

Pressure-Induced Sequential Magnetic Pole Inversion and Antiferromagnetic–Ferromagnetic Crossover in a Trimetallic Prussian Blue Analogue

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Prussian blue (PB) analogues display a wide range of important magnetic (e.g., room temperature magnetic ordering) and magneto-optical (e.g., piezoelectric ferromagnetism, photoinduced (de)magnetization) properties.¹ This stems from the flexibility of their framework structure which allows one to adjust at will the composition and tune the total magnetization of the system by selecting appropriate spin sources. In addition, the nature of the magnetic exchange can be anticipated in advance from basic orbital interaction arguments and the structure directing quality of the cyanide bridge. A notable example of this approach has been the design of magnetic materials (Néel's *N* phases)² displaying magnetic pole inversion below a compensation temperature, T_{comp} , by using competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions in trimetallic PB analogues, $(\text{Ni}_x\text{Mn}_{1-x})_{1.5}[\text{Cr}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ ($x \sim 0.4$).³ The reversible change of the sign of the spontaneous magnetization can be also observed as a response to an external stimulus, such as humidity and light irradiation.⁴

The application of hydrostatic pressure is also a powerful tool to modulate the properties of molecular magnets, including PB analogues, which show various responses, such as internal electron transfer, spin state transitions, and linkage isomerism of the cyanide bridge.⁵ In addition, pressure strongly influences the ground state magnetic properties by finely tuning the strength of the ligand field and the $d-\pi-d$ exchange interactions. Here we show that pressure can be also employed to induce a series of magnetic pole inversions in an appropriately chosen trimetallic PB ferrimagnet, $\text{Rb}_{0.64}\text{Ni}_{0.31}\text{Mn}_{0.87}[\text{Fe}(\text{CN})_6] \cdot 2.8\text{H}_2\text{O}$ (**1**).⁶ Depending on the experimental conditions, the magnetization of **1** can be reversibly switched sequentially from positive to negative and back to positive at very low pressures. At moderate pressures, a reversible internal charge transfer is also induced, leading to a crossover from ferrimagnetic to FM ordering.

1 is a member of the family of mixed ferri-ferromagnets, $\text{Rb}_y\text{Ni}_x^{\text{II}}\text{Mn}_{1-x}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_z \cdot n\text{H}_2\text{O}$, which incorporate both FM ($J_{\text{Ni-Fe}} > 0$) and AFM ($J_{\text{Mn-Fe}} < 0$) interactions and display a change in sign of the spontaneous magnetization for $x \approx 0.35-0.45$ below $T_{\text{comp}} \approx 6-8$ K. It was chosen in such a way as to be ferrimagnetic but with a value of x placing it at ambient P near Néel's *R-N* phase boundary for exhibiting magnetic pole inversion.² The magnetic response of **1** is consistent with overall AFM exchange interactions (Weiss temperature, $\theta = -7.5(1)$ K), while both the measured $\chi_{\text{M}}T$ at 300 K ($4.53 \text{ cm}^3 \text{ K mol}^{-1}$) and the saturation magnetization ($2.63 \mu_{\text{B}}$) are consistent with parallel alignment of the Ni^{II} ($S = 1$) and antiparallel alignment of Mn^{II} (HS, $S = 5/2$) spins with the Fe^{III} (LS, $S = 1/2$) spins. **1** is a

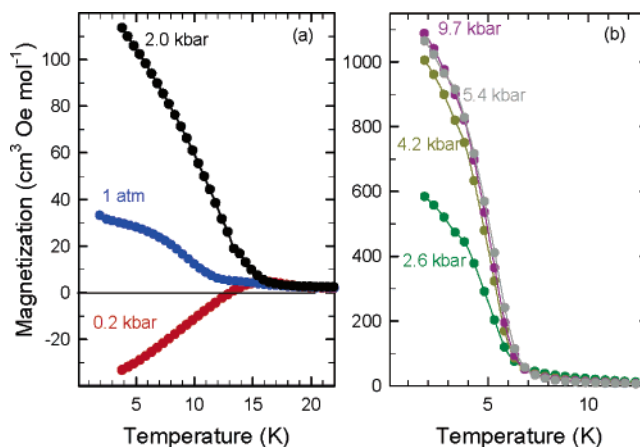


Figure 1. Temperature dependence of the magnetization ($H = 1$ mT, field cooling) of $\text{Rb}_{0.64}\text{Ni}_{0.31}\text{Mn}_{0.87}[\text{Fe}(\text{CN})_6] \cdot 2.8\text{H}_2\text{O}$ as a function of pressure. ferrimagnet, $T_{\text{N}} \approx 16$ K, with the temperature dependence of the spontaneous magnetization showing a double hump (Figure 1a).

The magnetic response of **1** proved extremely sensitive to pressure. Remarkably, upon pressurizing at *only* 0.2 kbar, the material exhibits magnetic pole inversion with the spontaneous magnetization reversing its sign to negative below $T_{\text{comp}} = 13$ K (Figure 1a).⁷ This is accompanied by an increase of the ordering temperature to 17.5 K and a decrease of both θ ($-5.9(1)$ K) and $\chi_{\text{M}}T$ at 300 K ($4.32 \text{ cm}^3 \text{ K mol}^{-1}$) (Figure 2b). These trends are consistent with the applied pressure enhancing the FM relative to the AFM exchange interactions [$(dJ_{\text{Ni-Fe}}/dP) > (dJ_{\text{Mn-Fe}}/dP)$], thereby shifting the material across the *R-N* phase boundary. The signature of the larger FM pressure coefficient is also evident when the applied pressure is increased further to 0.6 kbar. The low-field magnetization switches back to positive as the FM interactions are further enhanced, and the material crosses now the *N-P* boundary. The spontaneous magnetization continues to increase rapidly on further raising the pressure to 2.0 kbar as the FM interactions compete more effectively and θ now assuming a small positive value (Figure 1a).

However, the behavior of **1** changes even more dramatically when the pressure reaches 2.6 kbar. The spontaneous magnetization increases at an accelerated rate (Figure 1b), while the measured $\chi_{\text{M}}T$ at 300 K decreases considerably. This pressure-induced transformation is essentially complete by 4.2 kbar when the spontaneous magnetization approaches a value 40 times larger than that at 1 atm and the magnetic ordering temperature is ~ 5 K. The Weiss constant assumes a large positive value ($+16.4(2)$ K), and $\chi_{\text{M}}T$ (300 K) collapses to $2.6 \text{ cm}^3 \text{ K mol}^{-1}$. These changes provide the signature of a sudden switch from ferrimagnetic to FM order and a concomitant change in the metal ion spin configurations. The

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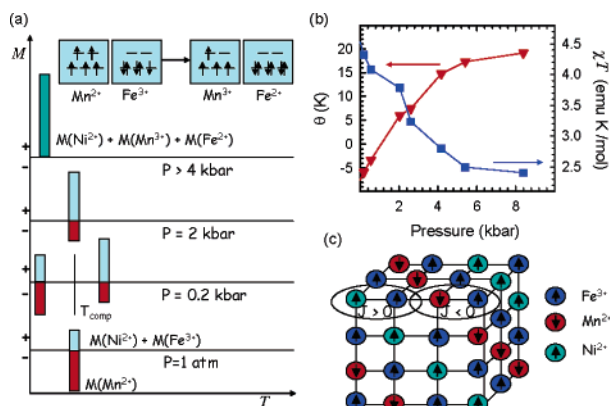


Figure 2. (a) Schematic diagram illustrating positive, $M(\text{Ni}^{2+}) + M(\text{Fe}^{3+})$, and negative, $M(\text{Mn}^{2+})$, magnetizations versus the direction of the external magnetic field as a function of temperature and pressure. Following the phase transition driven by the internal redox reaction above 4 kbar, all magnetic sublattices interact ferromagnetically. (b) Pressure dependence of $\chi_M T$ at 300 K (blue squares) and of the Weiss temperature, θ (red triangles), deduced by Curie–Weiss fits to $1/\chi_M(T)$ data between 50 and 300 K. (c) Schematic illustration of the coexistence of both FM and AFM superexchange interactions in the cubic PB-type structure of **1**.

only possible scenario consistent with the decrease in the effective magnetic moment is the internal metal-to-metal charge transfer $\text{Mn}^{\text{II}}(\text{HS}, d^5, S = 5/2) - \text{NC} - \text{Fe}^{\text{III}}(\text{LS}, d^5, S = 1/2) \rightarrow \text{Mn}^{\text{III}}(\text{HS}, d^4, S = 2) - \text{NC} - \text{Fe}^{\text{II}}(\text{LS}, d^6, S = 0)$,⁸ while alternative possibilities, such as metal-centered spin transitions and cyanide ligand flips, can be unambiguously excluded. Such a pressure-induced electronic transformation is also the driving force for the switch to bulk ferromagnetism. At low pressures, the $\text{Mn}^{\text{II}}(\text{HS})$ and $\text{Fe}^{\text{III}}(\text{LS})$ centers couple antiferromagnetically. In contrast, in the piezotransformed material, the exchange coupling between near-neighbor $\text{Mn}^{\text{III}}(\text{HS}, t_{2g}^3 e_g^1)$ ions, as mediated by the $\text{Fe}^{\text{II}}(\text{LS}, t_{2g}^6 e_g^0)$ t_{2g} orbitals, is FM in nature.⁹ As the pressure is increased further to 9.7 kbar, no other major changes are observed with T_C increasing slowly at ~ 0.1 K/kbar, reflecting the enhancement of the exchange interactions, which accompanies the decrease in near-neighbor metal–metal distances.

All transformations are fully reversible upon release of the pressure and are accompanied by hysteretic behavior (Figure 2S). The back internal electron transfer, $\text{Mn}^{\text{III}}(\text{HS}) - \text{NC} - \text{Fe}^{\text{II}}(\text{LS}) \rightarrow \text{Mn}^{\text{II}}(\text{HS}) - \text{NC} - \text{Fe}^{\text{III}}(\text{LS})$, is now observed at 3.6 kbar ($\Delta P \sim 0.6$ kbar) as is the reversal of the sign of the spontaneous magnetization just above atmospheric pressure ($\Delta P \sim 0.1$ kbar).

There are several prominent points arising from the present results. Pressure is proven to be an extremely efficient external stimulus for fine-tuning the properties of molecular magnets and for generating hidden electronic and magnetic states. The flexibility of the structure of PB analogues and its ability to incorporate a variety of competing magnetic interactions have allowed the design of mixed ferro-ferrimagnets (Figure 2c), which can span the whole spectrum of magnetic behavior, predicted by Néel,² including the rare phenomenon of magnetization reversal (in small magnetic fields) in response to a change in temperature.³ By synthesizing **1**, which exhibits positive magnetization but lies at the boundary between Néel's R and N ferrimagnetic phases, we were able to employ hydrostatic pressure to induce multiple reversals of the direction of the spontaneous magnetization. Remarkably, the magnetic response of **1** is so sensitive to pressure that the magnetization flips from positive to negative at only 0.2 kbar and then flips back to positive at 0.6 kbar. Such facile pressure-induced control of the magnetic poles is unprecedented and mirrors the effect of light illumination on the magnetic properties. It can be attributed to the rapid enhancement of the FM interactions with increasing

P , as also reflected in the substantial increase in the magnetic ordering temperature.

Figure 2a summarizes in a schematic way the evolution of the competition between the metal sublattice magnetizations with increasing pressure. As the applied pressure increases above ~ 4 kbar, the material becomes unstable, abruptly transforming to a phase in which an internal redox reaction, $\text{Mn}^{\text{II}}(\text{HS}) - \text{Fe}^{\text{III}}(\text{LS}) \rightarrow \text{Mn}^{\text{III}}(\text{HS}) - \text{Fe}^{\text{II}}(\text{LS})$, takes place with the effective magnetic moment at ambient temperature decreasing sharply and the magnetic order switching from ferrimagnetic to bulk FM. Although pressure-induced electron transfer has been observed before in PB analogues, the transformed state is also typically accessible thermally at ambient pressure.⁵ This is not the case for **1** as there is no hint of the presence of a thermal hysteresis loop in the χT versus T data, and pressure allows access to a hidden electronic state with drastically different magnetic properties.

In conclusion, the trimetallic mixed ferri-ferromagnet **1** shows an extreme (reversible) sensitivity to pressure with facile flipping of the magnetic poles and interconversion between electronic states with differing magnetic properties. The initial results presented here demonstrate that pressure is a powerful stimulus to tune and modulate the magnetic interactions in PB analogues and to allow trapping of novel inaccessible states.

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Supporting Information Available: Synchrotron X-ray powder diffraction profile of **1** at room temperature. Temperature dependence of the spontaneous magnetization obtained on releasing the pressure from 9.7 kbar to ambient. Temperature dependence of $\chi_M T$ and magnetic hysteresis M versus H loops at various pressures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (6) **1** was prepared as a brown solid by reaction of aqueous solutions of MnCl_2 (0.075 M), NiCl_2 (0.025 M), RbCl (1 M), and $\text{K}_3[\text{Fe}(\text{CN})_6]$ (0.1 M), and its stoichiometry was determined by elemental analysis (Rb:Ni:Mn:Fe: $\text{H}_2\text{O} = 0.64:0.31:0.87:1:2.8$). X-ray powder diffraction measurements are consistent with a single-phase material (Figure 1S). T - and H -dependent magnetization was measured in a QD MPMS SQUID magnetometer up to ~ 10 kbar. Two piston-cylinder high-pressure cells using Daphne mineral oil as pressure transmitting medium were employed: a home-built one (pressure calibrated by its external diameter) and the easyLab Mcell110 (pressure calibrated with the P -dependence of the T_C of Sn). The data were corrected for diamagnetic core contributions.
- (7) The required pressure to invert the magnetization direction is so small that it can be also reached by pelleting the material with a hand-operated press.
- (8) We restrict ourselves to the electron transfer occurring only between the Fe^{III} and Mn^{II} sublattices. Given the small Ni content, it is not possible to establish unambiguously with the present data whether the Ni^{II} sublattice is also oxidized. This does not affect our subsequent discussion as the coupling between the Ni and Fe sublattices remains always FM.
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