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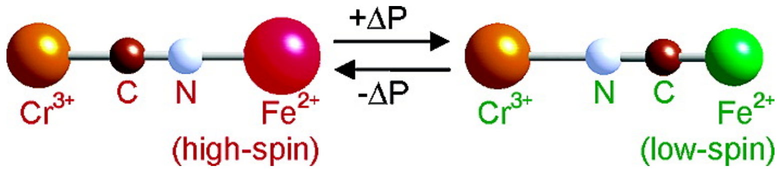

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Pressure-Tuning of Magnetism and Linkage Isomerism in Iron(II) Hexacyanochromate

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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.[1] 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.[2−5] Also, electrochemical tuning of the magnetic phase transition has been reported in a chromium cyanide thin film.[6] 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[7,8] with very rich electrochemical behavior.[9] 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.[10] Also, iron(II) hexacyanochromate(III) $Fe_3[Cr(CN)_6]_2$ transforms on heating[11−13] into the more stable chromium(III) hexacyanoferrate(II) $Cr_4[Fe(CN)_6]_3$. This reaction is nonreversible and can be also electrochemically induced in thin films.[14] We now report on the reversible pressure-induced linkage isomerization and magnetic properties of single crystals of $K_{0.4}Fe_4[Cr(CN)_6]_{2.8}\cdot 16H_2O$ (**1**).

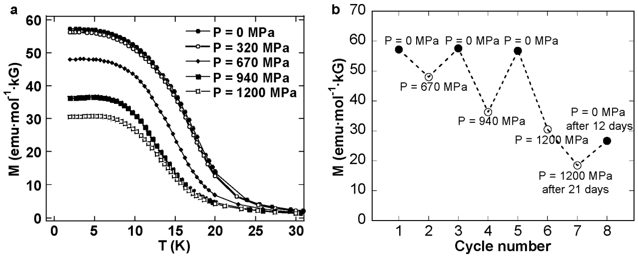

Figure 1. (a) Thermal dependence of the magnetization of **1** (applied field = 0.1 T) at different pressures. (b) Reversibility plot: magnetization changes induced upon alternating pressure application (○) and release (●).

1 crystallizes in the cubic $Fm\bar{3}m$ space group, and its structural features are typical of a Prussian blue analogue.[15] Fe^{2+} and 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 $[Cr(CN)_6]^{3-}$ fragment should be less than unity in order to account for the Fe:Cr stoichiometric ratio. The formula can be represented as $K_{0.4}Fe_4[Cr(CN)_6]_{2.8}\square_{1.2}\cdot 16H_2O$, where $\square$ represents the number of $[Cr(CN)_6]^{3-}$ vacancies in the system. Water occupies these vacant positions, and the mean Fe^{2+} coordination sphere is $N_{4.2}O_{1.8}$. The Fe−ligand bond distances are characteristic of a high-spin (HS) Fe^{2+} center, with Fe−N = 2.077(15) Å. Zeolitic water molecules and potassium ions fill the cavities, the latter ensuring electroneutrality.

The magnetic behavior of polycrystalline samples of **1** at ambient pressure is similar to that previously observed in powdered samples and thin films:[16] **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 emu mol^{-1} 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 μ_B at ambient pressure to 10 μ_B observed at 1200 MPa.

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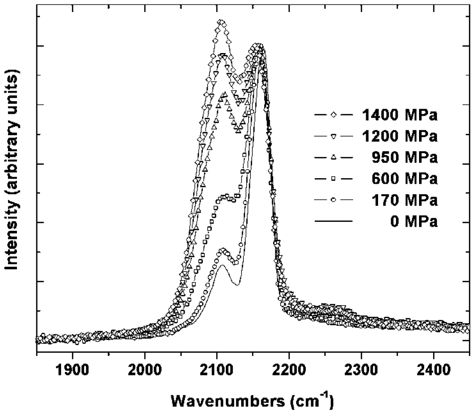
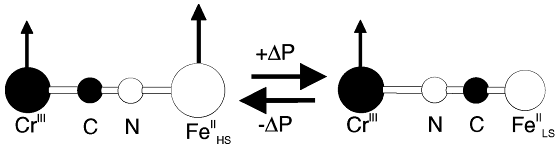


Figure 2. Raman spectra showing the evolution of the pressure-induced linkage isomerization of the cyanide ligand in **1**. Intensities are normalized with respect to the high-frequency band.

The magnetic 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, $\mathbf{Cr(III){-}C{\equiv}N{-}Fe(II)_{HS} \rightarrow Cr(III){-}C{\equiv}N{-}Fe(II)_{LS}}$; (B) metal-cyanide linkage isomerization (and subsequent spin change of Fe^{2+}), $\mathbf{Cr(III){-}C{\equiv}N{-}Fe(II)_{HS} \rightarrow Cr(III){-}N{\equiv}C{-}Fe(II)_{LS}}$; and (C) electron transfer, $\mathbf{Cr(III){-}C{\equiv}N{-}Fe(II)_{HS} \rightarrow Cr(II){-}C{\equiv}N{-}Fe(III)_{HS}}$. 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 cm^{-1}) to higher values.[17] Instead, for processes B and C, a significant shift (60 cm^{-1}) to lower frequencies (decrease in σ-bonding) should be observed. The Raman spectrum of **1** at ambient pressure (Figure 2) shows an intense band at 2164 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 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[18] 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.[13] 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 Δ and isomer shift values, indicating the presence of low-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 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 $Cr^{III}{-}C{\equiv}N{-}Fe^{II}$ to $Cr^{III}{-}N{\equiv}C{-}Fe^{II}$.

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



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 Fe^{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 $Fe_3[Cr(CN)_6]_2 \rightarrow Cr_4[Fe(CN)_6]_3$. 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.[19]

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.[20] 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 μ_B per Fe(II) center, the 8 μ_B decrease in magnetization suggests the presence of two (50%) 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.