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New Mn_{12} Clusters with Tunable Oxidation States via the Use of *N*,*N*,*N′*,*N′*-Tetrakis(2-hydroxyethyl)ethylenediamine

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Room-temperature reactions of *N*,*N*,*N′*,*N′*-tetrakis(2-hydroxyethyl)ethylenediamine with manganese(II) salts yield a novel family of Mn_{12} clusters incorporating the same $Mn_{12}O_4$ core and tunable oxidation states of $Mn^{III}{}_xMn^{II}{}_{12-x}$ ($x = 8$, 10, and 12). Magnetic susceptibility data indicate that the spin of the ground state increases as the number of Mn^{III} ions is increased, leading to increases in the magnitude of the out-of-phase ac susceptibility signal as the number of Mn^{III} ions is increased.

Because $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ (abbreviated Mn_{12}-Ac) was identified as a single-molecule magnet (SMM),[1] there has been much interest in high-nuclearity polyoxometalate complexes since they are promising materials for data storage and quantum computing.[2] The Mn_{12}Ac family has been expanded to include many complexes as a result of changes in the carboxylate and water ligands.[3] Geometric and Jahn–Teller (JT) isomeric forms of members of the Mn_{12}Ac family have been found[4] that exhibit appreciable changes in magnetization dynamics. The Mn_{12}Ac family has also been expanded to include monoanionic $[Mn_{12}]^-$ and dianionic $[Mn_{12}]^{2-}$ complexes.[5] While there have been some other dodecanuclear Mn SMMs reported,[6] there has not been a second extensive family of Mn_x SMMs characterized with such redox flexibility.

Herein we report three new members of a second Mn_{12} family: $[Mn^{II}{}_4Mn^{III}{}_8(\mu_4\text{-}O)_4(\mu\text{-}H_2O)_2(\mu\text{-}Cl)_4(\mu_5\text{-edte})_4Cl_4]\cdot 5MeCN\cdot H_2O$ (**1**), $[Mn^{II}{}_2Mn^{III}{}_{10}(\mu_4\text{-}O)_4(\mu\text{-}OH)(\mu\text{-}N_3)_5(\mu_5\text{-edte})_4(N_3)_4]\cdot THF\cdot 3H_2O$ (**2**; THF = tetrahydrofuran), and $[Mn^{III}{}_{12}(\mu_4\text{-}O)_4(\mu\text{-}OH)(\mu\text{-}N_3)_5(\mu_5\text{-edte})_4(N_3)_4](ClO_4)(N_3)\cdot 2H_2O$ (**3**). In this new Mn_{12} family, four new developments have been achieved: (1) the ligand *N*,*N*,*N′*,*N′*-tetrakis(2-hydroxyethyl)ethylenediamine (H_4edte) is used to form a polynuclear complex; (2) there is an unusual $[Mn_{12}(\mu_4\text{-}O)_4]$ topology; (3) these Mn_{12} complexes exhibit extremely rare tetragonally compressed Mn^{III} ions; (4) the plots of reduced magnetization ($M/N\beta$) versus H/T are unusual in that they show very little temperature dependence of ($M/N\beta$) at a given field. A Mn_{16} complex reported by Price et al.[7] in which 2 of the 16 Mn ions exhibit JT compression is the only other known example of tetragonally compressed Mn^{III} axes in polynuclear Mn complexes.

Room-temperature solution reactions of manganese(II) salts with H_4edte in MeOH or MeCN lead to dark-red block-shaped crystals of **1**–**3** in ca. 30–75% yield.[8]

Complex **1**[9] crystallizes in tetragonal space group *P*4/*ncc*, with the asymmetric unit containing one-fourth of the formula. Complex **1** consists of a neutral dodecanuclear $[Mn^{II}{}_4Mn^{III}{}_8(\mu_4\text{-}O)_4(\mu\text{-}H_2O)_2(\mu\text{-}Cl)_4(\mu_5\text{-edte})_4Cl_4]$ molecule (Figure 1a) and lattice MeCN and water molecules. The oxidation states of Mn1, Mn2, and Mn3 ions in **1** were established to be 3+, 3+, and 2+ by consideration of bond

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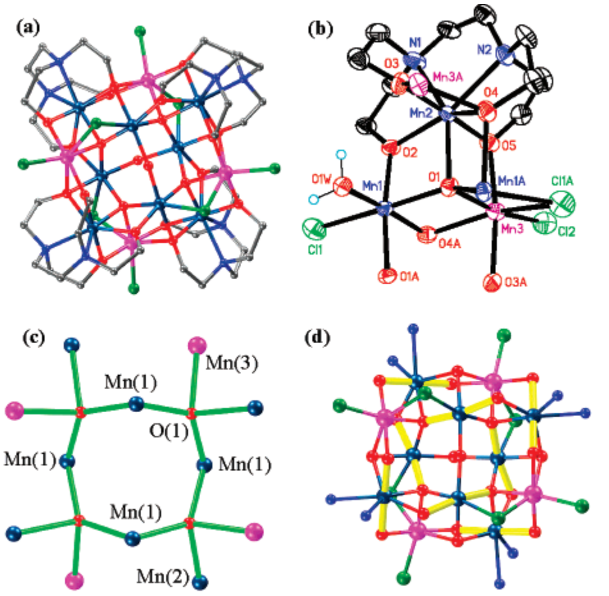

Figure 1. Molecular structure (a) and coordination environments of the Mn ions and bridging mode of the edte^{4-} ligands (b), the $Mn_{12}(\mu_4\text{-}O)_4$ core (c), and the JT compression axes highlighted in bold yellow (d) for complex **1**. Color code: navy blue, Mn^{III}; purple, Mn^{II}; green, Cl; red, O; blue, N; gray, C. H atoms have been omitted for clarity. Symmetry: a, $-y + 1$, $x + {}^1/_2$, $-z$.

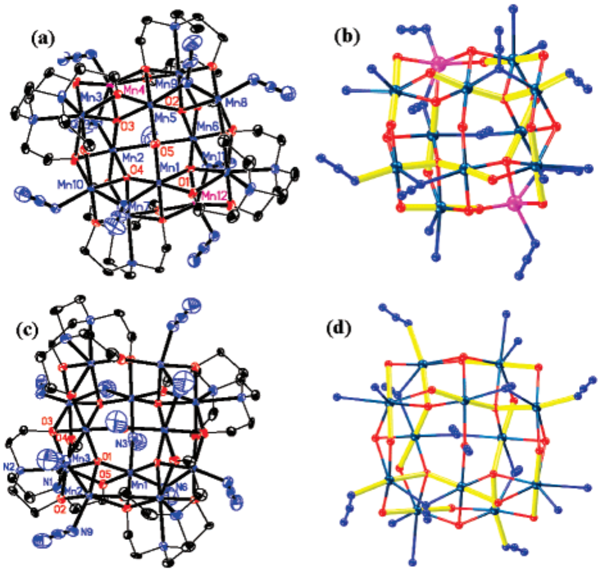

Figure 2. Molecular structure (a and c) and the JT compression highlighted by the bold yellow lines (b and d) for **2** (top) and **3** (bottom). Color code: navy blue, Mn^{III}; purple, Mn^{II}; green, Cl; red, O; blue, N; gray, C. H atoms have been omitted for clarity.

lengths, bond-valence-sum (BVS) calculations,[10] charge considerations, and the observation of JT distortions for the Mn^{III} centers. The four Mn^{II} and eight Mn^{III} ions are bridged by four μ_4-O^{2-} oxides, forming a $Mn_{12}O_4$ core (Figure 1c) that is capped by four μ_5-edte^{4-} ligands (Figure 1b), two μ_2-H_2O molecules, four μ-Cl^-, and four terminal Cl^- ions. The resulting Mn_{12} cluster resembles a twisted saddle capped by four μ_5-edte^{4-} ligands. The trivalent Mn1 ion is coordinated in a rare tetragonally compressed geometry, with the Mn1−O1a and Mn1−O2 bonds forming the JT-compressed axes with bond distances of 1.909(3) and 1.924(3) Å, respectively. The trivalent Mn2 ions are coordinated in a rare compressed pentagonal-bipyramidal geometry, with the Mn2−O3 [1.947(4) Å] and Mn2−O5 [1.973(4) Å] bonds forming the JT-compressed axes, by four alkyl O atoms and two N atoms from a hexadentate edte^{4-} ligand and one O^{2-} group. The divalent Mn3 is coordinated in a distorted octahedral geometry by three alkyl O atoms, two Cl^-, and one O^{2-} group with Mn3−O/N/Cl distances between 2.003(4) and 2.542(2) Å.

Complexes **2** and **3** crystallize in the monoclinic space group $P2_1/n$ and tetragonal space group $P\bar{4}2_1c$, respectively.[9] The structure of **2** consists of a dodecanuclear $[Mn^{II}_2Mn^{III}_{10}(\mu_4\text{-}O)_4(\mu\text{-}OH)(\mu\text{-}N_3)_5(\mu_5\text{-edte})_4(N_3)_4]$ molecule (Figure 2a) with THF and water solvent molecules. Of the 12 Mn atoms of the asymmetric unit of **2**, the Mn4 and Mn12 atoms are divalent, while the remaining 10 Mn atoms are trivalent and tetragonally compressed. The structure of **3** consists of $[Mn^{III}_{12}(\mu_4\text{-}O)_4(\mu\text{-}OH)(\mu\text{-}N_3)_5(\mu_5\text{-edte})_4(N_3)_4]^{2+}$ cations (Figure 2c), ClO_4^- and N_3^- anions, and lattice water molecules. The oxidation states of all Mn atoms in **3** are trivalent, and they are tetragonally compressed. Both **2** and **3** look like twisted-saddle structures, which are similar to that of **1** except that the μ-H_2O and μ-Cl bridges are substituted by μ-N_3^- or μ-OH^- bridges and four terminal Cl^- atoms are substituted by N_3^- groups. Complexes **1**−**3** all have the same $[Mn_{12}(\mu_4\text{-}O)_4]$ core (Figure 1c).

Magnetic susceptibility versus temperature (1.8−300 K) data were collected at 0.1 T for **1**−**3** (Figure 3). It can be seen that, as the number of Mn^{III} ions increases from **1**, **2**, to eventually **3** with all Mn^{III} ions, the χ_mT product increases at a given temperature. Unfortunately, it is not possible to employ the Kambe method to determine the ground-state

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(8) Synthesis of **1**. To a 20 mL MeCN solution of $MnCl_2 \cdot 4H_2O$ (0.600 g, 2 mmol) and $FeCl_3 \cdot 6H_2O$ (0.273 g, 1.0 mmol) was added a solution of H_4edte (0.236 g, 1 mmol) and 2-aminoethanol (0.240 g, 4.0 mmol) or NaOH (0.160 g, 4.0 mmol) in MeCN. After 4 h of stirring, the reaction was left undisturbed for 2 weeks, yielding dark square-block crystals of complex **1**, which were collected in ~30% yield. Synthesis of **2**. To a 20 mL MeCN solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (1.080 g, 3 mmol) was added a solution of H_4edte (0.236 g, 1 mmol), 2-aminoethanol (0.240 g, 4.0 mmol), and NaN_3 (0.130 g, 2.0 mmol) in MeOH. After 4 h and following diffusion with THF for 1 week, black sheet crystals of complex **2** were collected in ~75% yield. Synthesis of **3**. To a 20 mL MeCN solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (1.095 g, 3 mmol) was added a solution of H_4edte (0.133 g, 0.5 mmol), propane-1,3-diol (0.302 g, 4.0 mmol), and NaN_3 (0.385 g, 6.0 mmol) in MeCN. After 2 h and being left undisturbed for 2 days, large dark-black block crystals of complex **3** were collected in ~75% yield. $FeCl_3$ was added to accelerate the solubility of $MnCl_2$ in MeCN. 2-Aminoethanol acts as a base, while propane-1,3-diol was added to obtain good single crystals of **3**. ***Caution!*** *Perchlorate salts of metal complexes are potentially explosive and should be handled with care.*

(9) Crystal data for **1**: $C_{50}H_{101}Mn_{12}Cl_8N_{13}O_{23}$, $M_r = 2195.32$, tetragonal, space group $P4/ncc$, $a = 19.6410(16)$ Å, $c = 20.772(3)$ Å, $V = 8013.2(15)$ Å^3, $T = 123(2)$ K, $Z = 4$, 25 928 reflections collected, 3798 independent reflections ($R_{int} = 0.0974$), R1 = 0.0810, wR2 = 0.1954 [$I > 2\sigma(I)$]. Crystal data for **2**: $C_{44}H_{95}Mn_{12}O_{25}N_{35}$, $M_r = 2173.83$, monoclinic, space group $P2_1/n$, $a = 11.4017(7)$ Å, $b = 27.3994(17)$ Å, $c = 25.8015(16)$ Å, $\beta = 91.947(1)°$, $V = 8055.7(9)$ Å^3, $T = 123(2)$ K, $Z = 4$, 32 876 reflections collected, 15 422 independent reflections ($R_{int} = 0.0458$), R1 = 0.0604, wR2 = 0.1503 [$I > 2\sigma(I)$]. Crystal data for **3**: $C_{40}H_{85}Cl\ Mn_{12}N_{38}O_{27}$, $M_r = 2225.19$, tetragonal, space group $P\bar{4}2_1c$, $a = 14.1159(14)$ Å, $c = 22.067(3)$ Å, $V = 4397.1(9)$ Å^3, $T = 123(3)$ K, $Z = 2$, 16 707 reflections collected, 4778 independent reflections ($R_{int} = 0.0623$), R1 = 0.0639, wR2 = 0.1537 [$I > 2\sigma(I)$].

(10) (a) BVS calculations for Mn^{II} and Mn^{III} ions in **1** gave oxidation state values of 2.681 and 2.812−3.128, respectively. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102.

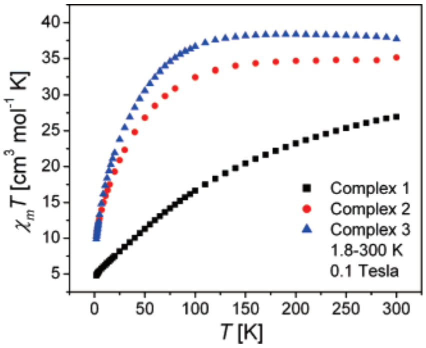

Figure 3. Plot of $\chi_m T$ versus absolute temperature dc magnetic susceptibility for complexes **1**−**3**.

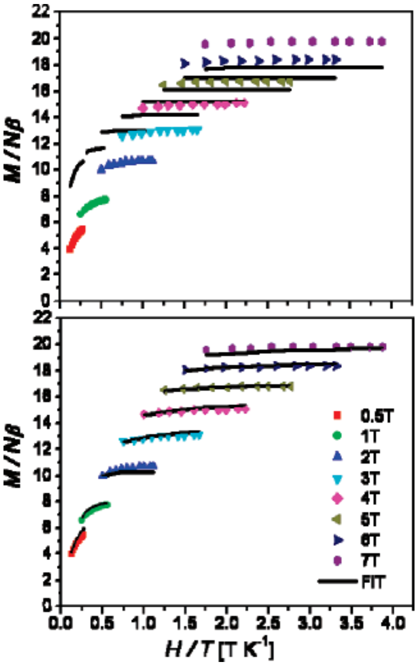

Figure 4. Plots of reduced magnetization ($M/N\beta$) versus H/T for complex **3** on a polycrystalline sample in the temperature range of 1.8−4.0 K in applied fields of 0.5−7 T fit to a single spin state ($S = 11$, top) and fit to two spin states ($S = 6$ and 11, bottom) separated by a 30 K energy barrier.

spins or exchange parameters. Through a combination of analysis of very low-temperature reduced magnetization data and in-phase alternating current (ac) susceptibilities at the lowest temperatures, we can determine the ground-state spins of **1**−**3**.

Figure 4 illustrates the reduced magnetization data, $M/N\beta$, plotted versus H/T for complex **3** in the temperature range of 1.8−4 K with applied external magnetic fields of 0.5−7 T. Examination of these data shows that they are unusual; for example, not only is there little temperature dependence at 7 T but also at 2 T. It is clear that more than one spin state is populated because, as shown in Figure 4 (top), you cannot fit all of the data by assuming there is only one spin state present experiencing some axial zero-field ($D\hat{S}_z^2$) splitting. A good fit of these data can be achieved, however, if there are two different spin states that are thermally populated. Fitting the data in the 5−7 T range suggests that there is an $S = 11$ state. Extrapolating the in-phase ac susceptibility data to $T = 0$ K indicates that in zero field there is an $S = 6$ state. Thus, as shown in Figure 4 (bottom), we could fit the $M/N\beta$ versus H/T data by assuming that two spin states ($S = 6$ and $S = 11$) separated by ΔE energy are present, each with an axial zero-field interaction. Least-squares fitting gives an $S = 6$ state with $D_1 = -0.30$ K with an $S = 11$ state with $D_2 = -0.32$ K at 30 K in energy. The $M/N\beta$ versus H/T data for complexes **1** and **2** are similar and can be fit, assuming two spin states in each case. If two or more spin states are close in energy in any complex, then the presence of an appreciable magnetic field and, for that matter, magnetic exchange interactions will mix the spin states. As such, S and M_s will no longer be good quantum numbers.

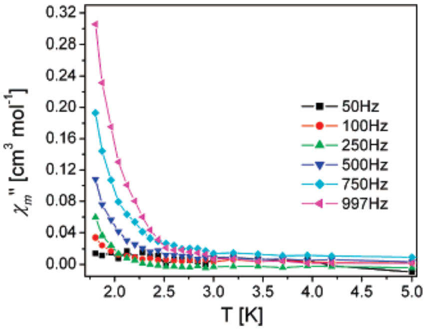

Figure 5. Plot of an out-of-phase portion of the ac magnetic susceptibility for complex **3** in the temperature range of 1.8−5 K.

ac magnetic susceptibility data for complexes **1**−**3** were collected on polycrystalline samples in the temperature range of 1.8−5 K in a 3 G ac field and a zero applied dc magnetic field. Figure 5 illustrates the onset of the frequency-dependent out-of-phase signal of the ac susceptibility for complex **3**. Similar frequency-dependent out-of-phase ac signals are seen for complexes **1** and **2**, and this is preliminary evidence for SMM behavior in all of these complexes.

Several additional experiments have been initiated on these new Mn_{12} complexes, such as a micro-SQUID determination of the presence of magnetization hysteresis and high-frequency electron paramagnetic resonance experiments to determine the spin of the low-lying states of each complex. It is hoped that these studies will elucidate the impact of the rare tetragonal compression seen at the Mn^{III} ions in these interesting Mn_{12} complexes.

In summary, $edte^{4-}$ is for the first time introduced into high-nuclearity manganese chemistry and has yielded three new Mn_{12} clusters with an unprecedented $Mn_{12}(\mu_4\text{-}O)_4$ core.

CCDC 650420, 650421, and 650422 contains crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: X-ray crystallography, BVS calculations, magnetic measurements, and magnetization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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