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Photoinduced Magnetization with a High Curie Temperature and a Large Coercive Field in a Cyano-Bridged Cobalt−Tungstate Bimetallic Assembly

Shin-ichi Ohkoshi,*,†,‡ Satoru Ikeda,† Toshiya Hozumi,† Toshinori Kashiwagi,† and
Kazuhito Hashimoto*,†

Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and PRESTO, JST, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

Received January 22, 2006; E-mail: ohkoshi@light.t.u-tokyo.ac.jp

Optical functionality is an attractive issue in the field of molecule-based magnets.[1−3] Photomagnetism has been observed in the photoinduced magnetization of cobalt−hexacyanoferrate, copper−octacyanomolybdate, etc. It has also been observed in the photodemagnetization of iron−hexacyanochromate and rubidium−manganese−hexacyanoferrate and in the photoinduced magnetic pole inversion of iron−manganese−hexacyanochromate. One possible method for achieving optical control of spontaneous magnetization is to change the electron spin state of a magnetic material. For example, when irradiating changes the oxidation numbers of transition metal ions in a magnetic material, its magnetization varies. From these viewpoints, octacyanometalate-based magnets are useful systems for preparing photomagnetic materials because octacyanometalates can adopt various valence states, such as W^{IV} and W^{V}.[4] In this paper, we report the synthesis, crystal structure, magnetic properties, and photofunctionality of a new type of three-dimensional Co−W bimetallic assembly, $Co^{II}_3[W^V(CN)_8]_2(pyrimidine)_4 \cdot 6H_2O$. This compound exhibits a photoinduced magnetization with a high Curie temperature (T_C) of 40 K and a large coercive field (H_c) of 12 000 G.

The target compound was prepared by adding a 2.5 cm^3 aqueous solution of $Cs^I_3[W^V(CN)_8] \cdot 2H_2O$ (0.258 g) to a 2.5 cm^3 mixed aqueous solution of $Co^{II}Cl_2 \cdot 6H_2O$ (0.112 g) and pyrimidine (0.050 g). The precipitated red powder was filtered and washed with water and then dried in air. A single crystal for X-ray structural analysis was prepared by a diffusion method in an H-shaped tube. Elemental analyses by inductively coupled plasma mass spectroscopy and standard microanalytical methods confirmed that the formula of the compound is $[\{Co^{II}(pyrimidine)(H_2O)\}_2\{Co^{II}(H_2O)_2\}\{W^V(CN)_8\}_2](pyrimidine)_2 \cdot 2H_2O$. Calcd: Co, 12.73; W, 26.46; C, 27.67; H, 2.03; N, 24.20%. Found: Co, 12.55; W, 26.44; C, 27.75; H, 1.92; N, 24.48%.

Single-crystal X-ray structural analysis[5] showed that the unit cell consists of four $[W(CN)_8]^{3-}$ anions, four $[Co1(pyrimidine)(H_2O)]^{2+}$ cations, two $[Co2(H_2O)_2]^{2+}$ cations, four zeolitic waters, and four noncoordinated pyrimidines (Figure 1a). The coordination geometries of the Co (Co1 and Co2) and W sites are pseudo-octahedron (D_{4h}) and bicapped trigonal prism (C_{2v}), respectively (Supporting Information). The four equatorial positions of Co1 are occupied by cyanide nitrogen atoms of $[W(CN)_8]$, while the apical positions are occupied by one nitrogen atom of the pyrimidine and one oxygen atom of the water ligand. Co2 is coordinated to two nitrogen atoms of $[W(CN)_8]$, two oxygen atoms of the water ligands, and two nitrogen atoms of the pyrimidines. The five CN groups of $[W(CN)_8]$ are bridged to four Co1 and one Co2, and the other three CN groups are free. The coordinated pyrimidine molecules bridge Co1 and Co2. The cyano-bridged Co1−W layers along the *ab* plane are linked by Co2. Noncoordinated pyrimidine molecules are located between the Co1−W grid layers.

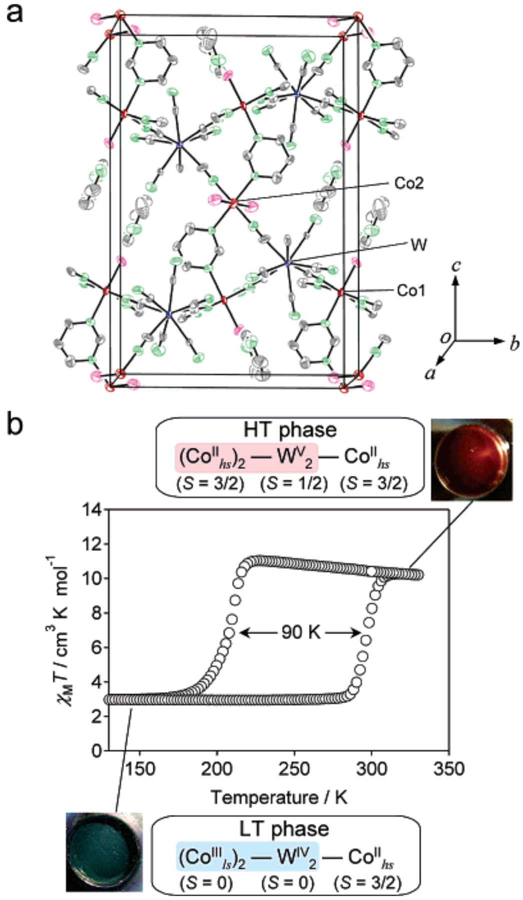

Figure 1. (a) The unit cell of $[\{Co^{II}(pyrimidine)(H_2O)\}_2\{Co^{II}(H_2O)_2\}\{W^V(CN)_8\}_2](pyrimidine)_2 \cdot 2H_2O$ at room temperature. Red, blue, gray, green, and pink ellipsoids represent Co, W, C, N, and O, respectively. Displacement ellipsoids are drawn at a 50% probability level. H atoms and zeolitic waters are omitted for clarity. (b) $\chi_M T-T$ plots at 5000 G.

Figure 1b shows the product of the molar magnetic susceptibility (χ_M) and temperature (T) versus T plots. The $\chi_M T$ value decreases at 208 K ($= T_{1/2\downarrow}$) as the sample is cooled at a cooling rate of -1.0 K min^{-1}. Conversely, as the sample is warmed, the $\chi_M T$ value increases around 298 K ($= T_{1/2\uparrow}$) and returns to the initial value. The thermal hysteresis value ($\Delta T \equiv T_{1/2\uparrow} - T_{1/2\downarrow}$) is a surprisingly large (90 K). The thermal phase transition changes the CN stretching peaks of $[W(CN)_8]$ (ν_{W-CN}) in the IR spectra, that is, $\nu_{W-CN} =$ 2185, 2182, 2171, and 2160 cm^{-1} at 300 K $\rightarrow$ $\nu_{W-CN} =$ 2196, 2166, 2161, 2143, 2128, and 2119 cm^{-1} at 150 K (Supporting Information). The observed ν_{W-CN} peaks at low temperature suggest that the valence state of the W ion is four.

[†] The University of Tokyo.
[‡] PRESTO, JST.

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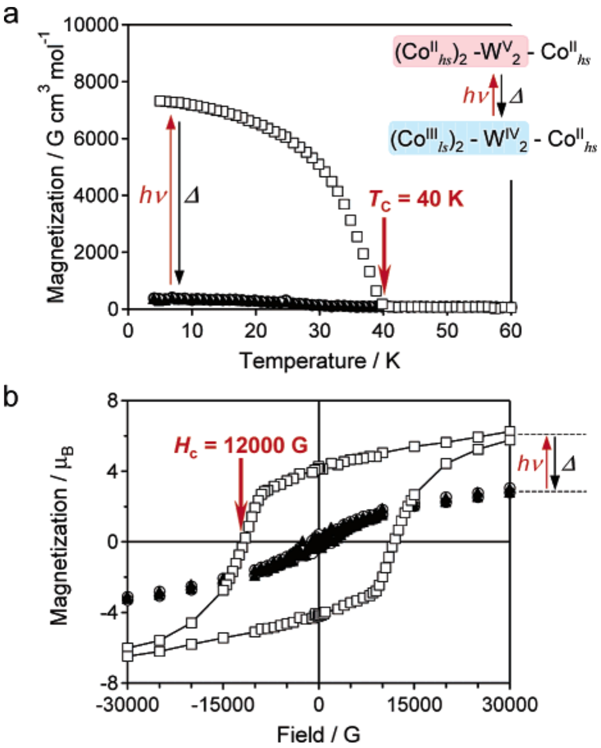

Figure 2. (a) Field-cooled magnetization curves at 10 G and (b) magnetic hysteresis loops at 2 K; before irradiating (▲), after irradiating (□), and after thermally treating up to 150 K (○).

The results of $\chi_M T-T$ plots and temperature dependence of IR spectra indicate that the observed temperature-induced phase transition from the high-temperature (HT) phase to the low-temperature (LT) phase is due to the electronic state change from $Co^{II}_{hs}(S = 3/2)-W^V(S = 1/2)$ to $Co^{III}_{ls}(S = 0)-W^{IV}(S = 0)$, where *hs* and *ls* are high-spin and low-spin states, respectively. Due to the stoichiometric limitation, 1/3 of the cobalt ions should remain as Co^{II}_{hs}, and thus the LT phase is expressed as $(Co^{II}_{hs})(Co^{III}_{ls})_2$-$[W^{IV}(CN)_8]_2(pyrimidine)_4 \cdot 6H_2O$.

The photomagnetic effect on the LT phase was investigated using a SQUID magnetometer. The powder-form sample was spread on a commercial transparent adhesive tape and placed on the edge of an optical fiber. Since the LT phase possesses an intervalence-transfer (IT) band between $Co^{III}-W^{IV}$ and $Co^{II}-W^V$ in the region of 600−1100 nm ($\lambda_{max} = 770$ nm) (Supporting Information), a continuous-wave diode laser of 840 nm was used as the light source (50 mW/cm^2). Figure 2a shows the field-cooled magnetization curves before and after irradiating for 160 min at 5 K in an external magnetic field of 10 G. The irradiated sample exhibits a spontaneous magnetization with a T_C of 40 K. The magnetization versus external magnetic field plots after irradiating for 120 min show a magnetic hysteresis loop with a H_c of 12 000 G at 2 K (Figure 2b). The magnetization value at 5 T is 7.2 μ_B, which suggests that Co^{II} and W^V ferromagnetically interact.[6] The photoinduced magnetization persists for at least 1 day after turning off the light. The photoinduced magnetization relaxes to the initial value upon a thermal treatment up to 150 K, indicating that the magnetization can be increased by irradiating with light and recovered with a thermal treatment.

The IR spectra after irradiating were measured to understand this photomagnetic behavior. Irradiating with a 840 nm laser light decreases the IR peaks due to LT phase and produces the spectra of HT phase (Supporting Information). Hence, in this photomagnetic effect, irradiating of the IT band between $Co^{III}-W^{IV}$ and $Co^{II}-W^V$ induces a valence state change from the $Co^{III}_{ls}(S = 0)-W^{IV}(S = 0)$ state to the $Co^{II}_{ls}(S = 1/2)-W^V(S = 1/2)$ state. Successively, the $Co^{II}_{ls}(S = 1/2)-W^V(S = 1/2)$ state changes to the $Co^{II}_{hs}(S = 3/2)-W^V(S = 1/2)$ state as Co^{II} favors a high-spin state, resulting that a spontaneous magnetization appears.

In summary, a new type of cyano-bridged Co−W bimetallic assembly was synthesized. This compound exhibited a temperature-induced phase transition with a large thermal hysteresis loop of 90 K and a photoinduced magnetization with a high T_C of 40 K and a large H_c of 12 000 G. These high performances are considered to be due to the octacyano-bridged 3-D network structure and the strong magnetic anisotropy of Co^{II}.

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Supporting Information Available: X-ray crystallographic file in CIF format. Information relating to the crystal structure, the temperature dependence of IR spectra, the IR spectra after irradiating, and the UV−vis diffuse reflectance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Verdaguer, M. *Science* **1996**, *272*, 698. (b) Ohkoshi, S.; Hashimoto, K. *J. Photochem. Photobiol. C* **2001**, *2*, 71. (c) Dei, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1160. (d) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (e) Ohkoshi, S.; Yorozu, S.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Appl. Phys. Lett.* **1997**, *70*, 1040. (f) Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **1999**, *121*, 10591. (g) Ohkoshi, S.; Einaga, Y.; Fujishima, A.; Hashimoto, K. *J. Electroanal. Chem.* **1999**, *473*, 245. (h) Pejaković, D. A.; Manson, J. L.; Miller, J. S.; Epstein, A. J. *Phys. Rev. Lett.* **2000**, *85*, 1994. (i) Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Moulin, C. C.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6648. (j) Tokoro, H.; Ohkoshi, S.; Hashimoto, K. *Appl. Phys. Lett.* **2003**, *82*, 1245. (k) Gawali-Salunke, S.; Varret, F.; Maurin, I.; Enachescu, C.; Malarova, M.; Boukheddaden, K.; Codjovi, E.; Tokoro, H.; Ohkoshi, S.; Hashimoto, K. *J. Phys. Chem. B* **2005**, *109*, 8251.

(2) (a) Ohkoshi, S.; Machida, N.; Zhong, Z. J.; Hashimoto, K. *Synth. Met.* **2001**, *122*, 523. (b) Rombaut, G.; Verelst, M.; Golhen, S.; Ouahab, L.; Mathonière, C.; Kahn, O. *Inorg. Chem.* **2001**, *40*, 1151. (c) Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 9240. (d) Hozumi, T.; Hashimoto, K.; Ohkoshi, S. *J. Am. Chem. Soc.* **2005**, *127*, 3864.

(3) Pejaković, D. A.; Kitamura, C.; Miller, J. S.; Epstein, A. J. *Phys. Rev. Lett.* **2002**, *88*, 057202.

(4) (a) Garde, R.; Desplanches, C.; Bleuzen, A.; Veillet, P.; Verdaguer, M. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 587. (b) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (c) Larionova, J.; Gross, M.; Pilkington, M.; Andres, H.; Stoeckli-Evans, H.; Güdel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605. (d) Sieklucka, B.; Szklarzewicz, J.; Kemp, T. J.; Errington, W. *Inorg. Chem.* **2000**, *39*, 5156. (e) Rombaut, G.; Golhen, S.; Ouahab, L.; Mathonière, C.; Kahn, O. *J. Chem. Soc., Dalton Trans.* **2000**, 3609. (f) Li, D. F.; Gao, S.; Zheng, L. M.; Tang, W. X. *J. Chem. Soc., Dalton Trans.* **2002**, 2805. (g) Ohkoshi, S.; Arimoto, Y.; Hozumi, T.; Seino, H.; Mizobe, Y.; Hashimoto, K. *Chem. Commun.* **2003**, 2772. (h) Herrera, J. M.; Bleuzen, A.; Dromzée, Y.; Julve, M.; Lloret, F.; Verdaguer, M. *Inorg. Chem.* **2003**, *42*, 7052. (i) Korzeniak, T.; Stadnicka, K.; Rams, M.; Sieklucka, B. *Inorg. Chem.* **2004**, *43*, 4811. (j) Kashiwagi, T.; Ohkoshi, S.; Seino, H.; Mizobe, Y.; Hashimoto, K. *J. Am. Chem. Soc.* **2004**, *126*, 5024. (k) Withers, J. R.; Ruschmann, C.; Bojang, P.; Parkin, S.; Holmes, S. M. *Inorg. Chem.* **2005**, *44*, 352.

(5) Crystal data for $[\{Co^{II}(pyrimidine)(H_2O)\}_2\{Co^{II}(H_2O)_2\}\{W^V(CN)_8\}_2]$-$(pyrimidine)_2 \cdot 2H_2O$: $C_{32}H_{28}Co_3N_{24}O_6W_2$, fw = 1389.23; monoclinic; space group $P2_1/n$; $a = 7.179(2)$ Å, $b = 14.634(5)$ Å, $c = 22.134(7)$ Å, $\beta = 91.121(14)°$; $V = 2324.9(13)$ Å^3; $Z = 2$; $d_{calcd} = 1.984$ g cm^{-3}; $T = 296$ K.; GOF = 0.987. The structure was solved by direct methods and refined on F^2 to $R1(wR2) = 0.0976(0.2241)$ using 3267 reflections with $I > 2.00\sigma(I)$. The non-hydrogen atoms were anisotropically refined. Hydrogen atoms of pyrimidine were refined isotropically. All calculations were performed using the CrystalStructure crystallographic software.

(6) Assuming that only the ground Kramers doublet of an octahedral Co^{II} is populated, the magnetic moment on Co^{II} is (13/6) μ_B ($g_{Co}J_{Co} = (13/3) \times (1/2)$). In contrast, the magnetic moment on W^V is 1 μ_B ($g_W J_W = 2 \times (1/2)$). Using these two magnetic moments, the saturation magnetization for the ferromagnetic ordering is estimated to be 8.5 μ_B (3 × (13/6) μ_B + 2 × 1 μ_B) for a given formula. Hence, the observed magnetization value suggests that the magnetic spins on Co^{II} and W^V ferromagnetically interact.

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