論文の内容の要旨

論文題目：Multifunctional molecular magnet based on octacyanometalate

(オクタシアノ金属錯体を構築素子とした多機能性分子磁性体)

氏名：井元　健太

Introduction

The research of molecule-based magnets is of intense interest because they can exhibit fascinating magnetic functionalities that have not been realized in existing magnets. Especially, cyano-bridged metal assemblies are attractive systems to demonstrate novel magnetic functionalities because of the large magnetic interaction between metal centers bridged by cyanide ligand. Octacyanometalates, $[M(CN)_8]$ (M = Mo, W, Nb), are useful for realizing magnetic functionalities due to the large numbers of routes for magnetic interaction and their diverse coordination geometry which is sensitive to the external chemical condition. Along this line, our laboratory has developed a lot of functional magnetic materials, such as, photo-magnets, chemically sensitive magnets, and non-linear magnetooptical materials. In this work, the following novel functional magnets are realized: (i) single crystal synthesis of Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly which is isostructural to light-induced spin-crossover magnet, (ii) two step spin-crossover and photo-induced spin-crossover ferromagnetism in Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly, and (iii) coexistence of high ionic conductivity and metamagnetism in a Mn^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly.

(i) Single crystal synthesis of Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly which is isostructural to light-induced spin-crossover magnet

In this work, single crystal of Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly with pyridine-4-aldehydeoxime, $Fe_2[Nb(CN)_8]$(pyridine-4-aldehydeoxime)$_2\cdot 2H_2O$ (**1**) is synthesized. The single crystal X-ray analysis indicated that the crystal structure of the compound was tetragonal, $I4_1/a$ space group. Two nitrogen atoms of cyano group and four nitrogen atoms on pyridine ring coordinate to the Fe site. The Nb site is coordinated by eight carbon atoms of CN group and four CN groups bridge to the neighboring Fe sites while other four are not bridged. The bond distance between Nb atom and C atom of bridged CN group is 2.25 Å, while the bond distance between Nb atom and C atom of non-bridged CN group is 2.24 Å. The Fe-N distances between Fe atom and N atom of CN group is 2.08 Å, between Fe atom and N atom of organic ligand is 2.24 Å and 2.27 A. These Fe-N distances are typical values for a high-spin Fe^{II} complex. The Fe-NC-Nb coordination framework forms a cyano-bridged three-dimensional (3D) network. The crystal structure of the present compound is isostructural to that of powder-form sample. Because powder-form sample shows a spin-crossover phenomenon between Fe^{II}_{HS} (S= 2) and Fe^{II}_{LS} (S= 0) around 130 K, and a large spontaneous magnetization with a Curie temperature (T_C) of 20 K and a coercive field (H_c) of 240 Oe by irradiating 473-nm light, the success of obtaining single crystal which is isomorphous to light-induced spin-crossover magnet opens up a new possibility of detailed and fruitful investigation about the crystal structure upon light-induced spin-crossover magnetization phenomenon.

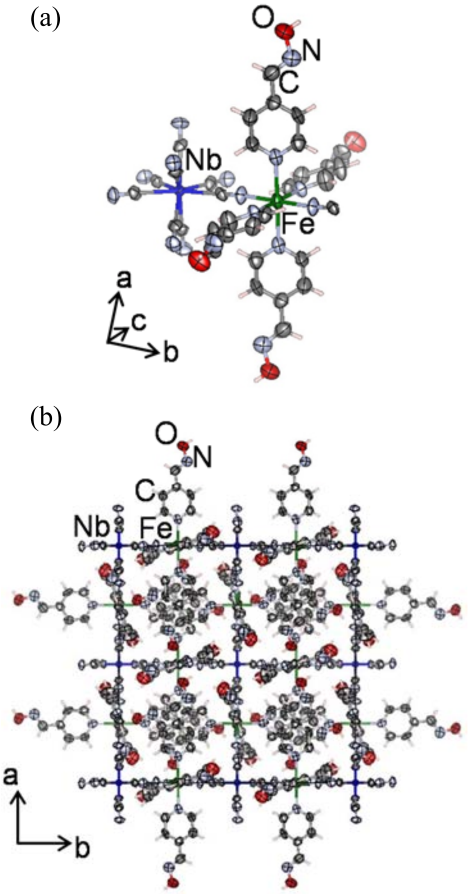

Fig. 1 (a) Assymetric unit of **1**. (b) Crystal structure of **1**.

(ii) Two step spin-crossover and photo-induced spin-crossover magnetism in Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly

In this work, I prepared Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly with organic ligand of 4-methylpyridine (**2**). The single crystal X-ray analysis indicated that the crystal structure of the compound was orthorhombic, *Fddd* space group. Two nitrogen atoms of CN groups and four nitrogen atoms on pyridine ring coordinate to the Fe site. Eight CN group coordinate to Nb site, and four of them bridge to the neighboring Fe sites while other four are not. The 3D network is constructed by Fe-NC-Nb moiety. The $\chi_M T$ vs T plot indicated the electronic states of metal ions are Fe^{II}_{HS} (S= 2) and Nb^{IV} (S= 1/2) at room temperature. As decreasing temperature, the $\chi_M T$ value decreased at 115 K, showed a plateau around 100 K, and then decreased again at 94 K. The latter transition showed a thermal hysteresis between 94 K and 96 K. The single crystal X-ray analysis and spectroscopic measurements indicated the spin-crossover transition. The thermodynamical analysis of the $\chi_M T$ vs T plot suggested the present spin transition behavior can be explained by an extended model of Slichter-Drickamer's model. The photo-irradiation of 532-nm light produced a bulk magnetization with a T_C of 14 K and a H_c of 2300 Oe. M_s

value indicated a ferrimagnetic coupling between Nb^{IV} (S= 1/2) and the photo-generated Fe^{II}_{HS} (S= 2). The UV-vis spectrum under photo-irradiation indicated the occurrence of light-induced spin-crossover phenomenon, supporting that the present compound is the second example of light-induced spin-crossover magnet.

(iii) Coexistence of high ionic conductivity and metamagnetism in a Mn^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly.

In this work, I synthesized a two-dimensional Mn^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly to examine both conductive properties and magnetic properties. The slow diffusion of a mixed aqueous solution of $MnCl_2 \cdot 4H_2O$ and 4-aminopyridine, and an aqueous solution of $K_4[Nb(CN)_8] \cdot 2H_2O$ gave yellow crystals of $Mn^{II}_3[Nb^{IV}(CN)_8]_2$(4-aminopyridine)$_{10}$(4-aminopyridinium)$_2 \cdot 12H_2O$ (**3**). The single crystal X-ray diffraction measurement indicated that $Mn^{II}_3[Nb^{IV}(CN)_8]_2$(4-aminopyridine)$_{10}$(4-aminopyridinium)$_2 \cdot 12H_2O$ belongs to the $C2/c$ space group in monoclinic system. The asymmetric unit contains a [Mn(4-aminopyridine)$_4$]$^{2+}$ cation (Mn1), a half of [Mn(4-aminopyridine)$_2$(H_2O)$_2$]$^{2+}$ cation (Mn2), a $[Nb(CN)_8]^{4-}$ anion, and five non-coordinated water molecules. The Mn1 site is coordinated by four pyridyl nitrogen atoms of 4-aminopyridine and two nitrogen atoms of $[Nb(CN)_8]$. The Mn2 site is coordinated by two pyridyl nitrogen atoms, two nitrogen atoms of CN, and two oxygen atoms of coordinated water molecules. The coordination geometry around $[Nb(CN)_8]$ was square-antiprism and three CN groups form cyano-bridged network to the neighboring Mn sites. The Mn−NC−Nb bridges form two-dimensional (2D) network structure. The non-coordinated 4-aminopyridinium molecules are placed inside the 2D network. In the crystal, 1D hydrogen-bonding networks are formed by O(water)−N(4-aminopyridinium), O(water)−O(water), and O(water)−N(cyano). In the magnetization vs. temperature plot under 100 Oe, the magnetization value increased below 20 K, showed a sharp maximum at 9 K, and then deareased below 9 K. The magnetization curve under different external magnetic field showed that a sharp maximum was observed below 400 Oe, but the magnetization shows a monotonical increase above 500 Oe. The initial magnetization curve

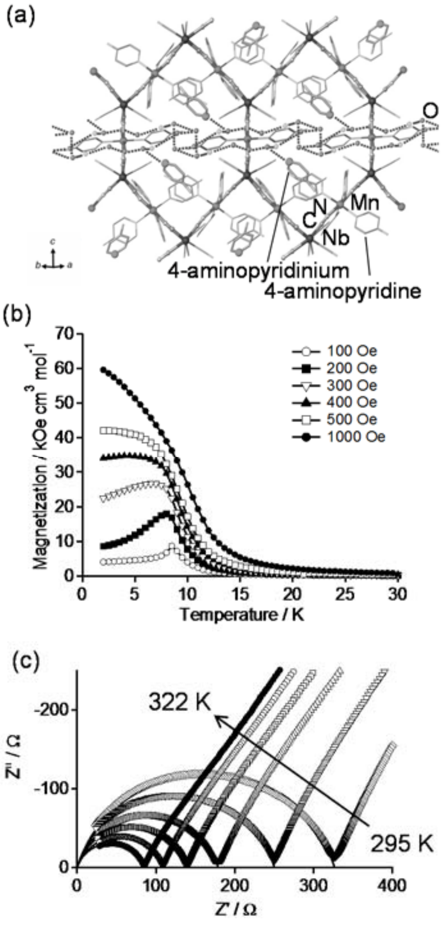

Fig. 3 (a) Crystal structure, (b) magnetization vs temperature curve under various magnetic field, (c) Cole-Cole plots of impedance measurements at various temperatures of **3**.

shows a spin-flip transition with a critical magnetic field around 200 Oe. The magnetization value at 50 kOe was 12.3 μ_B, which is close to the calculated saturation magnetization value of 13.0 μ_B for ferrimagnetic ordering of three Mn^{II} (S= 5/2, g= 2) and two Nb^{IV} (S= 1/2, g= 2). The observed magnetic properties are characteristic behavior of a metamagnet. At low external magnetic field, the magnetic moment of Mn and Nb sites gradually order below 20 K, while the magnetic moment on each layer, in which Mn and Nb sites are ferrimagnetically ordered, become antiparallel below 9 K, resulting in antiferromagnetism. By contrast, at a high external magnetic field, the magnetic moment on each layer parallely orders along the direction of magnetic field.

The conductive properties are investigated by impedance measurements. The half-circular arc fitting of the Cole-Cole plot showed that the conductivity (σ) of the sample is 1.0 × 10^{-4} S cm^{-1} at 295 K (100% RH). The σ value of the sample increases with increasing temperature and at 322 K, the σ value is 4.6 × 10^{-4} S cm^{-1}. The linear regression of the ln(σT) vs T plot indicated that the activation energy (E_a) is 0.48 eV. The humidity dependence of the conductivity showed that the σ value drastically changes from 1.0 × 10^{-4} S cm^{-1} (100% RH) to 3.2 × 10^{-8} S cm^{-1} (45% RH), indicating the occurrence of proton conduction. The σ value of 4.6 × 10^{-4} S cm^{-1} can be classified as super-ionic conductor. $Mn^{II}_3[Nb^{IV}(CN)_8]_2$(4-aminopyridine)$_{10}$(4-aminopyridinium)$_2$·$12H_2O$ has infinite hydrogen-bonding network based on ligand water molecules, non-coordinated water molecules, and 4-aminopyridinium cation, therefore, the mechanism of the proton conductivity is understood by Grotthus mechanism as follows: The deprotonation from the ligand water molecules are promoted by Lewis acidity of Mn ion, and the released proton is transported by the hydrogen-bonding network.

Conclusion

In this work, single crystal synthesis of Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly which is isostructural to light-induced spin-crossover magnet, two step spin-crossover and photo-induced spin-crossover ferromagnetism in Fe^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly, and the coexistence of high ionic conductivity and metamagnetism in a Mn^{II}-$[Nb^{IV}(CN)_8]$ bimetal assembly are realized. Using $[Nb^{IV}(CN)_8]$, a large magnetic interaction works between cyano-bridged metal centers, which leads to the coexistence of magnetic phase transition and other functionalities.