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A High-Spin Cyanide-Bridged Mn$_9$W$_6$ Cluster ($S = {}^{39}/_2$) with a Full-Capped Cubane Structure

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The design and synthesis of new molecule-based magnetic materials have become one of the most active areas in the molecular material chemistry.[2−8] One of the attractive targets in this field is to obtain tunable magnetic materials, with which magnetic properties can be controlled by external stimuli such as light.[9,10] Hexacyanometalate $[M(CN)_6]^{n-}$ is often used as a molecular building block for this purpose[9] as well as for obtaining high T_c molecule-based magnets.[11] Another current topic in this field is the so-called "single-molecule magnet" composed of a large metal cluster. There is an ongoing interest in this field for nanoscale magnetic materials, mainly stimulated by the potential high-density memory devices and unusual physcial properties such as quantum tunneling of the magnetization.[12] The most throughly studied example is a Mn$_{12}$ cluster, $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$.[13] This has been shown to function as a single-molecule magnet below a critical blocking temperature of 3 K, showing a hysteresis loop with quantum steps. This phenomenon is explained by the existence of a large energy barrier between the up- and down-spin states due to the high-spin multiplicity ($S = 10$) and strong uniaxial magnetic anisotropy (D).[14] Here the potential energy barrier is expressed as $|D|S^2$ and $|D|(S^2 - 1/4)$ for integer S and half integer S respectively in zero field according to the Hamiltonian $H = -DS_z^2 + g\mu_B S_z H_z$. So far, only a few molecular clusters with spin values as high as double figures have been reported. Besides the above example, a ground $S = 10$ state has also been proven for an Fe$^{III}_8$ cluster,[15] $S = 11$ for a Mn$^{II}_4$-Mn$^{III}_3$ cluster,[16] $S = 12$ for a Mn$^{III}_6$ or a Mn^{II}-radical$_6$ ring cluster and for a T_d symmetrical Mn$^{III}_6$ cluster,[17] $S = {}^{27}/_2$ for a CN bridged Mn$^{II}_6$Cr^{III} cluster,[18] $S = 14$ for a Mn$^{II}_6$Mn$^{III}_4$ cluster,[19] and $S = {}^{33}/_2$ for one of the clusters of cocrystallizing Fe$^{III}_{17}$ and Fe$^{III}_{19}$ species.[20] In this paper we demonstrate a new Mn$^{II}_9$W$^V_6$ cluster with a ground-state $S = {}^{39}/_2$, the highest to date.

The title complex $\{Mn_9[W(CN)_8]_6\cdot 24C_2H_5OH\}\cdot 12C_2H_5OH$ (**1**) was prepared by the reaction of 1 equiv of octacyanometalate $(HBu_3N)_3[W(CN)_8]$ (Bu_3N = tributylamine)[21] with 1.5 equiv of $Mn(ClO_4)_2\cdot 6H_2O$ in ethanol solution. A red-brown crystalline solid suitable for X-ray structure analysis was obtained after several days.[22] The crystal is highly efflorescent so that covering with liquid paraffin or sealing with a saturated solution of **1** in a glass capillary is necessary for physcial measurements.

The crystal consists of cyanide-bridged Mn$^{II}_9$W$^V_6$ units and ethanol molecules as crystal solvate. The structure of the centrosymmetric Mn$_9$W$_6$ unit is shown in Figure 1a. Eight Mn atoms are located at the eight corners of a distorted cubane and the remaining Mn1 atom at the center of the cubane, which is superimposed at the inversion center. A $[W(CN)_8]^{3-}$ unit spreads over each face of the cubane to function as a μ_5-bridge to link four Mn atoms at the corners and the central Mn 1 atom through its five CN groups, with the three remaining CN groups facing out. This is the first example of the so-called "full-capped cubane". A crystallographically imposed 3-fold axis runs through the center and Mn2, so that the cluster has an S_6 symmetry and the asymmetric unit consists of $^1/_6$ of the Mn$_9$W$_6$ unit (Figure 1b). The six $[W(CN)_8]^{3-}$ are equivalent and exhibit a geometry close to a bicapped trigonal prism. Conversely, three different Mn sites exist in this structure. The geometry of the central Mn1 is close to an octahedron with an N$_6$ donor set coming from μ-CN groups; both of Mn2 and Mn3 have a distorted octahedron with an N$_3$O$_3$ donor set, coming from three N atoms of μ-CNs and three O atoms from ethanol molecules, but the latter is much distorted due to a large derivation of bond angles (e.g., O2−Mn3−O3 = 80.2°) from the ideal 90°. The diameter of the cluster is about 17.5 Å, while the shortest inter-cluster contact between metal ions is 7.1 Å.

Magnetic susceptibities were measured in the temperature range of 1.9−300 K (Figure 2a). The sample was blocked at low temperature due to the use of liquid paraffin. The $\chi_m T$ at 300 K is 31.84 (cm^3 K mol^{-1}), smaller than the value (41.63) of the

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[2] Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

[3] Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385.

[4] Gatteschi, D. et al. *Magnetic Molecular Materials*; Kluwer: Dordrecht, 1991.

[5] Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiwa, N.; Hashimoto, Y.; Okawa, H. *J. Am. Chem. Soc.* **1992**, *114*, 6974.

[6] Mallah, T.; Thiebaut, S.; Verdaguer, M.; Veillet, P. *Science* **1993**, *262*, 1554.

[7] William, R. E.; Girolami, G. S. *Inorg. Chem.* **1994**, *33*, 5165.

[8] Ohkoshi, S.; Fujishima, K.; Hashimoto, K. *J. Am. Chem. Soc.* **1998**, *120*, 5349.

[9] (a) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (b) Ohkoshi, S.; Yorozu; S.; Sato, O.; Iyoda, T.; Fujishima, K.; Hashimoto, K. *Appl. Phys. Lett.* **1997**, *70*, 1040.

[10] Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024.

[11] Ferlay, S.; Mallah, T.; Quahes, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 701.

[12] (a) Awschalom, D. D.; Di Vicenzo, D. P. *Phys. Today* **1995**, *48*, 43. (b) Dahlberg, E. D.; Zhu, J.-G. *Phys. Today* **1995**, *48*, 34.

[13] (a) 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. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141. (c) Thomas, L.; Lionti, F.; Ballou, R.; Gatteschi, D.; Sessoli, R.; Babara, B. *Nature* **1996**, *383*, 145.

[14] Aubin, S. M. J.; Dilley, N. R.; Pardi, L.; Krzystek, J.; Wemple, M. W.; Brunel, L.-C.; Maple, M. B.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 4991.

[15] Barra, A. L.; Debrunner, P.; Gatteschi, D.; Schultz, C. E.; Sessoli, R. *Europhys. Lett.* **1996**, *35*, 133.

[16] Pilawa, B.; Kelemen, M. T.; Wanka, S.; Geisselmann, A.; Barra, A. L. *Europhys. Lett.* **1998**, *43*, 7.

[17] (a) Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1998**, *37*, 1430. (b) Caneschi, A.; Gatteschi, D.; Laugier, J.; Rey, P.; Sessoli, R.; Zanchini, C. *J. Am. Chem. Soc.* **1988**, *110*, 2759. (c) Aromi, G.; Claude, J.-P.; Knapp, M. J.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1998**, *120*, 2977.

[18] Scuillier, A.; Mallah, T.; Verdaguer, M.; Nivorozkhin; Tholence, J. L.; Veillet, P. *New J. Chem.* **1996**, *20*, 1.

[19] Goldberg, D. P.; Caneschi, A.; Delfs, C. D.; Sessoli, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 5789.

[20] Powell, A. K.; Heath. S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Giallo, F. D.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491.

[21] Leipoldt, J. G.; Bok, L. D. C.; Cilliers, P. J. *Z. Anorg. Allg. Chem.* **1974**, *407*, 350.

[22] Crystal data for $\{Mn_9[W(CN)_8]_6\cdot 24C_2H_5OH\}\cdot 12C_2H_5OH$: $C_{120}H_{216}N_{48}O_{36}Mn_9W_6$, fw = 4504.87; trigonal; space group $R\bar{3}$; a = 26.086(2) Å, c = 26.346 Å; V= 15526(2) Å^3; Z = 3; d_{calcd} = 1.445 g/cm^3; T =296 (1) K. The structure was solved by the heavy-atom Patterson methods and refined on F to $R(R_w)$= 0.047 (0.043) using 2513 reflections with $I > 3.00\ \sigma(I)$. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included at calculated positions. All calculations were performed using the teXan crystallographic software package of Molecular Structure Corporation.

[23] Castro, S. L.; Sun, Z.; Grant, C. M.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1998**, *120*, 2365.

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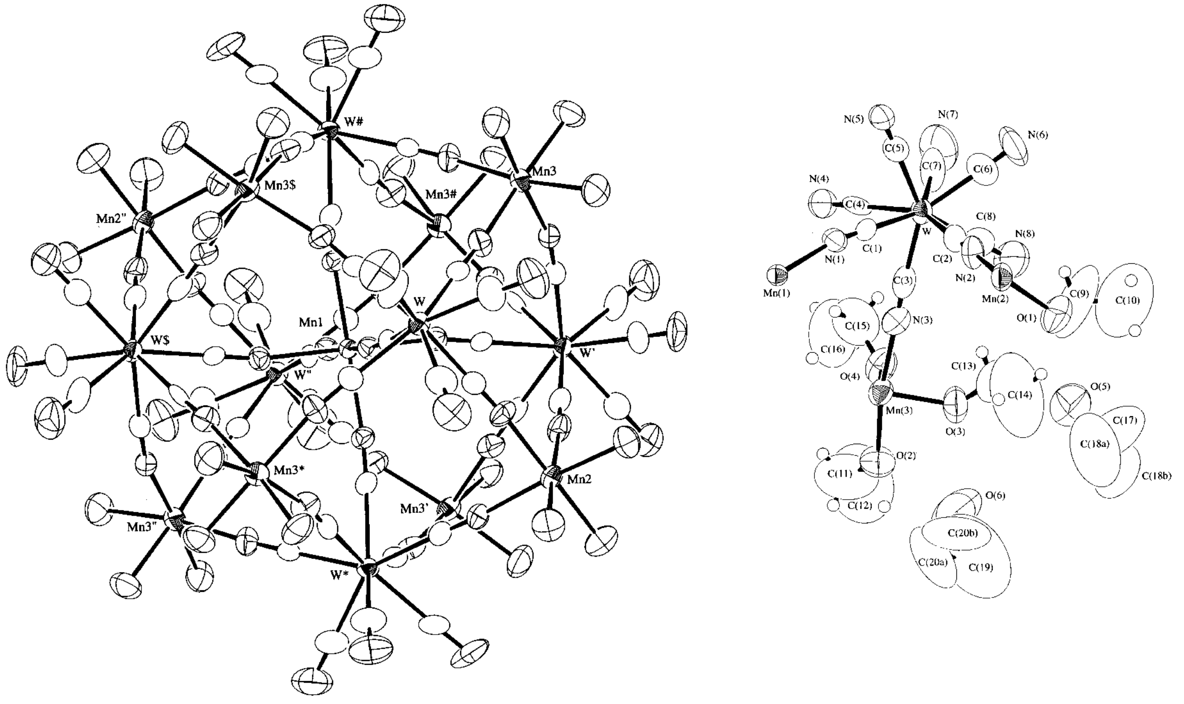

Figure 1. (a) Molecular structure of $\{Mn_9[W(CN)_8]_6\cdot24C_2H_5OH\}$ (The hydrogen atoms and carbon atoms of ethanol molecules are omitted for clarity). Selected distances (Å): Mn2−Mn3, 7.492(4); Mn2−Mn3′, 7.492(4); Mn2−Mn3*, 7.492(4);Mn3−Mn3, 7.085(4); Mn3−Mn3′, 7.085(4); Mn3−Mn3#, 7.085(4); Mn3#−Mn3$, 7.085(4); Mn1−Mn2, 6.590(4); Mn1−Mn3, 6.214(3); Mn1−W, 5.476(1); Mn2−W, 5.481(2); Mn3−W, 5.508(3); Mn3−W′, 5.420(2); Mn3−W#, 5.472(3); W−W′, 7.581(1); W−W*, 7.581(1); W−W#, 7.905(1); W−W$, 7.905(1). (b) The asymmetric unit of **1**.

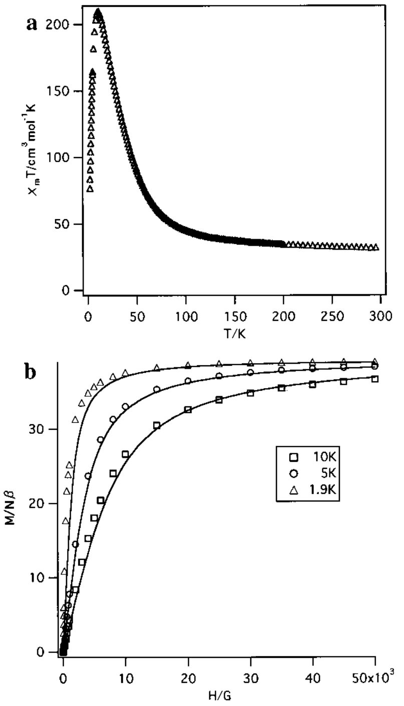

Figure 2. (a) Temperature dependence of $\chi_m T$ for **1** at an external field of 5000 G**.** (b) Field dependence of the magnetization of **1** at the indicated temperatures. The solid lines were theoretically calculated with Brillouin functions for a $S = {}^{39}/_{2}$ state with $g = 2.0$.

uncoupled nine Mn^{II} ($S = {}^{5}/_{2}$) ions and six W^{V} ($S = {}^{1}/_{2}$) ions, suggesting the presence of an appreciable antiferromagnetic interaction. On cooling it increased rapidly below 50 K to a maximum of 209.9 at 11 K and then decreased to 76.86 at 1.9 K. The maximum may be comparable with 200.0 for an $S = {}^{39}/_{2}$ state. The field dependence of the magnetization at 1.9, 5, and 10 K are shown in Figure 2b. The data agree with the Brillouin functions for an $S = {}^{39}/_{2}$ state with $g = 2.00$, although slightly larger error is seen in the case of 1.9 K.This may be because the *D* value is so small that it is only efficacious at very low temperature. The spin value *S* is just equal to the value where all of the Mn^{II} atoms are antiparallel with all of the W^{V} atoms ($S = 9S_{Mn} - 6S_{W} = {}^{39}/_{2}$). All of these data show the formation of the $S = {}^{39}/_{2}$ ground state due to the $Mn^{II}-W^{V}$ antiferromagntic couping through the CN bridges. To our knowledge, this is the largest spin multiplicity among the molecular clusters reported so far. The AC susceptibility data were collected in the 1.9−20 K range with zero DC field and a 1.0 G AC field oscillating at 50, 250, and 750 Hz. A peak of in-phase AC susceptibility χ' was observed at 2.2 K, and the out-of-phase AC susceptibility χ'' appeared and showed a rapid increase below about 2.5 K, indicative of slow relaxation of the magnetization.[14] In addition, it was frequency-dependent. This may be a signature of a single-molecule magnet. Since no χ'' peak was observed to 1.9 K, the blocking temperature is suggested to be lower than 1.9 K despite the large spin value. It may be due to the small anisotropy of the Mn^{II} ion and the high symmetry of the cluster, leading to a small $|D|$value.

In conclusion, a new type of spin cluster $\{Mn_9[W(CN)_8]_6\}$ with a novel full-capped cubane structure has been prepared and shown to have the largest spin value $S = {}^{39}/_{2}$ ground state. The work provides a simple way to a big spin cluster starting from octacyanometalates. Since it is not necessary to consider a spin frustration in this type of clusters, it would be possible to design and control the spin multiplicity *S* by selecting the constituent metal ions. The anisotropic factor *D* could be also controlled to some extent by introducing anisotropic metal ions and lowering the symmetry of cluster (e.g., by partial substution of metal ions). Therefore, the cluster can be a useful prototype for designing asingle-molecule magnet. Further studies are currently in progress along this line.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1** (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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