

Reversible Single Crystal-to-Amorphous Phase Transition upon Dehydration–Rehydration and Associated Magnetism in $[\text{Mn}^{\text{II}}(\text{enH})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$

Yusuke Yoshida,¹ Katsuya Inoue,^{*1} and Mohamedally Kurmoo^{*2}

¹Department of Chemistry and Institute for Advanced Materials Research, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526

²Laboratoire de Chimie de Coordination Organique, CNRS-UMR7140, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, 67000 Strasbourg Cedex 01, France

(Received January 17, 2008; CL-080057; E-mail: kxi@hiroshima-u.ac.jp)

We report the rare occurrence of a reversible loss of crystallinity upon dehydration and regain upon rehydration by in situ X-ray diffraction on a single crystal of $[\text{Mn}^{\text{II}}(\text{enH})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$ and the associated thermal and magnetic properties characterized by an increase of the Curie temperature of the soft ferrimagnet from 42 to 75 K.

The transformation of a single-crystal-to-single-crystal (SC–SC) upon external constraints is a subject of major importance in crystallography and thermodynamics, which has some bearing on the real world of applications.¹ While the success rate for achieving this goal is on the increase for systems where pores are generated by desolvation of a solid or where the structure collapses to one without pores in the SC–SC transformation, there is no example of reversible SC to amorphous phase. These SC–SC changes can influence the properties of the solids as has been reported; for example, guest-dependent magnetic interaction,² Curie temperature,³ and spin-crossover critical temperature.^{4,5} In developing our work on the search for the synergy in chiral magnets,⁶ we synthesized and studied the nonchiral magnetic system, $[\text{Mn}(\text{enH})(\text{H}_2\text{O})][\text{Cr}(\text{CN})_6]\cdot\text{H}_2\text{O}$ ($\mathbf{1}\cdot\text{2H}_2\text{O}$), as a test to some observed unusual magnetic phenomena for the chiral ones. This compound was found to show reversible single-crystal-to-amorphous phase transformation associated with increment and decrement of Curie temperature as a result of dehydration and rehydration, respectively. Here, we report its synthesis, in situ single-crystal structure determinations and the magnetic properties of $\mathbf{1}\cdot\text{2H}_2\text{O}$ and demonstrate the reversibility.

The complex $\mathbf{1}\cdot\text{2H}_2\text{O}$ was synthesized as green needles by layer-to-layer slow diffusion of $\text{en}\cdot\text{2HCl}$ (332 mg, 2.5 mmol) and $\text{K}_3[\text{Cr}(\text{CN})_6]$ (203 mg 0.625 mmol) in 2 mL of H_2O partially neutralized with 0.5 mL of 8 M KOH (4 mmol) in the bottom, 1.5 mL of H_2O –EtOH (3:1) as a buffer and 2.5 mL of H_2O –EtOH (1:3) solution of $\text{MnCl}_2\cdot\text{4H}_2\text{O}$ (372 mg 1.88 mmol) on the top. The tube was sealed under argon and kept in the dark. Anal. Calcd for $\mathbf{1}\cdot\text{2H}_2\text{O}$, $\text{C}_8\text{H}_{13}\text{CrMnN}_8\text{O}_2$: C, 26.68; H, 3.64; N, 31.11%. Found: C, 26.57; H, 3.98; N, 31.01%.

The thermogravimetric and differential thermal analyses of powdered samples for $\mathbf{1}\cdot\text{2H}_2\text{O}$ under nitrogen atmosphere show a weight loss of 9.69% starting at 340 K and ends at 370 K. This percentage loss is close to that for the departure of two water molecules, one coordinated and one noncoordinated, per formula unit (10.0%); that is the complete dehydration. Following cooling down to 291 K and exposure of the samples to air (relative humidity ca. 50%) for ca. 5 h, they absorb water and recover their initial weights, which we label as dehydrated $\mathbf{1}$

to rehydrated $\mathbf{1}\cdot\text{2H}_2\text{O}$. The disappearance of the associated water bands in the infrared spectra confirms the complete dehydration (See ESI).⁹

An in situ crystal structure study was undertaken starting from a virgin crystal of $\mathbf{1}\cdot\text{2H}_2\text{O}$. When the crystal was heated to 360 K in a flow of nitrogen, the diffraction spots disappeared (Figure 1), indicating dehydration results in an amorphous phase, $\mathbf{1}$. Unexpectedly, when the crystal was exposed to the air, the diffraction spots were recovered and the same crystal structure as the virgin sample was found on analysis of the recorded intensity data. However, the spots were slightly broadened and resulted in a lower resolution. This phenomenon was confirmed for the bulk by powder X-ray measurements (Figure 2). Analyses of the X-ray diffraction data on a single crystal of virgin ($a = 7.5177(8)$, $b = 14.6493(15)$, $c = 14.9539(15)$ Å) and the rehydrated $\mathbf{1}\cdot\text{2H}_2\text{O}$ ($a = 7.5298(9)$, $b = 14.6804(19)$, $c = 14.9760(19)$ Å) suggest they are isostructural with an orthorhombic $Pcmm$ space group (see ESI).^{8,9}

The crystal structures have a corrugated 2D-square grid of Mn and $\text{Cr}(\text{CN})_4$ where the Mn and Cr alternate in the ab plane and bridged by cyanide (Figure 3) as that found for $[\text{Mn}(\text{R-pnH})(\text{H}_2\text{O})][\text{Cr}(\text{CN})_6]\cdot\text{H}_2\text{O}$, $\text{pn} = \text{propanediamine}$.⁷ The remaining two cyanide groups complete the octahedral coordination of the Cr atom and pointing out of the layers while the statically disordered en and one water molecule are coordinated trans to each other to the Mn atom. Viewing along the c axis, we find that adjacent layers are staggered. It should be noted that oxygen atom O(1) of the coordinating water is found to have two hydrogen bonds to the nitrogen of cyanide groups of the neighboring layer ($\text{O}(1)\cdots\text{N}(3')$, 2.752(4) Å). The two hydrogen bonds are related by a mirror plane, which is thought to be the key to explain the reversible single crystal-to-amorphous phenomenon. Upon dehydration, the terminal cyanide

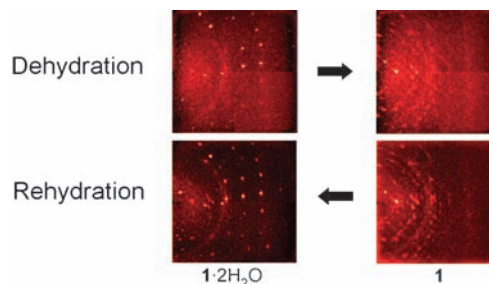


Figure 1. Observed Bragg diffraction spots of a single crystal before (top left, 295 K), after dehydration (top right, 360 K), upon exposure to air (bottom right, 295 K, $t = 0$ min) and after (bottom left, 295 K, $t = 12$ min).

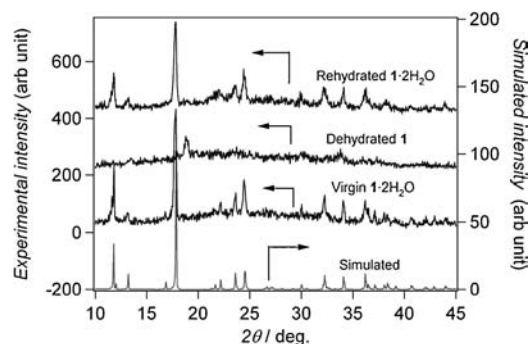


Figure 2. Experimental XRPD patterns for virgin $1 \cdot 2\text{H}_2\text{O}$, dehydrated **1**, and rehydrated $1 \cdot 2\text{H}_2\text{O}$ and that simulated for $1 \cdot 2\text{H}_2\text{O}$.⁶

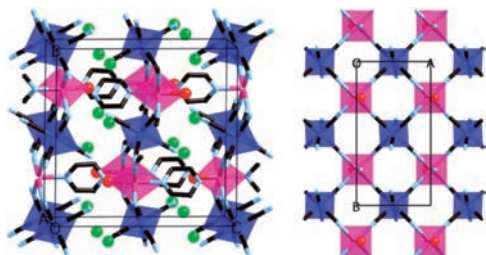


Figure 3. *a* Axis projection of the crystal structure of $1 \cdot 2\text{H}_2\text{O}$ (left) and a view of the square-grid layer (right) Mn (pink) and Cr (blue). Coordinated water (red oxygen atoms) and non-coordinated water (green oxygen atoms).

coordinates to the Mn as previously reported.^{3,5} There is equal probability for either cyanide to occupy the position of the leaving water molecule and consequently, causes severe disorder and loss of the crystallinity. On the other hand, rehydration repairs these faults and brings about a recovery of the order within the structure.

In the zero-field-cooled and field-cooled (5 Oe) measurements, spontaneous magnetization is observed at 42 K for the virgin $1 \cdot 2\text{H}_2\text{O}$, 75 K for the dehydrated **1** and 42 K for the rehydrated $1 \cdot 2\text{H}_2\text{O}$ (Figure 4). Rehydrated sample shows a trailing of the magnetization between the two Curie temperatures, suggesting that some fragments are not completely reversible. In the single-crystal X-ray measurements, these defects were very small and only contribute to the broadening of the Bragg reflections and are averaged out in the refinement. In all its states (hydrated, dehydrated, or rehydrated), the compounds are ferromagnets due to the negative Weiss constants and the saturation magnetizations of $2\mu_{\text{B}}$ in high field at low temperature (See ESI).⁹ The increment of the Curie temperature is understood as a consequence of the increase dimensionality through the randomly formed cyanide network between adjacent layers.

In summary, reversibility is demonstrated for loss and regain of crystallinity upon dehydration and rehydration of

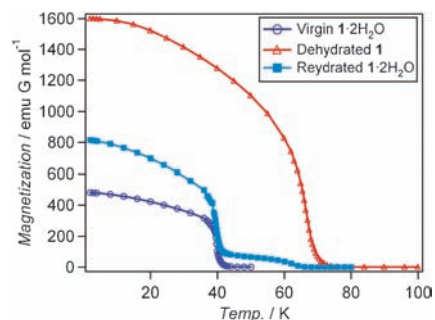


Figure 4. Field-cooled magnetization in an applied field of 5 Oe, for virgin $1 \cdot 2\text{H}_2\text{O}$ (blue), dehydrated **1** (red), and rehydrated $1 \cdot 2\text{H}_2\text{O}$ (pale-blue).

$[\text{Mn}(\text{enH})(\text{H}_2\text{O})][\text{Cr}(\text{CN})_6] \cdot \text{H}_2\text{O}$ by in situ X-ray diffraction, TGA, IR, and magnetic measurements. It is associated with the increment–decrement of Curie temperature.

This work was supported by a Grant-in-Aid for Science Research (A) (no. 18205023) from the Ministry of Education, Science, Sports, and Culture and the CNRS (France). YY thanks the Université Louis Pasteur for its hospitality during his stay in Strasbourg.

References and Notes

- 1 G. J. Halder, C. J. Kepert, *Aust. J. Chem.* **2006**, *59*, 597, and references therein.
- 2 M. Kurmoo, H. Kumagai, K. W. Chapman, C. J. Kepert, *Chem. Commun.* **2005**, 3012; M. Kurmoo, H. Kumagai, S. M. Hughes, C. J. Kepert, *Inorg. Chem.* **2003**, *42*, 6709.
- 3 W. Kaneko, M. Ohba, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 13706; S. Tanase, F. Tuna, P. Guionneau, T. Maris, G. Rombaut, C. Mathonière, M. Andruh, O. Kahn, J.-P. Sutter, *Inorg. Chem.* **2003**, *42*, 1625.
- 4 M. Nihei, L. Han, H. Oshio, *J. Am. Chem. Soc.* **2007**, *129*, 5312; G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762.
- 5 V. Niel, A. L. Thompson, M. C. Munoz, A. Galet, A. E. Goeta, J. A. Real, *Angew. Chem., Int. Ed.* **2003**, *42*, 3760.
- 6 The simulated pattern was calculated from the single crystal X-ray data using RIETAN-2000; F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321*, 198.
- 7 K. Inoue, K. Kikuchi, M. Ohba, H. Ōkawa, *Angew. Chem., Int. Ed.* **2003**, *42*, 4810.
- 8 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-674736 (virgin $1 \cdot 2\text{H}_2\text{O}$) and 674735 (hydrated $1 \cdot 2\text{H}_2\text{O}$).
- 9 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.