# Synthesis and Alcohol Vapor Sensitivity of a Ferromagnetic Copper−Tungsten Bimetallic Assembly

Shin-ichi Ohkoshi,*,† Yoshihide Tsunobuchi,†,‡ Hitomi Takahashi,†,‡ Toshiya Hozumi,†
Motoo Shiro,§ and Kazuhito Hashimoto‡

*Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033,
Japan, Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku,
Tokyo 113-8656, Japan, and Rigaku Corporation, 3-9-12 Matsubaracho, Akishima, Tokyo 196-8666, Japan*

Received December 29, 2006;  E-mail: ohkoshi@chem.s.u-tokyo.ac.jp

Synthesis of a porous coordination polymer has been aggressively studied since various attractive phenomena are expected in the materials of this category.[1,2] However, the preparation of porous magnetic materials is not so easy because magnetic coupling between spin sources is weak in the porous network. For the preparation of a ferromagnetic porous coordination polymer, an octacyanometalate-based assemble is a suitable system because an octacyanometalate complex has many exchange pathways owing to its high coordination numbers.[3] In this work, we prepared a ferromagnetic porous coordination polymer, $Cu_3[W(CN)_8]_2$-(pyrimidine)$_2$·8H$_2$O (**1**). Herein, we report the reversible variations in the crystal structure and magnetic properties of **1** upon exposure to *n*-propanol vapor.

Compound **1** was prepared by adding an aqueous solution of $Cs^I_3[W^V(CN)_8]$·2H$_2$O[4] to a mixed aqueous solution of $Cu^{II}Cl_2$·2H$_2$O and pyrimidine at room temperature. A single crystal for X-ray structural analysis was prepared by a diffusion method. Elemental analyses confirmed that the formula is $Cu_3[W(CN)_8]_2$(pyrimidine)$_2$·8H$_2$O:  (calcd) Cu, 14.9; W, 28.7; C, 22.5; H, 1.9; N, 21.9%; (found) Cu, 15.1; W, 28.7; C, 22.7; H, 1.7; N, 22.2%. Single-crystal structural analysis reveals that **1** consists of a three-dimensional cyanide-bridged network, in which Cu and W ions are linked in alternating fashion (orthorhombic, *Ibam*, $a = 11.419(2)$, $b = 24.830(4)$, $c = 30.005(4)$ Å, and $Z = 8$) (Figure 1a, left).[5] The coordination geometry of W is an 8-coordinated bicapped trigonal prism and six CN groups of [W(CN)$_8$] are bridged to Cu$^{2+}$ ions. The other two CN groups are free. The geometries of the two types of Cu$^{2+}$ ions (Cu1 and Cu2) are 6-coordinated pseudo-octahedron, that is, Cu1 is coordinated to four cyanide nitrogen atoms and two nitrogen atoms in pyrimidine molecules, and Cu2 is coordinated to four cyanide nitrogen atoms and two oxygen atoms in the water ligands (Figure 1a, right). This crystal has a cavity which is occupied by zeolitic water molecules.

We investigated the sensitivity to *n*-propanol vapor using **1** in the powder-form. When **1** is exposed to *n*-propanol vapor (11.5 Torr, 82% relative to saturated vapor) at room temperature, the sample changes from green to yellowish brown (**2**). As for IR spectra, the CN peak at 2203 cm$^{-1}$ of **1** decreases and a new CN peak appears at 2190 cm$^{-1}$. In **2**, the IR peaks due to the incorporated *n*-propanol molecules are also observed in the region of 950−1080 cm$^{-1}$ (Supporting Information, Figure S3). Elemental analyses showed that the formula of **2** is $Cu_3[W(CN)_8]_2$(pyrimidine)$_2$·$^3/_2$PrOH·$^9/_4$H$_2$O.[6] When **2** is exposed to water vapor (17.5 Torr, 100% RH), the IR spectrum is recovered. X-ray diffraction measurement shows the reversible variation of the crystal structure.
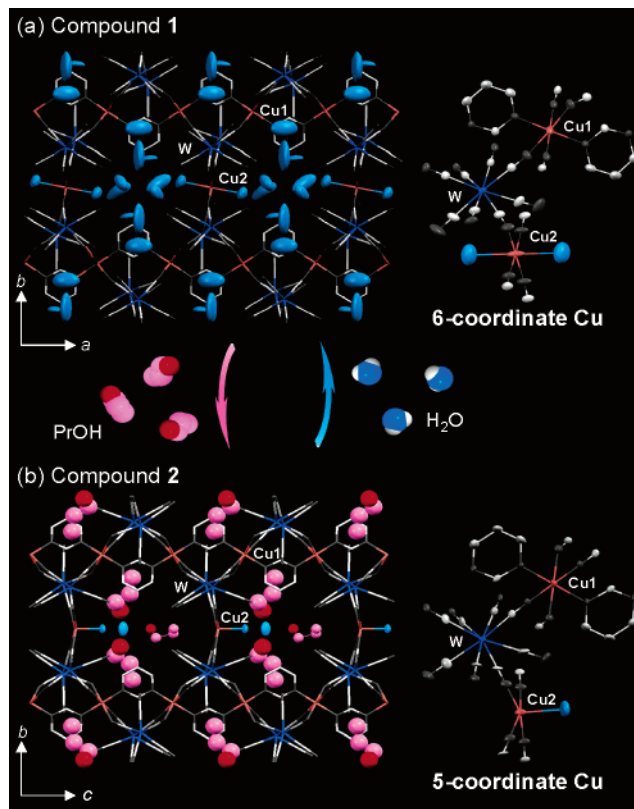
† Department of Chemistry, School of Science, The University of Tokyo.
‡ Department of Applied Chemistry, School of Engineering, The University of Tokyo.
§ Rigaku Corporation.

**Figure 1.** X-ray crystal structures for **1** and **2**. (a) (left) The projection of **1** in the *ab* plane (orthorhombic, *Ibam*). Cu, W, C, and N atoms are represented as orange, blue, light gray, and dark gray stick lines, respectively. Water O atoms are represented as sky blue ellipsoids. (right) ORTEP drawing of the coordination environments of **1** around the Cu1, Cu2, and W atoms. (b) (left) The projection of **2** in the *bc* plane (orthorhombic, *Pmmn*). C and O atoms of *n*-propanol molecules are represented as pink and red spheres, respectively. (right) ORTEP drawing of the coordination environments of **2** around the Cu1, Cu2, and W atoms. Displacement ellipsoids and spheres are drawn at a 50% probability level. All H atoms are omitted for clarify.

The orthorhombic structure (space group = *Ibam*) in **1** is converted to an orthorhombic structure (space group = *Pmmn*) in **2** (Figure S4).

To investigate the *n*-propanol sensitivity, a crystal structure of **2** was measured. Compound **2** consists of a three-dimensional cyanide-bridged network (orthorhombic, *Pmmn*, $a = 14.761(2)$, $b = 25.593(4)$, $c = 11.5284(19)$ Å, and $Z = 4$) (Figure 1b, left).[7] The coordination geometries of W is 8-coordinated bicapped trigonal prism. The geometry of Cu2 is 5-coordinated square pyramidal which is bridged to four cyanide nitrogen atoms and
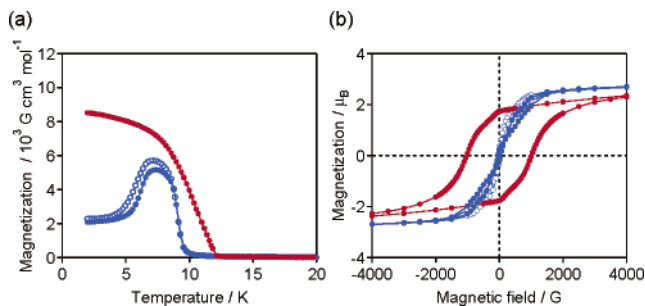
**Figure 2.** Magnetic properties for **1** (blue closed circle), **2** (red closed circle), and the recovered sample (blue open circle): (a) FCM curves in an applied field of 50 G; (b) magnetic hysteresis loops at 2 K.

one water oxygen atom, although that of Cu1 sites are 6-coordinated pseudo-octahedron (Figure 1b, right). The *n*-propanol molecules locate in the cavity. The significant difference between **1** and **2** is the coordination geometry of Cu2, that is, 6-coordinate for **1** and 5-coordinate for **2**.

The magnetic properties also change when **1** is exposed to *n*-propanol vapor. The product of the magnetic susceptibility and temperature ($\chi_M T$) at 293 K changes from 2.22 cm$^3$ K mol$^{-1}$ for **1** to 1.99 cm$^3$ K mol$^{-1}$ for **2**. The field-cooled magnetization (FCM) curve for powder-form **1** shows a spontaneous magnetization with a Curie temperature ($T_c$) of 9.5 K and then the magnetization decreases around 7.5 K (Figure 2a). The magnetization vs external magnetic field ($M-H$) curve for **1** at 2 K shows a saturation magnetization ($M_s$) value of 3.5 $\mu_B$ (Figure S6) for a given formula, and the magnetic hysteresis loop shows a coercive field ($H_c$) of 30 G (Figure 2b). The FCM curve of **2** has a $T_c$ value at 12.0 K and then spontaneous magnetization monotonously increases (Figure 2a). The $M-H$ curve of **2** shows that the $M_s$ and $H_c$ values are 3.6 $\mu_B$ (Figure S6) and 1000 G (Figure 2b) at 2 K, respectively. As shown in Figures 2a and 2b, the magnetic properties of **2** are recovered to those of **1** by exposing to water vapor.

On the basis of the structural difference between **1** and **2**, we considered the role of *n*-propanol in the change of the magnetic properties. The $M_s$ values of 3.5 $\mu_B$ for **1** and 3.6 $\mu_B$ for **2** indicate that these materials have a magnetic ordering, which consists of positive magnetizations for Cu1 ($S = 1/2$) and W ($S = 1/2$) and a negative magnetization for Cu2 ($S = 1/2$) against an applied magnetic field, that is, $M_s = 2(2S_{Cu1} + 2S_W - S_{Cu2})$. Hence, two types of exchange couplings, a ferromagnetic (Cu1$-$NC$-$W) and antiferromagnetic interaction (Cu2$-$NC$-$W), exist. Ferromagnetic Cu1$-$NC$-$W exchange coupling is assumed to be fixed at a particular positive value, since Cu1$-$NC$-$W geometry does not change between **1** and **2**. In contrast, antiferromagnetic Cu2$-$NC$-$W exchange coupling is considered to vary between **1** and **2** because Cu2 geometry changes from 6-coordinate to 5-coordinate. Along this scenario, using molecular-field theory[8] with particular exchange values, the observed $T_c$ values and the shapes of FCM curves are qualitatively reproduced (Figure S7).

In magnetic porous coordination polymers,[9] new magnetic functionalities are expected to be achieved, for example, magnetic gas-sensing and magnetic molecular recognizing. In the present work, we have prepared a ferromagnetic porous coordination polymer, Cu$_3$[W(CN)$_8$]$_2$(pyrimidine)$_2$·8H$_2$O. This material responds to *n*-propanol vapor. We are currently measuring the response with other alcohols (methanol and ethanol).

**Supporting Information Available:** X-ray crystallographic file in CIF format; information relating to the crystal structure, IR spectra, XRD patterns, saturation magnetization, and simulation of FCM curves based on molecular-field theory. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

(1) (a) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Cheerham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268. (c) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 369.

(2) (a) Kepert, C. J. *Chem. Commun.* **2006**, 695. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (c) Janiak, C. *Dalton Trans.* **2003**, 2781. (d) Ohkoshi, S.; Arai, K.; Sato, Y.; Hashimoto, K. *Nat. Mater.* **2004**, *3*, 857. (e) Mori, W.; Takamizawa, S.; Kato, C. N.; Ohmura, T.; Sato, T. *Microporous Mesoporous Mater.* **2004**, *73*, 31.

(3) (a) Garde, R.; Desplanches, C.; Bleuzen, A.; Veillet, P.; Verdaguer, M. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 587. (b) Podgajny, R.; Korzeniak, T.; Balanda, M.; Wasiutynski, T.; Errington, W.; Kemp, T. J.; Alcock, N. W.; Sieklucka, B. *Chem. Commun.* **2002**, 1138. (c) Bonadio, F.; Gross, M.; Evans, H. S.; Decurtins, S. *Inorg. Chem.* **2002**, *41*, 5891. (d) Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9240. (e) Willemin, S.; Larionova, J.; Clérac, R.; Donnadieu, B.; Henner, B.; Goff, X. F. L.; Guérin, C. *Eur. J. Inorg. Chem.* **2003**, 1866. (f) Herrena, J. M.; Marvaud, V.; Verdaguer, M.; Marrot, J.; Kalisz, M.; Mathonière, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5468. (g) Catala, L.; Mathonière, C.; Gloter, A.; Stephan, O.; Gacoin, T.; Boilot, J. P.; Mallah, T. *Chem. Commun.* **2005**, 746. (h) Ohkoshi, S.; Tokoro, H.; Hozumi, T.; Zhang, Y.; Hashimoto, K.; Mathonière, C.; Bord, I.; Rombaut, G.; Verelst, M.; Moulin, C. C.; Villain, F. *J. Am. Chem. Soc.* **2006**, *128*, 270. (i) Ohkoshi, S.; Ikeda, S.; Hozumi, T.; Kashiwagi, T.; Hashimoto, K. *J. Am. Chem. Soc.* **2006**, *128*, 5320. (j) Wang, Z. X.; Shen, X. F.; Wang, J.; Zhang, P.; Li, Y. Z.; Nfor, E. N.; Song, Y.; Ohkoshi, S.; Hashimoto, K.; You, X. Z. *Angew. Chem., Int. Ed.* **2006**, *45*, 3287. (k) Withers, J. R.; Li, D.; Triplet, J.; Ruschman, C.; Parkin, S.; Wang, G.; Yee, G. T.; Holmes, S. M. *Inorg. Chem.* **2006**, *45*, 4307. (l) Przychodzeń, P.; Korzeniak, T.; Podgajny, R.; Sieklucka, B. *Coord. Chem. Rev.* **2006**, *250*, 2234.

(4) Bok, L. D. C.; Leipoldt, J. G.; Basson, S. S. *Z. Anorg. Allg. Chem.* **1975**, *415*, 81.

(5) Crystal data for **1**: C$_{24}$H$_{24}$Cu$_3$N$_{20}$O$_8$W$_2$, fw = 1278.92, orthorhombic, space group *Ibam*, $a = 11.419(2)$ Å, $b = 24.830(4)$ Å, $c = 30.005(4)$ Å, $V = 8570(3)$ Å$^3$, $Z = 8$, $d_{calcd} = 1.972$ g cm$^{-3}$, $T = 296(1)$ K, $S = 1.071$. The structure was solved by direct methods and refined on $F^2$ to $R1$ ($wR2$) = 0.0253 (0.0614) using 4773 (4981) reflections. The non-hydrogen atoms were anisotropically refined. All calculations were performed using the CrystalStructure crystallographic software package.

(6) Cu$_3$[W$^V$(CN)$_8$]$_2$(pyrimidine)$_2$·3/2PrOH·9/4H$_2$O (**2**) in the powder-form was prepared by exposing **1** to *n*-propanol vapor (11.5 Torr, 82% relative to saturated vapor) for 1 h at room temperature. Anal. Calcd for **2** (%): Cu, 15.1; W, 29.1; C, 27.1; H, 2.0; N, 22.1. Found: Cu, 15.0; W, 29.5; C, 27.3; H, 2.0; N, 22.2. A single crystal of **2** was prepared by slow diffusion method using a mixed solvent of *n*-propanol and water (1:1 v/v). The XRD patterns of powder-form and crystal-form are completely coincident (Figure S5).

(7) Crystal data for **2**: C$_{28.5}$H$_{24.5}$Cu$_3$N$_{20}$O$_{3.75}$W$_2$, fw = 1265.48, orthorhombic, space group *Pmmn*, $a = 14.761(2)$ Å, $b = 25.593(4)$ Å, $c = 11.5284(19)$ Å, $V = 4355.1(12)$ Å$^3$, $Z = 4$, $d_{calcd} = 1.930$ g cm$^{-3}$, $T = 90(1)$ K, $S = 1.084$. The structure was solved by direct methods and refined on $F$ to $R1$ ($wR2$) = 0.0441 (0.1244) using 4350 (5285) reflections. Zeolitic water and *n*-propanol molecules were isotropically refined. All calculations were performed using the CrystalStructure crystallographic software package.

(8) (a) Ohkoshi, S.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Phys. Rev. B* **1997**, *56*, 11642. (b) Ohkoshi, S.; Abe, Y.; Fujishima, A.; Hashimoto, K. *Phys. Rev. Lett.* **1999**, *82*, 1285.

(9) (a) Kahn, O.; Larionova, J.; Yakhmi, J. V. *Chem.—Eur. J.* **1999**, *5*, 3443. (b) Kusaka, T.; Ishida, T.; Nogami, T. *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 259. (c) Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **2002**, *124*, 12096. (d) Usuki, N.; Ohba, M.; Okawa, H. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1693. (e) Maspoch, D.; Molina, D. R.; Wurst, K.; Domingo, N.; Cavallini, M.; Biscarini, F.; Tejada, J.; Rovira, C.; Veciana, J. *Nat. Mater.* **2003**, *2*, 190. (f) Kurmoo, M.; Kumagai, H.; Hughes, S. M.; Kepert, C. J. *Inorg. Chem.* **2003**, *42*, 6709. (g) Tian, Y. Q.; Cai, C. X.; Ren, X. M.; Duan, C. Y.; Xu, Y.; Gao, S.; You, X. Z. *Chem.—Eur. J.* **2003**, *9*, 5673. (h) Wang, Z.; Zhang, B.; Kurmoo, M.; Green, M. A.; Fujiwara, H.; Otsuka, T.; Kobayashi, H. *Inorg. Chem.* **2005**, *44*, 1230.

JA069353+