

Slow Magnetic Relaxation in a Trigonal Prismatic Uranium(III) Complex

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The discovery of slow magnetic relaxation in certain transition-metal–oxo clusters revealed a new family of magnetic materials known as single-molecule magnets.¹ Such molecules possess a high-spin ground state (with total spin S) for which spin–orbit coupling results in a zero-field splitting of the $(2S + 1)$ -fold degeneracy in a manner that creates a thermal relaxation barrier and gives rise to magnetic bistability at low temperature. Two major goals of research in this area are generating new molecules with larger relaxation barriers and understanding the quantum tunneling processes that can shortcut the barrier. Ultimately, realization of these efforts could lead to the viability of single-molecule magnets in applications such as information storage, quantum computing, and spin-based molecular electronics.²

Recently, a class of single-molecule magnets in which the molecule contains just a single paramagnetic metal ion has emerged. To date, the only examples of such species are the lanthanide ion complexes $[\text{LnPc}_2]^{n+}$ ($\text{Ln}^{\text{III}} = \text{Tb}, \text{Dy}, \text{Ho}; \text{H}_2\text{Pc} = \text{phthalocyanine}; n = -1, 0, 1$),³ $[\text{Ln}(\text{W}_5\text{O}_{18})_2]^{9-}$ ($\text{Ln}^{\text{III}} = \text{Ho}, \text{Er}$), and $[\text{Ln}(\beta_2\text{-SiW}_{11}\text{O}_{39})_2]^{13-}$ ($\text{Ln}^{\text{III}} = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$).⁴ Here, theoretical and experimental studies have shown that the zero-field splitting responsible for the relaxation barrier is due to removal of the $(2J + 1)$ -fold degeneracy of the spin–orbit-coupled ground state by the crystal field.⁵ In order to observe slow relaxation in such a situation, the lowest level of the ground-state manifold must have a highly anisotropic angular momentum and be well-separated in energy from excited levels. We have been pursuing the possibility that actinide ions, by virtue of their greater spin–orbit coupling and enhanced covalency relative to lanthanides, might be of utility in generating new single-molecule magnets.⁶ Herein, we show that a simple trigonal prismatic uranium(III) complex can indeed display slow magnetic relaxation.

In searching for this effect, we recognized that, as for the $4f^8$ Tb^{III} and $4f^9$ Dy^{III} ions, the $5f^3$ configuration of U^{III} can deliver an oblate single-ion anisotropy.⁷ For an axial ligand environment, strong spin–orbit coupling can then cause the spin to align preferentially along the unique molecular axis. This minimizes the crystal-field energy by reducing contacts between the equatorial f -element charge cloud and the ligand donor atom charges. Deviations from axial spin orientation would result in an increased crystal-field energy and a barrier to spin inversion. As an initial test of this hypothesis, we probed the magnetic behavior of the eightfold-symmetric complex $[\text{U}(\text{COT})_2]^-$ ($\text{COT}^{2-} = 1,3,5,7\text{-cyclooctatetraene}$) at low temperature. However, ac magnetic susceptibility measurements performed on $\text{K}[\text{U}(\text{COT})_2]$ indicated only a very small relaxation barrier, perhaps because of a lowering of symmetry caused by interactions between the K^+ cations and the complex. We therefore turned our attention to the neutral diphenylbis(pyrazolylborate) complex $\text{U}(\text{Ph}_2\text{BPz}_2)_3$ (**1**), which features the trigonal prismatic geometry depicted in Figure 1.⁸

The ac magnetic susceptibility data were collected on powder samples of **1** embedded in a frozen hexane matrix. The temperature dependence of the in-phase (χ'_M) and out-of-phase (χ''_M) ac susceptibility under zero applied dc field is shown in the top panel of Figure 2. The χ''_M signal displays frequency-dependent peaks characteristic of slow magnetic relaxation in discrete molecules. As previously observed for

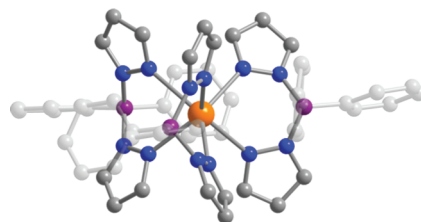


Figure 1. Structure of the trigonal prismatic complex $\text{U}(\text{Ph}_2\text{BPz}_2)_3$ (**1**).⁸ Orange, purple, gray, and blue spheres represent U, B, C, and N atoms, respectively; H atoms have been omitted for clarity. The coordination at the U^{III} center approximates D_{3h} symmetry, with U–N distances of 2.487(7)–2.568(7) Å and N–U–N angles of 73.2(2)–73.6(3) and 83.0(2)–95.1(2)°. The shortest intermolecular $\text{U}\cdots\text{U}$ distance is 10.791(2) Å.

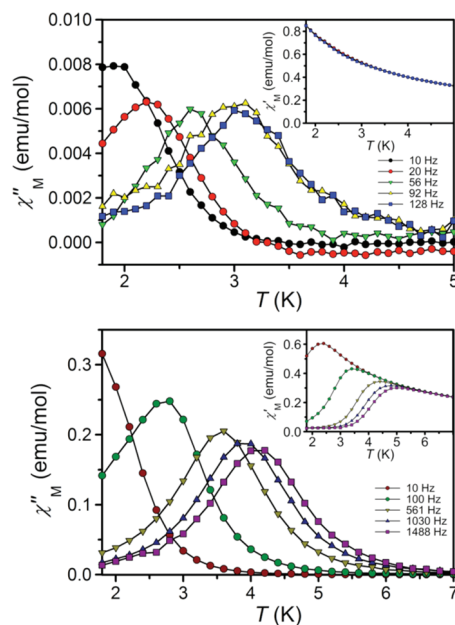


Figure 2. Temperature dependence of the in-phase (χ'_M , inset) and out-of-phase (χ''_M) components of the ac susceptibility of **1** under (top) zero and (bottom) 1000 Oe applied dc fields, collected at various ac frequencies.

lanthanide systems,^{3a,9} χ''_M represents only a small component of the total susceptibility under zero field. However, as exemplified in the bottom panel of Figure 2, application of a small dc magnetic field can change the relaxation dynamics and drastically increase the χ''_M to χ'_M ratio.

In order to obtain quantitative information regarding the spin relaxation barrier of **1**, the frequency dependence of χ'_M and χ''_M at fixed temperatures was examined. Cole–Cole plots were used to fit χ'_M and χ''_M and derive relaxation rates (see Figures S3–S9 in the Supporting Information). Figure 3 shows Arrhenius plots obtained under applied dc fields of 0, 100, and 1000 Oe. From these data, it is evident that the Arrhenius fit describes a thermally activated pathway independent of the small applied dc field. Values extracted from the linear region

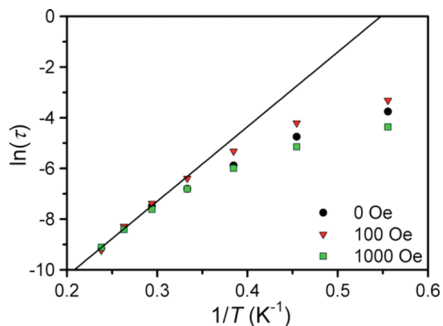


Figure 3. Arrhenius plot of **1** in the presence of applied dc fields of 0, 100, and 1000 Oe. The solid line represents an Arrhenius fit to the data in the thermally activated regime. Deviations of the data from linearity are due to quantum tunneling, as discussed in the text.

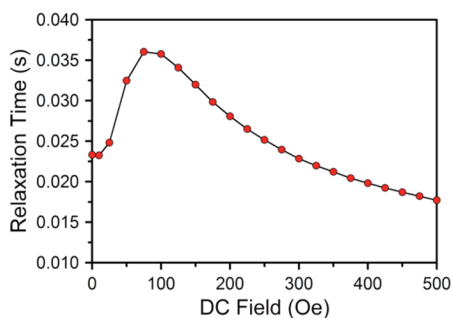


Figure 4. Dependence of the magnetic relaxation time of **1** on applied dc field strength at 1.8 K.

of the plot give an effective relaxation barrier of $U_{\text{eff}} = 20 \text{ cm}^{-1}$ and a lifetime of $\tau_0 = 1 \times 10^{-9} \text{ s}$ and are consistent with single-molecule-magnet behavior. Previous studies of LnPc₂ complexes suggest that the slow relaxation in such species occurs via an Orbach-type process, whereby phonon energy is transferred to the spin system via the spin-orbit interaction.^{3b} However, the energy-level structure for actinide-based molecules may differ considerably as a result of increased mixing of low-lying states. Further experimental and theoretical work is needed to determine the specific states constituting the thermal activation barrier in **1**.

Although the three sets of relaxation data shown in Figure 3 follow the same line at high temperatures, the temperature at which they deviate from linearity is dc-field-dependent. The deviation from linearity at low temperature can be used to describe the onset of a regime where quantum tunneling of the magnetization is the dominant process.^{1c} We were interested in further studying this aspect of the behavior of **1** since Kramers ions have been shown to display quantum tunneling between opposite orientations of the ground-state spin due to mixing of the levels by transverse components of internal magnetic fields.¹⁰ Such tunneling is maximized at zero applied magnetic field because of the near degeneracy of the levels. To test whether this occurs in **1**, variable-frequency ac susceptibility data at a number of applied dc fields in the range 0–500 Oe were collected. All of the data were acquired at 1.8 K, where the deviations from Arrhenius behavior suggest that quantum tunneling is the dominant process (see Figure 3). Hindrance of the tunneling should decrease the characteristic frequency as the frequency moves closer to the Arrhenius line. If quantum tunneling of the magnetization due to the Kramers ground state is present at 1.8 K, a significant drop should occur in the resonant frequency. Figure 4 shows a plot of the resonant frequencies at a number of applied dc fields between 0 and 500 Oe. As predicted, a

significant dip in frequency is observed, and a minimum in the tunneling rate (corresponding to a maximum in the relaxation time) is reached at an applied field between 75 and 100 Oe. This result is consistent with Figure 3, where the relaxation rate at an applied dc field of 100 Oe shows the least deviation from Arrhenius-type behavior.

The observed behavior is indicative of ground-state tunneling, yet the mechanism remains uncertain. In many systems, the tunneling can be attributed to intermolecular dipole or hyperfine interactions. To test whether the former are responsible for the tunneling, ac susceptibility experiments were performed on a frozen THF solution of **1**. These measurements revealed only a small shift in the peak locations relative to the data obtained for the solid sample (see Figure S2), which can be explained by slight differences between the solid-state and solution geometries of **1**. Thus, intermolecular interactions are unlikely to be the source of the observed tunneling. Additionally, our samples contain greater than 99% ²³⁸U (depleted uranium), which has no net nuclear spin, thus eliminating the possibility of a tunneling mechanism stemming from hyperfine interactions.

The foregoing results demonstrate that a simple uranium(III) complex with axial coordination can exhibit single-molecule-magnet behavior. It is unlikely that this result is unique, and given the large spin-orbit coupling and enhanced covalency of actinides relative to lanthanides, there is significant potential for identifying molecules with much larger relaxation barriers. Most importantly, the strategy of maximizing ligand-field contributions above and below the equatorial plane in various axial coordination geometries may provide a rational path toward this goal.

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Supporting Information Available: Complete experimental details, including additional magnetic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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