Crystal Structure and Magnetic Properties of Two-dimensional Cyanide-bridged Bimetallic Assembly Composed of $Cs^I[Mn^{II}(3\text{-cyanopyridine})_2\{W^V(CN)_8\}]\cdot H_2O$

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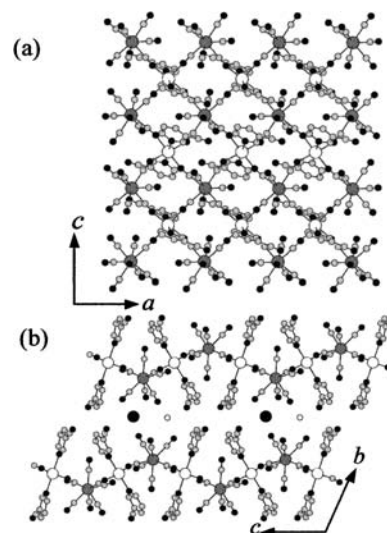[††]*Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505*

We have synthesized a two-dimensional manganese(II) octacyanotungstate(V)-based ferrimagnet with a magnetic ordering temperature of 35 K. Single crystal analysis showed that Mn^{II} ion was axially capped by 3-cyanopyridines, forming a two-dimensional structure. This bimetallic assembly showed ferrimagnetic properties due to the antiferromagnetic interaction between magnetic orbitals of d_{z^2} on W^V ion and $d_{x'y'}$ on Mn^{II} ion in the inside of the two dimensional layer.

There has been a great interest in the preparation of molecule-based magnets in the last 15 years.[1,2] Hexacyanometalates $[M(CN)_6]^{n-}$ have been often used as a molecular building block of molecule-based magnets. One of reasons of this is that a magnetic structure can be rationally designed because of the octahedral coordination geometry of $[M(CN)_6]^{n-}$.[3] Octacyanometalates $[M(CN)_8]^{n-}$ (M = Mo, W; n = 4, 5) are also an attractive building block.[4] They can take various coordination geometries such as square antiprism (D_{4h}), dodecahedron (D_{2d}), and bicapped trigonal prism (C_{2v}).[5] In addition, their assembled metal compounds could form various dimensional crystal structures, e.g., zero-, one-, two-, and three-dimensional structures. We may obtain such a various structures by choosing coordinated molecules. For example, in the system of cyano-bridged manganese(II) octacyano-tungstate(V) with a coordinated molecule of H_2O, a three-dimensional ferrimagnet $[Mn^{II}_6(H_2O)_9\{W^V(CN)_8\}_4\cdot13H_2O]_n$ with a magnetic ordering temperature (T_c) of 54 K was obtained.[6] In contrast, when a coordinated molecule was an ethanol, a zero-dimensional structural cluster $\{Mn^{II}_9[W^V(CN)_8]_6\cdot24C_2H_5OH\}$ ($S = 39/2$) was obtained.[7] In this paper, we report a two-dimensional cyano-bridged manganese(II)-tungsten(V)-based magnet, $Cs^I[Mn^{II}(3\text{-cyanopyridine})_2\{W^V(CN)_8\}]\cdot H_2O$ (**1**), and its magnetic properties.

The compound **1** was prepared by mixing an aqueous solution of $Cs_3[W(CN)_8]$ and an aqueous solution containing $MnCl_2$ and 3-cyanopyridine.[8] In the IR spectra, two CN stretching peaks of 3-cyanopyridine ($\nu_{C\equiv N}$ = 2246, and 2240 cm^{-1}) and seven peaks due to bridged CN ligands between W^V and Mn^{II} ions ($\nu_{C\equiv N}$ = 2182, 2177, 2161, 2155, 2150, 2145, and 2140 cm^{-1}) were observed.[9–11] The single crystal X-ray structural analysis showed that **1** consisted of a two-dimensional layer of cyano-bridged manganese(II)-tungstate(V) (Figure 1).[12] In the inside of layer, four CN ligands of $[W(CN)_8]^{3-}$ bridged to Mn ion and other four were free. In contrast, Mn ion was coordinated by six nitrogen atoms of two 3-cyanopyridine molecules and four CN groups. Cs^I ion and H_2O molecule intercalated between the layers. The shortest W–W and W–Mn distances between the layers were 9.33 Å and 11.25 Å, respectively. The average
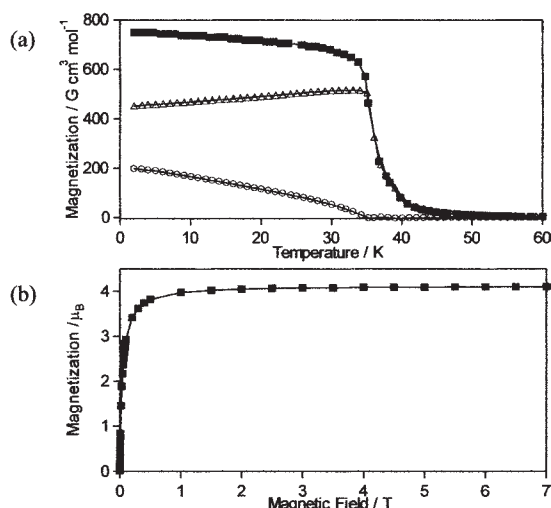

Figure 1. The crystal structure of **1**. (a) View of a layer along the b^* direction. (b) View of two layers along the a direction. Large white, large gray, large black, small black, small gray, and small white balls represent Mn, W, Cs, C, N, and O, respectively. H atoms are omitted for clarity.
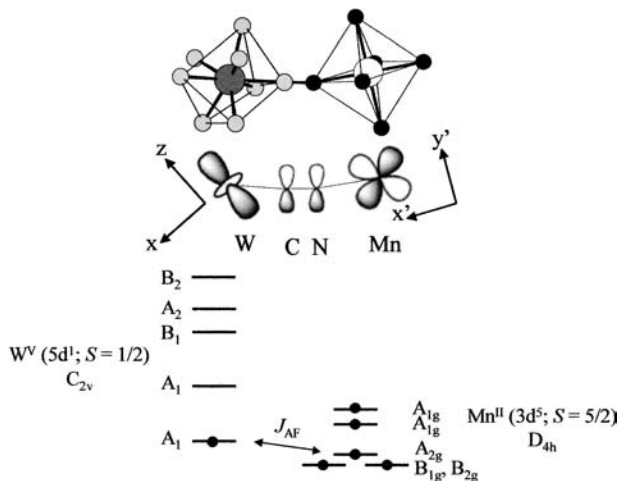
interlayer distance was 12.42 Å. The coordination geometries of W and Mn sites were bicapped trigonal prism (C_{2v}) and pseudo-octahedron (D_{4h}), respectively. The reason why the present compound forms a two-dimensional layer is that the axial positions of Mn ion are capped by 3-cyanopyridine molecules, and only equatorial positions are available for bridging with $[W(CN)_8]^{3-}$.

The magnetization vs temperature plots for **1** are shown in Figure 2a. The spontaneous magnetization appeared at a T_c of 35 K. The magnetization vs external magnetic field plot showed that the coercive field (H_c) was about 1 G[13] and the saturation magnetization (M_s) value was 4.1 μ_B at 5 K (Figure 2b). This M_s value is close to the expected saturation value of 4.0 μ_B assuming that the present compound is a ferrimagnet. This result suggests that an antiferromagnetic interaction operates between W^V ($S = 1/2$) and Mn^{II} ($S = 5/2$) ions in the inside of the layer[14] and a ferromagnetic interaction operates between the layers.

We considered the origin of the ferrimagnetism in this compound, based on the results of DV-Xα calculation[15] of $W(CN)_8$ and $Mn(NC)_4(3\text{-cyanopyridine})_2$ units. For the calculation, the atomic coordinates determined by X-ray analysis were used. A_1 (d_{z^2}) orbital is occupied by an unpaired electron of $[W(CN)_8]^{3-}$ and five 3d orbitals (B_{1g}, B_{2g}, A_{2g}, and two A_{1g}) are occupied by unpaired electrons of Mn^{II} as shown in Figure 3. Although the molecular symmetrical axes of these metal ions are twisted, the antiferromagnetic superexchange interaction (J_{AF}) is

Figure 2. (a) The magnetization vs temperature plots of **1**: (■) field-cooled magnetization obtained with decreasing temperature (60 K → 2 K) in an external magnetic field of 10 G; (△) zero-field-cooled magnetization with increasing temperature (2 K → 60 K) in the applied magnetic field of 10 G after the temperature was first lowered in zero field; (○) remanent magnetization obtained with increasing temperature (2 K → 60 K) after the temperature was first lowered in the applied magnetic field of 10 G. (b) Magnetization vs external magnetic field plots of **1** at 5 K.

Figure 3. Schematic illustration of π-like orbital interaction between W^V and Mn^{II} through the bridged cyanide (top), and the electronic configuration on W^V and Mn^{II} sites, based on the DV-Xα calculation of $W(CN)_8$ and $Mn(NC)_4$(3-cyanopyridine)$_2$ units (bottom).

expected to operate between the A_1 (d_{z^2}) magnetic orbital of W^V and A_{2g} ($d_{x'y'}$) one of Mn^{II} through the cyano-bridge, resulting in an antiparallel ordering of magnetic spins of W^V and Mn^{II} in the inside of the layer. In contrast, the dipole-dipole interaction may cause a ferromagnetic interaction among layers.[16]

In summary, we have prepared a new type of two-dimensional cyano-bridged Mn–W molecule-based magnet with a T_c of 35 K. So far, we have prepared a zero-, two-, and three-dimensional magnetic compounds in Mn–W cyano-bridged system. The key of the strategy to control the dimensionality in this system is the choice of an adequate coordinated molecule. It is theoretically predicted that a spontaneous magnetization should

not appear in the Heisenberg type of two-dimensional magnetic materials. However, the interlayer distance is not large enough to neglect the interactions operating between layers. If larger organic molecules are used as a coordinated molecule in this system, pure two-dimensional magnetic materials may be obtained. Furthermore, the structural and dimensional flexibilities of octacyanotungstate-based magnets allow us to design a new functional magnet such as photo-induced magnetization.[4a,4b,17] The works along this line are under way.

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8 The compound **1** was prepared by the reaction of $Cs_3[W(CN)_8] \cdot 2H_2O$ with 1 equiv of $MnCl_2 \cdot 4H_2O$ and 2 equiv of 3-cyanopyridine in an aqueous solution at room temperature. The obtained compound was a dark purple prismatic crystal. Its elemental analyses were carried out by standard microanalytical methods and inductively coupled plasma optical emission. Found: C, 29.8; H, 1.36; N, 20.7; Cs, 16.0; Mn, 6.83; W, 22.8. Calcd for: $C_{20}H_{10}CsMnN_{12}OW$: C, 29.9; H, 1.25; N, 20.9; Cs, 16.5; Mn, 6.82; W, 22.8.

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12 Crystal data for $Cs^I[Mn^{II}(3\text{-cyanopyridine})_2\{W^V(CN)_8\}] \cdot H_2O$: $C_{20}H_{10}N_{12}OMnCsW$, fw = 806.07; triclinic; space group $P\text{-}1$; $a = 7.3394(6)$ Å; $b = 13.907(1)$ Å, $c = 14.687(2)$ Å; $\alpha = 115.915(9)°$, $\beta = 90.076(10)°$, $\gamma = 96.058(9)°$; $V = 1339.0(3)$ Å^3; $Z = 4$; $d_{calcd} = 1.999$ g/cm^3; $T = 296(1)$ K. Of the collected 6622 reflections, 6143 were unique ($R_{int} = 0.026$). The structure was solved by the heavy-atom Patterson methods and refined on F to R (R_w) = 0.037 (0.042) using 4983 reflections with I > 3.00σ(I). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.

13 The small H_c value is due to small single ion anisotropy of Mn^{II} and W^V ions.[6]

14 The observed χT value of 3.70 G cm^3 mol^{-1} at $T = 300$ K was lower than spin-only value of 4.75 G cm^3 mol^{-1}. This result also indicates that the present compound is a ferrimagnet. Note that the local minimum point in the $\chi T - T$ plots was not observed in the temperature range of 35 K < T < 300 K. It is expected that the local minimum point may exist in higher temperature region.[6]

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