A Mn$_{17}$ Octahedron with a Giant Ground-State Spin: Occurrence in Discrete Form and as Multidimensional Coordination Polymers

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A [Mn$_{17}$(µ-$4$)-O-$6$]$_{25}^-$ ($L = N_3^-$ or OCN$^-$) octahedral unit is reported, occurring within 1D (1)$_{∞}$ and 2D (2)$_{∞}$ coordination polymers, as well as the corresponding 0D discrete cluster 3. It possesses a giant ground-state spin value, determined in the case of 3 to be $S = 37$, the second largest to be reported to date. In addition, compound 3 displays single-molecule magnet (SMM) behavior and is thus the largest-spin SMM.

Paramagnetic transition-metal clusters continue to attract great attention, mainly because of their often unusual and sometimes novel magnetic properties.\(^1\)\(^2\) Such molecules may exhibit high and sometimes abnormally high ground-state spin values, currently up to $S = \frac{83}{2}$.\(^3\) Several such clusters are now known, including the Mn$_{15}$ family with $S = \frac{83}{2}$ and \(\frac{73}{2}\) and the Mn$_{32}$ family with $S = \frac{51}{2}$ and \(\frac{61}{2}\), but it is still very difficult to predict what type of structure will give a large $S$. There are, however, some strategies that can assist the synthesis of new high-spin molecules, and these include the use of bridging ligands that result in ferromagnetic interactions. The best ligand for this is the N$_3^-$ group when it bridges metal ions in the end-on (1,1) fashion.\(^4\) We have thus included this group in our systematic investigation of the use of 1,3-propanediol (pdH$_2$) and its derivatives in manganese carboxylate chemistry.\(^5\) We herein report three new compounds that all contain the same new Mn$_{17}$ cluster but that differ in their dimensionality: the 1D [Mn$_{17}$O$_8$-(N$_3$)$_4$(O$_2$CMe)$_4$(pd)$_{10}$(py)$_{10}$(MeCN)$_2$(H$_2$O)$_2$(ClO$_4$)$_3$ (1)$_{∞}$ and 2D [Mn$_{17}$O$_8$(OCN)-N$_3$(O$_2$CMe)$_2$(pd)$_{10}$(py)$_{10}$]$_{∞}$ (2)$_{∞}$ coordination polymers and the corresponding 0D discrete cluster [Mn$_{17}$O$_8$(N$_3$)$_4$(O$_2$CMe)$_2$(pd)$_{10}$(py)$_{10}$](MeCN)$_2$(H$_2$O)$_2$(ClO$_4$)$_3$ (3). All three compounds contain the high-symmetry [Mn$_{17}$O$_8$-(µ-$4$)-O$_6$](µ-$3$)-L)$_{12}^{25+}$ [L = N$_3^-$ (1 and 3), OCN$^-$ (2)] octahedral unit, which possesses a giant ground-state spin that for discrete 3 was determined to be $S = 37$, the second largest to date. In addition, compound 3 displays single-molecule magnet (SMM) behavior and is thus the largest-spin SMM known to date.

Compound (1)$_{∞}$ was the first one isolated; it was obtained in 30% yield from the reaction of [Mn(O$_2$CMe)$_2$]-·4H$_2$O, pdH$_2$, and NaN$_3$ (1:5:1) in MeCN/py (py = pyridine). Magnetic susceptibility and X-ray crystallographic studies (vide infra) clearly suggested that the Mn$_{17}$ repeating unit of 1 possesses a large ground-state spin, but its exact value was impossible to determine because of the covalent linkage of neighboring Mn$_{17}$ units, which introduced intermolecular magnetic interactions. The isolation of this Mn$_{17}$ unit in a discrete form was thus targeted with high priority. Because the Mn$_{17}$ units in (1)$_{∞}$ were connected by 1,3-bridging N$_3^-$ groups, we explored the analogous reactions with OCN$^-$ with the hope that OCN$^-$ would still bridge intramolecularly but preclude the µ-1,3 (end-to-end) bridging of neighboring Mn$_{17}$ units and thus avoid the formation of a polymeric species. However, the use of OCN$^-$ gave instead the 2D coordination polymer (2)$_{∞}$ in 32% yield, with properties very similar to those of (1)$_{∞}$. The second and successful strategy was to include an excess of a poorly coordinating counteranion such as ClO$_4^-$ in order to stabilize a positively charged species that might contain neutral terminal ligands instead of the µ-1,3 N$_3^-$ groups. Thus, the reaction of [Mn(O$_2$CMe)$_2$]-·4H$_2$O with pdH$_2$ in the presence of NaN$_3$ and Mn(ClO$_4$)$_2$·6H$_2$O in a 1:5:1:1 molar ratio in MeCN/py and subsequent diffusion of Et$_2$O into the yellow solution led to the isolation of 3 in 30% yield after a few days.

The structures of (1)$_{∞}$ [Figure S1 in the Supporting Information (SI)], (2)$_{∞}$ (Figure S2 in the SI), and 3 (Figure 1,
Mn4 layers are nearly planar rectangles; the central Mn7 layer is also a rectangle, this time comprising six Mn ions with \( \mu \sim \) bridges Mn7 of one Mn17 unit to its symmetry-related Mn7 and Mn9 ions of a neighboring Mn17 unit, resulting in the formation of a 1D coordination polymer. The 17 Mn ions of the core (Figure 1, bottom) are disposed in alternating Mn/Mn4/Mn7/Mn4/Mn layers: the Mn4 layers are nearly planar rectangles; the central Mn7 layer is also a rectangle, this time comprising six Mn ions with a seventh at its center, and the remaining two Mn ions occupy the top and bottom capping positions. The Mn17 core is held together by eight \( \mu_4\text{-O}^- \) and four \( \mu_3\text{-1,1,1-N}_3^- \) (or OCN\(^-\)) bridging ligands. For compound C, the peripheral ligation is completed by six terminal pyridine, two carboxylate bridging ligands, and one \( \mu_4\text{-1,1,1-N}_3^- \) ligands. For compound 1, the peripheral ligation is completed by six terminal pyridine, two chelating acetate, and one \( \mu_3\text{-1,1,1-N}_3^- \) ligands. For compound 1, the peripheral ligation is completed by six terminal pyridine, two chelating acetate, and one \( \mu_3\text{-1,1,1-N}_3^- \) ligands.

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The χ_mT increases from 83.9 cm$^3$ mol$^{-1}$ K at 300 K to a maximum of 597.9 cm$^3$ mol$^{-1}$ K at 15 K before decreasing to 516.6 cm$^3$ mol$^{-1}$ K at 5 K. The maximum is consistent with an $S = 37$ ground state, the maximum possible for a Mn$^{II}_{11}$Mn$^{III}_{6}$ system, assuming a $g$ value of slightly less than 2. The low-temperature decrease is due to Zeeman effects, zero-field splitting, and/or weak intermolecular interactions. dc magnetization data were collected in the temperature and magnetic field ranges of 1.8–10 K and 0.1–7 T, respectively. The data were fit by assuming that only the ground state is populated and by including axial zero-field-splitting ($D_{x^2-y^2}$) and Zeeman interactions. For the two polymeric species (1)$_{ac}$ and (2)$_{ac}$, the intermolecular interactions of significant strength between neighboring Mn$_{17}$ molecules precluded a fit of the data to isolated units, but for 3, a good fit was obtained with $S = 37$, $g = 1.95$, and $D = -0.009$ cm$^{-1}$ (Figure 3, inset).

The conclusions from the dc studies were also confirmed by alternating current (ac) susceptibility experiments. The in-phase $\chi''_mT$ (Figure S3 in the SI) for the two polymeric species decreases almost linearly with decreasing temperature and is clearly heading to $\chi''_mT$ values close to zero at 0 K consistent with antiferromagnetic intermolecular interactions and a diamagnetic ground spin state. Extrapolation of the $\chi''_mT$ signal of 3 (Figure S3 in the SI) to 0 K from above 8 K to avoid the effects of intermolecular interactions gave $\chi_m'\sim 620$ cm$^3$ mol$^{-1}$ K, consistent with $S \sim 37$ and $g$ slightly less than 2.0 ($\chi_mT$ for an $S = 37$ state with $g = 1.88$ is 621.2 cm$^3$ mol$^{-1}$ K), as expected for a Mn$^{II}$/Mn$^{III}$ complex. The lowest temperature decrease is likely due to weak intermolecular interactions between neighboring Mn$_{17}$ units and is also typical of other high-spin molecules.

For all three complexes, there is no ac out-of-phase ($\chi''_m$) signal down to 1.8 K (Figures S4–S6 in the SI). The $S = 37$ ground state and negative $D$ value suggested that 3 might be an SMM. Single-crystal magnetic studies on 3·1.2H$_2$O were therefore performed using a micro-SQUID instrument and magnetization ($M$) vs dc field sweeps are shown in Figure 4. Hysteresis loops are evident below $\sim 0.7$ K, with their coercivities increasing with decreasing temperature, as expected for an SMM. An Arrhenius plot constructed from dc magnetization decay data gave $U_{eff} = 9.0$ cm$^{-1}$ = 13 K and $\tau_0 = 1.0 \times 10^{-13}$ s, where $\tau_0$ is the preexponential factor (Figures S7 and S8 in the SI). The small value of $\tau_0$, smaller than is typical for purely SMM behavior, is likely due to weak intermolecular interactions and low-lying excited states; large clusters often give smaller $\tau_0$ values. Note that adjacent Mn$_{17}$ clusters in 3 are hydrogen-bonded in one direction, but not directly, only via the lattice H$_2$O molecules. Thus, intermolecular exchange interactions will be very weak.

In summary, the use of N$_3^-$OCN$^-$ ligands in Mn-pdH$_2$ chemistry under various conditions has yielded essentially the same Mn$_{17}$ unit within 0D, 1D, and 2D compounds. The discrete form 3 was targeted once the polymeric form was identified, and it was obtained by a procedure containing some elements of synthetic control that could also prove useful for the isolation in discrete form of the repeating cluster of other coordination polymers. Compound 3 possesses a giant ground-state spin of $S = 37$ and is the largest spin-SMM to date. $S = 37$ is also the second-highest ground state yet identified, and it is the maximum for a [Mn$^{II}_{11}$Mn$^{III}_{6}$] species, thus indicating that most, if not all, of the interactions are ferromagnetic. This is consistent with the $\mu_2$-1,1,1-N$_3^-$ ligands, which are known to mediate ferromagnetic interactions. Finally, the labile terminal ligands on the Mn$_{17}$ units offer a variety of additional possibilities for crystal engineering, i.e., introducing interunit linkages of various types for the construction of multidimensional coordination polymers with interesting magnetic and/or structural properties. Compounds (1)$_{ac}$ and (2)$_{ac}$ provide a proof-of-feasibility of this strategy that encourages us to believe an expanded family of related polymeric species containing this high-spin Mn$_{17}$ unit should be possible.

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Supporting Information Available: Crystallographic details (CIF), structural representations, and magnetism plots. This material is available free of charge via the Internet at http://pubs.acs.org.