

# Metal-to-metal electron transfer and magnetic interactions in a mixed-valence Prussian Blue analogue

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Dedicated to Professor (Emeritus) Michio Sorai of Osaka University in honour of his 66th Birthday

## Abstract

In search of a new Prussian Blue analogue exhibiting fascinating magnetic properties, potassium manganese hexacyanoferrate,  $K_{0.2}Mn_{0.66}^{II}Mn_{1.44}^{III}[Fe_{0.2}^{II}Fe_{0.8}^{III}(CN)_6]O_{0.66}(CH_3COO)_{1.32} \cdot 7.6H_2O$ , has been synthesized. This compound undergoes a paramagnetic to ferrimagnetic transition at 10 K. Temperature and magnetic field-dependent magnetization studies of this compound have revealed different spin alignments below and above 3 K. The nature of possible magnetic interactions between the nearest neighbor magnetic centers has been discussed in order to explore the origin of the observed magnetic interactions. Mössbauer spectroscopic study at different temperatures demonstrates the presence of both  $Fe^{III}$  and  $Fe^{II}$  in low-spin states in this compound. Quantitative analysis of the  $Fe^{III}$  and  $Fe^{II}$  ions, and their temperature dependence exhibits the existence of an electron transfer phenomenon between Mn and Fe ions  $[Fe^{III} (t_{2g}^5, S = 1/2) - CN - Mn^{II} (t_{2g}^3 e_g^2, S = 5/2)] \leftrightarrow [Fe^{II} (t_{2g}^6, S = 0) - CN - Mn^{III} (t_{2g}^3 e_g^1, S = 2)]$ . This electron transfer has been remarkably enhanced in the magnetically ordered region.

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## 1. Introduction

The hexacyanometalate  $[B(CN)_6]^{x-}$  ions are well-known building blocks used for fabrication of the hetero-metal assemblies exhibiting bulk magnetization, where reaction of the  $[B(CN)_6]^{x-}$  ions with metal ions gives rise to the so-called ‘Prussian Blue’ analogues— $MA[B(CN)_6] \cdot (xH_2O)$  ( $M$  = monovalent alkali metal ion, and  $A, B$  = di- and trivalent transition metal ions) [1–11]. The magnetic super-exchange interaction between metal ions  $A$  and  $B$  are

mediated by the cyano-bridges. It is well known that the spins of  $A$  and  $B$  couple antiferromagnetically, if the spin-containing orbital of magnetic ions are of the same symmetry, whereas if the orbitals are orthogonal then ferromagnetic coupling appears [4]. Variations of  $A$  and  $B$  cations as well as the introduction of additional water/solvent molecule clusters change the type, strength and 3D topology of the magnetic coupling [1]. Modulating the nature of the interaction between the paramagnetic ions through the cyanide bridge, development of new molecule-based magnetic materials of the Prussian Blue family combined with fascinating physical properties are drawing much attention in recent times. These materials exhibit various magnetic properties depending on their transition metal combinations, e.g., high  $T_C$  magnet [2,4,12], magnetic pole reversal [5,13], spin glass behavior [14,15] and photo-induced magnetic transition [3,5,16–19].

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$\text{Co}_x^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$  and its alkali-doped analogues are one of the most extensively studied recent materials of the Prussian Blue family in regard to photo-induced [7,10,11,20–22] and pressure-induced [23] metal-to-metal electron transfer and magnetism. These compounds exhibited the foremost incidences of photo-/pressure-induced electron transfer in a 3D compound. In these Co–Fe cyanides, the observed magnetic transitions involve the electronic state change of Co between the trivalent low-spin and the divalent high-spin states. Kawamoto et al. [18] concluded that the transitions of this kind are initiated by the excitation of various Co sites.

Among other Prussian Blue analogues, Mn-ferrocyanides have been getting much interest in the contemporary research in this field [19,24,25].  $\text{Mn}_x^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$  is reported to be ferrimagnetic with  $T_N$  at 9 K [26,27].  $\text{RbMn}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$  has been reported to be ferrimagnetic below 12 K from magnetic measurements, where a thermal spin transition with a broad thermal hysteresis loop was observed [24,25]. X-ray emission spectroscopic study of this material led to conclude that the thermally induced phase transition takes place via the charge transfer between Fe and Mn, and that the electronic state of Mn changes between trivalent high-spin state at low temperatures and divalent high-spin state at high temperatures. A photo-induced phase transition has also been observed in this compound [19]. The spin transitions in Co–Fe and Mn–Fe cyanides have so far been reported to commonly originate from the metal-to-metal charge transfer phenomenon, however, no low-spin–high-spin transition has been seen in the Mn–Fe cyanides.

In search for another Prussian Blue analogue exhibiting fascinating magnetic properties, potassium manganese hexacyanoferrate  $\text{K}_{0.2}\text{Mn}_{0.66}^{\text{II}}\text{Mn}_{1.44}^{\text{III}}[\text{Fe}_{0.2}^{\text{II}}\text{Fe}_{0.8}^{\text{III}}(\text{CN})_6]\text{O}_{0.66}(\text{CH}_3\text{COO})_{1.32} \cdot 7.6\text{H}_2\text{O}$  has been synthesized. Magnetic studies of this compound exhibits ferrimagnetic ordering below 10 K and a magnetic field-induced phenomenon below 3 K. Mössbauer studies of this compound detected a thermally induced electron transfer between Mn and Fe, which is much enhanced in the magnetically ordered state, which is the first-ever observation of this kind in the Mn–Fe-type Prussian Blue materials. These results are discussed in the present paper.

## 2. Experimental details

The powdery material of potassium(I) manganese(II) manganese(III) hexacyanoferrate was synthesized by the following method. An aqueous solution of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (0.307 g, 0.0933 mmol) was slowly added to a vigorously stirred methanolic solution of  $\text{Mn}(\text{CH}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$  (0.25 g, 0.0933 mmol). A dark brown solid appears immediately on mixing the two solutions. The stirring was continued for 2–3 h for completion of precipitation. The solid was filtered and washed with copious amount of  $\text{H}_2\text{O}$  and finally by  $\text{CH}_3\text{OH}$ . The product was then dried under vacuum. The solid product thus obtained was

characterized by conventional elemental analysis for C, H, N, and atomic absorption spectroscopy for Mn and Fe. The AAS analysis showed Fe and Mn present in the sample, 19.1% and 7.2%, respectively. IR spectroscopic analysis showed two very intense bands for C–N vibration of the cyanide group at ca. 2148 and 2069  $\text{cm}^{-1}$ . A band at 1609  $\text{cm}^{-1}$  indicates the presence of acetate moiety in the sample while the IR band for Mn–O appears at ca. 990  $\text{cm}^{-1}$ . X-ray powder diffraction measurement shows that the sample possesses a BCC structure. The estimated compositions satisfy the proposed molecular formula of this compound as  $\text{K}_{0.2}\text{Mn}_{0.66}^{\text{II}}\text{Mn}_{1.44}^{\text{III}}[\text{Fe}_{0.2}^{\text{II}}\text{Fe}_{0.8}^{\text{III}}(\text{CN})_6]\text{O}_{0.66}(\text{CH}_3\text{COO})_{1.32} \cdot 7.6\text{H}_2\text{O}$  (say,  $[\text{KMnFe}]$ ).

The temperature- and magnetic field-dependent magnetization measurements in the 2–300 K range were made using a Quantum Design MPMS XL SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants.  $^{57}\text{Fe}$  Mössbauer spectra were measured at various temperatures in the 1.5–300 K range using a conventional constant-acceleration spectrometer with a liquid helium cryostat. The hyperfine parameters were obtained by least-squares fitting to the Lorentzian lines using the Recoil (1.03a) Mössbauer software analysis program.

## 3. Results and discussion

### 3.1. Magnetization study: temperature and field dependence

The temperature-dependent magnetization ( $M$ ) measurements for  $[\text{KMnFe}]$  were carried out in 2–300 K temperature range. The experimental  $M(T)$  data were used to estimate the molar magnetic susceptibility ( $\chi = M/H$ ). The  $\chi(T)$  plots obeyed the Curie–Weiss law in 150–300 K range with the Curie ( $C$ ) and Curie–Weiss ( $\theta$ ) constants as 8.2  $\text{emu mol}^{-1}\text{K}$  and  $-20\text{ K}$ , respectively indicating an antiferromagnetic interaction in this magnetic system. Fig. 1, plot (a) represents the  $\chi$  vs.  $T$  variation obtained under 1 kOe magnetic field ( $H$ ).

The observed room temperature value of the effective magnetic moment  $\mu_{\text{eff}} (= (8\chi T)^{1/2})$  is 7.8  $\mu_B/\text{f.u.}$  (f.u. = formula unit), which is in excellent agreement with the theoretically expected spin-only  $\mu_{\text{eff}}$  value of the present magnetic system (7.74  $\mu_B/\text{f.u.}$ ). With decreasing temperature the  $\mu_{\text{eff}}$  value decreases very slowly from its room temperature value and exhibits a knee-shaped variation around 30 K (see Fig. 1, plot (b)). Below this temperature,  $\mu_{\text{eff}}$  increases showing a maximum of 9.46  $\mu_B/\text{f.u.}$  at 8.6 K, followed by a rapid decrease down to the lowest measuring temperature. The knee-shaped round minimum at a temperature in  $\mu_{\text{eff}}(T)$  variation while cooling as observed in the present study is usually the signature of the onset of ferrimagnetic spin alignment while cooling below this temperature [28]. The magnetic transition temperature of  $[\text{KMnFe}]$  was determined to be 10 K by studying the temperature dependence of the remanent magnetization. For this purpose, the sample was slowly cooled down to

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