Communication

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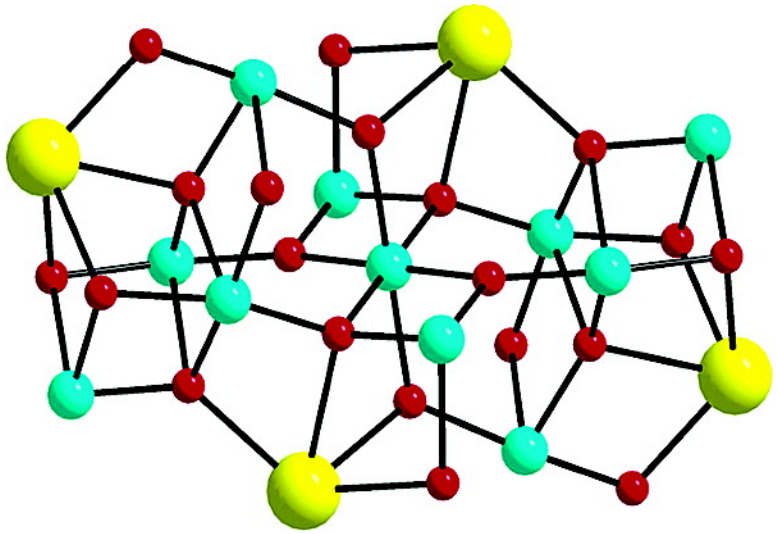

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Initial Observation of Magnetization Hysteresis and Quantum Tunneling in Mixed Manganese−Lanthanide Single-Molecule Magnets

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Single-molecule magnets (SMMs) are a growing class of materials that represents a molecular approach to nanoscale magnetic particles.[1,2] Such species derive their properties from the combination of a large ground-state spin (*S*) and a large magneto-anisotropy of the Ising (easy-axis) type (i.e. a negative zero-field splitting (ZFS) parameter, *D*). Since the initial discovery of the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ family of SMMs,[2] a number of other structural types have been discovered, almost all of them being transition metal clusters, and the majority of them being Mn clusters containing at least some Mn^{III} ions. In contrast, the synthesis of heterometallic transition metal−lanthanide SMMs is an almost completely unexplored area. Indeed, there are only two 3d/4f complexes of this type, a Cu_2Tb_2[3a] and a Dy_6Mn_6.[3b] In general, the presence of a lanthanide ion's (i) large spin such as the $S = {}^7/_2$ of Gd^{3+} and/or (ii) large anisotropy as reflected in a large *D* value, could serve to generate SMMs with properties significantly different from those of homometallic transition metal SMMs. We have thus joined ongoing efforts in this area and have focused to date primarily on Mn-containing species. Note that we have in the past described a $CeMn_8$ complex with $S = 16$ that is an SMM,[4] but this contains diamagnetic Ce^{4+}, and therefore we do not consider it a mixed 3d/4f SMM but instead a "homometallic" Mn SMM. Note also that the previous 3d/4f SMMs[3] displayed frequency-dependent out-of-phase AC signals, but not reported were magnetization hysteresis loops or quantum tunneling behavior, two confirmatory properties of a SMM; we have therefore sought these properties in our 3d/4f complexes. In the present work, we report access to a new family of mixed Mn^{3+}−Ln^{3+} polynuclear SMMs comprising a $[Mn_{11}Ln_4]^{45+}$ core. Five isostructural clusters have been synthesized, and all but the Eu complex display frequency-dependent out-of-phase AC susceptibility signals suggestive of SMMs. Furthermore, we have confirmed that these complexes are SMMs by observing magnetization hysteresis loops and have also established that they exhibit quantum tunneling of the magnetization (QTM).

The reaction of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ (1 equiv) with $Ln(NO_3)_3$ (2 equiv) (Ln = Nd, Gd, Dy, Ho, and Eu) in MeOH/MeCN (1:20 v/v) gave a dark-brown solution, which was filtered and concentrated by evaporation to give dark crystals in 55−60% isolated yield of complexes all containing the $[Mn_{11}Ln_4]^{45+}$ core, but differing slightly in the periphery. The Dy complex $[Mn_{11}Dy_4O_8(OH)_6(OMe)_2(O_2CPh)_{16}(NO_3)_5(H_2O)_3]\cdot 15MeCN$ (**1**·15MeCN) will be discussed here. Complex **1** crystallizes[5] in the triclinic space group $P\bar{1}$ and lies on an inversion center. The structure (Figure 1) consists of a $[Mn_{11}Ln_4]^{45+}$ core held together by 2 μ_3-O^{2-}, 6 μ_4-O^{2-}, 6 μ_3-OH^- and 2 μ-OMe^- ions. Peripheral ligation is provided by 12 μ- and 4 μ_3-benzoate groups, 5 chelating NO_3^- groups on the Dy ions, two H_2O molecules on Mn6 and Mn6a, and a water molecule on Dy2. The metal oxidation states (Mn^{3+} and Dy^{3+}) and the protonation levels of O^{2-} and OH^- ions were established by bond valence sum calculations,[6] charge considerations, inspection of metric parameters, and the observation of Mn^{III} Jahn−Teller (JT) elongation axes. The Mn and Dy atoms are six- and nine-coordinate, respectively. Closer inspection of the core (Figure 1) reveals two distorted $[DyMn_3O_4]$ cubanes, which are each linked by a Mn and Dy atom to a central linear Mn_3 unit. The same core structure is found in the Nd, Gd, Ho, and Eu complexes.

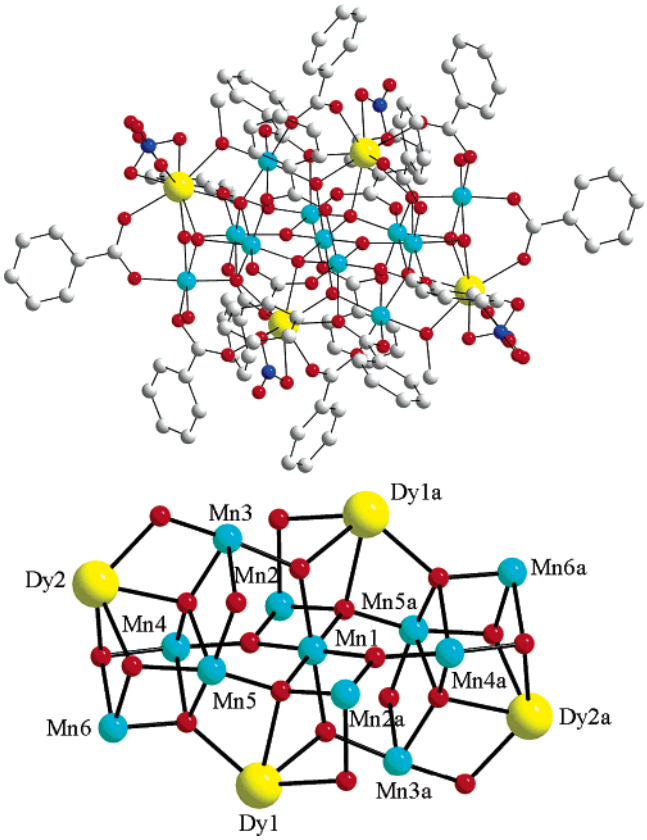

Figure 1. Molecular structure of **1** (top) and its centrosymmetric core (bottom). Color code: cyan, manganese; yellow, dysprosium; red, oxygen; blue, nitrogen; gray, carbon.

Solid-state DC magnetic susceptibility (χ_M) data were collected in the 5.0−300 K range in a 1 kG (0.1 T) field. The $\chi_M T$ value of 74.3 $cm^3\ mol^{-1}$ K at 300 K is less than the expected value for 11 Mn^{3+} ($S = 2$) and 4 Dy^{3+} ($S = {}^5/_2$, $L = 5$, $^6H_{15/2}$) noninteracting ions of 89.7 $cm^3\ mol^{-1}$ K, consistent with antiferromagnetic exchange interactions, and decreases to 57.1 $cm^3\ mol^{-1}$ K at 5.0 K, suggesting that **1** has a large ground-state spin value. To investigate whether **1** might be a SMM, AC susceptibility measurements were carried out in a 3.5 G AC field oscillating at 10−1000 Hz, and with a zero DC field (Figure 2).

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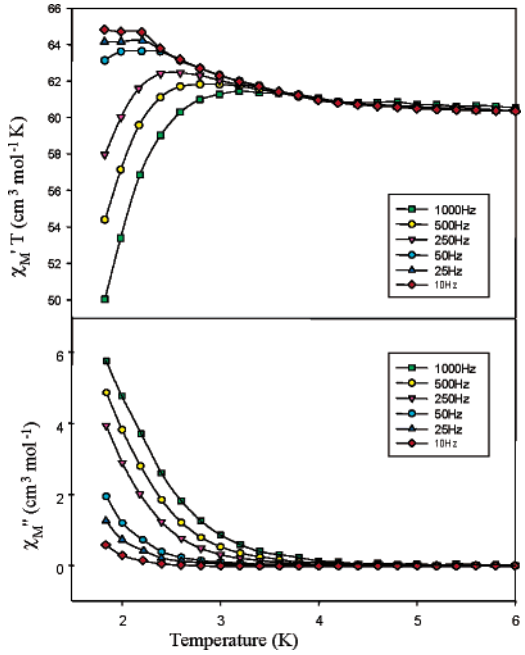

Figure 2. Plots of the in-phase ($\chi_M'T$) (top) and the out-of-phase (χ_M'') (bottom) AC susceptibility signals vs temperature for complex **1**.

A frequency-dependent decrease in the in-phase ($\chi_M'T$) signal and a concomitant increase in the out-of-phase (χ_M'') signal were observed, the latter merely "tails" of peaks that lie at <1.8 K, the operating limit of our SQUID. These are indicative of slow magnetization (M) relaxation. Such χ_M'' signals suggest the complex might be a SMM but do not prove it because intermolecular interactions and phonon bottlenecks can also give such signals.[7] Confirmation was therefore sought by magnetization vs DC field scans on single crystals of **1**·15MeCN using a micro-SQUID.[8] Magnetization hysteresis, the diagnostic property of a magnet, was indeed observed below ~1.0 K (Figure 3, top). The observed loops show superparamagnet-like increasing coercivity with decreasing temperature, confirming **1** to be a SMM. No steps due to quantum tunneling of magnetization (QTM) were seen, probably due to a distribution of molecular environments and/or intermolecular interactions.[9] To characterize the system further, DC magnetization decay data were collected in the 0.04−1.0 K range: at each temperature, the magnetization was saturated with a DC field, the temperature lowered to a chosen value, the field switched off, and the magnetization monitored with time. This gave relaxation time (τ) vs T data, which were used to construct the Arrhenius plot of Figure 3 (bottom), based on the Arrhenius relationship $\tau = \tau_0 \exp(U_{\text{eff}}/kT)$. The slope in the thermally activated region above ~0.5 K gave $\tau_0 = 4 \times 10^{-8}$ s and $U_{\text{eff}} = 9.3$ K. Below ~0.1 K, the relaxation time becomes essentially temperature-independent, consistent with the purely quantum regime where QTM through the anisotropy barrier is only via the lowest energy $\pm M_s$ levels.

Complex **1** is the first mixed-metal 3d/4f SMM to exhibit hysteresis loops and quantum tunneling of the magnetization. The ability to probe both classical (hysteresis) and quantum (QTM) magnetism behavior as a function of the lanthanide ion, as demonstrated by the extension of the synthetic method for **1** to several other lanthanides, should provide an invaluable means of improving our understanding of both the chemistry and physics of this area of bimetallic nanoscale magnetic materials. In addition, the large variation in spin and anisotropy within the lanthanide ions

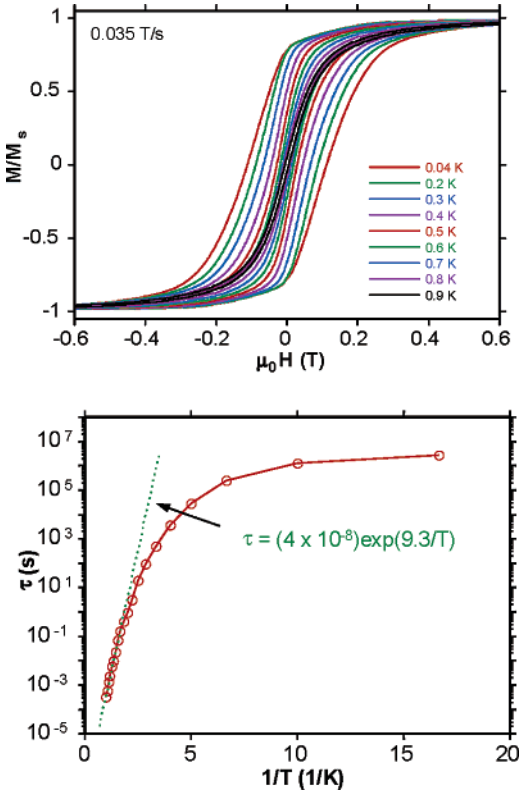

Figure 3. (Top) Magnetization (M) vs field hysteresis loops for **1**·15MeCN at the indicated temperatures; M is normalized to its saturation value, M_s. (Bottom) Arrhenius plot constructed from DC magnetization decay data. The dashed line is the fit of the thermally activated region to the Arrhenius relationship with the indicated parameters.

mentioned earlier offers the enticing possibility of being able to raise the blocking temperature (T_B) of SMMs to above that of the Mn_{12} family.

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Supporting Information Available: Crystallographic details in CIF format. Bond valence sums and magnetism data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bulletin* **2000**, *25*, 66−71 and references therein.
(2) (a) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804−1816. (b) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141−143.
(3) (a) Osa, S.; Kido, T.; Matsumoto, N.; Re, N.; Pochaba, A.; Mrozinski, J. *J. Am. Chem. Soc.* **2004**, *126*, 420−421. (b) Zaleski, C. M.; Depperman, E. C.; Kampf, J. W.; Kirk, M. L.; Pecoraro, V. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3912−3914.
(4) Tasiopoulos, A. J.; Wernsdorfer, W.; Moulton, B.; Zaworotko, M. J.; Christou, G. *J. Am. Chem. Soc.* **2003**, *125*, 15274−15275.
(5) (a) Anal. Calcd (Found) for dried **1** (solvent-free): C 35.75 (35.91), H 2.53 (2.56), N 1.83 (1.74). (b) Crystal data for **1**·15MeCN: $C_{142}H_{139}N_{20}O_{66}Mn_{11}Dy_4$, 4436.07 g mol^{-1}, triclinic $P\bar{1}$, $a = 16.5705(11)$ Å, $b = 17.2926(11)$ Å, $c = 18.6213(12)$ Å, $\alpha = 64.9700(10)°$, $\beta = 67.2950(10)°$, $\gamma = 65.6110(10)°$, $Z = 1$, $V = 4256.6(5)$ Å^3, $d_{\text{calc}} = 1.731$ g cm^{-3}, $T = 173$ K. Final R1 = 4.25 and wR2 = 10.06%.
(6) (a) Bond valence sums for Mn^{III} and Dy^{III} ions of **1** were 2.88−2.92 and 2.89−2.90, respectively. (b) Liu, W.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 4102−4105. (c) Palenik, G. J. *Inorg. Chem.* **1997**, *36*, 4888−4890.
(7) Chakov, N. E.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Inorg. Chem.* **2004**, *43*, 5919−5930.
(8) Wernsdorfer, W. *Adv. Chem. Phys.* **2001**, *118*, 99−190.
(9) Soler, M.; Wernsdorfer, W.; Folting, K.; Pink, M.; Christou, G. *J. Am. Chem. Soc.* **2004**, *126*, 2156−2165.

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