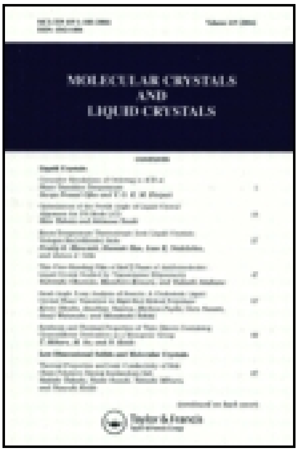

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Synthesis, Structure and Magnetic Properties of the Antiferromagnetic Hexamanganese Cluster $[Mn_6(\mu_4\text{-}O)_2(O_2CC_6HF_4)_{10}(HO_2CCH_3)_4]\cdot(C_7H_8)$

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Synthesis, Structure and Magnetic Properties of the Antiferromagnetic Hexamanganese Cluster $[Mn_6(\mu_4\text{-}O)_2(O_2CC_6HF_4)_{10}(HO_2CCH_3)_4]\cdot(C_7H_8)$

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A hexanuclear Mn^{II}-Mn^{III}-cluster, $[Mn_6(O)_2(O_2CC_6HF_4)_{10}(HO_2CCH_3)_4]\cdot(C_7H_8)$ (**1**), was synthesized by a typical acetate-substitution reaction of the well-known Mn_{12}-cluster, $[Mn_{12}(O)_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 2CH_3CO_2H\cdot 4H_2O$ in the presence of an excess of 2, 3, 5, 6-tetrafluorobenzoic acid. Each unpaired spin on Mn(II) and Mn(III) ions is promoted as to be antiferromagnetically cancelled to produce an $S = 0$ ground state.

Keywords: Manganese Cluster; Magnetic properties, Antiferromagnetic interaction; Single-Molecule Magnets;

INTRODUCTION

In recent years, nano-scale high-nuclear clusters have much attention in the field of physical chemistry and coordination chemistry. Because some of them realistically exhibit quantum phenomena expected in nano-scale, such as tunneling transition[1]. Such compounds are so-called as "single-molecule magnets". Among them, the well-known Mn_{12} cluster $[Mn_{12}(O)_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 2CH_3CO_2H\cdot 4H_2O$[2] revealed in 1980 have been accurately investigated so far on its characteristic physical properties by Gatteschi *et al.* This molecule was reported to have a $S = 10$ ground state and indicated slow relaxation time of the magnetization at low temperature. More recently, further efforts are energetically directing to developments of new single-molecule magnets and superparamagnets having giant-spin ground state, the highest ground state of a $S = 51/2$ reported up to date[3]. One of the representative synthetic methods is the acetate-substitution reaction of the above-mentioned compound. Several substituted compounds have been prepared, where the $Mn_{12}O_{12}$ cluster cores were maintained in the produced compounds, $[Mn_{12}(O)_{12}(O_2CR)_{16}(H_2O)_4]$ (R = CH_2CH_3, C_6H_5, $C(CH_3)_3$, CH_2Cl)[4-7]. These compounds were composed of external eight Mn^{III} ions around four Mn^{IV} ions having an internal-cuboidal motif as well as the acetate derivative. We performed here a acetate-substitution reaction of the $Mn_{12}O_{12}$ cluster in the presence of 2, 3, 5, 6-tetrafluorobenzoic acid and obtained a Mn_6O_2 cluster, $[Mn_6(O)_2(O_2CC_6HF_4)_{10}(HO_2CCH_3)_4]\cdot(C_7H_8)$ (**1**) as large rectangular crystals. Although structural analogues of **1** have already reported[8], which have a similar $[Mn_6O_2]^{10+}$ core bridged by acetate, benzoate and pivalate, etc, the rearranged formation of such cluster from the $Mn_{12}O_{12}$ cluster is the first report. Here, the structure and magnetic properties are presented.

EXPERIMNTAL

All synthetic procedures were performed under dried dinitrogen atmosphere and the solvents used were dried by the common practices before used. A toluene solution (25 mL) containing $[Mn_{12}(O)_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 2CH_3CO_2H\cdot 4H_2O$ (1.0 g, 0.5 mmol) and excess 2, 3, 5, 6-tetrafluorobenzoic acid (2.59 g, 13.3 mmol) was stirred at room temperature for 2 days. The resulting dark brown solution was filtered and dried *in vacuo*. To the dark brown residue, more toluene (25 mL) was added with a further amount of 2, 3, 5, 6-tetrafluorobenzoic acid (2.59 g), and the entire process repeated. The final residue was dissolved in toluene (25 mL) and transferred to the bottom of a narrow Schlenk tube. Hexane (40 mL) was carefully put on it to form large rectangular crystals of **1**. Compound **1** contains a toluene molecule as a crystallization solvent in the formulated molecule, however the crystallinity of **1** was relatively stable in air. Anal. Calcd for $C_{85}H_{34}F_{40}O_{30}Mn_6$: C, 38.90; H, 1.31. Found: C, 38.75; H, 1.52.

Crystal data: **1**: $C_{85}H_{34}F_{40}O_{30}Mn_6$, M = 2624.75, monoclinic, a = 25.5445(8), b = 13.8940(5), c = 27.209(1) Å, β = 105.808(2) °, U = 9291.6(6) Å^3, T = -170 °C, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo-Kα) = 9.53 cm^{-1}, 68561 reflections measured, 20853 unique (R_{int} = 0.100), refinement method: full-matrix least-squares on F^2. The final R indices: R_1 = 0.062 ($I > 3\sigma(I)$), R = 0.108, wR = 0.197 (all data), GOF = 1.61.

RESULTS AND DISCUSSION

Structure

Figure 1a shows ORTEP representation of the Mn_6 core of **1**. The Mn_6 core consists of two μ_4-O^{2-} and ten bridging $F_4HC_6CO_2^-$ moieties similar to the compounds reported previously[9]. Especially, the basic skeleton of $Mn_6(\mu_4\text{-}O)_2$ core is arranged in a edge-shared double tetrahedral geometry, where two vertexes located on the edge-shared

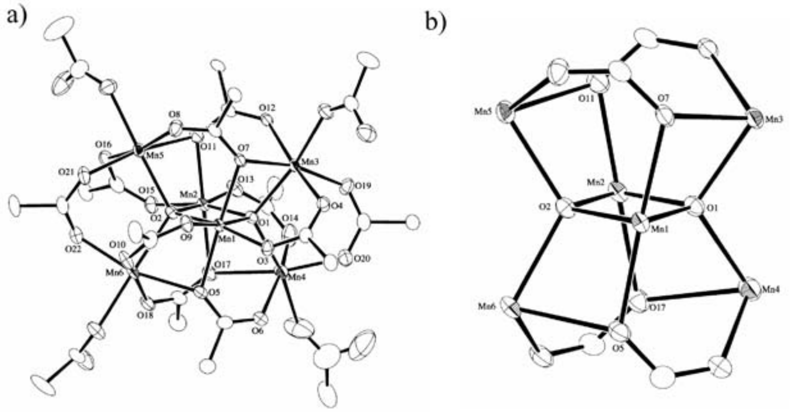

FIGURE 1 (a) ORTEP view of the **1** with the atom-numbering scheme, showing 30% probability. For clearty, only the *ipso* C atoms of the 2, 3, 5, 6-tetrafluorobenzoate phenyl groups are shown. (b) The bridging carboxylates of four $F_4HC_6CO_2^-$ moieties which support the $Mn_6(\mu_4\text{-}O)_2$ core is shown.

position are occupied by Mn^{III} ions and the other four vertexes are occupied by Mn^{II} ions, forming a $[Mn^{III}{}_2Mn^{II}{}_4(\mu_4\text{-}O)_2]^{10+}$ core. The center of tetrahedron sphere assumes the μ_4-oxo position. For this core, the Mn-O bonds around μ_4-O [O(1), O(2)] have two types: the distances between the inner Mn ions and the μ_4-O [Mn(1)-O(1) = 1.896(3)Å, Mn(1)-O(2) = 1.883(3)Å, Mn(2)-O(1) = 1.900(3)Å, and Mn(2)-O(2) = 1.874(3)Å] are shorter than those between the outer Mn ions and the μ_4-O [Mn(3)-O(1) = 2.172(3)Å, Mn(4)-O(1) = 2.180(3)Å, Mn(5)-O(2) = 2.208(3)Å, Mn(6)-O(2) = 2.214(3)Å], which clearly demonstrate that Mn(1) and Mn(2) are trivalent Mn ions with Jahn-Teller distortion and the other (the outer Mn ions) are divalent Mn ions. The Jahn-Teller axes around Mn(1) and (2) are perpendicularly arranged to the plane consisting of a set of [Mn(1), O(1), Mn(2), and O(2)] (the averaged distance; Mn-O = av. 1.888 Å). The bond angles in the above mentioned plane are found to be Mn(1)-O(1)-Mn(2) = 95.3(1)°, Mn(1)-O(2)-Mn(2) = 96.6(1)°, O(1)-Mn(1)-O(2) = 84.0°, and O(1)-Mn(2)-O(2) = 84.1(1)°. Four Mn ions around O(1) and O(2) arrange in distorted tetrahedral with the dihedral angles of ∠A·B =

76.002 ° and ∠A·C = 75.878 °, where the plane A, B and C are defined as Plane A [Mn(1)-O(1)-Mn(2)-O(2)], Plane B [Mn(3)-O(1)-Mn(4)], and Plane C [Mn(5)-O(2)-Mn(6)]. Four $F_4HC_6CO_2^-$ moieties of ten ones support the $Mn_6(\mu_4\text{-}O)_2$ core in the unsymmetric $\eta^1:\eta^2$ mode as shown in Figure 1b with the bond distances in the range of 2.20 – 2.33 Å. The other six $F_4HC_6CO_2^-$ moieties bridge each set of [Mn(1), Mn(3)], [Mn(1), Mn(6)], [Mn(2), Mn(4)], [Mn(2), Mn(5)], [Mn(3), Mn(4)], and [Mn(5), Mn(6)] in the symmetric $\eta^1:\eta^1$ mode and the external four Mn ions, Mn(3) – Mn(6), are capped by acetic acid.

Magnetic Properties

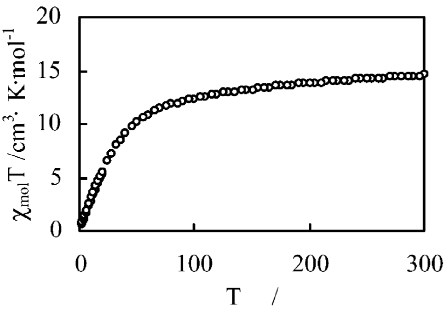

FIGURE 2 χ_mT vs T curve for **1**, where the measurement was carried out under the applied magnetic field of 1 T, and magnetic susceptibility per Mn6 cluster unit, respectively.

The temperature-dependence of direct-current (DC) magnetic susceptibility of the polycrystalline sample of **1** was measured under 1 T in the temperature range of 2.0 – 300 K. The χ_MT value 14.6 $cm^3 \cdot mol^{-1} \cdot K$ at 300 K gradually decreases upon lowering temperature and reaches to 0.738 $cm^3 \cdot mol^{-1} \cdot K$ at 2.0 K (Figure 2). This behavior shows that the unpaired electrons of **1** are antiferromagnetically coupled and could be finally converged to $S = 0$ ground state.

Reference

[1.] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature.*, **383**, 145 (1996)

[2.] T. Lis, *Acta Cryst.*, **B36**, 2042-2046 (1980)

[3.] L. Joulia, G. Mathias, P. Melanie, A. Hanspeer, S.-E. Helen, U. G. Hans, D. Silvio, *Angew. Chem. Int. ed.*, **39**, 1605 (2000)

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

[5.] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gtteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.*, **115**, 1804-1816 (1993)

[6.] Z. Sun, D. Ruiz, E. Rumberger, C. D. Incarvito, K. Folting, A. L. Rheingold, G. Christou, D. N. Hendrickson, *Inorg. Chem.*, **34**, 4758-4759 (1998)

[7.] H.-L. Tsai, T.-Y. Jwo, G.-H. Lee, Y. Wang, *Chemistry Letters.*, **346** (2000)

[8.] A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **28**, 1915-1923 (1989)

[9.] A. R. E. Baikie, A. J. Howes, M. B. Hursthouse, A. B. Quick, P. Thornton, *J. Chem. Soc., Chem. Commun.,* 1587 (1986)