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. 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. 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—as large as 50 cm$^{-1}$ for the planar complex ($\beta$-diketiminato)FeCH$_3$. After testing several such molecules for slow relaxation effects, we turned our attention to the trigonal pyramidal complex [$(tpa$Mes)Fe] depicted in Figure 1. 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 K[($tpa$Mes)Fe] (I) afforded a value of $\gamma_M T = 3.32$ cm$^3$ 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 2.06 afforded a value of $|D|$ $= -39.6$ cm$^{-1}$ and $E = -0.4$ 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 Fe–N$_{apical}$ distances and N$_{basal}$–Fe–N$_{basal}$ angles. Most importantly, the negative sign of $D$, together with its large magnitude, indicates a significant intrinsic spin-reversal barrier of $U = S^2|D| = 158$ cm$^{-1}$ and therefore the possibility of observing slow magnetic relaxation.

To probe the magnetization dynamics of I, variable-frequency ac susceptibility data were collected at multiple temperatures. In the absence of an applied dc field, no $\chi_{M''}$ 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 $\chi_{M''}$ vs $\nu$ with varying temperature (see Figure 3, bottom). Relaxation times were extracted from these peaks by fitting the $\chi_M'$ and $\chi_M''$ data to a generalized Debye model (see Figure S3 in the Supporting Information). 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 anisotropy barrier of $U_{\text{eff}} = 42$ 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. In addition, the value of $\tau_0$ indicates that phonon bottleneck effects are not the source of the slow relaxation. 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.

The absence of slow relaxation in I under zero applied field 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 and f-element complexes. 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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In 1, the slight distortion from threefold symmetry about the non-Kramers Fe$^{	ext{II}}$ 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 tunneling as the most facile relaxation pathway. Indeed, efforts are underway to generate more rigid high-spin iron(II) 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.

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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.

References


(9) The zero-applied-field Mössbauer spectra obtained at 4.2 K and above (see Figure 4) are paramagnetic quadrupole doublets characteristic of a low-coordinate high-spin iron(II) complex; this observation indicates a zero-field relaxation time of less than $5 \times 10^{-8}$ s.

