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

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A $[Mn^{III}_{11}Mn^{II}_{6}(\mu_4\text{-}O)_8(\mu_3\text{-}L)_4]^{25+}$ ($L = N_3^-$ or OCN^-) octahedral unit is reported, occurring within 1D $(\mathbf{1})_\infty$ and 2D $(\mathbf{2})_\infty$ 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.[1,2] Such molecules may exhibit high and sometimes abnormally high ground-state spin values, currently up to $S = {}^{83}/_{2}$.[1] Several such clusters are now known, including the Mn_{19} family with $S = {}^{83}/_{2}$[1] and ${}^{73}/_{2}$[3] and the Mn_{25} family with $S = {}^{51}/_{2}$[4] and ${}^{61}/_{2}$,[5] 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.[6] 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.[7] We herein report three new compounds that all contain the same new Mn_{17} cluster but that differ in their dimensionality: the 1D $[Mn_{17}O_8(N_3)_5(O_2CMe)_4(pd)_{10}(py)_6]_\infty$ $(\mathbf{1})_\infty$ and 2D $[Mn_{17}O_8(OCN)_7(O_2CMe)_2(pd)_{10}(py)_4]_\infty$ $(\mathbf{2})_\infty$ coordination polymers and the corresponding 0D discrete cluster $[Mn_{17}O_8(N_3)_4(O_2CMe)_2(pd)_{10}(py)_{10}(MeCN)_2(H_2O)_2](ClO_4)_3$ (**3**). All three compounds contain the high-symmetry $[Mn^{III}_{11}Mn^{II}_{6}(\mu_4\text{-}O)_8(\mu_3\text{-}L)_4]^{25+}$ [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 $(\mathbf{1})_\infty$ was the first one isolated: it was obtained in 30% yield from the reaction of $[Mn(O_2CMe)_2]\cdot 4H_2O$, 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 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 $(\mathbf{1})_\infty$ 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 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 $(\mathbf{2})_\infty$ in 32% yield, with properties very similar to those of $(\mathbf{1})_\infty$. 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 μ-1,3 N_3^- groups. Thus, the reaction of $[Mn(O_2CMe)_2]\cdot 4H_2O$ with pdH_2 in the presence of NaN_3 and $Mn(ClO_4)_2\cdot 6H_2O$ in a 1:5:1:1 molar ratio in MeCN/py and subsequent diffusion of Et_2O into the yellow solution led to the isolation of **3** in 30% yield after a few days.

The structures of $(\mathbf{1})_\infty$ [Figure S1 in the Supporting Information (SI)],[8] $(\mathbf{2})_\infty$ (Figure S2 in the SI),[8] and **3**[8] (Figure 1,

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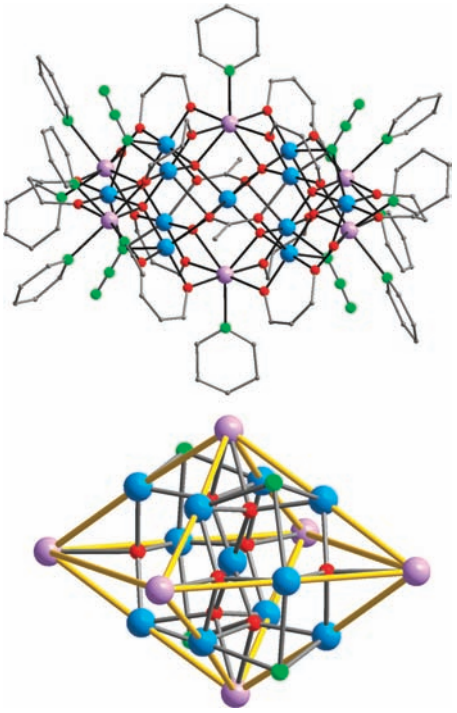

Figure 1. Structure of **3** (top) and its core (bottom). In the lower figure, the yellow line connecting the Mn ions is to emphasize the octahedral topology. Color scheme: Mn^{III}, blue; Mn^{II}, purple; O, red; N, green; C, gray. H atoms have been omitted for clarity.

top) all contain a $[Mn_{17}(\mu_4\text{-}O)_8(\mu_3\text{-}L)_4(pd)_{10}(O_2CMe)_2]^{3+}$ unit with a flattened octahedral topology. Bond valence sum (BVS) calculations,[9] charge considerations, and inspection of metric parameters reveal a mixed-valence $Mn^{III}_{11}Mn^{II}_6$ situation. The 17 Mn ions of the core (Figure 1, bottom) are disposed in alternating $Mn/Mn_4/Mn_7/Mn_4/Mn$ layers: the Mn_4 layers are nearly planar rectangles; the central Mn_7 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 Mn_{17} core is held together by eight μ_4-O^{2-} and four μ_3-1,1,1-N_3^- (or OCN^-) bridging ligands. The structures also contain 10 pd^{2-} and two carboxylate bridging ligands. For compound **1**, the peripheral ligation is completed by six terminal pyridine, two chelating acetate, and one μ-1,3-N_3^- ligands. The latter bridges Mn7 of one Mn_{17} unit to its symmetry-related Mn ion of a neighboring Mn_{17} unit, resulting in the formation of a 1D coordination polymer (Figure 2, top). The shortest Mn···Mn separation between different Mn_{17} units is ~6.24 Å. For compound **2**, the peripheral ligation is completed by four terminal pyridine and three μ-1,3-OCN^- ligands. The three OCN^- groups bridge two Mn ions of the Mn_{17} unit (Mn7 and Mn9) with Mn ions of two neighboring Mn_{17} units, resulting in a 2D coordination polymer (Figure 2, bottom). The shortest Mn···Mn separation between different Mn_{17} 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 terminally bound and lattice H_2O molecules and ClO_4^- counterions (O···O separations = 2.7−2.9 Å); i.e., there are no hydrogen bonds directly between neighboring Mn_{17} cations, and as a result, the shortest Mn···Mn separation between different Mn_{17} units is ~8.47 Å, significantly longer than those for $(\mathbf{1})_\infty$ and $(\mathbf{2})_\infty$.

(8) The Crystal data for $(\mathbf{1}\cdot 2H_2O\cdot 2MeCN)_\infty$, $(\mathbf{2}\cdot 1H_2O)_\infty$ and $\mathbf{3}\cdot 1.2H_2O$ are provided in the Supporting Information.

(9) (a) BVS calculations for the Mn[9b] ions of compounds $(\mathbf{1})_\infty$, $(\mathbf{2})_\infty$, and **3** gave oxidation state values of 2.83−3.16 (Mn^{III}) and 1.81−2.07 (Mn^{II}). (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993** *32*, 4102.

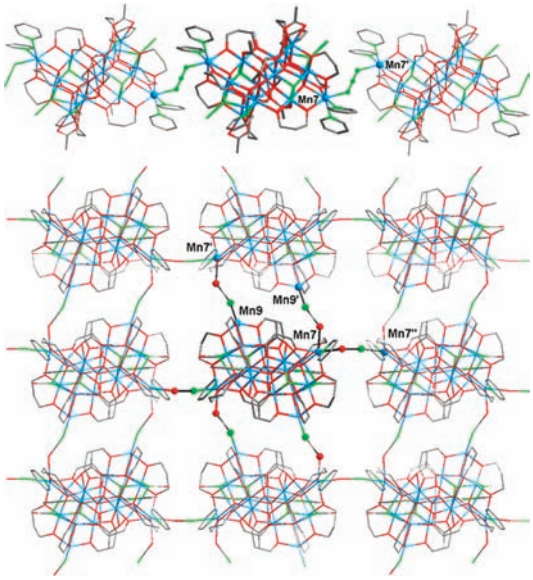

Figure 2. Wireframe representations of sections of $(\mathbf{1})_\infty$ (top) and $(\mathbf{2})_\infty$ (bottom) emphasizing the connection of Mn_{17} units into 1D and 2D polymeric networks, respectively. The color scheme is as in Figure 1.

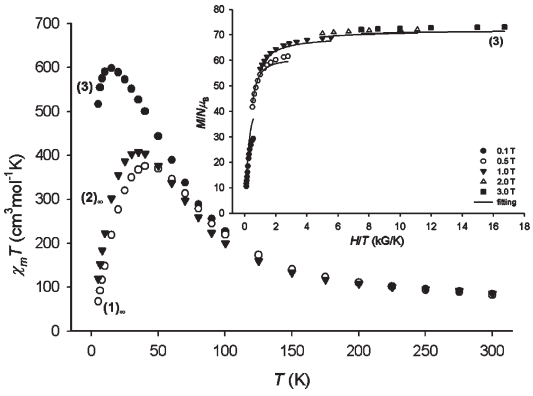

Figure 3. $\chi_m T$ vs T plots for $(\mathbf{1})_\infty$, $(\mathbf{2})_\infty$, and **3**. Inset: Plot of reduced magnetization, $M/N\mu_B$ vs H/T for **3**. The solid lines are the fit; see the text for the fit parameters.

Solid-state direct current (dc) magnetic susceptibility measurements were performed on vacuum-dried microcrystalline samples of $(\mathbf{1})_\infty$,[10a] $(\mathbf{2})_\infty$,[10b] and **3**[10c] in a 0.1 T field in the 5−300 K range. The obtained data are shown as $\chi_m T$ vs T plots in Figure 3, and they indicate the existence of predominantly ferromagnetic interactions and a resulting giant ground-state spin for the Mn_{17} units. For $(\mathbf{1})_\infty$ and $(\mathbf{2})_\infty$, $\chi_m T$ increases from 82.5 and 85.9 $cm^3\ mol^{-1}$ K at 300 K to maxima of 375.4 and 407.5 $cm^3\ mol^{-1}$ K at 40 and 35 K, respectively, before decreasing rapidly to 67.9 and 119.0 $cm^3\ mol^{-1}$ K at 5 K. The low-temperature decrease is very probably due to intermolecular antiferromagnetic exchange interactions mediated by the end-to-end N_3^- and OCN^- ligands, resulting in diamagnetic ground spin states for the two polymeric species. For **3**,

$\chi_m T$ 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 $Mn_{11}^{III}Mn_6^{II}$ 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 ($D\hat{S}_z^2$) and Zeeman interactions. For the two polymeric species $(\mathbf{1})_\infty$ and $(\mathbf{2})_\infty$, the intermolecular interactions of significant strength between neighboring Mn_{17} molecules precluded a fit of the data to isolated units,[7b] 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 $\chi_m'T$ (Figure S3 in the SI) for the two polymeric species decreases almost linearly with decreasing temperature and is clearly heading to $\chi_m'T$ 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 $\chi_m'T \sim 620$ cm^3 mol^{-1} K, consistent with $S \sim 37$ and g slightly less than 2.0 ($\chi_m T$ 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.[4,5] For all three complexes, there is no ac out-of-phase (χ_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 $\mathbf{3}\cdot 1.2H_2O$ 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 $U_{eff} = 9.0$ cm^{-1} = 13 K and $\tau_0 = 1.0 \times 10^{-13}$ s, where τ_0 is the preexponential factor (Figures S7 and S8 in the SI). The small value of τ_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 τ_0 values.[4,5] Note that adjacent Mn_{17} clusters in **3** are hydrogen-bonded in one direction, but not directly, only via the lattice H_2O molecules. Thus, intermolecular exchange interactions will be very weak,

(10) (a) It analyzes as $\mathbf{1}\cdot 2H_2O$. (b) It analyzes as $\mathbf{2}\cdot 6H_2O$. (c) It analyzes as $\mathbf{3}\cdot 4H_2O$.

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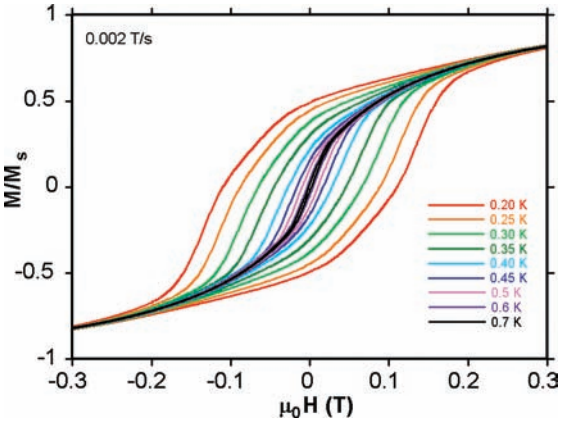

Figure 4. Magnetization (M) versus field hysteresis loops for single crystals of $\mathbf{3}\cdot 1.2H_2O$ at the indicated temperatures. The magnetization is normalized to its saturation value (M_s).

and they will represent merely perturbations of single-molecule properties. In addition, they will be antiferromagnetic and thus could not make **3** be a single-chain magnet rather than an SMM.

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,[1] and it is the maximum for a $[Mn_{11}^{III}Mn_6^{II}]$ species, thus indicating that most, if not all, of the interactions are ferromagnetic. This is consistent with the μ_3-1,1,1-N_3^- ligands, which are known to mediate ferromagnetic interactions.[6] 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 $(\mathbf{1})_\infty$ and $(\mathbf{2})_\infty$ 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.