

Reversible Single-Crystal to Single-Crystal Transformations and Associated Magnetism of a Cyanide-Bridged Chiral Magnet

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[Introduction] Over the last several decades, the exploring for multifunctional molecule-based magnetic materials to combine the additional functions to magnetism became popular also significant for both the applied and the fundamental interests. To the best of our knowledge, these combinations mainly include magnetism and dielectricity, conductivity, optical/nonlinear-optical activity, porosity with guest dependence or chirality. In particular, it caused increasing interests on the so-called chiral magnets^[1], that how does the structural chirality coupled to magnetic chirality.

Recently, a chiral magnet $[\text{Mn}^{\text{II}}(\text{S-pnH})(\text{H}_2\text{O})][\text{Mn}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$, **1S**·2H₂O, has been prepared which is slightly different from **1S**·3H₂O^[2] in the amount of the water molecule per unit (demonstrated by elemental analysis), although **1S**·2H₂O and **1S**·3H₂O have identical magnetic behaviors. The further structural and magnetic properties study reveal reversible structure transformation upon dehydration and rehydration. Different to the transformation exhibited by $[\text{Mn}^{\text{II}}(\text{enH})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$ and $[\text{Mn}^{\text{II}}(\text{rac-pnH})(\text{H}_2\text{O})][\text{Cr}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$ during the dehydration/rehydration process in our previous works^[3], **1S**·2H₂O altered reversibly from single-crystal phase to single-crystal phase. Here, we report the details study in regard to the reversible structural changes and the associated magnetic properties of this chiral magnet.

[Experiment] The single crystal of **1S**·2H₂O was prepared by using a slow diffusion method. To demonstrate the complete reversibility upon dehydration/rehydration of **1S**·2H₂O, one selected single crystal from the as-prepared **1S**·2H₂O was dehydrated to $[\text{Mn}^{\text{II}}(\text{S-pnH})][\text{Mn}^{\text{III}}(\text{CN})_6]$, **1S**, then rehydrated to $[\text{Mn}^{\text{II}}(\text{S-pnH})(\text{H}_2\text{O})][\text{Mn}^{\text{III}}(\text{CN})_6]\cdot\text{H}_2\text{O}$, **1S-HP**, and dehydrated again to $[\text{Mn}^{\text{II}}(\text{S-pnH})][\text{Mn}^{\text{III}}(\text{CN})_6]$, **1S-DeHP**. The X-ray diffraction measurements for each forms were performed using a Bruker SMART-APEX II diffractometer. The magnetic measurement for **1S**·2H₂O, **1S**, **1S-HP** and **1S-DeHP** were carried on using a Quantum Design MPMS-5S SQUID magnetometer.

[Results and Discussion] By using the X-ray analysis, all the crystal structures for **1S**·2H₂O, **1S**, **1S-HP** and **1S-DeHP** were solved successfully. The result showed that **1S-HP** and **1S-DeHP** have the same structures as **1S**·2H₂O and **1S**, respectively. The structures for **1S**·2H₂O and **1S** were shown in Figure 1.

1S·2H₂O crystallizes in the chiral space group $P2_12_12_1$ and has two-dimensional (2D) square network. Parallel to the *ab*-plane, four cyanide groups from the $[\text{Mn}^{\text{III}}(\text{CN})_6]^{3-}$ ion are ligated to adjacent Mn^{II} ions in the equatorial positions to form cyanide-bridged bimetallic 2D

corrugated layers which are stacked along *c*-axis. Viewing along the *c*-axis, we can find the adjacent layers are staggered. One oxygen atom O(1) from water molecule and one nitrogen atom N(2) on the β -carbon of the *S*-pnH anion coordinated to the Mn^{II} ion out of the 2D plane, to complete the octahedral coordination. Between the 2D sheets the non-coordinated nitrogen atom N(1) of on the α -carbon of the diamine is assumed to be protonated to balance the overall charge. And there is another one H₂O exists among the 2D sheet per molecule.

Compound **1S** crystallizes in the same orthorhombic space group $P 2_1 2_1 2_1$ as **1S**·2H₂O. But instead, it reveals three-dimensional (3D) cyanide-bridged bimetallic network which seems like the 2D sheets described for the structure of **1S**·2H₂O were connected via the previously non-bridging cyanides.

The dehydration is associated to a change in coordination of the *S*-pnH from one 2D layer to the neighbor one involving a proton transfer, and accompanies with a new cyanide bridging of Mn^{II} and Mn^{III} ions forming between the 2D sheets. Which, concretely, transforming from {Mn^{II}-NH₂CH(CH₃)₃CH₂N⁺H₃⁺·····(H₂O)Mn^{II}} for **1S**·2H₂O to {Mn^{II}-CN·····NH₃⁺CH(CH₃)₃CH₂H₂N⁺Mn^{II}} for **1S**, and therefore bring about the three-dimensional (3D) cyanide-bridged network structure of **1S**. Corresponding to the 2D to 3D structural transition, the study of magnetic properties reveals that the critical temperature of long range magnetic ordering (see Figure 2.) for **1S**·2H₂O ($T_C = 21$ K) more than doubled of that for **1S** ($T_C = 45$ K).

Our works discovered a junction of chirality, reversible crystal structure and switchable magnetism for the development of molecule-based magnet.

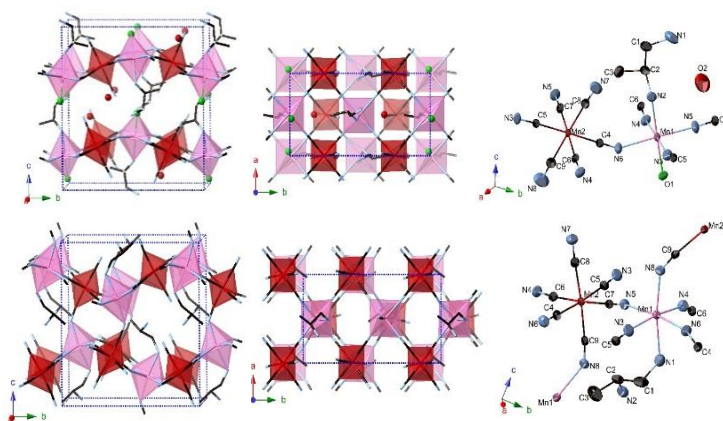


Figure 1. Projection of the crystal structures viewed along the *a*-axis (left), *c*-axis (middle) and ORTEP drawing for **1S**·2H₂O (top) and **1S** (bottom). The green and red balls represent the oxygen atoms of the coordinated and the non-coordinated water molecules, respectively.

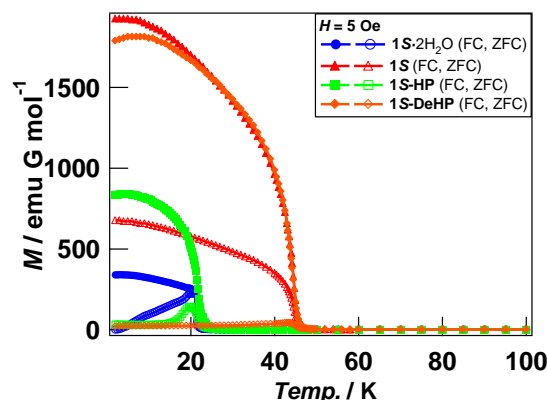


Figure 2. Temperature dependence of the FC-ZFC magnetization in an applied field of 5 Oe for **1S**·2H₂O, **1S**, **1S-HP** and **1S-DeHP**.

[Reference]

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- [3] Y. Yoshida, K. Inoue, M. Kurmoo, (a) *Inog. Chem.*, **2009**, 48, 267; (b) *Inog. Chem.*, **2009**, 48, 10726.