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Synthesis of a Chiral-structured Molecular Magnet Based on a Cyano-bridged Co–W Bimetal Assembly

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A three-dimensional chiral-structured molecular magnet based on a Co–W bimetal assembly, $[Co^{II}(H_2O)_2][Co^{II}(pyrimidine)\{(R)\text{-1-(4-pyridyl)ethanol}\}]_2[W^{V}(CN)_8]_2\cdot7.5H_2O$, is synthesized. This compound exhibits a spontaneous magnetization due to ferromagnetic ordering between Co^{II} ($S = 3/2$) and W^{V} ($S = 1/2$) with a Curie temperature of 19 K and coercive field of 3600 Oe.

One target in the field of molecular-based magnets is to obtain multifunctional magnetic materials that combine different physical properties[1,2] such as a ferroelectric-ferromagnet.[2] Because electric and magnetic polarizations coexist, one candidate to study multiferroics is a molecular magnet having structural chirality (called a chiral-structured molecular magnet)[3] which should exhibit various magnetoelectric effects, e.g., magneto chiral dichroism (MChD)[4a,4b] and magnetic second harmonic generation (MSHG).[4c,4d] Several methodologies have been used to synthesize chiral molecular magnets: incorporating a chiral coordinated (Δ or Λ) metal complex,[3h,3i] e.g., $[NBu_4][Mn(\Delta)Cr(\Lambda)(oxalate)_3]$, penetrating a chiral molecule as a coordinating ligand,[3b–3g] e.g., $K_{0.4}[Cr(CN)_6][Mn\{(S)\text{-1,2-diaminopropane}\}][(S)\text{-1,2-diaminopropaneH}]_{0.6}$[3c] and $[Cu\{(S)\text{-1,2-diaminopropane}\}H_2O]_4[Cu\{(S)\text{-1,2-diaminopropane}\}]_2[W(CN)_8]_4\cdot2.5H_2O$[3d] and introducing a chiral molecule as a guest molecule in the interstitial site of the magnetic framework, e.g., $Mn_3(HCOO)_6[(S)\text{-2-chloropropan-1-ol}]$.[3j] In this work, we employed a synthetic methodology which involves a chiral aromatic molecule as a coordinating ligand. Herein, we report the synthesis of $[Co^{II}(H_2O)_2][Co^{II}(pyrimidine)\{(R)\text{-1-(4-pyridyl)ethanol}\}]_2[W^{V}(CN)_8]_2\cdot7.5H_2O$, which exhibits ferromagnetic ordering with a Curie temperature of 19 K.

The target compound was prepared by slowly adding an aqueous solution of $Cs_3[W(CN)_8]\cdot2H_2O$ into an aqueous solution containing $CoCl_2\cdot6H_2O$, pyrimidine, and (*R*)-1-(4-pyridyl)ethanol at room temperature. After stirring overnight, the reddish pink powder was separated from the resulting dark magenta suspension by filtration. Elemental analyses by inductively coupled plasma mass spectrometry and standard microanalytical methods indicated that the formula of the compound was $[Co(H_2O)_2][Co(pyrimidine)\{(R)\text{-1-(4-pyridyl)ethanol}\}]_2[W(CN)_8]_2\cdot7.5H_2O$.[5,7]

The single-crystal X-ray analysis showed that the present compound crystallized in the C_2 space group ($a = 30.410(6)$ Å, $b = 17.909(3)$ Å, $c = 10.567(2)$ Å, $\beta = 107.10(3)°$, $Z = 4$).[6] Figure 1 shows the coordination environments around W and Co ions. The asymmetric unit consisted of $[W(CN)_8]^{3-}$, $[Co(H_2O)_2]^{2+}$, and $[Co(pyrimidine)\{(R)\text{-1-(4-pyridyl)ethanol}\}]^{2+}$. The coordination geometries around W and Co sites were bicapped trigonal prism and pseudo-octahedron, respectively. Five CN groups in $[W(CN)_8]^{3-}$ were bridged to cobalt ions (Co1, Co2, and Co3), and the other three were not bridged. Co1 (and Co2) was coordinated to one nitrogen atom of (*R*)-1-(4-pyridyl)ethanol, one nitrogen atom of pyrimidine, and four nitrogen atoms of $[W(CN)_8]$. The four equatorial positions of Co3 were occupied by two cyanide nitrogen atoms and two nitrogen atoms from pyrimidine molecules, while the two apical positions were occupied by two oxygen atoms from water molecules. The cyano-bridged Co1–W–Co2 layers along the *bc* plane were linked by Co3. The electric polarization (a twofold screw axis) was along the *b* axis (Figure 1c).

The present compound possessed optical absorption bands around 360 and 500 nm, which were assigned to the ligand-to-metal charge transfer (LMCT) of $CN–W^{V}$ ($^2B_1 \rightarrow {}^2A_2$, ^2E) band and the d–d transition of Co^{II} bands ($^4T_{1g} \rightarrow {}^4A_{2g}$, $^4T_{1g} \rightarrow {}^4T_{1g}$), respectively. Additionally, the temperature dependence of the magnetic susceptibility (χ_M) was measured in an applied field of 5000 Oe and a temperature range of 2–340 K. Although the $\chi_M T$ value at 340 K was 9.8 K cm^3 mol^{-1}, the extrapolated high-temperature value was 8.9 K cm^3 mol^{-1}. This $\chi_M T$ value agrees with the expected spin-only value (8.9 K cm^3 mol^{-1}) for three Co^{II} ($S_{Co} = 3/2$) and two W^{V} ($S_W = 1/2$) assuming *g* values of 2.4 and 2.0 for Co^{II} and W^{V}, respectively. The $\chi_M{}^{-1}$ vs. temperature plots showed a Weiss temperature (θ) of + 28 K, supporting ferromagnetic ordering.

In the field-cooled magnetization (FCM) curve at 10 Oe, spontaneous magnetization appeared at $T_C = 19$ K (Figure 2). The zero-field-cooled magnetization (ZFCM) and remnant magnetization (RM) curves supported this T_C value. The magnetization vs. external magnetic field plots at 2 K indicated that the saturation magnetization (M_S) value was 8.4 μ_B (Figure 2, inset). The magnetic moment on Co^{II} is $(13/6)\,\mu_B$ ($g_{Co}J_{Co} = (13/3) \times (1/2)$) assuming only the ground Kramers doublet of octahedral Co^{II} is populated, while the magnetic moment on W^{V} was 1 μ_B ($g_W J_W = 2 \times (1/2)$). Using these two magnetic moments, the estimated M_S value for ferromagnetic ordering is 8.5 μ_B for the given formula. The agreement between the observed and estimated M_s values indicates that the magnetic spins on Co^{II} and W^{V} ferromagnetically interact. The magnetic hysteresis loop exhibited a relatively large coercive field (H_C) value of 3600 Oe at 2 K, which may be due to the magnetic anisotropy of Co^{II}.

In summary, we have prepared a three-dimensional chiral-structured molecular magnet, $[Co(H_2O)_2][Co(pyrimidine)\{(R)\text{-1-(4-pyridyl)ethanol}\}]_2[W(CN)_8]_2\cdot7.5H_2O$, which displays $T_C = 19$ K and $H_C = 3600$ Oe. The synthetic methodology herein where a chiral aromatic molecule ligand coordinates to metal ions in a cyano-bridged metal assembly will be useful in the study of chiral magnets. We are currently studying the interaction between magnetic polarization and electric polarization due to structural chirality, for example, MSHG.

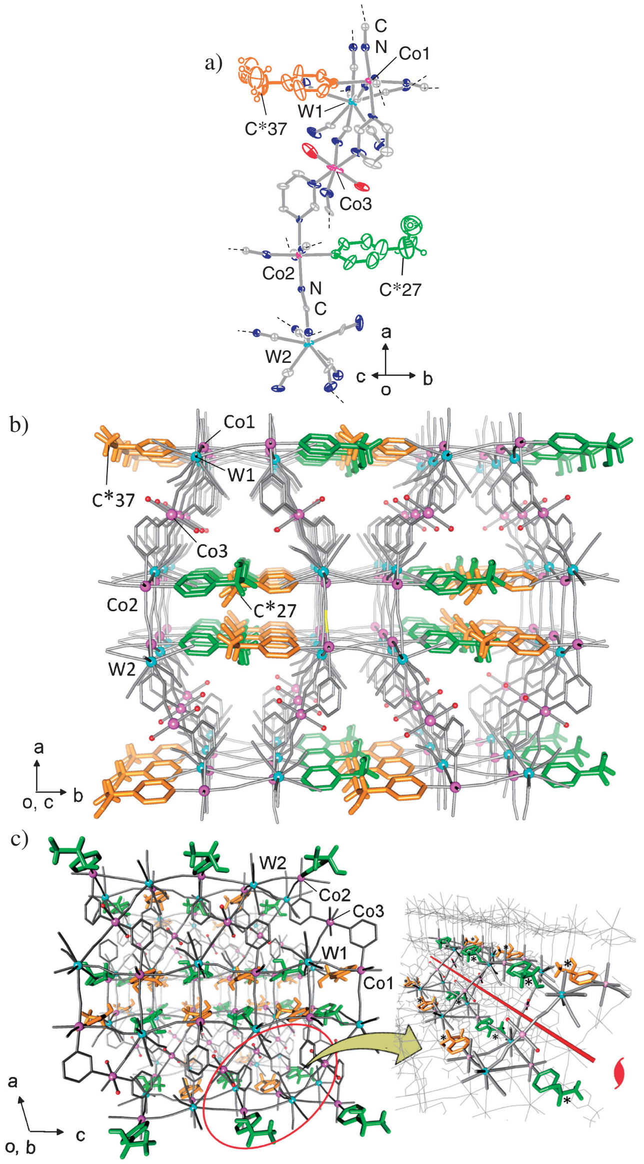

Figure 1. (a) The coordination environments around W and Co. Displacement ellipsoids are drawn at a 50% probability level. Light blue, pink, gray, navy, and red spheres represent W, Co, C, N, and O atoms, respectively. The green and orange colored molecules show (*R*)-1-(4-pyridyl)ethanol with C*27 and C*37 as a chiral center, respectively. Hydrogen atoms (except for the hydrogen atoms around the chiral atoms), noncoordinated water molecules, and disordered atoms are omitted for clarity. (b) Crystal structure along the *c* axis. Gray sticks represent the framework containing C and N atoms. (c) Crystal structure along the *b* axis and the enlarged view where chiral molecules are aligned along the twohold screw axis represented by a red line.

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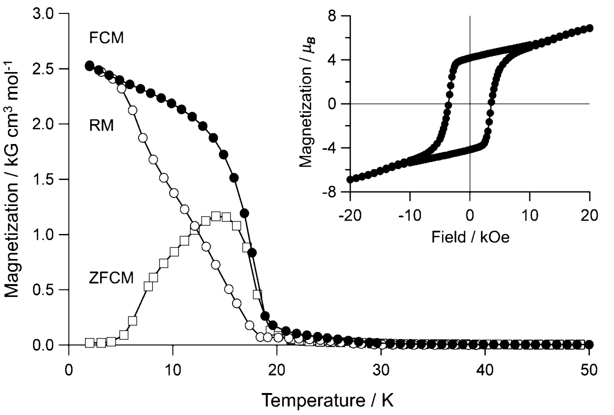

Figure 2. Field-cooled magnetization (FCM), zero-field-cooled magnetization (ZFCM) curves in an external applied field of 10 Oe, and remnant magnetization (RM) curve. Inset shows magnetic hysteresis loop at 2 K.

References and Notes

1 a) N. Usuki, M. Ohba, H. Ōkawa, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 1693. b) M. Nihei, L. Han, H. Oshio, *J. Am. Chem. Soc.* **2007**, *129*, 5312. c) N. Yanai, W. Kaneko, K. Yoneda, M. Ohba, S. Kitagawa, *J. Am. Chem. Soc.* **2007**, *129*, 3496. d) S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. e) T. Kusaka, T. Ishida, T. Nogami, *Mol. Cryst. Liq. Cryst.* **2003**, *379*, 259. f) S. Ohkoshi, K. Arai, Y. Sato, K. Hashimoto, *Nat. Mater.* **2004**, *3*, 857. g) S. Ohkoshi, K. Hashimoto, *J. Photochem. Photobiol., C* **2001**, *2*, 71.

2 a) H. Cui, Z. Wang, K. Takahashi, Y. Okano, H. Kobayashi, A. Kobayashi, *J. Am. Chem. Soc.* **2006**, *128*, 15074. b) S. Ohkoshi, H. Tokoro, T. Matsuda, H. Takahashi, H. Irie, K. Hashimoto, *Angew. Chem., Int. Ed.* **2007**, *46*, 3238. c) C.-M. Liu, R.-G. Xiong, D.-Q. Zhang, D.-B. Zhu, *J. Am. Chem. Soc.* **2010**, *132*, 4044.

3 a) K. Inoue, S. Ohkoshi, H. Imai, in *Magnetism: Molecules to Materials*, ed. by J. S. Miller, M. Drillon, WILEY-VCH, Weinheim, **2005**, Vol. 5, p. 41. b) W. Kaneko, S. Kitagawa, M. Ohba, *J. Am. Chem. Soc.* **2007**, *129*, 248. c) K. Inoue, H. Imai, P. S. Ghalsasi, K. Kikuchi, M. Ohba, H. Ōkawa, J. V. Yakhmi, *Angew. Chem., Int. Ed.* **2001**, *40*, 4242. d) H. Higashikawa, K. Okuda, J. Kishine, N. Masuhara, K. Inoue, *Chem. Lett.* **2007**, *36*, 1022. e) Y. Numata, K. Inoue, N. Baranov, M. Kurmoo, K. Kikuchi, *J. Am. Chem. Soc.* **2007**, *129*, 9902. f) H. Imai, K. Inoue, K. Kikuchi, Y. Yoshida, M. Ito, T. Sunahara, S. Onaka, *Angew. Chem., Int. Ed.* **2004**, *43*, 5618. g) J. Milon, M.-C. Daniel, A. Kaiba, P. Guionneau, S. Brandès, J.-P. Sutter, *J. Am. Chem. Soc.* **2007**, *129*, 13872. h) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, J. M. Martínez-Agudo, *Inorg. Chem.* **2001**, *40*, 113. i) R. Andrés, M. Gruselle, B. Malézieux, M. Verdaguer, J. Vaissermann, *Inorg. Chem.* **1999**, *38*, 4637. j) B. Zhang, Z. Wang, M. Kurmoo, S. Gao, K. Inoue, H. Kobayashi, *Adv. Funct. Mater.* **2007**, *17*, 577.

4 a) G. L. J. A. Rikken, E. Raupach, *Nature* **1997**, *390*, 493. b) C. Train, R. Gheorghe, V. Krstic, L.-M. Chamoreau, N. S. Ovanesyan, G. L. J. A. Rikken, M. Gruselle, M. Verdaguer, *Nat. Mater.* **2008**, *7*, 729. c) T. Nuida, T. Matsuda, H. Tokoro, S. Sakurai, K. Hashimoto, S. Ohkoshi, *J. Am. Chem. Soc.* **2005**, *127*, 11604. d) C. Train, T. Nuida, R. Gheorghe, M. Gruselle, S. Ohkoshi, *J. Am. Chem. Soc.* **2009**, *131*, 16838.

5 The detailed synthesis method is described in Supporting Information.[7] Elemental analysis; Calcd: Co, 11.48; W, 23.87; C, 29.67; H, 2.95; N, 20.04%. Found: Co, 11.48; W, 23.71; C, 29.75; H, 2.86; N, 19.87%. In the IR spectra in nujol, CN stretching peaks due to bridging CN (2205, 2191, 2170, and 2154 cm^{-1}) and terminal CN (2120 cm^{-1}) were observed.

6 The very small crystal size ($0.06 \times 0.02 \times 0.01\,\text{mm}^3$) and poor crystalinity resulted in synchrotron radiation being used. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-805038. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

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