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“Molecular Nanoclusters”: A 2-nm-Sized $\{Mn_{29}\}$ Cluster with a Spherical Structure

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Supporting Information

ABSTRACT: The comproportionation reaction between Mn^{II} and Mn^{VII} sources in the presence of 3,3-dimethylacrylic acid and azides has led to a new $\{Mn_{29}\}$ molecular cluster with a spherical structure and dimensions of ∼2.2 nm, comparable in size to the smallest classical and magnetic nanoparticles.

Molecular nanoscale materials continue to be at the forefront of chemistry, physics, and materials science not only because of their beautiful and unusual structures but also because of their potential applications in various fields of fundamental and applied research such as quantum physics, nanomagnetism, optics, spintronics, and quantum computation.[1] The synthesis of such polynuclear metal complexes (or metal clusters) can be achieved by molecular bottom-up approaches, which are distinctly different from the top-down approaches of the traditional nanoscale materials. The bottom-up approach to the nanoscale usually involves reactions between simple metal salts or oligonuclear metal complexes and bridging organic and/or inorganic ligands such as carboxylate ions and azides.[2] The bridging ligands serve to aggregate the metal ions into a molecular polymetallic array and simultaneously help to terminate extensive polymerization, which otherwise would lead to the formation of multidimensional coordination polymers or amorphous metal oxides. As a result, the bottom-up approach brings all of the advantages of molecular chemistry into the field of nanoscience, including solubility, crystallinity, monodispersity, low-energy (mild) synthetic conditions, and chemical reactivity. The latter comprises one of the most intriguing aspects of coordination cluster chemistry because it allows us to manipulate the structural, spectroscopic, and physical properties of the molecular materials by modifying the organic and inorganic ligands,[3] altering the reaction solvent, the metal-to-ligand ratio, the temperature, and the “pH” of the solution.[4]

Manganese in moderate-to-high oxidation states occupies its own special position within the fields of 3d metal cluster chemistry, bioinorganic chemistry, and molecular magnetism. The recent discovery of the gigantic $\{Mn_{84}\}$[5] and $\{Mn_{70}\}$[6] torus-like complexes and the $\{Mn_{49}\}$ cuboctahedron,[7] all with nanosized dimensions and single-molecule-magnet (SMM) behavior, has rendered manganese as one of the leading metals in molecular nanoscience and nanomagnetism. SMMs are molecular compounds with an energy barrier to magnetization reversal at low temperatures, resulting from a combination of a nonzero spin ground state (S) with an appreciable magnetoanisotropy of the easy-axis type (negative zero-field splitting, D).[8] These molecular nanomagnets have been proposed for several applications, ranging from high-density information storage to molecular spintronics and qubits for quantum computation.[9] Attempts to increase the S values and enhance the SMM properties of transition-metal-based complexes were sought by the use of bridging azides.[10] It is now established that end-on (EO) bridging azides can promote ferromagnetic exchange interactions between the metal spin carriers for a wide range of acute and slightly obtuse M−N−M angles, thus leading to high-spin molecules, SMMs, and molecule-based magnets with long-range ferromagnetic ordering or spin-canting behavior.[11]

In this work, we have combined a new carboxylate group in molecular chemistry, the anion of 3,3-dimethylacrylic acid (dmaH), with the versatile azido ligand, and we were able to synthesize and structurally and magnetically characterize a large $\{Mn_{29}\}$ cluster with a spherical topology and a diameter of ∼2.2 nm. The reported compound with the formula $[Mn_{29}O_{24}(N_3)_{10}(dma)_{28}]$ (**1**) is one of the largest 3d metal clusters reported to date and was isolated from the self-assembly, comproportionation reaction between $Mn(NO_3)_2\cdot 6H_2O$ and $NBu^n{}_4MnO_4$ in the presence of excess dmaH and Me_3SiN_3 (see the Supporting Information). The latter has proven to be an excellent precursor for the delivery of azido groups in 3d metal cluster chemistry, as was recently demonstrated by the synthesis of a new class of ferromagnetic inorganic materials with beautiful structures and SMM properties.[12]

Complex **1** crystallizes in the highly symmetric tetragonal space group $P4/nnc$. Bulk materials such as the important minerals rutile, pyrolusite, and zircon have been found to crystallize in similar high-symmetry space groups. The structure of **1** (Figure 1, top) comprises 29 Mn ions held together by 16 μ_3-O^{2-} and 8 μ_4-O^{2-} ions, as well as 8 μ-1,1 and 2 μ_4-1,1,1,1 EO bridging azido groups to yield an overall $[Mn_{29}(\mu_4\text{-}O)_8(\mu_3\text{-}O)_{16}(\mu_4\text{-}N_3)_2(\mu\text{-}N_3)_8]^{28+}$ core (Figure 1, bottom) with virtual D_{4h} symmetry. Peripheral ligation about the core is provided by a

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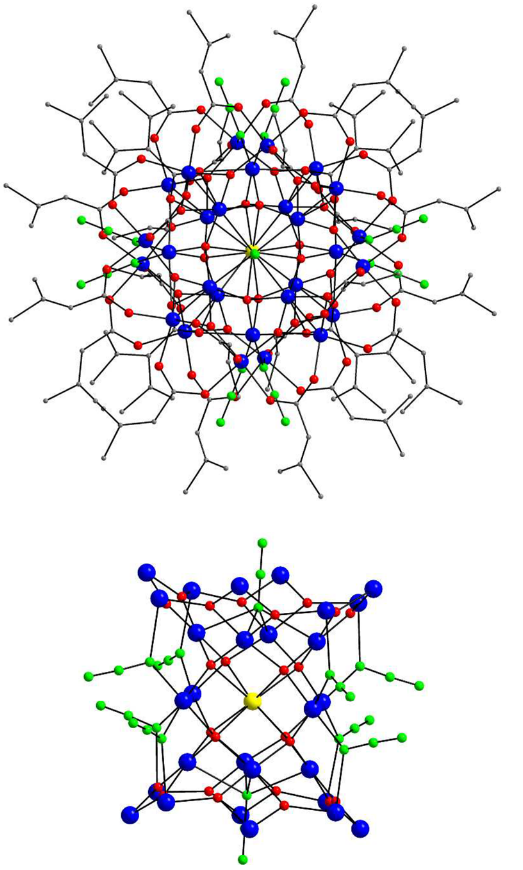

Figure 1. Structure of **1** along the crystallographic *c* axis (top) and its $[Mn_{29}(\mu_4\text{-}O)_8(\mu_3\text{-}O)_{16}(\mu_4\text{-}N_3)_2(\mu\text{-}N_3)_8]^{28+}$ core (bottom). H atoms have been omitted for clarity. Color scheme: Mn^{II}, yellow; Mn^{III}, blue; O, red; N, green; C, gray.

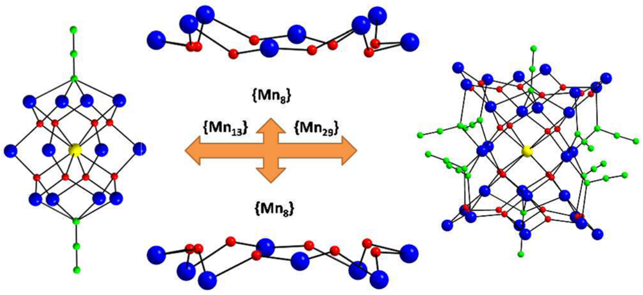

Figure 2. "Building up" the $\{Mn_{29}\}$ core of **1** from smaller $\{Mn_{13}\}$ and $\{Mn_8\}$ fragments. The color scheme is as in Figure 1.

total of 28 bridging carboxylate groups, which are arranged in two classes: 24 dma^- ligands bridge in a common *syn,syn*-η^1:η^1:μ fashion, while the remaining 4 dma^- groups adopt a rare η^2:η^2:μ_4 mode (Figure S1). Carboxylates as ancillary bridging and terminal ligands play an important role in the thermodynamic stability and crystallinity of metal−oxo clusters because (i) they are able to protect the central metal−oxo core upon extensive redox activity, (ii) they enhance the solubility of the species in most common organic solvents, and (iii) they are quite flexible, allowing for the performance of chemical reactivity studies and the observation of tunable properties because of their different steric and/or electronic properties.

The complete core of **1** appears to be organized into three layers. The central layer is a $\{Mn_{13}(\mu_4\text{-}O)_8(\mu_4\text{-}N_3)_2\}^{20+}$ unit, which can be described as consisting of eight edge-sharing $\{Mn^{II}Mn^{III}(\mu_4\text{-}O)\}$ tetrahedra, all with a shared common apex, the Mn^{II} atom. The μ_4-bridging azido groups act as capping ligands for eight Mn^{III} atoms at the two sides of the $\{Mn_{13}\}$ unit (Figure 2). Above and below the $\{Mn_{13}\}$ unit, there are the same two $\{Mn_8\}$ layers with a "crown"-like motif. These layers comprise a nonlinear array of 8 Mn^{III} atoms bridged by 8 μ-O^{2-} groups (Figure 2). The μ-O^{2-} groups are becoming μ_3-bridging, and with the additional presence of the 8 μ-N_3^- groups, they serve to link the three layers together. Charge-balance considerations, inspection of the metric parameters, and bond valence sum[13] calculations (Table S2) confirmed the $Mn^{II}Mn^{III}_{28}$ oxidation state description and the protonation levels of O^{2-} ions. The Mn^{III} atoms (Mn1, Mn2, and Mn4 and their symmetry equivalents) are six-coordinate with Jahn−Teller distorted octahedral geometries, whereas the remaining Mn^{III} atoms (Mn3 and its symmetry equivalents) are five-coordinate with distorted square-pyramidal geometry (τ = 0.40).[14] The central Mn^{II} atom (Mn5) is eight-coordinate with a slightly distorted cubic geometry (CShM = 1.19; *SHAPE* program; Figure S2).[15]

The overall spherical shape and nanometer size of the $\{Mn_{29}\}$ cluster are emphasized by the space-filling plot of Figure 3, which shows that the molecular compound has a thickness and a diameter of 2.2 nm, excluding the H atoms. Furthermore, as a result of the high crystallographic symmetry of **1**, the $\{Mn_{29}\}$ molecules are nicely packed in the crystal, forming a supramolecular gridlike structure (Figure S3). Complex **1** is the first icosaenneanuclear homometallic cluster compound reported to date. It also joins a very small family of manganese and other 3d metal clusters with nuclearities larger than 29.[5−7,16] It is also worth mentioning that the vast majority of manganese and other 3d metal clusters with large nuclearities contain an even number of metal ions. There are only a few high-nuclearity 3d metal clusters with an odd number of metal ions; in manganese chemistry, these are limited to the $\{Mn_{49}\}$ cuboctahedron and a few $\{Mn_{25}\}$ barrel-like compounds.[1] Possible reasons for this observation, which are tentatively rationalized in terms of structural comparisons between all odd-number (M_x; $x > 24$) cluster compounds, are the presence of high-order rotational axes passing from a metal ion and the size of the available vacant space at the center of the highly symmetric structure.

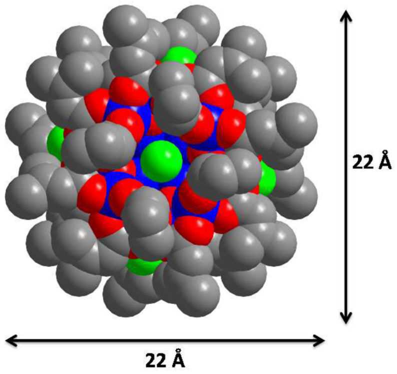

Figure 3. Space-filling representation of **1**, showing the dimensions of the molecule and its spherical structure.

Solid-state direct-current (dc) and alternating-current (ac) magnetic susceptibility (χ_M) studies were performed on $\mathbf{1}\cdot 3H_2O$ in a 1 kG (0.1 T) dc field in the 5.0−300 K range and with a 3.5 G ac field oscillating in the 1.8−15 K range, respectively. The obtained dc data are plotted as $\chi_M T$ versus T in Figure 4 and

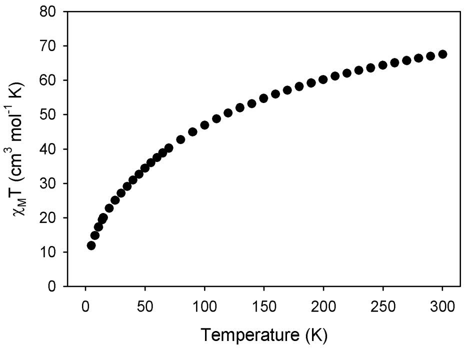

Figure 4. $\chi_M T$ versus T plot for complex **1**·3H_2O.

reveal predominantly antiferromagnetic exchange interactions between the metal centers. The $\chi_M T$ product at 300 K is 67.53 cm^3 K mol^{-1}, much less than the theoretical value of 88.38 cm^3 K mol^{-1} (calculated with $g = 2$) for 1 Mn^{II} and 28 Mn^{III} noninteracting ions, and it steadily decreases to a value of 11.86 cm^3 K mol^{-1} at 5.0 K. The overall shape of the curve and its low-temperature $\chi_M T$ value suggest a relatively small ground-state spin value, *S*, for **1**, probably mixed with low-lying excited states, as expected for a high-nuclearity system with many different repeating subunits. Although complex **1** contains an appreciable number of EO bridging azides within its repeating units, the average Mn−N−Mn angle is 111.4°, thus presaging the presence of antiferromagnetic interactions between the respective metal centers.[10] Furthermore, the concurrent presence of many bridging oxido groups, one of the strongest antiferromagnetic couplers in molecular magnetism, seems to support stabilization of a small spin ground state for **1**.

An alternative determination of *S* and a probe of the magnetization relaxation dynamics for **1** can be obtained from ac susceptibility measurements, which preclude complications from a dc field and/or low-lying excited states. The in-phase $\chi_M{}'T$ product of **1**·3H_2O (Figure S4) decreases almost linearly with decreasing temperature in the 6−15 K range, indicating depopulation of a high density of excited states with spin *S* greater than that of the ground state,[5−7,16] which is in agreement with the conclusion from the dc studies. Extrapolation of the in-phase $\chi_M{}'T$ versus T plot[16] from above ∼6 K to 0 K gives a value of ∼10 cm^3 K mol^{-1}, suggesting an $S = {}^9/_2$ ground state with $g \sim 1.8$, smaller than 2.0 as expected for mangaese. Finally, complex **1** did not exhibit an out-of-phase ac magnetic susceptibility signal down to 1.8 K (Figure S5), indicating that it does not possess a barrier large enough (vs *kT*) to show the superparamagnet-like slow relaxation of its magnetization vector; i.e., it is not an SMM. This behavior can be tentatively ascribed to the inherent high symmetry of **1**,[1] which limits the degree of magnetic anisotropy and/or the small spin ground state of the system.

In conclusion, we have shown that a comproportionation reaction comprising Mn^{II} and Mn^{VII} ions, in the presence of a new carboxylic acid and azides, leads to an unprecedented {Mn$_{29}$} molecular cluster of ∼2.2 nm size with a beautiful, spherical structure. The reported synthetic route appears to be a promising, bottom-up approach to the nanoscale and suggests that efforts toward its extension to various directions are worthy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02363.

Synthesis and various structural and magnetism figures (PDF)

Crystallographic data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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