

Construction of a One-Dimensional Chain Composed of Mn_6 Clusters and 4,4'-Bipyridine Linkers: The First Step for Creation of “Nano-Dots-Wires”

Kazuya Nakata, Hitoshi Miyasaka,^{*,†} Kunihisa Sugimoto,^{††} Tomohiko Ishii, Ken-ichi Sugiura, and Masahiro Yamashita*

Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, 1-1 Minamiohsawa, Hachioji, Tokyo 192-0397

[†]“Structural Ordering and Physical Properties”, PRESTO, Japan Science and Technology Corporation (JST)

^{††}X-ray Research Laboratory, Rigaku Co. Ltd., 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666

(Received March 4, 2002; CL-020199)

Treatment of a mixed-valence Mn_6 cluster, $[\text{Mn}_6\text{O}_2(t\text{-BuCO}_2)_{10}(t\text{-BuCO}_2\text{H})_4]$ (**1**), with 4,4'-bipyridine (bpy) in dichloromethane/1,2-dichloroethane solution gave a one-dimensional polymeric chain compound, $[\text{Mn}_6\text{O}_2(t\text{-BuCO}_2)_{10}(t\text{-BuCO}_2\text{H})_2(\text{bpy})]$ (**2**), in which the parent cluster core was maintained as a building block.

In recent years, nanosized clusters such as *single-molecule magnets* (SMMs) have received much attention in the field of physical chemistry and coordination chemistry because they realistically exhibit quantum phenomena such as quantum tunneling transition expected in nanoscale supraparticles.¹⁻⁸ SMMs have such essential magnetic factors as a large spin ground state (*S*) and a negative zero-field splitting (*D*) with an uni-axis anisotropy in molecular particles, which are responsible for their quantum magnetic behavior. Our next project is directed at the second-generated materials created based on the SMM's magnetic factors and quantum peculiarities. One of the second-generated materials is targeted at the fabrication of network compounds using SMM building blocks, particularly “one-dimensional (1-D) chains alternately connecting nanosized clusters as spin containers”. We call such materials “*nano-dots-wires*”. For the fabrication of ferromagnetic- or ferrimagnetic-exchanged “*nano-dots-wires* and -networks”, the preparation and selection of core-stable SMM building blocks are of utmost importance. In the initial synthetic methodology, the first step in fabricating such materials is to connect *stably* nanosized clusters without decomposition and rearrangement of cluster cores by adequate linkers even if the building blocks used are not SMMs. Christou and Hendrickson et al. succeeded in fabricating the first 1-D chain composed of Mn_4 antiferromagnetic cluster blocks and 4,4'-bipyridine (bpy) linkers.⁹ However, the target compounds constructed on the basis of the above concept are very rare, and to our knowledge, only Christou and Hendrickson et al.'s compound is known to date. We describe herein a structural model for *nano-dots-wires*, although its magnetic properties as new materials are excluded. We chose an Mn_6 cluster, $[\text{Mn}_6\text{O}_2(t\text{-BuCO}_2)_{10}(t\text{-BuCO}_2\text{H})_4]$ (**1**),¹⁰ as the candidate building block, and obtained, as expected, a 1-D polymeric chain compound with the 4,4'-bipyridine linkage, $[\text{Mn}_6\text{O}_2(t\text{-BuCO}_2)_{10}(t\text{-BuCO}_2\text{H})_2(\text{bpy})]$ (**2**). This compound, together with that of Christou and Hendrickson et al., may serve as an impetus for the creation of high-temperature metastable materials.

The single crystal of **2** was prepared by a slow diffusion of a dichloromethane (10 ml) solution containing 4,4'-bipyridine (5 mg, 0.03 mmol) into a 1,2-dichloroethane (10 ml) solution containing **1** (50 mg, 0.03 mmol) in a narrow glass tube.¹¹

An ORTEP view of **2** containing an Mn_6 cluster and a bridging

4,4'-bpy is depicted in Figure 1. **2** crystallizes in orthorhombic space group *Pnna* possessing a crystallographic C_2 symmetrical axis through O(7) and O(10) and the center of the C-C bond of the bpy molecule.¹² It is notable that the $[\text{Mn}_6\text{O}_2]^{10+}$ core of the parent cluster **1** is retained even in **2**. The Mn ions include two groups comprising the inner core of two Mn(III) ions and outer four Mn(II) ions to give a mixed valence of $\text{Mn}_4^{\text{II}}\text{Mn}_2^{\text{III}}$ (vide infra): the six Mn ions are positioned at the vertexes of an edge-shared double tetrahedron, where the two Mn(III) ions occupy the edge-shared positions and the other four Mn(II) ions occupy the outer vertexes with two $\mu_4\text{-O}^{2-}$ ions at the center of each tetrahedron. All Mn ions are surrounded by μ_2 - and μ_3 -pivalate groups to form the $\text{Mn}_6\text{O}_2(t\text{-BuCO}_2)_{10}$ cluster. Four vacant sites on the outer Mn(II) ions are distinguishably occupied by two species of ligands in a *cis* arrangement: Mn(1) and Mn(1)* are capped by monodentate pivalic acids, and Mn(3) and Mn(3)* are occupied by a bridging bpy molecule to form a 1-D zigzag chain having the [-bpy-(Mn_6)]_n repeating unit. The coordination geometry around the inner Mn(III) ions, Mn(2) and Mn(2)*, is elongated octahedral, where the six positions are occupied by oxygen atoms from four pivalate bridging groups and $\mu_4\text{-O}^{2-}$ ions: the distances of Mn(2)-O(8) = 2.240(4) Å and Mn(2)-O(11) = 2.254(4) Å (the elongated axis) are longer than those of Mn(2)-O(6) = 1.979(4) Å, Mn(2)-O(7) = 1.904(3) Å, Mn(2)-O(9) = 1.943(3) Å, and Mn(2)-O(10) = 1.891(3) Å (the equatorial plane), clearly demonstrating that Mn(2) and Mn(2)* are trivalent with Jahn-Teller distortion. The coordination geometry of two outer Mn(II) ions, Mn(1) and Mn(1)*, which have the capping

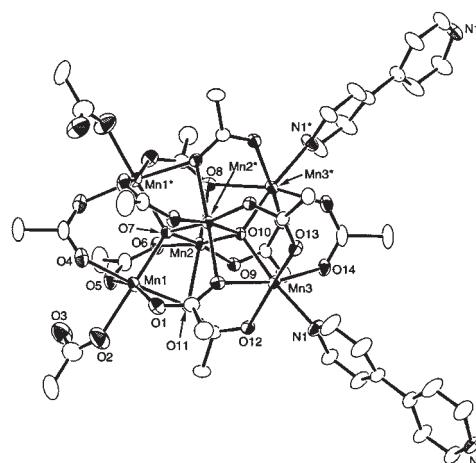


Figure 1. ORTEP drawing of **2** with an adjacent bpy molecule with the atom-numbering scheme (50% probability ellipsoid, symmetry operation: $^*x, 1/2-y, 1/2-z; ^{11}x, -y, z; ^{12}x, 1/2-y, 1/2-z$). Methyl groups of pivalic acid are omitted for clarity.

pivalic acid, is distorted octahedral, where the six positions are occupied by the oxygens from the four pivalate bridging groups [$\text{Mn}(1)-\text{O}(1) = 2.096(4) \text{ \AA}$, $\text{Mn}(1)-\text{O}(4) = 2.123(4) \text{ \AA}$, $\text{Mn}(1)-\text{O}(5) = 2.205(5) \text{ \AA}$, $\text{Mn}(1)-\text{O}(11) = 2.303(4) \text{ \AA}$], $\mu_4\text{-O}^{2-}$ ion [$\text{Mn}(1)-\text{O}(7) = 2.138(3) \text{ \AA}$] and a pivalic acid [$\text{Mn}(1)-\text{O}(2) = 2.207(6) \text{ \AA}$, $\text{O}(2)-\text{Mn}(1)-\text{O}(7) = 172.2(2)^\circ$]. On the other hand, the coordination geometry of the other two outer Mn(II) ions, Mn(3) and Mn(3)*, is also distorted octahedral, where five positions are occupied by oxygens from the four pivalate bridging groups [$\text{Mn}(3)-\text{O}(12) = 2.120(3) \text{ \AA}$, $\text{Mn}(3)-\text{O}(13) = 2.145(3) \text{ \AA}$, $\text{Mn}(3)-\text{O}(14) = 2.103(4) \text{ \AA}$, $\text{Mn}(3)-\text{O}(8)^* = 2.378(4) \text{ \AA}$] and $\mu_4\text{-O}^{2-}$ ion [$\text{Mn}(3)-\text{O}(10) = 2.180(2) \text{ \AA}$]. The sixth position is occupied by the nitrogen from bpy with the bond distance and bond angle of $\text{Mn}(3)-\text{N}(1) = 2.316(5) \text{ \AA}$ and $\text{N}(1)-\text{Mn}(3)-\text{O}(10) = 173.2(1)^\circ$, respectively.

Figure 2 shows a packing diagram of the chains. The adjacent chains run along the a axis with the same phase in the crystal lattice. The intra-chain inter-cluster distance ($\text{Mn} \cdots \text{Mn}$) is 11.68 \AA , and the inter-chain inter-cluster distance is 12.09 \AA (between clusters along the a axis) and 12.68 \AA (between clusters along the b axis). Therefore, even with its intra-chain relation (*via* bridging bpy), significant inter-cluster magnetic interaction is not expected from this molecular arrangement.

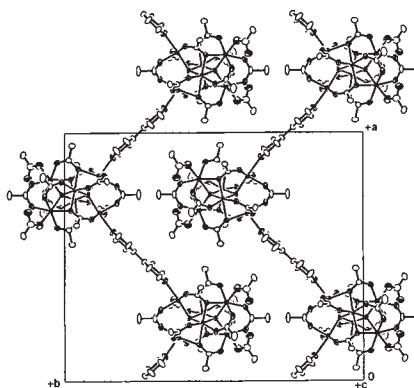


Figure 2. Packing diagram of the 1-D chain compound **2** projected along the c axis.

The temperature dependence of the magnetic susceptibility was measured in the temperature range of 2 to 300 K under the applied magnetic field of 1 T. The plot of $\chi_m T$ vs T is given in Figure 3. The $\chi_m T$ value for **2** is $14.2 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at room temperature, and decrease gradually upon cooling, particularly below ca. 50 K, to reach $0.317 \text{ cm}^{-1} \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K. As expected from the structural

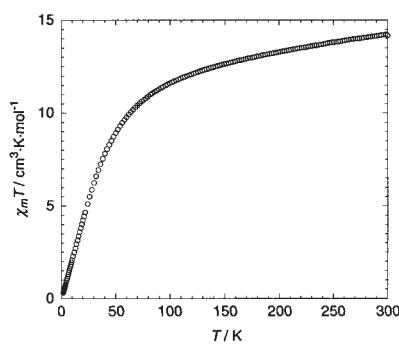


Figure 3. Temperature dependence of the $\chi_m T$ for **2**.

arrangement that the individual clusters are sufficiently separated, the overall magnetic behavior of **2** is nearly identical to that of the parent cluster **1**.¹³ Therefore, we conclude that the inter-cluster magnetic interaction, which arises from both intra-chain and inter-chain magnetic interactions, is negligible.

In summary, the reaction of an Mn_6 cluster with 4,4'-bipyridine gave a 1-D polymeric chain assembly while retaining the structure and magnetism of the parent Mn_6 cluster. Our final goal is to create ferromagnetic- or ferrimagnetic-exchanged nano-dots-wires and -networks, magnetic nature of which may be understood from the following parameters: the spin ground state S and the anisotropy D of the cluster, intra-cluster local exchange J_c , and inter-cluster exchange J_{c-c} . This work offers the first synthetic step toward creating such materials.¹⁴

References and Notes

- 1 D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, *Science*, **365**, 1054 (1994).
- 2 R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, *Nature*, **365**, 141 (1993); L. Thomas, F. Lioni, R. Ballou, D. Gatteschi, R. Sessoli, and B. Barbara, *Nature*, **383**, 145 (1996); Z. Sun, D. Ruiz, E. Rumberger, C. D. Incarvito, K. Folting, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **37**, 4758 (1998); D. Ruiz, Z. Sun, B. Albela, K. Folting, J. Ribas, G. Christou, and D. N. Hendrickson, *Angew. Chem. Int. Ed.*, **37**, 300 (1998); S. M. J. Aubin, Z. Sun, L. Pardi, J. Krzystek, K. Folting, L.-C. Brunel, A. L. Rheingold, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **38**, 5329 (1999); H. Andres, R. Basler, H.-U. Güdel, G. Aromi, G. Christou, H. Büttner, and B. Ruffé, *J. Am. Chem. Soc.*, **50**, 12469 (2000); T. Kuroda-Sowa, M. Lam, A. L. Rheingold, C. Frommen, W. M. Reiff, M. Nakano, J. Yoo, A. L. Maniero, L.-C. Brunel, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **25**, 6469 (2001).
- 3 S. M. J. Aubin, N. R. Dilley, L. Pardi, J. Krzystek, M. W. Wemple, L.-C. Brunel, M. B. Maple, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **120**, 4991 (1998).
- 4 J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A. L. Maniero, L.-C. Brunel, K. Awaga, H. Ishimoto, G. Christou, and D. N. Hendrickson, *Inorg. Chem.*, **16**, 3615 (2000).
- 5 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).
- 6 A. L. Barra, A. Caneschi, A. Cornia, F. F. de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli, and L. Sorace, *J. Am. Chem. Soc.*, **121**, 5302 (1999).
- 7 H. Oshio, N. Hoshino, and T. Ito, *J. Am. Chem. Soc.*, **122**, 12602 (2000).
- 8 S. L. Castro, Z. Sun, V. M. Grant, J. C. Bollinger, D. N. Hendrickson, and G. Christou, *J. Am. Chem. Soc.*, **120**, 2365 (1998).
- 9 S. Wang, H.-L. Tsai, K. Folting, J. D. Martin, D. N. Hendrickson, and G. Christou, *J. Chem. Soc., Chem. Commun.*, **1994**, 671.
- 10 A. R. E. Baikie, A. J. Howes, M. B. Hursthouse, A. B. Quick, and P. Thornton, *J. Chem. Soc., Chem. Commun.*, **1986**, 1587.
- 11 Analytical data: Calcd for $2 \cdot 5\text{H}_2\text{O}$: $\text{C}_{70}\text{H}_{130}\text{N}_2\text{O}_{32}\text{Mn}_6$: C, 46.16; H, 6.97; N, 1.54. Found: C, 46.14; H, 6.36; N, 1.67. IR (KBr) $\tilde{\nu}_{\text{max}}(\text{cm}^{-1})$: 3429 (OH, m), 2959, 2928, 2872 (C-H, s), 1693 (C=O, m), 1589, 1570 (CO₂, s), 1417 (C-O-H, s), 1226 (C-O, m).
- 12 Crystallographic data for $2 \cdot 5\text{H}_2\text{O}$: $\text{C}_{70}\text{H}_{130}\text{N}_2\text{O}_{32}\text{Mn}_6$, $M = 1841.42$, orthorhombic, $a = 29.406(2)$, $b = 24.651(2)$, $c = 13.1964(9) \text{ \AA}$, $V = 9565(1) \text{ \AA}^3$, $T = -150^\circ\text{C}$, space group $Pnna$ (#52), $Z = 4$, $\mu(\text{Mo K}\alpha) = 8.40 \text{ cm}^{-1}$, $D_{\text{calcd}} = 1.279 \text{ g/cm}^3$, 92203 reflections measured, 10945 unique ($R_{\text{int}} = 0.036$), refinement method: full-matrix least-squares on F^2 . The final R indicates: $R1 = 0.074$ ($I > 2\sigma(I)$), $R = 0.139$ and $wR2 = 0.241$ (all data), and GOF = 1.04.
- 13 Magnetic studies for **1** and similar Mn_6 compounds indicated that the presumable local exchanges within the cluster were all antiferromagnetic to converge to $S_T = 0$ ground state. See ref. 10 and A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson, and G. Christou, *Inorg. Chem.*, **28**, 1915 (1989).
- 14 W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, and G. Christou, *Nature*, **416**, 406 (2002). In that paper, exchange-biased quantum tunnelling derived from a dimerized SMMs having inter-cluster interaction is described.