

## Light- and Temperature-Induced Electron Transfer in Single Crystals of $\text{RbMn}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$

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Prussian Blue analogs (PBAs), materials of the generic formula  $\text{A}_x\text{M}[\text{M}'(\text{CN})_6]_y \cdot z\text{H}_2\text{O}$  ( $\text{A}$  = alkali cation or  $\text{NR}_4^+$ ;  $\text{M}$ ,  $\text{M}'$  = metal ion), are extremely versatile with respect to their physical properties upon variation of their constituents (in particular the choice of metal ions) and stoichiometry.<sup>1</sup> Their merits have been recognized at a very early stage when it was discovered that favorable electronic transitions or electron transfer between the metallic constituents gave rise to their use as pigments<sup>2</sup> and as components for batteries.<sup>3</sup> More recently, the observed changes in several physical properties induced by various types of external stimuli was anticipated to enable their implementation in molecular scale devices.<sup>4</sup> Of particular interest are magnets with two compensation temperatures<sup>5,6</sup> or the temperature dependent dual magnetic properties that are combined within mixed ferro-ferrimagnets.<sup>5,7</sup> Unique in PBAs is the extended range of light-induced phenomena, such as magnetic pole inversion,<sup>5,8</sup> (de)magnetization,<sup>9,10</sup> spin crossover<sup>11</sup> of  $\text{Fe}^{\text{II}}$ , and electron transfer.<sup>10,12</sup> For instance, in  $\text{RbMn}[\text{Fe}(\text{CN})_6]$ , a 532 nm pulse at 3 K induces an electron transfer from low-spin  $\text{Fe}^{\text{II}}$  and

high-spin  $\text{Mn}^{\text{III}}$  to low-spin  $\text{Fe}^{\text{III}}$  and high spin  $\text{Mn}^{\text{II}}$ .<sup>13</sup> These physical phenomena may be coupled to other unique properties such as negative thermal expansion<sup>14</sup> and porosity.<sup>15–17</sup> The latter offers a further parameter for tuning the magneto-optical behavior by solvatochromism,<sup>15</sup> as well as providing reversible storage capability for, e.g.,  $\text{N}_2$ <sup>16</sup> or  $\text{H}_2$ .<sup>17</sup>

Arguably, there is no other class of three-dimensional, inorganic materials for which so many current and forthcoming applications are available. A further development of the field would highly benefit from an extended knowledge on the relationship between structural features and the material's physical properties, which ideally requires single crystals. Nevertheless, the number of crystal structures of PBAs with  $\text{AM}[\text{M}'(\text{CN})_6] \cdot z\text{H}_2\text{O}$  stoichiometry known to date is small and limited to compounds that do not exhibit physical properties relevant in terms of applications.<sup>18–20</sup> This also applied to single crystals of a rubidium manganese hexacyanoferrate which have been obtained recently.<sup>21</sup> Its inactivity in displaying electron transfer is probably due to the unbalanced redox potentials of the individual metal sites, which is a consequence of the unfavorable stoichiometry ( $\text{Rb}_{0.61}\text{Mn}[\text{Fe}(\text{CN})_6]_{0.87} \cdot 1.7\text{H}_2\text{O}$ ) involving  $\text{Fe}(\text{CN})_6$  vacancies and an associated number of water molecules as has been suggested previously.<sup>22</sup> Our efforts have now resulted in obtaining single crystals of  $\text{RbMn}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$ , which show light- and temperature-induced switching, in which only 50% of the metal ions participate.

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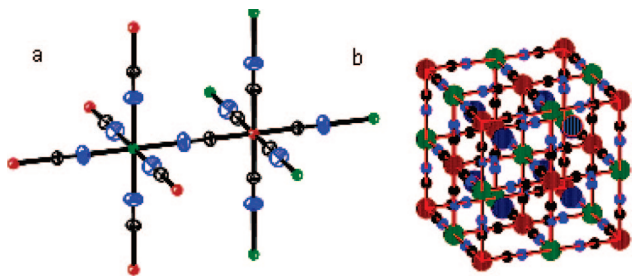
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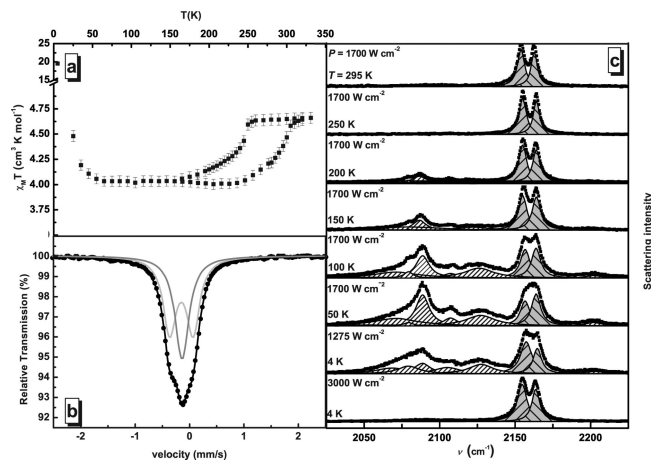
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**Figure 1.** (a) Perspective ORTEP drawing of part of **1** (50% probability level). (b) Representation of the unit cell of **1** ( $F-43m$ ). Mn, green; Fe, red; Rb or O, dark blue; N, blue; C, black.

Cube-shaped, dark brown crystals of  $\text{RbMn}[\text{Fe}(\text{CN})_6] \cdot \text{H}_2\text{O}$  (**1**) have been obtained by a modified version of the crystallization method developed by Kepert et al.<sup>23</sup> The best structural model at 293(1) K is based on the cubic space group  $F-43m$  ( $a = 10.521(2)$  Å, Figure 1). Fe is in an octahedral environment formed by 6 C atoms of the cyano ligands bridging the Fe and Mn ions. Rb and O ( $\text{H}_2\text{O}$ ) are stoichiometrically present and located in the fully occupied interstitial sites. Rb is distributed over two positions ( $4c$ , sof 0.7512(4) and  $4d$ , sof 0.2488(4)). The interatomic distances of 1.929(4) Å for Fe–C and 2.205(5) Å for Mn–N are indicative for low-spin (LS)  $\text{Fe}^{\text{III}}$  and high-spin (HS)  $\text{Mn}^{\text{II}}$ , respectively,<sup>20,24,25</sup> forming the high-temperature (HT) configuration of the material.<sup>26</sup> Unfortunately, we have not yet been able to elucidate the structure at low temperatures, despite numerous efforts. The data recorded at 100 K yielded an inconclusive structural model, caused by the diffraction measurements revealing many diffuse spots that did not result in a realistic unit cell. In addition, about 20% of the reflections did not fit in this orientation matrix.<sup>27</sup>

The temperature dependence of  $\chi_{\text{M}}T$  (with  $\chi_{\text{M}}$  being the molar magnetic susceptibility per formula unit and  $T$  the temperature) of **1** is shown in Figure 2a. At room temperature the  $\chi_{\text{M}}T$  value is  $4.7 \text{ cm}^3 \text{ K mol}^{-1}$ . This corresponds well to the  $\chi_{\text{M}}T$  value of  $4.8 \text{ cm}^3 \text{ K mol}^{-1}$  expected for a weakly coupled paramagnetic  $\{S_1; S_2\} = \{5/2; 1/2\}$  material (the HT configuration, assuming a  $g$  value of 2). Upon cooling  $\chi_{\text{M}}T$  decreases around 250 K until it reaches a value of  $4.0 \text{ cm}^3 \text{ K mol}^{-1}$  at 150 K. The  $T_{1/2}$  value for this process is 237 K. For a paramagnetic  $\{S_1; S_2\} = \{2; 0\}$  material (HS  $\text{Mn}^{\text{III}}$  and LS  $\text{Fe}^{\text{II}}$ , the low-temperature (LT) configuration), a  $\chi_{\text{M}}T$  value of  $3.0 \text{ cm}^3 \text{ K mol}^{-1}$  is expected, which is lower than the value observed in the experiment. If exactly 50% of the material is switched from the HT to the LT configuration, the expected  $\chi_{\text{M}}T$  value is  $3.9 \text{ cm}^3 \text{ K mol}^{-1}$ ; this is close to the value found in our experiment. It therefore seems feasible that approximately 50% of the MnFe pairs have transformed to the LT configuration on cooling, which is intriguing considering that microcrystalline samples of comparable



**Figure 2.** (a) Temperature dependence of  $\chi_{\text{M}}T$  versus  $T$  of **1**. (b) Room-temperature  $^{57}\text{Fe}$  Mössbauer spectrum (black circles) of **1** with fitted line (black line) consisting of two different subspectra (grey lines). (c) Raman scattering spectra (black squares) of a single crystal of **1** at various temperatures. Multiple Lorentzian lineshapes (filled) were combined to obtain a fit. The grey and white filled peaks represent vibrations characteristic for the HT and LT configuration, respectively. The excitation density ( $P$ ) is indicated. The spectra are normalized with respect to the integrated intensity of the HT lines and are shown with an offset for clarity.

stoichiometry exhibit a virtually complete conversion.<sup>22</sup> The reverse process takes place at a  $T_{1/2}$  of 292 K. The broad hysteresis of 55 K reflects the cooperativity of the electron transfer process. The magnetic ordering in the LT phase occurring below 12 K, and hence the observed increase in  $\chi_{\text{M}}T$ , has been proposed to arise from a mechanism of mixed-valence electron delocalization of the Mn ions similar as reported for the  $\text{Fe}^{\text{III}}$  ions in Prussian Blue  $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$ .<sup>26,28</sup>

We have several reasons to believe that the consistently observed partial switching is an intrinsic property of the crystals. At first, magnetic susceptibility measurements recorded for independently prepared samples confirm the approximately 50% switching ratio. Second, it is also detected by  $^{57}\text{Fe}$  Mössbauer spectroscopy and Raman spectroscopy. The latter technique is therefore crucial and is in this instance very conclusive, as the spectra evidencing reproducible extents of partial switching have repeatedly been recorded on different single crystals. In addition, a sample made of powdered crystals also shows the same ratio in switching.

The partial switching can be explained by proposing two or more distinct iron sites differing in electron transfer capability. This is supported by the  $^{57}\text{Fe}$  Mössbauer spectrum recorded at 293 K (Figure 2b) revealing approximately equal area fractions for two different LS  $\text{Fe}^{\text{III}}$  sites (site 1,  $\delta = 0.138(2) \text{ mm s}^{-1}$ ,  $\Delta = 0 \text{ mm s}^{-1}$ ,  $\Gamma/2 = 0.16(2) \text{ mm s}^{-1}$ ; site 2,  $\delta = 0.150(2) \text{ mm s}^{-1}$ ,  $\Delta = 0.43(1) \text{ mm s}^{-1}$ ,  $\Gamma/2 = 0.145(7) \text{ mm s}^{-1}$ ). Inequivalent Fe and Mn environments may be generated by a particular distribution of the different unit cells that originate from the observed disorder of the Rb ions (and water molecules) over the two interstitial sites,  $4c$  and  $4d$ , in the spacegroup  $F-43m$ , in a 3:1 ratio.<sup>27</sup>

Figure 2c shows the evolution of the 532 nm excited Raman spectrum of the CN stretch vibrations in a single

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crystal of **1** upon cooling. At temperatures above the phase transition ( $T > 250$  K) two strong bands are observed at 2155 and 2164  $\text{cm}^{-1}$ . These peaks originate from the stretching modes of the CN moiety in the HT phase. At lower temperatures, new spectral features appear at the cost of the HT lines, mostly at lower energies. These evolve into several new peaks at 2086, 2091, 2110, 2130, and 2202  $\text{cm}^{-1}$ . Since CN vibrations generally decrease in frequency upon lowering of the oxidation state of the C-bound metal ion,<sup>27,29</sup> these modes are assigned to the CN stretching modes of the LT phase, unambiguously confirming the charge transfer in the HT  $\rightarrow$  LT phase transition. It is clear from Figure 2c that spectra below the transition (100, 50 and 4 K ( $P = 1275$  W  $\text{cm}^{-2}$ )) show lines characteristic for both the LT and HT configuration, indicating a partial switching, consistent with the magnetic susceptibility and  $^{57}\text{Fe}$  Mössbauer data. The partial electron transfer process is also apparent by the line at 2202  $\text{cm}^{-1}$ , which is assigned to  $\text{Fe}^{\text{III}}\text{--CN--Mn}^{\text{III}}$ . This band can be present only if the compound has contributions of both the LT and HT configuration.

In contrast, the 4 K spectrum recorded with  $P = 3000$  W  $\text{cm}^{-2}$  shows lines originating from the HT configuration only. This is quite understandable in view of the photoactivity of the material. This allows for optical switching from the LT configuration to a metastable HT configuration, above a certain excitation power density.<sup>13</sup> Here, the 4 K spectra

demonstrate complete optical switching using 532 nm excitation light. The c.w. excitation power threshold for complete switching at 4 K is found to be  $\sim 2000$  W  $\text{cm}^{-2}$  for 532 nm light.

In summary, we have determined the crystal structure of the Prussian Blue analog  $\text{RbMn}[\text{Fe}(\text{CN})_6]\cdot\text{H}_2\text{O}$ , and shown that the crystals undergo a partial, reversible valence transfer between the HS  $\text{Mn}^{\text{II}}$ , LS  $\text{Fe}^{\text{III}}$  and the HS  $\text{Mn}^{\text{III}}$ , LS  $\text{Fe}^{\text{II}}$  configuration under the influence of temperature. Raman spectroscopy also shows a transition from the LT to the HT configuration upon irradiation with light in single crystals. The partial switching of the crystals may be assigned to distinctly different Fe sites brought about by unequal Rb/ $\text{H}_2\text{O}$  distributions. With these single crystals in hand, current efforts are focused on an extensive exploration of the mechanisms and opportunities for optical and thermal control of the physical properties of these materials.

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**Supporting Information Available:** Synthetic procedures, experimental details of magnetic,  $^{57}\text{Fe}$  Mössbauer, and Raman measurements, crystallographic data of **1**, interpretation of Raman spectra and Mössbauer data and possible model for generation of two different Fe sites (PDF) and crystallographic information files (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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