

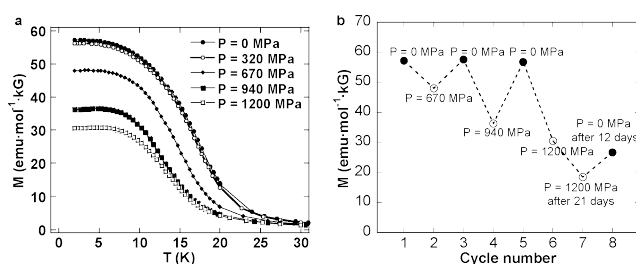
# Pressure-Tuning of Magnetism and Linkage Isomerism in Iron(II) Hexacyanochromate

Eugenio Coronado,<sup>\*,†</sup> Mari Carmen Giménez-López,<sup>†</sup> Georgiy Levchenko,<sup>†</sup> Francisco M. Romero,<sup>\*,†</sup> Valentín García-Baonza,<sup>‡</sup> Alla Milner,<sup>§</sup> and Moshe Paz-Pasternak<sup>§</sup>

*Institut de Ciència Molecular, Universitat de València, Dr. Moliner 50, 46100 Burjassot, Spain, Departamento de Química Física I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain, and School of Physics and Astronomy, Tel Aviv University, 69978 Tel Aviv, Israel*

E-mail: fmm@uv.es

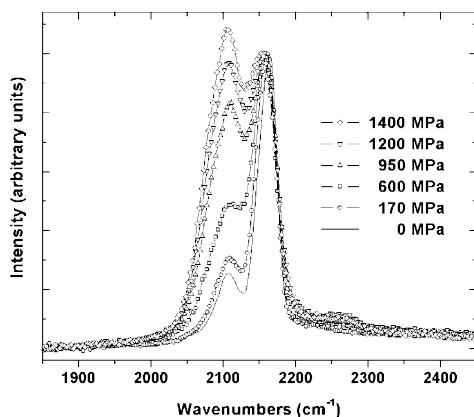
The ability of certain molecules and molecule-based materials to change the nature of their electronic ground state under the presence of an external perturbation is well-known. This leads to functional materials in which a physical property (absorption of light, magnetic moment, electrical conductivity, etc.) can be tuned through the application of an external stimulus. Examples of materials that undergo abrupt changes in magnetic moment under thermal treatment, light irradiation, or mechanical compression are abundant in the literature on spin crossover compounds.<sup>1</sup> Less common is the observation of this behavior in magnetically ordered molecule-based materials. In this context, photoinduced and pressure-induced switching of bulk magnetization have been observed in a cobalt-iron cyanide.<sup>2-5</sup> Also, electrochemical tuning of the magnetic phase transition has been reported in a chromium cyanide thin film.<sup>6</sup> The three phenomena bear some features in common: the materials under study are all Prussian blue analogues, a family of compounds that can combine high- $T_C$  molecule-based magnetism<sup>7,8</sup> with very rich electrochemical behavior.<sup>9</sup> Indeed, the key step in all these processes is always an electron-transfer reaction. Surprisingly, the possibility of tuning the magnetization via structural rearrangements has not yet been explored despite the fact that cyanide is a nonsymmetric ligand and linkage isomerization can be operative in these systems, as evidenced by Miller et al. in an iron-manganese cyanide.<sup>10</sup> Also, iron(II) hexacyanochromate-(III)  $\text{Fe}_3[\text{Cr}(\text{CN})_6]_2$  transformations on heating<sup>11-13</sup> into more stable chromium(III) hexacyanoferrate(II)  $\text{Cr}[\text{Fe}(\text{CN})_6]$ . This reaction is nonreversible and can be also electrochemically induced in thin films. We now report on the reversible pressure-induced linkage isomerization and magnetic properties of single crystals of  $\text{K}_{0.4}\text{Fe}_4[\text{Cr}(\text{CN})_6]_{2.8} \cdot 16\text{H}_2\text{O}$  (**1**).



**Figure 1.** (a) Thermal dependence of the magnetization of **1** (applied field) 0.1 T at different pressures. (b) Reversibility plot: magnetization changes induced upon alternating pressure

application (O) and release (b).

**1** crystallizes in the cubic  $Fm\bar{3}m$  space group, and its structural features are typical of a Prussian blue analogue.<sup>15</sup>  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  cations sit, respectively, at the (0, 0, 0) and (1/2, 1/2, 1/2) special positions of a face-centered cubic unit cell of 10.6720(2) Å parameter. Cyanide ligands bridge the metal ions in a linear arrangement, giving rise to a three-dimensional perovskite-like structure. Within this picture, the occupancy of the  $[\text{Cr}(\text{CN})_6]^{3-}$  fragment should be less than unity in order to account for the Fe:Cr stoichiometric ratio. The formula can be represented as  $\text{K}_{0.4}\text{Fe}_4[\text{Cr}(\text{CN})_6]_{2.8}0_{1.2}16\text{H}_2\text{O}$ , where 0 represents the number of  $[\text{Cr}(\text{CN})_6]^{3-}$  vacancies in the system. Water occupies these vacant positions, and the mean  $\text{Fe}^{2+}$  coordination sphere is  $\text{N}_{4.2}\text{O}_{1.8}$ . The Fe-ligand bond distances are characteristic of a high-spin (HS)  $\text{Fe}^{2+}$  center, with Fe-N ) 2.077(15) Å. Zeolitic water molecules and potassium ions fill the cavities, the latter ensuring electroneutrality.



**Figure 2.** Raman spectra showing the evolution of the pressure-induced linkage isomerization of the cyanide ligand in **1**. Intensities are normalized with respect to the high-frequency band.

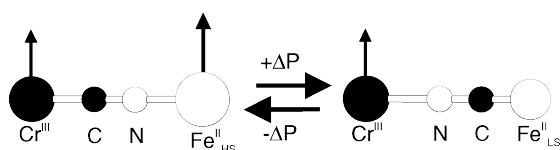
The magnetic behavior of polycrystalline samples of **1** at ambient pressure is similar to that previously observed in powdered samples and thin films:<sup>16</sup> **1** is a soft ferromagnet with critical temperature  $T_C$  ) 19 K and coercive field (at 2 K)  $H_c$  ) 0.06 T. Upon application of external pressure ( $P$ ) in the 0–1200 MPa range, the magnetization decreases considerably and initiates saturation at lower temperatures (Figure 1a). At 1200 MPa,  $T_C$  is 13 K and the saturation value of the magnetization ( $30 \text{ emu mol}^{-1} \text{ kG}$ ) is halved compared to that at ambient pressure. The phenomenon is reversible: releasing the pressure results in a thermal dependence of the magnetization that matches that of the original sample (Figure 1b). An additional and irreversible decrease of the magnetization and ordering temperature ( $T_C$  ) 8 K) is observed after prolonged treatment (21 days) at 1200 MPa. Pressure-dependent magnetization hysteresis loops are also observed. Application of pressure results in a decrease of the magnetization at saturation from a value of  $18 \mu_B$  at ambient

pressure to  $10 \mu_B$  observed at 1200 MPa.

The magnetic properties point to the existence of a pressure-induced partial structural transformation that is accompanied by a decrease of the magnetic moment. In principle, three transformations can be envisaged: (A) spin crossover of the  $Fe^{2+}$  cations,  $Cr(III)-C\equiv N-Fe(II)_{HS} \longrightarrow Cr(III)-C\equiv N-Fe(II)_{LS}$ ; (B) metal-cyanide linkage isomerization (and subsequent spin change of  $Fe^{2+}$ ),  $Cr(III)-C\equiv N-Fe(II)_{HS} \longrightarrow Cr(III)-N\equiv C-Fe(II)_{LS}$ ; and (C) electron transfer,  $Cr(III)-C\equiv N-Fe(II)_{HS} \longrightarrow Cr(II)-C\equiv N-Fe(III)_{HS}$ . Cyanide stretching vibrations are very dependent on the oxidation state of the bonded metal ions and they can be used here as a local probe. Process A, with no change in oxidation states, should be accompanied by a small frequency shift ( $6-7 \text{ cm}^{-1}$ ) to higher values.<sup>17</sup> Instead, for processes B and C, a significant shift ( $60 \text{ cm}^{-1}$ ) to lower frequencies (decrease in  $\sigma$ -bonding) should be observed. The Raman spectrum of **1** at ambient pressure (Figure 2) shows an intense band at  $2164 \text{ cm}^{-1}$  that can be ascribed to cyanide stretching vibration in the  $Cr^{III}-C\equiv N-Fe^{II}$  configuration. A small peak at  $2108 \text{ cm}^{-1}$  indicates the presence of  $M^{III}-N\equiv C-M^{II}$  defects. On pressure treatment, the intensity of this band increases and a concomitant decrease of the high-frequency band is observed. The process is completely reversible. According to the relative Raman intensities, at around 1300 MPa both  $Cr^{III}-C\equiv N-Fe^{II}$  (initial) and  $M^{III}-N\equiv C-M^{II}$  (final) configurations are present in the solid in approximately equal amounts. The Raman study excludes an “intrinsic” spin crossover (A), but reactions B and C are equally possible. However, the significant decrease in magnetization<sup>18</sup> and ordering temperatures clearly indicates a pressure-induced linkage isomerization of the cyanide ligand (B) with subsequent spin change (Scheme 1) and seems to discard a simple electron-transfer process C.

Mössbauer spectroscopy has been used to distinguish between these two possible phenomena. The Mössbauer spectrum of iron(II) hexacyanochromate at ambient conditions was previously described.<sup>13</sup> Mössbauer spectra of **1** recorded at room temperature and different pressures (Supporting Information) show the appearance at 2000 MPa of a new spectral component characterized by small  $\Delta$  and isomer shift values, indicating the presence of low-

**Scheme 1.** Pressure-Induced Control of the Exchange Coupling in **1**



spin iron(II) centers. With pressure increase, the relative abundance of this signal increases. Measurements at 6 K and  $P > 2000$  MPa show that the high-spin components are magnetically ordered as manifested by the complex hyperfine splitting. This phenomenon is not observed for the new signal, providing clear evidence for a pressure-induced magnetic transition. Finally, at 2500 MPa, the splitting disappears, suggesting a  $T_C < 6$  K. These data point to a pressure-driven  $\text{Fe}^{2+}$  spin crossover. The combined Raman and Mössbauer analyses show that this spin change is not intrinsic but subsequent to a pressure-induced linkage isomerization of the cyanide-metal bond from an initial state  $\text{Cr}^{\text{III}}-\text{C}\equiv\text{N}-\text{Fe}^{\text{II}}$  to  $\text{Cr}^{\text{III}}-\text{N}\equiv\text{C}-\text{Fe}^{\text{II}}$ .

As a result, the electronic configuration of the iron(II) cations changes from high-spin (HS,  $S = 2$ ) to low-spin (LS,  $S = 0$ ) upon mechanical compression (Scheme 1). The appearance of diamagnetic  $\text{Fe}^{\text{II}}$  centers results in a decrease of the magnetic moment and interrupts the connectivity of the magnetic lattice, leading to lower ordering temperatures.

It is interesting to compare the reversible piezomagnetic process with the previously reported thermally induced linkage isomerization reaction  $\text{Fe}_3[\text{Cr}(\text{CN})_6]_2 \longrightarrow \text{Cr}_4[\text{Fe}(\text{CN})_6]_3$ . The latter is accompanied by a severe contraction of the cell parameter from 10.65 to 10.05 Å. This contraction is clearly the driving force of the piezomagnetic process: application of pressure results in stabilization of the most compact structure and leads to isomerization.<sup>19</sup>

This chromium-iron compound joins a selected group of bimetallic cyanides in which magnetic ordering can be tuned by external stimuli. In the previously reported examples, the material undergoes electron transfer when the external perturbation is applied. In the present case, pressure induces a more drastic but reversible structural transformation in the solid.<sup>20</sup> At the local level, the rotational movement of the cyanide anions can be considered as a molecular switch of the magnetic interaction between nearest neighbors. The old family of Prussian blue still deserves attention and will probably afford more fascinating examples of structurally driven switching magnets such as **1**.

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**Supporting Information Available:** Raman spectra, field dependence of the magnetization, AC susceptibility and Mössbauer spectra ( $T = 300$  and 6 K) at different pressures, Experimental Section, and crystallographic data (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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  - (18) Assuming a contribution of  $4 \mu\text{B}$  per Fe(II) center, the  $8 \mu\text{B}$  decrease in magnetization suggests the presence of two (50%)  $\text{Fe}^{2+}$  cations per formula in their low-spin configuration (Supporting Information).
  - (19) Reversibility is possible because the Fe:Cr stoichiometry does not change along the process. In the thermally induced reaction, however, the excess iron is released as ferric oxyhydroxide; see ref 13.
  - (20) Electron transfer might be involved in the mechanism of isomerisation.

## SUPPORTING INFORMATION

### Assignment of bands in the Raman spectra:

The IR-Raman absorption properties of cyanometallates and Prussian blue analogues have been studied in detail. Standard textbooks like Nakamoto's (**Infrared and Raman Spectra of Inorganic and Coordination Compounds. John Wiley & Sons, New York, 1986**) or Socrates' (**Infrared Characteristic Group Frequencies. Tables and Charts. John Wiley & Sons, New York, 1994.**) are good references to see that the frequency of the cyanide stretching vibration is highly sensitive to the oxidation state of the bonded metal ions. In particular, in both textbooks and in our ref. 11-13, reference is given to the so-called "red" and "green" isomers of the iron-chromium cyanide system. It is stated that:

The red isomer is iron(II) hexacyanochromate(III) ( $\text{Fe}_3[\text{Cr}(\text{CN})_6]_2$ ) and its cyanide stretching vibration is equal to  $2168\text{ cm}^{-1}$ . Clearly, our starting material (red single crystals) is the red isomer and the principal band located at  $2164\text{ cm}^{-1}$  corresponds to the initial Cr(III)-C $\equiv$ N-Fe(II) configuration.

The green isomer is chromium(III) hexacyanoferrate(II) ( $\text{Cr}_4[\text{Fe}(\text{CN})_6]_3$ ) and its cyanide stretching vibration is equal to  $2092\text{ cm}^{-1}$ . By comparison, the new band that we observe at  $2108\text{ cm}^{-1}$  can be tentatively assigned to the presence of some Cr(III)-N $\equiv$ C-Fe(II) bridges (defaults). As it has been pointed out in the paper, the final assignment is only possible after examination of the Mössbauer spectra and the magnetic data.

Upon pressure application, the intensity of the low-frequency band increases, and a concomitant decrease of the intensity of the high-frequency band is observed. (For experimental reasons, it is necessary to use a new sample for each experiment at a different pressure. That is why intensities have been normalized to the value of the high-frequency band). The frequency of this band, assigned to the Cr(III)-C $\equiv$ N-Fe(II) initial configuration, shifts to lower values. This is also a consequence of the isomerization reaction. Actually, there is a linear correlation between the frequency of this band and the intensity of the new band corresponding to the isomerized Cr(III)-N $\equiv$ C-Fe(II) configuration (Figure S1).

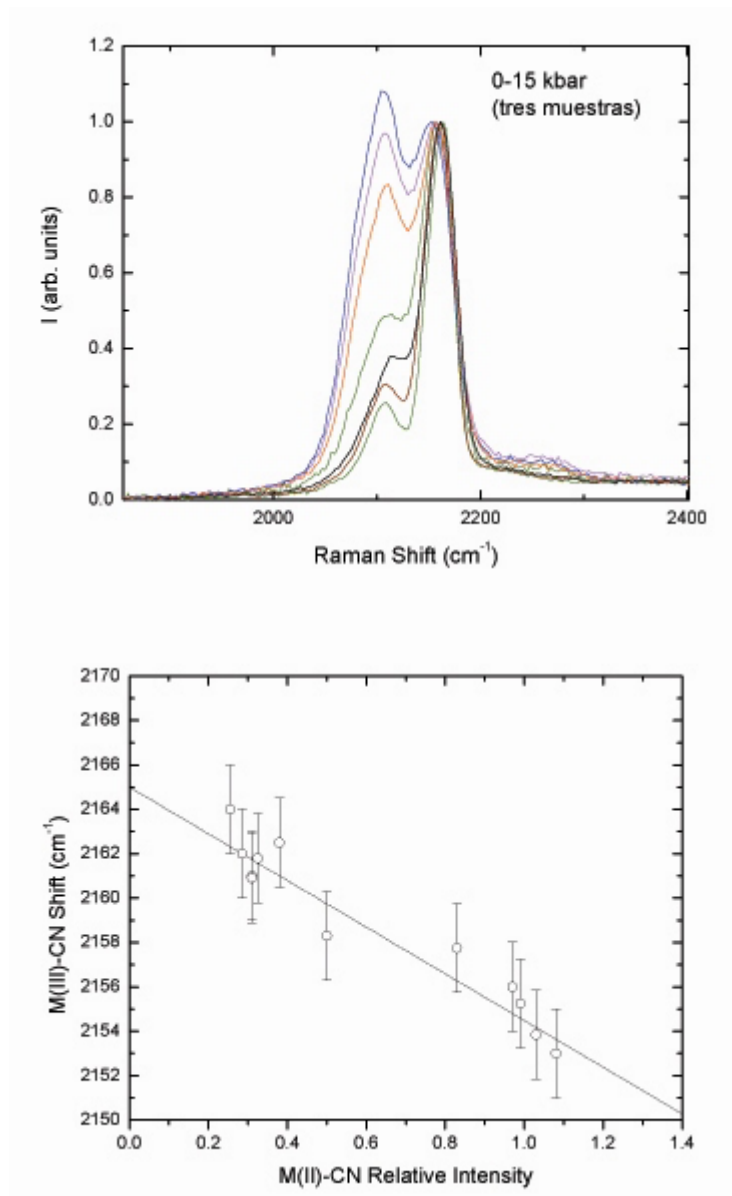
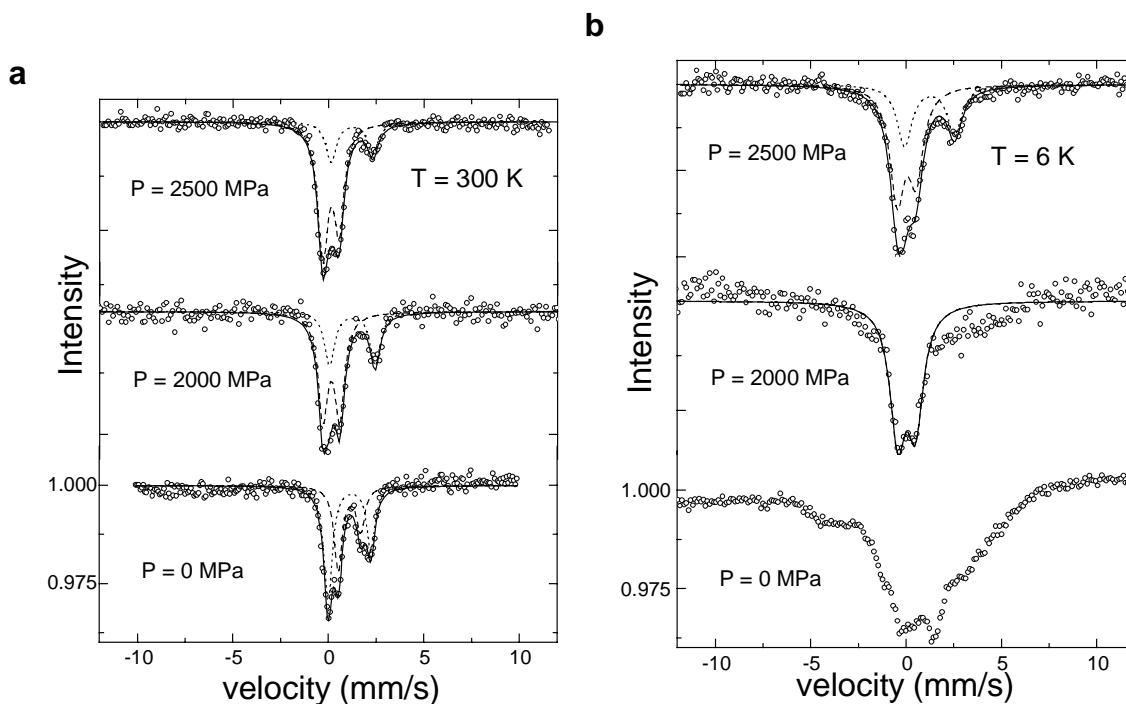


Figure S1.

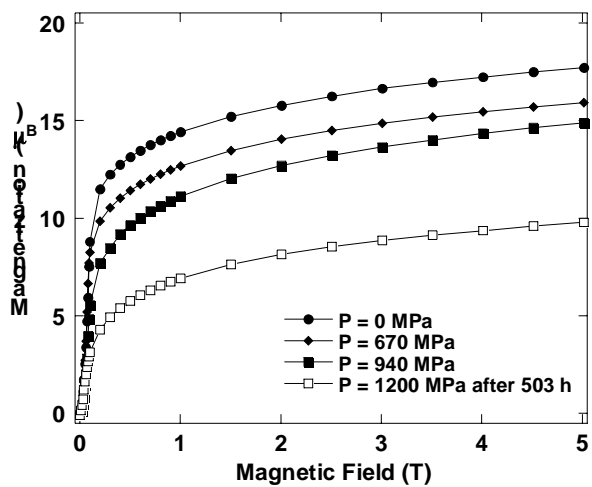
## Mössbauer spectroscopy:

The Mössbauer spectrum of iron(II) hexacyanochromate at ambient conditions was previously described (our ref. 13). It shows two quadrupole doublets corresponding to non-equivalent high-spin  $\text{Fe}^{2+}$  cations (see Figure S2a, down). These doublets have been attributed to the different  $\text{FeN}_6$  and  $\text{FeN}_4\text{O}_2$  metal surroundings. The Mössbauer spectra of **1** recorded at room temperature and different pressures show the appearance at 2000 MPa of a new spectral component characterized by small  $\Delta$  and isomer shift values, indicating the presence of low-spin iron(II) centers (Figure S2a, middle). With pressure increase, the relative abundance of this signal increases (Figure S2a, top). Measurements at 6 K show that the two ambient pressure high-spin components are magnetically ordered as manifested by the complex hyperfine splitting (Figure S2b, down). This phenomenon is not observed for the new signal that appears at 2000 MPa, providing clear evidence for a pressure-induced magnetic transition (Figure S2b, middle). At this pressure, the remaining high-spin centers exhibit a reduced hyperfine splitting indicative of lower ordering temperatures. Finally, at 2500 MPa (Figure S2b, top), the splitting disappears suggesting a  $T_C < 6$  K.

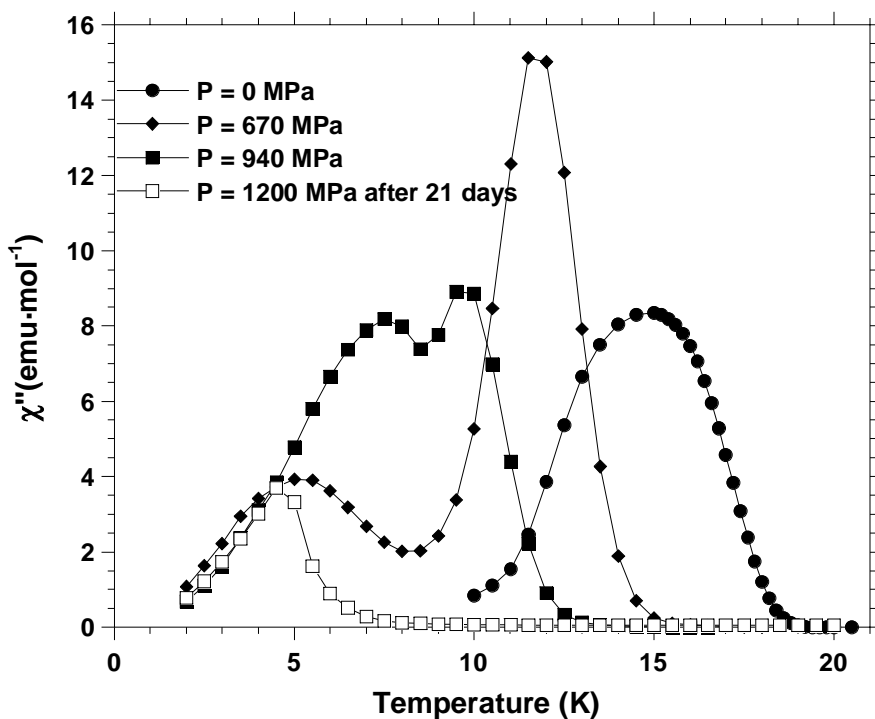


**Figure S2.** Mössbauer spectra at  $T = 300$  K (a) and  $T = 6$  K (b) as a function of external pressure.

Magnetic properties:



**Figure S3.** Field dependence of the magnetization at 2 K and different pressures.



**Figure S4.** Temperature dependence of the out-of-phase component of the AC susceptibility (110 Hz) at different pressures.

**1** was obtained by slow diffusion in an H-shaped tube of two ethanolic aqueous solutions containing  $\text{K}_3[\text{Cr}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$  and  $\text{Fe}[\text{ClO}_4]_2\cdot 6\text{H}_2\text{O}$ . After a few weeks, red cube-shaped single crystals were formed. The yield was 3-6 mg (15-30%). The mean relative metal composition was evaluated by SEM analysis. The water content was determined by thermogravimetric analysis. Elem. Anal. Found (calcd for  $\text{K}_{0.4}\text{Fe}_4[\text{Cr}(\text{CN})_6]_{2.8}\cdot 16\text{H}_2\text{O}$ ): C, 19.16 (18.18); H, 2.94 (2.91); N, 19.26 (21.20). (calcd for  $\text{K}_{0.4}\text{Fe}_4[\text{Cr}(\text{CN})_6]_{2.8}\cdot 16\text{H}_2\text{O}\cdot \text{EtOH}$ ): C, 19.53; H, 3.31; N, 20.36. CSD-391283 contains the details of crystal structure solution and refinement which can be obtained from the Inorganic Crystal Structure Database (<http://icsdweb.fiz-karlsruhe.de/index.php>).

Variable-temperature (applied field: 1000 Oe) and field-dependent ( $T = 2$  K) magnetization measurements were carried out in a Quantum Design MPMS Squid magnetometer. The hydrostatic pressure cell made of hardened beryllium bronze with silicone oil as the transmitting medium operates under pressures lower than 1300 MPa. The dimensions of the cylindrically shaped sample holder are 1 mm in diameter and 8 mm in length. The pressure was measured using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of high purity tin.

Raman spectra were measured at room temperature using a sapphire anvil cell (SAC). Raman spectra were excited using the 488 nm line of an ILT air-cooled  $\text{Ar}^+$  laser. The scattered radiation was spatially filtered and collected in backscattering into an ISA HR460 spectrograph coupled to a liquid nitrogen cooled CCD multi-channel detector. Raman spectra were collected at  $4\text{ cm}^{-1}$  spectral resolution. The pressure on the sample was determined by measuring the shift of the Raman band of the microcrystalline diamonds with an absolute uncertainty of 100 MPa.

Mössbauer measurements were carried out in a top-loaded LHe cryostat in the 5–300 K temperature range up to  $\sim 50$  GPa using a  $^{57}\text{Co}(\text{Rh})$  point source. Samples were loaded into a miniature *opposing-plates* diamond anvil cell. The initial dimensions of the sample cavities in the Re gasket were  $250 \times 35$

$\mu\text{m}$ . Typically about 24h was required for each Mössbauer spectrum. The final spectra were analyzed using least-squares-fitting programs to obtain the hyperfine interaction parameters and components abundance.

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