Manganese(II) Octacyanotungstate(V)-Based Magnet Containing a Noncoordinated Aromatic Molecule

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Transition metal complex-assemblages containing noncoordinated molecules have drawn attention due to functionalities such as gas storage and molecular recognition.[1,2] When such materials have a ferromagnetic character, various novel magnetic functionalities may be realized. However, the preparation of ferromagnetic metal-assembled complexes that contain a noncoordinated molecule is difficult because problems such as weak magnetic coupling between spin sources and low coordinate numbers around metal ions must be overcome. In particular, there are few reports of ferromagnetic metal-assembled complexes containing a noncoordinated aromatic molecule.[3] Polycyanometalates have received attention in the synthesis of new molecule-based magnets due to their high T_C and interesting functionalities.[4,5] Recently, octacyanometalate-based magnets have been aggressively studied. The materials of this series can take various coordination geometries in the crystal structure, that is, zero-dimensional (0-D), 1-D, 2-D, and 3-D.[6] For example, a $Cs^I[\{Mn^{II}(3\text{-cyanopyridine})_2\}\{W^V(CN)_8\}]\cdot H_2O$ ferrimagnet (T_C = 35 K) consists of a 2-D grid layer structure. If such a 2-D cyano-bridged bimetallic layer is linked with a pillar molecule, one can obtain a high T_C magnetic material containing a noncoordinated molecule or having a channel structure. Herein, we report a manganese(II) octacyanotungsten(V)-based magnet (T_C = 47 K) which contains a noncoordinated aromatic molecule, $[\{Mn^{II}(pyrimidine)(H_2O)\}_2\{Mn^{II}(H_2O)_2\}\{W^V(CN)_8\}_2](pyrimidine)_2\cdot 2H_2O$.

This compound was prepared by adding a 5 cm³ aqueous solution of $Cs^I_3[W^V(CN)_8]\cdot 2H_2O^7$ (0.516 g, 0.620 mmol) to a 5 cm³ mixed aqueous solution of $Mn^{II}Cl_2\cdot 4H_2O$ (0.191 g, 0.936 mmol) and pyrimidine (0.100 g, 1.25 mmol) at room temperature. The resulting dark yellow solution was left in the dark for 12 h, and dark brown prismatic crystals were obtained. These crystals were separated by filtration, washed with water, and dried in air. This procedure resulted in a 36% yield. In the IR spectra, CN stretching peaks due to $W^V(CN)_8$ were observed at 2183, 2176, 2172, 2168, 2164, 2160, and 2153 cm⁻¹. Elemental analyses by inductively coupled plasma mass spectroscopy and a standard microanalytical method confirmed that the formula of the compound is $[\{Mn^{II}(pyrimidine)(H_2O)\}_2$-$\{Mn^{II}(H_2O)_2\}\{W^V(CN)_8\}_2](pyrimidine)_2\cdot 2H_2O$. Anal. Calcd: Mn, 12.0; W, 26.7; C, 27.9; H, 2.1; N, 24.4. Found: Mn, 12.3; W, 26.3; C, 27.8; H, 2.1; N, 24.6.

Single-crystal X-ray structural analysis[8] shows that the asymmetric unit consists of a $[W(CN)_8]^{3-}$ anion, a $[Mn1(pyrimidine)$-$(H_2O)]^{2+}$ cation, one-half of a $[Mn2(H_2O)_2]^{2+}$ cation, a water molecule, and a noncoordinated pyrimidine (Figure 1a). The coordination geometries of Mn (Mn1 and Mn2) and W sites are pseudo-
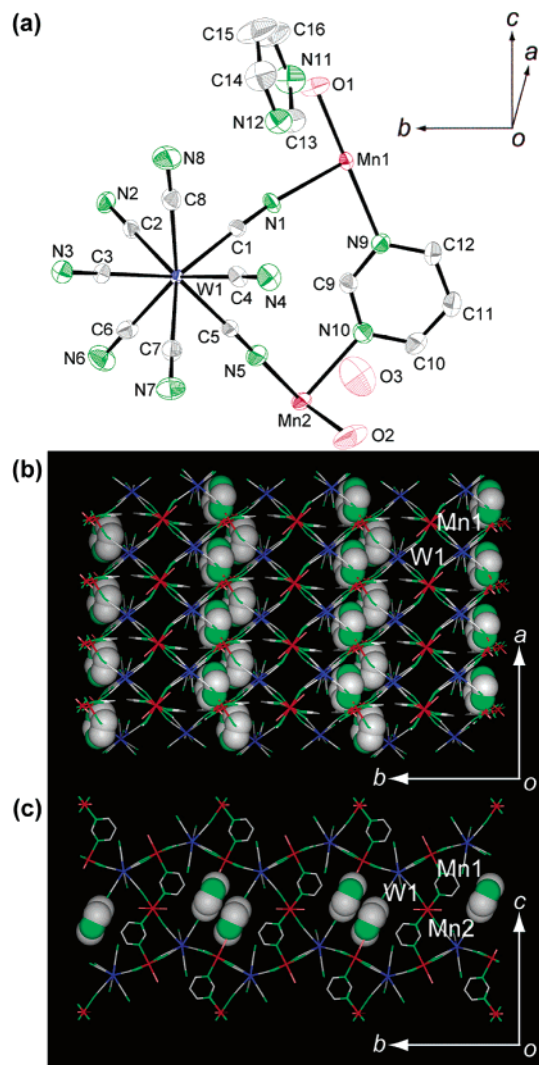

Figure 1. The X-ray crystal structure at 293 K for the complex [{Mn^II-(pyrimidine)(H_2O)}_2{Mn^II(H_2O)_2}{W^V(CN)_8}_2](pyrimidine)_2·2H_2O; the framework atoms are represented as sticks, and the atoms of noncoordinated pyrimidine molecules are represented as spheres. Blue, red, white, green, and pink balls represent W, Mn (Mn1 or Mn2), C, N, and O, respectively. Zeolitic water molecules and hydrogen atoms are omitted for clarity. (a) Thermal ellipsoid plot showing the asymmetric unit and atom numbering scheme. (b) A view perpendicular to the grid layer. (c) A view parallel to the grid layer.

octahedron (D_{4h}) and bicapped trigonal prism (C_{2v}), respectively. The four equatorial positions of Mn1 are occupied by cyanide nitrogen atoms of $[W(CN)_8]$, while the apical positions are occupied

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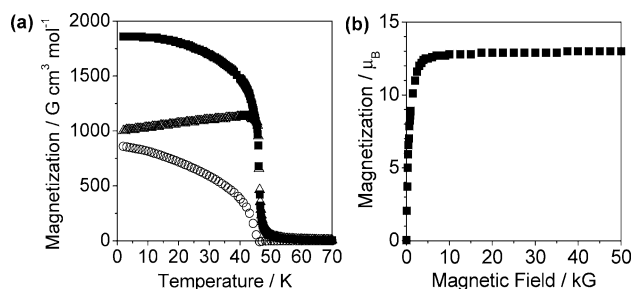§ Institute of Industrial Science, The University of Tokyo.

Figure 2. (a) The magnetization versus temperature plots: (■) field-cooled magnetization (FCM) obtained with decreasing temperature (70 K → 2 K) in an external magnetic field of 10 G; (△) zero-field-cooled magnetization (ZFCM) with increasing temperature (2 K → 70 K) in an applied magnetic field of 10 G after the temperature was first lowered in the zero field; (○) remanent magnetization (RM) obtained with increasing temperature (2 K → 70 K) after the temperature was first lowered in an applied magnetic field of 10 G. (b) Magnetization versus external magnetic field plots at 2 K.

by one nitrogen atom of the pyrimidine and one oxygen atom of the water ligand. Mn2 is coordinated to two nitrogen atoms of [W(CN)$_8$], two oxygen atoms of water ligands, and two nitrogen atoms of pyrimidines. Five CN groups of [W(CN)$_8$] bridge to four Mn1 and one Mn2, and the other three CN groups are free. The shortest Mn1–W and Mn2–W distances are 5.43 and 5.49 Å, respectively. The cyano-bridged Mn1–W layer (Figure 1b) is linked by Mn2 pillar unit (Figure 1c). The average interlayer distance through the pillar moiety is 11.24 Å. There exists a 1-D channel structure along the *a* axis between the 2-D grid layers. The size and volume of this channel are estimated to be 6.2 × 2.1 Å and 7.7% of crystal volume, respectively, calculated by subtracting the van der Waals radii of the framework atoms. This channel is occupied by noncoordinated pyrimidine molecules. The positions of the nitrogen atoms of noncoordinated pyrimidine molecules are governed by the hydrogen bond between the nitrogen atom of pyrimidine and the ligand water molecule of Mn1 (N(pyrimidine)···H$_2$O = 2.813(7) Å).

The magnetizations versus temperature plots of this compound are shown in Figure 2a. In the field-cooled magnetization (FCM) curve at $B_0 = 10$ G, spontaneous magnetization appeared at $T_C = 47$ K. The zero-field-cooled magnetization (ZFCM) and remanent magnetization (RM) curves supported this T_C value. The magnetization versus external magnetic field plots showed that the saturation magnetization (M_S) value was 13.0 μ_B at 2 K (Figure 2b). The magnetic hysteresis loop showed that the coercive field (H_C) was 17 G at 2 K. The product of molar magnetic susceptibility (χ_M) and temperature, $\chi_M T$, value was 13.3 cm^3 K mol^{-1} (10.3 μ_B) at room temperature. This value corresponds to the spin-only value of 13.9 cm^3 K mol^{-1} (10.5 μ_B) for 3 × Mn^{II} ($S = {}^5/_2$) and 2 × W^V ($S = {}^1/_2$) (Supporting Information). The M_S value agrees with the expected saturation value of 13.0 μ_B, assuming that this compound is a ferrimagnet, indicating that an antiferromagnetic interaction operates between the W^V and Mn^{II} ions. Weiss temperature (θ) was estimated to be −45 K from the temperature dependence of χ_M^{-1} values. This value also supports the ferrimagnetism. This mechanism of ferrimagnetism is discussed on the basis of the DV-Xα calculation[9] in the Supporting Information.

In summary, we have prepared a pillared layer magnetic material containing pyrimidine as a noncoordinated aromatic molecule, [{Mn^{II}(pyrimidine)(H$_2$O)}$_2${Mn^{II}(H$_2$O)$_2$}{W^V(CN)$_8$}$_2$](pyrimidine)$_2$·

2H$_2$O. In this system, a magnetic 2-D cyano-bridged Mn1–W grid layer was linked by a pillar complex of Mn2, and a ferromagnetic metal-assembled complex ($T_C = 47$ K) containing a noncoordinated aromatic molecule was obtained. Because new building blocks for cyanide-bridged metal complexes are currently being prepared,[10] various pillared layer materials will be generated using cyanide-bridged metal complexes soon.

Supporting Information Available: X-ray crystallographic file in CIF format. Information relating to the unit cell, the magnetic hysteresis loop, and the mechanism of ferrimagnetism (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for [{Mn^{II}(pyrimidine)(H$_2$O)}$_2${Mn^{II}(H$_2$O)$_2$}{W^V(CN)$_8$}$_2$]-(pyrimidine)$_2$·2H$_2$O: C$_{32}$H$_{28}$ N$_{24}$Mn$_3$O$_6$W$_2$, FW 1377.24; monoclinic; space group *P*2$_1$/*n* (No. 14); *a* = 7.247(2) Å; *b* = 14.983(5) Å; *c* = 22.489-(7) Å; *β* = 90.905(3)°; *V* = 2441.4(13) Å^3; *Z* = 2; d_{calcd} = 1.87 g/cm^3; *T* = 293(1) K. Of the 20 926 reflections that were collected, 5815 were unique (R_{int} = 0.054). The structure was solved by heavy-atom Patterson methods and refined on *F* to *R* (R_W) = 0.026 (0.073) using 3708 reflections with *I* > 3.00σ(*I*). The non-hydrogen atoms were anisotropically refined. Hydrogen atoms of pyrimidine were refined isotropically. All calculations were performed using the CrystalStructure crystallographic software package.
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