Synthesis and Magnetic Properties of a New Prussian Blue Analog Composed of $K_{0.9}Mn^{II}_{1.05}[Mo^{I}(CN)_5(NO)]\cdot5H_2O\cdot1.9MeOH$

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We have prepared a new molybdenum polycyanide $K_{0.9}Mn^{II}_{1.05}[Mo^{I}(CN)_5(NO)]\cdot5H_2O$ 1.9MeOH with a face-centered cubic structure with a lattice constant of 10.72 Å. This compound exhibited a spontaneous magnetization with a Curie temperature of 39 K and a saturated magnetization value (I_s) of 3.8 μ_B. This I_s value and magnetic susceptibility measurements indicate that the magnetic coupling between Mn^{II} and Mo^{I} ions is antiferromagnetic.

There has been a great interest in a preparation of new molecule-based magnets.[1-6] Prussian blue analogs comprise one of the most attractive classes of molecule-based magnets, some of which show high Curie temperature (T_C).[7-9] For example, Verdaguer et al. have reported that $V[Cr(CN)_6]_{0.86}\cdot2.8H_2O$ exhibited a spontaneous magnetization with $T_C = 315$ K.[9] In addition, their common face-centered cubic (fcc) structures allow us easily to understand the superexchange interactions among transition metal ions.[7-11] Furthermore, we have developed various functional magnets composed of Prussian blue analogs, ex., photomagnets,[12,13] colored magnetic thin films,[14] and a magnet flipping its magnetic pole twice.[15] For these Prussian blue analogs, the first transition series element ions such as chromium and iron ions are mainly used as their precursors [A(CN)$_6$]$^{n-}$, where A is a transition metal ion. In the present work, we focus our attention on a new type of building blocks incorporating molybdenum ion. The first molybdenum polycyanide has recently reported in the system of $Mn^{II}_2(H_2O)_5[Mo^{III}(CN)_7]\cdot nH_2O$ ($S_{Mn} = 5/2$, $S_{Mo} = 1/2$) by Kahn et al.[16,17] This compound shows a parallel spin ordering with $T_C = 51$ K and a strong magnetic anisotropy. A heptacyanomolybdenate(III) ion is used as its precursor in this compound and hence its structure is a ladder type, not a cubic type. The object of the present work is to prepare a cubic type of a molybdenum polycyanide exhibiting a spontaneous magnetization. For this attempt, we have chosen a

pentacyanonitrosylmolybdenate ion, [Mo^I(CN)$_5$(NO)]$^{3-}$(4d^5, S = 1/2), as a building block. We here report the synthesis and magnetic properties of this new Prussian blue analog, $K_{0.9}Mn^{II}_{1.05}$ [Mo^I(CN)$_5$(NO)]·5H$_2$O·1.9MeOH (1).

The compound 1 was obtained by the oxidation of K_4[Mo^0(CN)$_5$(NO)]·2H$_2$O[18] with Mn(ClO$_4$)$_2$·nH$_2$O.[19] Its elemental analyses were carried out by standard microanalytical methods and inductively coupled plasma optical emission. Under our typical experimental conditions,[19] the formula for 1 was $K_{0.9}Mn^{II}_{1.05}$[Mo^I(CN)$_5$(NO)] ·5H$_2$O·1.9MeOH. Note that the fraction of Mn^{II} and Mo^I in the prepared compound slightly depended on the mixing ratio of the starting materials. The X-ray diffraction patterns of this compound showed the fcc structure with a lattice constant of 10.72 Å (Figure 1). In addition, the CN and NO stretching frequencies in the IR spectra were observed at 2127 cm^{-1} and 1649 cm^{-1}, respectively. This NO stretching frequency is different from that of a free [Mo^I(CN)$_5$(NO)]$^{3-}$ ion ($\nu_{NO} = 1585$ cm^{-1})[20]. All these data show that a cubic type of molybdenum polycyanide containing Mo^I-NO-Mn^{II} bridges is obtained.

The field-cooled magnetization vs. temperature plots for 1 in the external magnetic field of 10 G showed an abrupt break at $T_C = 39$ K (Figure 2). The magnetization against the external magnetic field showed that the saturation magnetization (I_s) value was 3.8 μ_B per the obtained formula of 1, assuming the g factor of 2.0 (Figure 3). When this compound is a ferrimagnet, the I_s value should be 4.3 μ_B. The observed I_s value is close to this calculated value, and hence this observed I_s value suggests that the magnetic coupling between Mo^I(4d^5, S = 1/2) and Mn^{II}(3d^5, S = 5/2) is antiferromagnetic. In addition, the $\chi_M T$ vs. T plots had a minimum value around 255 K and then approached infinity at T_C. This type of $\chi_M T$ vs. T curve also indicates that this compound is a ferrimagnet. The coercive field (H_C) was 14 G at 5 K. This small H_C value is due to the isotropy of magnetic orbitals of a Mn^{II} ion in octahedral surroundings.
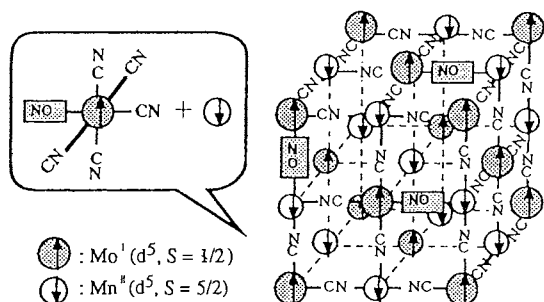

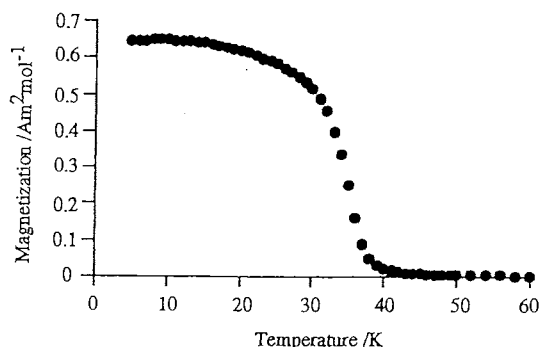Figure 1. Schematic illustration of $K_{0.9}Mn_{1.05}[Mo(CN)_5(NO)]\cdot5H_2O\cdot$1.9MeOH(1).

Legend:
⊕ : Mo^I(d^5, S = 1/2)
⊕ : Mn^{II}(d^5, S = 5/2)

Temperature /K

Figure 2. Field-cooled magnetization (FCM) curve for 1 (field = 10^{-3} T).
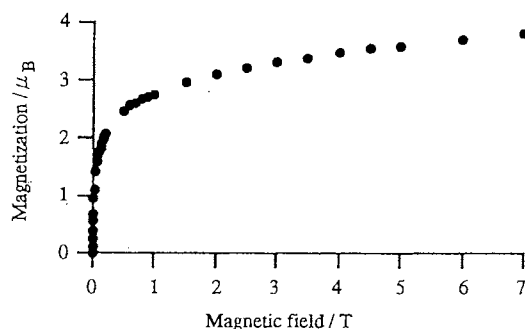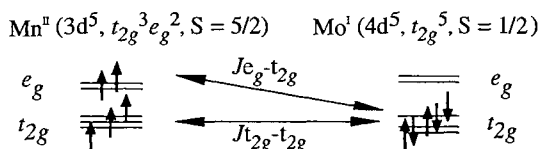
Figure 3. Field dependence of the magnetization at 5 K for **1**.

Next, let us consider the origin of the antiferromagnetic interaction between Mn^{II} and Mo^{I} ions (J_{MnMo}) of this system. The point group of each metal ion for **1** is close to O_h group due to its fcc structure. Therefore, the d-orbitals of Mn^{II} and Mo^{I} split into e_g and t_{2g} orbitals and unpaired electrons occupy these orbitals as follows.

$$Mn^{II} (3d^5, t_{2g}{}^3 e_g{}^2, S = 5/2) \qquad Mo^{I} (4d^5, t_{2g}{}^5, S = 1/2)$$

In this unpaired electron configuration, several superexchange pathways among unpaired electrons exist. These pathways are roughly devided into two categories. One is the antiferromagnetic contribution ($Jt_{2g}-t_{2g}$) between $t_{2g}(Mn^{II})$ and $t_{2g}(Mo^{I})$ magnetic orbitals, and the other is the ferromagnetic contribution (Je_g-t_{2g}) between $e_g(Mn^{II})$ and $t_{2g}(Mo^{I})$ magnetic orbitals. Usually, the absolute value of $Jt_{2g}-t_{2g}$ is much larger than the Je_g-t_{2g} value.[21] Therefore, the sum of these two contributions could be negative; $J_{MnMo} = Jt_{2g}-t_{2g} + Je_g-t_{2g} < 0$, resulting that the superexchange interaction between Mn^{II} and Mo^{I} is antiferromagnetic.

We can estimate this J_{MnMo} value, which is the weight average of five CN bridged and one NO bridged superexchange interactions. For Prussian blue analogs, the magnitude of the superexchange interaction relates to the T_C value.[11] Using this relationship, we evaluated the J_{MnMo} value of -2.7 cm^{-1}. This value is as large as the J_{MnCr} value of -2.3 cm^{-1} for $K_{0.5}Mn^{II}[Cr^{I}(CN)_5(NO)]_{0.83}\cdot4H_2O\cdot1.5MeOH$.[22] This suggests that the $[Mo^{I}(CN)_5(NO)]^{3-}$ candidate is not less useful than the $[Cr^{I}(CN)_5(NO)]^{3-}$ candidate as a building block to obtain high T_C Prussian blue analog-based magnets.

In summary, we have succeeded in preparing a new type of Prussian blue based magnet containing Mo-NO-Mn bridges. The superexchange interaction between Mn^{II} and Mo^{I} was estimated to be -2.7 cm^{-1}. For this system, the ferromagnetic and antiferromagnetic contributions compete with each other. Therefore, when we choose a $Ni^{II}(t_{2g}{}^6 e_g{}^2)$ or a $Cu^{II}(t_{2g}{}^6 e_g{}^3)$ ion

instead of a Mn^{II} ion, only the ferromagnetic contribution operates to the superexchange interaction and hence ferromagnets can be obtained. Conversely, when we choose a $V^{II}(t_{2g}{}^3)$ or a $Cr^{II}(t_{2g}{}^4)$ ion, only the antiferromagnetic contribution operates, and hence we can obtain higher T_C ferrimagnets. In addition, it is known that a nitroprusside ion, $[Fe^{II}(CN)_5(NO)]^{2-}$, exhibits photo-induced charge transfer.[23-25] Hence, the present compound may show a photo-induced magnetization change. The works under these lines are under way.

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19 The compound **1** was prepared by the reaction of $K_4[Mo(CN)_5(NO)]\cdot2H_2O$ with 4 equiv. of $NaClO_4\cdot H_2O$, 1.2 equiv. of pyridinium tribromide, and 4 equiv. of $Mn(ClO_4)_2\cdot nH_2O$ in $H_2O/MeOH$ (1:1, v/v) under Ar atmosphere. The obtained compound **1** was a brown powder. Found: C, 16.8; H, 3.7; N, 17.0%; K, 6.8; Mn, 11.2; Mo, 18.6. Calcd for: $C_{6.9}H_{17.6}K_{0.9}Mn_{1.05}MoN_6O_{7.9}$: C, 16.58; H, 3.55; N, 16.82%; K, 7.04; Mn, 11.54; Mo, 19.19. FT-IR spectrum of **1** was recorded on a Shimadzu FT-IR 8200PC spectrometer. The powder X-ray diffraction was measured using a Rigaku PW 1400 powder diffractometer. Magnetization measurements were carried out using a Quantum Design MPMS 7S superconducting quantum interference device (SQUID) magnetometer.

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