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

Eleni E. Moushi,† Theocaris C. Stamatatos,‡ Wolfgang Wernsdorfer,§ Vassilios Nastopoulos,‖ George Christou,* and Anastasios J. Tasiopoulos*†

†Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus, ‡Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, §Institut Néel, CNRS, BP-166, Grenoble Cedex 9, France, and ‖Department of Chemistry, University of Patras, 26500 Patras, Greece

Received September 19, 2008

A [Mn$^{11+}$Mn$^{11+}$($\mu_4$-O$_2$)$_4$($\mu_3$-L)$_4$]$_{25+}$ ($L = N_3^-$ or OCN$^-$) octahedral unit is reported, occurring within 1D (1)$_\infty$ and 2D (2)$_\infty$ 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. Such molecules may exhibit high and sometimes abnormally high ground-state spin values, currently up to $S = \frac{83}{2}$. Several such clusters are now known, including the Mn$_{16}$ family with $S = \frac{83}{2}$; and the Mn$_{32}$ family with $S = \frac{61}{2}$ 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. 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. 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$_3$O$_{12}$Mn$_{17}$O$_{8-}$N$_3$O$_{12}$Mn$_{17}$O$_{8-}$N$_3$O$_{12}$]$_\infty$ (1)$_\infty$ and 2D [Mn$_{17}$O$_8$(OCN$_2$)$_2$(ClO$_4$)$_2$(pd)$_{10}$(py)$_6$]$_\infty$ (2)$_\infty$ coordination polymers and the corresponding 0D discrete cluster [Mn$_{17}$O$_8$(N$_3$)$_4$(O$_2$CMe)$_2$(pd)$_{10}$(py)$_6$]$_\infty$ (Fig. 1, 2). All three compounds contain the high-symmetry [Mn$_{17}$]$_2$[Mn$_{17}$($\mu_4$-O)$_2$]$_4$($\mu_3$-L)$_4$$_{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)$_\infty$ 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 crystallography studies (vide infra) clearly suggested that the Mn$_{17}$ repeating unit of 1 possesses a large ground-state spin $S$, 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)$_\infty$ 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 $\mu$-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)$_\infty$ in 32% yield, with properties very similar to those of (1)$_\infty$. 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 $\mu$-1,3 $N_3^-$ groups. Thus, the reaction of [Mn(O$_2$CMe)$_2$]-4H$_2$O with pdH$_2$ in the presence of Na$_2$O and Mn(ClO$_4$)$_2$·6H$_2$O in a 1:5:1 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)$_\infty$ (Figure S1 in the Supporting Information (SI)), (2)$_\infty$ (Figure S2 in the SI), and (3) (Figure 1,
Mn4 layers are nearly planar rectangles; the central Mn7 layer completed by four terminal pyridine and three μ∼ ligands at the top and bottom capping positions. The Mn17 core is held together by eight μ4-O2− and four μ2,1,1,1-N3− (or OCN−) bridging ligands. The structures also contain 10 pd2 bridges Mn7 of one Mn17 unit to its symmetry-related Mn ion of a neighboring Mn17 unit, resulting in the formation of a seventh Mn7 at its center, and the remaining two Mn ions occupy the top and bottom ligation positions. The Mn17 core is held together by eight μ4-O2− and four μ2,1,1,1-N3− (or OCN−) bridging ligands. The three OCN− groups bridge two Mn ions of the Mn17 unit (Mn7 and Mn9) with Mn ions of two neighboring Mn17 units, resulting in a 2D coordination polymer (Figure 2, top). The shortest Mn⋯Mn separation between different Mn17 units is ~6.24 Å. For compound 2, the peripheral ligation is completed by four terminal pyridine and three μ2,1,3-OCN− ligands. The three OCN− groups bridge two Mn ions of the Mn17 unit (Mn7 and Mn9) with Mn ions of two neighboring Mn17 units, resulting in a 2D coordination polymer (Figure 2, bottom). The shortest Mn⋯Mn separation between different Mn17 units is ~6.36 Å. For compound 3, the peripheral ligation is completed by 10 pyridine, 2 water and 2 MeCN ligands, all terminal. A close examination of the packing of 3 reveals the existence of intermolecular hydrogen-bonding interactions involving terminal bound and lattice H2O molecules and ClO4− counterions (O⋯·O separations = 2.7−2.9 Å); i.e., there are no hydrogen bonds directly between neighboring Mn17 cations, and as a result, the shortest Mn⋯Mn separation between different Mn17 units is ~8.47 Å, significantly longer than those for (1)∞ and (2)∞.

Solid-state direct current (dc) magnetic susceptibility measurements were performed on vacuum-dried microcrystalline samples of (1)∞, (2)∞ and (3)∞ in a 0.1 T field in the 5−300 K range. The obtained data are shown as χmT vs T plots in Figure 3, and they indicate the existence of predominantly ferromagnetic interactions and a resulting giant ground-state spin for the Mn17 units. For (1)∞ and (2)∞, χmT increases from 82.5 and 85.9 cm3 mol−1 K at 300 K to maxima of 375.4 and 407.5 cm3 mol−1 K at 40 and 35 K, respectively, before decreasing rapidly to 67.9 and 119.0 cm3 mol−1 K at 5 K. The low-temperature decrease is very probably due to intermolecular antiferromagnetic exchange interactions mediated by the end-to-end N3− and OCN− ligands, resulting in diamagnetic ground spin states for the two polymeric species. For 3,
\( \chi_mT \) 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 \( \text{Mn}^{III}_{17} \) 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 (\( D_{\perp} \)) and Zeeman interactions. For the two polymeric species (1) and (2), the intermolecular interactions of significant strength between neighboring \( \text{Mn}^{17} \) molecules precluded a fit of the data to isolated \( \text{Mn}^{III} \) molecules.

The conclusions from the dc studies were also confirmed by alternating current (ac) susceptibility experiments. The in-phase \( \chi_m' \) (Figure S3 in the SI) for the two polymeric species decreases almost linearly with decreasing temperature and is clearly heading to \( \chi_m' \) values close to zero at 0 K consistent with antiferromagnetic intermolecular interactions and a diamagnetic ground spin state. Extrapolation of the \( \chi_m''/T \) signal of 3 (Figure S3 in the SI) to 0 K from above 8 K to avoid the effects of intermolecular interactions gave \( \chi_m' \) ~ 620 cm\(^3\) mol\(^{-1}\) K, consistent with \( S = 37 \) and \( g \) slightly less than 2.0 (\( \chi_m' \) for an \( S = 37 \) state with \( g = 1.88 \) is 621.2 cm\(^3\) mol\(^{-1}\) K), as expected for a \( \text{Mn}^{II}/\text{Mn}^{III} \) complex. The lowest temperature decrease is likely due to weak intermolecular interactions between neighboring \( \text{Mn}^{17} \) 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\(^{11}\) and magnetization \( (M) \) vs dc field sweeps are shown in Figure 4. Hysteresis loops are evident below ~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 \( U_{\text{eff}} = 9.0 \) 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,\(^{2} \) is likely due to weak intermolecular interactions and low-lying excited states; large clusters often give smaller \( \tau_0 \) values.\(^{4,5} \) Note that adjacent \( \text{Mn}^{17} \) 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, and they will represent merely perturbations of single-molecule properties. In addition, they will be antiferromagnetic and thus could not make 3 a single-chain magnet rather than an SMM.

In summary, the use of \( \text{N}_3^{-}/\text{OCN}^- \) ligands in Mn-pdH\(_2\) chemistry under various conditions has yielded essentially the same \( \text{Mn}^{17} \) 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 SMM to date. \( S = 37 \) is also the second-highest ground state yet identified,\(^{1} \) and it is the maximum for a \([\text{Mn}^{III}_{17}\text{Mn}^{II}_6]\) species, thus indicating that most, if not all, of the interactions are ferromagnetic. This is consistent with the \( \mu_3\text{-1,1,1-N}_3^- \) ligands, which are known to mediate ferromagnetic interactions.\(^{6} \) Finally, the labile terminal ligands on the \( \text{Mn}^{17} \) 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) and (2) provide a proof-of-feasibility of this strategy that encourages us to believe an expanded family of related polymeric species containing this high-spin \( \text{Mn}^{17} \) unit should be possible.

**Acknowledgment.** This work was supported by the Cyprus Research Promotion Foundation and the National Science Foundation.

**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.

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\(^{10}\) (a) It analyzes as 1·2H\(_2\)O. (b) It analyzes as 2·6H\(_2\)O. (c) It analyzes as 3·4H\(_2\)O.