Porous Magnets Based on Copper–Octacyanotungsten Containing Noncoordinated Alcohol Molecules

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Two types of molecule-based magnets $Cu^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_2\cdot 2\text{-propanol}\cdot 6H_2O$ (**1**) and $Cu^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_2\cdot 1\text{-butanol}\cdot 5H_2O$ (**2**) are prepared. These compounds have a 3-dimensional porous structure, in which a noncoordinated 2-propanol or 1-butanol molecule is penetrated. These compounds show long-range magnetic ordering with Curie temperatures of 8.2 K (**1**) and 8.4 K (**2**) although large organic molecules are packed.

The study of porous magnetic materials is an attractive issue from the angle of new magnetic functionalities such as chemically sensitive magnetism.[1] The magnetic materials composed of cyano-bridged bimetallic assemblies are a suitable system for this objective. Among them, we have focused our attention on an octacyanometalate-based magnet, since it can form a crystal structure containing a pore at the interstitial site and its Curie temperature (T_C) is relatively high,[2] e.g., $T_C = 50\,K$ in $Cu_3[W(CN)_8]_2\cdot 3.4H_2O$[2a] and $T_C = 54\,K$ in $Mn_6(H_2O)_9[W(CN)_8]_4\cdot 13H_2O$.[2b] One of the interests in the study of porous magnetic materials is whether a bulky molecule can be incorporated into the pore with keeping a long-range magnetic ordering. In our previous paper, we reported $Cu_3[W(CN)_8]_2(pyrimidine)_2\cdot 3/2(1\text{-propanol})\cdot 9/4H_2O$, which shows ferrimagnetism.[2g] In this work, we tried to prepare two types of porous magnets containing bulky molecules, 2-propanol and 1-butanol (Figure 1); $Cu^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_2\cdot 2\text{-propanol}\cdot 6H_2O$ (**1**) and $Cu^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_2\cdot 1\text{-butanol}\cdot 5H_2O$ (**2**). Although large organic molecules are penetrated to the interstitial site, these two compounds keep the long-range magnetic ordering. Their Curie temperatures are 8.2 K (**1**) and 8.4 K (**2**).

Single crystals of **1** and **2** were obtained by slow diffusion of a solution of $Cs_3[W(CN)_8]\cdot 2H_2O$ into a mixed solution of $CuCl_2\cdot 2H_2O$ and pyrimidine with solvents of alcohols (2-propanol; **1**, 1-butanol; **2**) and water. The elemental analyses show that the formulas of the obtained single crystals **1** and **2** are $Cu^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_2\cdot 2\text{-propanol}\cdot 6H_2O$ and $Cu^{II}_3[W^{V}(CN)_8]_2(pyrimidine)_2\cdot 1\text{-butanol}\cdot 5H_2O$, respectively.[3] Figure 2 shows the crystal structures of **1** and **2** determined by single-crystal X-ray structural analysis.[4] The asymmetric unit of **1** consists of one-half of a $[W1(CN)_8]^{3-}$ anion, one-half of a $[W2(CN)_8]^{3-}$ anion, one-half of a $[Cu1A(pyrimidine)]^{2+}$ cation, one-half of a $[Cu1B(pyrimidine)]^{2+}$ cation, one-half of a $[Cu2(H_2O)_2]^{2+}$ cation, two zeolitic water molecules, and one-half of a 2-propanol molecule (Figure 2a, upper). The coordination geometry of W (W1 and W2) is eight-coordinated square antiprism (D_{4d}). Six cyano groups of $[W(CN)_8]$ bridge to Cu^{2+} ions and the other two cyano groups are free (Figure S1).[5] The geometries of two types of Cu^{2+} ions (Cu1 and Cu2) are six-coordinated pseudo-octahedron (D_{4h}), i.e., Cu1 is coordinated to

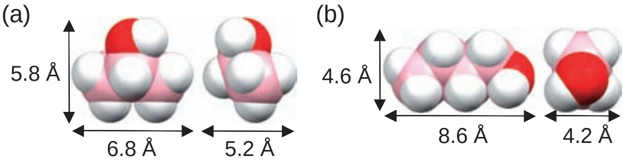

Figure 1. Molecular size of (a) 2-propanol and (b) 1-butanol. C, O, and H atoms of alcohol molecules are represented by pink, red, and white spheres considering van der Waals radii, respectively.

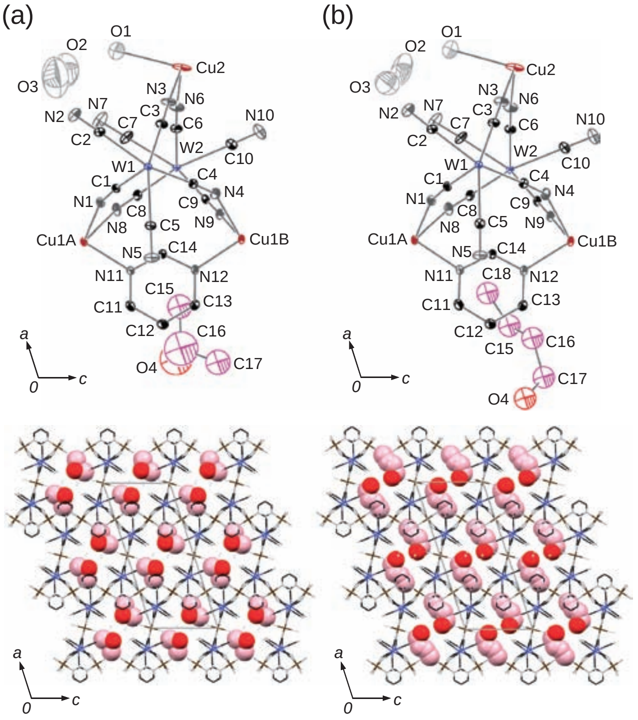

Figure 2. (a) The crystal structure of **1**. ORTEP drawing of the asymmetric unit (upper). The projection in the *ac* plane (lower). 2-Propanol molecules are represented as spheres considering van der Waals radii. (b) The crystal structure of **2**. ORTEP drawing of the asymmetric unit (upper). The projection in the *ac* plane (lower). 1-Butanol molecules are represented as spheres considering van der Waals radii. Displacement ellipsoids are drawn at a 20% probability level. Cu, W, C, N, and water O atoms are represented by brown, blue, black, dark gray, and light gray ellipsoids, respectively. C and O atoms of alcohol molecules are represented by pink and red spheres, respectively. H atoms are omitted for clarify.

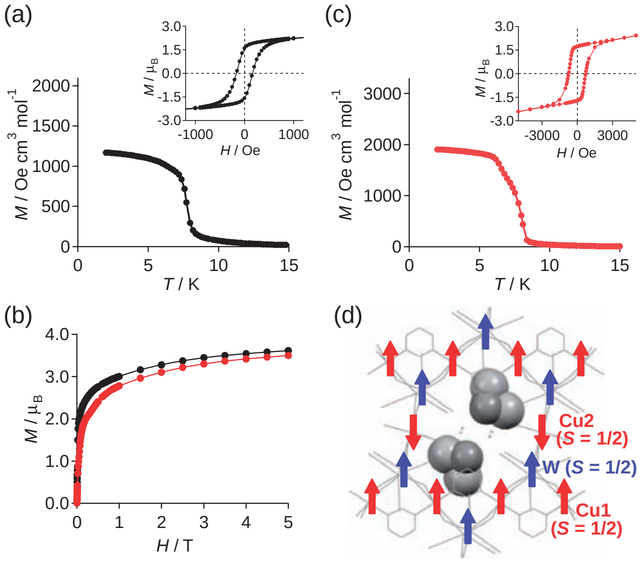

Figure 3. (a) FCM curve of **1** at 10 Oe. Magnetic hysteresis loop of **1** at 2 K (inset). (b) Magnetic field dependence of magnetization of **1** (●) and **2** (●) at 2 K. (c) FCM curve of **2** at 10 Oe. Magnetic hysteresis loop of **2** at 2 K (inset). (d) The schematic illustration of the ferrimagnetic spin alignment.

four cyanide nitrogen atoms and two nitrogen atoms of pyrimidine molecules and Cu2 is coordinated to four cyanide nitrogen atoms and two oxygen atoms of water ligands (Figure S1).[5] This crystal has a three-dimensional porous structure with a cavity along the *b* axis. In the cavity, noncoordinated 2-propanol molecules are packed (Figure 2a, lower). The position of O atoms of the 2-propanol molecules is determined by the hydrogen bond. The distance between the hydrogen bonded atoms is O4···O3 = 2.79 Å. For **2**, the framework is basically similar to **1**, but 1-butanol molecule instead of 2-propanol molecule is penetrated in the cavity (Figures 2b and S2).[4,5] The position of O atoms of the 1-butanol molecules is determined by the hydrogen bond. The distances between the hydrogen-bonded atoms are O4···O1 = 2.78 Å and O4···N2 = 2.86 Å.

Figure 3 shows the magnetic properties of **1** and **2**. In the field-cooled magnetization (FCM) curve at 10 Oe for **1**, spontaneous magnetization was observed with a T_C of 8.2 K (Figure 3a). Zero-field-cooled magnetization (ZFCM) and remanent magnetization (RM) curves are shown in Figure S3.[5] The magnetization versus external magnetic field (M–H) curve showed that the coercive field (H_c) was 150 Oe (Figure 3a, inset) and the saturation magnetization (M_s) value was 3.6 μ_B at 2 K (Figure 3b). **2** showed similar magnetic properties to **1**. In the FCM curve of **2** at 10 Oe, spontaneous magnetization was observed with a T_C of 8.4 K (Figure 3c). ZFCM and RM curves are shown in Figure S4.[5] The M–H curve showed that the H_c was 700 Oe (Figure 3c, inset) and the M_s value was 3.5 μ_B at 2 K (Figure 3b). The observed M_s values indicate that these compounds are ferrimagnets, in which sublattice magnetizations of Cu1 ($S = 1/2$) and W ($S = 1/2$) are positive but that of Cu2 ($S = 1/2$) is negative as shown in Figure 3d.

We prepared $Cu^{II}_3[W^V(CN)_8]_2(pyrimidine)_2\cdot$2-propanol$\cdot 6H_2O$ and $Cu^{II}_3[W^V(CN)_8]_2(pyrimidine)_2\cdot$1-butanol$\cdot 5H_2O$ magnetic materials. Although large-size molecules are incorporated in the interstitial site, these two compounds maintain a long-range magnetic ordering. Magnetic properties of the present CuW framework depend on the penetrated molecules. We summarized the difference in crystal structures and magnetic properties of a series of CuW porous magnets in Table S4.[5] In such ferromagnetic complexes, host–guest chemistry of large organic molecules is expected to be realized.

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References and Notes

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3 Synthesis: **1**: A single crystal of compound **1** was obtained by slow diffusion of a solution (50 mL) of $Cs_3[W(CN)_8]\cdot 2H_2O$ (0.16 mmol) into a mixed solution (50 mL) of $CuCl_2\cdot 2H_2O$ (0.24 mmol) and pyrimidine (0.16 mmol) with solvents of 2-propanol and water (1:1 v/v) at room temperature for one week. Calcd: Cu, 14.63; W, 28.21; C, 24.89; H, 2.17; N, 21.51%. Found: Cu, 14.41; W, 28.85; C, 24.97; H, 2.12; N, 21.59%. IR (Nujor, cm^{-1}): ν(CN) 2190, 2165, and 2159. **2**: This compound was prepared by the same method as that of **1**, except that solvents of 1-butanol and water (1:20 v/v) was used. Calcd: Cu, 14.68; W, 28.30; C, 25.89; H, 2.17; N: 21.57%. Found: Cu, 14.58; W, 28.14; C, 25.75; H, 2.19; N, 21.79%. IR (Nujor, cm^{-1}): ν(CN) 2191, 2166, and 2158.

4 Detailed crystallographic data of compounds, **1** and **2**, were deposited in Supporting Information.[5] All calculations were performed using the CrystalStructure crystallographic software package. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-645281 (**1**) and 656506 (**2**).

5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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