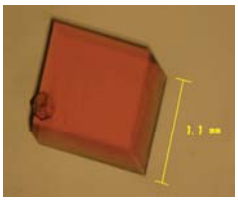
（ ※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。 ）

CROSS TOKAI **Experimental Report** J-PARC	承認日 Date of Approval 2018/2/16 承認者 Approver Takashi Ohhara 提出日 Date of Report 2018/2/15
課題番号 Project No.2017B0105 実験課題名 Title of experiment: Single-crystal neutron structure analysis of a charge-transfer salt of hexacyanidoferrate(II) with protons as a counter-cation 実験責任者名 Name of principal investigator Nobuyuki MATSUSHITA 所属 Affiliation Department of Chemistry, Rikkyo University	装置責任者 Name of Instrument scientist Takashi OHHARA 装置名 Name of Instrument/（BL No.） Extreme Environment Single Crystal Neutron Diffractometer (SENJU) (BL-18) 実施日 Date of Experiment 2017/12/16-12/22

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

We measured neutron diffraction data of a single crystal of (4,4'-bipyridine-1,1'-diium) hexahydrogen bis[hexacyanidoferrate(II)] tetrahydrate, $(C_{10}H_{10}N_2)(H)_6[Fe(CN)_6]_2{\cdot}4H_2O$ using SENJU (BL-18) on MLF, J-PARC. The present ionic molecular crystal comprising a bulky anion with a high negative charge, $[Fe(CN)_6]^{4-}$, and a bulky cation with a lower positive charge, $(C_{10}H_{10}N_2)^{2+}$, includes protons (H^+) as small cations to supplement the deficient positive charge. However, atomic parameters of the X-ray invisible protons have not been precisely determined on X-ray crystallography (Crystal data: monoclinic, $P2_1/c$, a=11.9985(3) Å, b=11.2857(3) Å, c=12.2196(7) Å, β=112.7946(8)°, V=1525.44(10) Å^3, Z=2). Thus, we have attempted this single-crystal neutron structure analysis in order to determine the precise atomic parameters of the protons as counter cations.



2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

A 1.1 x 1.1 x 0.3 mm sized single crystal of $(C_{10}H_{10}N_2)(H)_6[Fe(CN)_6]_2{\cdot}4H_2O$ which was coated by the Apiezon type N grease and fixed on an aluminum pin was mounted at the end of a closed-type cryostat and installed into the sample chamber of SENJU. Neutron diffraction data was measured at 100 K with 11 crystal orientations. Exposure time for one orientation was 12 hours. Diffraction data was processed with a data processing software for SENJU, STARGazer, and finally integrated intensities of 11271 Bragg reflections were obtained.

We have successfully obtained structure factors based on the single-crystal measured neutron diffraction data. Then, we have plainly determined the positions of the protons as counter cations as well as the hydrogen atoms of the water molecules and 4,4'-bipyridine-1,1'-diium cations on the difference Fourier map calculated on the neutron structure factors. In the difference Fourier synthesis,

atomic parameters based on X-ray crystallography were used for non H-atoms.

Refinement was performed on F^2 based on the single-crystal neutron diffraction data by full-matrix least-squares methods with anisotropic displacement parameters for all atoms. The refinement converged to $R1$ = 0.1017 for 2870 reflections with $Fo > 4\sigma(Fo)$. We have successfully obtained the precise atomic parameters with the anisotropic displacement parameters for the protons including in the crystal as counter cations. A software, SHELXL2014 was used for the calculation of the difference Fourier synthesis and the refinement.

The molecular structure and the crystal packing of $(C_{10}H_{10}N_2)(H)_6[Fe(CN)_6]_2\cdot 4H_2O$ refined based on the single-crystal neutron diffraction data are shown in Figures 1 and 2, respectively.

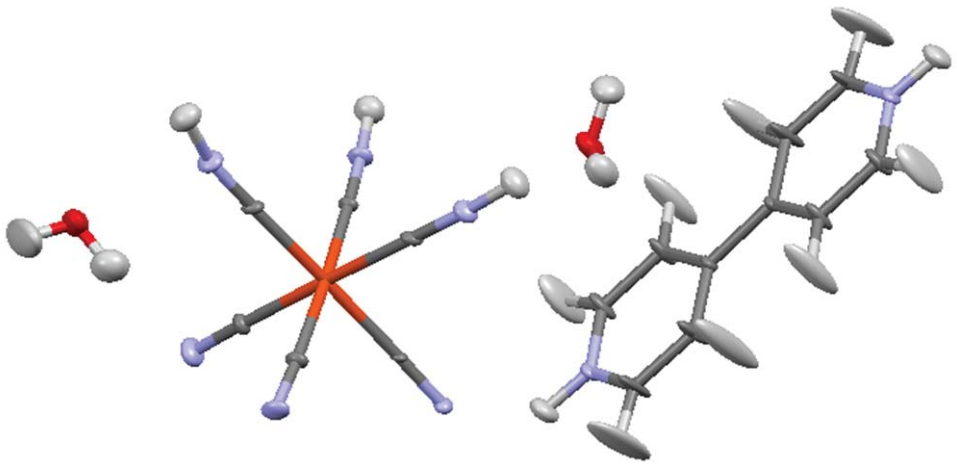


Figure 1 A thermal-ellipsoid-plots view of the molecular structure of $(C_{10}H_{10}N_2)(H)_6[Fe(CN)_6]_2\cdot 4H_2O$. Displacement ellipsoids are drawn at the 50% probability level for all atoms.

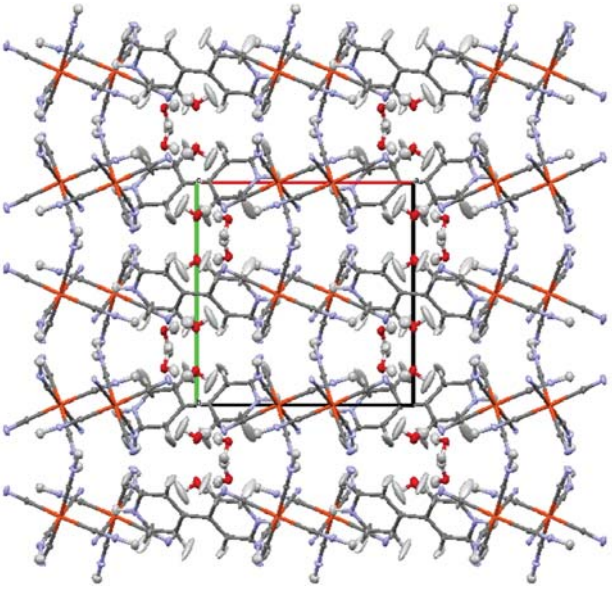


Figure 2 A packing view of $(C_{10}H_{10}N_2)(H)_6[Fe(CN)_6]_2\cdot 4H_2O$.