Crystal Structures and Magnetic Properties of $[Mn^{II}(rac\text{-}pnH)(H_2O)Cr^{III}(CN)_6]\cdot H_2O$ and Its Dehydrated Form

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An irreversible single-crystal-to-single-crystal transformation is observed upon dehydration of $[Mn^{II}(rac\text{-}pnH)(H_2O)Cr^{III}(CN)_6]\cdot H_2O$. The virgin, dehydrated, and rehydrated phases are ferrimagnets with Curie temperature of 36, 70, and 36 K, respectively.

Understanding the crystallography of solids has always been essential in providing a thorough meaning to the chemistry and physics of their properties for subsequent development of practical materials. Recently, coordination polymers have been of interest to chemists, physicists, and materials scientists as they show promise in application for gas-storage and catalysis.[1] In the field of molecule-based magnetism, certain compounds show dynamic structural transformation through desolvation–resolvation accompanied by changes of Curie temperature, magnet ground state, spin-crossover (SCO) transition temperature, or emerging SCO phenomenon, pole inversion.[2–4] In addition, a handful of compounds displays in-situ single-crystal-to-single-crystal transformation.[4] In developing our work on the search for the synergy in chiral magnets,[5] we synthesized and studied the non-chiral magnetic system, $[Mn^{II}(enH)(H_2O)][Cr^{III}(CN)_6]\cdot H_2O$ ($\mathbf{1}\cdot 2H_2O$),[6] and $[Mn^{II}(rac\text{-}pnH)(H_2O)Cr^{III}(CN)_6]\cdot H_2O$ ($\mathbf{2}\cdot 2H_2O$) as a test to some observed unusual magnetic phenomena for the chiral ones and we found a rare case where the as-prepared hydrated crystals of $\mathbf{1}\cdot 2H_2O$ lose both coordinated and non-coordinated water molecules to an amorphous phase which when rehydrated regain the original crystal structure.[6] Ohba et al. found a transformation from single-crystal-to-single-crystal for a related compound $[Mn^{II}(NNdmenH)(H_2O)Cr^{III}(CN)_6]\cdot H_2O$, (NNdmen = *N*,*N*-dimethylethylenediamine, $\mathbf{3}\cdot 2H_2O$).[3] In both cases, an increase of the Curie temperature of these ferrimagnets upon dehydration was observed.

Here, we report a new phenomenon in which $\mathbf{2}\cdot 2H_2O$ shows an irreversible single-crystal-to-single-crystal transformation upon dehydration and disorder is introduced upon rehydration.

The complex $\mathbf{2}\cdot 2H_2O$ was synthesized as green plates by layer-to-layer slow diffusion of *rac*-pn·2HCl (147 mg, 1 mmol) and $K_3[Cr(CN)_6]$ (16.3 mg 0.05 mmol) in 0.5 mL H_2O partially neutralized with 0.1 mL of 8 M KOH (0.8 mmol) in the bottom, 0.4 mL of H_2O–EtOH (3:1) as a buffer and 0.5 mL of H_2O–EtOH (1:3) solution of $MnCl_2\cdot 4H_2O$ (74.2 mg 0.375 mmol) on the top. The tube was sealed under argon and kept in the dark. Yeild 14.1 mg. Anal. Calcd. for $\mathbf{2}\cdot 2H_2O$, $C_9H_{15}CrMnN_8O_2$: C, 28.89; H, 4.04; N, 29.94%. Found: C, 28.84; H, 4.37; N, 29.97%.

The thermogravimetric and differential thermal analyses of powdered samples for $\mathbf{2}\cdot 2H_2O$ under nitrogen atmosphere show a weight loss of 9.6% starting at 350 K to a stable state up to 450 K. This weight loss is close to that for the departure of two water molecules, one coordinated and one non-coordinated, per formula unit (9.63%); that is the complete dehydration. Subsequent exposure of the samples to air (relative humidity ca. 50%) for ca. 5 h at 291 K, they absorb water and recover their initial weights, which we label as dehydrated **2** to rehydrated $\mathbf{2'}\cdot 2H_2O$. The disappearance of the associated water bands in the infrared spectra confirms the complete dehydration (See ESI).[7]

The first dehydration process causes large change of the positions and intensity of the Bragg reflections in the XRPD pattern without noticeable broadening. Subsequent rehydration indicates a reversal of the process but some reflections were severely broadened (Figure 1).

An in-situ crystal structure study was undertaken starting with the determination of the structure of a virgin crystal of $\mathbf{2}\cdot 2H_2O$ ($P2_1/m$, $a = 7.6945(14)$, $b = 14.543(3)$, $c = 7.9749(14)$ Å, $\beta = 110.918(3)°$). When the crystal was heated to 360 K in a flow of nitrogen, the diffraction pattern changed and the crystal structure of **2** ($Pmnb$, $a = 7.730(4)$, $b = 13.627(7)$, $c = 14.064(7)$ Å) was determined (Figure 1). Upon rehydration, the unit cell parameters for rehydrated $\mathbf{2'}\cdot 2H_2O$ ($P2_1/m$, $a = 7.631(5)$, $b = 14.430(9)$, $c = 7.925(5)$ Å, $\beta = 110.958(11)°$) were close to those of $\mathbf{2}\cdot 2H_2O$ but the diffraction spots were severely broadened and only metal positions were located in a full crystal structure analysis.

The crystal structure of $\mathbf{2}\cdot 2H_2O$ is similar to that reported for $\mathbf{3}\cdot 2H_2O$, except for the slight differences in some dimensions due to the different size of the amine (Figure 2).[3] The structure consists of layers of Mn and Cr in a pseudo square-grid with cyanide bridges. The amines of the asymmetric carbon and a water molecule coordinate to Mn atoms in the axial positions thus completing its octahedral coordination. The amine is

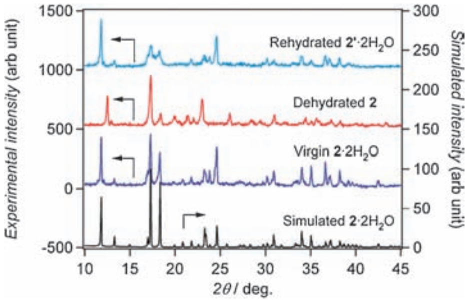

Figure 1. Experimental XRPD patterns for virgin $\mathbf{2}\cdot 2H_2O$, dehydrated **2**, and rehydrated $\mathbf{2'}\cdot 2H_2O$ and that simulated for $\mathbf{2}\cdot 2H_2O$.[8]

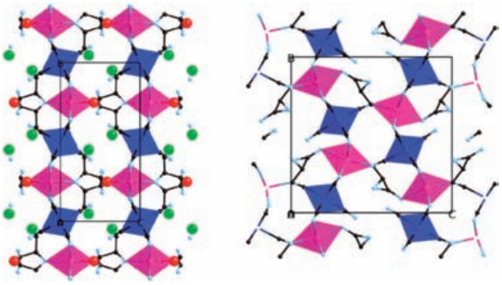

Figure 2. *a* Axis projection of the crystal structure of **2**•$2H_2O$ (left) and **2** (right); Mn (pink) and Cr (blue). Coordinated water (red oxygen atoms) and non-coordinated water (green oxygen atoms).

disordered on two positions (one is the *S* the other is the *R* enantiomer) with only the nitrogen atom being common to the two amines. The lattice water molecule is hydrogen bonded to the amine.

Upon dehydration the crystal structure of **2** adopts a higher symmetry but retains the layer geometry with some deviations. The position of the departing coordinated water is taken by the terminal cyanide in **2**•$2H_2O$, resulting in a 3D-network of Mn–CN–Cr (Figure 2). Interestingly, the amine has changed its mode of coordination. That is the nitrogen on the alpha carbon is now coordinated to the Mn. The consequence of this is that the two symmetry related amines (*R*/*S* enantiomer) have now one nitrogen and one carbon atoms in common. The most energetically plausible way for this to happen is that the amine is deconnected from the Mn and then connected to Mn on adjacent layer through the other nitrogen without rotation. We note that the position of the amine in **2** is equidistant to two different Mn atoms on the adjacent layer by symmetry. Consequently, the equal probability of the nitrogen to coordinate to the Mn atom during the rehydration process imposes the severe disorder as well as broadening of certain Bragg peaks, indicating irreversible dehydration–rehydration process of **2**•$2H_2O$. However, the amine NNdmen of **3**•$2H_2O$, has only one monodentate site and difficult to change the coordinating position to Mn on adjacent layer, and this situation is thought to prevent the transformation from being irreversible.

In the field-cooled (5 Oe) measurements, spontaneous magnetization is observed at 36 K for the virgin **2**•$2H_2O$, 70 K for the dehydrated **2**, and 36 K for the rehydrated **2′**•$2H_2O$ (Figure 3), Rehydrated sample shows some non-reversible anomaly that may be from some remaining defects.

In all its states (virgin **2**•$2H_2O$, dehydrated **2**, and rehydrated **2′**•$2H_2O$), the compounds are ferrimagnets due to the negative Weiss constants (−76.4 K for **2**•$2H_2O$, −103 K for **2**, and −77.5 K for **2′**•$2H_2O$) and the saturation magnetizations of $2\mu_B$ in high field at low temperature are in good agreement with antiferromagnetically coupled Mn^{II} ($5\mu_B$) and Cr^{III} ($3\mu_B$) (See ESI).[7] The increment and decrement of the Curie temperature is understood as a consequence of the increase and decrease dimensionality through formation and dissociation of cyanide network between adjacent layers.

In summary, single-crystal-to-single-crystal transformation upon dehydration and its irreversibility upon rehydration of $[Mn^{II}(rac\text{-}pnH)(H_2O)][Cr^{III}(CN)_6]\cdot H_2O$, associating with the increment–decrement of Curie temperature are demonstrated by in-situ X-ray diffraction, TGA, IR, and magnetic measurements.

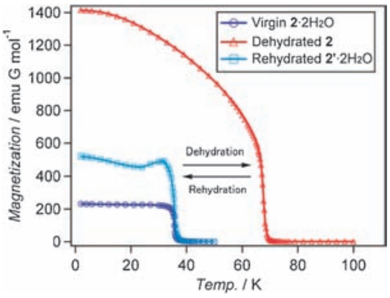

Figure 3. Field-cooled magnetization in an applied field of 5 Oe, for virgin **2**•$2H_2O$ (squares), dehydrated **2** (triangles), and rehydrated **2′**•$2H_2O$ (circles).

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7 Experimental details were deposited in ESI.[9] Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-676444 (virgin **2**•$2H_2O$) and CCDC-676445 (dehydrated **2**).
8 The simulated pattern was calculated from the single-crystal X-ray data using RIETAN-2000: F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321–324*, 198.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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