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A Large $[Mn_{10}Na]_4$ Loop of Four Linked Mn_{10} Loops

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A large $[Mn_{10}Na]_4$ loop-of-loops aggregate was prepared from the use of 1,3-propanediol (pdH_2) in manganese carboxylate chemistry. It is constructed from four $[Mn_{10}(\mu_3\text{-}O)_2(O_2CMe)_{13}(pd)_6(py)_2]^-$ loops linked through Na^+ ions and exhibits a saddlelike topology. Magnetic characterization showed that the Mn_{10} loop has an $S \sim 4$ ground-state spin and displays frequency-dependent in-phase and out-of-phase alternating current signals and also hysteresis loops that, however, are not typical of single-molecule magnets because of the existence of intermolecular interactions between the Mn_{10} units.

The current intense interest in paramagnetic 3d transition-metal clusters has resulted in a number of beautiful complexes, some of which contain a large number of metal ions (up to 84).[1] The main reason for this interest is the fact that such molecules can function as magnets below a critical temperature, providing a new "bottom-up" approach to nanoscale magnetic materials.[2] Although there are now many species displaying single-molecule magnet (SMM) behavior, most of them from manganese carboxylate chemistry,[1c−6] there is a continuing need for new structural types. One of the most successful synthetic approaches to new polynuclear clusters involves the use of chelates containing alcohol groups because alkoxides are good bridging groups and thus favor the formation of polynuclear products.[1b,4−6] Recently, we have been investigating the use of 1,3-propanediol (pdH_2) in manganese carboxylate chemistry.[6] We herein report the synthesis, crystal structure, and magnetic properties of a molecular aggregate that consists of four repeating units of the new $[Mn_{10}Na(\mu_3\text{-}O)_2(O_2CMe)_{13}(pd)_6(py)_2]$ (**1**) loop linked through the Na^+ ions. This novel tetrameric $[\mathbf{1}]_4$ loop-of-loops is the second-largest Mn cluster reported to date,[1c] has a saddlelike topology, and crystallizes in an aesthetically pleasing manner, forming egg-shaped stacks.

The reaction of $[Mn_3O(O_2CMe)_6(py)_3]\cdot py$ (py = pyridine) with pdH_2 and NaN_3[7] in a 1:4:1 molar ratio in MeCN resulted in a dark-brown slurry, which was filtered to give a brown filtrate and a brown powder. The filtrate was left undisturbed at room temperature for a few days and slowly gave red-brown crystals of $[\mathbf{1}\cdot 2.4H_2O]_4$ in 32% yield; dried solid was hygroscopic and analyzed as $[\mathbf{1}\cdot 10H_2O]_4$. The crystal structure[8] of $[\mathbf{1}\cdot 2.4H_2O]_4$ consists of a mixed-valent loop (Figure 1) containing two Mn^{II} and eight Mn^{III} ions, as determined by bond valence sum (BVS) calculations,[9] charge considerations, and inspection of metric parameters. Compound **1** can be described as a dimer of Mn_5 units (Mn atoms 1,2,8,9,10 and 3,4,5,6,7) linked between Mn7/Mn8 by two μ-O atoms of different pd^{2-} groups and between Mn2/Mn3

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(7) When this reaction was repeated with other Na^+ sources like NaCN, NaSCN, and $Na[N(CN)_2]$, the same product was isolated in slightly smaller yields. However, when $NaClO_4$ was used as a Na^+ source, the product that was isolated was the $\{Mn_{19}\}_\infty$ 3D coordination polymer reported elsewhere.[6]

(8) Crystal structure data for $[\mathbf{1}\cdot 2.4H_2O]_4$: $C_{216}H_{359.2}O_{169.60}N_8Na_4Mn_{40}$, $M = 8071.49$, tetragonal, $I4_1/a$, $a = 25.0996(5)$ Å, $c = 70.929(2)$ Å, $V = 44685(2)$ Å^3, $T = 100$ (2) K, $Z = 4$, $\rho_{calcd} = 1.197$ g cm^{-3}, 102 512 reflections collected, 20 625 unique ($R_{av} = 0.0655$), R1 = 0.0545, wR2 = 0.1537, using 10 737 reflections with $I > 2\sigma(I)$.

(9) (a) BVS calculations for the Mn ions of **1** gave oxidation state values of 2.88−2.94 (Mn^{III}) and 2.05 (Mn^{II}). (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102.

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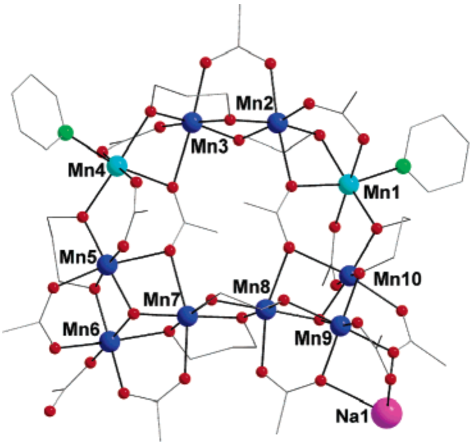

Figure 1. Molecular structure of **1**. Color code: Mn^{III}, blue; Mn^{II}, cyan; O, red; N, green; Na, purple. H atoms are omitted for clarity.

again by two pd^{2-} μ-O atoms and also a μ-O_2CMe^- group. Each Mn_5 unit consists of triangular $[Mn^{III}_3O]^{7+}$ and dinuclear Mn^{II}Mn^{III} subunits linked by μ-O_2CMe^- and η^2:η^2:μ_4-$MeCO_2^-$ groups and a pd^{2-} μ-O atom. The peripheral ligation of the Mn^{II}Mn^{III} subunit is completed by μ-O_2CMe^- and pd^{2-} μ-O atoms, which bridge the Mn^{II} and Mn^{III} ions, and a terminal py ligand. The Mn ions of the triangular unit are bridged by a μ_3-O^{2-} ion, two pd^{2-} and one O_2CMe^- μ-O atoms, and two μ_3-$MeCO_2^-$ ligands. The latter and an additional acetate group link each triangular unit to a Na^+ ion. The two Na^+ ions attached to the Mn_{10} loop then each connect in an equivalent way to a different neighboring Mn_{10} loop, resulting in the formation of a tetrameric$[\mathbf{1}]_4$ loop-of-loops (Figure 2a). This aggregate is not planar but instead folds to give a saddlelike conformation, as shown in Figure 2b. Note that although there are a few examples of discrete and polymeric aggregates of 3d metal clusters linked through alkali- or alkaline-earth-metal ions with an overall nuclearity >6, none of them has a nuclearity >20.[5a,6,10] It is also interesting that $[\mathbf{1}]_4$ represents the first example of a loop constructed from smaller loops. The shortest Mn⋯Mn separation between different Mn_{10} units of $[\mathbf{1}]_4$ is relatively large at 6.382 Å. A close examination of the crystal packing reveals that the $[\mathbf{1}]_4$ aggregates pack as tail-to-tail $\{[\mathbf{1}]_4\}_2$ dimers, thus giving aesthetically pleasing egg-shaped stacks (Figure 3). The central cavity of the $\{[\mathbf{1}]_4\}_2$ dimer has dimensions of approximately 8 × 17 Å and contains a small amount of H_2O of crystallization. The $[\mathbf{1}]_4$ units within a dimer and between different dimers are similarly spaced (the shortest separation between the tails of two different $[\mathbf{1}]_4$ units and between the heads of two different $[\mathbf{1}]_4$ units is ~3.2−3.4 Å).

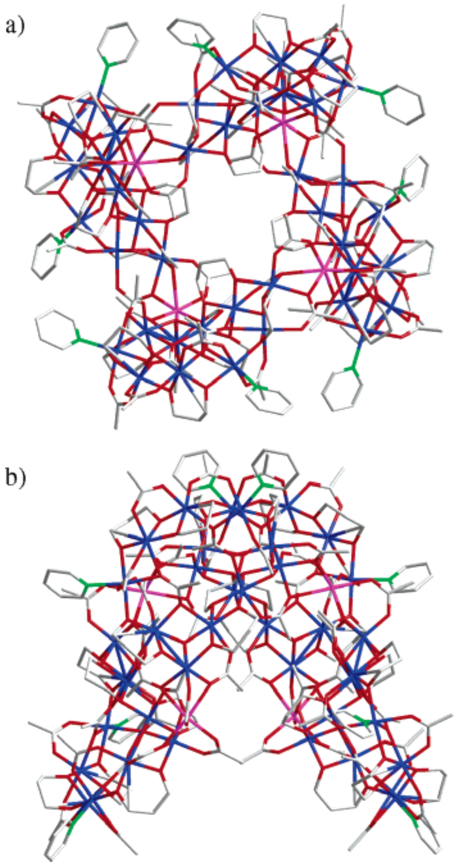

Figure 2. Wire-frame representations of $[\mathbf{1}]_4$ from viewpoints that emphasize (a) the tetrameric loop-of-loops structure and (b) the saddlelike folding. Color code: Mn, blue; O, red; N, green; Na, purple. H atoms are omitted for clarity.

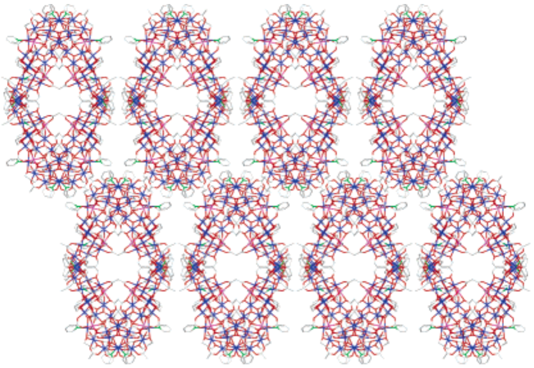

Figure 3. Wire-frame representation viewed along the *a* axis of the packing of $[\mathbf{1}]_4$ as $\{[\mathbf{1}]_4\}_2$ dimers. H atoms and H_2O molecules of crystallization are omitted for clarity. The color code is as in Figure 2.

Direct current (dc) magnetic susceptibility data on a microcrystalline powdered sample of $\mathbf{1}\cdot 10H_2O$ were recorded in the 5.0−300 K temperature range using an applied field of 0.1 T. The $\chi_M T$ value per Mn_{10} at 300 K is 28.42 cm^3 mol^{-1} K, and it decreases steadily with decreasing temperature to 8.48 cm^3 mol^{-1} K at 5.0 K. These data suggest the existence of strong antiferromagnetic interactions within **1**, with the value at 5.0 K being in the region expected for an $S = 4$ ground state (spin-only value of 10 cm^3 mol^{-1} K). In order to confirm the ground state, magnetization data were collected in the temperature and magnetic field ranges of 1.8−10.0 K and 0.1−7.0 T, respectively. Attempts were made to fit the resulting data using the program *MAGNET*,[11] which assumes that only the ground state is populated at these temperatures and includes axial zero-field-splitting

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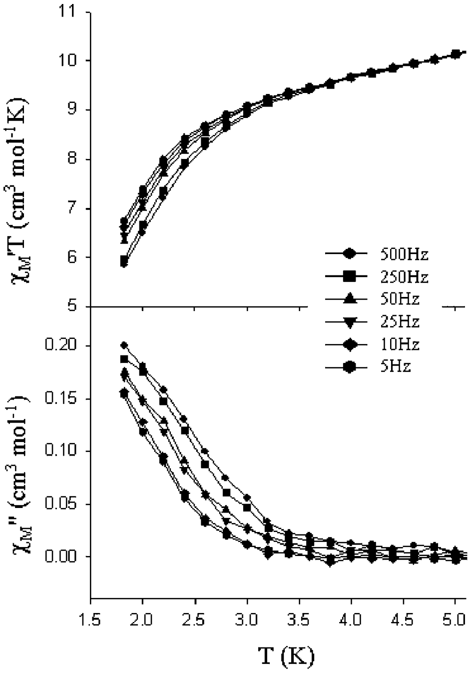

Figure 4. In-phase χ_m' (as $\chi_m'T$) (top) and out-of-phase χ_m'' (bottom) ac magnetic susceptibilities for $\mathbf{1}\cdot 10H_2O$.

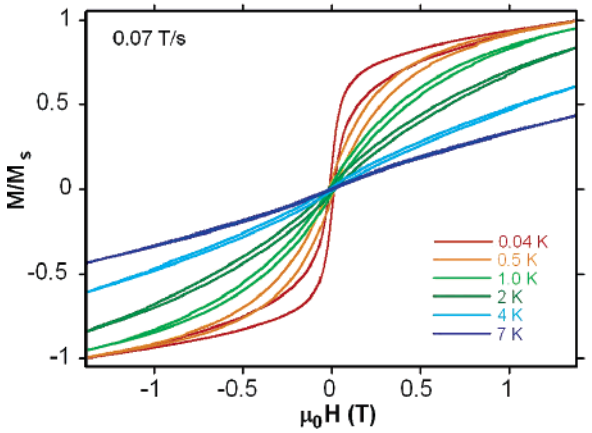

Figure 5. Magnetization (M) vs field hysteresis loops for single crystals of $[\mathbf{1}\cdot 2.4H_2O]_4$ at the indicated temperatures. The magnetization is normalized to its saturation value (M_S).

($D\hat{S}_z^2$) and Zeeman interactions. However, it was not possible to obtain a good fit. This is likely due to the presence of low-lying excited states that are populated even at these low temperatures (as indeed is expected for such a large molecule containing Mn^{II}) and intermolecular interactions between the neighboring Mn_{10} units, which are not included in the fitting model.[1c,4a,12]

Reliable conclusions about the ground state S value can, nevertheless, be reached by using alternating current (ac) magnetic susceptibility measurements,[3a,4a] which also can detect the slow magnetization relaxation suggestive of SMMs. The in-phase $\chi_m'T$ increases with increasing temperature, confirming low-lying excited states (Figure 4, top). Extrapolation of the $\chi_m'T$ vs T plots to 0 K (from $T > 4$ K to avoid the effects of slow relaxation at lower T) gives a value of $\sim$8.5 cm^3 mol^{-1} K, which is consistent with $S = 4$ (assuming $g \sim 1.85$). Below 3 K, $\chi_m'T$ is frequency-dependent, and there is a concomitant frequency-dependent, out-of-phase ac susceptibility (χ_m'') signal for **1**, whose peaks clearly lie at $T < 1.8$ K (Figure 4, bottom). This suggests that **1** might be a SMM, and in order to confirm this, magnetization vs applied dc field data down to 0.04 K were collected on single crystals of $[\mathbf{1}\cdot 2.4H_2O]_4$ using a micro-SQUID apparatus.[13] The resulting magnetization responses at different temperatures and a fixed-field sweep rate of 0.070 T s^{-1} are shown in Figure 5. Hysteresis loops become evident in the scans at 4 K, but they only have a small coercivity. The latter increases, but only slightly, with decreasing temperature down to 0.04 K. This is not typical SMM behavior, for which one would normally expect a greater dependence of the coercivity on the temperature. It is likely that this behavior is instead due to a combination of an intrinsic barrier to magnetization relaxation for each Mn_{10} unit, and exchange interactions between the neighboring Mn_{10} units of the same $[\mathbf{1}]_4$ cluster (mediated through the connecting Na^+ ions) as well as of different tetrameric units.[14]

In summary, the use of pdH_2 has yielded a large $Mn_{40}Na_4$ loop-of-loops aggregate of four Mn_{10} loops with an aesthetically pleasing saddlelike topology. Because the Na^+ ions are intimately associated with the Mn_{10} loops, the compound can also accurately be described as a mixed-metal M_{44} cluster, the second-largest Mn cluster reported to date.[1c] Each Mn_{10} loop has a ground-state spin of $S = 4$ and displays hysteresis loops in magnetization vs dc field scans that, however, are not typical of an SMM due to intermolecular interactions between the neighboring Mn_{10} units. Substitution of the Na^+ ions with paramagnetic 3d or 4f metal ions could lead to a magnetically interesting single $Mn_{40}M_4$ aggregate rather than four weakly interacting Mn_{10} units, and such studies are in progress. Finally, the tetrameric $[Mn_{10}]_4$ loop-of-loops suggests that other related aggregates of metal-linked loops or even discrete supramolecular assemblies of loops might also be possible as this work, and the chemistry of loop/wheel complexes in general,[15] is extended in the future.

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Supporting Information Available: X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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