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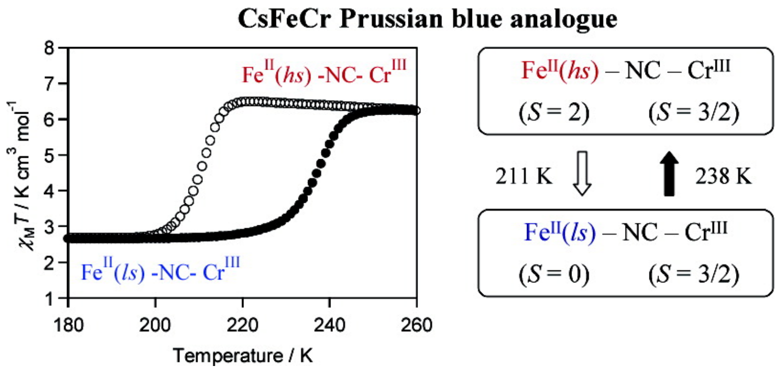

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Observation of an Fe(II) Spin-Crossover in a Cesium Iron Hexacyanochromate

Wataru Kosaka,[†] Kiyoshi Nomura,[†] Kazuhito Hashimoto,*,[†] and Shin-ichi Ohkoshi*,[†,‡]

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

Received January 8, 2005; E-mail: hashimoto@light.t.u-tokyo.ac.jp; ohkoshi@light.t.u-tokyo.ac.jp

Thermal phase transition phenomenon, which is caused by spin-crossover, has been extensively investigated in solid-state chemistry. The spin-crossover phase transition has been observed in d^4−d^7 octahedral coordination transition metal ions.[1,2] In a spin-crossover complex, a transition metal ion can be in either the low-spin (*ls*) or the high-spin (*hs*) state depending on the strength of the ligand field. When the thermal energy is close to the exchange energy that corresponds to the crossover, a spin transition occurs between the two spin states. In the field of solid-state chemistry, studies on functionalized molecule-based magnets have also received much attention. Cyano-bridged metal assemblies[3] are good systems for novel functional magnetic materials since they exhibit responses to external stimuli such as humidity[4] and light.[5,6] In this work, we observed a spin-crossover phenomenon in a cesium iron hexacyanochromate, which is a Prussian blue analogue. This compound exhibited a thermal phase transition with transition temperatures of 211 K ($T_{1/2\downarrow}$) and 238 K ($T_{1/2\uparrow}$) due to a spin-crossover on Fe^{II} sites. This spin-crossover phase transition is accompanied by a lattice contraction of 0.38 Å, but maintains a face-centered cubic (fcc) structure $F\bar{4}3m$. This is the first observation of Fe^{II} spin-crossover in a series of Prussian blue analogues.

The target compound was prepared by reacting a mixed aqueous solution of $\mathrm{K_3[Cr^{III}(CN)_6]}$ (0.01 mol dm^{-3}) and $\mathrm{Cs^{I}Cl}$ (1 mol dm^{-3}) with a mixed aqueous solution of $\mathrm{Fe^{II}Cl_2}$ (0.01 mol dm^{-3}) and $\mathrm{Cs^{I}Cl}$ (1 mol dm^{-3}). The obtained precipitate was a brown powder, and elemental analyses by inductively coupled plasma mass spectrometry and standard microanalytical methods showed that it had a composition of $\mathrm{CsFeCr(CN)_6\cdot 1.3H_2O}$. Calcd: Cs, 31.6; Fe, 13.3; Cr, 12.4; C, 17.1; H, 0.6; N, 20.0. Found: Cs, 31.5; Fe, 13.3; Cr, 12.4; C, 17.3; H, 0.6; N, 19.9. Scanning electron microscope (SEM) images showed that the prepared sample consists of cubic microcrystals of ca. 200 nm (Supporting Information).

Magnetic measurements were conducted using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5). Figure 1 shows the temperature dependence of the product of the molar magnetic susceptibility (χ_M) and the temperature (T) at a rate of 1 K min^{-1} in an external magnetic field of 5000 G. The $\chi_M T$ value was 6.11 K cm^3 mol^{-1} (high-temperature (HT) phase) at 280 K. As the temperature decreased, the $\chi_M T$ value sharply decreased around 210 K and reached a local minimum of 2.66 K cm^3 mol^{-1} at 188 K (low-temperature (LT) phase). Conversely, as the sample in the LT phase was warmed, the $\chi_M T$ value increased around 230 K and returned to the HT phase value at 250 K. The transition temperatures of HT → LT ($T_{1/2\downarrow}$) and LT → HT ($T_{1/2\uparrow}$) were 211 and 238 K, respectively, and the width of the thermal hysteresis loop ($\Delta T = T_{1/2\uparrow} - T_{1/2\downarrow}$) was 27 K. This thermal phase transition was repeatedly observed several times.

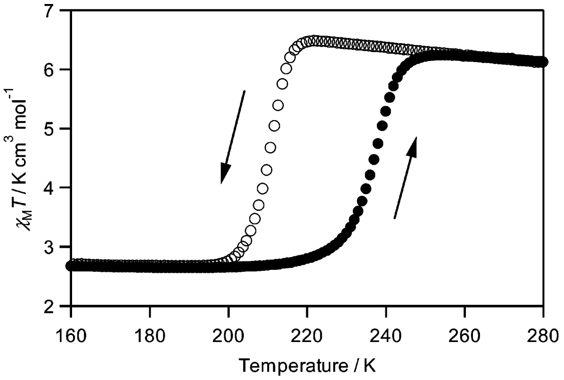

Figure 1. Temperature dependence of $\chi_M T - T$ plots of cesium iron hexacyanochromate in an external magnetic field of 5000 G; measured while cooling (○) and warming (●).

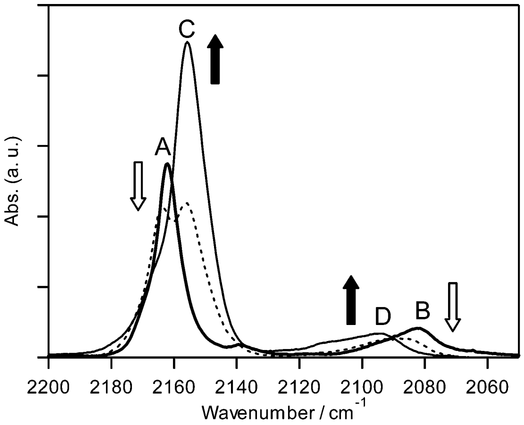

Figure 2. Temperature dependence of the CN$^-$ stretching frequencies in the IR spectra as the temperature decreases; measured at 280 K (bold line), 205 K (dotted line), and 180 K (fine line).

Figure 2 shows the temperature dependence of the CN$^-$ stretching frequencies in the IR spectra. In the HT phase at 280 K, a strong peak at 2163 cm^{-1} (A) and a weak peak at 2083 cm^{-1} (B) were observed. Peaks A and B are assigned to $\mathrm{Cr^{III}{-}CN{-}Fe^{II}}_{hs}$ and $\mathrm{Cr^{III}{-}NC{-}Fe^{II}}_{ls}$ of the cyano flip,[7] respectively. As the temperature decreased, these two peaks decreased, and two new peaks appeared at 2156 cm^{-1} (C) and 2095 cm^{-1} (D) around $T_{1/2\downarrow}$. Peak C is assigned to $\mathrm{Cr^{III}{-}CN{-}Fe^{II}}_{ls}$, which is converted from peak A. Peak D is $\mathrm{Cr^{III}{-}NC{-}Fe^{II}}_{ls}$, which is from a shift in peak B due to the variation in the cyano group between the HT and LT phases. The IR spectra indicate that the electronic states of HT and LT phases are $\mathrm{Cs^{I}\{Fe^{II}}_{hs}\mathrm{[Cr^{III}(CN)_6]\}_{0.94}\{Fe^{II}}_{ls}\mathrm{[Cr^{III}(NC)_6]\}_{0.06}\cdot 1.3H_2O}$ and $\mathrm{Cs^{I}\{Fe^{II}}_{hs0.12}\mathrm{Fe^{II}}_{ls0.88}\mathrm{[Cr^{III}(CN)_6]\}_{0.94}\{Fe^{II}}_{ls}\mathrm{[Cr^{III}(NC)_6]\}_{0.06}\cdot 1.3H_2O}$, respectively.[8] In the HT phase, 94% of Fe^{II} is in the *hs* state and 6% is the *ls* state. In contrast, 11% (= (0.12 × 0.94) × 100) of Fe^{II} is the *hs* state and 89% (= (0.88 × 0.94 + 0.06) × 100) of Fe^{II} is the *ls* state in the LT phase.

The Fe^{II} spin-crossover was also confirmed by ^{57}Fe Mössbauer spectroscopy (Supporting Information). In the HT phase, a doublet

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[†] The University of Tokyo.
[‡] PRESTO, JST.

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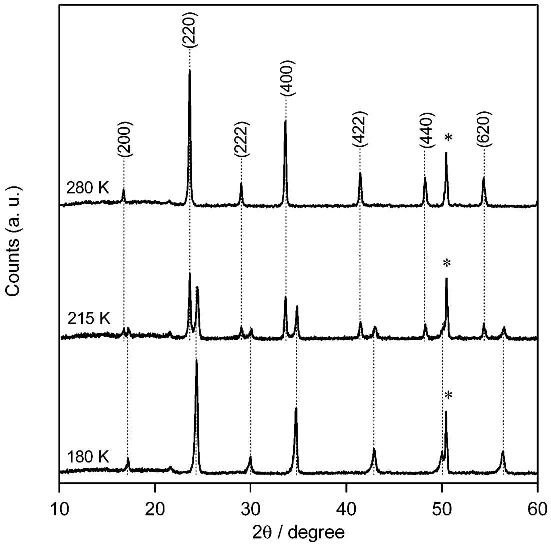

Figure 3. Temperature dependences of XRD spectra for cesium iron hexacyanochromate as the temperature decreases. (* indicates Cu from the sample holder).

peak was mainly observed (isomer shift = 1.07; quadrupole splitting = 0.74), which is assigned to Fe^{II}_{hs}. In the LT phase, this doublet peak disappeared and a singlet peak appeared (isomer shift = 0.44), which is assigned to Fe^{II}_{ls}. These results show that the spin-crossover actually occurred on Fe^{II} sites.

The temperature dependence of the X-ray powder diffraction (XRD) patterns showed that the present spin-crossover is accompanied by a structural phase transition (Figure 3). The XRD patterns of the HT phase at 280 K showed an fcc $F\bar{4}3m$ structure with a lattice constant of 10.708(1) Å. In contrast, the LT phase showed XRD patterns of an fcc $F\bar{4}3m$ structure with a lattice constant of 10.330(1) Å. The lattice constant in the LT phase decreased by about 0.38 Å compared to that in the HT phase. This structural phase transition was repeatedly observed.

The CsFeCr Prussian blue analogue clearly showed a spin-crossover transition, but in the analogue compound of $Fe[Cr(CN)_6]_{2/3}\cdot 5H_2O$ a spin-crossover was not observed.[5] In this analogue compound, typically Fe^{II} is coordinated by four N atoms from cyano groups and two O atoms from ligand waters and the statistical probabilities of each coordinate geometry are 8.8% ($Fe^{II}N_6$), 26.4% ($Fe^{II}N_5O$), 33.0% ($Fe^{II}N_4O_2$), 22.0% ($Fe^{II}N_3O_3$), 8.2% ($Fe^{II}N_2O_4$), and 1.6% ($Fe^{II}NO_5$) (Supporting Information). For the spin-crossover phenomenon to appear, the number of cyanonitrogen around Fe^{II} must be significant. Maybe in $Fe[Cr(CN)_6]_{2/3}\cdot 5H_2O$ the strength of the ligand field is insufficient to cause the spin-crossover. In contrast, $Fe^{II}N_6$ in the CsFeCr Prussian blue analogue is an environmental advantage for the spin-crossover. Furthermore, since both Fe^{II} and Cr^{III} are bridged by a CN^- group with six-coordinate, the interaction between spin-crossover sites should be stronger in the 3D structure.

The field-cooled magnetization curve at an external magnetic field of 10 G revealed that the LT phase had a spontaneous magnetization with a magnetic ordering temperature of 9 K and the saturation magnetization (M_S) at 2 K was 3.3 μ_B (Supporting Information). The observed M_S value of 3.3 μ_B is consistent with the expected M_S value of 3.4 μ_B due to the sum of sublattice magnetization of Cr^{III} and the remaining Fe^{II}_{hs} for a given formula of the LT phase.

In summary, we found that a cesium iron hexacyanochromate showed a spin-crossover behavior. The spin-crossover phenomenon in a Prussian blue analogue allows a variety of new functionalities to be considered. For example, the observation of photoinduced magnetization caused by a light-induced excited spin state trapping effect[9] is expected since this material has a spontaneous magnetization.

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Supporting Information Available: SEM image of the precipitate, ^{57}Fe Mössbauer spectra of HT and LT phases, statistical probabilities of coordinate geometries around Fe in $Fe[Cr(CN)_6]_{2/3}\cdot 5H_2O$, analysis of $\chi_M T - T$ curves, magnetization versus temperature plots, and magnetization versus external magnetic field plots of the LT phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The estimated oscillator strength ratio of peak A ($Cr^{III}-CN-Fe^{II}_{hs}$) to peak C ($Cr^{III}-CN-Fe^{II}_{ls}$) in the IR spectra was 1.8. A compound that contains more cyano flips can be obtained by heating. In this heated sample, peak A was converted to peak B ($Cr^{III}-NC-Fe^{II}_{ls}$). Comparing the IR spectra of the heated sample and the original sample, we estimated that the oscillator strength ratio of peak A to peak B was 2.1.

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