

Single-Molecule-Magnet Behavior in a Fe₁₂Sm₄ Cluster

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Received May 15, 2010

Through the combination of Sm^{III} spin carriers with a Fe^{III} system, the largest Fe–Ln cluster so far has been synthesized. To our knowledge, the new complex, Fe₁₂Sm₄, is the first Sm^{III} single-molecule magnet. Furthermore, Fe₁₂La₄ and Fe₁₂Gd₄ have also been synthesized to help understand the magnetic exchange interactions and origin of magnetic anisotropy in Fe₁₂Sm₄.

The phenomena of slow magnetization relaxation and quantum effects displayed by single-molecule magnets (SMMs) make them very promising for possible applications in high-density information storage, quantum computing, and molecular spintronics, which have evoked researchers' great interest.^{1–3} Strictly, the two fundamental requirements for a 3d system to be an SMM are a large spin ground state (*S*) and large magnetic anisotropy (gauged by a negative zero-field-splitting parameter *D*).⁴ For 3d SMMs, the combination of these two properties results in an energy barrier (*U*) to magnetization relaxation, which is defined as *S*²|*D*| or (*S*² – 1/4)|*D*| for integer and half-integer spins, respectively.⁵ Recently, some propose that the energy barrier for reversal of the magnetization depends on |*D*|*S*^o; thus, efforts should be

focused on increasing the anisotropy of the cluster in order to obtain higher energy barriers.^{5c} To date, many nanomagnets reported are polynuclear transition-metal clusters containing Mn^{III}⁶ or Co^{II},⁷ in which their inherent single-ion magnetic anisotropy plays a significant role in determining the molecule's SMM behavior. However, the magnetic anisotropy of Fe^{III} clusters exhibiting slow relaxation of the magnetization is greatly dependent on the biased exchange in the molecular structures, which is not easily controlled.⁸ Considering the large anisotropy of the lanthanide ions (Ln^{III}),^{9–11} they are good candidates in the search for new SMMs. Mononuclear Ln^{III} SMMs display slow relaxation of the magnetization with an energy barrier that has its origin in the splitting of the total angular momentum (*J*) levels of the lanthanide.^{12,13} Integrating the Ln^{III} spin carriers into Fe^{III} systems may induce enough magnetic anisotropy to display SMM behavior. Some explorations on the Fe–Ln system have afforded Fe₂Ln₂, Fe₃Ln₈, Fe₄Ln₂, Fe₃Ln₇, and Fe₃Ln.¹⁴

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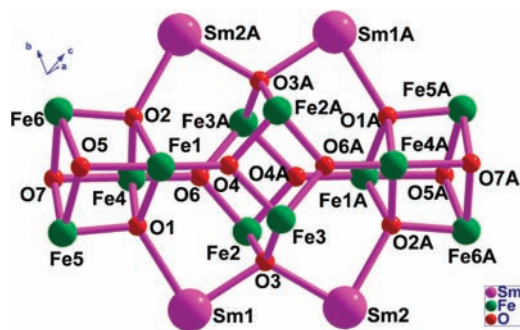


Figure 1. $\text{Fe}_{12}\text{Sm}_4$ core for **1**.

Here, we have succeeded in introducing Ln^{III} ions within a Fe^{III} system with no magnetic anisotropy. To our knowledge, the title compound $[\text{Fe}_{12}\text{Sm}_4(\mu_4\text{-O})_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{PhCO}_2)_{24}]$ ($\text{Fe}_{12}\text{Sm}_4$, **1**) is the largest Fe–Ln cluster complex reported to date. Alternating-current (ac) signals show the appearance of a frequency-dependent slow relaxation process for complex **1**, which also exhibits step hysteresis loop of the magnetization versus field at low temperatures. To gain insight into the complicated magnetic interactions and origin of the molecular magnetic anisotropy in **1**, the analogues of $\text{Fe}_{12}\text{La}_4$ (**2**) and $\text{Fe}_{12}\text{Gd}_4$ (**3**) have also been explored.

Because of the structural similarity for **1**–**3**, only the structure of **1** is described in detail here, its molecular structure is shown in Figure S1 in the Supporting Information (SI). In **1**, all of the Fe^{III} centers are in a distorted octahedral fashion and all of the Sm^{III} ions display distorted square-antiprism coordination geometries (Figure S2 in the SI). As shown in Figure 1, two $\mu_3\text{-OH}^-$ (O5 and O7) and two O^{2-} (O1 and O2) anions bridge four Fe^{III} ions (Fe1, Fe4, Fe5, and Fe6) to form $\text{Fe}_4\text{O}_2(\text{OH})_2$ cubane units, and two of these cubane units “sandwich” four Fe^{III} centers (Fe2, Fe3, Fe2A, and Fe3A) via four $\mu_3\text{-O}^{2-}$ bridges (O4, O6, O4A, and O6A). The connections between Fe2 and Fe3 and between Fe2A and Fe3A centers are achieved by two O^{2-} anion bridges (O3 and O3A), which form a $\text{Fe}_{12}\text{O}_{10}(\text{OH})_4$ core along with the two $\text{Fe}_4\text{O}_2(\text{OH})_2$ cubane units. Four Sm^{III} ions are linked to $\text{Fe}_{12}\text{O}_{10}(\text{OH})_4$ through six $\mu_4\text{-O}^{2-}$ anions (O1, O1A, O2, O2A, O3, and O3A), forming the $\text{Fe}_{12}\text{Sm}_4$ core of **1**. To the best of our knowledge, **1** is the largest Fe–Ln cluster reported by far. Twenty $\mu_2\text{-PhCO}_2^-$ and four $\mu_3\text{-PhCO}_2^-$ occupy the periphery of the $\text{Fe}_{12}\text{Sm}_4$ core and complete the coordination spheres of the Fe^{III} and Sm^{III} centers by the oxygen atoms of the carboxylate group (Figure S3 in the SI).

Magnetic susceptibility data of **1**–**3** were measured at 10 kOe in the 100–300 K range and at 200 Oe between 2 and 100 K to avoid saturation effects (Figure S4 in the SI). The magnetic data for **2** are equal to those of the Fe–O core, because La^{III} has no unpaired f electrons. The expected $\chi_{\text{M}}T$ value at 300 K for 12 noninteracting Fe^{III} ions with $g = 2.0$ and $S = 5/2$ is $52.5 \text{ cm}^3 \text{ K mol}^{-1}$; however, the observed value for **2** is only $22.5 \text{ cm}^3 \text{ K mol}^{-1}$, indicating dominant anti-

ferromagnetic coupling between the Fe^{III} ions. Upon cooling, the $\chi_{\text{M}}T$ value remains nearly constant, decreasing to $21.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 150 K, and then rises up to a value of $36.3 \text{ cm}^3 \text{ K mol}^{-1}$ at 15 K. Below this temperature, a sharp decrease is observed, indicating a combination of ferro- and antiferromagnetic interactions leading to a nonzero spin ground state. This is further confirmed by the M vs H measurements at 2.0 K (Figure S5 in the SI). The magnetization at 2 K tends to saturation at a value of $16.4 \text{ cm}^3 \text{ K mol}^{-1}$ at 50 kOe and is fairly well modeled by the Brillouin curve (solid line in Figure S5 in the SI) for $S = 8$ ground state with $g = 2.0$, which indicates an $S = 8$ ground state for **2** with very little anisotropy associated to the Fe–O core. ac magnetic susceptibility data were collected at various frequencies for **2** in order to ascertain whether it has enough anisotropy to be an SMM. However, there is no signal in the out-of-phase ac magnetic susceptibility, indicating that **2** is not an SMM. Thus, the Fe–O core of **1**–**3** does not possess enough magnetic anisotropy to display slow relaxation of the magnetization.

Table S1 in the SI contains the susceptibility data at 300 K for **1**–**3**. The room temperature $\chi_{\text{M}}T$ values are well in agreement with that of one Fe_{12} unit and four Ln ions. Figure S6 in the SI shows $\Delta\chi_{\text{M}}T$, the contribution to the $\chi_{\text{M}}T$ value of the Ln_4 part in $\text{Fe}_{12}\text{Ln}_4$, calculated as $\chi_{\text{M}}T(\text{Fe}_{12}\text{Ln}_4) - \chi_{\text{M}}T(\text{2})$. For **3**, the $\chi_{\text{M}}T$ value at 300 K is below that expected for a Fe_{12} unit and four Gd^{III} ions and the $\Delta\chi_{\text{M}}T$ vs T plot is very similar to what would be expected for four Gd^{III} ions, indicating that the magnetic exchange between the Gd^{III} and Fe^{III} ions in **3** is very weak. For **1**, the $\chi_{\text{M}}T$ value at 300 K is $21.3 \text{ cm}^3 \text{ K mol}^{-1}$, which is slightly below that expected for the $[\text{Fe}_{12}]$ unit and four isolated Sm^{III} ions,¹⁵ and the $\Delta\chi_{\text{M}}T$ vs T plot is not that expected for four Sm^{III} ions ($^6\text{H}_{5/2}$, with a low-lying $^6\text{H}_{7/2}$ excited state) with strong spin–orbit coupling. This indicates that there is magnetic coupling between the Sm^{III} ions¹⁶ and possibly between the Sm^{III} and Fe^{III} ions in **1**, in spite of the fact that the magnetic coupling between 4f and 3d ions is known to be extremely weak.

The M vs H plot for $\text{Fe}_{12}\text{Ln}_4$ is shown in Figure S5 in the SI along with that of **2**. Figure S7 in the SI shows ΔM , the contribution to the M value of the Ln_4 part in $\text{Fe}_{12}\text{Ln}_4$, calculated as $M(\text{Fe}_{12}\text{Ln}_4) - M(\text{2})$. The M vs H data for **1** practically overlap that of **2**, indicating antiferromagnetic coupling between the Sm^{III} ion and an $S = 8$ spin ground state for complex **1**. Because of the large number of paramagnetic centers and exchange interactions, the magnetic susceptibility for these complexes cannot be modeled, not even that of **2** and **3**. The method developed by Tangoulis et al.¹⁷ to study the nature of the magnetic interaction implies the synthesis of a Co^{III} analogue for each of the Ln^{III} ions; that is, $\text{Co}_{12}\text{Ln}_4$ clusters should be synthesized. Unfortunately, this is not possible in the present case. It is not common to find Ln^{III}_2 complexes with only two carboxylates and an oxide bridge; furthermore, most of the times the carboxylate bridges are not in the syn–syn bridging mode

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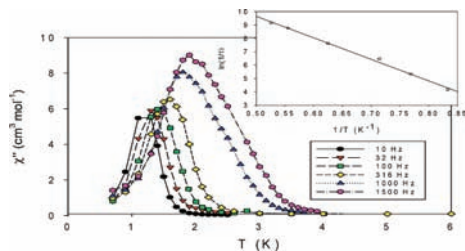


Figure 2. ac magnetic susceptibility plot for **1** at different frequencies. Inset: Arrhenius plot for complex **1**. See the text for fitting parameters.

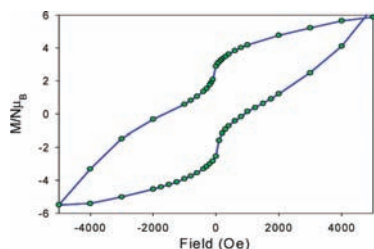


Figure 3. Magnetization vs field hysteresis loop for **1** at 0.5 K.

found in complexes **1**–**3**. One similar example of a Gd dimer with two bridging carboxylato ligands displayed extremely weak antiferromagnetic coupling,¹⁸ in agreement with the observations on the $\text{Fe}_{12}\text{Ln}_4$ complexes reported here.

By introducing Ln^{III} ions with unquenched spin–orbital momentum, we expected to induce enough magnetic anisotropy in the resulting complexes to obtain new examples of slow-relaxing species. In fact, that is exactly what we observe for **1**. ac susceptibility for **1** displayed a strong frequency-dependent out-of-phase signal, shown in Figure 2, centered around 1.5 K. This is similar to the expected response for a SMM with an effective barrier for magnetization reversal. The energy barrier for relaxation of the magnetization and the preexponential factor τ_0 can be obtained from the fitting of the relaxation time versus temperature using the Arrhenius equation, shown in Figure 2 (inset). The effective energy barrier for **1** is 16 K and $\tau_0 = 2 \times 10^{-8}$ s, values that are in agreement with the observed preexponential factors and effective energy barriers for Ln^{III} -containing SMMs¹⁹ and for 3d metal SMMs with low-lying excited states, as is the case for **1**.²⁰ To the best of our knowledge, complex **1** not only is one of the largest 3d–4f SMMs²¹ but also represents the first Sm^{III} SMM. Furthermore, **1** displays a hysteresis loop of the magnetization at 0.5 K, shown in Figure 3, with a step at

zero field, because of quantum tunneling of the magnetization, as expected for species where the slow relaxation is of molecular origin. Because of the absence of out-of-phase ac signals in **2** and **3**, the slow relaxation in **1** can be attributed to magnetic anisotropy induced by the introduction of Sm^{III} ions with unquenched spin–orbital coupling. As shown by Ishikawa and co-workers, for certain ligand-field (LF) symmetries, such splitting can stabilize sublevels with a large $|J_z|$ value, thus achieving an “easy axis” of the magnetization.^{12,13} In the SMM Ln^{III} monomers,^{12,22} the slow relaxation process inherent to the Ln ion J ground state was enhanced by the LF with an unpaired electron, and the quantum tunneling of the magnetization is due to entangled states $|J_z > |I_z\rangle$ of the electron and nuclear spin system. The $\text{Fe}_{12}\text{Sm}_4$ complex presented here, **1**, is not a Sm^{III} mononuclear species, but it is formed of 16 ions: 4 Sm^{III} ions and 12 Fe^{III} . The $[\text{Fe}_{12}]$ unit acts as a bridging ligand with a large $S = 8$ to the two dinuclear $[\text{Sm}_2]$ units. Thus, the LF of the Sm^{III} ion is accompanied by a spin ground state of $S = 8$ of the Fe_{12} moiety. Even though the J_z value of Sm^{III} is not larger than that of Dy^{III} or Tb^{III} , it still has a value of $5/2$. Moreover, there are excited states with larger J_z values for each Sm^{III} ion lying low in energy. The zero-field splitting of the Sm^{III} ion J ground state when placed in a LF must be taken into account, as well as the nuclear spin of the ^{147}Sm (15%, $I = 7/2$) and ^{149}Sm (13.8%, $I = 7/2$) isotopes. $\text{Fe}_{12}\text{Sm}_4$ displays a frequency-dependent out-of-phase ac signal and a magnetization vs field hysteresis loop at 0.5 K, indicating a slow relaxation process of molecular origin. The hysteresis loop is similar in shape to those observed for mononuclear Ln^{III} complexes with slow relaxation of the magnetization reported by Ishikawa et al.,²² in which the magnetism is due to both orbital and spin angular momenta of the single ion. In the present case, a combination of the very weak magnetic exchange between the 3d and 4f ions, the large spin state of the $[\text{Fe}_{12}]$ ligand, and the orbital momentum of the 4f ions causes the SMM behavior.

In summary, the incorporation of Sm^{III} into a Fe^{III} system results in the largest Fe–4f cluster and the first Sm^{III} SMM that displays step hysteresis loop. Furthermore, the magnetic properties of **2** and **3** have been explored to help understand the magnetic exchange interactions and origin of magnetic anisotropy in $\text{Fe}_{12}\text{Sm}_4$. Further studies on this system are under way in our group.

Acknowledgment. This work was supported by the 973 Program of China (Grant 2007CB815305) and NSFC (Grants 20773068 and 21003078). E.C.S. acknowledges financial support from the Spanish Government (Grant CTQ2006/03949BQU and a Ramón y Cajal Fellowship).

Supporting Information Available: Experimental details, X-ray crystallographic files (CIF), Figures S1–S8, including PXRD of **1**–**3**, and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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