

Single-Molecule Magnets: A Mn₂₅ 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.¹ They derive their properties from a combination of a large spin (S) and an Ising (easy-axis) magnetoanisotropy (negative zero-field splitting parameter, D). Several classes of SMMs are now known,^{1–3} 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 Mn₂₅ 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 $S > 10$.⁴

A stirred slurry of MnCl₂·4H₂O (3 equiv), pyridine-2,6-dimethanol (pdmH₂; 10 equiv), and NaN₃ (10 equiv) in MeOH/MeCN (1:2 v/v) was treated with NMe₄OH (1 equiv). This gave a dark brown solution from which slowly crystallized [Mn₂₅O₁₈(OH)₂(N₃)₁₂-(pdm)₆(pdmH)₆](Cl)₂·12MeCN (1·12MeCN) in ~30% yield. Complex **1** crystallizes⁵ in triclinic space group $P\bar{1}$. The Mn₂₅ cation lies on an inversion center and has a barrel-like cage structure (Figure 1). The 12 μ_4 -O²⁻, 6 μ_3 -O²⁻, and 2 μ_3 -OH⁻ ions hold the

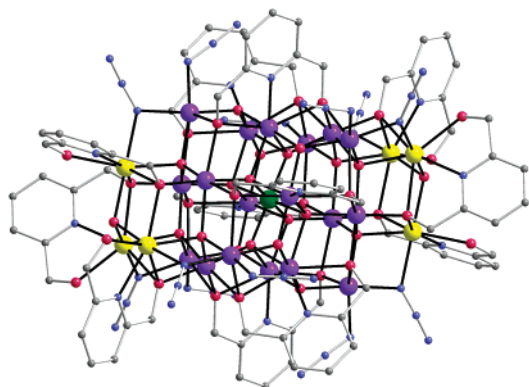


Figure 1. Structure of the cation of **1**. Color code: green, Mn^{IV}; purple, Mn^{III}; yellow, Mn^{II}; red, O; blue, N; gray, C.

core together, as well as chelating/bridging pdm²⁻/pdmH⁻ and both terminal and bridging N₃⁻ groups. The metal oxidation states and the protonation levels of O²⁻, OH⁻, pdm²⁻, and pdmH⁻ O atoms were established by Mn and O bond valence sum calculations,⁶ 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^{II}₃ triangular unit (Mn1, Mn2, Mn4) with a capping μ_3 -OH⁻ ion; layer **B** is a Mn^{III}₆ triangle (Mn3, Mn5, Mn6, Mn7,

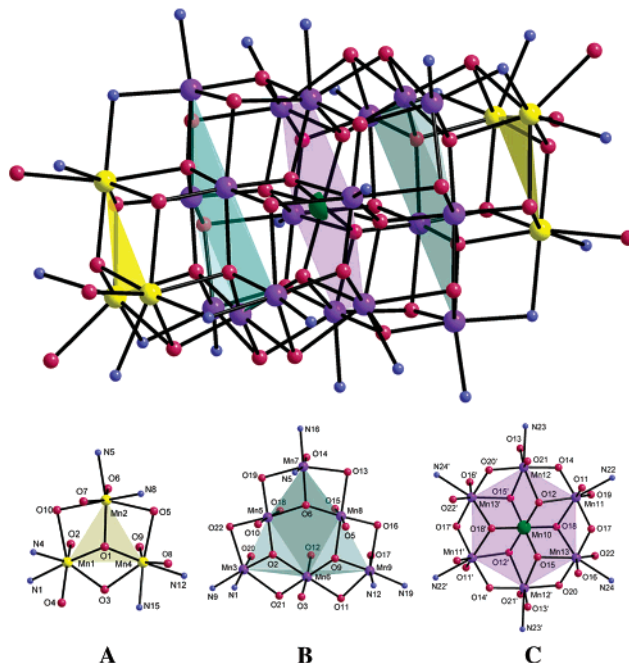


Figure 2. Centrosymmetric core of the cation of **1** (top) and its three types of constituent layers (bottom), color coded for clarity. Atom color code: green, Mn^{IV}; purple, Mn^{III}; yellow, Mn^{II}; red, O; blue, N.

Mn8, Mn9) comprising three corner-sharing Mn^{III}₃ triangles; and layer **C** is a Mn^{IV}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.^{4f} 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 pdm²⁻, pdmH⁻, and terminal azide ligands (Figure 1). Each Cl⁻ anion is hydrogen-bonded to a single μ_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 (χ_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 cm³ K mol⁻¹ at 300 K to a maximum of 310 cm³ K mol⁻¹ at 15 K, before dropping to 289 cm³ 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 in the 47/2–53/2 range, depending on g . To identify the ground state, magnetization (M) data collected in the 1.8–4.0 K and 1–8 kG ranges were fit by matrix diagonalization to a model that assumes only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and

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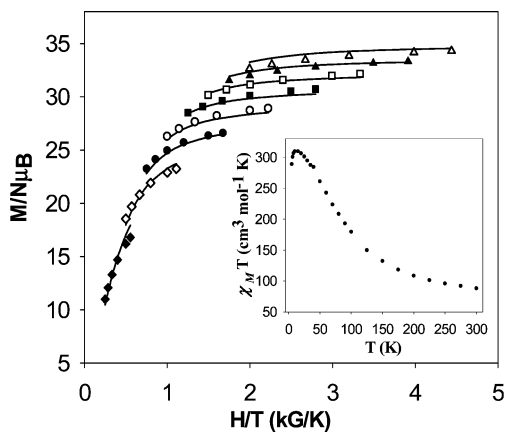


Figure 3. Plot of reduced magnetization ($M/N\mu_B$) vs H/T for **1** at 8 (Δ), 7 (\blacktriangle), 6 (\square), 5 (\blacksquare), 4 (\circ), 3 (\bullet), 2 (\diamond), and 1 (\blacklozenge) kG. Solid lines are the fits; see the text for the fitting parameters. Inset: Plot of χ_{MT} vs T at 1 kG.

Zeeman interactions, and incorporates a full powder average. We used only low fields (≤ 8 kG) to avoid problems associated with M_S 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 $S = 51/2$, $D = -0.022(1) \text{ cm}^{-1}$, 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 **1** is $S = 51/2 \pm 1$. 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 $\sim 315 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K, indicating the large χ_{MT} value of Figure 3 not to be an artifact of the applied DC field.

In fact, an $S = 51/2$ ground state is also 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^{II} 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^{IV} 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 $S = 15/2 + 21/2 + 15/2 = 51/2$,⁷ rationalizing the high observed S value and supporting a conclusion that **1** has an $S = 51/2$ ground state.

The $S = 51/2$ ground state and negative D value suggested that **1** 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 **1**, but the actual (or effective) barrier (U_{eff}) will be significantly less due to magnetization quantum tunneling through the barrier. Single crystals of **1**·12MeCN were therefore investigated using a micro-SQUID,⁸ and the obtained M vs. applied DC field sweeps (Figure 4) exhibited hysteresis below ~ 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 $U_{\text{eff}} = 8.3 \text{ cm}^{-1} = 12 \text{ K}$. The low temperature at which **1** 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 $\text{Mn}^{\text{II}}/\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ 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; $[\text{Mo}_6\text{Mn}_9(\text{CN})_{48}(\text{MeOH})_{24}]$ has also been suggested to

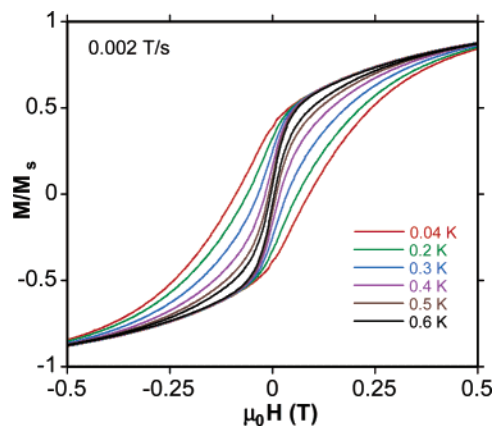


Figure 4. Magnetization (M) vs applied DC field sweeps at the indicated sweep rate and temperatures. M is normalized to its saturation value, M_s , at 1 T.

be $S = 51/2$, although the situation is unfortunately complicated by strong intermolecular interactions and long-range ferromagnetic ordering below 44 K.^{4e} The related W complex has an $S = 39/2$ ground state.^{4c} The next largest spin for any molecule after $S = 51/2$ is the $S = 23$ of a recently reported Fe_{14} complex.^{4d}

Acknowledgment. This work was supported by the National Science Foundation.

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>.

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- (5) (a) Anal. Calcd (Found) for dried **1**: C, 25.72 (26.01); H, 2.36 (2.68); N, 17.14 (17.15). (b) Crystal data for **1**·12MeCN: $\text{C}_{108}\text{H}_{128}\text{Cl}_2\text{Mn}_{25}\text{N}_{60}\text{O}_{44}$, 4415.10 g mol^{-1} , triclinic $P1$, $a = 15.8921(8)$, $b = 16.5027(8)$, $c = 17.2565(8) \text{ \AA}$, $\alpha = 98.881(2)$, $\beta = 99.923(2)$, $\gamma = 117.003(2)^\circ$, $Z = 1$, $V = 3830.0(3) \text{ \AA}^3$, $d_{\text{calc}} = 1.914 \text{ g cm}^{-3}$, $T = 173 \text{ K}$. 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 3.99, respectively. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, 32, 4102.
- (7) Of course, other ways of qualitatively rationalizing an $S = 51/2$ state in such a large molecule are also feasible.
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JA0316824