Single-Molecule Magnets: A Family of Mn\textsuperscript{III}/Ce\textsuperscript{IV} Complexes with a [Mn\textsubscript{8}CeO\textsubscript{8}]\textsuperscript{12+} Core

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Received January 21, 2008

Four heterometallic, enneanuclear Mn- Ce clusters [Mn\textsubscript{8}CeO\textsubscript{8}(O\textsubscript{4}CMe)\textsubscript{12}(H\textsubscript{2}O)\textsubscript{4}] (4), [Mn\textsubscript{8}CeO\textsubscript{8}(O\textsubscript{4}CMe)\textsubscript{12}(py)\textsubscript{4}] (5), [Mn\textsubscript{8}CeO\textsubscript{8}(O\textsubscript{4}CPh)\textsubscript{12}(MeCN)\textsubscript{4}] (6), and [Mn\textsubscript{8}CeO\textsubscript{8}(O\textsubscript{4}CPh)\textsubscript{12}(dioxane)\textsubscript{4}] (7) have been prepared by various methods. Their cores are essentially isostructural and comprise a nonplanar, saddlelike [Mn\textsubscript{8}O\textsubscript{8}]\textsuperscript{8-} loop containing a central Ce\textsuperscript{IV} ion attached to the eight Mn\textsuperscript{III} ions. Peripheral ligation around the [Mn\textsubscript{8}CeO\textsubscript{8}]\textsuperscript{12+} core is provided by eight µ- and four µ\textsubscript{3}-O\textsubscript{2}CR\textsuperscript{-} groups. Terminal ligation on four Mn\textsuperscript{III} atoms is provided by H\textsubscript{2}O in 4 and 7, pyridine in 5, and MeCN/dioxane in 6. Solid-state magnetic susceptibility studies, fits of dc magnetization vs field and temperature data, and in-phase ac susceptibility studies in a zero dc field have established that complexes 4, 5, and 7 possess S = 16, S = 4 or 5, and S = 6 ± 1 spin ground states, respectively, but in all cases there are very low-lying excited states. The large variation in the ground-state spins for this isostructural family is rationalized as due to a combination of weak exchange interactions between the constituent Mn\textsuperscript{III} atoms, and the presence of both nearest-neighbor and next-nearest-interactions of comparable magnitudes. Magnetization vs applied dc field sweeps on single crystals of 4·4H\textsubscript{2}O and 7·4H\textsubscript{2}O·3MeCN·2CH\textsubscript{2}Cl\textsubscript{2} down to 0.04 K have established that these two complexes are new single-molecule magnets (SMMs). The former also shows an exchange-bias, a perturbation of its single-molecule properties from very weak intermolecular interactions mediated by hydrogen-bonding interactions with lattice–water molecules of crystallization.

Introduction

One of the motivating themes in our polynuclear cluster chemistry is the identification of new high nuclearity manganese carboxylate clusters that can function as nanoscale magnetic materials. Because such species are molecular in nature, fall in the nanoscale size regime, and display superparamagnetlike slow magnetization relaxation as a result of intrinsic properties of individual molecules, they have been called single-molecule magnets (SMMs) or molecular nanomagnets. SMMs thus represent a molecular or “bottom-up” approach to nanomagnetism. They exhibit hysteresis in magnetization versus dc field scans below their blocking temperature ($T\textsubscript{B}$), with the relaxation barrier arising from the combination of a large ground-state spin ($S$) and a large and negative Ising- (easy-axis-) type of magnetoanisotropy, as measured by the axial zero-field splitting parameter, $D$. This leads to a significant barrier ($U$) to magnetization reversal, its maximum value given by $S(S^2-1)/2$ or $(S^2-\frac{1}{4})D$ for integer and half-integer spin, respectively. However, in practice, quantum tunneling of the magnetization (QTM) through the barrier via higher lying $M\textsubscript{S}$ levels of the spin $S$ manifold results in the actual or effective barrier ($U\textsubscript{eff}$) being less than $U$. Indeed, a primary reason that SMMs have been of interest to scientists of various disciplines is this combination of their

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10.1021/ic8001064 CCC: $40.75 © 2008 American Chemical Society Published on Web 04/15/2008
often aesthetically pleasing structures and their ability to display classical magnetic bistability and quantum properties, while at the same time retaining all the advantages of molecular species, such as crystallinity, solubility, and easy chemical modification in targeted ways.\(^2\) The first SMM discovered was $[\text{Mn}_{12} \text{O}_{12} (\text{O}_2 \text{CMe})_16 (\text{H}_2 \text{O})_4] (\text{Mn}_{12}; \text{R} = \text{Me})$.\(^{2,3}\) There are also many other structural types of SMMs known, spanning several metals, but most of them are completely or primarily Mn$^{III}$ complexes.\(^4-7\)

As part of a continuing development of new synthetic routes to novel structural types that can function as SMMs, we and several other groups have been exploring 3d/4d, 3d/5d, and 3d/4f mixed-metal cluster complexes that have the appropriate properties to function as SMMs.\(^8\) Our own contributions to this relatively new field have included $\text{Mn}_3 \text{Mn}_{11} \text{Mn}_{12} \text{Dy}^{109}$, $\text{Mn}_3 \text{Dy}^{109}$, and Fe-Dy$^{110}$ SMMs. Our original communication of the Mn$_{12}$ SMM, which possesses an $S = 16$ ground state, described how it was obtained by a template synthesis using a Ce$^{IV}$ ion around which was formed a ferromagnetically coupled loop of Mn$^{II}$ ions. We have since extended and expanded this work and in this paper report full details of the syntheses, structures, magnetic characterization, and reactivity of four structurally related Mn$_{12}$Ce complexes. We shall show that some are new SMMs and that they also demonstrate extensive spin-variability within the family.

Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. $[\text{Mn(OH)}_2 (\text{OMe})_2]_2 (\text{MeCO}_2 \text{H})_6 (\text{H}_2 \text{O})_4] (1)^{11}$, $[\text{Mn}_2 \text{O}_2 (\text{O}_2 \text{CPh})_9 (\text{H}_2 \text{O})] (3)^{12b}$ were prepared as previously described.

\begin{itemize}
  \item \([\text{Mn}_2 \text{O}_2 (\text{O}_2 \text{CMe})_9 (\text{H}_2 \text{O})]_2 \text{(4)}\)
  \item Method A. To a slurry of 1 (2.00 g, 7.46 mmol) in MeCN (35 mL) was added solid (NH$_4$)$_2 \text{Ce(NO}_3)_6$ (0.51 g, 0.93 mmol), and the mixture was left under magnetic stirring for 8 h. This gave some brown powder and a reddish-brown solution, which were separated by filtration. To the filtrate was added Et$_2$O (40 mL), and the solution left under magnetic stirring for 5 min and refiltered. This filtrate was
\end{itemize}
concentrated slowly by evaporation over a few days to yield red-brown crystals of $4\cdot$H$_2$O$\cdot$4MeCN, which were collected by filtration, washed with Me$_2$CO and Et$_2$O, and dried in vacuo; the yield was 60%. Anal. Calcd (Found) for $C_{32}H_52O_{40}Mn_8Ce$: C, 18.49 (18.47); H, 3.36 (3.32). Selected IR data (KBr, cm$^{-1}$): 3392(s, br), 1576(s), 1539(s), 1444(s), 1029(w), 680(s), 657(m), 619(m), 589(s, br), 551(m), 496(w), 432(w).

Method B. $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CMe})_{12}(\text{py})_4]$ (5). To a slurry of 2 (1.00 g, 1.29 mmol) in MeCN (50 mL) was added solid (NH$_4$)$_2$Ce(NO$_3$)$_6$ (0.24 g, 0.62 mmol) and the mixture stirred overnight. To the resulting solution was added toluene, and removal of solvent by rotoevaporation were carried out. The resulting solid was then redissolved in MeCN (20 mL), and the solution left to concentrate by slow evaporation to give large, well-formed black crystals. These were recrystallized from a CHCl$_3$/heptanes layering, which gave black crystals of $7\cdot$H$_2$O$\cdot$3MeCN$\cdot$2CHCl$_3$; after 1 week. The crystals were collected by filtration, washed with heptanes and dried in vacuo; the overall yield was 60%. The synthesis can also be performed using complex 5 instead of 4 as the starting material. Vacuum-dried solid analyzed as $7\cdot$H$_2$O. Anal. Calcd (Found) for $C_{32}H_64N_4O_{40}Mn_8Ce$: C, 47.82 (48.00); H, 2.81 (2.54). Selected IR data (KBr, cm$^{-1}$): 3430(s, br), 1600(m), 1560(s), 1527(m), 1494(w), 1404(s), 1032(w), 745(m), 697(s), 650(m), 580(s, br), 433(w).

X-ray Crystallography. For $4\cdot$H$_2$O, $5\cdot$C$_6$H$_{12}$O$_7$, $6\cdot$12C$_4$H$_8$O$_2$$\cdot$4MeOH and $7\cdot$H$_2$O$\cdot$3MeCN$\cdot$2CHCl$_3$, data were collected on a Siemens SMART PLATFORM whereas for $4\cdot$H$_2$O$\cdot$4MeCN data were collected on an Oxford-Diffraction Xcalibur diffractometer, both equipped with a CCD area detector and a graphite monochromator utilizing Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Suitable crystals were attached to glass fibers using silicone grease and transferred to a goniostat where they were cooled for data collection. Cell parameters were refined using up to 12766 reflections. The first 50 frames were remeasured at the end of data collection to monitor crystal stability (maximum correction on $I$ was <1%). Absorption corrections by integration were applied based on measured indexed crystal faces. The structures were solved by direct methods, and refined on $F^2$ using full-matrix least-squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms. Unit-cell data and structure refinement details are listed in Table 1.

For $4\cdot$H$_2$O and $4\cdot$H$_2$O$\cdot$4MeCN, there are two symmetry-independent molecules in the unit cell, both lying on $S_4$ symmetry axes parallel to the crystal c axis. The two molecules are essentially superimposable. The water molecules of crystallization each hydrogen-bond to two adjacent MnCe clusters and form one-dimensional, hydrogen-bonded chains of MnCe clusters parallel to the crystal c axis. Thus, O1W hydrogen-bonds to bound water O6 (O1W···O6 = 2.645 Å for $4\cdot$H$_2$O and 2.750 Å for $4\cdot$H$_2$O$\cdot$4MeCN), $\mu_3$-$O^-$ ion O1 (O1W···O1 = 2.616 and 2.756 Å).

### Table 1. Crystallographic Data for Complexes 4–6

| Compound | $a$ Å | $b$ Å | $c$ Å | $\beta$ (deg) | $V$ Å$^3$ | $Z$ | $T$ K | $\rho$ | $\mu$ (mm$^{-1}$) | R1 | wR2 | aGraphite monochromator. b$R = 2\sigma(I)$. cR1 = 100[$\sum||F_o| - |F_c||]/\sum|F_o|. d wR2 = 100[$\sum(w(F_o^2 - F_c^2)^2)/\sum[w(F_o^2)^2]|^{1/2}$, where $p = [\max(F_o^2, O)] + 2F_c^2]/3. |
|---------|------|------|------|------------|--------|-----|------|------|-------------|-----|------|------|
| $4\cdot$H$_2$O | 23.947(6) | 24.6153(6) | 10.1274(2) | 90.0 | 5708(4) | 4 | 100(2) | 0.71073 | 2.908 | 0.0899 | 0.2115 | 0.0899 |
| $4\cdot$H$_2$O$\cdot$4MeCN | 23.947(6) | 24.6153(6) | 10.1274(2) | 90.0 | 6136(3) | 4 | 100(2) | 0.71073 | 2.908 | 0.0899 | 0.2115 | 0.0899 |
| $5\cdot$C$_6$H$_{12}$O$_7$ | 9.593(5) | 19.847(1) | 23.485(2) | 90.0 | 3809.8(4) | 1 | 173(2) | 0.71073 | 1.784 | 1.953 | 0.0497 | 0.1165 |
| $6\cdot$12C$_4$H$_8$O$_2$$\cdot$4MeOH | 9.593(5) | 19.847(1) | 23.485(2) | 90.0 | 3809.8(4) | 1 | 173(2) | 0.71073 | 1.784 | 1.953 | 0.0497 | 0.1165 |

MnIII/CeIV Complexes with a [Mn8CeOs]2+ Core

because the magnetic studies were performed on 4·4H2O, whereas the structure of 4·4H2O·4MeCN was obtained more recently to provide more reliable metric parameters. The low quality crystal and CH2Cl2 solvent molecules are severely disordered, and the · which however did not affect the magnetism studies. For R1 and wR2 were 8.91 and 21.36%, respectively. These values and remove its contribution to the overall intensity data. The final program SQUEEZE was used to calculate the solvent disorder area and differing in the identity of the bound solvent molecules (MeCN vs dioxane). There are also three dioxane molecules, lying on a 2-fold rotation axis or a S4 axis. A total of 258 parameters were included in the refinement using 23703 reflections with I > 2o(I). For 6·12C4H8O2·4MeOH, there are two types of molecules, both lying on a S4 symmetry axis parallel to the crystal c axis and differing in the identity of the bound solvent molecules (MeCN vs dioxane). There are also three dioxane and one MeOH molecules in the asymmetric unit that are disordered and could not be modeled properly. Thus program SQUEEZE,14c a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. A total of 646 parameters were included in the refinement using 6920 reflections with I > 2o(I).

For 7·4H2O·3MeCN·2C2H5Cl2, the structure could not be refined to a satisfactory, publishable level because of poor diffraction and extensive ligand and solvent disorder, but we were able to confirm that it contains a Mn4Ce core analogous to those of 4–6. The asymmetric unit contains a complete Mn4Ce cluster in a general position, and four H2O, three MeCN, and two CH2Cl2 molecules. Most of the phenyl rings display considerable displacement motions but not large enough to allow resolution of different sites. Consequently, large thermal parameters are observed for their C atoms, and they were thus refined with isotropic thermal parameters. The cluster has four coordinated water molecules, as in 4, which hydrogen bond to the four water molecules of crystallization. The latter are thus ordered, and do not bridge neighboring molecules, unlike the situation in 4·4H2O and 4·4H2O·4MeCN. The MeCN and CH2Cl2 solvent molecules are severely disordered, and the program SQUEEZE was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The final R1 and wR2 were 8.91 and 21.36%, respectively. These values are similar to those for 4·4H2O, which is why we sought and obtained better crystals of what proved to be 4·4H2O·4MeCN; we were unable to obtain improved crystals of complex 7.

Other Studies. Infrared spectra were recorded in the solid state (KBr pellets) on a Nicolet Nexus 670 FTIR spectrometer in the 400–4000 cm⁻¹ range. Elemental analyses (C, H and N) were performed by the in-house facilities of the University of Florida Chemistry Department. Variable-temperature dc and ac magnetic susceptibility data were collected at the University of Florida using a Quantum Design MPMS-XL SQUID susceptometer equipped with a 7 T magnet and operating in the 1.8–300 K range. Samples were embedded in solid eicosane to prevent torquing. Magnetization vs field and temperature data were fit using the program MAGNET.15 Pascal’s constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χm). Studies at ultralow temperatures (<1.8 K) were performed on single crystals at Grenoble using an array of micro-SQUIDs.16 The high sensitivity of this magnetometer allows the study of single crystals of the order of 10–500 μm; the field can be applied in any direction by separately driving three orthogonal coils.

Results and Discussion

Syntheses. [Mn8CeO6(O2CMe)3(H2O)3] (4) was originally obtained by accident in very small yield (5%) from an MeCN/Et2O solution of [Mn8CeO6(O2CMe)3(NO3)(H2O)2]13 (MnIV,CeIV) that had been left undisturbed for some time (Method B in the Experimental Section). Once the identity of 4 had been established as a MnIII8 loop with a central CeIV (vide infra) and its interesting magnetic properties identified in preliminary studies, it was considered essential to develop a rational, high-yield synthetic procedure. This was successfully developed using the linear polymer [(Mn(OH)(O2CMe)2)·(MeCO2H)·(H2O)]n (1) shown below.11,17 This contains all the components found in 4, namely MnIII, carboxylate and O2⁻ (as OH⁻) groups, except the CeIV ion. It was thus suspected that a reaction between the polymer and a source of oxophilic CeIV with a Ce:Mn ratio of 1:8 might lead to formation of 4 as Ce⁴⁺−OH⁻ contacts develop during the reaction and the chain essentially wraps around the CeIV ion, followed by deprotonation of OH⁻ in the presence of carboxylate groups as H⁺ acceptors. Thus, the reaction between 1 and (NH4)2Ce(NO3)6 in MeCN was investigated, and this did indeed give a high isolated yield of 4 (55%), as 4·4H2O·4MeCN (eq 1). The reaction is essentially thus a template procedure involving a Ce⁴⁺ template (8/n)[Mn(OH)(O2CMe)2]ₙ + Ce⁴⁺ + 4H₂O → [Mn₈Ce₄O₆(O2CMe)₃(H₂O)]ₙ + 4H⁺ + 4MeCO₂H (1) around which the chain wraps. This is the overall, net process, and we make no mechanistic claims that the reaction actually involves chains in solution wrapping around the Ce⁴⁺ ion. In any case, polymer 1 is very insoluble in MeCN, slowly dissolving completely during the reaction, and the mechanism is likely a complicated heterogeneous one involving fragmentation of the polymer as Ce⁴⁺ binds.

Once the magnetic studies had established that there are weak intermolecular interactions in 4 (vide infra), derivatives of 4 were sought that (i) might have weaker intermolecular interactions as a result of replacement with other groups of


the complexes. Indeed, the reaction of previous work to be good stepping-stones to higher nuclearity 
$$[\text{Mn}_3\text{O(O}_2\text{CMe)}_6(\text{py})_3] $$
3Ce4+ in $\text{H}_2\text{O}$ (1). The structure can be described as a nonplanar, saddlelike
point (ii), we employed bulky carboxylate groups. Since the corresponding polymer 1 was not available at the time with different carboxylates, other MnIII sources were explored as routes to the desired complexes. These included $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{H}_2\text{O})_4] $ (3) and $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{MeCN})_4] $ (4) in 60% isolated yield (eq 2).

Other ratios in the 2:1 to 5:1 range gave the same product, but in lower yield. Complex 5 is the same as 4 except that the bound water groups have been replaced by pyridines. The benzoate derivative 6 was obtained from the reaction of complex 3 with (NH4)$_2$Ce(NO$_3$)$_6$ in various ratios. Both the 2:1 and 1:1 ratios gave 6, but the latter ratio gave the cleanest isolated product. However, 6 is $[[\text{Mn}_9\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{MeCN})_4] $, the unit cell containing two different molecules differing in the
bound solvent groups but, interestingly, without any disorder. The manifestation of two complexes cocrystallizing indicates the complexity of this reaction with several species likely to be in equilibrium in the reaction solution.

Finally, a derivative with very bulky diphenylacetate groups was prepared by a different procedure than those used above, because the corresponding complexes 1–3 with this carboxylate were not available. Instead, a carboxylate substitution reaction\textsuperscript{3a} on complex 4 was employed; complex 4 was treated with 12–20 equiv of diphenylacetic acid in MeCN, and the reaction driven to completion by removal under vacuum of the generated acetic acid as its toluene azeotrope.\textsuperscript{3} An excess of diphenylacetic acid also favors complete substitution, as does the higher acidity of Ph$_2$CHCO$_2$H ($pK_a = 3.94$) versus acetic acid (4.75). The substitution is summarized in eq 3.

$$[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}\text{CH}_2\text{CO}_2\text{H}]^- + 12\text{Ph}_2\text{CHCO}_2\text{H} \rightarrow [\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}]^\text{2+}(\text{H}_2\text{O})_4] + 12\text{MeCO}_2\text{H} (3) $$

We were pleased to see that only ligand substitution occurred during this reaction, giving the desired $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CPh})_{12}(\text{H}_2\text{O})_4] $ (7) in 60% isolated yield, rather than cluster fragmentation.

**Description of Structures.** A PovRay representation and stereoview of 4 are presented in Figure 1, and a side-view of the common $[\text{Mn}_8\text{CeO}_8]$ core present in complexes 4–7 is shown in Figure 2 for 4. A PovRay representation of one of the molecules in complex 6 is presented in Figure 3; the structures of 5 and 7 are available in the Supporting Information. Selected metric parameters for complexes 4·4H$_2$O, 4·4H$_2$O·4MeCN, 5·3C$_2$H$_4$O$_2$, and 6·12C$_2$H$_4$O$_2$·4MeOH are compared in Table 2.

Complex 4·4H$_2$O and 4·4H$_2$O·4MeCN crystallize in the tetragonal space group $I$4 with the $[\text{Mn}_8\text{CeO}_8(\text{O}_2\text{CMe})_{12}(\text{H}_2\text{O})_4] $ molecule lying on a crystallographic $S_4$ symmetry axis. The cluster contains one CeIV and eight MnIII ions bridged by eight $\mu_3$-O$^2-$ and 12 CH$_2$CO$_2$ groups (Figure 1). The structure can be described as a nonplanar, saddellike

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**Figure 1.** PovRay representation at the 50% probability level of the structure of 4 (top) and a stereoview (bottom), viewed approximately along the $S_4$ axis. Color scheme: Mn, green; Ce, cyan; O, red; C, grey. H atoms have been omitted for clarity.

**Figure 2.** $[\text{Mn}_8\text{CeO}_8]$ core of 4, which is common to complexes 4–7. Color scheme: Mn, green; Ce, cyan; O, red.


Table 2. Comparison of Selected Interatomic Distances (Å) and Angles (deg) for 4-6

<table>
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<tr>
<th>atom</th>
<th>MnIV</th>
<th>MnVI</th>
<th>CeIV</th>
<th>angle (deg)</th>
<th>Manganese-Ce distance (Å)</th>
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<td>2.95</td>
<td>3.10</td>
<td>Ce2</td>
<td>4.35</td>
</tr>
</tbody>
</table>

* Underlined values are the ones closest to the charge for which they were calculated. The oxidation state of a particular atom can be taken as the nearest whole number to the underlined value.

Figure 3. PovRay representation at the 50% probability level of [MnCeO8(O2CPh)12(MeCN)4], one component of the structure of 6. Color scheme: Mn, green; Ce, cyan; N, dark blue; O, red; C, grey. H atoms have been omitted for clarity.

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a nonplanar [Mn8O8] loop that is attached via the oxide ions are eight metal-oxide bonds between the [Mn8O8] loop and smaller Ce atom (Figure 4). In both cases, therefore, there which are SMMs with

\[ \text{[Mn12O12]}^{48}_{\text{48}} \text{Inorganic Chemistry, Vol. 47, No. 11, 2008} \]

[52x345]relative alignment of their MnIII Jahn–Teller (JT) elongation complexes lead to another difference between them, the [Mn12O12(O2CR)16(H2O)4](Mn12) family of complexes, (Figure 4).

Figure 4. Comparison of the [Mn8CeO8]^{12}_{12} core (top) with the [Mn8O8]^{12}_{12} core (bottom). Color scheme: MnIII, green; MnIV, violet; Ce, cyan; O, red.

[52x321]In contrast, the JT axes in 4–7 have no preferred orientation. The JT axes are shown in Figure 5 as solid black bonds, and they can be seen to be disposed essentially equally with respect to any chosen reference direction. This is facilitated by the fact that they occur in four symmetry-related pairs of JT axes that intersect at the same O atom and thus are nearly perpendicular, with the Mn2–O4–Mn1 angle being 83.9°. Indeed, for all the complexes 4–7, the eight JT axes occur in sets of two with the Mn–O–Mn intersection angle being in the range of 80–84°. This and the actual or virtual \( S_i \) symmetry are expected to lead to a very low anisotropy (small \( |D| \) value), and this was borne out by the experiment (vide infra).

**DC Magnetic Susceptibility Studies for Complexes 4, 5, and 7.** Solid-state variable temperature magnetic susceptibility measurements were performed on vacuum-dried microcrystalline samples of representative complexes 4·4H2O, 5·3C6H5O2, and 7·4H2O suspended in eicosane to prevent torquing. The dc magnetic susceptibility (\( \chi_M \)) data were collected in the 5.0–300 K range in a 0.1 T magnetic field and are plotted as \( \chi_M T \) vs \( T \) in Figure 6. For 4, the \( \chi_M T \) value of 39.36 cm\(^3\) K mol\(^{-1}\) at 300 K remains essentially constant down to 70 K and then steadily increases with decreasing temperature to 69.28 cm\(^3\) K mol\(^{-1}\) at 5.0 K indicating predominantly ferromagnetic coupling in 4 and a large ground-state spin \( S \). For 5, the \( \chi_M T \) value of 28.31 cm\(^3\) K mol\(^{-1}\) at 300 K also remains essentially constant to 70 K and then steadily decreases with decreasing temperature to 17.08 cm\(^3\) K mol\(^{-1}\) at 5.0 K indicating a relatively small ground state \( S \) for 5. For 7, the \( \chi_M T \) of 28.00 cm\(^3\) K mol\(^{-1}\) at 300 K is essentially constant down to \( \sim 120 \) K and then increases to a maximum of 32.47 cm\(^3\) K mol\(^{-1}\) at 70 K, and then decreases to 19.85 cm\(^3\) K mol\(^{-1}\) at 5.0 K, again indicating a relatively small ground state \( S \) for 7. The spin-only (\( g = 2.0 \)) value for eight noninteracting, high-spin MnIII ions is 24.00 cm\(^3\) K mol\(^{-1}\) (CeIV is diamagnetic, \( f \)). For each compound, the high-temperature \( \chi_M T \) values are above this, most notably for 4. This suggests that the dominant exchange interaction within the molecules is ferromagnetic, and then

\[ -0.468(2) \text{ cm}^{-1} \text{ for [Mn12O12(O2CCH2Br)16(H2O)4]·4CH2Cl2}. \]

Weaker interactions (antiferro- and/or ferromagnetic) assume greater importance at lower temperatures (vide infra).

The eight Mnill centers in 4, 5, and 7 will give total S values in the range 0 to 16. Owing to the size and low symmetry of the molecules, a matrix diagonalization method to evaluate the various Mn2 pairwise exchange parameters (Jij) within the MnillCe cores is not easy. Similarly, application of the equivalent operator approach based on the Kambe vector coupling method is not possible.22 Therefore, we focused only on identifying the ground state S values for the complexes since these would in any case dominate the low temperature studies we performed. Hence, magnetization (M) data were collected in the 0.1–7 T magnetic field and 1.8–10 K temperature ranges. The data were fit, using the program MAGNET,13 by diagonalization of the spin Hamiltonian matrix assuming only the ground-state is populated, incorporating axial anisotropy (DSz2) and Zeeman terms, and employing a full powder average. The corresponding spin Hamiltonian (H) is given by eq 4,

\[
H = DS_z^2 + g\mu_B\mu_0SH
\]  

where D is the axial anisotropy (ZFS) constant, \(\mu_B\) is the Bohr magneton, \(S\) is the easy-axis spin operator, g is the electronic g factor, \(\mu_0\) is the vacuum permeability, and H is the applied field. The last term in eq 4 is the Zeeman energy associated with an applied magnetic field. The data for 4 are plotted as reduced magnetization (M/N\(\mu_B\)) versus H/T in Figure 7, and the fit (solid lines) gave \(S = 16, D = -0.10\) cm\(^{-1}\), and \(g = 1.98\). When data collected at fields <3.0 T were included, a satisfactory fit could not be obtained, which is as expected from the crystal structure described above, which revealed intermolecular hydrogen-bond linkages between MnillCe clusters that will introduce intermolecular exchange interactions that are not included in the fitting model; the use of only higher field data overcomes the intermolecular exchange interactions and their effect on the observed magnetization. The small D value of only \(-0.1\) cm\(^{-1}\) is consistent with the complex having the JT axes almost perpendicular, as stated earlier, and the g < 2 value is as expected for Mn.

For complexes \(5 \cdot 3C_4H_2O\) and \(7 \cdot 4H_2O\), which from Figure 6 clearly have smaller spin ground states than \(4 \cdot 4H_2O\), we could not get satisfactory fits using all the data. For 5, a somewhat reasonable fit was obtained when only data collected in the 0.1–2 T applied field range were used, and this gave \(S = 5, D \approx -0.30\) cm\(^{-1}\) and \(g \approx 1.83\) (see the Supporting Information). For 7, a slightly better fit was obtained with data collected in the 0.1–0.8 T range, and this gave \(S = 6, D \approx -0.34\) cm\(^{-1}\) and \(g \approx 1.89\). Although the values of D and g carry significant estimated uncertainty (±20%), the ground state S values are considered reliable to ± 1 units, and are consistent with the estimates from the dc magnetic susceptibility plots in Figure 6. Such problems in fitting dc magnetization data are commonly encountered when there are low-lying excited-states (relative to \(kT\)), some of which have S values greater than that of the ground state; this is typical of systems that contain weakly antiferromagnetic interactions and/or have high nuclearity and there is thus a high density of spin states. Thus, low-lying excited states are populated, even at these relatively low temperatures, and/or the Ms levels from nearby excited states with S greater than that of the ground-state are sufficiently stabilized by the applied dc field that they thus approach or even cross the ground-state levels. Since the fitting routine assumes population of only the ground state, these excited states complicate the fitting. This is undoubtedly the problem with complexes 5 and 7, and this is supported by the slope observed in the in-phase ac susceptibility vs temperature data (vide infra). As will be described below, ac susceptibility studies, which avoid the complications from a dc field, support the conclusions from the magnetization fits of the ground state S values for 5 and 7.

**AC Magnetic Susceptibility Studies.** The values of S = 16 and D = \(-0.10\) cm\(^{-1}\) obtained for \(4 \cdot 4H_2O\) suggested an upper limit to its barrier \(U\) to magnetization relaxation (reorientation) of \(U = S^2|D| = 25.6\) cm\(^{-1}\). Even though the

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true, or effective barrier \( U_{\text{eff}} \), would be significantly smaller due to quantum tunneling of the magnetization (QTM) through the barrier, it still suggested that at least 4·4H₂O, and perhaps even 5 and 7, might display slow relaxation at low enough temperatures, and this was explored using ac susceptibility measurements.

Alternating current magnetic susceptibility studies were performed on vacuum-dried microcrystalline samples of 4·4H₂O, 5·3C₃H₆O₂, and 7·4H₂O in a zero dc field in the temperature range 1.8–10 K, using a 3.5 G ac field oscillating at frequencies between 5 and 1000 Hz. If the magnetization vector can relax fast enough to keep up with the oscillating field, then there is no imaginary (out-of-phase) susceptibility signal (\( \chi'' \)), and the real (in-phase) susceptibility (\( \chi' \)) is equal to the dc susceptibility. However, if the barrier to magnetization relaxation is significant compared to thermal energy (\( kT \)), then there is a nonzero \( \chi'' \) signal and the in-phase signal decreases. In addition, the \( \chi'' \) signal will be frequency-dependent. For complexes 4–7, there were no significant out-of-phase \( \chi'' \) signals observed down to 1.8 K, the operating minimum of our SQUID magnetometer; only the very beginnings of a \( \chi'' \) signal was observed for each compound to this temperature, the most evident being for 4. This suggested that temperatures much lower than 1.8 K would have to be employed to better gauge whether 4–7 might be single-molecule magnets (SMMs).

Since the in-phase susceptibility (\( \chi' \)) is equal to the dc susceptibility (\( \chi'_{\text{dc}} \)) when there is no \( \chi'' \) component, the \( \chi' \) signal is a useful way of determining (or confirming) the ground state will be populated, using data from \( \chi' \) and \( \chi'' \) plots of Figure 6. The plots show a steady decrease with increasing temperature, and \( \chi' \) plots of 4·4H₂O, 5·3C₃H₆O₂, and 7·4H₂O are similar to those for 5 and 7, respectively. Linear extrapolation to 0 K gives values of \( \sim 6.7 \) and \( \sim 16 \) cm³ mol⁻¹ K⁻¹ for 5 and 7, respectively. The latter suggests an \( S = 6 \pm 1 \) ground state for 7, with \( g < 2 \) as expected for Mn; the spin-only \( (g = 2.0) \) values for 5, 6, or 7 are 15, 21, and 28 cm³ mol⁻¹ K⁻¹. The value for 5 of \( g = 2.0 \) is suggestive of an \( S = 4 \) or 5 ground state; the spin-only \( (g = 2.0) \) values for 3, 4, or 5 are 6, 10, and 21 cm³ mol⁻¹ K⁻¹. For both compounds, the \( \chi' \) increases with increasing temperature indicating population of low-lying excited states with \( S \) greater than that of the ground state, and rationalizes the problems in fitting the dc magnetization data, which assumes population of only a single state.

Because complex 4 displays the beginnings of frequency-dependent out-of-phase \( \chi'' \) signals, which are an indication of the superparamagnet-like slow magnetization relaxation of a SMM, we decided to investigate this further. Out-of-phase \( \chi'' \) signals are a necessary but not sufficient proof of an SMM, and thus we collected dc magnetization data to lower temperature (\( < 1.8 \) K).

**Hysteresis Studies below 1.8 K.** The observation of hysteresis loops in magnetization vs applied dc field studies represents the diagnostic property of a magnet, including SMMs and superparamagnets below their blocking temperature (\( T_B \)). Thus, such data were collected down to 0.04 K on single crystals of 4·4H₂O, 5·3C₃H₆O₂ and 7·4H₂O·
loops for a single crystal of \( \text{Mn}^{III}/\text{Ce}^{IV} \) complexes with a [\( \text{Mn}_{8}\text{Ce}_{2} \text{O}_{8} \)]\(^{2+} \) core.

Figure 9. (top) Magnetization (\( M \)) vs applied magnetic field (\( H \)) hysteresis loops for a single crystal of \( 4\cdot\text{H}_2\text{O} \) at a 0.004 T/s sweep rate in the 0.04–0.6 K temperature range; and (bottom) expansion of the 0.2 to –0.2 T field range showing the exchange-bias measurement positions. \( M \) is normalized to its saturation value, \( M_s \).

Figure 10. Magnetization (\( M \)) vs applied magnetic field (\( H \)) hysteresis loops for a single crystal of \( 5\cdot3\text{C}_{2}\text{H}_{4}\text{O}_{2}\) at 0.04 K for the indicated field sweep rates. \( M \) is normalized to its saturation value, \( M_s \).

3MeCN·2CH\(_2\)Cl\(_2\) (stored in mother liquor) using a micro-SQUID apparatus.\(^{16}\) The observed magnetization responses for complex 4 are shown in Figure 9 at a sweep rate of 0.004 T/s and at different temperatures. Hysteresis loops are clearly evident below 0.6 K, with the coercivity (half the loop width at \( H/M_s = 0 \)) increasing with decreasing temperature, as expected for the superparamagnet-like properties of a SMM. A dominating feature in the loops is the two-step profile of the QTM and the fact that on sweeping the field back from either extreme toward zero field, the magnetization begins to decrease before reaching zero field. This shift from zero field is indicative of an exchange bias from neighboring molecules, i.e., the influence of intermolecular antiferromagnetic exchange interactions on the magnetization relaxation dynamics of a molecule. This is totally consistent with the observation in the crystal structure of \( 4\cdot\text{H}_2\text{O} \) of one-dimensional chains of \( \text{Mn}_{8}\text{Ce} \) molecules linked by hydrogen-bonded bridging solvate water molecules (see Figure S5 of the Supporting Information), and there are likely also some bonded bridging solvate water molecules (see Figure S5 of the Supporting Information). The observed magnetization responses are as defined for eq 4.\(^{28}\) This gives \( J = -0.0012 \) K, and from this can be calculated the exchange interaction energy \(-2JS^2 \) of 0.65 K. The interaction is thus antiferromagnetic, as expected, and very weak. Complex 4 is thus a SMM that also exhibits weak antiferromagnetic interactions along a one-dimensional hydrogen-bonded chain. Note that the latter half of this statement does not contradict the former: no assembly of SMM molecules in a crystal can ever be completely free of all possible interactions with neighbors (otherwise it would be a gas), and the important question is then exactly how strong are these interactions from a magnetic point of view. If they are weak, as they are for 4, then they are merely a perturbation of the single-molecule magnetic properties, and a compound such as 4 can be described as an exchange-biased SMM.\(^{26}\) If intermolecular interactions are relatively strong, however, then the crystal is best described as containing antiferromagnetically ordered 1-, 2- or 3D extended networks.

The magnetization vs field responses for complex \( 5\cdot3\text{C}_{2}\text{H}_{4}\text{O}_{2}\cdot\text{O}_{2} \) at 0.04 K and different scan rates are shown in Figure 10. There is essentially no hysteresis observed even at the highest scan rates, and there is also a strongly sloping background as the field is increased from zero. These observations confirm that 5 is not a SMM, and that there are very low lying excited states with \( S \) greater than that of the ground state whose levels cross with those of the latter leading to increased values of the magnetization at increasing fields. These data support the conclusions from the ac in-phase data.

The magnetization vs field responses for complex \( 7\cdot4\text{H}_2\text{O}\cdot3\text{MeCN}\cdot2\text{CH}_2\text{Cl}_2 \) are plotted in Figure 11, showing both the temperature dependence at 0.14 T/s and the scan-rate dependence at 0.04 K. Hysteresis is observed whose coercivity increases with decreasing temperature and increasing scan rate, as expected for a superparamagnetlike SMM. In

\[ J = -g\mu_B H_{ex}/k_B S \]  

where \( H_{ex} \) is the exchange-bias field (i.e., the shift from zero field), \( k_B \) is the Boltzmann constant, and the other symbols are as defined for eq 4.\(^{28}\) This gives \( J = -0.0012 \) K, and from this can be calculated the exchange interaction energy

\[ -2JS^2 \]  

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and leads to correspondingly increased tunneling rates.29

significant transverse term in the spin Hamiltonian, which 

the low site-symmetry of this molecule; unlike complexes 

large size of this step corresponds to most (75–80%) of the 

due to quantum tunneling of the magnetization (QTM). The 

dominating feature in the loops is the large step at zero field 

structure, which shows noninteracting molecules. The clearly 

there is no noticeable exchange-bias and thus no significant 

begin to relax until zero field is reached. This shows that 

contrast to the behavior of 4, the magnetization does not 

begin to relax until zero field is reached. This shows that 

regimes exchange-bias and thus no significant 

intermolecular interactions, as expected from the crystal 

structure, which shows noninteracting molecules. The clearly 

dominating feature in the loops is the large step at zero field 

due to quantum tunneling of the magnetization (QTM). The 

large size of this step corresponds to most (75–80%) of the 

magnetization reversing, and thus the only other observed 

large size of this step corresponds to most (75–80%) of the 

magnetization fit. Note that, as stated, eq 6 gives the lower limit to $D$ because of the strong mixing of levels 

due to the low symmetry; this causes the large step at zero 

field, but there will be even stronger mixing at the first 

nonzero step and the magnetization therefore relaxes completely before the field reaches the value of the first nonzero 

field step. It thus makes sense that the obtained value of $D$ 

= −0.28 cm$^{-1}$ is less than the $D = −0.34$ cm$^{-1}$ from the magnetization fit.

Rationalization of the Variable Spin in Mn8Ce Complexes. One of the results of this work that warrants specific 

comment is the ability of the Mn8Ce complexes to possess different ground state $S$ values. Inspection of Figure 1 shows 

that the Mn8Ce core with $S_4$ symmetry contains only two types of near-neighbor $J_{ij}$ exchange constants, $J_{12}$ and $J_{12'}$ 

(and their symmetry partners). If next-nearest-neighbor 

interactions are assumed to be zero or negligible, there are only two possibilities: (i) if $J_{12}$ and $J_{12'}$ are both ferromagnetic, 

they will give an $S = 16$ ground state, as seen for 4; 

and (ii) if they are both antiferromagnetic, or one is antiferromagnetic and the other is ferromagnetic, they will 

give an $S = 0$ ground state. Therefore, the only way to 

rationalize the intermediate spin values found for 5 and 7 is 

to accept that next-nearest-neighbor interactions are not, in 

fact, negligible relative to $J_{12}$ and $J_{12'}$. No doubt this is 

facilitated by the CeIV ion providing additional pathways for 

next-nearest-neighbor interactions than would be available 

in an Mn$2^+$ wheel with nothing in the center. There are four 

symmetry-independent next-nearest-neighbor interactions, 

and the magnetic properties of the Mn8Ce complexes are 

thus determined by a total of six interactions, some of which 

will be competing. The two types of nearest-neighbor Mn2 

interactions are both propagated via $[\text{Mn}_2(\mu-O_2^-\mu-O_2\text{CR})]_2$ 

bridges, but differ in that one case (e.g., Mn1–Mn2′ for 4 

in Figure 1) there is one monoatomically bridging carboxy-

late in addition to the monoatomically bridging O2$^{-}$, whereas 

in the other case only the O2$^{-}$ is monoatomically bridging.

As a result: (i) the Mn⋯Mn separations in the former case 

($∼3.0$ Å) are slightly shorter than in the latter ($∼3.2$ Å); 

and (ii) the angles at monoatomically bridging ligands in the 

former (for 4, Mn1−O1−Mn2′ = 106.33° and Mn1−O4−

Mn2′ = 83.93°, average 95.13°) are much more acute than in 

the latter (Mn1−O3−Mn2 = 121.98°). Two monoatomic 

bridges between a pair of metal atoms, and the resulting acute 

bridging angles they foster, can often give ferromagnetic 

coupling for many metals including dinuclear MnIII 

complexes.30 The other symmetry type of Mn2 pair has a single 

monatomic $\mu$-O2$^{-}$ bridge as well as two carboxylate bridges, 

and such units in dinuclear MnIII chemistry are known to 

typically have Mn2Mn angles of $123°$ ± $5°$ and to give 

weakly ferro- or antiferromagnetic interactions in the $−5 < J < +10$ cm$^{-1}$ range.

On the basis of the above observations, our rationalization for the ground states seen for the Mn8Ce complexes is as

(29) (a) Beghidja, C.; Rogez, G.; Kortus, J.; Wesolek, M.; Welter, R. J. Am. 

Chem. Soc. 2006, 128, 3140. (b) Clerac, R.; Miyasaka, H.; Yamashita, 

follows: the coupling within both types of nearest-neighbor Mn2 pairs is weakly ferromagnetic in complex 4, and sufficiently stronger than the (presumably) antiferromagnetic next-nearest-neighbor interactions to give the observed S = 16 ground state, but with very low-lying excited states. In 5 and 7, however, one or both of the nearest-neighbor interactions is antiferromagnetic and comparable with next-nearest-neighbor interactions; as a result, there are competing interactions of comparable magnitude within the core, and thus spin frustration effects give a ground-state that is intermediate between the maximum (S = 16) and minimum (S = 0) possible. The exact ground-state is acutely sensitive in such situations to the relative magnitudes of the competing interactions, and thus small structural differences between 5 and 7 lead to different ground states for the two complexes. In both cases, there will again be low-lying excited states. Alternatively, one could argue that perhaps the nearest-neighbor interactions are ferromagnetic in all cases and what is varying is the strength of antiferromagnetic next-nearest-neighbor interactions. This is certainly also a possibility, but we see no reason why the next-nearest-neighbor interactions should be relatively more sensitive to small structural changes than the nearest-neighbor ones. In any event, the safest conclusion to be drawn is that the precise ground states in this family of Mn8Ce complexes are determined by the relative magnitudes of several weak-to-very-weak exchange interactions either side of zero, and thus are acutely sensitive to what in an absolute sense are small changes of perhaps only 1 or 2 cm\(^{-1}\) in either direction.

The logical next step is to try to identify which structural change(s) is (are) primarily responsible for the change in the magnetic properties, with the likeliest candidates being the Mn–O–Mn angles. The comparative listings in Table 2 are therefore of some interest. However, within the estimated standard deviations in the crystallographic structural parameters, and the poor quality of the structure of 7, it is not possible to identify one or more real and statistically significant structural differences between the complexes. In any case, on the basis of the above discussion, the changes in the exchange interactions required to cause the observed change in magnetic properties will be small, and thus can be caused by small structural perturbations difficult to identify above experimental uncertainties.

**Conclusions**

We have shown that convenient, high-yield methods are available that allow access into a new family of Mn8Ce complexes that are new additions to the area of single-molecule magnetism. The prototype of this family was complex 4, an SMM with S = 16, which displays hysteresis in magnetization vs dc field sweeps, albeit with the characteristic signature of exchange-bias, i.e. a perturbation to its single-molecule properties from the hydrogen bonding that forms 1D chains in the crystal. In an attempt to remove these intermolecular interactions, we have developed methods to derivatives of 4 in which the terminal water molecules have been replaced by pyridines, or in which the acetate groups have been replaced with other, bulkier carboxylates. These have indeed successfully provided other Mn8Ce complexes that are SMMs. However, these changes have also had an unforeseen consequence in that they have altered the magnitude of the intramolecular exchange interactions sufficiently to lead to major changes in the ground state S values of the complexes, from the S = 16 for 4, to S = 4 or 5 for 5, and S = 6 ± 1 for 7. This prevents a detailed study of the hysteresis response and other properties of these complexes as a function of the molecular separations, our original objective. Nevertheless, the work did provide a second SMM, complex 7, with no exchange-bias and with faster QTM rates as a consequence of its lower site-symmetry. From an alternative viewpoint, it is of course interesting and unusual for a given structural type to be capable of adopting such different spin ground states, and in some ways is another example of the “spin tweaking” phenomenon, as recently reported for a Mn32 SMM, which can be prepared as S = 51/2 or S = 61/2, depending on the peripheral ligands.\(^{31}\)

Finally, we note that the use of a highly charged Ce IV ion has led to significantly different structural chemistry than would be found with just Mn III and carboxylate groups alone, and we are investigating further the new chemistry that remains to be discovered with this combination, which is also complementary to the related Mn IV/Ce IV and Mn III/Ce III/Ce IV chemistry we have recently reported.\(^{13,25b}\)

**Acknowledgment.** We thank the National Science Foundation (CHE-0414555) for support of this work.

**Supporting Information Available:** X-ray crystallographic data in CIF format for complexes 4·4H2O, 4·4H2O·4MeCN, 5·3C4H4O6·12C4H8O2·4MeOH, and 7·4H2O·3MeCN·2CH2Cl2; Pov-Ray representations of 5 and 7, and the reduced magnetization fits for 5 and 7 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC8001064