

A Ferromagnetically Coupled Octanuclear Manganese(III) Cluster: A Single-Molecule Magnet with a Spin Ground State of $S = 16$

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Polynuclear complex, Single-molecule magnet, Magnetism, Manganese, Ferromagnetic interactions.

Supporting Information Placeholder

ABSTRACT: An octanuclear manganese complex, $[\text{Mn}^{\text{III}}_8(\mu_4\text{-O})_4(\text{L})_4(\text{OMe})_4(\text{OAc})_4(\text{OCH}_2\text{CH}_2\text{NH}_3)_4]$ (**1**) [$\text{H}_2\text{L} = 3$ -(dimethoxymethyl)-2-hydroxybenzoic acid], was synthesized with an extended cubane core structure consisting of eight manganese ions bridged by oxo atoms. Cryomagnetic studies revealed that **1** showed a single-molecule magnetic behavior with an $S = 16$ spin ground state.

Transition-metal clusters have been extensively investigated for their potential magnetic properties.¹ Many single-molecule magnets (SMMs) have been reported, and their unique magnetic properties have been explored.² Two basic requirements for constructing an SMM are a large ground spin state S and a large negative magnetic anisotropy D . However, it is difficult to control both the magnetic exchange and the magnetic anisotropy of cluster molecules. Consequently, appropriate synthetic strategies for SMMs are still important, and sophisticated spin systems are highly required. The family of $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ is one of the most intensively studied group of SMMs.³ The manganese ion is a useful metal ion for constructing molecular magnetic materials because of its variety of oxidation/spin states [Mn(II), Mn(III), and Mn(IV)] and the significant magnetic anisotropy of the Mn(III) ion. Therefore, several SMMs composed of manganese ions have been reported, and it is known that the complexity of their structures has tended to increase with increasing molecular size.⁴ A number of spin clusters have been developed by using various ligands. For examples, the Mn_{84} complex, $[\text{Mn}_{84}\text{O}_{72}(\text{OH})_6(\text{CH}_3\text{CO}_2)_{78}(\text{OMe})_{24}(\text{MeOH})_{12}(\text{H}_2\text{O})_{42}]$, has a giant wheel structure with a spin ground state of $S = 6$.⁵ The Mn_{19} complex, $[\text{Mn}^{\text{II}}_7\text{Mn}^{\text{III}}_{12}\text{O}_8(\text{N}_3)_8(\text{Hbhmmp})_{12}(\text{MeCN})_6]\text{Cl}_2$ [$\text{H}_2\text{bhmmp} = 2,6$ -bis(hydroxymethyl)-4-methylphenol], has an $S = 83/2$ spin ground state and a low blocking temperature

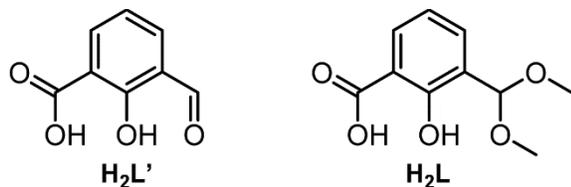
(T_B) of 0.5 K, which is due to its small magnetic anisotropy.⁶ It was previously suggested that a balance between a high spin ground state and a large negative magnetic anisotropy is difficult to achieve by means of serendipitous synthetic methods.² To prepare SMMs with a high blocking temperature, it is important to explore new cluster cores constructed with proper ligands.

In constructions of polynuclear complexes with high ground spin states, it is known that cubanes and stacked triangles are excellent magnetic cores. A tetranuclear cubane core consisting of four metal ions bridged by oxygen atoms is a well-known structural motif. Such cubane cores tend to display ferromagnetic interactions, which is due to the accidental orthogonality of the magnetic orbitals.⁷ We have previously reported several examples of alkoxo-bridged tetranuclear ferrous cubes, derived from Schiff-base ligands, that display superparamagnetic behavior.⁸ On the other hand, stacked triangle cores consisting of six metal ions bridged by $\mu_3\text{-O}$ and oxime groups have also been well investigated. Brechin and co-workers reported a series of Mn_6 SMMs with the stacked triangle core.⁹ In such systems, intramolecular magnetic exchange interactions are sensitive to the Mn–N–O–Mn torsion angles of the oxime bridges, resulting in various spin ground state from $S = 4$ to $S = 12$. However, these complexes have a large and negative magnetic anisotropy associated with the presence of Jahn–Teller-distorted Mn(III) ions aligned in the direction perpendicular to the plane of the $\{\text{Mn}_3\text{O}\}$ triangle.

With this background in mind, we attempted to synthesize various polynuclear complexes containing regular arrays of metal ions, such as triangles, cubes, rings, wheels, grids, helices, or Keggin, by using several rigid and planar ligands.¹⁰ In our search for polynuclear manganese complexes with high ground spin states, we obtained a new manganese complex by serendipitous supramolecular assembly through hydrogen

bonds, accompanied by acetalization of the ligand. Here, we report the synthesis, structure, and magnetic properties of an octanuclear manganese cluster, $[\text{Mn}^{\text{III}}_8(\mu_4\text{-O})_4(\text{L})_4(\text{OMe})_4(\text{OAc})_4(\text{OCH}_2\text{CH}_2\text{NH}_3)_4]$ (**1**) [$\text{H}_2\text{L} = 3$ -(dimethoxymethyl)-2-hydroxybenzoic acid], which has a high spin ground state of $S = 16$, and showed SMM behavior.

Chart 1. Structures of the Ligands Used in This Work



The reaction of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with $\text{H}_2\text{L}'$ ($\text{H}_2\text{L}' = 3$ -formylsalicylic acid), 2-aminoethanol, and Et_3N in methanol gave the octanuclear manganese complex **1** after recrystallization from acetonitrile. During the synthesis of complex **1**, the formyl group of $\text{H}_2\text{L}'$ was transformed into a dimethoxymethyl group by acetalization.¹¹ Complex **1** crystallized in the monoclinic space group $C2/c$ (Table S1). The asymmetric unit consists of a half of $[\text{Mn}^{\text{III}}_8(\mu_4\text{-O})_4(\text{L})_4(\text{OMe})_4(\text{OAc})_4(\text{OCH}_2\text{CH}_2\text{NH}_3)_4]$, and three acetonitrile molecules. In this structure, the amino group of 2-aminoethanol is protonated to form an ammonium cation, whereas the hydroxy group is deprotonated and coordinates to two manganese ions in a μ_2 -bridging mode. The structure of **1** contains a $[\text{Mn}^{\text{III}}_8(\mu_4\text{-O})_4(\mu_2\text{-O})_8]$ core in which four $\mu_4\text{-O}$ are oxide ion, four $\mu_2\text{-O}$ atoms are derived from the 2-aminoethanol moiety and four $\mu_2\text{-O}$ atoms are derived from the methoxide anion. The core can be considered as a face-shared defective pentacubane, which appears to be an extended cubane structure. There are four crystallographically independent manganese(III) ions with Jahn-Teller distortion; these are classified into peripheral ions (Mn1 and Mn3) and central ions (Mn2 and Mn4). The Mn1 and Mn3 ions are in an O_6 coordination sphere of peripheral sites, with two oxygen atoms from the ligand, one oxygen atom from the 2-aminoethanol moiety, one oxygen atom from the methoxide anion, one $\mu_4\text{-O}$ atom, and one oxygen atom from the acetate anion. The Mn2 and Mn4 ions are in an O_6 coordination sphere of the central Mn_4O_4 cubane core, with three $\mu_4\text{-O}$ atoms, one oxygen atom from the 2-aminoethanol moiety, one oxygen atom from the methoxide anion, and one oxygen atom from the acetate anion. The manganese(III) oxidation states were established by considering bond lengths, bond valence sum calculations (Table S2), and the presence of elongated Jahn-Teller distortions, as expected for octahedral manganese(III) centers. The Jahn-Teller axes of the four manganese ions in peripheral sites are approximately parallel to each other with an elongated Mn1-O6 , Mn1-O17 , Mn3-O3 , and Mn3-O19 bond lengths. In contrast, the Jahn-Teller axes (Mn2-O1 , Mn2-O2 , Mn4-O4 , and Mn4-O5) of the four manganese ions in central sites lie perpendicular to the pseudo molecular S_4 axis, resulting in a uniaxial magnetic easy axis (Figure S1). In the Mn_4O_4 cubane core, the Mn-O-Mn bond angles are in the range $90.94\text{--}104.73^\circ$, whereas the Mn-O-Mn bond angles between the manganese ions of the central and peripheral sites are in the range $92.35\text{--}103.96^\circ$. The

neighboring $\text{Mn}\cdots\text{Mn}$ separations in the octanuclear core are in the range $2.963\text{--}3.194 \text{ \AA}$. The shortest intermolecular $\text{Mn}\cdots\text{Mn}$ separation is 8.129 \AA . Methyl group of AcO^- ion interacts with phenyl ring of neighboring Mn_8 cluster through $\text{CH}\cdots\pi$ interactions (Figure S2).

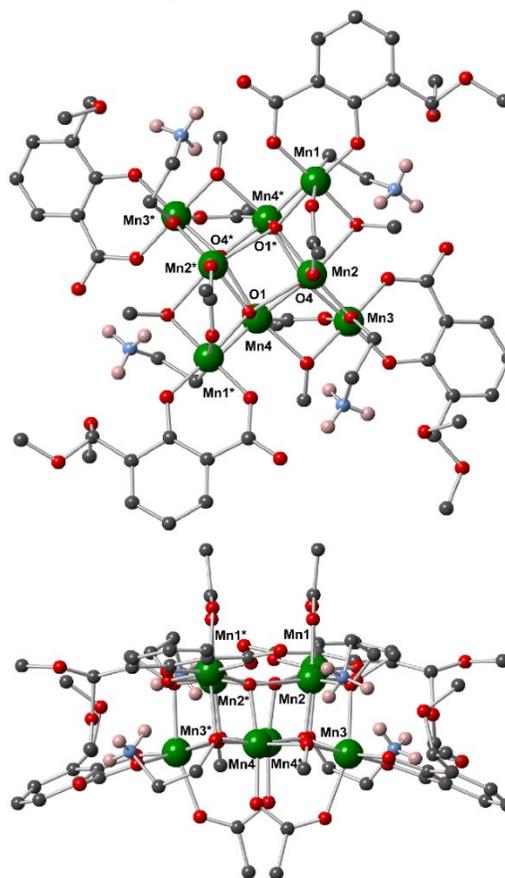


Figure 1. Molecular structure of **1**. Top: top view. Bottom: side view. Only the H atoms that are part of the ammonium group of 2-aminoethanol are shown. Color code: C, gray; N, light blue; Mn^{III} , green. Symmetry code: * 2 - x, +y, 3/2 - z. Solvent molecules are excluded for clarity.

Complex **1** has a unique intramolecular hydrogen bond, $\text{N-H}\cdots\text{O}-\text{C}$, between the ammonium group of the 2-aminoethanol moiety and the oxygen of the ligand (Table S3). The formation of this intramolecular interaction contributes to the stability of the octanuclear cluster structure.

Magnetic susceptibility measurements for **1** were performed in the temperature range $1.8\text{--}300 \text{ K}$ with an applied magnetic field of 500 Oe . Plots of $\chi_m T$ versus T are shown in Figure 2. At room temperature, the values of the $\chi_m T$ product ($28.137 \text{ emu mol}^{-1} \text{ K}$) are larger than the expected spin-only value ($24 \text{ emu mol}^{-1} \text{ K}$) for eight magnetically isolated manganese(III) ions ($S = 2$). The $\chi_m T$ values gradually increased with decreasing temperature to a maximum value of $136.0 \text{ emu mol}^{-1} \text{ K}$ at 5.5 K . The value of $\chi_m T$ decreased to $112.9 \text{ emu mol}^{-1} \text{ K}$ at 1.8 K due to zero-field splitting. This magnetic behavior is indicative of the presence of intramolecular ferromagnetic interactions between manganese(III) ions. The magnetic behavior above 5 K was fitted by MAGPACK, based on an eight-center spin

model with two kinds of magnetic exchange interactions J_1 and J_2 without magnetic anisotropy terms (Figure 2, inset) with the following spin Hamiltonian:²²

$$H = -2J_1(S_2 \cdot S_4 + S_2 \cdot S_6 + S_2 \cdot S_8 + S_4 \cdot S_6 + S_4 \cdot S_8 + S_6 \cdot S_8) - 2J_2(S_1 \cdot S_2 + S_1 \cdot S_8 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_5 + S_5 \cdot S_6 + S_6 \cdot S_7 + S_7 \cdot S_8).$$

Ferromagnetic interactions were estimated with $J_1 = +5.0$ K and $J_2 = +2.3$ K with $g = 1.98$. The discrepancy factor $R(\chi_m)$ was 3.56×10^{-2} and $R(\chi_m T)$ was 2.98×10^{-2} . **1** has a perpendicular alignment of Jahn-Teller axis through μ -O bridges, thus the ferromagnetic interactions are expected.¹³ Magnetization experiments for **1** were carried out and the reduced magnetization versus H/T plots are shown in Figure 2 (right). The magnetization of **1** saturated with a value of $29.8 N\beta$ when the magnetic field exceeded 5.0 T at 1.8 K. The reduced magnetization data in the 1.8–3.0 K and 2–5 T ranges were fitted by assuming an $S = 16$ spin ground state with $g = 1.98$, $D/k_B = -0.15$ K, $E/k_B = 0.05$ K, and $B_4^0 = 3.0 \times 10^{-5}$ K.

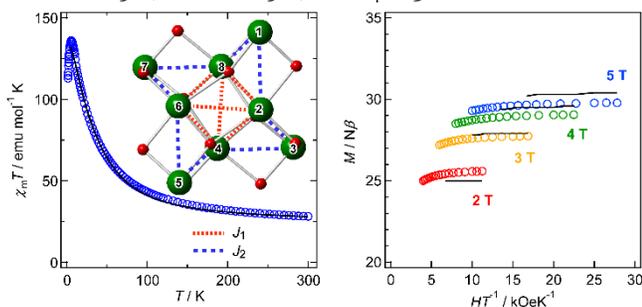


Figure 2. Left: Plots of $\chi_m T$ versus T for **1**. The solid line represents the fit of the data to the theoretical model. The schematic in the inset is a spin model for fitting of the magnetic data. Right: The reduced magnetization $M/N\beta$ versus H/T plots for **1** at 2–5 T. The solid lines correspond to the fit of the data (see text for details).

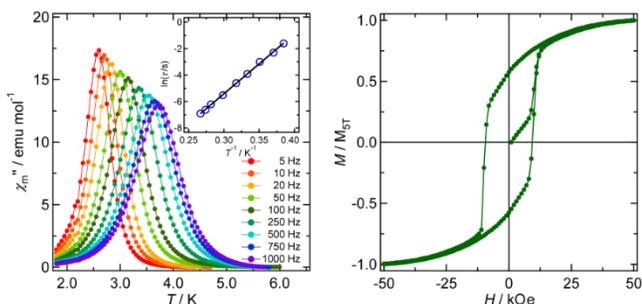


Figure 3. Left: Frequency dependences of the out-of-plane magnetic susceptibility (χ_m'') for **1** at various temperatures between 1.8 and 6.0 K under zero external magnetic dc field. An Arrhenius plot from the position of the χ_m'' peaks is shown in the inset. Right: Magnetization versus magnetic field for aligned single crystals of **1** at 450 mK ($H \perp a$ axis).

We carried out ac magnetic susceptibility studies under zero external dc field (Figure 3, left; Figure S1). The χ_m'' versus T plots for various frequencies led to well-defined maxima in the temperature range 1.8–6.0 K. Analysis of the linear variation of **1** with the Arrhenius law $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ gave $U_{\text{eff}}/k_B = 45.14$ K with $\tau_0 = 5.85 \times 10^{-9}$ s. Magnetizations in the

direction perpendicular to the magnetization hard axis were measured for aligned single crystals of **1** in a static magnetic field at 450 mK (Figure 3, right). The M/M_{5T} versus H plots showed a distinct hysteresis loops with a step at 9 kOe.

The high-field EPR spectra obtained with a pulsed magnetic field are shown in Figure 4 (left) and Figure S2. The temperature dependences of the EPR spectra for the powder sample were collected at 190 GHz (Figure 4, left). The spectrum at 4.2 K showed the most intense band at 3.9 T, and more fine structure was observed for the EPR signals at higher temperatures in the higher-magnetic-field region. This is due to the appreciable thermal energy needed to populate higher-energy M_S levels; moreover, the temperature dependence of the EPR signals indicates that **1** has a negative D value. Zeeman splitting of the $S = 16$ state, calculated with $D = -0.15$ K, $E = 0.05$ K, $B_4^0 = 3.0 \times 10^{-5}$ K, and $g = 1.98$ by using the Hamiltonian below:

$$H = g\mu_B H + D[S_z - 1/3 S(S+1)] + E(S_x - S_y) + B_4^0 O_4$$

The expected resonance lines were plotted with the observed peaks (Figure 4, right). These parameters are consistent with the above-mentioned magnetic-fitting parameters.

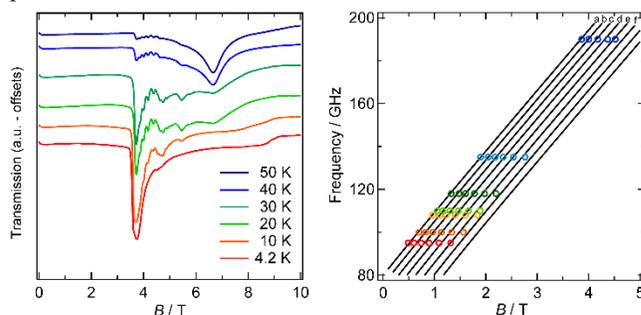


Figure 4. Left: Temperature dependences of high-field EPR spectra of a powder sample of **1** measured at 190 GHz. Right: Plots of the frequency versus the resonance magnetic field B for the observed peaks. Solid lines on the frequency versus magnetic field plots were calculated from $S = 16$, $D = -0.15$ K, $E = 0.05$ K, and $B_4^0 = 3.0 \times 10^{-5}$ K (see text for details). Assignments: a, $m = -16 \rightarrow -15$; b, $m = -15 \rightarrow -14$; c, $m = -14 \rightarrow -13$; d, $m = -13 \rightarrow -12$; e, $m = -12 \rightarrow -11$; f, $m = -11 \rightarrow -10$.

In summary, an octanuclear manganese complex with an extended cubane core structure consisting of eight manganese ions bridged by oxo atoms was synthesized. Cryomagnetic studies revealed that **1** displays a single-molecule magnetic behavior with an $S = 16$ spin ground state and a negative magnetic anisotropy of $D = -0.15$ K, as confirmed by the magnetization hysteresis and high-field EPR measurements. The obtained octanuclear Mn(III) complex has a maximum spin ground state of $S = 16$, which is the first case among known octanuclear Mn(III) complexes (Table S4). The present study shows that the extended cubane core structure is a good motif for constructing high-performance SMMs due to the presence of effective ferromagnetic interactions.

ASSOCIATED CONTENT

Supporting Information

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

Experimental and characterization details, detail synthetic procedure, crystal data, a real part of ac magnetic susceptibility data and EPR spectra of **1**.

Accession Codes

CCDC 1959643 contains the supplementary crystallographic data for **1** at 200 K. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written with contributions by all authors.

Notes

The authors declare no competing financial interests.

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An Octanuclear Manganese(III) Single-Molecule Magnet

