Spin-Crossover Magnets

DOI: 10.1002/ange.200802266

Observation of an Iron(II) Spin-Crossover in an Iron Octacyanoniobate-Based Magnet**

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The spin-crossover phenomenon has been extensively studied for metal complexes containing octahedrally coordinated transition-metal ions by both inorganic and physical chemists.[1–3] The research of ferromagnetism has been developed using coordination polymers containing magnetic transition-metal ions.[4] A variety of attractive functions should be observed if spin-crossover and ferromagnetism coexist in a compound. However, bulk magnetization has proved difficult to observe in the spin-crossover complexes reported to date because the spin-carrier molecules are isolated in the crystal, which results in a very weak magnetic coupling between the spin-crossover sites. To generate magnetic ordering in a spin-crossover system, the spin sites should be directly bridged by a small coordinating ligand into a three-dimensional network. A cyano-bridged bimetallic assembly is a suitable system in this context.[5] Octacyanometalate-based networks, for example, are good candidates[6–10] because they have multiple pathways for magnetic coupling through the CN ligand and can take various coordination geometries in the crystal structure, ranging from zero-dimensional (0D)[7] to 1-,[8] 2-,[9] and 3D.[10] Herein we report the preparation of the octacyano-bridged Fe–Nb bimetallic assembly $Fe_2[Nb(CN)_8]\cdot(3\text{-}pyCH_2OH)_8\cdot 4.6H_2O$ (3-py = 3-pyridyl), which displays both spin-crossover on Fe^{II} and ferrimagnetic ordering between Fe^{II} and Nb^{IV}.

Rietveld analysis of the XRD pattern of a powder sample (Figure 1a) indicated that the sample has a cubic crystal structure in the $Ia\bar{3}d$ space group ($a = 35.157(11)$ Å; refinements $R_{wp} = 0887$ and $R_p = 0685$; see Tables S1 and S2, and Figure S1 in the Supporting Information). Figure 1b shows the cyano-bridged bimetallic framework (-Fe^{II}-NC-Nb^{IV}-) of the unit cell and the coordination geometries of the Fe and Nb sites (pseudo-octahedral, D_{4h}, and dodecahedral, D_{2d}, respectively). The two axial positions of Fe are occupied by cyanide nitrogen atoms of $[Nb^{IV}(CN)_8]$ whereas the equatorial positions are occupied by four nitrogen atoms from (3-pyridyl)methanol ligands. The four equatorial CN groups of $[Nb^{IV}(CN)_8]$ bridge four Fe centers whilst the four axial CN groups are free.

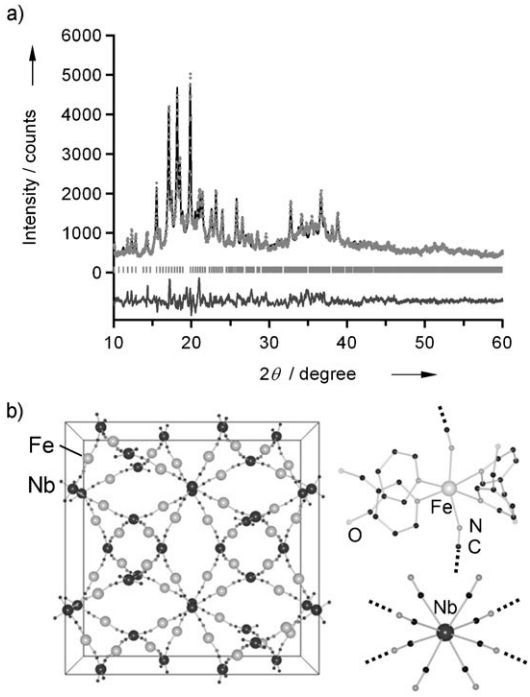

Figure 1. a) XRD pattern at 296 K and Rietveld analysis. Dots, top line, and bottom line are the observed plots, calculated pattern, and their difference, respectively. Central bars represent the calculated positions of the Bragg reflections. b) Cyano-bridged Fe–Nb 3D framework and coordination geometries of the Fe and Nb sites; (3-pyridyl)methanol ligands, terminal CN ligands, and water molecules have been omitted for clarity.

The molar magnetic susceptibility (χ_M) was determined as a function of the temperature (T) at a cooling (or warming) rate of $1\,K\,min^{-1}$ (Figure 2a). The $\chi_M T$ value is $7.37\,K\,cm^3\,mol^{-1}$ [high-temperature (HT) phase] at 330 K and slowly decreases with temperature in the range 330–180 K. The $\chi_M T$ value at 100 K is $4.17\,K\,cm^3\,mol^{-1}$ [low-temperature (LT) phase]. The $\chi_M T$ value observed in the warming process corresponds to that obtained in the cooling process at each temperature, in other words there is no thermal hysteresis involved in this transition.

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[**] We thank Dr. H. Tokoro for helpful discussions. The present research was supported, in part, by a Grant for the Global COE Program, "Chemistry Innovation through Cooperation of Science and Engineering", a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, the Royal Society Joint Project Programme, the Iketani Science and Technology Foundation, the Inamori Foundation, the Kurata Memorial Hitachi Science and Technology Foundation, and the Murata Science Foundation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200802266.

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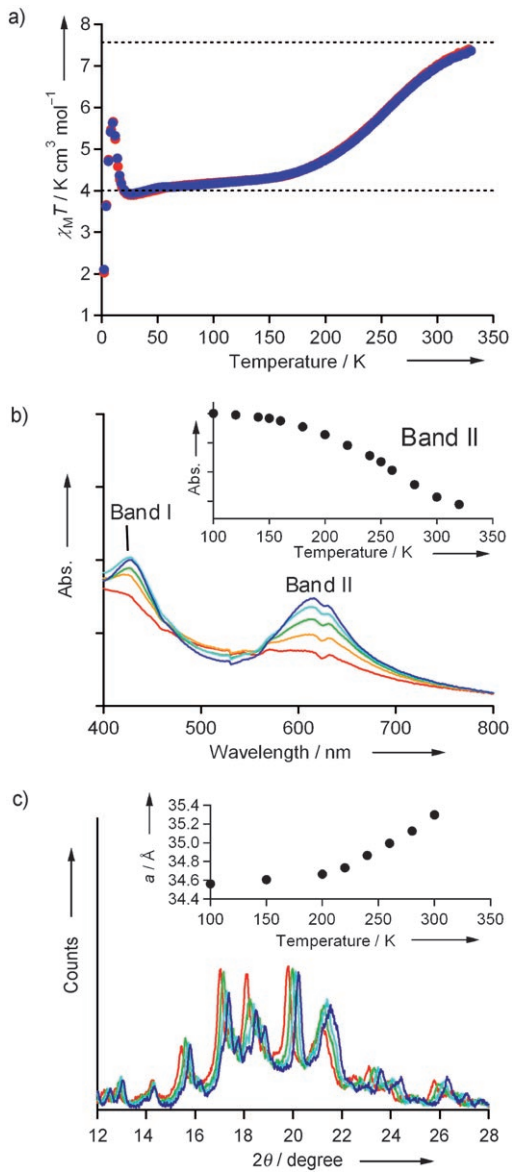

Figure 2. a) $\chi_M T$ vs. T plots measured while cooling (blue) and warming (red) in an external field of 5000 Oe. Dashed lines indicate the estimated $\chi_M T$ values for the HT and LT phase. b) Temperature dependence of the UV/Vis spectra at 300 (red), 260 (orange), 220 (green), 180 (cyan), and 100 K (blue); inset: temperature dependence of the absorption intensity of band II. c) Temperature dependence of the XRD patterns at 300 (red), 260 (green), 220 (cyan), and 100 K (blue); inset: temperature dependence of the lattice constant *a*.

Absorption bands appear at 430 (band I) and 610 nm (band II) upon lowering the temperature in the temperature-dependent UV/Vis absorption spectra (Figure 2b). These bands were assigned to $^1A_1 \rightarrow {}^1T_2$ (band I) and $^1A_1 \rightarrow {}^1T_1$ transitions (band II) in the low-spin (ls) state of Fe^{II}. The temperature dependence of the intensity of these bands corresponds to the temperature dependence of the $\chi_M T$ values (inset of Figure 2b), thus indicating that the change in the $\chi_M T$ vs. T plots is due to the spin-crossover on Fe^{II}. The XRD peaks shift continuously with temperature in the variable-temperature XRD measurements but remain in accord with a cubic crystal structure (Figure 2c). The continuous decrease of the lattice constant is consistent with the $\chi_M T$ vs. T plots. This result suggests that the spin-crossover in this case is not the result of a first-order phase transition but is a continuous transition.

The electronic states in the HT and LT phases were assigned as follows. The $\chi_M T$ value observed for the HT phase (7.37 K cm^3 mol^{-1}) is close to the $\chi_M T$ value due to the sum (7.64 K cm^3 mol^{-1}) of Fe^{II}_{hs}(S=2) and Nb^{IV}(S=1/2) assuming that the g-values of Fe^{II}_{hs} and Nb^{IV} are 2.2[11] and 2.0, respectively.[12] In contrast, the $\chi_M T$ value (4.17 K cm^3 mol^{-1}) observed for the LT phase is close to the value of 4.01 K cm^3 mol^{-1} obtained for a phase in which half of the Fe^{II}_{hs} centers transit to Fe^{II}_{ls}. Hence, the electronic states of the HT and LT phases are close to the formulae $(Fe^{II}_{hs})_2$-$[Nb^{IV}(CN)_8]\cdot(3\text{-py}CH_2OH)_8\cdot 4.6\,H_2O$ and $Fe^{II}_{hs}Fe^{II}_{ls}$-$[Nb^{IV}(CN)_8]\cdot(3\text{-py}CH_2OH)_8\cdot 4.6\,H_2O$, respectively.

The magnetization vs. temperature plots for the LT phase at very low temperature (Figure 3) reveal that this phase has a spontaneous magnetization with a Curie temperature (T_C) of 12 K. The magnetization vs. external magnetic field plots at 2 K (Figure 3, inset) indicate that the saturation magnetization (M_S) is 3.1 μ_B and the magnetic coercive field 600 Oe. The observed M_S value of 3.1 μ_B for the LT phase at 2 K is consistent with the expected M_S value of 3.4 μ_B due to antiferromagnetic coupling between the sub-lattice magnetization of the remaining Fe^{II}_{hs} and Nb^{IV}, assuming g values of 2.2 and 2.0 for Fe^{II}_{hs} and Nb^{IV}, respectively; the LT phase is therefore a ferrimagnet.

In summary, we have prepared the iron octacyanoniobate $Fe_2[Nb(CN)_8]\cdot(3\text{-py}CH_2OH)_8\cdot 4.6\,H_2O$. This compound exhibits a spin-crossover between Fe^{II}(S=2)-Nb^{IV}(S=1/2)-Fe^{II}-(S=2) and Fe^{II}(S=0)-Nb^{IV}(S=1/2)-Fe^{II}(S=2) with a continuous transition. The low-temperature phase shows ferrimagnetism with a T_C of 12 K due to an antiferromagnetic interaction between the remaining high-spin Fe^{II} and the Nb^{IV} centers (Figure 4). A variety of new functionalities, such as photo-induced magnetization caused by a light-induced

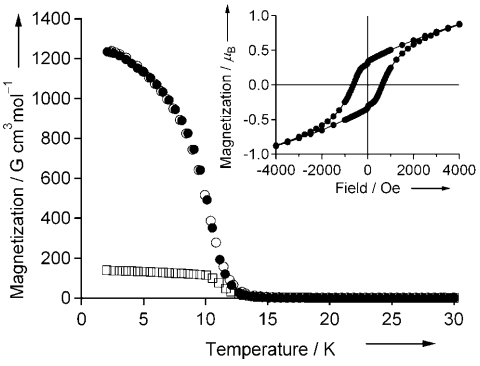

Figure 3. Field-cooled (○), zero-field-cooled (□), and remnant (●) magnetization in an external magnetic field of 10 Oe; inset: magnetic hysteresis loop at 2 K.

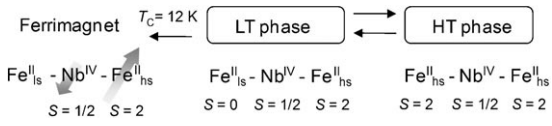

Figure 4. Electronic states of the HT and LT phases and magnetic ordering of the LT phase.

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excited-spin-state trapping effect, could be expected for such a spin-crossover magnet.

Experimental Section

Materials: The target compound was prepared by treating a mixed aqueous solution of $FeCl_2$ (0.1 M) and (3-pyridyl)methanol (2 M) with an aqueous solution of $K_4[Nb(CN)_8]$ (0.05 M). The resulting precipitate was an indigo-colored powder. Elemental analyses by inductively coupled plasma mass spectrometry and standard microanalytical methods indicated that this compound had the composition $Fe_2[Nb(CN)_8]\cdot(3\text{-}pyCH_2OH)_8\cdot 4.6\,H_2O$ (calcd C 49.1, H 4.8, Fe 8.2, N 16.4, Nb 6.8; found C 48.8, H 4.8, Fe 8.1, N 16.6, Nb 7.0). Scanning electron microscopy images showed that the prepared sample consisted of microcrystals approximately 600 nm in diameter. CN stretching peaks were observed at 2136 and 2148 cm^{-1} in the IR spectra, whereas peaks due to (3-pyridyl)methanol were observed at 707, 801, 1037, and 1432 cm^{-1}.

Characterization: The morphologies of the compounds were measured with a Hitachi S 4200 scanning electron microscope at an accelerating voltage of 10 kV. IR spectra were recorded with a Shimadzu FT-IR 8200PC spectrometer with samples as KBr pellets in the 4000–400 cm^{-1} region. XRD measurements were conducted with a Rigaku RINT2100 diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å) within the range $10° \le 2\theta \le 60°$. Rietveld analyses were performed using the RIETAN-FP program.[13] Magnetic measurements on a polycrystalline sample were carried out with a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Pascal's constants were used to determine the diamagnetic contribution. UV/Vis absorption spectra were recorded with a Shimadzu UV-3100 spectrometer.

Received: May 15, 2008
Published online: August 5, 2008

Keywords: coordination polymers · iron · magnetic properties · niobium

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