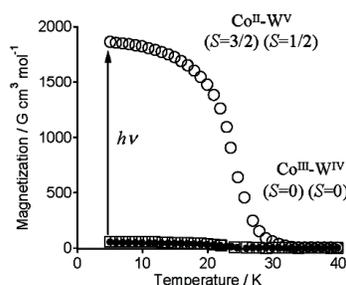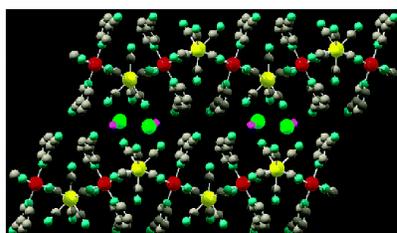## Communication

# Photoinduced Magnetization in a Two-Dimensional Cobalt Octacyanotungstate

Yoichi Arimoto, Shin-ichi Ohkoshi, Zhuang Jin Zhong,
Hidetake Seino, Yasushi Mizobe, and Kazuhito Hashimoto

## More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 18 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

# Photoinduced Magnetization in a Two-Dimensional Cobalt Octacyanotungstate

Yoichi Arimoto,† Shin-ichi Ohkoshi,*,†,‡ Zhuang Jin Zhong,† Hidetake Seino,§ Yasushi Mizobe,§ and Kazuhito Hashimoto*,†

*Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan, and PRESTO, JST, Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan*

Received February 24, 2003; E-mail: ohkoshi@fchem.chem.t.u-tokyo.ac.jp; kazuhito@fchem.chem.t.u-tokyo.ac.jp.

One of the goals in the field of molecule-based magnets is to develop a novel type of functionalized magnet. The optical functionality, such as photomagnetism or magnetooptics, is one of the especially attractive issues.[1−5] Photomagnetism was observed in the photoinduced magnetization in $K_{0.2}Co_{1.4}[Fe(CN)_6] \cdot 6.9H_2O$[2a] and $Cu_2[Mo(CN)_8] \cdot 8H_2O$,[3a] photodemagnetization in $RbMn[Fe(CN)_6]$,[4] and a photoinduced magnetic pole inversion in $(Fe_{0.40}Mn_{0.60})_{1.5}[Cr(CN)_6] \cdot 7.5H_2O$.[5] One way to achieve optical control of magnetization is to change the electron spin state of a magnetic material. The bistability of the electronic states is indispensable for observing photoinduced persistent magnetization since the energy barrier between these bistable states maintains the photo-produced state even after photoirradiation is stopped. From these viewpoints, octacyanometalates $[M(CN)_8]$ (M = Mo, W, and so forth) are useful building blocks for preparing a photomagnetic material, because octacyanometalates can adopt various valence states, e.g., $M^{IV}$ and $M^V$, and coordination geometries, e.g., square antiprism, dodecahedron, and bicapped trigonal prism.[6,7] In this work, a new type of two-dimensional $Cs[\{Co(3\text{-cyanopyridine})_2\}\{W(CN)_8\}] \cdot H_2O$ is prepared, and its magnetic functionalities are investigated. Here, the crystal structure, the temperature-induced phase transition, and photoinduced magnetization of this compound are reported.

The target compound was prepared by adding an aqueous solution of $Cs^I_3[W^V(CN)_8]$ (0.1 mol $L^{-1}$) to a mixed aqueous solution of $Co^{II}Cl_2$ (0.1 mol $L^{-1}$) and 3-cyanopyridine (0.2 mol $L^{-1}$) at room temperature. After 24 h, the precipitated powder was removed and washed with water. A single crystal for X-ray structural analysis was prepared by a slow evaporation method. The elemental analyses by an inductively coupled plasma mass spectroscopy and a standard microanalytical method confirmed that the formula is $Cs^I[\{Co^{II}(3\text{-cyanopyridine})_2\}\{W^V(CN)_8\}] \cdot H_2O$: Calcd Cs, 16.4; Co, 7.27; W, 22.7; C, 30.0; H, 1.24; N, 20.8; Found Cs, 15.9; Co, 7.24; W, 22.6; C, 30.0; H, 1.38; N, 20.7.

X-ray structural analysis showed that this compound consisted of two-dimensional cyano-bridged $Co^{II}-W^V$ layers (Figure 1a).[8] Four CN groups of $[W^V(CN)_8]^{3-}$ are linked to $Co^{II}$ ions and another four are free. In contrast, two nitrogen atoms of 3-cyanopyridine molecules and four nitrogen atoms of CN groups coordinate to the $Co^{II}$ ions. The coordination geometries of $W^V$ and $Co^{II}$ ions are bicapped trigonal prism and pseudo-octahedron, respectively. $Cs^I$ ions and $H_2O$ molecules are intercalated between the layers as shown in Figure 1b. The distance between the two layers is 12.42 Å.
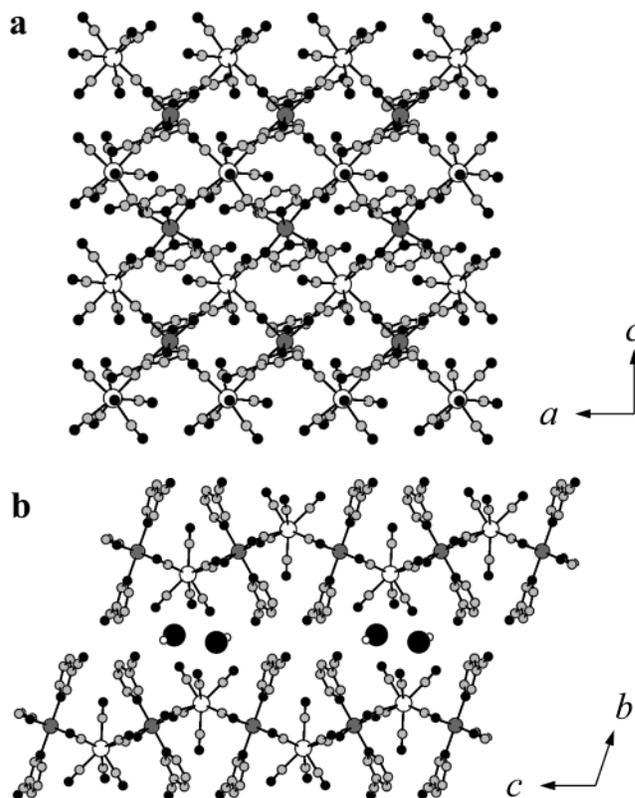
† Research Center for Advanced Science and Technology, The University of Tokyo.
‡ PRESTO, JST.
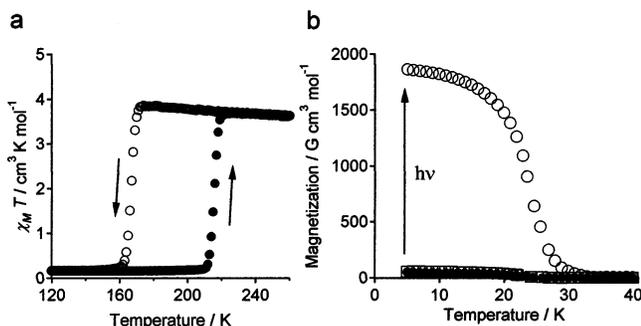§ Institute of Industrial Science, The University of Tokyo.

**Figure 1.** The crystal structure of $Cs^I[\{Co^{II}(3\text{-cyanopyridine})_2\}\{W^V(CN)_8\}] \cdot H_2O$ at room temperature. (a) A view perpendicular to the layer. (b) A side view of the layers. Large black, large gray, large white, small gray, small black, and small white balls represent $Cs^I$, $Co^{II}$, $W^V$, C, N, and O, respectively. H atoms are omitted for clarity.

Magnetic measurements were conducted using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-7). The temperature dependence of the molar magnetic susceptibility ($\chi_M$) at a rate of 1 K $min^{-1}$ determined that the obtained compound exhibited a temperature-induced phase transition with a wide thermal hysteresis loop (Figure 2a). The transition temperatures from high-temperature (HT) phase to low-temperature (LT) phase and from LT phase to HT phase were 167 and 216 K, respectively. The $\chi_M T$ values of HT phase at 300 K and LT phase at 130 K were 3.57 and 0.17 $cm^3$ K $mol^{-1}$, respectively. Temperature dependence of the IR spectra of this compound was measured using a Shimadzu FT-IR 8200PC spectrometer with a Daikin PS22 cryostat. The thermal phase transition drastically changed the CN stretching frequency peaks of 3-cyanopyridine ($\nu_{CN-py}$) and $[W(CN)_8]$ ($\nu_{W-CN}$) i.e., $\nu_{CN-py} =$ 2247, 2242 and $\nu_{W-CN} =$ 2187, 2179, 2166, 2157, and 2141 $cm^{-1}$

**Figure 2.** (a) Temperature dependence of $\chi_M T$ value of Cs[{Co(3-cyanopyridine)$_2$}{W(CN)$_8$}]·H$_2$O in the external magnetic field of 5000 G; measured when cooling (○) and warming(●). (b) Field-cooled magnetization curve for Cs[{Co(3-cyanopyridine)$_2$}{W(CN)$_8$}]·H$_2$O in an external magnetic field of 10 G before irradiating with light (□), after irradiating (○), and after thermally treating (5 K → 120 K → 5 K) (●).

at 300 K (HT phase) → $\nu_{CN-py}$ = 2257, 2252 and $\nu_{W-CN}$ = 2191, 2171, 2161, 2152, 2140, 2124, 2120, and 2102 cm$^{-1}$ at 120 K (LT phase). The observed $\nu_{W-CN}$ peaks of LT phase suggest that the valence state of the W ion is four.[9] In addition, the octet splitting of $\nu_{W-CN}$ peaks of LT phase suggests the coordination symmetry around [W$^{IV}$(CN)$_8$]$^{4-}$ of LT phase is lower than that of HT phase. These IR data indicate that the observed temperature-induced phase transition from HT to LT phases 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$^{IV}$($S = 0$). It is noteworthy that a small amount of HT phase was retained even at 10 K. Analyzing the IR spectra, the valence state of LT phase was assigned to Cs$^I$[{Co$^{II}_{0.05}$Co$^{III}_{0.95}$(3-cyanopyridine)$_2$}-{W$^{IV}_{0.95}$W$^V_{0.05}$(CN)$_8$}]·H$_2$O. In an analogous compound Cs$_{0.8}$-Co$_{1.1}$W(CN)$_8$(3-cyanopyridine)$_{1.9}$·2.1H$_2$O with metal vacancies, a similarly temperature-induced phase transition was observed in the measurement of the X-ray absorption near edge structure.[10]

The photomagnetic effect on the LT phase was investigated using a SQUID magnetometer. The vis−near-IR spectra demonstrated that the LT phase possesses an intervalence-transfer (IT) band between Co$^{III}$−W$^{IV}$ and Co$^{II}$−W$^V$ around 800 nm. To irradiate a powder sample, it was supported on a commercial transparent adhesive tape that was placed on the edge of an optical fiber. The filtered red light (600−750 nm, 12.5 mW cm$^{-2}$) of a Xe lamp was guided via an optical fiber into the sample of the SQUID magnetometer. Figure 2b shows the field-cooled magnetization curves before and after irradiating at 5 K in the external magnetic field of 10 G. Upon irradiating, the magnetization value continuously increased as follows; 280 (10 min), 660 (20 min), 1170 (40 min), 1400 (60 min), 1660 (120 min), and 1840 G cm$^3$ mol$^{-1}$ (240 min). After irradiating for 240 min, the sample exhibited a magnetic phase transition temperature ($T_C$) at 30 K. This photoinduced magnetization persisted for at least 1 day even after turning off the light at 5 K. The magnetization vs external magnetic field plots at 5 K showed that a magnetization ($M_s$) value of 3.3 $\mu_B$ at 7 T and a coercive field of 2500 G. The observed $M_s$ value showed that the magnetic spins on Co$^{II}$ ($S = ^3/_2$) and W$^V$ ($S = ^1/_2$) ions ferromagnetically interacted. Thermal treating (5 K → 120 K → 5 K) relaxed this photoinduced magnetization to the initial value, which indicates that the magnetization can be repeatedly increased by irradiating with light and recovering with a thermal treatment. The efficiencies of photoinduced magnetization varied when different lights were employed. For example, the quantum yield for green light (480−580 nm) was one-fifth of that for red light (600−750 nm), when the absorbed photon energy was equivalent. This indicates that the present photoinduced magnetization phenomenon is not due to photothermal reaction, but is due to a

*photochemical reaction* via a photoexcited state. Furthermore, the IR and X-ray powder diffraction spectra of the irradiated sample at 10 K almost corresponded to those of the HT phase. Therefore, the observed photoinduced magnetization is caused by the photoinduced phase transition from the LT phase (Co$^{III}$(LS; $S = 0$)−W$^{IV}$($S = 0$)) to the HT phase (Co$^{II}$(LS; $S = ^1/_2$)−W$^V$($S = ^1/_2$)). In this photomagnetic effect, irradiating with light induced a charge transfer from Co$^{III}$(LS; $S = 0$)−W$^{IV}$($S = 0$) to Co$^{II}$(LS; $S = ^1/_2$)−W$^V$($S = ^1/_2$) states. Successively, this charge transfer state of Co$^{II}$-(LS; $S = ^1/_2$)−W$^V$($S = ^1/_2$) will change to Co$^{II}$(HS; $S = ^3/_2$)−W$^V$($S = ^1/_2$) state because Co$^{II}$ favors a high-spin state. This photoproduced phase Co$^{II}$(HS; $S = ^3/_2$)−W$^V$($S = ^1/_2$) and the initial Co$^{III}$-(LS; $S = 0$)−W$^{IV}$($S = 0$) phase are considered to be sufficiently separated by the energy barrier, which is caused by the bistability due to the changes of valence state and coordination geometry of [W(CN)$_8$]$^{n-}$.

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 and photoinduced magnetization. Such phenomena are due to the bistability between Co$^{II}$(HS, $S = ^3/_2$)−W$^V$($S = ^1/_2$) and Co$^{III}$(LS, $S = 0$)−W$^{IV}$($S = 0$) phases of this compound.

**Supporting Information Available:** An X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

**References**

(1) (a) Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2273. (b) Roux, C.; Zarembowitch, J.; Gallois, B.; Granier, T.; Claude, R. *Inorg. Chem.* **1994**, *33*, 2273. (c) Adams, D. M.; Li, B.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 11515. (d) Ohkoshi, S.; Hashimoto, K. *J. Photochem. Photobiol., C* **2001**, *2*, 71.

(2) (a) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (b) Bleuzen, A.; Lomenech, C.; Escax, V.; Villain, F.; Varret, F.; Cartier, dit Moulin, C.; Verdaguer, M. *J. Am. Chem. Soc.* **2000**, *122*, 6648. (c) Pejakovic, D. A.; Manson, J. L.; Miller, J. S.; Epstein, A. J. *Phys. Rev. Lett.* **2000**, *85*, 1994.

(3) (a) Ohkoshi, S.; Machida, N.; Zhong, Z. J.; Hashimoto, K. *Synth. Met.* **2001**, *122*, 523. (b) Rombaut, G.; Verelst, M.; Golhen, S.; Ouahab, L.; Mathoniere, C.; Kahn, O. *Inorg. Chem.* **2001**, *40*, 1151.

(4) Tokoro, H.; Ohkoshi, S.; Hashimoto, K. *Appl. Phys. Lett.* **2003**, *82*, 1245.

(5) Ohkoshi, S.; Yorozu, S.; Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Appl. Phys. Lett.* **1997**, *70*, 1040.

(6) Leipoldt, J. G.; Basson, S. S.; Roodt, A. *Adv. Inorg. Chem.* **1993**, *40*, 241.

(7) (a) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hidai, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (b) Larionova, J.; Gross, M.; Pilkington, M.; Andres, H.; Stoeckli-Evans, H.; Güdel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605. (c) Podganjy, R.; Korzeniak, T.; Balanda, M.; Wasiutynski, W.; Errington, W.; Kemp, T. J.; Alcock, N. W.; Siekucka, B. *Chem. Commun.* **2002**, 1138. (d) Arimoto, Y.; Ohkoshi, S.; Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hashimoto. K. *Chem. Lett.* **2002**, 832.

(8) Crystal data for Cs[{Co(3-cyanopyridine)$_2$}{W(CN)$_8$}]·H$_2$O: C$_{20}$H$_{10}$N$_{12}$-OCoCsW, fw = 810.07; triclinic; space group *P*-1; *a* = 7.2979(7) Å, *b* = 13.937(3) Å, *c* = 14.381(3) Å, α = 116.30(1)°, β = 90.02(1)°, γ = 96.97(1)°; *V* = 1299.2(4) Å$^3$; *Z* = 2; $d_{calcd}$ = 2.071 g cm$^{-3}$; *T* = 298 K. The structure was solved by the heavy-atom Patterson methods and refined on *F* to R1(wR2) = 0.033(0.088) using 5070 reflections with *I* > 3.00σ-(*I*). The non-hydrogen atoms were anisotropically refined. Hydrogen atoms of 3-cyanopyridine were refined isotropically. All calculations were performed using the CrystalStructure crystallographic software package.

(9) Rombaut, G.; Mathonière, C.; Guionneau, P.; Golhen, S.; Ouahab, L.; Verelst, M.; Lecante, P. *Inorg. Chim. Acta* **2001**, *326*, 27.

(10) Yokoyama, T.; Okamoto, K.; Ohta, T.; Ohkoshi, S.; Hashimoto, K. *Phys. Rev. B* **2002**, *65*, 64438.

JA030130I