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Synthesis of Ferromagnetic CsCuCr Prussian Blue Analogue with a Tetragonal Structure

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We report a crystal structure, bond lengths, and magnetic properties of a Prussian blue analogue, $CsCu[Cr(CN)_6]\cdot 2.1H_2O$. This compound has a tetragonal structure ($I\bar{4}m2$), which is caused by the strong cooperativity due to the Jahn–Teller effect of Cu^{II} and shows ferromagnetism with Curie temperature of 65 K.

A series of Prussian blue analogues have attracted a lot of attention as functional molecule-based magnets.[1,2] For example, $RbMn[Fe(CN)_6]$ shows a temperature-induced phase transition, which is caused by a metal-to-metal charge transfer and a Jahn–Teller distortion on Mn^{III}.[3] The Jahn–Teller effect will be important in the interaction between the metal ion and lattice strain. Since the Jahn–Teller effect is observed in octahedrally-coordinated Cu^{II}, high-spin Mn^{III}, low-spin Co^{II}, and so on,[4] we focused on Prussian blue analogues that contain Cu^{II}. Verdaguer et al. reported that $Cu[Cr(CN)_6]_{2/3}\cdot 5.3H_2O$ is a ferromagnet with a Curie temperature (T_C) = 66 K and has a cubic structure.[5] This compound has vacancies of $[Cr(CN)_6]$ to maintain the charge neutrality.[6] In contrast, Prussian blue analogues with alkali ions allow divalent ions to coordinate with six cyanonitrogen atoms.[3,7] In this work, we synthesized CsCuCr Prussian blue analogue, and studied its crystal structure, bond lengths, and magnetic properties.

The target compound was prepared by reacting a mixed aqueous solution of $K_3[Cr^{III}(CN)_6]$ ($0.05\,mol\,dm^{-3}$) and $Cs^{I}Cl$ ($2\,mol\,dm^{-3}$) with a mixed aqueous solution of $Cu^{II}Cl_2$ ($0.05\,mol\,dm^{-3}$) and $Cs^{I}Cl$ ($2\,mol\,dm^{-3}$) at 50 °C. The obtained precipitate was light blue and the CN^- stretching frequency was observed at $2186\,cm^{-1}$ in the IR spectra. Elemental analyses determined by inductively coupled plasma mass spectrometry and standard microanalytical methods showed that the formula was $CsCu[Cr(CN)_6]\cdot 2.1H_2O$: Calcd: Cs, 30.0; Cu, 14.4; Cr, 11.8; C, 16.3; N, 19.0. Found: Cs, 30.2; Cu, 14.4; Cr, 11.7; C, 16.8; N, 18.8. Scanning electron microscope (SEM) images showed that the prepared sample consisted of cubic microcrystals of ca. 100 nm.

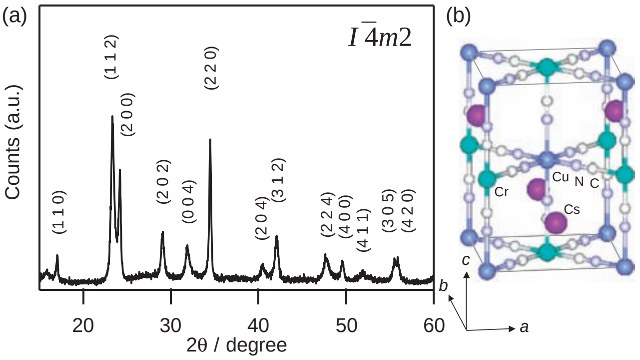

Figure 1. (a) XRD pattern of $CsCu[Cr(CN)_6]\cdot 2.1H_2O$ with Miller indices of a tetragonal structure, (b) Unit cell of $I\bar{4}m2$.

Figure 1a shows the X-ray powder diffraction (XRD) patterns of the prepared compound. The diffraction patterns were assigned to the tetragonal structure of $I\bar{4}m2$ with lattice parameters of $a = b = 7.345(1)$ Å, and $c = 11.208(2)$ Å. (These values correspond to $\sqrt{a^2 + b^2} = 10.389(1)$ Å, and $c = 11.208(2)$ Å in the cubic lattice of a Prussian blue structure.). The unit cell of this crystal structure is shown in Figure 1b. The local structures around Cu and Cr were measured by extended X-ray absorption fine structure (EXAFS) spectroscopy.[8] The EXAFS Fourier transform at the Cu K-edge showed three dominant contributions near 1.5, 2.5, and 4.6 Å (Figure 2a), which were attributed to the Cu–N, Cu–C, and Cu–Cr shells, respectively. The curve-fitting analysis of this Cu K-edge data was performed in *k* space for the Cu–N shell (0.7–1.9 Å), using the backscattering amplitudes and phase shifts based on the FEFF calculation.[9] Analyses of bond lengths were performed with a (4 + 2)-coordinate model and showed that the Cu–N bond distances of

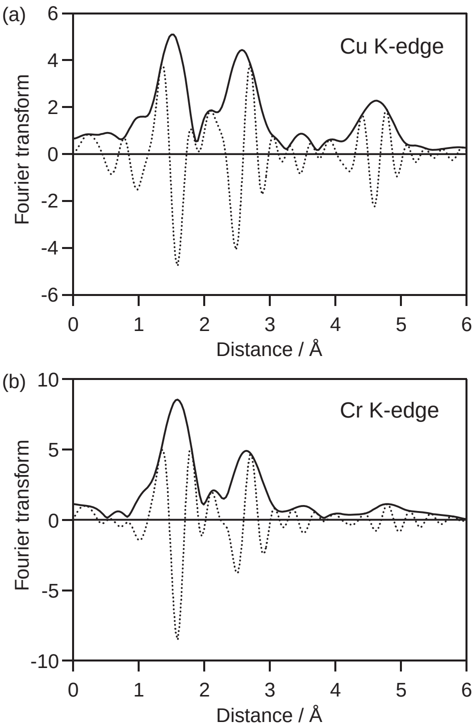

Figure 2. EXAFS Fourier transforms of $CsCu[Cr(CN)_6]\cdot 2.1H_2O$ including modules (——) and imaginary parts (······); (a) Cu K-edge, (b) Cr K-edge.

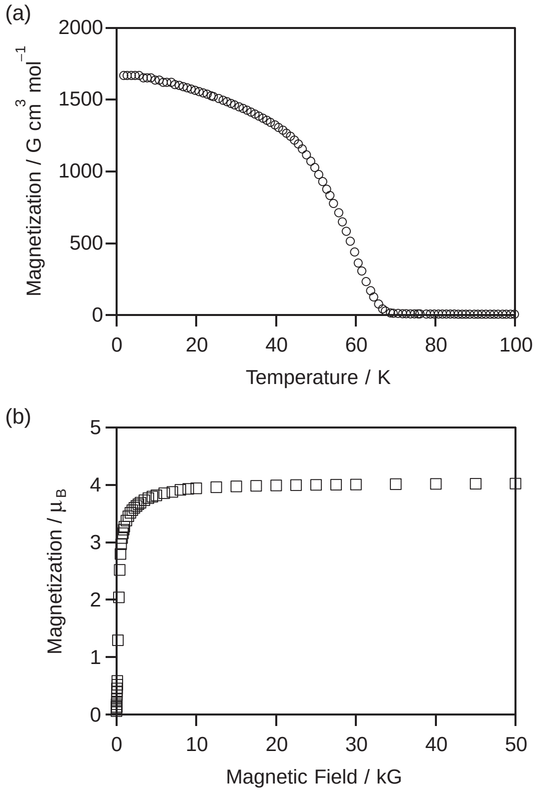

Figure 3. (a) Field-cooled magnetization curves of CsCu[Cr(CN)$_6$]$\cdot$2.1H$_2$O in an external magnetic field of 10 G. (b) Magnetization vs external magnetic field plots.

the four shorter and two longer were 1.94(1) and 2.44(3) Å, respectively. Figure 2b shows the EXAFS Fourier transform at the Cr K-edge. Two dominant contributions were observed around 1.5 and 2.7 Å, which were attributed to Cr–C and Cr–N shells, respectively. The curve-fitting analysis with a 6-coordinate model for the Cr–C shell (1.2–2.0 Å) gave a bond distance of 2.050(4) Å. EXAFS data clearly revealed that the tetragonal crystal structure of CsCu[Cr(CN)$_6$]$\cdot$2.1H$_2$O was caused by the Jahn–Teller distortion on Cu^{II}. In the CsCuCr Prussian blue analogue, the Jahn–Teller elongation of Cu^{II} occurred in only one direction of the lattice. Thus, the compound exhibited a tetragonal structure.

The field-cooled magnetization curve at an external magnetic field of 10 G showed that this compound exhibited a spontaneous magnetization with a T_C value of 65 K (Figure 3a). The magnetization vs magnetic field showed that the coercive field was 100 G and the saturation magnetization (M_S) at 2 K was 4.0 μ_B (Figure 3b). This observed M_S value was consistent with the expected M_S value of 4.0 μ_B assuming the ferromagnetic ordering between Cu^{II} ($S = 1/2$) and Cr^{III} ($S = 3/2$) with $g = 2$. A positive Weiss temperature value of +98.3 K, which was obtained from the magnetic susceptibility in the temperature range of 200–300 K, also supported the ferromagnetic coupling between Cu^{II} and Cr^{III} magnetic spins.

In summary, we synthesized a ferromagnetic Prussian blue analogue, CsCu[Cr(CN)$_6$]$\cdot$2.1H$_2$O with a tetragonal structure, which was caused by the strong cooperativity due to the Jahn–Teller effect of Cu^{II}. This is the first Prussian blue analogue-based ferromagnet in which a Cu^{II} Jahn–Teller effect influences its crystal structure. Superexchange pathways of this system are in *ab* plane, i.e., ($d_{xy,\mathrm{Cr}} \parallel p_x \perp p_y \parallel d_{x^2-y^2,\mathrm{Cu}}$), ($d_{xy,\mathrm{Cr}} \parallel p_y \perp p_x \parallel d_{x^2-y^2,\mathrm{Cu}}$), ($d_{xz,\mathrm{Cr}} \parallel p_z \perp p_x \parallel d_{x^2-y^2,\mathrm{Cu}}$), and ($d_{yz,\mathrm{Cr}} \parallel p_z \perp p_y \parallel d_{x^2-y^2,\mathrm{Cu}}$) where x, y, and z axis are parallel to [110], [$\bar{1}$10], and [001], respectively. To understand this, we plan to measure the neutron diffraction pattern and investigate the magnetic ordering of this system in the future.

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8 EXAFS measurements were performed using a Rigaku Laboratory XAFS measurement system (RIGAKU R-XAS Looper). Cu K-edge and Cr K-edge XAFS spectra were measured at room temperature in the conventional transmission mode. The transmitted X-rays were measured using a gas-filled proportional counter and a scintillation counter, respectively. The sample was diluted with BN and pressed into a tablet with a 15-mm diameter prior to XAFS measurements.

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