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Mn^{III} Salen-type Single-molecule Magnet Fixed in a Two-dimensional Network

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A two-dimensional network compound, $[\{Mn(saltmen)\}_4\{Co(CN)_6\}](ClO_4)\cdot 9H_2O$ (**2**) ($saltmen^{2-} = N,N'$-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)), was synthesized. Magnetic measurements characterized the $[Mn_2(saltmen)_2]^{2+}$ subunit as a single-molecule magnet with an $S_T = 4$ spin ground state, indicating that the Mn^{III} dimer is magnetically isolated not only by the diamagnetic $[Co(CN)_6]^{3-}$ unit but also by the space between the layers.

The multiple degrees of freedom in molecules have a great advantage, even in the design of magnetic materials for example, since magnetic properties can be controlled simply by choice of metal ions in a fixed structure. Such a simple methodology is still very important because, as recently demonstrated, it enables the tuning of a spin ground state with collective phenomena between bulk magnetic behavior and superparamagnetic behavior owing to change of the metal-intrinsic magnetic anisotropy or magnetic exchange. Polycyanometalate $[M^{n+}(CN)_x]^{(n-x)}$ is an intriguing building block for the construction of magnetic materials since it can exhibit a wide variety of magnetic properties depending on the choice of the metal center and partners for assemblies as metal ions or coordination-acceptor building blocks.[1] As a partner, Mn^{III}–salen analogs are efficient due to their high-spin $S = 2$ ground state, relatively large uniaxial anisotropy, and high binding affinity in the axial positions. Thus, the combination of polycyanometalate and Mn^{III}–salen analogs could provide various magnetic materials.[1,2] In a hexacyanoferrate-based compound, $[\{Mn(saltmen)\}_4\{Fe(CN)_6\}](ClO_4)\cdot nH_2O$ (**1**),[3] the $[Fe(CN)_6]^{3-}$ unit organizes Mn^{III}–salen-type dimers into a 2D sheet structure, in which two types of ferromagnetic couplings between Fe^{III} and Mn^{III} ions and between Mn^{III} ions in the dimers resulted in ferromagnetic ordering with $T_c = 4.5$ K. Meanwhile, Mn^{III}–salen-type dimers, $[Mn_2(saltmen)_2(X)_2]$ ($X = ReO_4^-$, CH_3COO^-, and N_3^-), are potential candidates for single-molecule magnets (SMMs).[4] Thus, **1** could be considered as a ferromagnetically coupled network of Mn^{III} dimers, potentially with the ability to function as an SMM as well as $[Mn_4]$–SMM networks.[5] To isolate the intrinsic SMM character from the 2D network, we synthesized the Co-substituted compound, $[\{Mn(saltmen)\}_4\{Co(CN)_6\}](ClO_4)\cdot 9H_2O$ (**2**). This compound is isostructural with **1**: the Mn^{III}–salen-type dimers are connected by the diamagnetic $[Co(CN)_6]^{3-}$ unit. Herein, we demonstrate a modification of the magnetic properties from a long-range order in **1** to SMM behavior in **2** by choice of the metal ion in an identical network.

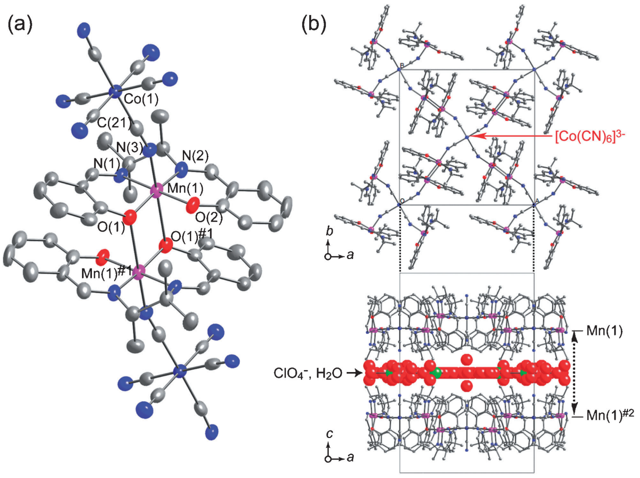

Figure 1. (a) A bonding form of Mn^{III} dimer with $[Co(CN)_6]^{3-}$ units and (b) packing diagrams of **2**, where hydrogen atoms were omitted for clarity. Symmetry operations: #1 ($1.5 - x$, $0.5 - y$, $0.5 - z$), #2 (x, y, $1 - z$).

A crystalline sample of **2** was obtained by the slow evaporation method from a methanol/water mixed solution with a mole ratio of $Mn:Co = 1:1$.[6] The crystal exhibited the same space group as **1**, with tetragonal $I4/m$ (Table S1). Four cyanide groups in the equatorial positions of $[Co(CN)_6]^{3-}$ coordinate to an axial position of a $[Mn(saltmen)]^+$ unit to form a four-blade propeller-like motif of Mn_4Co (Figure 1). The pentanuclear Mn_4Co units are connected by dimerizing in the $[Mn(saltmen)]^+$ parts as $[-Mn^{III}-(O_{Ph})_2-Mn^{III}-]$ ($-(O_{Ph})_2-$ is a biphenolate bridge), forming an infinite 2D network. The dimerization of $[Mn(saltmen)]^+$ is similar to that found in general Mn–salen-type dimers.[4,7] The bond distances for axial coordinates, Mn(1)–N(3)(cyanide) and Mn(1)–O(1)$^{\#1}$(phenolate), are significantly longer than equatorial ones, which is consistent with a distortion due to Jahn–Teller effects in the d^4 Mn^{III} ion: $\langle Mn-O_{equatorial}\rangle_{av} = 1.876$ Å, $\langle Mn-N_{equatorial}\rangle_{av} = 1.982$ Å, Mn(1)–N(3) = 2.199(6) Å, Mn(1)–O(1)$^{\#1}$ = 2.737(5) Å (Table S2). In the 2D network, there are two orientations of $[Mn_2(saltmen)_2]^{2+}$ in which the Jahn–Teller axes (N(3)–Mn(1)–O(1)$^{\#1}$ direction) are almost perpendicular to each other. The layers are stacked, sandwiching a layer composed of ClO_4^- and water molecules with van der Waals contacts. Each Mn_4Co layer is well separated from neighboring layers with a minimum inter-layer Mn(1)···Mn(1)$^{\#2}$ distance of 11.853(2) Å (Figure 1b).

DC magnetic measurements were performed on a polycrystalline sample in the temperature range 2.0–300 K applying a DC field of 1 kOe (Figure S1). The χT product gradually increases to a maximum of 7.99 $cm^3\,K\,mol^{-1}$ at 7.4 K with decreasing temperature and finally decreases to 7.30 cm^3 K mol^{-1} at 2.0 K. The susceptibility obeys the Curie–Weiss law above 200 K. The obtained Curie constant (C) is 5.84 cm^3 K mol^{-1}, which is in agreement with the spin-only value of 6.0 cm^3 K mol^{-1} calculated by assuming $g = 2.0$ for two Mn^{III} ($S = 2$) ions. Thus, the Co^{III} center, as expected, is diamagnetic. The positive Weiss constant of +4.8 K indicates the presence of ferromagnetic interactions between Mn^{III} centers, typical for $[Mn_2(saltmen)_2]^{2+}$ dimeric complexes.[4,7] The decrease at low temperatures is probably due to magnetic anisotropy, i.e., zero-field splitting of Mn^{III} ion (D_{Mn}), and/or inter-dimer interaction (zJ'). The magnetic data was, therefore, simulated using a dimer model with the following spin Hamiltonian: $H = -2J_{Mn\text{–}Mn*}(S_{Mn}\cdot S_{Mn*}) + 2D_{Mn}S_{Mn,z}{}^2$, taking into account zJ' in the framework of the mean-field approximation.[8] Nevertheless, the best-fit was obtained without zJ' and with $g = 1.9604(7)$, $J_{Mn\text{–}Mn*}/k_B = +1.48(1)$ K and $D_{Mn}/k_B = -4.06(6)$ K (Figure S1). The $J_{Mn\text{–}Mn*}$ and D_{Mn} values are similar to those reported in the literature.[4,7] This result demonstrates that the inter-dimer and interlayer magnetic interactions are almost negligible, implying that the Mn^{III} dimers are magnetically isolated not only by the diamagnetic $[Co(CN)_6]^{3-}$ unit but also by the spacer layer of $ClO_4{}^-$ and water molecules.

The field dependence of the magnetization was measured using oriented single crystals at 0.5 K on a commercial SQUID magnetometer equipped with a ^{3}He cryostat (Figure 2a). When the magnetic field was applied parallel to one of the two Mn(1)–O(1)[#1] directions (i.e., Jahn–Teller axis), a butterfly-type hysteresis loop was observed, which is typical SMM behavior confirmed in $S_T = 4$ Mn^{III}–salen-type dimers and other systems.[4,9] The absence of any anomaly at around zero-field indicates that inter-dimer interactions are negligible, consistent with the simulation of χT.

The slow relaxation of magnetization was studied using techniques of AC susceptibility measurement at several DC fields with an oscillating 2 Oe AC field as a function of frequency (0.5–1500 Hz) at 2 K (Figures 2b and S2). Both χ' and χ'' components show a frequency dependence indicative of slow relaxation of the magnetization. The relaxation time was deduced from the maximum of the χ'' curves and from a least-squares fitting taking into account the distribution of a single-relaxation process.[10] The obtained relaxation time obeys a thermally activated Arrhenius relation with $\tau_0 = 4.8 \times 10^{-7}$ s and $\varDelta_{eff}/k_B = 10$ K (Figure S3). The effective energy barrier $\varDelta_{eff}$ is significantly smaller than the theoretical value of 27 K estimated from $\varDelta = |D_{ST}|S_T{}^2$ using $D_{ST}/k_B = -1.68$ K for the dimer deduced from an M–H curve for a polycrystalline sample at 2 K (Figure S1).[9a] The reduction of the energy barrier and a linear-shaped M–H curve at around $H = 0$ indicate a "short-cut" of the thermal barrier by quantum tunneling of the magnetization (QTM). Indeed, AC susceptibility measurements under DC fields revealed saturation of the relaxation time above 2000 Oe at which $\varDelta_{eff}$ was ca. 28 K owing to the lifting of the degeneracy of the $\pm m_s$ states to suppress QTM (Figure S4). Thus, even in a position-fixed network, the SMM character of Mn^{III}–salen-type dimers was preserved.[4,9]

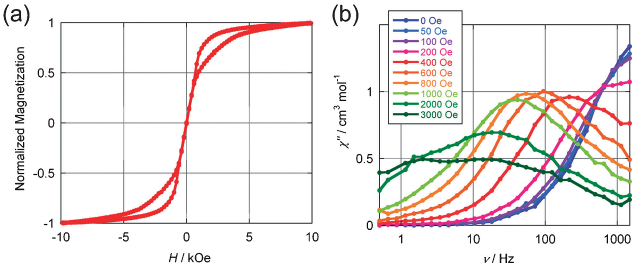

Figure 2. (a) Field dependence of the magnetization in oriented single crystals of **2** at 0.5 K with a scan rate of 2 Oe/ s^{-1} and (b) frequency dependence of the imaginary part (χ'') of AC susceptibility under several magnetic fields at 2.0 K.

In conclusion, we demonstrated a magnetic change from ferromagnet to SMM in a fixed network by changing the metal center from Fe^{III} to Co^{III}. Concomitantly, we noticed that further detailed investigations are needed of even the Mn$^{III}{}_4$Fe^{III} system, **1**, to reveal the specific behavior of anisotropic spins at the ordering points. These experiments are now in progress.

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References and Notes

1 a) H. Weihe, H. U. Güdel, *Comments Inorg. Chem.* **2000**, *22*, 75. b) L. M. C. Beltran, J. R. Long, *Acc. Chem. Res.* **2005**, *38*, 325.

2 a) H. Miyasaka, H. Takahashi, T. Madanbashi, K. Sugiura, R. Clérac, H. Nojiri, *Inorg. Chem.* **2005**, *44*, 5969. b) R. Ababei, Y.-G. Li, O. Roubeau, M. Kalisz, N. Bréfuel, C. Coulon, E. Harté, X. Liu, C. Mathonière, R. Clérac, *New J. Chem.* **2009**, *33*, 1237. c) X. Liu, O. Roubeau, R. Clérac, *C. R. Chim.* **2008**, *11*, 1182.

3 H. Miyasaka, N. Matsumoto, H. Ōkawa, N. Re, E. Gallo, C. Floriani, *J. Am. Chem. Soc.* **1996**, *118*, 981.

4 a) H. Miyasaka, R. Clérac, W. Wernsdorfer, L. Lecren, C. Bonhomme, K. Sugiura, M. Yamashita, *Angew. Chem., Int. Ed.* **2004**, *43*, 2801. b) Z. L. Lü, M. Yuan, F. Pan, S. Gao, D. Q. Zhang, D. B. Zhu, *Inorg. Chem.* **2006**, *45*, 3538.

5 H. Miyasaka, K. Nakata, L. Lecren, C. Coulon, Y. Nakazawa, T. Fujisaki, K. Sugiura, M. Yamashita, R. Clérac, *J. Am. Chem. Soc.* **2006**, *128*, 3770.

6 Supporting Information is available electronically on the CSJ-Journal Website, http://www.csj.jp/journals/chem-lett/index.html. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-755553. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

7 H. Miyasaka, R. Clérac, T. Ishii, H.-C. Chang, S. Kitagawa, M. Yamashita, *J. Chem. Soc., Dalton Trans.* **2002**, 1528.

8 C. J. O'Connor, *Prog. Inorg. Chem.* **1982**, *29*, 203.

9 a) C. Kachi-Terajima, H. Miyasaka, K. Sugiura, R. Clérac, H. Nojiri, *Inorg. Chem.* **2006**, *45*, 4381. b) C. Kachi-Terajima, H. Miyasaka, A. Saitoh, N. Shirakawa, M. Yamashita, R. Clérac, *Inorg. Chem.* **2007**, *46*, 5861.

10 a) S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L.-C. Brunel, A. L. Rheingold, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **1999**, *38*, 5329. b) K. S. Cole, R. H. Cole, *J. Chem. Phys.* **1941**, *9*, 341.