Slow magnetic relaxation in homoleptic trispyrazolylborate complexes of neodymium(III) and uranium(III)†

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Lanthanide- and actinide-based single-molecule magnets are rapidly gaining prominence due to the unique properties of f-orbitals, yet no direct comparison of slow magnetic relaxation of an isostructural and valence isoelectronic lanthanide and actinide complex exists. We present the dynamic magnetic properties of two f-element single-molecule magnets, NdTp3 and UTp3 (Tp− = trispyrazolylborate), demonstrating that, although neither complex displays the full anisotropy barrier predicted from its electronic structure, relaxation is slower in the uranium congener. Magnetic dilution studies performed with NdTp3 reveal that, while intermolecular interactions partially account for the faster relaxation dynamics, they are not uniquely responsible.

The recent abundance of lanthanide1 and actinide2 single-molecule magnets demonstrates the advantages that f-elements can bring to the synthesis of new molecular magnetic materials. Namely, unprecedented single-ion anisotropy and high-moment ground states offer the promise of achieving longer magnetic relaxation times by manipulating the ligand field environment around a small cluster or mononuclear complex. The enhanced magnetic coupling and larger crystal field splittings that are possible for the actinides3 make them an intriguing target for future single-molecule magnet research. However, to date, the magnetic relaxation properties of the lanthanides have eclipsed those of the actinides in benchmark properties of anisotropy barrier and hysteresis temperature. This discrepancy can to some extent be explained by the concerted effort devoted to the lanthanides, yet no direct comparison has been made between an isostructural, valence isoelectronic lanthanide and actinide compound. Here, we present the dynamic magnetic properties of the 4f3 complex NdTp3 (Tp− = trispyrazolylborate), and its isostructural 5f3 congener, UTp3. In an attempt to rationalize the experimentally observed behavior in terms of previously reported electronic structure data,4 magnetic dilution experiments were performed on the NdTp3 complex, revealing a significant increase in the relaxation time with dilution, yet very little effect on the temperature dependence of the relaxation time.

The compound NdTp3 was prepared by reaction of NdCl3 with KTp in water, as previously described,5 while UTp3 was synthesized using a modification of a published procedure,4b involving the reaction of UI3 with KTp in THF. Previous structural characterization revealed crystallographic three-fold symmetry with a tri-capped trigonal prismatic first coordination sphere (see Fig. 1). Studies of the low temperature absorption spectra for both compounds have determined the extent to which the lowest energy spin–orbit coupled 4I9/2 state is split by the ligand field environment into its component MJ levels.5 The ordering of these MJ levels indicates that while the splitting of the 4I9/2 state is similar for NdTp3 and UTp3, the energy spacing between levels is more than twice as large for UTp3. Of particular interest to single-molecule magnetism is the energy difference between the ground MJ level and the first-excited MJ level, as this gap indicates the lowest energy two-state transition by which magnetic relaxation can theoretically occur. This spin-lattice energy transfer, known as an Orbach process, defines the Arrhenius temperature dependence of the magnetic relaxation for mononuclear f-element single-molecule magnets. As with the total splitting, the lowest energy Orbach transition for UTp3 is

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Fig. 1 Left: Crystal structure of NdTp3. Orange, blue, purple, and gray spheres represent Nd, N, C, and B atoms, respectively; H atoms omitted for clarity. Right: Splitting of 4I9/2 states of UTp3 and NdTp3 by the crystal field. Labels represent the projections of total angular momentum (MJ) for each Kramers doublet. Ground MJ states for UTp3 and NdTp3 are set to 0 cm−1.
over twice as large as that of NdTP$_3$ (267 vs. 115 cm$^{-1}$, respectively).

To determine whether the experimental magnetic relaxation matches that predicted by the electronic structure, variable frequency ac magnetic susceptibility experiments were performed. Both NdTP$_3$ and UTp$_3$ display signatures of slow magnetic relaxation under an applied dc field of 100 Oe (see Fig. 2 and S2 and Tables S1–S2†). The magnetic relaxation of UTp$_3$ is an order of magnitude slower than that of NdTP$_3$, in agreement with the electronic structure prediction; however, the Arrhenius plots for both compounds are consistent with anisotropy barriers that are far lower than those suggested by the electronic structure ($U_{\text{eff}} = 2.84(7)$ and $3.81(8)$ cm$^{-1}$ for NdTP$_3$ and UTp$_3$, respectively). This discrepancy between the low-lying electronic structure and the observed relaxation behavior is common for f-element single-molecule magnets and can result from intermolecular dipolar interactions, nuclear coupling, and mixing of low-lying excited states.$^{1a,2,6}$ Further corroborating the lack of an Orbach mechanism for relaxation are the large $\tau_0$ values of $4.2(2) \times 10^{-5}$ and $7.0(4) \times 10^{-5}$ s for NdTP$_3$ and UTp$_3$, respectively. These values are several orders of magnitude larger than expected for an Orbach mechanism, and have a much weaker temperature dependence. Such factors indicate that higher temperatures (and thus higher frequencies) would be required to observe Orbach behavior (see Fig. 3 and S3†).

It has been shown that in many cases, intermolecular interactions can have a strong effect on the magnetic relaxation of single-molecule magnets, especially in mononuclear and f-element systems. To study these effects, NdTP$_3$ was incorporated into a LaTP$_3$ matrix to increase the average distance between paramagnetic centers and weaken intermolecular effects. An undiluted NdTP$_3$ sample was compared to samples diluted to 59, 15, and 3.8 mol% NdTP$_3$ (see Table S1 and Fig. S4–S6†). A plot of relaxation time vs. concentration of NdTP$_3$ reveals that increasing the separation between Nd$^{3+}$ ions slows the magnetic relaxation by over an order of magnitude (see Fig. 3, lower). However, dilution does not significantly affect the temperature dependence of the relaxation behavior. Arrhenius plots for each dilution show an increase of only 0.9(1) cm$^{-1}$ in the anisotropy barrier, affording a barrier that is still far lower than the 115 cm$^{-1}$ expected from the electronic structure. This indicates that either the extent of the magnetic dilution was not great enough to force relaxation by an Orbach process, or other factors are responsible for the observed deviation. In the axial threefold symmetry of NdTP$_3$, the excited $M_J = \pm 7/2$ levels belong to the same irreducible representation as the ground $M_J = \pm 5/2$ levels, meaning that mixing could be leading to the fast relaxation.$^4$

Conclusions

With these results we expand the range of single-molecule magnets to include neodymium and provide the first direct comparison between an isostructural and valence iso-electronic lanthanide and actinide single-molecule magnet. Although the relaxation barriers are modest compared to many compounds, these data provide experimental evidence that the stronger crystal field interactions of the actinides may give rise to an advantage
over lanthanides in the construction of single-molecule magnets that operate at higher temperatures.

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Notes and references


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