

DOI: 10.1002/ange.200601467

A Ferromagnetically Coupled Mn₁₉ Aggregate with a Record $S = 83/2$ Ground Spin State**

Ayuk M. Ako, Ian J. Hewitt, Valeriu Mereacre,
Rodolphe Clérac, Wolfgang Wernsdorfer,
Christopher E. Anson, and Annie K. Powell*

*Dedicated to Professor Hansgeorg Schnöckel
on the occasion of his 65th birthday.*

The first evidence of single molecule magnet (SMM) behavior was discovered in the mixed-valence compounds $[\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ ($\text{R} = \text{Ph}, \text{Me}$), which possess the structural motif originally reported by Lis for $\text{R} = \text{Me}$ in 1980.^[1] In the quest to synthesize SMMs that show hysteresis at higher temperatures, it has been recognized that large ground-state spins and a uniaxial anisotropy (large negative D and small E considering the following Hamiltonian anisotropy term: $H = DS_z^2 + E(S_x^2 - S_y^2)$) are required.^[1c,2,3] It is thus of interest to discover how to obtain the largest-spin ground state possible for a given size of aggregate. As well as having four unpaired electrons in its high-spin state, the Mn^{III} ion is particularly useful for introducing large anisotropies through the presence of Jahn–Teller distortions in this configuration and has been the most thoroughly studied candidate for synthesizing new SMMs. Amongst the large number of aggregates containing manganese(III) in the literature, a Mn_{25} cluster has been reported as having a ground spin state of $51/2$.^[4] Herein we report on the realization of the maximum-spin ground state of $83/2$ for the aggregate $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8(\mu_3\eta^1\text{-N}_3)_8(\text{HL})_{12}(\text{MeCN})_6]\text{Cl}_2 \cdot 10\text{MeOH} \cdot \text{MeCN}$ (**1**; $\text{H}_3\text{L} = 2,6\text{-bis}(\text{hydroxymethyl})\text{-4-methylphenol}$).

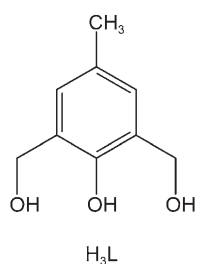
[*] Dr. A. M. Ako, Dr. I. J. Hewitt, Dr. V. Mereacre, Dr. C. E. Anson,
Prof. A. K. Powell
Institut für Anorganische Chemie der Universität Karlsruhe
Engesserstrasse Geb. 30.45, 76128 Karlsruhe (Germany)
Fax: (+49) 721-608-8142
E-mail: powell@chemie.uni-karlsruhe.de

Dr. R. Clérac
Centre de Recherche Paul Pascal
CNRS–UPR 8641
115 Avenue Dr. A. Schweitzer, 33600 Pessac (France)
Dr. W. Wernsdorfer
Laboratoire Louis Néel–CNRS, BP 166
25 Avenue des Martyrs, 38042 Grenoble Cedex 9 (France)

[**] This work was supported by Bordeaux 1 University, the CNRS, the Region Aquitaine, the DFG (SPP 1137 and the Center for Functional Nanostructures), QuEMolNa (MRTN-CT2003-504880), MAGMA-Net (NMP3-CT-2005-515767), and the Alexander von Humboldt Foundation.



Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



The crystal structure of compound **1** (Figure 1) reveals that the aggregate is mixed-valent and contains seven Mn^{II} centers and twelve Mn^{III} centers, as derived from the metric parameters and BVS (bond valence sum) calculations.^[5] The core of compound **1** (Figure 2a) can be described as being based on two Mn_9 fragments that are linked through a central Mn^{II} center, Mn1 ,

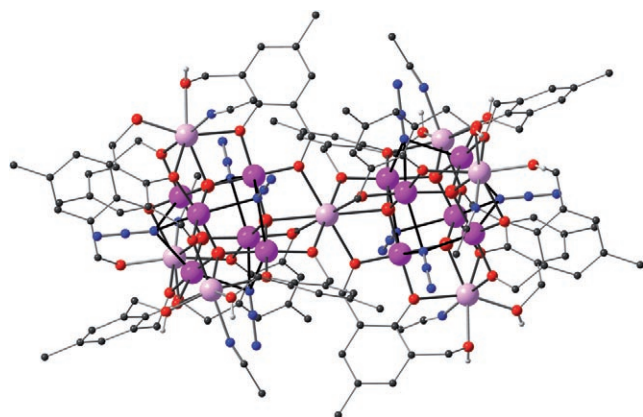


Figure 1. Molecular structure of **1** in the crystal (Mn^{III} dark pink, Mn^{II} pale pink, O red, N blue, C gray, H white). Carbon-bound hydrogen atoms and noncoordinated solvent molecules have been omitted for clarity.

which is coordinated to six $\mu\text{-O}$ and two $\mu_4\text{-O}$ donor atoms. Each half of the molecule is derived from an almost perfect cube in which the vertices consist alternately of Mn^{II} centers and central N atoms of the terminally coordinating $\mu_3\text{-N}_3$ units. Thus, the Mn^{II} centers define a tetrahedron in each half. At the center of each of the faces of the cube there is a Mn^{III} center defining an octahedron such that the faces of the octahedron are capped alternately by $\mu_3\text{-N}_3$ and $\mu_4\text{-O}$ ligands, the latter of which is linked to the Mn^{II} centers. Closer inspection of the Mn^{III} geometries reveals that the Jahn–Teller elongation axes are those involving the two azido ligands (Figure 2b,c) which result in a trigonal arrangement for each Mn^{III} octahedron. The resulting nanosized particle has a structural arrangement corresponding to that found in Chevrel phases.^[6]

The magnetic properties were measured on a polycrystalline sample of **1**. At room temperature, the $\chi'T$ product (Figure 3a) is $93\text{ cm}^3\text{ K mol}^{-1}$, which is higher than the expected value ($66.625\text{ cm}^3\text{ K mol}^{-1}$ taking $g_{\text{av}} = 2$) for twelve Mn^{III} centers ($S = 2$) and seven Mn^{II} centers ($S = 5/2$). Owing to the large magnetic susceptibility of the molecule and in order to stay below the upper limit of detection of our SQUID magnetometer, the mass of the sample had to be decreased from 17.79 mg to 6.38 mg, and the temperature dependence of susceptibility had to be measured in zero field by using the ac technique. On decreasing the temperature, the $\chi'T$ product continuously increases to reach $894\text{ cm}^3\text{ K mol}^{-1}$ at 1.8 K, thus indicating dominant ferromagnetic interactions in the poly-

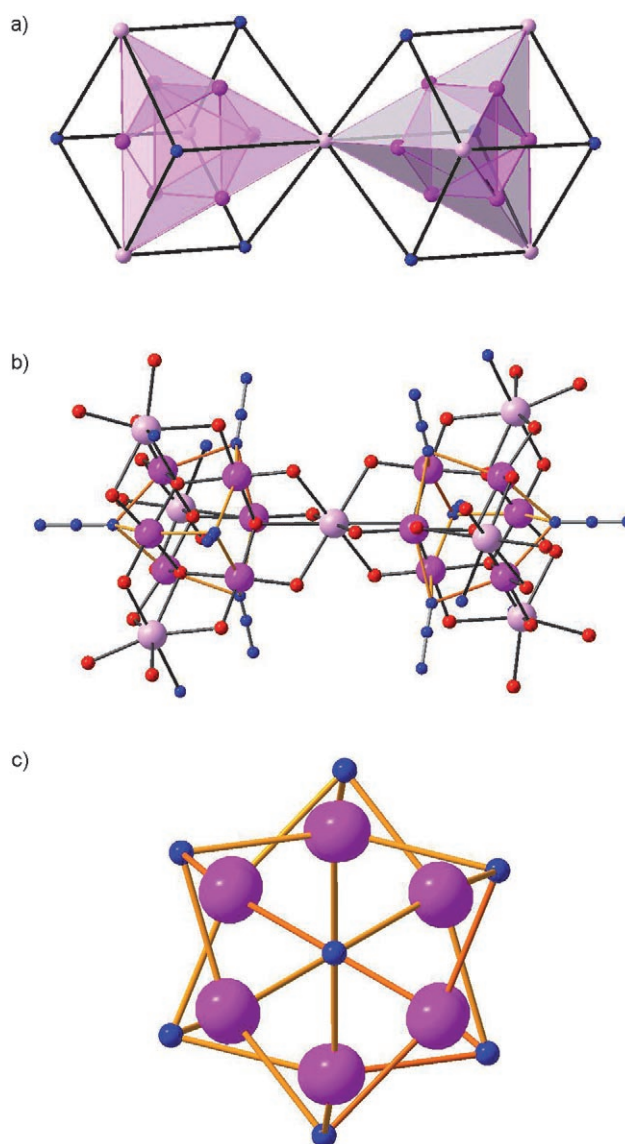


Figure 2. a) Polyhedral representation of the core of **1** with emphasis on the cubic-derived symmetry (same color scheme as above). b) Highlighted Jahn–Teller axes (yellow) on the Mn^{III} centers within the core. c) The trigonal arrangement of the Jahn–Teller axes as viewed along the crystallographic c axis.

nuclear complex. This value is close to the one expected when all the spins composing the Mn aggregate are parallel, thus for a ground spin state of $S_T = 83/2$ ($881.875\text{ cm}^3\text{ K mol}^{-1}$ taking $g_{\text{av}} = 2$). The presence of strong ferromagnetic interactions easily explains the high $\chi'T$ product at room temperature. Indeed, this unusually large magnetic susceptibility allows crystals of **1** to be moved easily at room temperature by using only a simple permanent magnet of 0.35 T. At 1.8 K, the field dependence of the magnetization saturates very fast above 1.5 T to reach about $84.5\text{ }\mu_{\text{B}}$ (inset of Figure 3a), a value in good agreement with the expected value of $83\text{ }\mu_{\text{B}}$ (with $g_{\text{av}} = 2$) for a ground spin state of $S_T = 83/2$. At this temperature, the linear part of the plot of M versus H does not exceed 300 Oe, thus justifying the use of the ac technique.

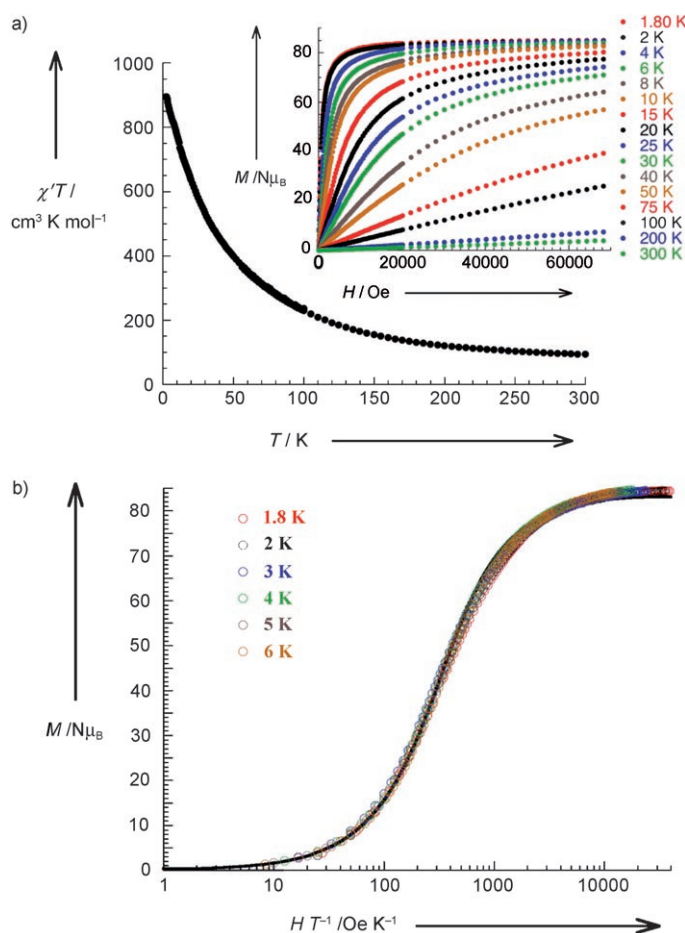


Figure 3. a) Temperature dependence of the $\chi'T$ product (where $\chi' = dM/dH$) measured in $H_{ac} = 0$ Oe, $H_{dc} = 3$ Oe, and $\nu = 100$ Hz (inset: field dependence of the magnetization from 1.8 K to 300 K). b) Semilogarithmic M versus H/T plot with data between 1.8 and 6 K; the solid line is the best fit obtained with an $S = 83/2$ Brillouin function.

At high field, the magnetization is fully saturated and no slope is observed, which proves the absence of significant anisotropy in the material. The ferromagnetic exchange energies thus seem to be much higher than the local anisotropic energies, forcing the spins to be parallel. Moreover, the presence of isotropic Mn^{II} metal ions and the triangular geometrical arrangement of the Mn^{III} centers probably make a significant contribution to the minimization of the magnetic anisotropy. In agreement with this conclusion, the data below 6 K which are presented as a plot of M versus H/T (Figure 3b) are all superposed on one single master curve. This result indicates that the ground state is essentially the only one populated below this temperature. This interpretation is further confirmed qualitatively by the plot of $\chi'T$ versus T , which is weakly temperature-dependent below 6 K (see the Supporting Information).

In order to prove definitively the unprecedented $S_T = 83/2$ ground spin state, the M versus H/T data below 6 K have been fitted to a Brillouin function. The agreement with the theoretical curve is close to perfect and represents a textbook example of a paramagnetic $S = 83/2$ unit with an average

g value of 2.00(6). Additional field dependences of the magnetization were measured below 1.8 K by using the micro-SQUID technique on single crystals. Below 0.5 K, the magnetization, which is independent of the field orientation, shows hysteresis effects with a coercive field that reaches 300 Oe at 0.04 K (Supporting Information). The two obvious possible sources of the hysteresis are the anisotropy of the Mn^{III} centers which is not completely compensated and the anisotropy of the dipolar interactions that is induced by the nonspherical shape of the molecule. This finding together with the fact that the system also shows relaxation (Supporting Information) suggests that the molecule is, indeed, an SMM but is dramatically influenced by the intermolecular dipolar interactions which are always present in SMM-based materials. However, in conventional SMMs the dipolar coupling energy is much smaller than the anisotropy energy while in compound **1** both energies are probably of the same order of magnitude. The situation is further complicated by the fact that all large molecules have small disorders which give a distribution of easy-axis directions, thus making it impossible to locate the easy axis by using the micro-SQUID technique.

Azido ligands in the terminal μ_3 -bridging mode as in compound **1** are known to favor ferromagnetic interactions,^[7] and the μ_4 -O bridges are likely to mediate weaker interactions.^[8] Thus, the combination of using an organic ligand which can bridge to multiple metal centers and using azido ligands has resulted in a Mn_{19} aggregate that exhibits dominant ferromagnetic interactions with the maximum-spin ground state possible, here 83/2. Achieving such a high ground spin state is clearly one of the elusive goals in the search for obtaining superior SMMs. However, although the Mn^{III} centers in **1** show a high degree of Jahn–Teller distortion, their geometrical arrangement and the strong ferromagnetic interactions between spin carriers lead to a system with a very low anisotropy. The challenge now is to find a means of introducing not only maximum spin but also greater anisotropy. Nevertheless, **1** represents a remarkable milestone in the quest for high-temperature SMMs.

Experimental Section

A solution of NaN_3 (0.2 g, 3 mmol) in MeOH (5 mL) was added with stirring to a slurry of 2,6-dihydroxymethyl-4-methylphenol (1 g, 6 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.4 g, 2 mmol), and NaO_2CMe (0.14 g, 1 mmol) in MeCN (20 mL). After the mixture had been stirred for 1 h at room temperature, the mixture was heated at reflux for 2 h. The resulting dark brown solution was allowed to cool and was filtered. After the solution had been left to stand in a sealed vessel for one week, well-formed black crystals of **1** were obtained. Yield: 350 mg, 40%. Selected IR data (KBr disk): $\tilde{\nu} = 3352$ (b), 2922 (w), 2847 (w), 2062 (s), 1610 (w), 1469 (s), 1251 (m), 1224 (m), 1160 (m), 1026 (m), 989 (m), 863 (m), 810 (m), 634 (b,s), 556 (m), 475 cm^{-1} (w). Compound **1** can also be synthesized by heating the reaction mixture directly after adding NaN_3 , but this procedure results in a lower yield and microcrystalline product. The compound can also be obtained without the addition of NaO_2CMe , but analysis of the resulting crystals showed heavily disordered Cl^- and N_3^- ions, thus making a satisfactory refinement not possible. The two compounds were otherwise isostructural.

Crystal data for **1**: $C_{132}H_{181}Cl_2Mn_{19}N_{31}O_{54}$, $M_r = 4180.84$, rhombohedral, space group $R\bar{3}$, $a = 20.9989(6)$, $c = 34.7489(14)$ Å, $V = 13269.8(8)$ Å³, $T = 100$ K, $Z = 3$, $\mu = 1.418$ mm⁻¹, $F(000) = 6393$, $\rho_{\text{calcd}} = 1.570$ Mg m⁻³, 22436 data measured, 6751 unique ($R_{\text{int}} = 0.0253$), final $wR_2(F^2, \text{all data}) = 0.1283$, $S = 1.036$, $R_1(4991 \text{ with } I > 2\sigma(I)) = 0.0414$. The structure was solved by direct methods and refined by using the SHELXTL program suite.^[9] The two chloride counteranions were refined as disordered over the twelve lattice solvent sites per Mn_{19} cluster to which the ligand OH groups form hydrogen bonds through O5 and O8. CCDC-604216 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The measurements of magnetic susceptibility were obtained with a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on two finely ground crystalline samples of 6.38 and 17.79 mg. Measurements of M versus H were performed at 100 K to check for the presence of ferromagnetic impurities, which were found to be systematically absent. Measurements of ac susceptibility were made with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz without applied dc fields. It is worth noting that the ac susceptibility shows no out-of-phase signal above 1.85 K and no frequency dependence of the in-phase component. The magnetic data were corrected for the sample holder and the diamagnetic contribution which was calculated from Pascal's constants.^[10] Magnetization measurements on single crystals were performed with an array of micro-SQUIDS.^[11] This magnetometer works in the temperature range of 0.04 to ca. 7 K and in fields of up to 0.8 T with sweeping rates as high as 0.28 T s⁻¹, and exhibits field stability of better than μ T. The time resolution is approximately 1 ms. The field can be applied in any direction of the micro-SQUID plane with precision much better than 0.1° by separately driving three orthogonal coils. In order to ensure good thermalization, a single crystal was fixed with apiezon grease.

Received: April 13, 2006

Published online: July 4, 2006

Keywords: cluster compounds · magnetic properties · manganese · molecular magnets · structure elucidation

- Vicente, M. Font-Bardia, X. Solans, S. P. Perlepes, *Chem. Commun.* **2001**, 2414; c) G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans, *Angew. Chem.* **2001**, *113*, 908; *Angew. Chem. Int. Ed.* **2001**, *40*, 894.
- [8] See, for example: C. Dendrinou-Samara, M. Alexiou, C. M. Zaleski, J. W. Kampf, M. L. Kirk, D. P. Kessissoglou, V. L. Pecoraro, *Angew. Chem.* **2003**, *115*, 3893; *Angew. Chem. Int. Ed.* **2003**, *42*, 3763.
- [9] G. M. Sheldrick, SHELXTL 5.1, Bruker AXS, Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA, **1997**.
- [10] *Theory and Applications of Molecular Paramagnetism*, (Eds.: E. A. Boudreaux, L. N. Mulay), Wiley, New York, **1976**.
- [11] W. Wernsdorfer, *Adv. Chem. Phys.* **2001**, *118*, 99.

- [1] a) T. Lis, *Acta Crystallogr. Sect. B* **1980**, *36*, 2042; b) P. D. W. Boyd, Q. Li, J. B. Vincent, K. Folting, H.-R. Chang, W. E. Streib, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1988**, *110*, 8537; c) A. Caneschi, D. Gatteschi, R. Sessoli, *J. Am. Chem. Soc.* **1991**, *113*, 5873; d) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804; e) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141.
- [2] a) G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66; b) D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268; c) M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789.
- [3] G. Aromí, E. K. Brechin, *Struct. Bonding (Berlin)* **2006**, *122*, 1.
- [4] M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 4766.
- [5] W. Liu, H. H. Thorp, *Inorg. Chem.* **1993**, *32*, 4102 and see supplementary data.
- [6] a) R. Chevrel, M. Sergent, J. Prigent, *J. Solid State Chem.* **1971**, *3*, 315; b) T. Hughbanks, R. Hoffman, *J. Am. Chem. Soc.* **1983**, *105*, 1150.
- [7] See, for example: a) G. S. Papaefstathiou, A. Escuer, C. P. Raptopoulou, A. Terzis, S. P. Perlepes, R. Vicente, *Eur. J. Inorg. Chem.* **2001**, 1567; b) G. S. Papaefstathiou, A. Escuer, R.