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Vanadium(II) Heptacyanomolybdate(III)-Based Magnet Exhibiting a High Curie Temperature of 110 K

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We prepared a vanadium heptacyanomolybdate-based magnet, $V^{II}_2[Mo^{III}(CN)_7]\cdot(pyrimidine)_2\cdot 4.5H_2O$ (**VMo**), with a Curie temperature (T_C) of 110 K, which is the highest T_C value in $[Mo^{III}(CN)_7]$-based magnets. Additionally, $Mn^{II}_2[Mo^{III}(CN)_7]\cdot(pyrimidine)_2\cdot 2H_2O$ (**MnMo**) of a monoclinic structure ($P2_1/n$) with T_C = 47 K was prepared to confirm the crystal structure of **VMo**.

In molecule-based magnets,[1] preparing compounds with a high Curie temperature (T_C) is a challenging issue.[2,3] In cyano-bridged metal assemblies,[4] high T_C values have been reported using a V^{II}-containing system.[5] Recently, octacyanometalate $[M(CN)_8]$ (M = Mo, W, Nb)-based magnets have been aggressively studied because of their high T_C and functionalities such as photomagnetism and chemically sensitive magnetism.[6] Heptacyanometalate $[Mo(CN)_7]$-based magnets have also attracted attention because of their high coordination numbers around the metal ions and various coordination geometries, e.g., pentagonal bipyramid (D_{5h}), monocapped octahedron (C_{3v}), and capped trigonal prism (C_{2v}).[7g] In addition, heptacyanomolybdate has a large magnetic anisotropy, which hexacyanometalate and octacyanometalate lack. However, because of handling difficulties, heptacyanometalate-based magnets are not as well researched. Some heptacyanomolybdate-based magnets, including $Mn_2[Mo(CN)_7]\cdot nH_2O$ and $[Mn(N,N\text{-dimethylalaninolH})]_2Mn[Mo(CN)_7]_2\cdot nH_2O$, have been

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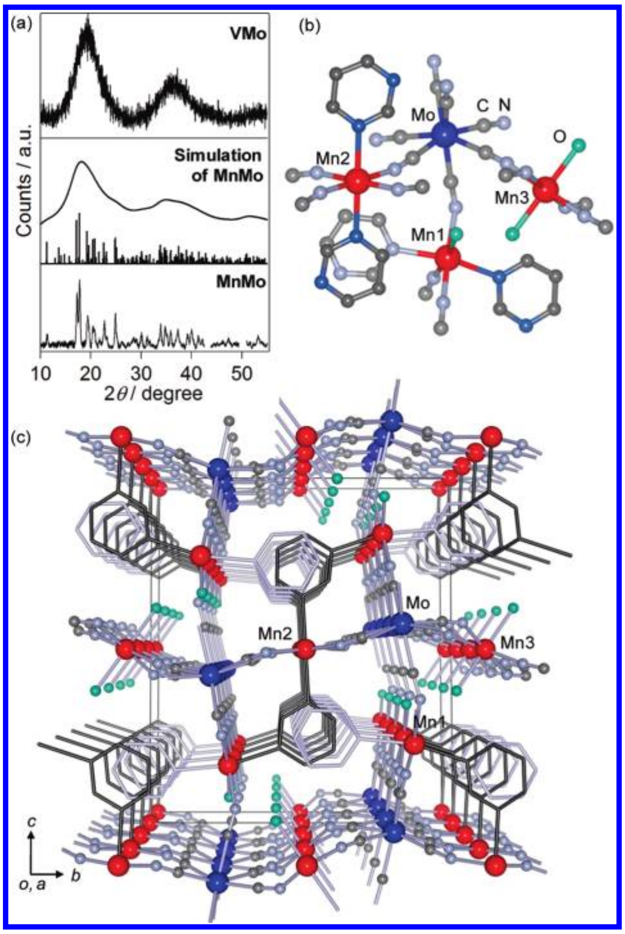

Figure 1. (a) Powder XRD pattern of **VMo** (top), simulated diffraction pattern and intensities of the Bragg reflections based on the crystal structure of **MnMo** (middle; line and sticks), and the powder XRD pattern of powder-form **MnMo** (bottom). The peaks of a Cu sample holder are omitted for clarity. (b) Coordination environments around Mo and Mn. (c) Crystal structure of the 3D $Mn^{II}-Mo^{III}$ framework. H atoms are omitted for clarity. Blue, red, gray, light-blue, and light-green balls represent Mo, Mn, C, N, and O, respectively. Dark and light hexagons represent bidentate and monodentate pyrimidines, respectively.

reported.[7] Although the combination of V^{II} and heptacyanomolybdate has the potential of realizing high-T_C molecular magnets, a $V^{II}[Mo(CN)_7]$-based magnet has yet to be reported. Herein we report a $V^{II}[Mo(CN)_7]$-based ferrimagnet, $V^{II}_2[Mo^{III}(CN)_7]\cdot(\text{pyrimidine})_2\cdot 4.5H_2O$ (**VMo**), which has a high Curie temperature of 110 K. In addition, to confirm the crystal structure of **VMo**, $Mn^{II}_2[Mo^{III}(CN)_7]\cdot(\text{pyrimidine})_2\cdot 2H_2O$ (**MnMo**) (T_C = 47 K) was synthesized.

The powder form of **VMo** was obtained by adding 2.5 mL of a deoxygenated aqueous solution of $K_4[Mo(CN)_7]\cdot 2H_2O$[8] (5×10^{-2} mol dm^{-3}) to 2.5 mL of a mixed deoxygenated aqueous solution of $(NH_4)_2V(SO_4)_2\cdot 6H_2O$ (1×10^{-1} mol dm^{-3}) and pyrimidine (2 mol dm^{-3}) under an argon atmosphere. The purplish-black precipitate was filtered, washed with water, and then dried in argon. The IR spectrum displayed a CN stretching peak at 2074 cm^{-1}. Our attempts to prepare a single crystal were unsuccessful. Elemental analyses by the standard microanalytical method, inductively coupled plasma mass spectroscopy, and ion chromatography analysis confirmed that the formula was $V^{II}_2[Mo^{III}(CN)_7]\cdot(\text{pyrimidine})_2\cdot 4.5H_2O$ with a small amount of impurity of $0.08K_2SO_4$. Calcd: V, 16.4; Mo, 15.5; C, 29.0; H, 2.8; N, 24.8. Found: V, 16.4; Mo, 15.2; C, 29.2; H, 2.8; N, 24.6. To confirm the crystal structure of the powder form of **VMo**, a single crystal of **MnMo** was prepared.[9] The formula was $Mn^{II}_2[Mo^{III}(CN)_7]\cdot(\text{pyrimidine})_2\cdot 2H_2O$. Calcd: Mn, 18.8; Mo, 16.4; C, 30.8; H, 2.1; N, 26.4. Found: Mn, 18.7; Mo, 16.6; C, 30.5; H, 2.4; N, 26.3.

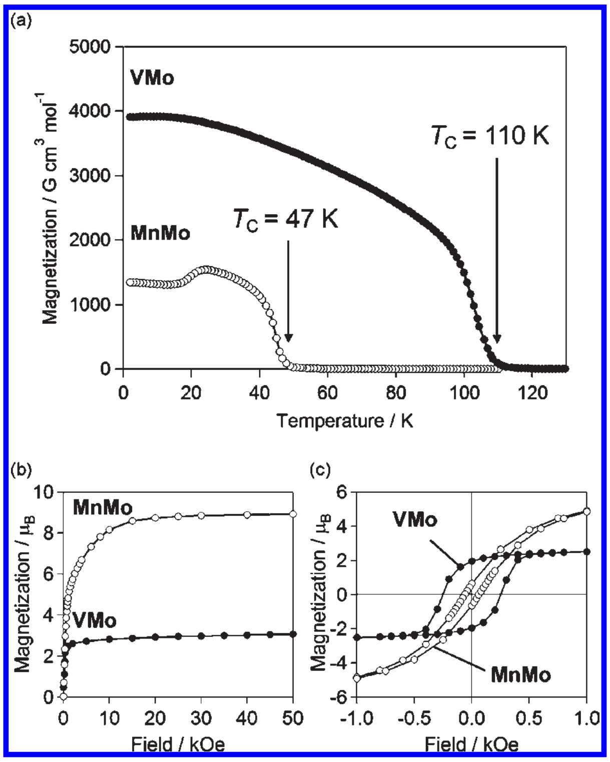

Figure 2. Magnetic properties of **VMo** (filled circles) and **MnMo** (open circles). (a) FCM versus temperature plots in an external magnetic field of 10 G. (b) Saturation magnetization curves at 2 K. (c) Magnetic hysteresis loops at 2 K.

The powder X-ray diffraction (XRD) pattern of **VMo** displayed broad peaks around 19, 37, and 54° (Figure 1a, top). To determine the crystal structure, the XRD pattern of **VMo** was compared to the single-crystal X-ray analysis data of **MnMo**.[10] Single-crystal X-ray analysis of **MnMo** indicated that this compound belonged to the monoclinic structure of space group $P2_1/n$ [a = 7.20778(13) Å, b = 15.7128(3) Å, c = 18.1688(3) Å, β = 95.0877(7)°, and Z = 4]. The coordination

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(9) Reacting a deoxygenated aqueous solution of $K_4[Mo(CN)_7]\cdot 2H_2O$ (5×10^{-3} mol dm^{-3}) with a deoxygenated aqueous solution of $Mn(NO_3)_2\cdot 6H_2O$ (1×10^{-2} mol dm^{-3}) containing pyrimidine (2×10^{-1} mol dm^{-3}) in an H-shaped tube under an argon atmosphere gave a green-brown single crystal of **MnMo**. The IR spectrum had a CN stretching peak at 2084 cm^{-1}.

(10) Single-crystal X-ray analysis of **MnMo** indicated that this compound belonged to the monoclinic structure of space group $P2_1/n$ [a = 7.20778(13) Å, b = 15.7128(3) Å, c = 18.1688(3) Å, β = 95.0877(7)°, and Z = 4]. The structure was solved by direct methods and refined on F^2 to R1 (wR2) = 0.0196 (0.0631) using 4365 reflections with $F^2 > 2.0\sigma(F^2)$ (Table S1 in the Supporting Information). The non-H atoms were anisotropically refined. The H atoms of pyrimidine and water were refined isotropically. The asymmetric unit consisted of a $[Mo(CN)_7]^{4-}$ anion, a $[Mn1(\text{pyrimidine})(H_2O)]^{2+}$ cation, half of a $[Mn2(\text{pyrimidine})_2]^{2+}$ cation, and half of a $[Mn3(H_2O)_2]^{2+}$ cation (Figure S1 in the Supporting Information).

geometries of Mn (Mn1, Mn2, and Mn3) and Mo were near to an octahedron (O_h) and near to a capped octahedron (C_{3v}), respectively. The seven CN ligands of $[Mo(CN)_7]^{4-}$ were bridged to three Mn1, two Mn2, and two Mn3. The four equatorial positions of Mn1 were occupied by three N atoms of $[Mo(CN)_7]$ and one O atom of a water ligand, while the apical positions were occupied by two N atoms from pyrimidine molecules. Mn2 was coordinated by four cyanide N atoms and two N atoms from pyrimidine. Mn3 was coordinated by four cyanide N atoms and two O atoms from the water ligands (Figure 1b). Figure 1c shows the crystal structure of **MnMo**. $[Mo^{III}(CN)_7]^{4-}$ and Mn^{II} formed a three-dimensional (3D) cyano-bridged network. The middle and bottom XRD patterns of Figure 1a show the simulated XRD pattern and the experimental powder XRD pattern of the powder-form **MnMo**, respectively. The observed XRD pattern of **VMo** and the calculated pattern of **MnMo** agree well, suggesting that the crystal structure of **VMo** is same as the 3D structure of **MnMo**.[11]

The value of the product of the molar magnetic susceptibility (χ_M) and temperature, $\chi_M T$, of **VMo** was 3.9 cm^3 K mol^{-1} at room temperature (Figure S3 in the Supporting Information), which corresponds to the spin-only value of 4.1 cm^3 K mol^{-1} for Mo^{III} ($S = {}^1/_2$) and $2V^{II}$ ($S = {}^3/_2$). Figure 2 shows the magnetization versus temperature plots of **VMo**. In the field-cooled magnetization (FCM) curve at 10 Oe, spontaneous magnetization appeared at $T_C = 110$ K.[12] The magnetization versus external magnetic field plots at 2 K showed that the M_S value was 3.0 μ_B,[13] while the magnetic hysteresis loop had a coercive field (H_c) of 300 Oe at 2 K (Figure 2b,c). The magnetic properties of **MnMo**, which is a sample composed of numerous single crystals, exhibited ferrimagnetism with $T_C = 47$ K, $M_S = 9.0\ \mu_B$, and $H_c = 60$ Oe at 2 K. The high T_C of **VMo** is likely due to (i) the diffuse 4d orbitals of Mo, which enable an effective superexchange interaction through the cyano groups, and (ii) the high-energy 3d orbitals of V, which lead to a good energy match with the magnetic orbital of $[Mo(CN)_7]^{4-}$.[5,6a]

In conclusion, we prepared $V^{II}_2[Mo^{III}(CN)_7]\cdot(pyrimidine)_2\cdot 4.5H_2O$, a heptacyanomolybdate-based ferrimagnet with a high Curie temperature of 110 K. The observed T_C is the highest value among reported heptacyanomolybdate-based magnets. We believe that a higher T_C will be realized in $[Mo^{III}(CN)_7]$-based magnets by controlling the coordination geometries of V and Mo and by selecting the appropriate organic ligand.

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Supporting Information Available: Instrumentation, single-crystal X-ray structural analysis for **MnMo**, $\chi_M T-T$ plots of **VMo**, and a crystallographic information data file in CIF format for **MnMo**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The broadening of the XRD pattern in **VMo** is considered to be due to the low crystallinity derived from the lack of V^{2+} and $[Mo(CN)_7]^{4-}$ from the lattice. The defects will be occupied by water molecules, resulting in the number of water molecules on **VMo** being higher than that of **MnMo**.

(12) Five batches of **VMo** synthesis under the same reaction conditions showed the same magnetic properties, indicating that the present **VMo** can be obtained reproducibly.

(13) This M_S value of **VMo** is closed to the expected saturation value of 5.0 μ_B, assuming that this compound is a ferrimagnet with antiferromagnetic interaction between V^{II} ($S = {}^3/_2$) and Mo^{III} ($S = {}^1/_2$). This difference of M_S values may be due to the low crystallinity of the prepared sample.