Vanadium Octacyanoniobate-based magnet with a Curie Temperature of 138 K

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SUPPORTING INFORMATION

EPR spectrum:

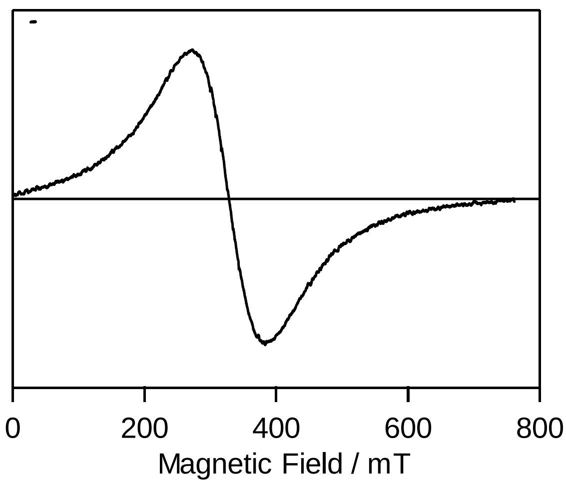

Figure S1. EPR spectrum measured at 300 K.

χ_M***T*-*T* plots:**

The $\chi_M T$ value at 300 K is 6.2 K cm^3 mol^{-1}, which is much larger than the expected spin-only value of 2.5 K cm^3 mol^{-1} for one Nb^{IV} (S_{Nb} = 1/2), 1.24 V^{III} (S_V^{III} = 1), and 0.54 V^{II} (S_V^{II} = 3/2) with *g* value of 2.0. This is because T_C value of this compound is high and the contribution of the magnetic ordering remains even at room temperature. In addition, a minimum in the $\chi_M T$-*T* plots, which is characteristic in ferrimagnet, was not observed below 300 K. The minimum $\chi_M T$ will be located above 300 K.

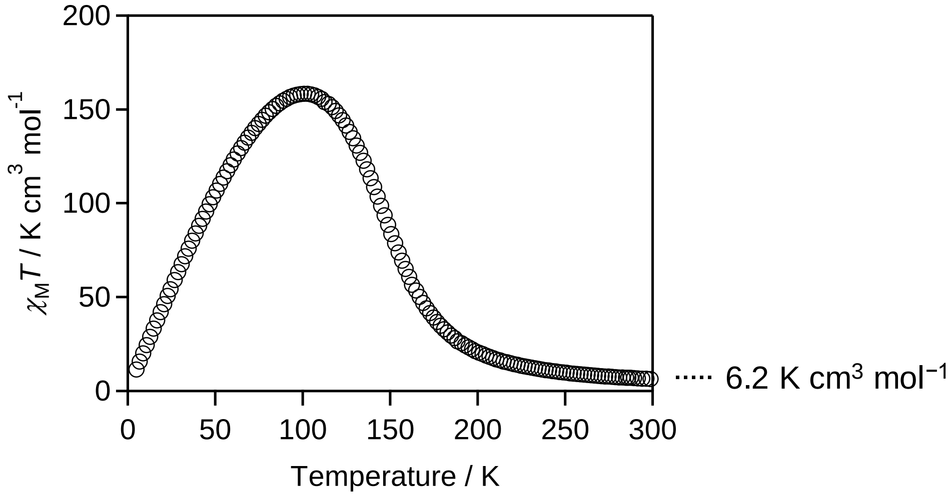

Figure S2. $\chi_M T$-*T* plots in an external magnetic field of 5000 Oe.

Estimation of superexchange constant based on molecular-field theory:

The values of the superexchange interaction constants (J_{ij}, $\hat{H} = -J_{ij}S_i \cdot S_j$) between the *i* site and the nearest neighbor *j* site in $V^{II}_x V^{III}_y [Nb^{IV}(CN)_8]$ are related to the T_C value via the following equation:[S1]

$$T_C = \frac{\left\{ S_{Nb}(S_{Nb}+1)\left[\left| J_{V^{II}Nb} \right|^2 Z_{NbV^{II}} Z_{V^{II}Nb} S_{V^{II}} (S_{V^{II}}+1) + \left| J_{V^{III}Nb} \right|^2 Z_{NbV^{III}} Z_{V^{III}Nb} S_{V^{III}} (S_{V^{III}}+1) \right] \right\}^{0.5}}{3k_B} \quad (1)$$

where S_i is the spin quantum number ($S_{Nb} = 1/2$, $S_{V^{II}} = 3/2$, and $S_{V^{III}} = 1$), Z_{ij} is the number of the nearest neighbor *j* site around *i* site, and k_B is the Boltzmann constant. In the case of $K_{0.10}V^{II}_{0.54}V^{III}_{1.24}[Nb^{IV}(CN)_8]\cdot(SO_4)_{0.45}\cdot 6.8H_2O$, Z_{ij} is as follows: $Z_{V^{II}Nb} = Z_{V^{III}Nb} = 4$, $Z_{NbV^{II}} = 8\times(x/2)$, $Z_{NbV^{III}} = 8\times(y/2)$, $x = 0.54$, $y = 1.24$. In addition to the present compound, we used $V^{II}_{0.20}V^{III}_{1.20}[Nb^{IV}(CN)_8]\cdot 9.4H_2O$ (T_C = 98 K) to calculate $J_{V^{II}Nb}$ and $J_{V^{III}Nb}$. This another compound was prepared by mixing an aqueous solution of $K_4[Nb(CN)_8]\cdot 2H_2O$ with that of VCl_2. Calcd. V, 13.2; Nb, 17.1. Found: V, 13.3; Nb, 17.0. Consequently, $J_{V^{II}Nb}$ and $J_{V^{III}Nb}$ are estimated to be −51 cm^{-1} and −25 cm^{-1}, respectively.

In contrast, the $J_{V^{II}Cr^{III}}$ value in a Prussian blue analog, $KV^{II}[Cr^{III}(CN)_6]\cdot 2H_2O\cdot 0.1(KOSO_2CF_3)$, reported by Holmes[S2] is related to the T_C value via the following equation:[S1]

$$T_C = \frac{\left| J_{V^{II}Cr^{III}} \right| \left\{ Z_{Cr^{III}V^{II}} Z_{V^{II}Cr^{III}} S_{V^{II}} (S_{V^{II}}+1) S_{Cr^{III}} (S_{Cr^{III}}+1) \right\}^{0.5}}{3k_B} \quad (2)$$

where $Z_{Cr^{III}V^{II}} = Z_{V^{II}Cr} = 6$, $S_{Cr^{III}} = 3/2$, $S_{V^{II}} = 3/2$, and T_C = 376 K. From equation (2), $J_{V^{II}Cr^{III}}$ is estimated to be −35 cm^{-1}.

S1) Ohkoshi, S.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Phys. Rev. B* **1997**, *56*, 11642.

S2) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593.