A High Compensation Temperature of 175 K in a Vanadium Hexacyanochromate-based Magnet

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We observed a high compensation temperature (T_{comp}) of 175 K in a vanadium hexacyanochromate-based ferrimagnet, $\text{K}^{\text{I}}{}_{0.19}\text{V}^{\text{II}}{}_{0.64}(\text{V}^{\text{IV}}\text{O})_{0.36}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.73}\cdot 7.5\text{H}_2\text{O}$. The observed phenomenon is understood by the compensation of the positive sublattice magnetization of Cr^{III} ($S = 3/2$) and the negative sublattice magnetizations of V^{II} ($S = 3/2$) and V^{IV} ($S = 1/2$). A T_{comp} value of 175 K is the highest value among molecule-based magnets reported to date.

For the last two decades, molecule-based magnets have been aggressively studied.[1] The advantages of molecule-based magnets compared to conventional ones such as metal alloys or metal oxides are that magnetic ordering can be designed through the proper selection of spin sources and bridging ligands. Prussian blue analog-based magnets have drawn attention owing to their high magnetic critical temperature (T_c), especially a series of vanadium hexacyanochromate-based ferrimagnets, which shows high T_c values above room temperature.[2] Furthermore, compensation of magnetization has been observed, i.e., the spontaneous magnetization changes its sign at a particular temperature (the so-called compensation temperature, T_{comp}),[3] with multimetal Prussian blue analogs.[4] For example, T_{comp} values of 38 and 42 K have been reported for $(\text{Ni}^{\text{II}}{}_{0.38}\text{Mn}^{\text{II}}{}_{0.62})[\text{Cr}^{\text{III}}(\text{CN})_6]_{2/3}\cdot 5.0\text{H}_2\text{O}$[4a] and $(\text{Co}^{\text{II}}{}_{0.41}\text{Mn}^{\text{II}}{}_{0.59})[\text{Cr}^{\text{III}}(\text{CN})_6]_{2/3}\cdot 5.1\text{H}_2\text{O}$,[4f] respectively. Two compensation temperatures have also been observed in $(\text{Ni}^{\text{II}}{}_{0.22}\text{Mn}^{\text{II}}{}_{0.60}\text{Fe}^{\text{II}}{}_{0.18})[\text{Cr}^{\text{III}}(\text{CN})_6]_{2/3}\cdot 5.1\text{H}_2\text{O}$ ($T_{\text{comp}} = 35$ and 53 K).[4d] In this work, we observed a high T_{comp} value of 175 K using $\text{K}^{\text{I}}{}_{0.19}\text{V}^{\text{II}}{}_{0.64}(\text{V}^{\text{IV}}\text{O})_{0.36}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.73}\cdot 7.5\text{H}_2\text{O}$, which is the highest value among molecule-based magnets reported to date.

The target compound was prepared by quickly adding an aqueous solution of VCl_3 (10 mmol dm^{-3}) to an aqueous solution of $\text{K}_3[\text{Cr}(\text{CN})_6]$ (10 mmol dm^{-3}) at room temperature. The mixed solution was left for four hours, and then the precipitate was filtered off, washed four times with water, and dried. All of the synthetic procedures were carried out under an Ar atmosphere using a glovebox (MBRAUN, UNILab). Samples for each measurement were also prepared under an Ar atmosphere. The obtained precipitate was a dark blue powder, and elemental analysis by inductively coupled plasma-mass spectroscopy confirmed that the formula is $\text{K}^{\text{I}}{}_{0.19}\text{V}^{\text{II}}{}_{0.64}(\text{V}^{\text{IV}}\text{O})_{0.36}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.73}\cdot 7.5\text{H}_2\text{O}$. Calcd: K, 2.1; V, 14.5; Cr, 10.8%. Found: K, 2.3; V, 14.3; Cr, 11.0%. The infrared (IR) spectrum of the obtained compound shows two CN stretching bands at 2117 and 2165 cm^{-1}, which are assigned to $\text{Cr}^{\text{III}}\text{–CN–V}^{\text{II}}$ and $\text{Cr}^{\text{III}}\text{–CN–V}^{\text{IV}}\text{O}$, respectively (Figure S1).[2c,2h,8] A V=O stretching band is observed at 987 cm^{-1}. The estimated ratio of V^{II} to V^{IV} is 0.64 to 0.36 from the analysis of the IR spectra,[5] indicating that valence state of this compound is $\text{K}^{\text{I}}{}_{0.19}\text{V}^{\text{II}}{}_{0.64}(\text{V}^{\text{IV}}\text{O})_{0.36}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.73}\cdot 7.5\text{H}_2\text{O}$. The X-ray powder diffraction shows that the crystal structure is indexed as a face-centered cubic structure ($Fm\bar{3}m$, $a = b = c = 10.62(2)$ Å) (Figure S2).[8] Figure 1a shows the field-cooled magnetization (FCM) curve of this compound in a 10 Oe field. Spontaneous magnetization is observed below 250 K ($=T_c$) but vanishes at 175 K ($=T_{\text{comp}}$), and then a negative magnetization appears. When FCM curve is measured with an applied field of 50 Oe, the magnetization value is close to zero at T_{comp} but increases as temperature decreases. The magnetic hysteresis loop at 50 K shows that the coercive field is 33 Oe (Figure 1b). The magnetization vs. external magnetic field plots at 5 K shows that the saturation magnetization (M_s) is 0.097 μ_B (Figure S3),[8] which is close to the calculated value of 0.09 μ_B when the sublattice magnetizations of V^{II} ($S = 3/2$) and V^{IV} ($S = 1/2$) are antiparallelly ordered to the sublattice magnetization of Cr^{III} ($S = 3/2$).

To understand the compensation behavior, a model calculation was carried out on the basis of the molecular field theory with three sublattice sites of V^{II} ($S = 3/2$), V^{IV} ($S = 1/2$), and Cr^{III} ($S = 3/2$). In the case of Prussian blue analogs, only superexchange coupling between the nearest-neighbor sites effectively contributes to magnetic ordering. Hence, in the present system, the molecular fields of $H_{\text{V}^{\text{II}}}$, $H_{\text{V}^{\text{IV}}}$, and $H_{\text{Cr}^{\text{III}}}$, which act on the three sublattice sites are expressed as follows: $H_{\text{V}^{\text{II}}} =$

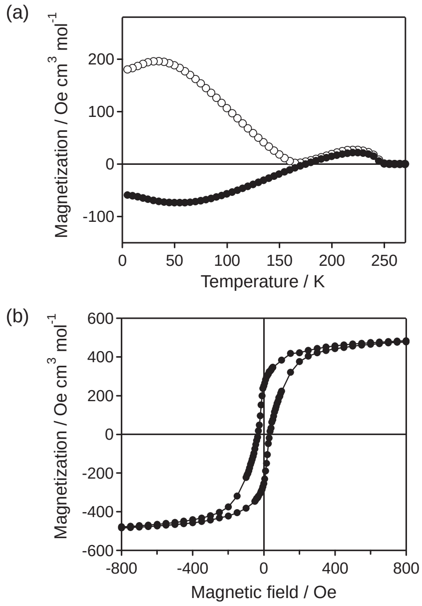

Figure 1. (a) Field-cooled magnetization curves in a field of 10 Oe (●) and 50 Oe (○). (b) Magnetic hysteresis loop measured at 50 K.

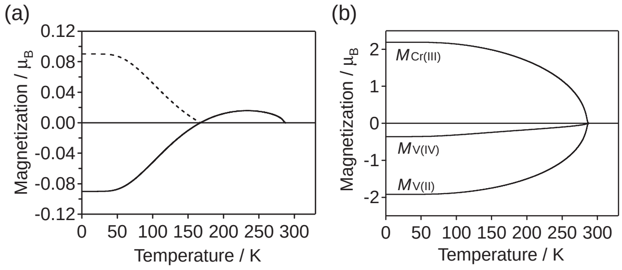

Figure 2. (a) Calculated temperature dependence of M_{total} (solid line) and $|M_{\mathrm{total}}|$ (dashed line). (b) Calculated temperature dependence of sublattice magnetizations ($M_{\mathrm{V^{II}}}$, $M_{\mathrm{V^{IV}}}$, and $M_{\mathrm{Cr^{III}}}$).

Table 1. The reported T_{comp} values in molecule-based magnets

Compound[a]	T_{comp}/K	Ref.
$(\mathrm{Mn^{III}TPP})(\mathrm{TCNE})$	5	7a
$\mathrm{Ni^{II}(HCOO)_2 \cdot 2H_2O}$	8.5	7g
$\mathrm{(NBu_4)_2Mn^{II}{}_2[Cu^{II}(opba)]_3}$	11.5	7c
$\mathrm{Rb^{I}{}_{0.64}Ni^{II}{}_{0.31}Mn^{II}{}_{0.87}[Fe^{III}(CN)_6] \cdot 2.8H_2O}$	13	4g
$\mathrm{[K\{Mn^{III}(3\text{-}MeO\text{-}salen)\}_2\{Mn^{III}(CN)_6\}]}$	13.5	7d
$\mathrm{[rad_2Ni^{II}{}_2\{Cu^{II}(opba)\}_3]}$	15	7f
$\mathrm{NBu_4[Fe^{II}Fe^{III}(C_2O_4)_3]}$	30	7b
$\mathrm{(Ni^{II}{}_{0.38}Mn^{II}{}_{0.62})[Cr^{III}(CN)_6]_{2/3} \cdot 5.0H_2O}$	38	4a
$\mathrm{(Fe^{II}{}_{0.42}Mn^{II}{}_{0.58})[Cr^{III}(CN)_6]_{2/3} \cdot 5.0H_2O}$	40	4b
$\mathrm{(Co^{II}{}_{0.41}Mn^{II}{}_{0.59})[Cr^{III}(CN)_6]_{2/3} \cdot 5.1H_2O}$	42	4f
$\mathrm{(Ni^{II}{}_{0.22}Mn^{II}{}_{0.60}\ Fe^{II}{}_{0.18})[Cr^{III}(CN)_6]_{2/3} \cdot 5.1H_2O}$	35, 53	4d
$\mathrm{(Fe^{II}{}_{0.15}Cr^{II}{}_{0.85})[Cr^{III}(CN)_6]_{2/3} \cdot \mathit{z}H_2O}$	110	4c
$\mathrm{K^{I}{}_{0.19}V^{II}{}_{0.64}(V^{IV}O)_{0.36}[Cr^{III}(CN)_6]_{0.73} \cdot 7.5H_2O}$	175	This work

[a] TPP = *meso*-tetraphenylporphinato, TCNE = tetracyanoethylene, opba = *o*-phenylenebis(oxamato), rad = 2-(1-ethylpyridinium-4-yl)-4,4,5,5-tetramethylimidazolin-1-oxyl-3-oxide, salen = *N*,*N*′-ethylenebis(salicylideneaminato) dianion.

$H_0 + n_{\mathrm{V^{II}Cr^{III}}} M_{\mathrm{Cr^{III}}}$, $H_{\mathrm{V^{IV}}} = H_0 + n_{\mathrm{V^{IV}Cr^{III}}} M_{\mathrm{Cr^{III}}}$, and $H_{\mathrm{Cr^{III}}} = H_0 + n_{\mathrm{V^{II}Cr^{III}}} M_{\mathrm{V^{II}}} + n_{\mathrm{V^{IV}Cr^{III}}} M_{\mathrm{V^{IV}}}$ where H_0 is the external magnetic field, n_{ij} are the molecular-field coefficients relating to the exchange coefficients (J_{ij}), and $M_{\mathrm{V^{II}}}$, $M_{\mathrm{V^{IV}}}$, and $M_{\mathrm{Cr^{III}}}$ are the sublattice magnetizations per unit volume for the $\mathrm{V^{II}}$, $\mathrm{V^{IV}}$, and $\mathrm{Cr^{III}}$ sites, respectively.[6] From the experimental T_c values of the binary compounds of $\mathrm{V^{II}[Cr^{III}(CN)_6]_{2/3} \cdot 3.5H_2O \cdot 0.1[NEt_4][CF_3SO_3]}$ ($T_c = 330\,\mathrm{K}$) and $\mathrm{(V^{IV}O)[Cr^{III}(CN)_6]_{2/3} \cdot 10/3H_2O}$ ($T_c = 115\,\mathrm{K}$) reported in previous reports,[2c,2h] $J_{\mathrm{V^{II}Cr^{III}}}$ and $J_{\mathrm{V^{IV}Cr^{III}}}$ values are estimated to be -28.1 and $-21.9\,\mathrm{cm^{-1}}$, respectively. Using these parameters, the total magnetization ($M_{\mathrm{total}} = -M_{\mathrm{V^{II}}} - M_{\mathrm{V^{IV}}} + M_{\mathrm{Cr^{III}}}$) was calculated (Figure 2a). The calculated M_{total} reproduces the compensation behavior. As shown in the calculated sublattice magnetization curves in Figure 2b, the compensation behavior is observed because between T_c and T_{comp}, the positive magnetization of $\mathrm{Cr^{III}}$ site dominates, but below T_{comp}, the negative magnetizations of $\mathrm{V^{II}}$ and $\mathrm{V^{IV}}$ sites dominate. When the FCM curve is measured in a large magnetic field compared to the coercive field, the negative magnetization below T_{comp} is upset by the applied magnetic field, which results in two hills being observed.

In summary, $\mathrm{K^{I}{}_{0.19}V^{II}{}_{0.64}(V^{IV}O)_{0.36}[Cr^{III}(CN)_6]_{0.73} \cdot 7.5H_2O}$ exhibits a high T_{comp} value of 175 K. The compensation of magnetization has been reported in other molecule-based magnets,[7] e.g., $\mathrm{(NBu_4)_2Mn^{II}{}_2[Cu^{II}(opba)]_3}$ (opba = *o*-phenylenebis(oxamato)) ($T_{\mathrm{comp}} = 11.5\,\mathrm{K}$)[7c] and $\mathrm{NBu_4[Fe^{II}Fe^{III}(C_2O_4)_3]}$ ($T_{\mathrm{comp}} = 30\,\mathrm{K}$).[7b] Table 1 summarizes the T_{comp} values reported for molecule-based magnets. The observed T_{comp} value in the present system is the highest value among molecule-based magnets reported to date.

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5 By comparing the electrochemically synthesized $\mathrm{K}_a\mathrm{V^{II/III}[Cr(CN)_6]}_b \cdot n\mathrm{H_2O}$ compound and its oxidized compound, the peak area ratio of $\mathrm{Cr^{III}\text{–}CN\text{–}V^{II/III}}$ to $\mathrm{Cr^{III}\text{–}CN\text{–}V^{IV}}$ is 1.3 to 1. Based on this result, we estimated that the ratio of $\mathrm{V^{II}}$ to $\mathrm{V^{IV}}$ in the present compound is 0.64 to 0.36.

6 The molecular-field coefficients n_{ij} are expressed by $n_{\mathrm{V^{II}Cr^{III}}} = 2Z_{\mathrm{V^{II}Cr^{III}}} J_{\mathrm{V^{II}Cr^{III}}} / (\mu N g^2 {\mu_B}^2)$, $n_{\mathrm{V^{IV}Cr^{III}}} = 2Z_{\mathrm{V^{IV}Cr^{III}}} J_{\mathrm{V^{IV}Cr^{III}}} / (\mu N g^2 {\mu_B}^2)$, $n_{\mathrm{Cr^{III}V^{II}}} = 2Z_{\mathrm{Cr^{III}V^{II}}} J_{\mathrm{Cr^{III}V^{II}}} / (\lambda x N g^2 {\mu_B}^2)$, and $n_{\mathrm{Cr^{III}V^{IV}}} = 2Z_{\mathrm{Cr^{III}V^{IV}}} J_{\mathrm{Cr^{III}V^{IV}}} / (\lambda(1-x) N g^2 {\mu_B}^2)$ where μ_B is the Bohr magneton, Z_{ij} are the numbers of the nearest neighbor j-site ions surrounding an i-site ion, N is the total number of all types of metal ions per unit volume, g is the g-factor, x is the mole fraction for $\mathrm{V^{II}}$, and λ and μ are the mole fractions for V (total of the mole fractions for $\mathrm{V^{II}}$ and $\mathrm{V^{IV}}$) and for $\mathrm{Cr^{III}}$, respectively. In the case of $\mathrm{K^{I}{}_{0.19}V^{II}{}_{0.64}(V^{IV}O)_{0.36}[Cr^{III}(CN)_6]_{0.73} \cdot 7.5H_2O}$, these parameters are as follows: $Z_{\mathrm{V^{II}Cr^{III}}} = Z_{\mathrm{V^{IV}Cr^{III}}} = 6 \times 0.73 = 4.38$, $Z_{\mathrm{Cr^{III}V^{II}}} = 3.84$, $Z_{\mathrm{Cr^{III}V^{IV}}} = 2.16$, $x = 0.64$, $\lambda = 1$, and $\mu = 0.73$. In this model, the spin Hamiltonian ($\hat{H}$) with J_{ij} is defined as $\hat{H} = -2J_{ij}S_iS_j$.

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8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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