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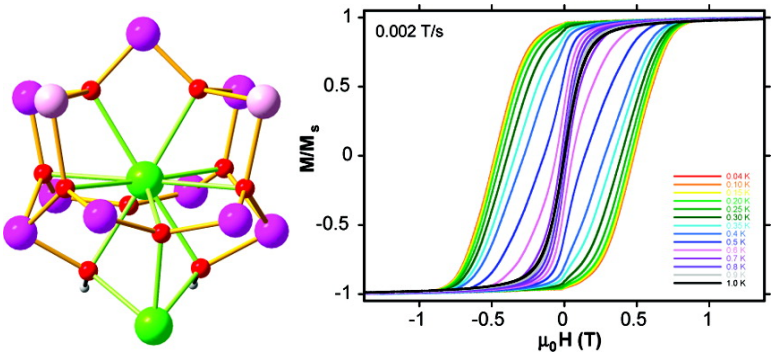

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A Bell-Shaped $Mn_{11}Gd_2$ Single-Molecule Magnet

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The synthesis of transition-metal clusters with unusual magnetic properties has become an area of intense research activity since the discovery of single-molecule magnets (SMMs).[1] The quest for new SMMs displaying high blocking temperatures has focused mainly on the use of paramagnetic 3d metal ions.[2−5] SMM behavior results from the favorable arrangement of metal ions with single ion anisotropy in a high-ground-spin state molecule, and some recent synthetic efforts have turned attention to combining 3d and 4f ions in complexes to enhance both spin and anisotropy. Recent success in synthesizing mixed transition metal and lanthanide SMMs presenting various core topologies includes Cu_2Tb_2[6] and Mn_6Dy_6[7], which have been described as SMMs on the observation of frequency-dependent out-of-phase *ac* signals, and $Mn_{11}Dy_4$[8], Mn_2Dy_2[9], Fe_2Dy_2[10], and Fe_2Ho_2[10], which additionally show hysteresis loops in the magnetization.

Recently we reported on triangular dysprosium compounds showing SMM behavior of thermally excited spin states[11] which has attracted us to exploring mixed d/f compounds as a means of enhancing anisotropy and/or spin state. Herein we report an efficient procedure toward the isolation of high-nuclearity heterometallic complexes using a preformed hexanuclear Mn complex, $[Mn^{III}_2Mn^{II}_4O_2(piv)_{10}(4\text{-Me-py})_{2.5}(pivH)_{1.5}]$[12] (**1**) (pivH = $^tBuCO_2H$), as a source of $Mn^{II/III}$ ions. Reaction of **1** with $Gd(NO_3)_3\cdot 6H_2O$ in the presence of 2-furan-carboxylic acid (fcaH) in CH_3CN results in the formation of the high-nuclearity complex $[Mn^{III}_9Mn^{II}_2Gd_2(O)_8(OH)_2(piv)_{10.6}(fca)_{6.4}(NO_3)_2(H_2O)]\cdot 13CH_3CN\cdot H_2O$ (**2**·13MeCN·H_2O).[13]

The $Mn_{11}Gd_2$ aggregate **2** crystallizes[14] in the triclinic space group $P\bar{1}$, and its molecular structure is shown in Figure 1. The oxidation states of the Mn centers were determined by bond-valence sum (BVS) calculations,[15] with Mn(1)−Mn(9) assigned as Mn^{III} and Mn(10) and Mn(11) as Mn^{II}. The assignments of O(10) as $(\mu_3\text{-}O)^{2-}$ and of O(2) and O(3) as $(\mu_3\text{-}OH)^-$ were also confirmed by BVS calculations; the H-atoms on O(2) and O(3) could be located and refined. The core of the complex **2** can be described as bell-shaped. The Mn^{III} and Mn^{II} centers form the shell of the bell, with Mn(9) at the apex, Mn(5), Mn(8), Mn(10), and Mn(11) at the shoulder of the bell, and the remaining six Mn^{III} centers forming the rim of the bell. The two Gd centers can be thought of as forming the bell's clapper, and since the Gd···Gd vector is inclined with respect to the axis of the bell, this gives the impression that the bell is ringing. Gd(1) is ten-coordinate and is connected to each of the eleven Mn atoms through the six $(\mu_4\text{-}O)$, one $(\mu_3\text{-}O)$, and two $(\mu_3\text{-}OH)$ bridges. Its coordination polyhedron may be best described as a bicapped square antiprism. The second Gd is nine-coordinate and hangs below the rim of the bell. It is connected to the other Gd and four of the Mn^{III} atoms through one $(\mu_4\text{-}O)$ and the two $(\mu_3\text{-}OH)$ bridges, and two oxygen atoms from two $(\mu_3$-carboxylate) bridges. Its coordination sphere is completed by two chelating nitrate ions. The Mn centers all have octahedral coordination geometries except for Mn(6), which is square-pyramidal, with the Mn^{III} all showing the expected Jahn−Teller distortions. Of the 17 carboxylate ligands (ten pivalate, six furoate, and one that is a disordered superposition), the unusual (μ_4,η^2,η^2) bridging mode is seen for one furoate and one pivalate ligand. In addition to these μ_4-bridging carboxylates, four of the furoates adopt a (μ_3, η^2, η^1) triply bridging mode, while the sixth furoate and all the remaining pivalates form simple bridges between two metal centers. In other words, five of the six furoates bridge between three or four metal centers, whereas all but one of the pivalates adopt a simple μ_2-bridging mode. The Mn^{III} Jahn−Teller axes have an irregular

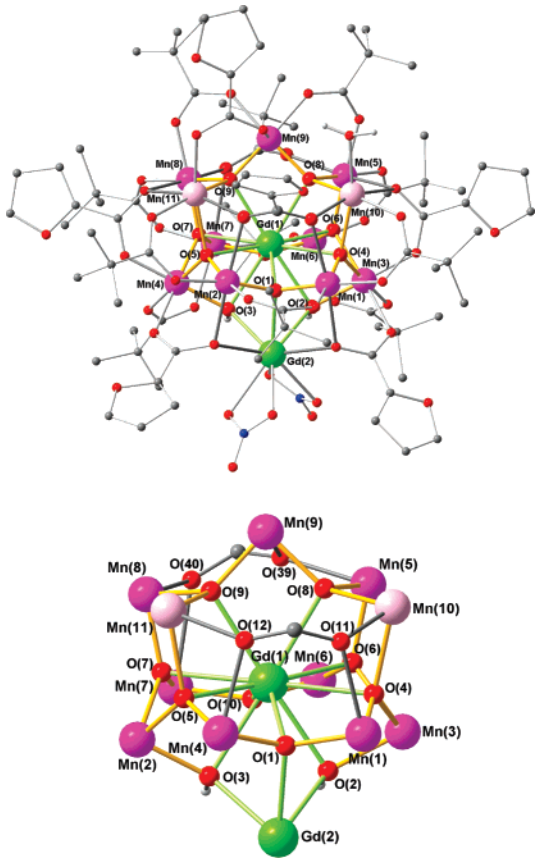

Figure 1. Molecular structure of **2** (above) and its core (below). Disorder and organic H-atoms omitted for clarity: Gd, green; Mn^{III}, purple; Mn^{II}, pink; O, red; N, blue; C, gray.

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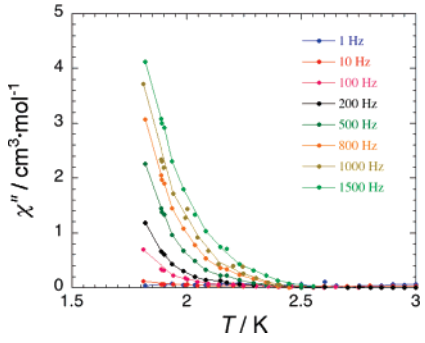

Figure 2. Plots of the out-of-phase (χ'') ac susceptibility signals versus temperature for complex **2** with an applied 3 Oe ac field in zero dc field.

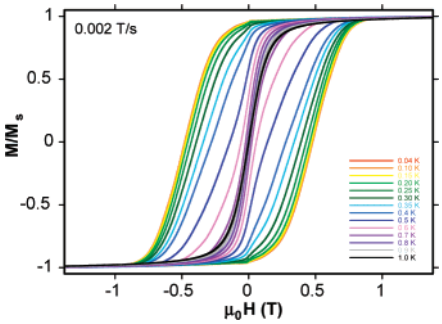

Figure 3. Magnetization (M) versus applied dc field ($\mu_o H$) for **2**.

arrangement within the aggregate core (Figure S1). In addition to the bell-shaped core topology, **2** is the first mixed-valence $Mn^{II,III}$-Ln^{III} d/f complex and only the second synthesized Mn-Ln cluster with as many as eleven Mn centers.[8]

The dc magnetic susceptibility of **2** measured at 1000 Oe in the 1.8−300 K temperature range, reveals a room temperature χT value per complex of 46.9 cm^3 K/mol. On lowering the temperature, χT first continuously decreases reaching 35.2 cm^3 K/mol at 37 K and then increases to a maximum value at 1.81 K of 74.5 cm^3 K/mol. The fact that the χT product starts to saturate at 1.81 K suggests that below this temperature a well-defined high-spin ground state is almost exclusively thermally populated (Figure S2). The fit of the experimental data to a Curie Weiss law above 30 K (Figure S3) leads to a Curie constant of 50.8 cm^3 K/mol and a Weiss constant of −28.1 K indicating dominant antiferromagnetic interactions between spin carriers. The Curie constant is close to the expected value for nine Mn^{III} ($S = 2$), two Mn^{II} ($S = {}^5/_2$) and two Gd^{III} ($S = {}^7/_2$) noninteracting ions (51.5 cm^3 K/mol).

The ac susceptibility measurements taken over the frequency range 1−1500 Hz and at temperatures of 1.8−3 K display frequency-dependent out-of-phase signals (Figure 2) suggesting that the complex exhibits slow relaxation of its magnetization and potential SMM behavior. To investigate this further, single-crystal magnetization measurements were performed using an array of micro-SQUIDs at temperatures down to 40 mK.[16] Hysteresis loops collected for complex **2** at varying temperatures and sweep rates (Figure 3) show a superparamagnet-like increasing coercivity with decreasing temperature confirming **2** to be a SMM. No steps due to quantum tunneling of magnetization (QTM) were observed, probably as a result of ligand and lattice solvent disorder, as there are no obvious pathways for intermolecular interactions. The 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 decay monitored with time. The data were scaled in a single master curve to construct the Arrhenius plot, and the fit of the thermally activated region above ∼0.5 K gave $\tau_0 = 2 \times 10^{-12}$ s and an effective barrier $\Delta_{eff} = 18.4$ K, which is the highest value reported so far for 3d-4f SMMs.[8,9] Given the lack of obvious intermolecular interactions, the relatively low value of τ_0 compared with other 3d-4f SMMs might be the result of the presence of a higher spin state. Below ∼0.16 K, the relaxation time becomes essentially temperature-independent, consistent with the purely quantum regime where QTM is only via the lowest energy $\pm m_s$ levels. Probably the Jahn−Teller distortions of the Mn^{III} centers make the major contribution to the anisotropy with the Mn^{II} and Gd^{III} centers contributing to the spin.

In conclusion, this tridecanuclear manganese−lanthanide complex has an unusual topology and SMM properties. The synthetic method allows for the assembly of related materials.

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

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(12) See Supporting Information.
(13) Anal. Found (calcd for **2**·CH_3CN·H_2O): C, 34.39 (34.12); H, 4.21 (4.00); N, 1.19 (1.37).
(14) Crystal data for **2**·13CH_3CN·H_2O: $C_{111}H_{157.6}Gd_2Mn_{11}N_2O_{58.4}$, 3555.36 g mol^{-1}, triclinic, $P\bar{1}$, $a = 15.8893(10)$ Å, $b = 17.5285(11)$ Å, $c = 27.2474(17)$ Å, $\alpha = 86.985(1)$, $\beta = 78.083(1)$, $\gamma = 72.737(1)°$, $Z = 2$, $V = 7090.5(8)$ $Å^3$, $T = 100$ K, $\rho_{calcd} = 1.665$ g cm^{-3}, $F(000) = 3598$, μ(Mo Kα) = 1.957 mm^{-1}; $2\theta_{max} = 52.7°$, 33399 data, 28136 unique ($R_{int} = 0.0246$), 1408 parameters, final $wR_2 = 0.0907$, $S = 0.992$ (all data), R_1 (18636 data with $I > 2\sigma(I)$) = 0.0409. See Supporting Information for refinement details; CCDC 637050.
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