A Novel Mn_{12} Single-molecule Magnet with a μ_3-Methanesulfonate Bridge

Takayoshi Kuroda-Sowa,* Tetsuji Handa, Takehiro Kotera, Masahiko Maekawa, Megumu Munakata,
Hitoshi Miyasaka,† and Masahiro Yamashita†
Department of Chemistry, Faculty of Science and Engineering, Kinki University, Higashi-Osaka, Osaka
†*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Minami-Osawa, Hachioji, Tokyo*

(Received February 16, 2004; CL-040176)

The first Mn_{12} complex with μ_3-methanesulfonate bridge was observed and its single-molecular magnetic property was characterised.

Recently much attention is focused on the so-called single-molecule magnets (SMM's). SMM's are superparamagnets with a relatively slow magnetization relaxation which enables them to behave as "magnets" below blocking temperatures (T_B). Since the molecule itself behaves as a small magnet, it is expected to be an ultimate high-density memory device. Another aspect of SMM's is a candidate for the element of a qubit for a quantum computer. The observation of steps in the hysteresis loop of $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (**1**) is attributed to macroscopic quantum tunneling of magnetization.[1] The magnetic property of **1** is characterized by a large ground state spin S (=10), and a negative D (= − 0.72 K).[2] In order to understand its chemistry and property more thoroughly, many works have been devoted to the chemical modifications of **1** including the substitution of bridging acetates to other carboxylates[3–5] and the partial substitution of peripheral manganese(III) ions.[6,7] Recently, the substitution of bridging carboxylates to non-carboxylate bridges such as nitrate,[8] phosphinate,[9] phosphate,[10] and benzenesulfonate[11] have been reported. Although these results show that the substitution affects a little on their magnetic properties, the important point is to show the possibility of oxo-bridges other than carboxylates to be substituted for acetates in Mn_{12} complexes. Oxo-bridges, mostly having stronger acidity than acetates, tend to replace acetate ions in axial positions of Mn_{12} complexes.[8] Expanding the variety of axially substituted Mn_{12} complexes can be a starting point for the construction of an assemblage of Mn_{12} complexes connected in axial direction with the aim of getting an SMM having a greater S value. We report here the first example of an axially substituted Mn_{12} complex with μ_3-methanesulfonate ions, which is also the first example of the μ_3-bridging fashion in manganese coordination complexes.[12]

The μ_3-methanesulfonate-bridged Mn_{12} complex $[Mn_{12}O_{12}(O_2CMe)_{12}(O_3SMe)_3(\mu_3\text{-}O_3SMe)(H_2O)_3]$ (**2**) was synthesized by reaction of **1** with four equivalence of methanesulfonic acid in acetonitrile.[13] Complex **2** crystallizes in the orthorhombic space group *Pbca* with an asymmetric unit consisting of one Mn_{12} molecule and seven solvent molecules as $\mathbf{2}\cdot 3CH_3CN\cdot 4H_2O$.[14] The molecular structure of **2** is shown in Figure 1 together with the numbering of some selected atoms. Four methanesulfonate ions are introduced by replacing four axial acetate ions and one water molecule. Among four methanesulfonate ions, one of them containing the S(2) sulfur atom coordinates to three Mn^{III} ions through three oxygen atoms with μ_3(-O, -O′, -O″) bridging fashion while the rest bridge two Mn^{III} ions through two oxygen atoms. Although many metal complexes with μ_3-bridging sulfonate ions are known so far,[12] this is the first observation of a manganese complex with a μ_3-sulfonate bridge.

Since all Mn–O (sulfonate) bonds are in the axial position and their lengths are all longer than those of Mn–O (equatorial carboxylate) bonds, Jahn–Teller (JT) axes of Mn^{III} ions in **2** seem to be roughly parallel to each other. Three Mn–O bond lengths involved in the μ_3-coordination are 2.167(3) Å, 2.312(3) Å, and 2.306(3) Å for Mn(5)–O(37), Mn(6)–O(38), and Mn(12)–O(36), respectively. The first bond is the shortest one and the latter two are the longest and the second longest ones among the nine Mn–O (sulfonate) bonds in **2**. The average of the nine Mn–O (sulfonate) lengths is 2.22 Å, which is similar to the average of eight axial Mn–O (sulfonate) lengths (2.20 Å) in $[Mn_{12}O_{12}(O_2CMe)_8(O_3SPh)_8(H_2O)_4]$[11] but appreciably longer than the average of eight Mn–O (phosphate) lengths (2.14 Å) in $[Mn_{12}O_{12}(O_2CPh)_{12}(O_2P(OPh)_2)_4(H_2O)_4]$.[10]

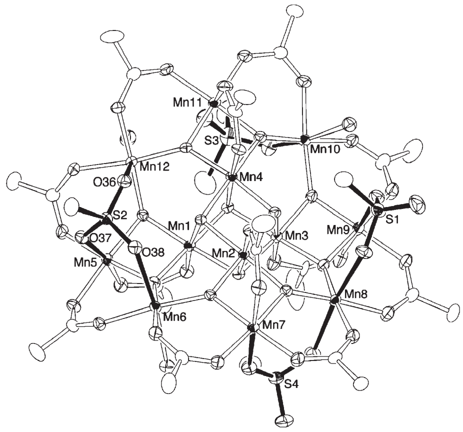

Figure 1. ORTEP drawing of a molecular structure of **2** with the atom numbering scheme for selected atoms. Hydrogen atoms are omitted for clarity.

The Mn(5) ion is apparently displaced downward (about 0.36 Å) from the line connecting Mn(1) and Mn(3) ions. Additionally, the distance between Mn(6) and Mn(12) is 5.37 Å, which is 11% shorter than 6.05 Å of that between Mn(8) and Mn(10). These lengths should be the same if the core structure maintains S_4 symmetry like **1**. Thus, the μ_3-sulfonate bridge pushes the Mn(5) ion downward and pulls Mn(6) and Mn(12) ions inside. Although these geometrical changes affect the orientation of JT axes of Mn^{III} ions, the effect on the magnetic property is rather small as stated later.

Since the space group of the crystal is *Pbca*, there are eight independent molecules with four unique orientations in the unit cell. Four unique molecular z axes are making angles between 104–116° (average 110°) each other, just like a tetrahedral orientation.

Ac magnetic susceptibility of **2** was measured at 1.7–10 K with 5–997 Hz frequencies. The out-of-phase signal χ''_M at 997 Hz frequency shows two peak-maxima at 2.8 and 7.2 K although the intensity of the latter is much greater than the former. These two peaks correspond to "low-temperature" (LT) and "high-temperature" (HT) phases, respectively. On the basis of the Arrhenius plots of the logarithm of the relaxation time τ versus the inverse of peak temperature T, the activation energies U_{eff} for the reversal of the magnetization spin are estimated to be 35 and 68 K for LT and HT phases, respectively. The latter value is slightly larger than 61 K for that of **1**.[2] To estimate the ground state spin S and the zero-field splitting parameter D of **2**, dc magnetization data were collected for randomly oriented sample at low temperatures (1.9 to 4.5 K) with multiple-field strength (1.0 to 7.0 T). The results were fitted by using a fitting program "axfit"[15] for the axially symmetric system. The fitting is not perfect especially at high-temperature region, probably because of the configuration mixing of excited states into the ground state. The best-fit parameters using low temperature data below 3 K are $g = 1.93$ and $D = -0.54$ K for the $S = 9$ ground state. We also tried fittings for rhombic system considering an E term, but no clear improvement was observed with E values within the range of ± 0.005 K and with E values out of this range, fittings were getting worse. These parameters are in the range of those of Mn_{12} complexes reported so far,[2–11] indicating that the effect of the μ_3-bridge on the magnetic property is not so large. Using the obtained S and D, we can estimate a theoretical energy barrier for the reversal of the magnetization spin as $U = |D|S^2 = 44$ K. Since U defines the upper limit of the energy barrier, it is reasonable to assign the sample used for the magnetization measurements is the LT phase. Removal of lattice solvent probably induces a drastic change of the LT/HT ratio.[16]

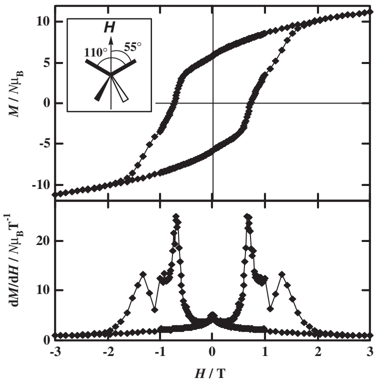

Figure 2. Top: Magnetization hysteresis loop measured at 1.9 K for microcrystals of **2**. The inset shows the orientation of four unique molecular z axes under a field H. Bottom: The first derivative of the magnetization hysteresis loop.

The molecular packing with four unique orientations in the unit cell affects the appearance of the hysteresis loop. At 1.9 K, **2** shows a hysteresis loop as shown in Figure 2 (top). Although microcrystalline samples were aligned under the 7 T field and fixed by eicosane wax before measurement, the magnetization is not saturated at 3.0 T, where the magnetization value is ca. 12 $N\mu_B$. Since there are four independent molecular orientations in the unit cell, each molecular easy axis can not align with the external field but the easy axis of each microcrystal aligns as shown in the inset of the Figure 2. The first derivative of the hysteresis loop is shown in the bottom part of Figure 2. Two peaks can be observed at 0.71 and 1.32 T, which correspond to steps observed in the hysteresis loop. The true step interval ΔH_0 for a single molecule with a field applied parallel to the molecular z axis can be estimated by $H \cos 55°$ where H is the field that step was observed. The value is calculated to be 0.41 T by using $H = 0.71$ T, and is a good agreement with the value of 0.42 T estimated from $|D|/(g\mu_B)$ derived from the condition for the magnetization tunneling,[1] indicating the validity of the above reduced magnetization analysis.

References and Notes

1 J. R. Friedman, M. P. Sarachik, J. Tejada, and R. Ziolo, *Phys. Rev. Lett.*, **76**, 3830 (1996).

2 R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature*, **365**, 141 (1993).

3 R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **115**, 1804 (1993).

4 H. J. Eppley, H.-L. Tsai, N. D. Vries, K. Folting, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **117**, 301 (1995).

5 T. Kuroda-Sowa, T. Nogami, H. Konaka, M. Maekawa, M. Munakata, H. Miyasaka, and M. Yamashita, *Polyhedron*, **22**, 1795 (2003).

6 A. R. Schake, H.-L. Tsai, N. D. Vries, K. Folting, D. N. Hendrickson, and G. Christou, *J. Chem. Soc., Chem. Commun.*, **1992**, 181.

7 L. Jin-Yu, X. Hao, Z. Jian-Zhong, X. Zheng, Y. Xiao-Zeng, and Y. Kai-Pei, *Polyhedron*, **15**, 3325 (1996).

8 P. Artus, C. Boskovic, J. Yoo, W. E. Streib, L.-C. Brunel, D. N. Hendrickson, and G. Christou, *Inorg. Chem.*, **40**, 4199 (2001).

9 C. Boskovic, M. Pink, J. C. Huffman, D. N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.*, **123**, 9914 (2001).

10 T. Kuroda-Sowa, S. Fukuda, S. Miyoshi, M. Maekawa, M. Munakata, H. Miyasaka, and M. Yamashita, *Chem. Lett.*, **2002**, 682.

11 N. E. Chakov, W. Wernsdorfer, K. A. Abboud, D. N. Hendrickson, and G. Christou, *J. Chem. Soc., Dalton Trans.*, **2003**, 2243.

12 F. H. Allen, S. A. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers, and D. G. Watson, *Acta Crystallogr., Sect. B*, **35**, 2331 (1979); F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).

13 An acetonitrile solution (20 mL) containing Mn_{12}-ac (0.50 g, 0.27 mmol) and methanesulfonic acid (0.10 g, 1.08 mmol, 4 equiv.) was stirred for 1 h at room temperature. The resulting black solution was filtered to remove a slight amount of insoluble Mn_{12}-ac. After the filtrate was transferred into a glass tube, the same amount of Et_2O was placed on the solution and the glass tube was sealed. After 6 days, black brick crystals were obtained. (Yield ca. 20% as crystal). Anal. Calcd for $C_{28}H_{54}Mn_{12}O_{51}S_4$(**2** after dry); C, 16.86; H, 2.73. Found: C, 16.94; H, 2.77%. Similar procedures with 8 or 16 equiv. of methanesulfonic acid gave no crystalline products.

14 Crystal data: $C_{34}H_{71}Mn_{12}N_3O_{55}S_4$, $M_r = 2189.45$, orthorhombic, space group *Pbca* (no.61), $a = 23.5561(7)$, $b = 25.2409(7)$, $c = 27.4660(7)$ Å, $V = 16330.7(8)$ Å^3, $T = 120$ K, $Z = 8$, $D_{calcd} = 1.769$ gcm^{-3}, $\mu(\mathrm{MoK}\alpha) = 1.990$ cm^{-1}, 97853 reflections measured, 18382 unique ($R_{int} = 0.020$), $R = 0.0548$, $R_w = 0.1491$. CCDC-193221 contains the supplementary crystallographic data for this complex.

15 J. Yoo, A. Yamaguchi, M. Nakano, J. Krzystek, W. E. Streib, L.-C. Brunel, H. Ishimoto, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **40**, 4604 (2001).

16 S. M. J. Aubin, Z. Sun, H. J. Eppley, E. M. Runmberger. I. A. Gunzei, K. Folting, P. K. Gantzel, A. L. Reingold, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **40**, 2127 (2001).

Published on the web (Advance View) April 5, 2004; DOI 10.1246/cl.2004.540