<div align="center">

論文の内容の要旨

</div>

論文題目: Synthesis, crystal structure, and first-principles calculations of a cyanide-bridged copper-molybdate bimetallic assembly

<div align="center">

（銅－オクタシアノモリブデン錯体の合成、結晶構造、および第一原理計算）

氏　名　　　梅　田　喜　一

</div>

**Introduction**

Molecular magnetism has been studied as an interdisciplinary theme on the border of chemistry, materials science, and physics. In this area, control of physical properties by external stimuli is aggressively studied as an important target. Photomagnetism, control of magnetic properties by light irradiation, is attracting attention due to its potential toward applications in information storage and processing. Among photomagnetic materials, bimetallic copper octacyanidomolybdate with the general formula of $Cu^{II}_2[Mo^{IV}(CN)_8] \cdot nH_2O$ is known as a classical photo magnet, for which our group firstly reported photo-induced reversible magnetization with a Curie temperature of 30 K in 2001. After the report, various copper octacyanidomolybdate bimetal assemblies have been studied as photoresponsive magnetic materials. The mechanism of photomagnetism has been considered as the metal to metal charge transfer from $Mo^{IV}$ ($S = 0$) to $Cu^{II}$ ($S = 1/2$). The charge transfer produces $Mo^V$ ($S = 1/2$) and $Cu^I$ ($S = 0$), while the other $Cu^{II}$ centers remain due to 2:1 Cu/Mo stoichiometry. The ferromagnetic interaction between $S = 1/2$ spins of $Cu^{II}$ and $Mo^V$ has been considered to be the origin of photomagnetism. However, the mechanism of photomagnetism in copper octacyanidomolybdate is the issue under discussions due to absence of the precise structural analysis for $Cu^{II}_2[Mo^{IV}(CN)_8] \cdot nH_2O$. There are some efforts to reveal the structure, and it was estimated to be the analogous of $M^{II}_2[Mo^{IV}(CN)_8] \cdot nH_2O$ ($M^{II} = Mn^{II}$, $Fe^{II}$, and $Co^{II}$) assemblies with tetragonal crystal system by wide-angle X-ray analysis and X-ray absorption spectroscopic analysis. As the structure is highly symmetrical and simple, it is expected to be a suitable model for calculations to examine the mechanism of photomagnetism. However, due to its poor crystallinity, a single crystal X-ray analysis was unavailable, and desired for further studies. In this study, the synthesis towards the single crystals, crystal structure, and first-principles calculations by a GGA + $U$ method of a copper(II) octacyanidomolybdate(IV) bimetallic assembly $\{[Cu^{II}(H_2O)]_2[Mo^{IV}(CN)_8]\} \cdot 2H_2O$ (**CuMo**) are reported.

**Result and discussions**

Synthesis and characterization

A single-crystalline form of the target material was obtained by using a gel method. The gel was obtained by mixing a portion of $Na_2SiO_3 \cdot 9H_2O$, acetic acid, and $K_4[Mo^{IV}(CN)_8] \cdot 2H_2O$ powder. The aqueous solution of $Cu(NO)_3 \cdot 3H_2O$ was added on the top of the gel. After the system was kept in dark for ca. 6 months, black block crystals were obtained. The elemental analyses by inductively coupled plasma mass spectrometer, a standard micro-analytical method, and a thermo-gravimetrical (TG) measurement confirmed that the formula is $Cu_2MoC_8H_8N_8O_4$. Calcd. Cu: 25.3%; Mo: 19.1%; C: 19.1%; H: 1.6%; N: 22.3%. Found Cu: 25.3%; Mo: 19.0%; C: 19.2%; H: 1.7%; N: 22.5%. The TG measurement shows two steps of weight loss in the range of 30−40 (step 1) and 120−130 °C (step 2). The weight loss of both steps are about 7.2%. Steps 1 and 2 correspond to desorption of coordinated and non-coordinated water, respectively. The infrared spectrum showed two peaks due to cyanide stretching vibration modes at 2185 and 2167 $cm^{-1}$.

Crystal structure

The single crystal X-ray diffraction analysis revealed that **CuMo** has tetragonal $I4/mcm$ space group with the lattice constants of $a = 11.2833(6)$ Å, $c = 12.8491(8)$ Å. **CuMo** possesses a three-dimensional network structure, in which $Cu^{II}$ and $Mo^{IV}$ centers are alternately bridged by cyanide (Figure 1). The skeleton of the cyanido-bridged network is an analogue of other 3d transition metal assemblies, $\{[M^{II}(H_2O)_2]_2[Mo^{IV}(CN)_8] \cdot nH_2O$ ($M^{II} = Mn^{II}$, $Fe^{II}$, and $Co^{II}$). **CuMo** shows a tetragonal crystal system with unit cell parameters similar to the analogues. However, **CuMo** reveals higher symmetry and fewer coordinated waters than that of the analogues. The independent unit consists of one $Cu^{II}$



**Figure 1.** Crystal structure of **CuMo** (the view from $a$ axis).

center and one $Mo^{IV}$ center. The coordination geometry of $Mo^{IV}$ center is 8-coordinated square antiprism ($D_{4d}$), which is the highest symmetry for 8-coordinate centers. The coordination geometry of $Cu^{II}$ center is 5-coordinated square pyramid. The equatorial positions of the square pyramid are occupied by four nitrogen atoms from bridging cyanides, and the axial position is occupied by one oxygen atom from coordinated water. The position of the coordinated water is disordered into two positions with the occupancy of 50%. The non-coordinated water molecules are located in the structural pores along $c$ axis. Coordinated and non-coordinated water molecules are forming hydrogen bonding network extending along $c$ axis. The crystal structure of **CuMo** is stabilized by both the hydrogen bonding and cyanide bridging.
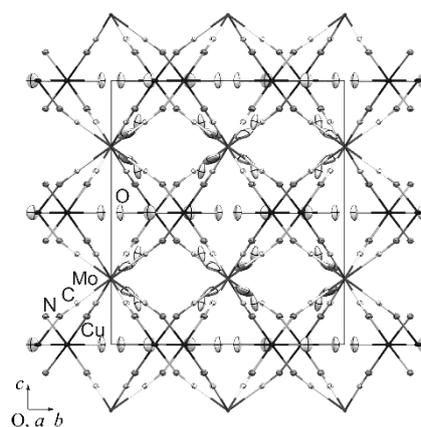
First-principles band calculations

The first-principles calculations were conducted by using Vienna ab initio simulation package (VASP) with a GGA + $U$ method. Structural optimization from the result of the single crystal X-ray diffraction analysis as the initial structure was applied. The calculated band structure is shown in Figure 2. **CuMo** reveals a direct optical transition at the $\Gamma$ point with a band gap of 1.2 eV. The conduction bands above 1.0 eV are occupied by two $Mo^{IV}$ 4d-based bands. Although these bands show energy splitting, the charge density of these bands are very similar. This splitting can be attributed to a difference in phases of the atomic orbitals for equivalent atoms in the calculated primitive unit cell. The valence bands below 1.8 eV are occupied by two $Cu^{II}$ 3d-based bands. The energy splitting between the same spins is originated from the difference in phase like for the valence bands. In addition, the splitting between the different spins are caused by the difference of coordination geometry due to the disordered coordinated waters. The valence bands in the range of $-2.0$ to $-1.0$ eV consist of the oxygen 2p-based bands from the non-coordinated water. The conduction bands above 1.8 eV are composed of the carbon and nitrogen atoms of cyanide ligands with a slight contribution from $Mo^{IV}$. As a result of an absorption spectrum calculation, the optical transition between the highest valence band and the lowest conduction band are found to be the main contribution to absorption in the visible range. The direction dependence of absorption strength indicates the strongest absorption along [1 1 1] crystallographic direction, where the cyanide ligands are aligned in parallel. The charge density map of the highest valence band and the lowest conduction band are shown in Figure 3. The highest valence band consists of $Mo^{IV}$ $d_{z^2}$ orbital and nitrogen $p_z$ orbital, while the lowest conduction band is composed of $Cu^{II}$ $d_{x^2-y^2}$ orbital, nitrogen $sp_x$ orbital, and carbon $sp_x$ orbital. Among these bands, orbital overlap exists only around the nitrogen center. The transition of $p_z \rightarrow sp_x$ of nitrogen gives the strong transition moment due to the orbital difference in the orbital angular momentum and parity. This result confirms the charge transfer from $Mo^{IV}$ to $Cu^{II}$ is realized through the transition moment on nitrogen atom of cyanide ligand, which results also in the anisotropy of the optical transition.
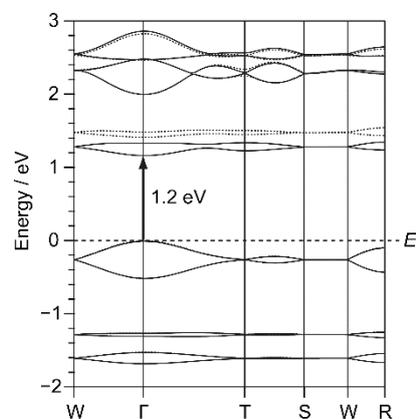


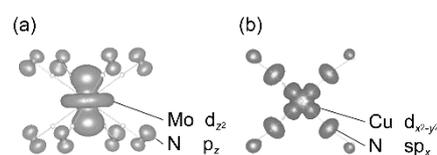**Figure 2.** Calculated band structure of **CuMo**.



**Figure 3.** Charge density maps of (a) the highest valence band and (b) the lowest conduction band.

**Conclusions**

In this work, the single crystalline form of a three-dimensional copper(II) octacyanido-molybdate(IV) was successfully synthesized, and the crystal structure was determined. The crystal structure is a tetragonal three-dimensional network structure similar to analogues with other s3d transition metals. Using the experimentally determined crystal structure, first principles calculations

with a GGA + *U* method were performed. **CuMo** shows a direct transition at the $\Gamma$ point with a band gap of 1.2 eV, and the optical transitions in the visible range were assigned to the charge transfer from $Mo^{IV}$ to $Cu^{II}$. The absorption strength analysis suggests the anisotropic absorption along [1 1 1] crystallographic axis, which is parallel to the arrangement of cyanides. In addition, as the result of the charge density analysis, the charge transfer between $Mo^{IV}$ and $Cu^{II}$ in the visible range was found to be facilitated by the optical transition of nitrogen from bridging cyanides, i.e. the changes of the parity and the symmetry caused by the $p_z \rightarrow sp_x$ transition of nitrogen enable the efficient charge transfer. The results in this work are expected to give a design criteria for new functional copper octacyanidomolybdate-based and other related photomagnetic materials.