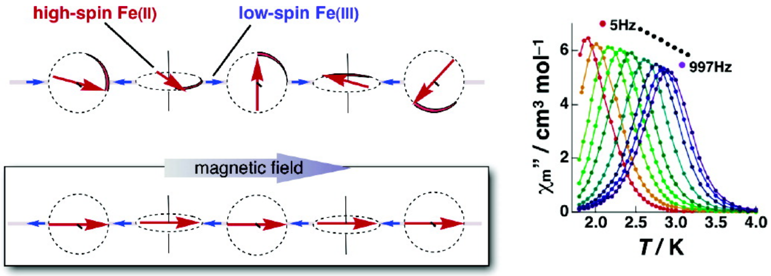
Communication

A Single-Chain Magnet Formed by a Twisted Arrangement of Ions with Easy-Plane Magnetic Anisotropy

Takashi Kajiwara, Motohiro Nakano, Yukihiro Kaneko, Shinya Takaishi, Tasuku Ito, Masahiro Yamashita, Asako Igashira-Kamiyama, Hiroyuki Nojiri, Yuuki Ono, and Norimichi Kojima

J. Am. Chem. Soc., **2005**, 127 (29), 10150-10151• DOI: 10.1021/ja052653r • Publication Date (Web): 02 July 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

A Single-Chain Magnet Formed by a Twisted Arrangement of Ions with Easy-Plane Magnetic Anisotropy

Takashi Kajiwara,*,† Motohiro Nakano,*,‡ Yukihiro Kaneko,† Shinya Takaishi,† Tasuku Ito,†
Masahiro Yamashita,† Asako Igashira-Kamiyama,§ Hiroyuki Nojiri,‖ Yuuki Ono,⊥ and
Norimichi Kojima⊥

Department of Chemistry, Graduate School of Science, Tohoku University and CREST, Japan Science and Technology Agency (JST), Aramaki, Aoba-ku, Sendai 980-8578, Japan, Department of Molecular Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan, Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan, Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan, and Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 113-8654, Japan

Received April 24, 2005; E-mail: kajiwara@agnus.chem.tohoku.ac.jp; moto@ch.wani.osaka-u.ac.jp

The attention of nanoscientists is currently directed toward the behaviors of nanomagnets, such as single-molecule magnets (SMMs)[1] and single-chain magnets (SCMs),[2] since they show unique physical properties, such as quantum tunneling of magnetization[1a,b] and quantum phase interference,[1c] that are not observed in bulk magnets. Those molecular quantum nanomagnets have a well-defined structure and exhibit well-characterized easy-axis magnetic anisotropy ($D < 0$), forming a "double-well potential" which prevents reversal of the molecular magnetization. SCMs are strategically constructed nanomagnets based on an alignment of the spin-carrier components possessing easy-axis anisotropy, such as nitronyl nitroxide radical/Co^{II},[2a] Ni^{II}/Mn^{III},[2b] Fe^{III}/Co^{II},[2c] or uniform Co^{II} chains,[2d] to realize one-dimensional Ising-type chains. Although only a few are known currently, SCMs are attracting considerable attention not only because of their synthetic interest but also because of their physical properties, including exhibition of Glauber's dynamics.[3] We have developed a synthetic method for the preparation of homo- and heterometal chain systems using $\{M(bpca)_2\}$[4a−c] and $\{M'(bpca)_2\}^{+}$[4d,e] ($M = Mn^{II}, Fe^{II}, Ni^{II}$; $M' = Cr^{III}, Fe^{III}, Co^{III}$; Hbpca = bis(2-pyridylcarbonyl)amine), and for the first time, we have synthesized a novel SCM using spin-carrier components possessing hard-axis anisotropy (or easy-plane anisotropy, $D > 0$). The compound, an alternating high-spin Fe^{II} and low-spin Fe^{III} chain complex, *catena*-[Fe^{II}(ClO$_4$)$_2$\{Fe^{III}(bpca)$_2$\}]ClO$_4$ (**1**), behaves as an SCM, although the constituent ions do not attain any bistability arising from the double-well potential, which seems to be required for an Ising system. Here, we report an unusual SCM which is derived from a twisted arrangement of easy-planes of Fe^{II} along the chain axis, which, as a result, generates a novel type of one-dimensional Ising system.

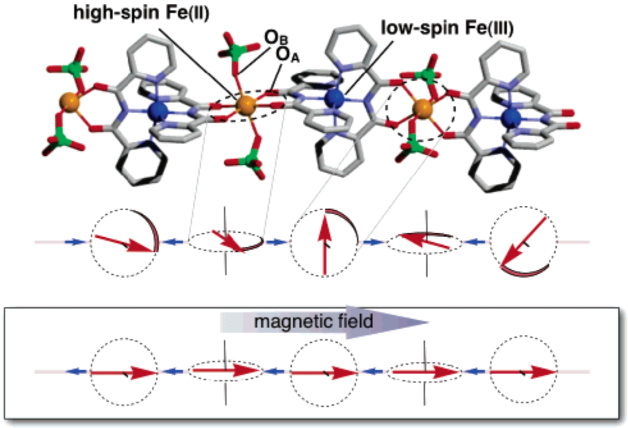


Figure 1. Crystal structure and spin arrangement of high-spin Fe^{II} and low-spin Fe^{III} alternating chain complex **1**. Each atom is depicted as follows: Fe^{III} blue, Fe^{II} orange, Cl green, O red, N pale blue, and C gray.

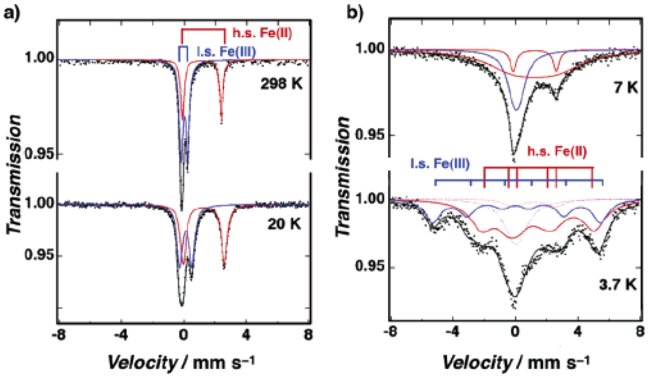


Figure 2. Temperature dependence of the ^{57}Fe Mössbauer spectra of **1**. (a) At ambient temperature, the isomer shift (δ) and the quadrupole splitting (ΔE_Q) are estimated to be 1.15 and 2.49 mm s^{-1} for the Fe^{II} site and 0.03 and 0.41 mm s^{-1} for the Fe^{III} site, respectively. (b) From the data at 3.7 K, the hyperfine parameters are estimated as $H_n = 192$ kOe and $V_{zz} = 12.6 \times 10^{21}$ V m^{-1} for Fe^{II} and $H_n = 335$ kOe and $V_{zz} = 1.7 \times 10^{21}$ V m^{-1} for Fe^{III}.

Complex **1** (Figure 1) was synthesized in a manner similar to the published procedure.[4d,5] The Mössbauer spectrum of **1** at ambient temperature (Figure 2) confirmed the presence of low-spin Fe^{III} and high-spin Fe^{II} ions in a 1:1 molar ratio with typical δ and ΔE_Q values for these oxidation and spin states. The low-spin Fe^{III} ions (blue spheres in Figure 1) are coordinated by six N donor atoms in a slightly compressed octahedron along the chain axis. The high-spin Fe^{II} ions (orange spheres) have an axially elongated geometry with four equatorial carbonyl oxygen atoms (O$_A$, Fe−O$_A$ = 2.0275(14)−2.0659(13) Å) and two axial ClO$_4^-$ oxygen atoms (O$_B$, 2.1208(14) and 2.1516(14) Å). The π-donor character of O$_A$ splits the t$_{2g}$ orbitals into e$_g$ and b$_{2g}$ orbitals, and therefore, the orbital angular momentum is fully quenched. The ground state of the Fe^{II} ions is $^5B_{2g}$ rather than $^5T_{2g}$. Taking into account spin−orbit coupling, the quintet is split into one singly and two doubly degenerate energy levels which are consistent with a uniaxial zero-field splitting parameter of $D > 0$. Thus the $S = 2$ spin on the Fe^{II} ions would have a hard-axis-type anisotropy along the O$_B$−Fe−O$_B$ axis, that is, easy-plane-type anisotropy in the

---

† Graduate School of Science, Tohoku University.
‡ Graduate School of Engineering, Osaka University.
§ Graduate School of Science, Osaka University.
‖ Institute for Materials Research, Tohoku University.
⊥ The University of Tokyo.

10.1021/ja052653r CCC: $30.25

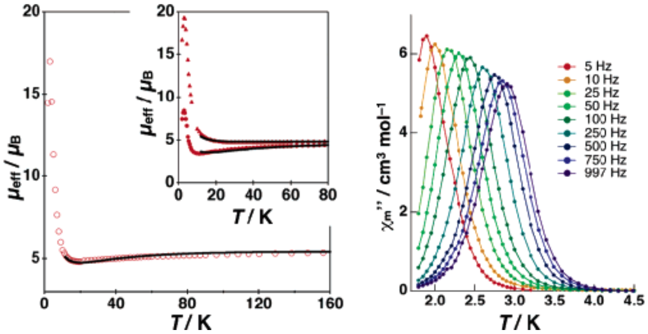


Figure 3. (Left) Temperature dependence of μ_{eff} (○) for the powder sample. (Inset) Magnetic measurements on an oriented single crystal of **1** in the dc field applied along the chain (▲) and perpendicular to the chain (●). The solid lines are theoretical curves. (Right) Out-of-phase (χ_m'') ac magnetic susceptibility versus temperature in a 3.0 Oe ac field oscillating at the indicated frequencies and with a zero dc field. The solid lines are a guide for the eyes.

equatorial plane involving four O_A atoms. The easy-plane spins are coupled to the nearly isotropic Fe^{III} $S = 1/2$ spins in a ferrimagnetic arrangement, forming a unique *XY* spin chain with twisting of the axis of anisotropy. The chain lies along a crystallographic $a-c$ vector, and the crystals grow along this axis. The chains are well separated without any contacts.

The field dependence of the magnetization was investigated for the single crystal (Figure S2). When the dc field was applied parallel to the chain, the magnetization rapidly saturated above 0.5 kOe. However, when the dc field was perpendicular to the chain, the magnetization did not saturate until 50 kOe. The temperature dependence of the effective magnetic moment, μ_{eff}, for microcrystalline **1** (Figure 3, left) is clearly consistent with the presence of a ferrimagnetic ground state, showing a minimum at 20 K (4.8 μ_B) and a maximum at 3 K (17.0 μ_B). No evidence for long-range ordering was observed. Anisotropy of the susceptibility was observed for the single-crystal sample (Figure 3, inset), which was analyzed on the basis of the following spin Hamiltonian:

$$H = -2J\sum_i [S_{4i}\cdot S_{4i+1} + S_{4i+1}\cdot S_{4i+2} + S_{4i+2}\cdot S_{4i+3} + S_{4i+3}\cdot S_{4i+4}] + D\sum_i [(S^x_{4i})^2 + (S^y_{4i+2})^2] + H_{Zeeman} \quad (1)$$

where S_j is either an $S = 2$ spin for Fe^{II} for even values of *j* or an $S = 1/2$ spin for Fe^{III} for odd values of *j*, *J* is the superexchange interaction between neighboring Fe^{II} and Fe^{III} ions in the chain, and *D* is the uniaxial zero-field splitting parameter for Fe^{II} spins. From a mean-field approximation of the Hamiltonian, the parameters J/k_B and D/k_B were estimated to be -10.0 and 14.9 K, respectively. Although the anisotropic saturation of the magnetization suggests an easy-axis-type anisotropy for the entire crystal, the estimated single-site anisotropy, *D*, is of easy-plane-type, which is consistent with the expectation for an Fe^{II} ion based on ligand field considerations. Moreover, this positive *D* is directly confirmed by HF-EPR spectroscopy.[6] Thus, it is likely that the large easy-plane anisotropies of the Fe^{II} ions are added together noting the mutual orthogonality of the quantization axes to afford a net easy-axis anisotropy along the chain.

Ac magnetic susceptibility measurements were performed with a powder sample to observe the frequency dependence. With cooling, the in-phase signal, χ_m', increased in accordance with the Curie law to a maximum value and then decreased, eventually approaching zero (Figure S3), with the corresponding appearance of the out-of-phase signal, χ_m'' (Figure 3, right). As the frequency was swept from 1000 to 5 Hz, the temperature of maximum χ_m'' shifted from 2.9 to 1.9 K. This frequency dependence clearly indicates that the χ_m' drop arises from a kinetic restraint, not due to long-range ordering. At fixed temperatures between 2.0 and 3.4 K, semicircle Cole–Cole plots were obtained with small α parameters in the range of 0.09–0.13, which indicates that relaxation occurs via a single process (Figure S4).[1d] This is a typical SCM behavior and should be attributed to a mutually orthogonal arrangement of the Fe^{II} molecular axes inducing Ising interactions along the chain.[7] The slow reversal of molecular spins characteristic of Ising chains was also confirmed by the temperature-dependent Mössbauer spectra (Figure 2).[8] Broadening due to a paramagnetic relaxation occurred below 7 K, and two sets of sextet signals appeared at 3.7 K, where the spin reversal slows down below the Mössbauer time scale of 10^{-7} s and the Fe nuclei feel quasi-static hyperfine fields, H_n, of 192 kOe for Fe^{II} and 335 kOe for Fe^{III}. The relaxation times $\tau(T)$ extracted from the ac susceptibility and Mössbauer data were used to construct an Arrhenius plot (Figure S5), giving an estimated activation energy Δ of 27(1) K. This Δ value is smaller than the $8J$ expected for pure Glauber's dynamics,[3a] suggesting that the transverse magnetization of the Fe^{II} spins in an easy-plane is responsible for the magnetic relaxation. Extrapolating the Arrhenius plot, the blocking temperature ($\tau(T_B) = 100$ s) was estimated as $T_B = 1.3$ K.

In conclusion, an alternating Fe^{II} (high-spin)/Fe^{III} (low-spin) mixed valence single-chain magnet was prepared using the complexed ligand $\{Fe(bpca)_2\}^+$. This twisting easy plane system is unique in that it exhibits easy-axis anisotropy over the whole chain, giving rise to slow magnetization reversal despite single ion anisotropy of the constituent Fe^{II} ions with easy-plane.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental procedure and detail of X-ray crystallographic analyses (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Barbara, B. *Nature* **1996**, *383*, 145. (b) Gatteschi, D.; Sessoli, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 268. (c) Wernsdorfer, W.; Sessoli, R. *Science* **1999**, *284*, 133. (d) Aubin, S. M. J.; Sun, Z.; Pardi, L.; Krzystek, J.; Folting, K.; Brunel, L.-C.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1999**, *38*, 5329.

(2) (a) Caneschi, A.; Gatteschi, D.; Lalioti, N.; Sangregorio C.; Sessoli, R.; Venture, G.; Vindigni, A.; Rettori, A.; Pini, M. G.; Novak, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1760. (b) Clérac, R.; Miyasaka, H.; Yamashita, M.; Coulon, C. *J. Am. Chem. Soc.* **2002**, *124*, 12837. (c) Lescouëzec, R.; Vaissermann, J.; Ruiz-Pérez, C.; Lloret, F.; Carrasco, R.; Julve, M.; Verdaguer, M.; Dromzee, Y.; Gatteschi, D.; Wernsdorfer, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1483. (d) Liu, T.-F.; Fu, D.; Gao, S.; Zhang, Y.-Z.; Sun, H.-L.; Su, G.; Liu, Y.-J. *J. Am. Chem. Soc.* **2003**, *125*, 13976.

(3) (a) Glauber, R. J. *J. Math. Phys.* **1963**, *4*, 294. (b) Coulon, C.; Clérac, R.; Lecren, L.; Wernsdorfer, W.; Miyasaka, H. *Phys. Rev.* **2004**, *B69*, 132408.

(4) (a) Kamiyama, A.; Noguchi, T.; Kajiwara, T.; Ito, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3130. (b) Kamiyama, A.; Noguchi, T.; Kajiwara, T.; Ito, T. *Inorg. Chem.* **2002**, *41*, 507. (c) Kamiyama, A.; Noguchi, T.; Kajiwara, T.; Ito, T. *Cryst. Eng. Commun.* **2003**, *5*, 231. (d) Kajiwara, T.; Sensui, R.; Noguchi, T.; Kamiyama, A.; Ito, T. *Inorg. Chim. Acta* **2002**, *337*, 299. (e) Kajiwara, T.; Ito, T. *Mol. Cryst. Liq. Cryst.* **1999**, *335*, 73.

(5) Crystallographic data for **1**: Monoclinic, space group $P2_1/n$, $a = 13.719(3)$ Å, $b = 18.428(4)$ Å, $c = 15.355(4)$ Å, $\beta = 90.189(5)°$, $U = 3882.1(15)$ Å^3, $T = 240$ K, $Z = 4$, $D_{calcd} = 1.786$ g/cm^3, 26 631 reflections were observed, of which 8875 were independent, $R1 = 0.0690$ ($I > 2\sigma(I)$) and $wR2 = 0.1849$ (all data) for 559 parameters.

(6) Nojiri, H. Unpublished data.

(7) Nakano, M.; Matsubayashi, G.; Muramatsu, T.; Kobayashi, T. C.; Amaya, K.; Yoo, J.; Christou, G.; Hendrickson, D. N. *Mol. Cryst. Liq. Cryst.* **2002**, *376*, 405.

(8) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Chittipeddi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769.

JA052653R