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Slow Magnetic Relaxation in a High-Spin Iron(II) Complex

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Over the past two decades, a number of transition metal clusters, known as single-molecule magnets, have been shown to exhibit slow magnetic relaxation at low temperature.[1] This phenomenon stems from a negative uniaxial magnetic anisotropy (D) acting on a high-spin ground state (S) to generate an energy barrier to spin inversion ($U = S^2|D|$). Recently, a new class of single-molecule magnets in which the molecule contains a single paramagnetic lanthanide or actinide center has emerged.[2,3] In these systems, the slow relaxation stems from a highly anisotropic ground state arising from the strong spin−orbit coupling associated with the f-element ion. In principle, slow relaxation in a mononuclear complex should also be possible for species incorporating high-anisotropy transition metal ions. Of particular interest here are molecules exhibiting a ground state with an unquenched orbital angular momentum together with the maximal possible spin of $S = 2$. Indeed, for certain high-spin iron(II) complexes, this situation has been shown to give rise to D values of extraordinarily large magnitude[4]—as large as 50 cm^{-1} for the planar complex (β-diketiminate)FeCH_3.[4a] After testing several such molecules for slow relaxation effects, we turned our attention to the trigonal pyramidal complex $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$ depicted in Figure 1.[5] Herein, we report the observation of slow magnetic relaxation for this species, providing the first example of a mononuclear transition metal based single-molecule magnet.

A dc magnetic susceptibility measurement performed on $\text{K}[(\text{tpa}^{\text{Mes}})\text{Fe}]$ (**1**) afforded a value of $\chi_M T = 3.32\ \text{cm}^3\ \text{K/mol}$ at 298 K, confirming the $S = 2$ ground state spin of the complex. Variable-field magnetization data were then collected to probe the magnetic anisotropy of the ground state. The resulting magnetization plot (see Figure 2) exhibits significant separation between the isofield curves, indicative of strong magnetic anisotropy. Indeed, a fit to the data using ANISOFIT 2.0[6] afforded axial and transverse zero-field-splitting parameters of $D = -39.6\ \text{cm}^{-1}$ and $E = -0.4\ \text{cm}^{-1}$, respectively, with $g = 2.21$. The large magnitude of D stems from the presence of three electrons residing in the 1e orbital set (see Figure 1, right), which generates orbital angular momentum and thus magnetic anisotropy. The nonzero value of E likely arises from the slight distortion away from threefold symmetry at the Fe^{II} center, as reflected in the variation of the $\text{Fe}-\text{N}_{\text{basal}}$ distances and $\text{N}_{\text{basal}}-\text{Fe}-\text{N}_{\text{basal}}$ angles. Most importantly, the negative sign of D, together with its large magnitude, indicates a significant intrinsic spin-reversal barrier of $U = S^2|D| = 158\ \text{cm}^{-1}$ and therefore the possibility of observing slow magnetic relaxation.

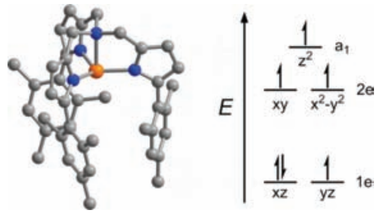

Figure 1. Left: Structure of the trigonal pyramidal complex $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$, as observed in **1**.[5] Orange, blue, and gray spheres represent Fe, N, and C atoms, respectively; H atoms have been omitted for clarity. The coordination at the Fe^{II} center deviates slightly from C_{3v} symmetry, with the following interatomic distances (Å) and angles (deg): $\text{Fe}-\text{N}_{\text{apical}}$ 2.1717(2); $\text{Fe}-\text{N}_{\text{basal}}$ 2.024(3), 2.008(3), 2.041(2); $\text{N}_{\text{basal}}-\text{Fe}-\text{N}_{\text{basal}}$ 122.4(1), 115.3(1), 117.4(1). Right: Splitting of the 3d orbital energies for a high-spin Fe^{II} center in a trigonal pyramidal ligand field.

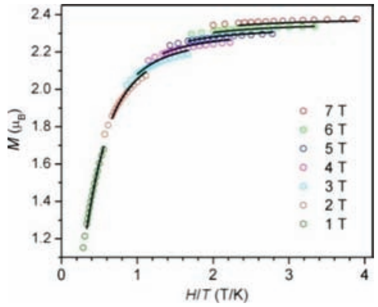

Figure 2. Low-temperature magnetization data for **1** collected under various applied dc fields. The black lines represent fits to the data.

To probe the magnetization dynamics of **1**, variable-frequency ac susceptibility data were collected at multiple temperatures. In the absence of an applied dc field, no χ_M'' signal was observed at frequencies up to 1500 Hz and temperatures down to 1.8 K. Application of a dc field, however, resulted in a set of frequency-dependent peaks in plots of χ_M'' vs ν with varying temperature (see Figure 3, bottom). Relaxation times were extracted from these peaks by fitting the χ_M' and χ_M'' data to a generalized Debye model (see Figure S3 in the Supporting Information).[7] The resulting Arrhenius plot is shown in the top panel of Figure 3. The plot features a linear region at high temperature, and a fit to these data yielded an effective spin-reversal barrier of $U_{\text{eff}} = 42\ \text{cm}^{-1}$ and a preexponential factor of $\tau_0 = 2 \times 10^{-9}$ s. These values are consistent with those previously reported for single-molecule magnets.[1] In addition, the value of τ_0 indicates that phonon bottleneck effects are not the source of the slow relaxation.[8] Notably, despite its considerable magnitude compared with other reported single-molecule magnets, this effective barrier falls well short of the theoretical barrier of 158 cm^{-1}, which would represent a nearly 3-fold increase over the current record for a transition metal based species.[1e]

The absence of slow relaxation in **1** under zero applied field[9] can most likely be attributed to quantum tunneling of the magnetization through the spin-reversal barrier, a phenomenon previously reported for a number of transition metal clusters[10] and f-element complexes.[3,11] In a molecule exhibiting only axial anisotropy, the wave functions associated with the energy levels constituting each $\pm M_S$ pair are orthogonal to one another, thereby eliminating quantum tunneling as a possible relaxation pathway. However, introduction of transverse magnetic anisotropy allows mixing of the $\pm M_S$ levels, allowing an

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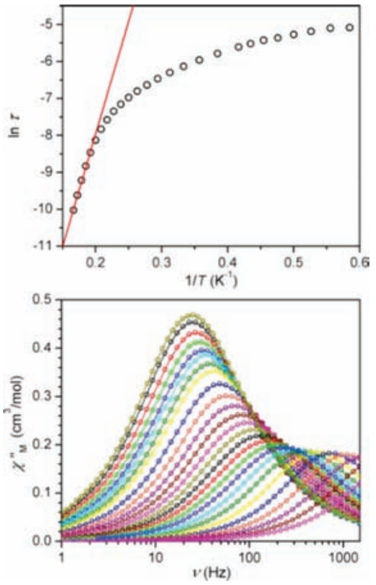

Figure 3. Bottom: Variable-frequency out-of-phase ac susceptibility data for **1**, collected under a 1500 Oe dc field over the temperature range 1.7 (dark yellow) to 6.0 (magenta) K. Data were collected in temperature increments of 0.1 (1.7−2.4 K) and 0.2 (2.6−6.0 K) K. The solid lines are guides for the eye. Top: Arrhenius plot constructed from data obtained under a dc field of 1500 Oe. The solid red line corresponds to a linear fit to the thermally activated region, as described in the text.

electron to tunnel from $+M_S$ through the thermal barrier to $-M_S$.[1c,10d] In **1**, the slight distortion from threefold symmetry about the non-Kramers Fe$^{\text{II}}$ center likely induces a transverse component of the anisotropy, leading to mixing of the +2 and −2 levels and of the +1 and −1 levels and, as a result, the formation of tunneling pathways. Indeed, the nonzero value of E obtained from the reduced magnetization data supports the presence of transverse anisotropy. Moreover, the clear dominance of the tunneling pathway over the thermal pathway in the absence of a field is not surprising in view of the small ground-state spin of the molecule, because the probability of tunneling increases with decreasing magnitude of M_S.[10d,12]

Emergence of slow relaxation upon application of a dc field occurs through removal of the degeneracy of the $\pm M_S$ levels. Splitting of these energy levels decreases their mixing with one another, thereby diminishing the rate of tunneling between them. While the high-temperature data in the Arrhenius plot for **1** illustrate a thermally activated relaxation mechanism, the data deviate from linearity as the temperature decreases, tending toward temperature independence of the relaxation time. This deviation from linearity likely stems from thermal depopulation of the $M_S = 0, \pm 1$ levels, ultimately leading to ground-state tunneling as the most facile relaxation pathway. Indeed, the existence of two distinct regimes in the Arrhenius plot has been observed previously for a number of molecules exhibiting quantum tunneling of the magnetization.[3,10c,11]

To further probe the effect of applied magnetic field on tunneling in **1**, relaxation times were extracted from variable-frequency ac susceptibility data obtained at 2.0 K under various dc fields (see Figure 4). As expected, the relaxation time increased with applied dc field, reaching a maximum at ∼1500 Oe. The subsequent downturn for $H > 1500$ Oe was unexpected, as the relative energies of the $M_S = \pm 2$ levels continue to diverge and do not approach the $M_S = \pm 1$ levels until much higher fields. An explanation for this behavior is not immediately forthcoming.

The foregoing results demonstrate that slow magnetic relaxation can indeed occur in a mononuclear transition metal complex. In view of the very large spin-reversal barrier expected for [(tpa$^{\text{Mes}}$)Fe]$^-$ in the absence of magnetic quantum tunneling, the synthesis of similar complexes that inhibit this effect at zero field may lead to single-molecule magnets that function at practical temperatures. Toward this end, efforts are underway to generate more rigid high-spin iron(II) complexes in which rigorous threefold symmetry eliminates the transverse magnetic anisotropy.

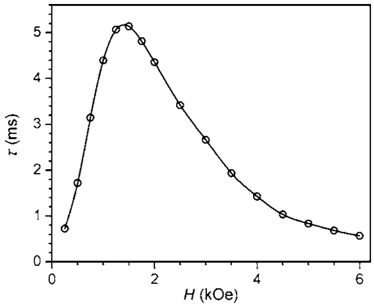

Figure 4. Dc field dependence of the relaxation time for **1** at 2.0 K. The solid line is a guide for the eye.

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

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