Single-Molecule Magnets: A Mn$_{25}$ Complex with a Record S = 51/2 Spin for a Molecular Species

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Single-molecule magnets (SMMs) offer a molecular (or “bottom-up”) approach to nanoscale magnetic materials.† They derive their properties from a combination of a large spin (S) and an Ising (easy-axis) magnetooanisotropy (negative zero-field splitting parameter, D). Several classes of SMMs are now known,‡ in most containing Mn$^{III}$, but there is a continuing need for new SMMs to improve our understanding of this phenomenon. We now report a new Mn$_{25}$ SMM, which (i) is mixed-valent 6Mn$^{II}$, 18Mn$^{III}$, Mn$^{IV}$; (ii) has an unusual five-layer structure; and (iii) possesses a record S = 51/2 ground-state spin for a molecular species. In the latter context, this complex is a new addition to the family of high-spin molecules, only some of which are also SMMs; most contain Mn$^{II,III}$ or Fe$^{III}$, and only very few possess S > 10.‡

A stirred slurry of MnCl$_2$
•H$_2$O (3 equiv), pyridine-2,6-dimethanol (pdmH$_2$; 10 equiv), and NaN$_3$ (10 equiv) in MeOH/MeCN (1:2 v/v) was treated with NMe$_4$OH (1 equiv). This gave a dark brown solution from which slowly crystallized [Mn$_{25}$O$_{18}$(OH)$_2$(N$_3$)$_{12}$]$_{3-}$Cl$_2$(pdm)$_6$(pdmH)$_6$(Cl)$_2$•12MeCN (1:12MeCN in ~30% yield). Complex I crystallizes in triclinic space group P1. The Mn$_{25}$ cation lies on an inversion center and has a barrel-like cage structure (Figure 1). The $12\mu_2$-O$^2-$, $6\mu_3$-O$^2-$, and $2\mu_3$-OH$^-$ ions hold the core together, as well as chelating/bridging pdm$^{2-}$/pdmH$^-$ and both terminal and bridging N$_3^-$ groups. The metal oxidation states and the protonation levels of O$_2^-$, OH$^-$, and pdmH$-$ O atoms were established by Mn and O bond valence sum calculations,§ inspection of metric parameters, and detection of Mn$^{III}$ Jahn–Teller (JT) elongation axes. The core (Figure 2) may be dissected into five parallel layers of three types with an ABCBA arrangement. Layer A is a Mn$^{III}_3$ triangular unit (Mn1, Mn2, Mn4) with a capping $\mu_3$-OH$^-$ ion; layer B is a Mn$^{III}_6$ triangle (Mn3, Mn5, Mn6, Mn7, Mn8, Mn9) comprising three corner-sharing Mn$^{III}_3$ triangles; and layer C is a Mn$^{III}_6$ hexagon (Mn11−Mn13, Mn11a−Mn13a) with a central Mn$^{IV}$ ion (Mn10). Layer C has the Anderson-type structure seen in some Mn complexes.¶ Each layer is held together and linked to its neighboring layers by a combination of oxide, alkoxide, and/or azide bridges. The outer coordination shell is occupied by pdm$^{2-}$, pdmH$^-$, and terminal azide ligands (Figure 1). Each Cl$^-$ anion is hydrogen-bonded to a single $\mu_3$-OH$^-$ group. There are no significant intermolecular interactions. There are two types of Mn$^{III}$ ions: those in layer B are nearly octahedral with JT axially elongated Mn$^{III}$−O bonds (2.147(3)−2.360(4) Å), whereas those in layer C are seven-coordinate and nearly pentagonal bipyramidal, with axially elongated Mn$^{III}$−O bonds (2.283(4)−2.331(4) Å).

Solid-state DC magnetic susceptibility ($\chi_M$) data were collected in the 5.0−300 K range in a 1 kG (0.1 T) field. The $\chi_M$T value steadily increases from 88.4 cm$^3$ K mol$^{-1}$ at 300 K to a maximum of 310 cm$^3$ K mol$^{-1}$ at 15 K, before dropping to 289 cm$^3$ K mol$^{-1}$ at 5.0 K (Figure 3, inset). The data strongly suggest a very large ground-state spin; the 5 K value suggests an S = 51/2 value.

To identify the ground state, magnetization ($M$) data collected in the 1.8−4.0 K and 1−8 K ranges were fit by matrix diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting (D$\Delta$S$^2$) and

Figure 1. Structure of the cation of I. Color code: green, Mn$^{IV}$; purple, Mn$^{III}$; yellow, Mn$^{II}$; red, O; blue, N; gray, C.

Figure 2. Centrosymmetric core of the cation of I (top) and its three types of constituent layers (bottom), color coded for clarity. Atom color code: green, Mn$^{IV}$; purple, Mn$^{III}$; yellow, Mn$^{II}$; red, O; blue, N.
Zeeman interactions, and incorporates a full powder average. We used only low fields (≤8 kG) to avoid problems associated with $M_D$ levels from excited states with higher $S$ values crossing with the ground state, which would lead to an erroneously high value for the ground-state $S$. The fit (solid lines in Figure 3) gave $S = 51/2$, $D = -0.022(1)$ cm$^{-1}$, and $g = 1.72(1)$. But the fits for $S = 49/2$ and $53/2$ were only slightly inferior, and we thus conclude that the ground-state spin of $I$ is $S = 51/2 ± 1$. Data collected up to 4 or 7 T could not be satisfactorily fit. Such a large $S$ value is supported by the in-phase AC susceptibility signal (in zero DC field) of $\sim 315$ cm$^{-1}$ K mol$^{-1}$ at 5 K, indicating the large $\chi_M$T value of Figure 3 not to be an artifact of the applied DC field.

In fact, an $S = 51/2$ ground state is consistent with the expected spins of layers A, B, and C of 15/2, 0, and 21/2, respectively. These are the values calculated for (i) three ferromagnetically coupled Mn$^{III}$ spins in layer A, (ii) an antiferromagnetically coupled Mn$^{III}$ triangle in layer B; and (iii) six Mn$^{III}$ spins in layer C strongly antiferromagnetically coupled to the central Mn$^{III}$ spin and thus aligned parallel to each other. Parallel alignment of the spins of layers A and C as a result of antiferromagnetic interactions with Mn ions in layer B then predicts a molecular spin of $S = 15/2 + 21/2 + 15/2 = 51/2$, rationalizing the high observed $S$ value and supporting a conclusion that I has an $S = 51/2$ ground state.

The $S = 51/2$ ground state and negative $D$ value suggested that I might be an SMM. The upper limit to the relaxation barrier is $(S^2 - 1/4)D$ for a half-integer spin, or only 14.3 cm$^{-1}$ for I, but the actual (or effective) barrier ($U_{rel}$) will be significantly less due to magnetization quantum tunneling through the barrier. Single crystals of 1-12MeCN were therefore investigated using a micro-SQUID,$^9$ and the obtained $M$ vs applied DC field sweeps (Figure 4) exhibited hysteresis below $\sim 0.6$ K, their coercivities increasing with decreasing temperature as expected for an SMM. Fitting of magnetization decay data collected in the 0.04–1.0 K range gave $U_{rel} = 8.3$ cm$^{-1} = 12$ K. The low temperature at which I is an SMM is clearly due to the small $D$ value, consistent with the nearly perpendicular disposition of the Mn$^{III}$ anisotropy axes.

Complex 1 is the largest mixed-valent Mn$^{II}$/Mn$^{III}$/Mn$^{IV}$ cluster and the largest spin SMM to date (the next highest being an Fe$_{19}$ SMM with $S = 33/2$). It also possesses the largest $S$ for an isolated molecule: [Mo$_2$Mn$_9$(CN)$_{24}$(MeOH)$_{12}$] has also been suggested to have $S = 51/2$, although the situation is unfortunately complicated by strong intermolecular interactions and long-range ferromagnetic ordering below 44 K.$^M$ The related W complex has an $S = 39/2$ ground state.$^M$ The next largest spin for any molecule after $S = 51/2$ is the $S = 23$ of a recently reported Fe$_{14}$ complex.$^M$

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Supporting Information Available: Crystallographic details (CIF), Mn bond valence sums, and magnetism data. This material is available free of charge via the Internet at http://pubs.acs.org.

References


(5) (a) Anal. Calcd (Found) for doped I: C, 25.72 (25.61); H, 2.36 (2.68); N, 17.14 (17.15). (b) Crystal data for I-12MeCN: $c_{04}=\text{Cu}_{0.34}^{2+}\text{Cl}_{0.66}\text{Me}_{0.50}\text{S}_{0.44}$ $\mu_{eq}=15.892(18)$, $R=16.502(9)$, $c = 17.2565(8)$, $\alpha = 98.881(2)$, $\beta = 99.923(2)$, $\gamma = 117.003(2)$, $Z = 1$, $V = 3830(3)$, $D = 1.494$ g cm$^{-3}$, $F_{000} = 173$. Final $R_1 = 5.55$ and $wR_2 = 15.31$. The crystal was a small dark brown plate; an absorption correction was applied.

(6) (a) Bond valence sum calculations for Mn$^{II}$, Mn$^{III}$, and Mn$^{IV}$ ions gave oxidation state values of 1.95–2.02, 2.90–3.02, and 3.90, respectively.

(7) Of course, other ways of qualitatively rationalizing an $S = 51/2$ state in such a large molecule are also feasible.