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Vanadium Octacyanoniobate-Based Magnet with a Curie Temperature of 138 K

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In this work, we prepared a three-dimensional vanadium octacyanoniobate-based magnet, $K_{0.10}V^{II}_{0.54}V^{III}_{1.24}[Nb^{IV}(CN)_8]\cdot(SO_4)_{0.45}\cdot 6.8H_2O$. This compound exhibits ferrimagnetism with a Curie temperature of 138 K, in which the sublattice magnetizations of V^{II} ($S = {}^3/_2$) and V^{III} ($S = 1$) are antiparallelly ordered to that of Nb^{IV} ($S = {}^1/_2$). The estimated superexchange interaction constants of $V^{II}-Nb^{IV}$ and $V^{III}-Nb^{IV}$ are -51 and -25 cm^{-1}, respectively.

In molecule-based magnets,[1] it is challenging to synthesize compounds with a high Curie temperature (T_C).[2−6] In cyano-bridged metal assemblies, high-T_C values have been reported using a V^{II}-containing system.[2−4] Because the diffuse d orbitals on 4d and 5d transition metals enhance the superexchange interaction through coordinating ligands, metal complexes based on 4d and 5d transition metals are effective in high-T_C magnets.[7−9] In recent years, octacyanometalate-based magnets have received much attention.[9] Octacyanometalates $[M(CN)_8]^{n-}$ (M = Mo, W, Nb, etc.) are a versatile class of building blocks that can adopt different spatial configurations that depend on the surrounding ligands. Thus, octacyanometalate-based compounds take various coordination geometries in the crystal structure from zero-dimensional to three-dimensional (3D).[10−13] Up to date, several octacyanoniobate-based magnets have been reported,[14−18] e.g., $[Mn(H_2O)_2]_2[Nb(CN)_8]\cdot 4H_2O$ (T_C = 50 K),[14] $\{Mn_2(2,2'\text{-bipyrimidine})(H_2O)_2[Nb(CN)_8]\}$ (T_C = 50 K),[15] $[Mn(pyrazine)(H_2O)_2][Mn(H_2O)_2][Nb(CN)_8]\cdot 4H_2O$ (T_C = 48 K),[16] and $\{Mn_2(imidazole)_2(H_2O)_4[Nb(CN)_8]\}$

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(T_C = 62 K).[17] Herein we prepared a 3D vanadium octacyanoniobate-based magnet, $K_{0.10}V^{II}_{0.54}V^{III}_{1.24}$ $[Nb^{IV}(CN)_8]\cdot(SO_4)_{0.45}\cdot6.8H_2O$ (**1**). This compound exhibits ferrimagnetism with a Curie temperature of 138 K, in which the sublattice magnetizations of V^{II} (S = $^3/_2$) and V^{III} (S = 1) are antiparallelly ordered to that of Nb^{IV} (S = $^1/_2$).

The target compound was obtained by mixing 2 mL of an aqueous solution of $K_4[Nb(CN)_8]\cdot2H_2O$[19] (0.1 mmol) with 2 mL of an aqueous solution of $(NH_4)_2V(SO_4)_2\cdot6H_2O$ (0.2 mmol) under an Ar atmosphere, which produced a dark-blue precipitate. In the IR spectra, CN^- stretching peaks were observed at 2088 cm^{-1} ($V^{II}-NC-Nb^{IV}$) and 2118 cm^{-1} ($V^{III}-NC-Nb^{IV}$).[20] Elemental analyses using the standard microanalytical method and inductively coupled plasma mass spectroscopy indicated that **1** had a formula of $K_{0.10}V^{II}_{0.54}V^{III}_{1.24}[Nb^{IV}(CN)_8]\cdot(SO_4)_{0.45}\cdot6.8H_2O$. Calcd: C, 17.1; H, 2.4; N, 20.0; V, 16.2; Nb, 16.6; K 0.7. Found: C, 17.0; H, 2.4; N, 20.1; V, 16.2; Nb, 16.7; K 0.6. In the powder X-ray diffraction (XRD) pattern, broad peaks were observed at 19, 25, and 35°, indicating that the crystallinity of the prepared sample is low (Figure 1a). To understand the crystal structure, the XRD pattern of **1** was compared to that of $[Mn(H_2O)_2]_2[Mo(CN)_8]\cdot4H_2O$ (**2**) as a reference sample.[21] Figure 1b shows the stick diagram and calculated XRD patterns of **2** (tetragonal structure in the $I4/mcm$ space group, a = 11.679 Å, and c = 13.276 Å, where each Mo is bridged to eight Mn and each Mn is bridged to four Mo through cyano groups). The observed XRD pattern and calculated pattern for the reference sample agree well, suggesting that the crystal structure of the present compound is close to the 3D tetragonal crystal structure shown in Figure 1c.

The electron paramagnetic resonance (EPR) spectrum showed one broad dispersive signal with a g value of 2.0 at 300 K (Figure S1 in the Supporting Information). In the magnetization vs temperature curves in an external magnetic field of 10 Oe, the magnetization abruptly increased below 140 K (Figure 2). Extrapolating the straight line in the remanent magnetization plots (Figure 2, inset) showed that the T_C value was 138 K. In the magnetization vs magnetic field plots at 2 K (Figure 3a, inset), the magnetic hysteresis loop with a coercive field of 90 Oe was observed. The saturated magnetization (M_s) value at 2 K was 2.8 μ_B (Figure 3a). This M_s value is close to the expected M_s value of 3.1 μ_B due to the antiferromagnetic coupling of the sublattice magnetizations of V^{II} and V^{III} with that of Nb^{IV}, with g values of 2.0. From the observed T_C value, the superexchange interaction constants J_{ij} between the i site and the nearest-neighbor j site of $H = -J_{ij}S_i\cdot S_j$ was estimated based on the molecular-field theory (Supporting Information), and $J_{V^{II}Nb}$ and $J_{V^{III}Nb}$ were evaluated to be −51 and −25 cm^{-1}, respectively (Figure 3b). The $J_{V^{II}Nb}$ value of **1** is higher than the $J_{V^{II}Cr^{III}}$ value of −35 cm^{-1} in a high-T_C V−Cr Prussian blue analogue.[4c]

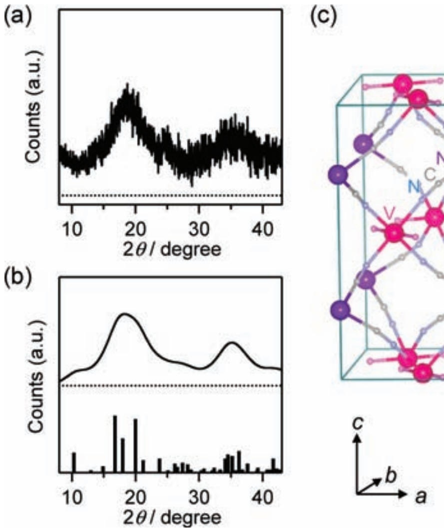

Figure 1. (a) Powder XRD pattern of the compound. (b) Simulated diffraction pattern based on the crystal structure of **2** with a half-width value of 5° (top) and calculated intensities of the Bragg reflections (bottom). (c) Schematic crystal structure of the compound. Purple, magenta, gray, light blue, and pink balls represent Nb, V, C, N, and O, respectively.

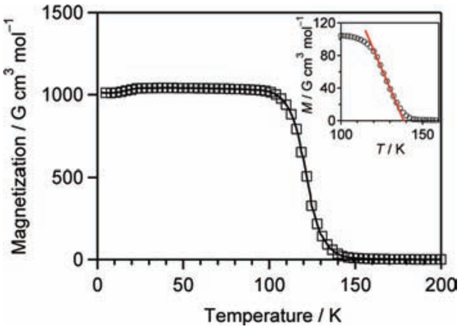

Figure 2. Field-cooled magnetization curve in an external magnetic field of 10 Oe. Inset: Remanent magnetization plot near T_C.

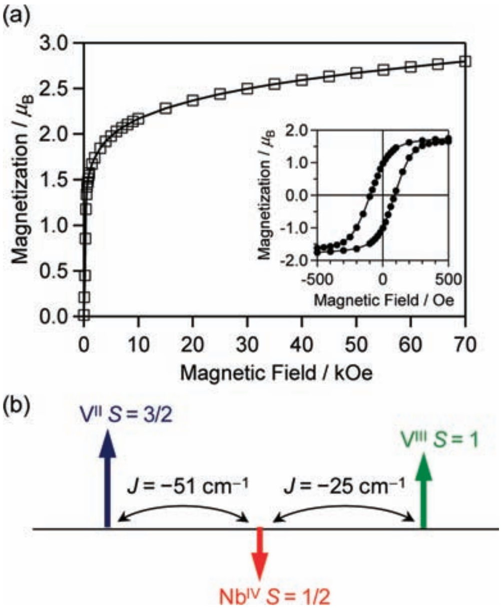

Figure 3. (a) Saturation magnetization curve measured at 2 K. Inset: Magnetic hysteresis loop at 2 K. (b) Schematic diagram of ferrimagnetic ordering of V^{II} (S = $^3/_2$), V^{III} (S = 1), and Nb^{IV} (S = $^1/_2$).

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[20] Elemental analyses and IR spectra showed that part of V^{II} originally contained in the precursor was oxidized to V^{III} during the reaction. When the sample was exposed to air, the IR intensity of the two peaks decreased, a new CN stretching peak appeared at 2147 cm^{-1} ($V^{IV}-CN-Nb^{IV}$) and a $V^{IV}O$ stretching peak was observed at 975 cm^{-1}, indicating that the compound is air-sensitive.

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In conclusion, we prepared vanadium octacyanoniobate, $K_{0.10}V^{II}_{0.54}V^{III}_{1.24}[Nb^{IV}(CN)_8]\cdot(SO_4)_{0.45}\cdot6.8H_2O$, which is a ferrimagnet with T_C equal to 138 K. This T_C value is the highest among 4d and 5d metal-based complexes reported to date. The high J value of **1** is due to (i) the diffuse 4d orbitals of Nb, which enable an effective superexchange interaction through the cyano groups, and (ii) high-energy 3d orbitals of V, which lead to a good energy matching with the magnetic orbital of $[Nb(CN)_8]^{4-}$. The combination of the V ion with the Nb ion should be a promising system for high-T_C compounds.

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Supporting Information Available: EPR spectrum of the compound at 300 K, $\chi_M T-T$ plot of the compound, and estimation of the superexchange constants based on the molecular-field theory. This material is available free of charge via the Internet at http://pubs.acs.org.