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Observation of a Secondary Slow Relaxation Process for the Field-Induced Single-Molecule Magnet $U(H_2BPz_2)_3$

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The field of single-molecule magnetism,[1] once dominated by the search for strongly coupled transition metal clusters with a high-spin, high-anisotropy ground state, has diversified as our understanding of the factors governing slow magnetic relaxation in molecules grows. One approach gaining in prominence is the study of single-ion molecular magnets, wherein magnetic anisotropy generated from the interaction between a single metal ion and its ligand field creates a strong preferential orientation of the magnetic moment. This type of molecular magnetism, which arises from a large unquenched orbital moment, was first recognized in lanthanide-based systems, including $[LnPc_2]^{n+}$ (Ln^{III} = Tb, Dy, Ho; H_2Pc = phthalocyanine; $n = -1, 0, 1$),[2] $[Ln(W_5O_{18})_2]^{9-}$ (Ln^{III} = Ho, Er), and $[Ln(\beta_2\text{-}SiW_{11}O_{39})_2]^{13-}$ (Ln^{III} = Dy, Ho, Er, Yb),[3] but has recently been extended to the trigonal pyramidal transition metal complex $[(tpa^{Mes})Fe]^-$ (H_3tpa^{Mes} = trismesityltris(pyrrolylmethyl)-amine)[4] and the trigonal prismatic actinide complex $U(Ph_2BPz_2)_3$.[5,6] Such compounds further the prospects for single-molecule magnets, potentially bringing the goals of molecule-based information storage, quantum computing, and spin-based electronics closer to reality.[7]

Additional mechanisms for magnetic relaxation can arise in single-ion molecular magnets that are not typically apparent for multinuclear clusters. In particular, the strong spin−orbit coupling and generally lower spin can facilitate phonon-based relaxation mechanisms involving only the ground state (direct relaxation) or the ground state and some real or virtual excited state (Orbach and Raman relaxation, respectively).[2b,8] The detailed characterization of such processes is of utmost importance, since a gain in knowledge may enable the magnetic relaxation times to be manipulated through simple alterations of the ligand field. To date, however, no compound has been shown to exhibit more than one well-resolved pathway for slow magnetic relaxation at a given temperature. Herein, we demonstrate that the dihydrobispyrazolylborate complex $U(H_2BPz_2)_3$ (**1**)[9] displays multiple relaxation pathways, including an extremely slow relaxation process that becomes dominant at low temperature under an applied magnetic field.

Compound **1** was crystallized from a saturated solution of hexanes and toluene. X-ray analysis of a single crystal revealed a trigonal prismatic coordination of the U^{III} center by the pyrazolate nitrogen atoms (Figure 1), similar to that observed previously for $U(Ph_2BPz_2)_3$.[10] Although the locations of the H atoms are not precisely determined, the calculated positions are in agreement with the results of a previous analysis in which the B−H stretching modes in the infrared spectrum were taken to be consistent with U···H interactions at the lateral faces of the trigonal prism.[9] Such an arrangement accounts for the increased axial elongation of the trigonal prism in the crystal structure of **1** compared with that of $U(Ph_2BPz_2)_3$.[10] By a simple electrostatic model,[5,11] this axial elongation should lead to a decreased splitting of the $2J+1$-fold degeneracy of the spin−orbit coupled ground state by the crystal field and, consequently, a smaller relaxation barrier. However, the generality of such effects are as yet poorly understood, especially for actinide complexes where this simple electrostatic model may be perturbed by covalency in the interactions with the ligands.

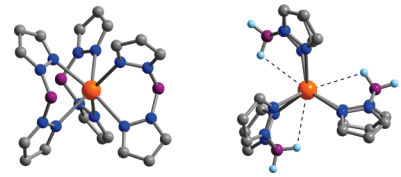

Figure 1. Side (left) and top (right) views of the crystal structure of the trigonal prismatic complex $U(H_2BPz_2)_3$ (**1**). Orange, purple, gray, and blue spheres represent U, B, C, and N atoms, respectively; H atoms are omitted for clarity except for those bound to B atoms in the depiction at the right. The molecule has approximate C_{3h} symmetry, with U−N distances of 2.4983(4)−2.5754(5) Å, calculated U···H distances of 2.8321(6)−2.9010(6) Å, and N−U−N angles of 77.192(7)°−80.208(8)° and 80.444(8)°−88.395(8)°. The shortest intermolecular U···U separation in the structure is 8.167(2) Å.

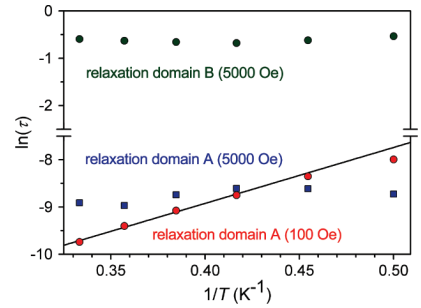

Figure 2. Arrhenius plot for **1** in the presence of applied dc fields of 100 and 5000 Oe. Relaxation domains A and B refer to the high frequency and low frequency relaxation processes, as described in the text. The solid line represents a fit to the linear range of frequency region A at 100 Oe.

To compare the spin relaxation behavior of **1** to that of $U(Ph_2BPz_2)_3$, the frequency dependence of χ'_M and χ''_M was examined at multiple fixed temperatures. Consistent with a low moment and a smaller relaxation barrier, **1** lacks the zero-field response displayed by $U(Ph_2BPz_2)_3$.[5] Under an applied dc field of greater than 30 Oe, however, a frequency dependent out-of-phase susceptibility signal is clearly observed, indicating slow magnetic relaxation. Cole−Cole plots (Figures S1−S9) were used to fit χ'_M and χ''_M in the temperature range 1.8−3.0 K at fields of 100 and 5000 Oe to characterize the magnetic relaxation in the frequency range 1−1500 Hz (hereafter referred to as relaxation domain A). From the 100 Oe data in Figure 2, the Arrhenius activation barrier to magnetic relaxation for **1** was determined to be 8 cm^{-1}, as compared to the barrier of U_{eff} = 20 cm^{-1} observed for $U(Ph_2BPz_2)_3$.[5] We note, however, that the accuracy of the value for the barrier in **1** is somewhat uncertain, since the relaxation data begin to deviate from Arrhenius behavior at lower temperatures. Additionally, the associated attempt frequency of $\tau_0 = 1.2 \times 10^{-6}$ s is large for a single-molecule magnet,[1c] suggesting that the temperature range probed may be intermediate between a high-temperature Arrhenius regime and a low-temperature regime involving relaxation directly between

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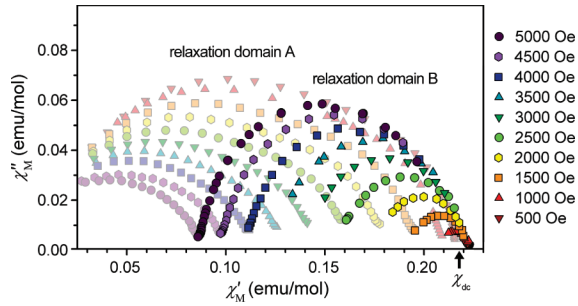

Figure 3. Cole−Cole plots showing the field dependence of multiple relaxation processes occurring in **1** at 1.8 K. Relaxation domains A and B correspond to the ac frequency ranges of 1−1500 and 0.06−1 Hz, respectively. Data in domain A are faded to facilitate visualization. The value of χ_{dc} at an applied dc field of 5000 Oe is marked with an arrow to indicate its relation to the low-frequency ac susceptibility data.

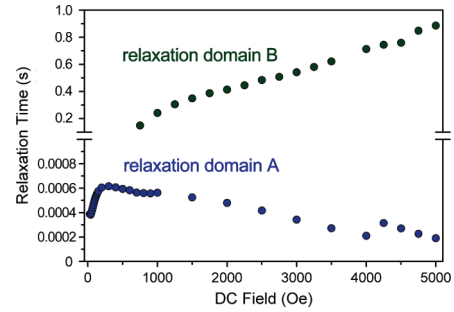

Figure 4. Field dependence of the magnetic relaxation time at 1.8 K for processes occurring in relaxation domains A and B.

opposite orientations of the magnetic ground state. Increasing the dc field from 100 to 5000 Oe eliminates any strong thermal dependence of the relaxation rate, suggesting that under a 5000 Oe field relaxation does not involve an excited state, as was evident at lower applied fields.

To further investigate the low-temperature relaxation behavior, variable-frequency ac susceptibility data were collected at 1.8 K under a wide range of applied dc fields (Figure 3). At each dc field above 500 Oe, two independent relaxation domains were observed: one at high and one at low frequency (hereafter referred to as relaxation domains A and B, respectively). Relaxation domain A roughly includes frequencies from 1 to 1500 Hz and shows a pronounced asymmetry for the Cole−Cole plot semicircles. This asymmetry suggests the presence of multiple, closely spaced relaxation processes within relaxation domain A. Owing to their proximity, relaxation times for the individual processes occurring at a given field could not be extracted from the overall curve. Instead, an average of these overlapping relaxation times was calculated by fitting the data to a distribution of relaxation processes using the generalized Debye model.[1c] Interestingly, as the dc field is increased, the asymmetry in the Cole−Cole plot disappears and a smooth semicircular arc is observed. We attribute this to the applied field eliminating one of the relaxation processes. The nature of the remaining process in relaxation domain A at 5000 Oe is unclear; however, the lack of thermal dependence (Figure 2) and prominence at higher fields suggests a direct process within the ground state Kramers doublet.[8]

Relaxation domain B, shown as unfaded symbols in Figure 3, involves extremely low frequencies (0.06−1 Hz). This process operates at the same temperatures and dc fields as those for the process in domain A; however, its relaxation time is drastically increased, such that it can be characterized by fitting a completely independent Cole−Cole semicircle. Such resolution of multiple processes at a given temperature is, to our knowledge, without precedent in molecular magnetism. The process occurs at a rate that is 3 orders of magnitude slower than that of the relaxation pathways operational in domain A and displays no asymmetry indicative of multiple overlapping processes. Figure 4 illustrates the vast difference in relaxation times, as well as the essentially linear increase in the relaxation time for the new process with an applied field. The new process displays a weak temperature dependence similar to that observed in the high field data for relaxation domain A (Figure 2), but instead of a decrease in relaxation time with increasing dc field, a dramatic and steady increase in relaxation time occurs up to 5000 Oe. This indicates a fundamental difference between the direct relaxation behavior observed in the high-field relaxation domain A data and that of the as yet unexplained low-frequency process.

The multiple relaxation processes displayed by $U(H_2BPz_2)_3$ attest to the complexity of the magnetic response in single-ion molecular magnets. Further characterization of this system will require measurements at lower frequencies and temperatures, as well as mapping out the low-lying electronic states to correlate our data with the available relaxation pathways. Analogous experiments performed on other single-ion molecular magnets will reveal whether the behavior observed here is common and might account for the discrepancies between crystal field energy splitting calculations and fits to relaxation barriers.[2b] Most critically, the results demonstrate that simply correlating temperature-scanned peak location to relaxation time may conceal a wealth of information about the magnetic relaxation properties of the system, which only a detailed investigation of frequency, dc field, and temperature space can elucidate. Ultimately, obtaining a comprehensive picture of the relaxation pathway manifold may prove essential to efforts aimed at slowing the relaxation dynamics within single-molecule magnets to facilitate their potential applications.

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Supporting Information Available: Additional data and complete experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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