

A One-Dimensional Magnet Based on $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ Xiao-Qin Wei,^{†,‡} Kun Qian,[†] Hai-Yan Wei,^{*,‡} and Xin-Yi Wang^{*,†}[†]State Key Laboratory of Coordination Chemistry, Collaborative Innovation Center of Advanced Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Chemistry Building, 22 Hankou Road, Nanjing, 210023, China[‡]Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing, 210023, China

S Supporting Information

ABSTRACT: Self-assembly of the $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ anion and the Mn^{II} unit with a macrocyclic ligand results in the first example of a one-dimensional (1D) chain compound based on the heptacyanomolybdate, $[\text{Mn}(\text{L}_{\text{NSC10}})]_2[\text{Mo}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ ($\text{L}_{\text{NSC10}} = 1,4,7,10,13$ -pentaazacyclopentadecane). Because of the existence of the interchain magnetic coupling, long-range magnetic ordering was observed in this compound.

Molecular magnetic materials have attracted enormous attention over the past two decades due to their potential applications in the information storage, spintronics, and quantum computing.¹ In this field, the cyanometallates have played major role as they offer a number of distinct advantages, including the tunable coordination modes and predictable magnetic coupling.² Thus, many interesting cyanide-based magnetic materials have been reported, including high T_c magnets,³ photomagnetism,⁴ bistable molecular nanomagnets such as single-molecule magnets (SMMs) and single-chain magnets (SCMs),^{5,6} spin crossover materials,⁷ and multifunctional magnets showing other properties such as chirality, porosity, conductivity, and so on.⁸

Among all the cyanometallates, the 4d and 5d cyanometallate precursors are very attractive due to their stronger magnetic coupling and magnetic anisotropy compared to their 3d congeners. While the octacyanomolybdates $[\text{M}^{\text{IV/V}}(\text{CN})_8]^{4-/3-}$ ($\text{M} = \text{Nb}, \text{Mo}, \text{W}$)⁹ are largely studied, reports on the hexacyanomolybdate and heptacyanomolybdate of trivalent Mo^{III} center ($[\text{Mo}^{\text{III}}(\text{CN})_6]^{3-}$ and $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$) are few, albeit their importance. On one hand, both the theoretical and experimental results had revealed the very strong magnetic coupling between the Mo^{III} and other metal centers, which is promising for the synthesis of high T_c molecular magnets.¹⁰ On the other hand, magnetic anisotropy, arising from both the single-ion magnetic anisotropy and the anisotropic magnetic coupling, for the Mo^{III} centers in the $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ unit is very significant, which has a great potential for the construction of anisotropic magnets, SMMs and SCMs.¹¹ However, although the synthesis of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ was reported in the 1930s, the preparation of the $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ -based molecular magnets was not reported in the late 1990s by Kahn.¹² Because of its large amount of CN groups and a high negative charge, most of the reported $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ -based materials are high dimensional magnets with relatively high T_c for some of them.^{12–14} Low dimensional materials of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ are extremely

scarce, with only two examples reported by some of us, namely a dicosanuclear $\text{Mo}_8\text{Mn}_{14}$ cluster and three trinuclear Mn_2Mo clusters.¹⁵ Interestingly, the $\text{Mo}_8\text{Mn}_{14}$ cluster has a very high ground state spin $S = 31$, which is only lower than the recently reported highest value of $S = 45$.¹⁶ One Mn_2Mo compound is a SMM with the highest energy barrier (40.5 cm^{-1}) for the cyano-bridged SMMs. Because of the similar requirements for the construction of SMMs and SCMs, it is very promising to construct SCMs with the $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ unit. However, to the best of our knowledge, no 1D compound based on the $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ unit has been reported.

The success in the synthesis of clusters of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ using the macrocyclic ligands prompts us to perform further reactions with similar ligands, hoping to prepare new low-dimensional materials of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$. Using another macrocyclic ligand L_{NSC10} , we obtained the first 1D compound of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$, $[\text{Mn}^{\text{II}}(\text{L}_{\text{NSC10}})]_2[\text{Mo}^{\text{III}}(\text{CN})_7] \cdot 2\text{H}_2\text{O}$ (**1**). Magnetic studies on **1** revealed the long-range magnetic ordering rather than the SCM behavior below 5.6 K. Because of the severe disorder of the L_{NSC10} ligand, **1** exhibits spin-glass like behavior, as confirmed by the frequency dependence in the ac data.

Compound **1** was prepared by self-assembly reaction of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ and $[\text{Mn}(\text{L}_{\text{NSC10}})]^{2+}$ in solution under a nitrogen environment (see details in the Supporting Information (SI)). Although the solution of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ is very air sensitive, **1** is stable in the air for at least two months (checked by the X-ray diffraction on the same single crystal). This makes the handling of **1** much easier.

Single-crystal X-ray study revealed that compound **1** crystallizes in the orthorhombic space group $Pnma$ (SI Table S1) and has a 1D structure. In the crystal structure, there are one unique $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ unit, two Mn^{II} centers with two 2-fold disordered L_{NSC10} ligands, and two crystallized water molecules (Figure 1 and SI Figure S1). The $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ anion is slightly distorted from the ideal pentagonal bipyramidal geometry with a continuous shape measure (CSHM) calculated to be 1.410 (SI Table S3).¹⁷ Using two CN groups in the equatorial *meta*-1,3 positions and one CN group in the axial position, each Mo^{III} center is bridged to three Mn^{2+} centers. One of the Mn^{II} centers, Mn1, is also hepta-coordinated by seven N atoms, five of which are from the macrocyclic ligand in the equatorial position and the remaining two are from the CN

Received: March 30, 2016

Published: May 13, 2016

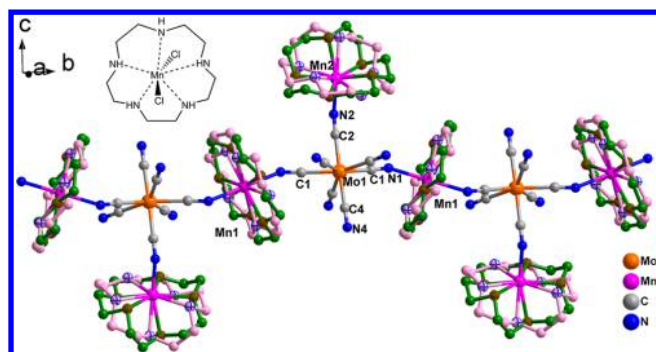


Figure 1. 1D chain structure of **1**. The pink and green colors represent the 2-fold disordered ligands.

groups of two $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ anions. On the other hand, the other Mn^{II} center, $\text{Mn}2$, is in a distorted octahedron, where the $\text{L}_{\text{NSC}10}$ ligand is twisted and no longer in a planar geometry. Bridged by two *meta*-1,3 CN groups, the $\text{Mo}1$ and $\text{Mn}1$ centers form a 1D chain along the *b* direction with a $\text{Mn}1\text{--Mo}1$ distance of 5.353(1) Å, while $\text{Mn}2$ is dangling on both sides of the chain with $\text{Mn}2\text{--Mo}1$ distance of 5.148(1) Å. The 1D chains of **1** were further connected to four others by abundant $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bonds involving the crystallized water molecules and the CN^- groups of $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$, forming the 3D hydrogen bonded framework (SI Figure S2). The shortest interchain $\text{Mn}^{\text{II}}\cdots\text{Mo}^{\text{III}}$ distance is 10.707(2) Å. The existence of these large amounts of H-bonds should account for the non-negligible interchain magnetic interaction and the 3D magnetic ordering observed for **1** (vide post).

The temperature-dependent magnetic susceptibility data under a 1000 Oe dc field for the grounded crystalline samples of **1** are shown in Figure 2. The $\chi_{\text{M}}T$ value at 300 K is 8.86 cm^3

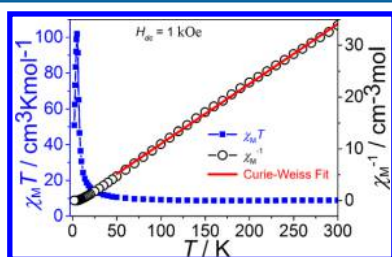


Figure 2. Temperature dependent $\chi_{\text{M}}T$ and χ^{-1} for **1** measured at 1 kOe. The red line represents Curie-Weiss fit.

Kmol^{-1} , which is slightly smaller than the spin-only value of $9.125 \text{ cm}^3 \text{ Kmol}^{-1}$ for the $\text{Mn}^{\text{II}}\text{Mo}^{\text{III}}$ unit ($S_{\text{Mo}} = 1/2$, $S_{\text{Mn}} = 5/2$, $g = 2.0$). Upon cooling, the $\chi_{\text{M}}T$ value increases slowly until about 25 K and then it increases abruptly to a maximal value of $102.2 \text{ cm}^3 \text{ Kmol}^{-1}$ at 5 K with a further rapid decrease to a value of $50.88 \text{ cm}^3 \text{ Kmol}^{-1}$ at 2 K. A Curie-Weiss fit of the data above 50 K gives the Curie constant $C = 8.63 \text{ cm}^3 \text{ Kmol}^{-1}$ and Weiss constant $\theta = 5.26 \text{ K}$. As has been confirmed by the neutron diffraction experiment on a $\text{Mn}^{\text{II}}\text{--}[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ compound,¹⁸ the observed increase of the $\chi_{\text{M}}T$ plot upon cooling at high-temperature region and the positive θ value are not necessarily corresponding to the ferromagnetic $\text{Mn}^{\text{II}}\text{--Mo}^{\text{III}}$ interactions. Actually, antiferromagnetic interactions have been confirmed in several low-dimensional $\text{Mn}^{\text{II}}\text{--}[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ compounds.¹⁵ The sharp peak at 5 K in the $\chi_{\text{M}}T$ plot indicates the blocking of the magnetic moments, which is further confirmed by the field-cooled (FC) and zero-field-cooled

(ZFC) magnetization measured at $H_{\text{dc}} = 10 \text{ Oe}$. As can be seen in Figure 3, the ZFC data exhibits a peak and diverges from the

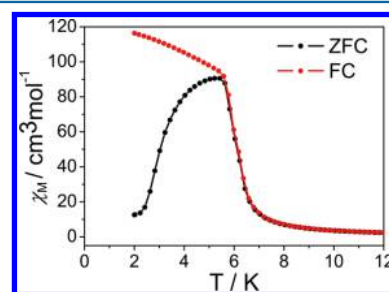


Figure 3. Temperature dependence of ZFCM and FCM of **1**.

FC curve at about 5.6 K. These results suggest the existence of either the long-range magnetic ordering or slow magnetic relaxation, such as that found for glassy magnets or SCMs, by considering the chain structure of **1**.

To further verify the nature of the magnetic blocking of **1**, ac susceptibility data were performed under a zero dc field with $H_{\text{ac}} = 2 \text{ Oe}$ at different frequencies (Figure 4). Both the in-

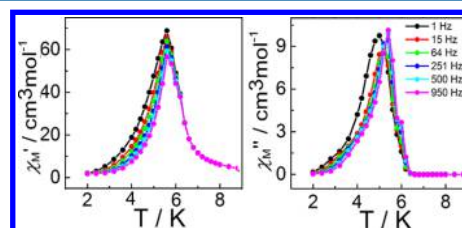


Figure 4. Temperature dependent ac susceptibility of **1** at different frequencies under $H_{\text{dc}} = 0 \text{ Oe}$ and $H_{\text{ac}} = 2 \text{ Oe}$.

phase (χ') and out-of-phase (χ'') signals show sharp peaks. The peak temperatures (T_{p}) in the χ' curve of 5.6 K are in accordance with the peak temperature in ZFCM curve. In addition, a very small frequency dependence for both the χ' and χ'' data was observed, with a small Mydosh parameter $\phi = (\Delta T_{\text{p}}/T_{\text{p}})/(\Delta \log f) = 0.005$. This small ϕ value is typical for a spin glass and much smaller than that expected for a superparamagnet such as a SCM.¹⁹ This result rules out the possibility of the SCM behavior of **1**. From a structural point of view, the large amounts of interchain H-bonds should lead to the interchain magnetic coupling and the long-range magnetic ordering of **1**, while the severe disorder of the $\text{L}_{\text{NSC}10}$ ligand accounts for the glassy behavior as observed.

Finally, the field dependent magnetization $M(H)$ of **1** was measured (Figure 5). At 2.0 K, M increases rapidly at low fields and reaches a value of $9.47 \mu_{\text{B}}$ at 70 kOe. This value is

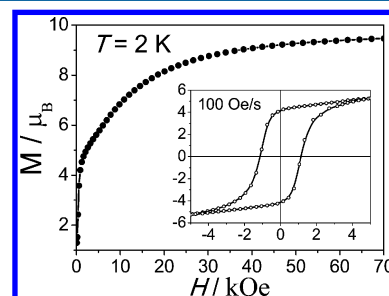


Figure 5. Field dependent magnetization and the hysteresis loop of **1**.

obviously lower than $11.0 \mu_B$ for the ferromagnetically coupled two Mn^{II} and one Mo^{III} ions, while close to the $9.00 \mu_B$ for the ferrimagnetic arrangement. This further confirms the anti-ferromagnetic coupling between the Mn^{II} and Mo^{III} centers. Interestingly, an obvious magnetic hysteresis loop was observed, with a coercive field H_c of 1150 Oe and a remnant magnetization M_R of $4.18 \mu_B$ (Figure 5).

In summary, we have reported here the synthesis, structure, and magnetic characterization of the first 1D magnetic compound based on the heptacyanomolybdate. Because of the interchain magnetic coupling and the inherent disorder, long-range magnetic ordering with a spin glass character, rather than a SCM behavior, was observed for **1**. Together with our former low-dimensional $[Mo^{III}(CN)_7]^{4-}$ based complexes, results reported here clearly demonstrate the feasibility by using a macrocyclic ligand to efficiently block the available coordination sites and to prepare new low-dimensional $[Mo^{III}(CN)_7]^{4-}$ based materials such as SMMs and SCMs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00787.

Experimental details, crystallographic data, additional structural figures, XRD, TG (PDF)
X-ray crystallographic file (CIF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: weihaiyan@nju.edu.cn (H.-Y.W.).

*E-mail: wangxy66@nju.edu.cn (X.-Y.W.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Major State Basic Research Development Program (2013CB922102), NSFC (21522103, 21471077), and the NSF of Jiangsu province (BK20150017).

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