JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
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A N_2^{3-} Radical-Bridged Terbium Complex Exhibiting Magnetic Hysteresis at 14 K

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S Supporting Information

ABSTRACT: The synthesis and magnetic properties of three new N_2^{3-} radical-bridged dilanthanide complexes, $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)^-$ (Ln = Tb, Ho, Er), are reported. All three display signatures of single-molecule-magnet behavior, with the terbium congener exhibiting magnetic hysteresis at 14 K and a 100 s blocking temperature of 13.9 K. The results show how synergizing the strong magnetic anisotropy of terbium(III) with the effective exchange-coupling ability of the N_2^{3-} radical can create the hardest molecular magnet discovered to date. Through comparisons with non-radical-bridged ac magnetic susceptibility measurements, we show that the magnetic exchange coupling hinders zero-field fast relaxation pathways, forcing thermally activated relaxation behavior over a much broader temperature range.

With spintronics and nanotechnology pushing well below the 100 nm size regime,[1] the utility of discrete molecules as device components is becoming apparent,[2] and f elements, with their highly anisotropic magnetic moments, will almost certainly play an important role.[3] In fact, the f elements have been responsible for many of the recent advances in single-molecule magnetism, pushing the frontiers to longer relaxation times and higher temperature regimes.[4] While molecule-based devices will differ in function and requirement from current technologies, certain key attributes of molecular components will undoubtedly be of interest. In particular, the *blocking temperature* (the temperature at which magnetic information is lost within a certain time threshold) and the *coercive field* (the magnetic field required to counteract remnant magnetization) are two criteria of hard magnets that scientists working in the field of molecular magnetism have struggled to improve.

We have synthesized thermally stable, air-sensitive salts of three new dilanthanide complexes, $[K(18\text{-crown-6})(THF)_2][\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)]$ [Ln = Tb (**1**), Ho (**3**), Er (**5**); see Figure 1 and Figures S1−S3 in the Supporting Information], that highlight the importance of single-ion anisotropy and magnetic exchange coupling in molecular magnetic behavior. Similar to the previously reported Y(III), Gd(III), and Dy(III) analogues, compounds **1**, **3**, and **5** can be isolated upon reduction of the N_2^{2-}-bridged complexes $\{[(Me_3Si)_2N]_2(THF)Ln\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ [Ln = Tb (**2**), Ho (**4**), Er (**6**)][4h,5] with potassium graphite. The reduction introduces radical character into the bridging dinitrogen unit, drastically enhancing the magnetic properties of the molecules.

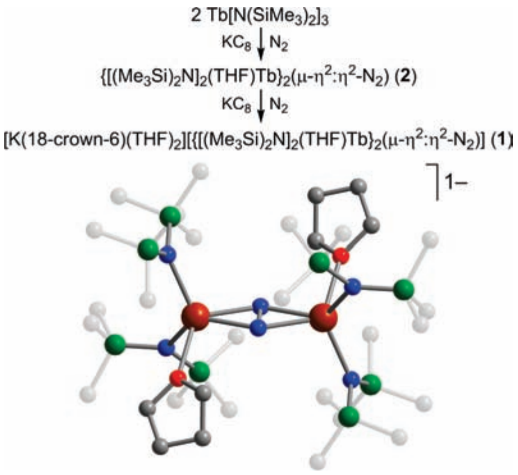

Figure 1. (top) Synthetic scheme for **1** and **2**. (bottom) Structure of the N_2^{3-} radical-bridged complex in **1**. Brown, green, red, blue, and gray spheres represent Tb, Si, O, N, and C atoms, respectively; H atoms have been omitted and methyl groups faded for clarity. The complexes in **2**−**6** exhibit analogous structures. Selected interatomic distances (Å) for **1**−**6**, respectively: N−N = 1.3940(3), 1.2705(3), 1.4045(3), 1.2637(3), 1.4085(3), 1.2750(4); mean Ln−N(N_2^{n-}) = 2.2200(2), 2.3147(2), 2.1989(3), 2.3058(2), 2.1905(3), 2.2863(3); Ln···Ln = 4.2155(2), 4.4517(3), 4.1675(3), 4.4351(2), 4.1485(3), 4.3914(5).

The unprecedented magnetic behavior of **1** was first apparent when the product of magnetic susceptibility and temperature ($\chi_M T$) was plotted versus temperature (see Figure 2). A typical gentle decline[6] in $\chi_M T$ had been observed for **2**, corresponding to a combination of weak magnetic coupling and thermal depopulation of low-lying crystal-field states. In stark contrast, **1** displays a pronounced rise from a room-temperature value of $\chi_M T = 23.1$ emu·K/mol ($\chi_M T_{\text{free-ion}} = 24$ emu·K/mol) to a maximum of $\chi_M T = 34.5$ emu·K/mol at 55 K. This rise is followed by a precipitous drop to $\chi_M T = 2.0$ emu·K/mol at 9 K. Here, the rise in $\chi_M T$ is ascribed to exceptionally strong magnetic exchange coupling between the Tb(III) ions and the central N_2^{3-} radical ligand, as was observed and quantified previously for the Gd(III) analogue.[4h] The sudden drop at low temperature suggests that the orientation of the total molecular spin of each molecule has been pinned by the strong molecular anisotropy and can no

Received: July 13, 2011
Published: August 12, 2011

dx.doi.org/10.1021/ja206286h | *J. Am. Chem. Soc.* 2011, 133, 14236–14239

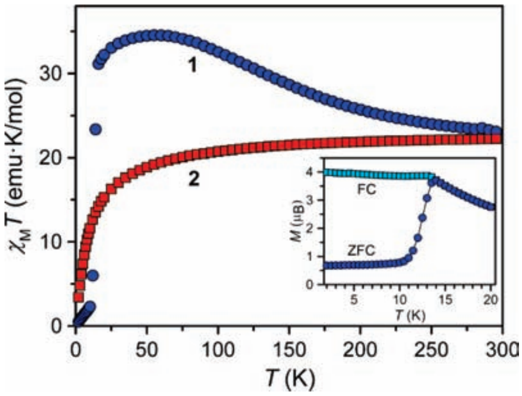

Figure 2. Temperature dependence of the product of magnetic susceptibility and temperature ($\chi_M T$) for **1** and **2**. Inset: plot of magnetization vs temperature for **1** during field-cooled (teal squares) and zero-field-cooled (blue circles) measurements displaying the thermoremnant magnetization.

longer respond to a magnetic field. This interpretation is corroborated by comparison of field- and zero-field-cooled magnetic susceptibility data (see the Figure 2 inset). Here, the field-cooled data do not show the same low-temperature decrease in $\chi_M T$, indicating that the behavior is indeed the result of magnetic blocking. The temperature at which the field-cooled and zero-field-cooled plots converge (14 K) corresponds to the peak in the zero-field-cooled magnetization, indicating a very narrow range of relaxation times, consistent with molecular relaxation behavior. Plots of $\chi_M T$ versus T for compounds **3** and **5** show similar high-temperature rises but lack the precipitous decline observed for **1** (see Figure S4).

To probe the slow magnetic relaxation behavior further, dynamic magnetic measurements were performed on compounds **1**, **3**, and **5**. When **1** was subjected to an ac magnetic field (1–1500 Hz) at temperatures between 20 and 34 K, a peak in the out-of-phase component (χ''; Figure 3 bottom) and a concurrent decrease in the in-phase component (χ'; Figure 3 top) of the susceptibility were observed, confirming magnetic blocking on a millisecond to second time scale. These data could be fit to a generalized Debye function to extract temperature-dependent relaxation times (see Figure 4, red circles), which fit an Arrhenius temperature law with an energy barrier to spin relaxation of $U_{\mathrm{eff}} = 227.0(4)\ \mathrm{cm}^{-1}$ and an attempt time of $\tau_0 = 8.2(1) \times 10^{-9}$ s. This places **1** among the small collection of terbium-based single-molecule magnets.[7] While the non-Kramers electronic ground state (${}^7F_6$; $S = 3$, $L = 3$, $J = 6$) does not ensure bistability,[8] terbium compounds have to date exhibited the highest energy barriers among all single-molecule magnets.[7a,f,h] Its strong single-ion anisotropy can be exploited by either enforcing a high-symmetry environment or coupling the terbium ions to other spin centers in a molecular cluster.

Similar analyses for **3** and **5** (see the Figure 4 inset) yielded barriers to magnetic relaxation of $U_{\mathrm{eff}} = 73(6)$ and $36(1)\ \mathrm{cm}^{-1}$, respectively.[9] Compound **5**, however, required the application of a 1000 Oe dc field to observe slow relaxation behavior. While these values are much lower than that observed for **1**, the barrier of **3** is the highest observed to date for a holmium-based single-molecule magnet. Interestingly, the magnetic relaxation of both **3** and **5** shows strong deviations from Arrhenius behavior on the ac susceptibility time scale. This may be the result of either weaker magnetic anisotropy or weaker exchange coupling arising from the contracted, more spherical f-electron densities of holmium and erbium.[10]

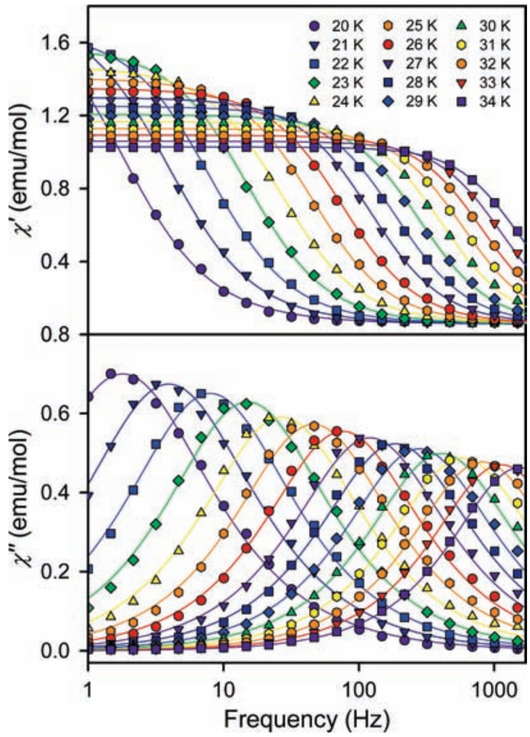

Figure 3. In-phase (χ', top) and out-of-phase (χ'', bottom) components of the ac magnetic susceptibility for **1** under zero applied dc field from 20 K (purple circles) to 34 K (purple squares). Solid lines represent a fit to the data.

While terbium compounds have proven to provide high relaxation barriers, at low temperature they tend to deviate strongly from Arrhenius behavior, leading to maximum relaxation times on the order of seconds to milliseconds. To probe the relaxation behavior of **1** on a longer time scale, the magnetic field was scanned and the sample response monitored for signs of magnetic hysteresis (see Figure 5). At an average sweep rate of 0.9 mT/s, an open magnetic hysteresis curve was observed at 14 K with a coercive field reaching 5 T below 11 K. This hysteretic behavior occurs at nearly twice the highest temperature recorded for any previous molecule.[4b,h]

Because of differences in sweep rates and measurement techniques, the maximum hysteresis temperature provides an imperfect comparison of the slow relaxation dynamics of different compounds. It has therefore been suggested that a more quantitative measure be implemented by defining the blocking temperature as the temperature at which the magnetic relaxation time is 100 s.[11] By fitting the time-dependent decay of the magnetization to an exponential function, we can extend the Arrhenius plot constructed from ac susceptibility data to much lower temperatures and longer relaxation times (see Figure 4, blue circles). From the lowest-temperature ac susceptibility point (20 K) and the highest-temperature dc susceptibility point (14 K) on the Arrhenius plot, a 100 s blocking temperature of 13.9 K can be estimated for **1**. Very few single-molecule magnets reach relaxation times in this domain. To the best of our knowledge, the next highest blocking temperatures by this definition are 6.7 K for $[\{[(\mathrm{Me_3Si})_2\mathrm{N}]_2(\mathrm{THF})\mathrm{Dy}\}_2(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{N}_2)]^{-}$[4h] (see Figure S5)

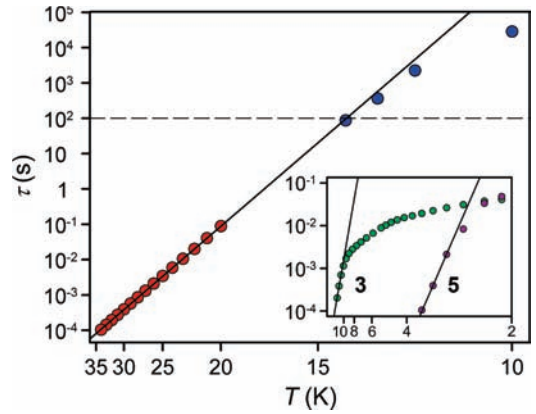

Figure 4. Plot of relaxation time (τ, natural logarithmic scale) vs temperature (reciprocal scale) extracted from fitting the χ'_M and χ''_M values obtained for **1**. Red and blue circles represent data extracted from ac and dc susceptibility measurements, respectively. The black line represents a linear fit to the Arrhenius equation based on the ac susceptibility data, affording an effective energy barrier to relaxation of $U_{\mathrm{eff}} = 227.0(4)$ cm^{-1} [326.7(6) K] with an attempt time of $\tau_0 = 8.2(1) \times 10^{-9}$ s. Inset: plots of τ (logarithmic scale) vs temperature (reciprocal scale) for **3** [$U_{\mathrm{eff}} = 73(6)$ cm^{-1}, $\tau_0 = 3(3) \times 10^{-8}$ s] and **5** [$U_{\mathrm{eff}} = 36(1)$ cm^{-1}, $\tau_0 = 4(2) \times 10^{-11}$ s].

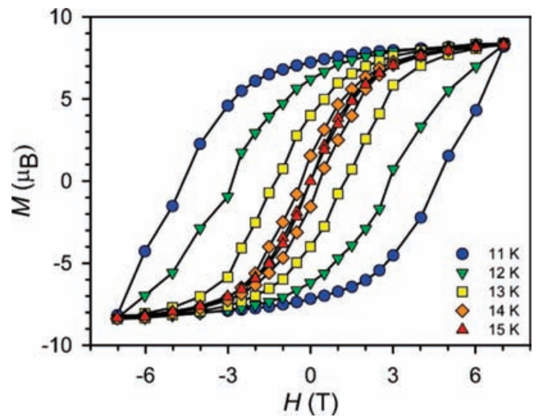

Figure 5. Plot of magnetization (M) vs dc magnetic field (H) for **1** from 11 to 15 K at an average sweep rate of 0.9 mT/s. At 15 K, the hysteretic behavior effectively disappears, corresponding to a calculated relaxation time of $\tau = 20$ s. Hysteresis measurements below 11 K were hindered by the strong coercive field.

and 3.2 K for [$Mn_6O_2(sao)_6(O_2CPh)_2(EtOH)_4$] ($saoH_2$ = 2-hydroxybenzaldehyde oxime).[12]

Interestingly, compound **1** shows evidence of multiple relaxation processes, as observed for many f-element single-molecule magnets.[4b,d−f,13] However, because of the extremely slow dynamics, this behavior was observed only in the dc relaxation experiment at 8 K. At this temperature, the magnetic relaxation of **1** could be fit satisfactorily only by using two separate exponential functions, corresponding to relaxation times of 14.33(3) and 3.0(2) h (see Figure S6). Neither of these values lie on the line predicted by the Arrhenius law, possibly indicating that some combination of long-range dipolar interactions, low-symmetry components of the ligand field, and nuclear tunneling shortcuts the molecular relaxation barrier. The presence of one short and one long relaxation time is consistent with an intermolecular dipolar mechanism for relaxation when the system is magnetically concentrated. As the individual moments in the molecular ensemble randomize, the strong dipolar field weakens, and the molecular electronic structure assumes sole responsibility for the relaxation kinetics.

In summary, we have extended the series of N_2^{3-} radical-bridged dilanthanide complexes to include three new analogues. Among the series, the terbium congener **1** was found to possess extraordinarily slow molecular magnetic relaxation properties, with a blocking temperature of 13.9 K. With the recently reported dysprosium analogue, the previous record for blocking temperature of a molecule was doubled, and with **1** it has now been quadrupled. This rapid advancement of a key single-molecule-magnet property emphasizes the role that the f elements are beginning to play in the field. Given the profound effect that altering the coordination environment has had on other terbium-based single-molecule magnets,[7f,h] we anticipate that this system can be altered to yield even stronger single-molecule-magnet behavior. Additionally, the properties of **1** indicate that coordination of a radical ligand could improve upon the already impressive properties of many mononuclear single-molecule magnets, including those containing transition-metal[14] and actinide ions.[13a,15] Although there is currently substantial effort to investigate the physics of individual molecular magnets, the molecules under study largely are species synthesized decades ago. The current advance demonstrates the vital role that synthetic chemistry can play, namely, the targeting and improvement of specific technologically desirable properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed synthetic, crystallographic, and magnetic data for all compounds and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank Dr. Grégory Nocton and Dr. Wayne Lukens for assistance collecting dc magnetic relaxation data and the National Science Foundation for support of this research through Grants CHE-0617063 and CHE-1010002.

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