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A Mn_{12} Single-Molecule Magnet $[Mn_{12}O_{12}(OAc)_{12}(dpp)_4]$ (dppH = Diphenyl Phosphate) with No Coordinating Water Molecules

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The preparation and physical characterization are reported for a novel single-molecule magnet $[Mn_{12}O_{12}(OAc)_{12}(dpp)_4]$ (dppH = diphenyl phosphate) with no coordinating water molecules. The crystal structure analysis reveals that there are four five-coordinate Mn^{III} ions with $Mn\cdots H$ approaches. Addition of water in CD_2Cl_2 solution was monitored by ^1H NMR, which showed that H_2O could coordinate to a vacant site of a five-coordinate Mn^{III} ion in solution. The measurements and analyses of magnetization hysteresis and ac magnetic susceptibility indicate that the title complex is a single-molecule magnet with a quantum tunneling behavior, whose ground state was tentatively assigned to $S = 10$ with $g = 1.78$ and $D = -0.60$ K.

Single-molecule magnets (SMMs) provide a tantalizing glimpse of the future possibilities for data storage technology because of both the slow relaxation of the magnetization with a magnetic hysteresis and the quantum tunneling of magnetization.[1] The combination of a large ground-state spin (S) value and an Ising (easy-axis) type of magnetic anisotropy (negative zero-field splitting parameter, D), which leads to an energy barrier U ($=S^2|D|$) for the reorientation of the magnetic moment, is the essential feature for a molecule to function as an SMM. A twelve-nucleus manganese complex $[Mn_{12}O_{12}(OAc)_{16}(H_2O)_4]$ (Mn_{12}-ac) is one of the most extensively studied SMMs with the largest energy barrier of 66 K due to its $S = 10$ ground state and a large negative D parameter.[2] Chemical modifications so far done for this complex include substitutions of bridging acetates to other carboxylates[1,3] and partial substitutions of a peripheral Mn^{III} ion to an Fe^{III} ion[4a] or a Cr^{III} ion.[4b] A substitution of carboxylate anions to non-carboxylate oxo anions such as NO_3^-, RSO_3^-, and $R_2PO_2^-$ would expand the possibility of the chemical modification in Mn_{12} complexes.[5] Although most Mn_{12} complexes have four coordinating water molecules, only a few examples[6] are known to have three or two coordinating water molecules. Herein, we report a

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(1) (a) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (b) Sessoli, R.; Tsai, H.-L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804. (c) Wernsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature* **2002**, *416*, 406. (d) Coronado, E.; Palacio, F.; Veciana, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 2570. (e) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.

(2) Mirebeau, I.; Hennion, M.; Casalta, H.; Andres, H.; Gudel, H. U.; Irodova, A. V.; Caneschi, A. *Phys. Rev. Lett.* **1999**, *83*, 628.

(3) (a) Eppley, H. J.; Tsai, H.-L.; Vries, N. D.; Folting, K.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 301. (b) Kuroda-Sowa, T.; Nogami, T.; Maekawa, M.; Munakata, M., *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 179. (c) Kuroda-Sowa, T.; Lam, M.; Rheingold, A. L.; Frommen, C.; Reiff, W. M.; Nakano, M.; Yoo, J.; Maniero, A. L.; Brunel, L.-C.; Christou, G.; Hendrickson, D. N., *Inorg. Chem.* **2001**, *40*, 6469. (d) Aubin, S. M. J.; Wemple, M. W.; Adams, D. A.; Tsai, H.-L.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 7746. (e) Soler, M.; Wernsdorfer, W.; Abboud, K. A.; Huffman, J. C.; Davidson, E, R.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2003**, *125*, 3576. (f) Kuroda-Sowa, T.; Nogami, T.; Konaka, H.; Maekawa, M.; Munakata, M.; Miyasaka, H.; Yamashita, M. *Polyhedron* **2003**, *22*, 1795.

(4) (a) Schake, A. R.; Tsai, H. L.; Vires, N. D.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1992**,181. (b) Li, J. Y.; Xu, H.; Zou, J. Z.; Xu, Z.; You, X. Z.; Yu, K. B. *Polyhedron* **1996**, *15*, 3325.

(5) (a) Artus, P.; Boskovic, C.; Yoo, J.; Streib, W. E.; Brune, L. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **2001**, *40*, 4199. (b) Boskovic, C.; Pink, M.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2001**, *123*, 9914. (c) Kuroda-Sowa, T.; Fukuda, S.; Miyoshi, S.; Maekawa, M.; Munakata, M.; Miyasaka, H.; Yamashita, M. *Chem. Lett.* **2002**, 682. (d) Chakov, N. E.; Wernsdorfer, W.; Abboud, K. A.; Hendrickson, D. N.; Christou, G. *Dalton Trans.* **2003**, 2243. (e) Kuroda-Sowa, T.; Handa, T.; Kotera, T.; Maekawa, M.; Munakata, M.; Miyasaka, H.; Yamashita, M. *Chem. Lett.* **2004**, *33*, 540.

(6) (a) Following is a list of Mn_{12} complexes with three or two coordinating water molecules known so far: $[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_3]\cdot 4H_2O$,[3a] $[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_3]$,[6b] $(PPh_4)[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$,[6c] $(PPh_4)_2[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$,[6d] and $(PPh_4)[Mn_{12}O_{12}(O_2CC_4H_3S)_{16}(H_2O)_2]$.[3c] (b) Aubin, S. M. J.; Sun, Z. M.; Eppley, H. J.; Rumberger, E. M.; Guzei, I. A.; Folting, K.; Gantzel, P. K.; Rheingold, A, L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **2001**, *40*, 2127. (c) Tsai, H. L.; Jwo, T. Y.; Lee, G. H.; Wang, Y. *Chem. Lett.* **2000**, 346. (d) Soler, M.; Chandra, S. K.; Ruiz, D.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2001**, *20*, 1279.

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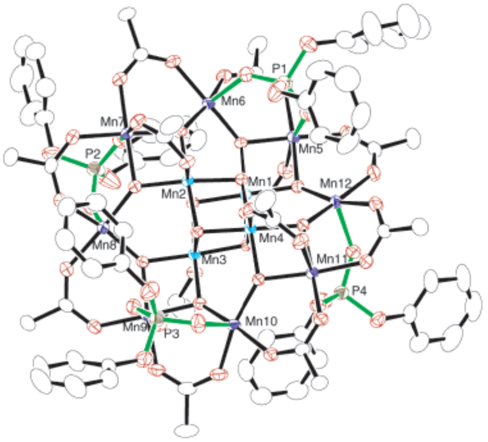

Figure 1. An ORTEP drawing of a molecular structure of complex **1**, with the atom numbering scheme for selected atoms. Four Mn^{III} ions, Mn6, Mn8, Mn10, and Mn12, show five-coordination. Hydrogen atoms are omitted for clarity.

structure of a novel Mn_{12} derivative with diphenylphosphate bridges, which shows the presence of four five-coordinate Mn^{III} centers with no coordinating water molecules.

The title complex was obtained from the reaction of Mn_{12}-ac with 4 equiv of dppH in CH_3CN followed by a vacuum distillation of the azeotrope of acetic acid and toluene. Crystallization from CH_2Cl_2/hexanes yields black block crystals of $[Mn_{12}O_{12}(OAc)_{12}(dpp)_4]$ (**1**). Single-crystal X-ray structure analysis[7] revealed that **1** crystallizes in the monoclinic space group $P2_1/n$. The structure of **1** is shown in Figure 1 together with the atom numbering scheme for some selected atoms. The most interesting feature of this complex is the absence of any coordinating water molecules. This is the first observation in Mn_{12} complexes so far reported. The central $[Mn^{IV}_4O_4]^{8+}$ cubane and the outer ring of eight Mn^{III} ions are connected by eight μ_3-O^{2-} bridges. The eight Mn^{III} ions can be divided into two groups: four Mn^{III} ions with six-coordination and four Mn^{III} ions with square pyramidal five-coordination, which are arranged alternately. The peripheral bridging ligands are categorized in three groups. They are eight equatorial acetates, four axial acetates, and four axial phosphates. The axial acetate groups are bridging Mn^{IV} and Mn^{III} ions whereas the phosphates are bridging two types of Mn^{III} ions with alternating up and down positions similar to $[Mn_{12}O_{12}(O_2CPh)_{12}(dpp)_4(H_2O)_4]$ (**2**).[5c] Each Mn^{III} ion in square pyramidal coordination is located about 0.2 Å above from the basal plane toward the apical oxygen atom. It should be noted that one phenoxy hydrogen atom of each dpp ligand is located near the vacant site of each five-coordinate Mn^{III} ion, as if it blocked water coordination. Those Mn···H distances are 3.373, 3.490, 3.170, and 3.158 Å for Mn6, Mn8, Mn10, and Mn12, respectively. This situation is different from the case of **2**, where all phenoxy groups of dpp are directed to the outside of the molecule.

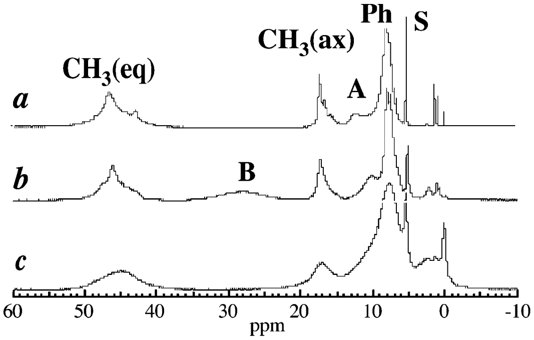

Figure 2. The ^1H NMR spectra of complex **1** in CD_2Cl_2 during addition of water: (a) initial, (b) after addition of a small amount of H_2O, and (c) after a subsequent addition of a small amount of D_2O.

The ^1H NMR spectrum of **1** in CD_2Cl_2 is shown in Figure 2a. A broad signal **A** at 12.2 ppm was observed together with CH_3 (equatorial) protons (40−50 ppm), CH_3 (axial) protons (15−18 ppm), and phenyl protons (6−10 ppm). When a small amount of H_2O was added (Figure 2b), a broad signal **B** due to coordinated water protons appeared at 28.5 ppm and the signal **A** shifted to higher field (10.3 ppm). A subsequent addition of a small amount of D_2O induced a disappearance of the signal **B** and a coalescence of the signal **A** into phenyl protons (Figure 2c). These observations suggest that the signal **A** is due to a part of phenyl protons in the vicinity of Mn^{III} vacant sites, which are affected by the water coordination. Changes in the spectral features of both CH_3 protons during the addition of water together with the observation of the signal **A** indicate that at least one phenoxy group of each dpp is almost fixed near the Mn^{III} vacant site during the NMR time scale. This is the first observation of a Mn_{12} complex with stable vacant sites on Mn^{III} ions in solution, which implies that **1** is a good candidate for a building block to form an assemblage of a Mn_{12} SMM.

The magnetic susceptibility of a crystalline sample of **1** was measured at four frequencies (25−997 Hz) for the temperature range of 1.7−10.0 K. As expected for SMM, **1** shows frequency-dependent ac out-of-phase signals as shown in Figure 3. The frequency-dependence of the χ''_M peak temperature can be analyzed by the Arrhenius equation[1] to give the effective energy barrier (U_{eff}) for the reversal of the magnetization spin, which was estimated to be 62.5 K. In order to determine S and D values, magnetization data $M/(N\mu_B)$ were collected for a sample fixed with an eicosane matrix under a 2−7 T field at temperatures between 1.9 and 4.5 K. The observed data were fitted with a magnetization fitting program "axfit"[8] assuming an $S = 10$ ground state. The lines in Figure 4 show the best fit for an $S = 10$ ground state with the parameters of $g = 1.78$ and $D = -0.60$ K. Although a fit with a similar quality was also obtained by using $g = 1.98$ and $D = -0.74$ K assuming an $S = 9$ ground state, this possibility might be excluded because the largest $|D|$ value of 0.74 K so far reported for Mn_{12} complexes is somewhat mysterious for **1** containing four five-coordinate

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(7) Crystal data for $\mathbf{1}\cdot 6.1CH_2Cl_2\cdot 0.4H_2O$: $C_{78.1}H_{89.0}Cl_{12.2}Mn_{12}O_{52.4}P_4$, 3081.81 g mol^{-1}, monoclinic, $P2_1/n$, $a = 14.8881(7)$ Å, $b = 29.168(1)$ Å, $c = 27.426(1)$ Å, $\beta = 94.468(3)°$, $Z = 4$, $V = 11873.8(10)$ Å^3, $D_{calc} = 1.724$ g cm^{-3}, $T = -123$ °C. The structure was solved by direct methods (SHELXS-97) and refined (on F) using 23234 observed reflections with ($I > 2\sigma(I)$) to R (R_w) values of 0.073 (0.168).

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

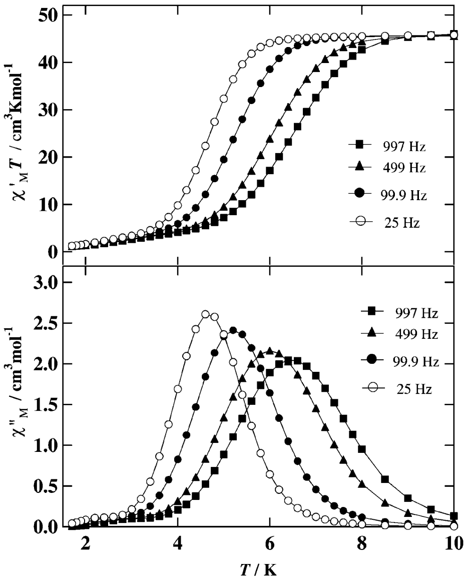

Figure 3. Plots of $\chi'_M T$ vs T (top) and χ''_M vs T (bottom) for a polycrystalline sample of complex **1** in a 0.3 mT ac field oscillating at the indicated frequencies, where χ'_M and χ''_M are the in-phase and the out-of-phase magnetic susceptibilities, respectively.

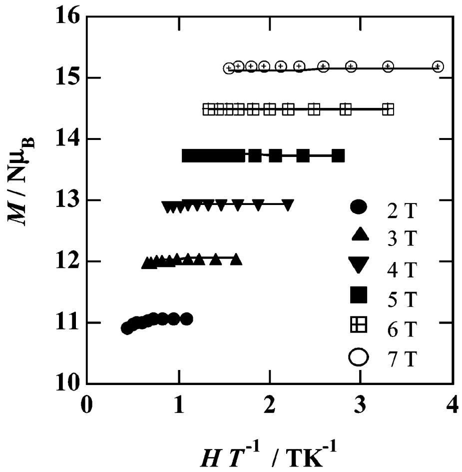

Figure 4. Reduced magnetization data for **1** with different external fields. Lines show the best fit assuming $S = 10$, $g = 1.78$, and $D = -0.60$ K.

Mn^{III} ions. Our model calculations using the AOM method[9] showed that a single ion $|D|$ value for a five-coordinate Mn^{III} ion (2.0 cm^{-1}) is clearly smaller than those for six-coordinate Mn^{III} ions (2.3−3.2 cm^{-1}). HF-EPR measurements will give a more definitive conclusion.

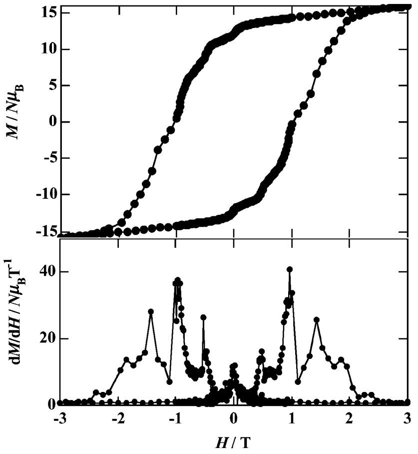

Figure 5. A magnetization hysteresis loop for oriented crystals of **1** in an eicosane matrix measured at 1.9 K (top) and the corresponding first derivatives dM/dH (bottom).

The magnetization hysteresis loop measured for the field-oriented single crystals of **1** at 1.9 K is shown in Figure 5. The magnetization saturates completely at fields above 2.3 T to ca. 16$N\mu_B$. Hysteresis is seen with a coercive field of 1.0 T. In the bottom of Figure 5 is shown the first derivative of the hysteresis plot. As the field is decreased from +3 T, the first step can be seen at zero field, followed by steps at −0.49, −0.98, −1.43, and −2.38 T. The steps correspond to increases in the rate of the change of the magnetization, and are attributable to resonant tunnelings between quantum spin states.[10]

In conclusion, we have carried out the characterization of the first Mn$_{12}$ derivative with no coordinating waters. The crystal structure analysis indicates that there are four five-coordinate Mn^{III} ions with Mn···H approaches at the vacant sites. The magnetic susceptibility and magnetization hysteresis of this complex reveal that it is an SMM and show the quantum magnetization tunneling behavior.

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Supporting Information Available: Crystallographic data for **1** in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) A program ZAOM was used for calculation. AOM parameters were adopted from the following paper. (b) Cornia, A.; Sessoli, R.; Gatteschi, D.; Barra, A. L.; Daiguebonne, C. *Phys. Rev. Lett.* **2002**, *89*, 257201.

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