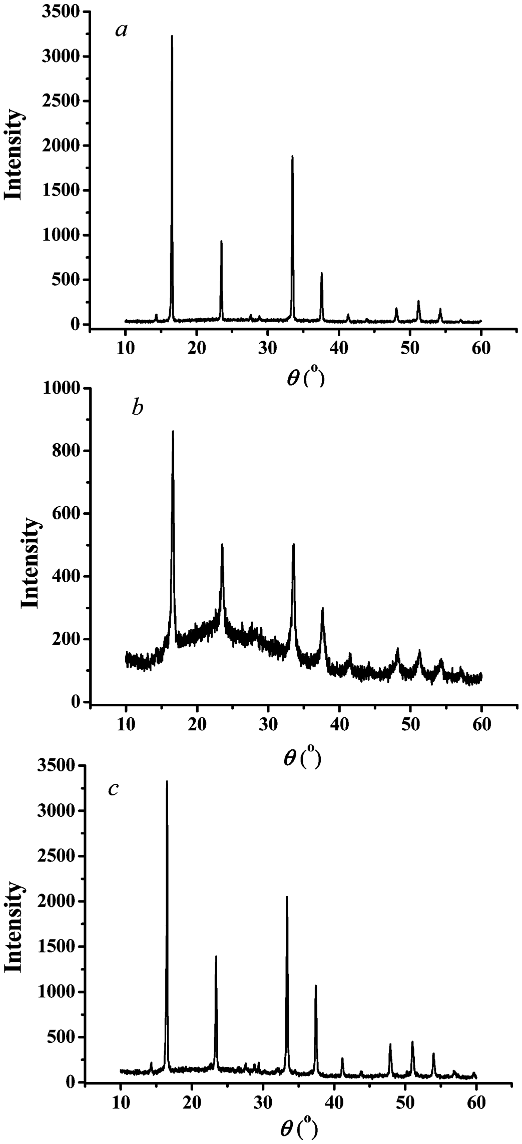

Figure 4. XRD patterns of (a) a fresh sample of complex **1**, (b) the same sample after removal of 87% of the water molecules (almost dehydrated sample), and (c) the same sample after rehydration.

Magnetic Properties. (i) Fresh Sample of Complex 1. Figure 5 shows the temperature dependence of the molar magnetic susceptibility, which is represented by the formula unit $K_{0.2}Mn_{1.4}Cr(CN)_6 \cdot 6H_2O$, for the fresh sample of complex **1** (black squares). The $1/\chi_M$ versus T plot in the range from 300 to 120 K obeys the Curie−Weiss law well [$\chi_M = C/(T - \theta)$] with a Curie constant $C = 7.46$ cm^3 K mol^{-1} and a Weiss constant θ of −30 K. The negative Weiss constant

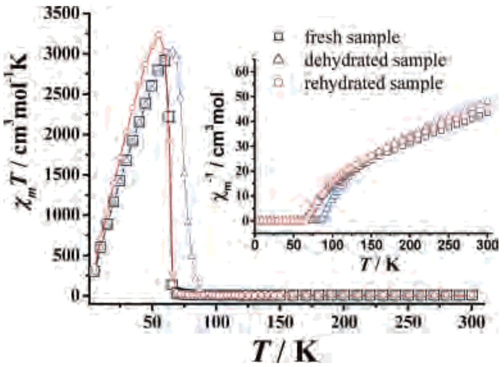

Figure 5. Plot of $\chi_m T$ vs T for the fresh sample (black squares), almost dehydrated sample (blue triangles), and rehydrated sample (red circles) of complex **1**. The inset shows the reciprocal of χ_m vs T for the fresh sample (black squares), almost dehydrated sample (blue triangles), and rehydrated sample (red circles) of complex **1**.

indicates an antiferromagnetic interaction between adjacent Cr(III) and Mn(II) ions through the cyanide bridge, similarly to that found for previously reported complexes.[7a,7c,7h] The $\chi_M T$ value is 6.9 cm^3 K mol^{-1} at 300 K and decreases as the temperature is reduced, reaching a minimum value of 6.1 cm^3 K mol^{-1} at ca. 125 K, below which it increases abruptly and reaches a maximum value of 2926 cm^3 K mol^{-1} at ca. 61 K. The abrupt increase of the $\chi_M T$ around 70 K suggests the onset of three-dimensional magnetic ordering. The decrease of the $\chi_M T$ below 61 K might result from a field saturation effect of the magnetization. This is characteristic of a ferrimagnetic behavior.

Alternating-current susceptibility measurements were performed with a zero applied dc field at different frequencies. The observed in-phase (χ') and out-of-phase (χ'') ac responses are plotted in Figure 6. The presence of both χ' and nonzero χ'' also suggests three-dimensional magnetic ordering for the fresh sample of complex **1**. Moreover, the plot of χ' vs T is independent of frequency, but the plot of χ'' vs T is slightly dependent on frequency. From the plot of χ'' vs T at different frequencies (Figure 6), the T_c value for the fresh sample of complex **1** was determined to be 66 K, at which the emergence of a nonzero value of χ'' was observed.

The field dependence of the magnetization (0−50 kOe) measured at 5.0 K shows rapid saturation of magnetization reaching a value of 4.16 $N\beta$ (saturated magnetization M_s) at 4.0 kOe with almost no coercive field, as shown in Figure 7. If the Cr(1) and Mn(1) ions were antiferromagntically coupled, the saturated magnetization below critical temperature would be $M_s = 4.0\ N\beta$ per formula unit of $K_{0.2}Mn_{1.4}Cr(CN)_6{\cdot}6H_2O$, which is close to the experimental value (4.16 $N\beta$). This result supports the assumption that the Cr(1) and Mn(1) ions of complex **1** are antiferromagntically coupled.

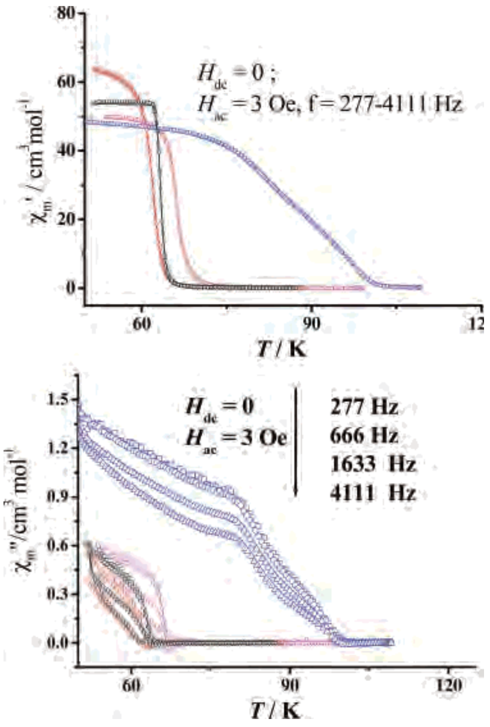

Figure 6. Real (χ') and imaginary (χ'') ac magnetic susceptibilities as a function of temperature at 277, 666, 1633, and 4111 Hz for complex **1**: fresh sample, black; almost dehydrated sample, blue; rehydrated sample, red; partially rehydrated sample, pink.

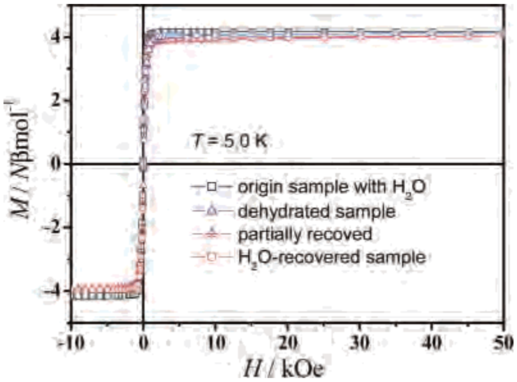

Figure 7. $M-H$ hysteresis loop for the fresh sample (black squares), almost dehydrated sample (blue triangles), partially rehydrated sample (pink triangles), and rehydrated sample (red circles) of complex **1** at 5.0 K.

(ii) Almost Dehydrated Sample of Complex 1. After removal of 87% of the water molecules (by mass), the magnetic behavior of complex **1** changed substantially. From the plots of χ' vs T and χ'' vs T (see Figure 6), the T_c value for the almost dehydrated sample of complex **1** was determined to be 99 K, 33 K higher than that for the fresh sample of complex **1**. The temperature dependence of the magnetic susceptibility, plots of both $\chi_M T$ and $1/\chi_M$ vs T, as shown in Figure 5, differed from that prior to dehydration, indicating that the magnetic interactions among Cr(III) and Mn(II) ions were modulated after dehydration. Nevertheless, the saturated magnetization (4.15 $N\beta$) was found to be close to that of the fresh sample of complex **1** (see Figure 7).

When the almost dehydrated sample was mixed with water and air-dried, the sample became rehydrated (see the Experimental Section). Interestingly, the T_c value of this rehydrated sample, which was again determined from plots of χ' vs T and χ'' vs T (see Figure 6), decreased back to the initial T_c value of the fresh sample of **1**. Concomitantly, the temperature dependence of the magnetic susceptibility and the saturated magnetization were almost recovered, as shown in Figures 5 and 7, respectively. Moreover, the magnetic behavior of the sample of complex **1** was found to be dependent on the degree of hydration. For example, the T_c

value of the partially rehydrated sample (see the Experimental Section), which corresponded to the formula of $K_{0.2}$ $Mn_{1.4}Cr(CN)_6 \cdot 4H_2O$ based on the elemental analysis, was found to be 70 K.

When the rehydrated sample was subjected to heating leading to dehydration [after the removal of 87% of the water molecules (by mass)], the T_c value of the sample was again enhanced to ca. 99 K. The dehydration/rehydration treatment can be repeated as mentioned above, so the magnetic properties of complex **1** can be almost reversibly tuned by such a dehydration/rehydration treatment.

Discussion. Kahn et al. reported the dramatic modification of the magnetic properties of molecular magnetic sponges through a dehydration/rehydration treatment, and they proposed that dehydration resulted in polymerization and an increase of dimensionality, leading to an enhancement of the magnetic transition temperature T_c.[14] The magnetic behaviors of a few magnets of Prussian blue analogues could also be substantially modified through dehydration/rehydration treatments.[12,13] Such phenomena were mainly ascribed to variations of the coordination geometry of the metal ions after dehydration or rehydration treatments. Although the crystal structure of complex **1** after dehydration could not be determined, it is preferred to attribute the reversible modulation of magnetic properties of complex **1** to the alteration of the coordination geometry of the Mn(II) ion after the dehydration/rehydration treatments. Probably, for the dehydrated sample of complex **1**, some of the water molecules coordinated to Mn(II) ions were removed,[17] and concomitantly, the coordination geometry of the Mn(II) ions deviated from an octahedron, giving rise to stronger antiferromagnetic coupling between Cr(III) and Mn(II) ions and, hence, a higher ordering temperature.

Conclusion

A new ferrimagnet of a Prussian blue derivative with the composition of $K_{0.2}Mn_{1.4}Cr(CN)_6 \cdot 6H_2O$ was prepared and characterized. The X-ray single-crystal structure of this new ferrimagnet was obtained. It should be noted that only a few Prussian blue magnets have been characterized by single-crystal structural analysis. The T_c value of this new ferrimagnet was determined to be 66 K on the basis of magnetic measurements. Importantly, the T_c value of this ferrimagnet increased to 99 K after removal of 87% of the water molecules from complex **1**. Moreover, the T_c value can be restored after rehydration, and this reversible modulation of the magnetic behavior of complex **1** can be repeated. By reference to previous studies, a possible explanation for this tuning of the magnetic behavior through dehydration/rehydration treatments was proposed. Further investigations of this new ferrimagnet include neutron diffraction analysis and the determination of the crystal structure of complex **1** after dehydration. These studies will help us to define the origin of the reversible modulation of the magnetic behavior after dehydration/rehydration observed for complex **1**.

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Supporting Information Available: CIF file of the crystal structure of complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) For the almost dehydrated sample, the average coordination number of the Mn(II) ion is estimated to be 4.84 based on the six CN ligands from $Cr(CN)_6$ and the 0.78 H_2O ligand from the 13% of water molecules remaining.