

論文の内容の要旨

論文題目: オクタシアノ CoW 錯体における外場応答性
(External-stimuli responsivity in an octacyano-CoW bimetal assembly)

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Introduction

Cyano-bridged assemblies, in which two or more kinds of metal ions are bridged by cyanido ligands to assemblies, are a versatile class of compounds to synthesize functional materials, because their properties or functionalities can be designed rationally by choosing suitable transition metal ions and ligands. Furthermore, octacyanometalates, $[M(\text{CN})_8]$ ($M = \text{Mo}, \text{W}, \text{Nb}$), have flexibility in their coordination geometry around the metal ions, and therefore, variable crystal structures can be constructed. In this context, we have developed many functional molecular-based materials using octacyanometalate, such as photo-induced magnets, chemically sensitive magnets, and so on. In my master thesis, I reported the photo-induced magnetization effect in an octacyano-CoW bimetal assembly, $\text{Co}_3[\text{W}(\text{CN})_8]_2(4\text{-methylpyridine})_2(\text{pyrimidine})_2 \cdot 7.5\text{H}_2\text{O}$. In this doctor thesis, I draw my attention to external-stimuli responsivity in an octacyano-CoW bimetal assembly.

Phase transition materials accompanied by large thermal hysteresis are not only useful for the study of cooperative effects in solids, but also attractive due to its potential for applications such as sensors, displays, or memory devices. In this context, porous coordination polymers and metal-organic frameworks are good targets because their physical properties are often affected by chemical environment, and when they exhibit thermal phase transition, the transition temperature and thermal hysteresis can be tuned by the chemical environment. In this study, a porous octacyano-CoW bimetal

assembly, $\text{Co}_3[\text{W}(\text{CN})_8]_2(4\text{-methylpyridine})_2(\text{pyrimidine})_2 \cdot 7.5\text{H}_2\text{O}$ was synthesized, and the humidity dependency of its phase transition behavior was observed.

Result and discussion

Synthesis and characterization

The powder-form sample of the target material was synthesized by mixing $\text{Co}^{\text{II}}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$, 4-methylpyridine, pyrimidine, and $\text{Cs}^{\text{I}}_3[\text{W}^{\text{V}}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ in H_2O at 40°C for 30 minutes. Elemental analysis by inductively coupled plasma mass spectrometer and the standard micro analytical method confirmed that the present compound has a chemical formula of $\text{Co}_3[\text{W}(\text{CN})_8]_2(4\text{-methylpyridine})_2(\text{pyrimidine})_2 \cdot 7.5\text{H}_2\text{O}$ at 60% RH: calcd.: Co 12.26, W 25.50, C 29.96, H 2.57, N 21.36; found: Co 12.23, W 25.48, C 29.87, H 2.47, N 21.40. The humidity dependence of the sample weight and the Infrared (IR) spectra indicated that the present compound absorb (or desorb) water molecules depending on the ambient humidity, i.e., the number of the water molecules contained in the present compound was 8.0 at 80% RH, while it was 5.3 at 5% RH.

The crystal structure was determined by powder X-ray diffraction (XRD) and Rietveld analysis (Figure 1). The present compound has triclinic $P-1$ symmetry with lattice constants of $a = 7.610(1) \text{ \AA}$, $b = 14.980(2) \text{ \AA}$, $c = 20.897(8) \text{ \AA}$, $\alpha = 90.90(8)^\circ$, $\beta = 98.34(2)^\circ$, and $\gamma = 90.55(2)^\circ$ at 80% RH. In the structure, Co and W ions are bridged by CN ligands, and forms a two-dimensional grid layer in the crystallographic ab -plane. These layers are bridged by different Co ions and construct a three-dimensional network structure. 2.0 H_2O molecules are coordinated to Co ions, and the remaining 6.0 H_2O molecules are contained in the pores between the grid layers as zeolitic water and forms hydrogen bond networks with the other H_2O molecules or non-bridged CN ligands. XRD patterns were also measured at 80% RH, 60% RH, 40% RH, 20% RH, and 5% RH. As the humidity decreased, some XRD peaks shifted to higher angles, while the others did not shift, which indicates an anisotropic contraction of the crystal lattice. Rietveld analysis revealed that the contraction occurs in a - and b -axes,

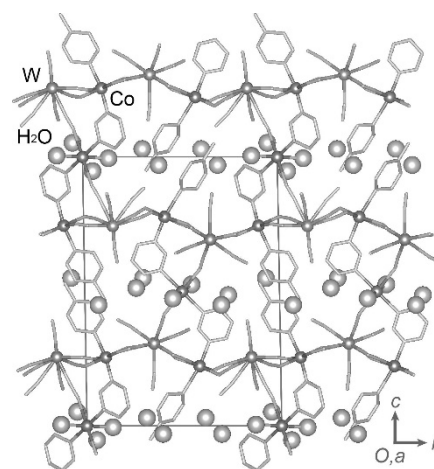


Fig. 1. Crystal structure of the target compound viewed along a -axis.

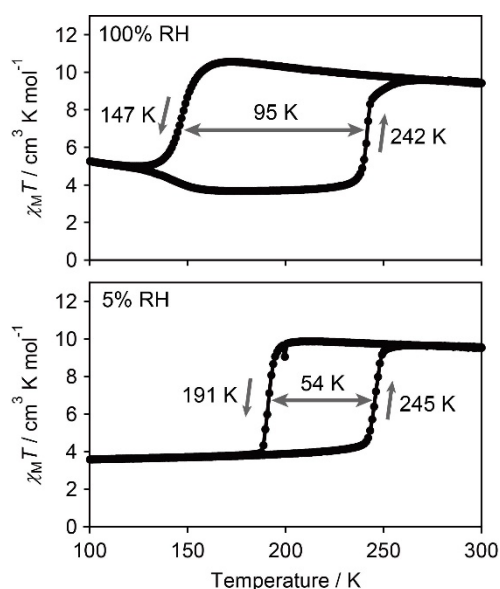


Fig. 2. Temperature dependence of $\chi_M T$ value at 100% RH (upper) and 5% RH (lower).

and c -axis did not contract; the lattice constants at 5% RH were $a = 7.588(1) \text{ \AA}$, $b = 14.949(2) \text{ \AA}$, and $c = 20.837(7) \text{ \AA}$, showing the contraction of 0.20%, 0.18%, and 0.00%, respectively, compared to those at 80% RH.

Phase transition and its humidity dependency

In my master thesis, I reported that the present compound shows thermal phase transition between high-temperature (HT, $3\text{Co}^{\text{II}}_{hs}-2\text{W}^{\text{V}}$) and low-temperature (LT, $\text{Co}^{\text{II}}_{hs}-2\text{Co}^{\text{III}}_{ls}-2\text{W}^{\text{IV}}$) phases. In this study, the product of magnetic susceptibility and temperature ($\chi_{\text{M}}T$) versus temperature (T) plot ($\chi_{\text{M}}T$ - T plot) was measured at variable humidity of 100% RH, 80% RH, 60% RH, 40% RH, 20% RH, and 5% RH. At 100% RH, $\chi_{\text{M}}T$ value abruptly decreased around 150 K with decreasing temperature, and conversely, the value abruptly increased around 240 K with increasing temperature (Figure 2). The phase transition behaviors, such as the phase transition temperatures ($T_{1/2\downarrow}$ and $T_{1/2\uparrow}$: the temperatures at which half of the compound is in HT or LT phase), T_{p} ($\equiv (T_{1/2\downarrow} + T_{1/2\uparrow})/2$), and ΔT ($\equiv T_{1/2\uparrow} - T_{1/2\downarrow}$), were $T_{1/2\uparrow} = 147 \text{ K}$, $T_{1/2\downarrow} = 242 \text{ K}$, $T_{\text{p}} = 195 \text{ K}$, and $\Delta T = 95 \text{ K}$. As the humidity decreased, T_{p} value increased from 195 K at 100% RH to 218 K at 5% RH, and ΔT value decreased from 95 K at 100% RH to 54 K at 5% RH.

Thermodynamic analysis

Differential scanning calorimetry (DSC) measurement was conducted in N_2 atmosphere for decreasing and increasing temperature. Sharp peaks, which is characteristic in first-order phase transitions, appeared at 183 K and 238 K, which correspond to the transition temperature observed in $\chi_{\text{M}}T$ - T plots. T_{p} was 211 K, and the transition enthalpy (ΔH) and the transition entropy (ΔS) were measured to be 25.6 kJ mol^{-1} and $116 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Then, thermodynamical analysis using Slichter-Drickamer mean-field model was conducted based on the obtained ΔH and ΔS values. In this model, Gibbs energy (G) is expressed as $G = \alpha\Delta H + \gamma\alpha(1 - \alpha) + T\{R[\alpha \ln \alpha + (1 - \alpha) \ln (1 - \alpha)] - \alpha\Delta S\}$, where α is the fraction of the HT phase, γ is the interaction parameter, and R is the gas constant. The DSC measurement was conducted in N_2 atmosphere, and therefore, the obtained ΔH and ΔS were close to those of 5% RH. When γ was 9.0 kJ mol^{-1} , the energy minimum disappeared at 189 K and 244 K with decreasing and increasing temperature, respectively which well explains the phase transition behavior observed in the $\chi_{\text{M}}T$ - T plot

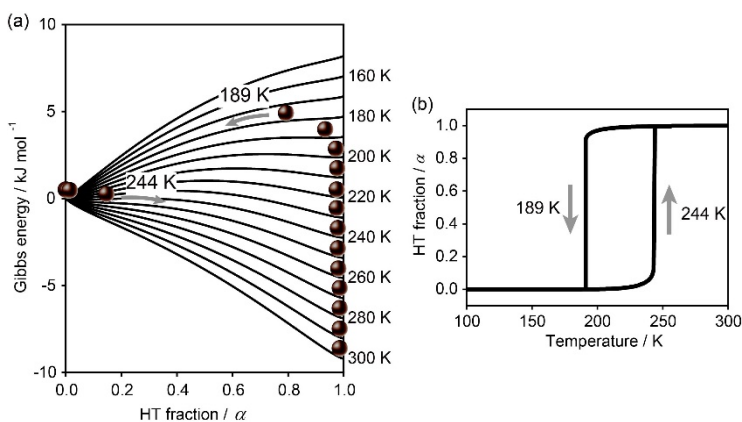


Fig. 3. (a) Temperature dependence of the calculated Gibbs energy curve and (b) the fraction vs. temperature curve based on Slichter-Drickamer mean-field model.

(Figure 3).

Conclusions

In this work, humidity dependency of the phase transition behavior of an octacyano-CoW bimetal assembly, $\text{Co}_3[\text{W}(\text{CN})_8]_2(4\text{-methylpyridine})_2(\text{pyrimidine})_2 \cdot 7.5\text{H}_2\text{O}$, was investigated. The observed humidity dependency, i.e., the change in $T_{1/2\downarrow}$ was larger than that of $T_{1/2\uparrow}$, is a characteristic when the interaction parameter γ changes. Therefore, the origin of the humidity dependency is mainly attributed to the change in the cooperative effect based on the hydrogen bond network in the system due to the absorption (or desorption) of water molecules in the interstitial sites of the pores of the present material.