

Slow magnetic relaxation in homoleptic trispyrazolylborate complexes of neodymium(III) and uranium(III)[†]Jeffrey D. Rinehart^{a,b} and Jeffrey R. Long^{*b}

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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 ⁴I_{9/2} state is split by the ligand field environment into its component *M_J* levels.⁴ The ordering of these *M_J* levels indicates that while the splitting of the ⁴I_{9/2} 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 *M_J* level and the first-excited *M_J* 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

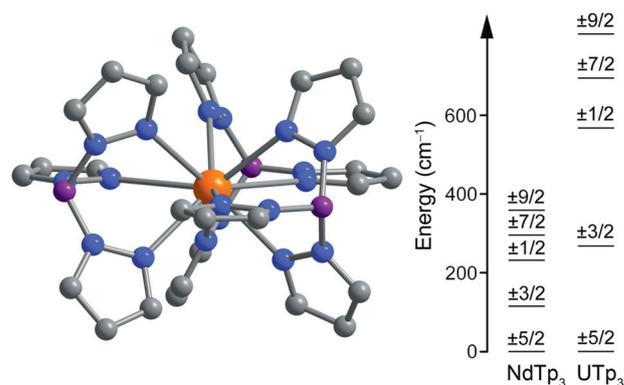


Fig. 1 Left: Crystal structure of NdTp₃. Orange, blue, purple, and gray spheres represent Nd, N, C, and B atoms, respectively; H atoms omitted for clarity. Right: Splitting of ⁴I_{9/2} states of UTp₃ and NdTp₃ by the crystal field. Labels represent the projections of total angular momentum (*M_J*) for each Kramers doublet. Ground *M_J* states for UTp₃ and NdTp₃ are set to 0 cm⁻¹.

^aDepartment of Chemistry, University of Washington, WA 98195, USA. E-mail: jdr44@uw.edu; Tel: +1 (206) 616-8754

^bDepartment of Chemistry, University of California, Berkeley, CA 94720, USA. E-mail: jrlong@berkeley.edu; Fax: +1 (510) 642-8369; Tel: +1 (510) 642-0860

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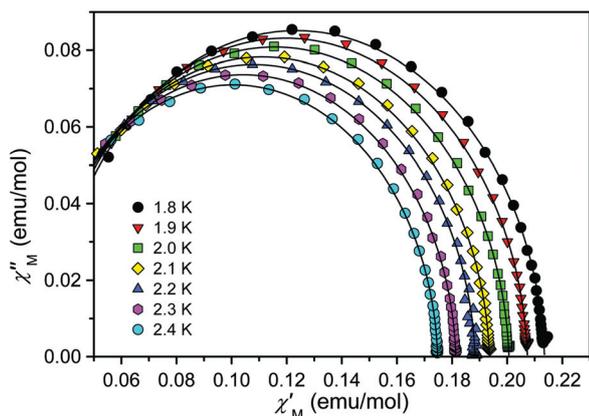


Fig. 2 Cole–Cole (Argand) plots for ac susceptibility data collected on undiluted NdTp₃ at 100 Oe and varying temperatures. Experimental data points are represented by symbols with the black line representing a fit to a generalized Debye equation.

over twice as large as that of NdTp₃ (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 NdTp₃ and UTP₃ 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 UTP₃ is an order of magnitude slower than that of NdTp₃, 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 NdTp₃ and UTP₃, 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,j,2f,6} Further corroborating the lack of an Orbach mechanism for relaxation are the large τ_0 values of $4.2(2) \times 10^{-5}$ and $7.0(4) \times 10^{-5}$ s for NdTp₃ and UTP₃, 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, NdTp₃ was incorporated into a LaTp₃ matrix to increase the average distance between paramagnetic centers and weaken intermolecular effects. An undiluted NdTp₃ sample was compared to samples diluted to 59, 15, and 3.8 mol% NdTp₃ (see Table S1 and Fig. S4–S6†). A plot of relaxation time vs. concentration of NdTp₃ reveals that increasing the separation between Nd³⁺ 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

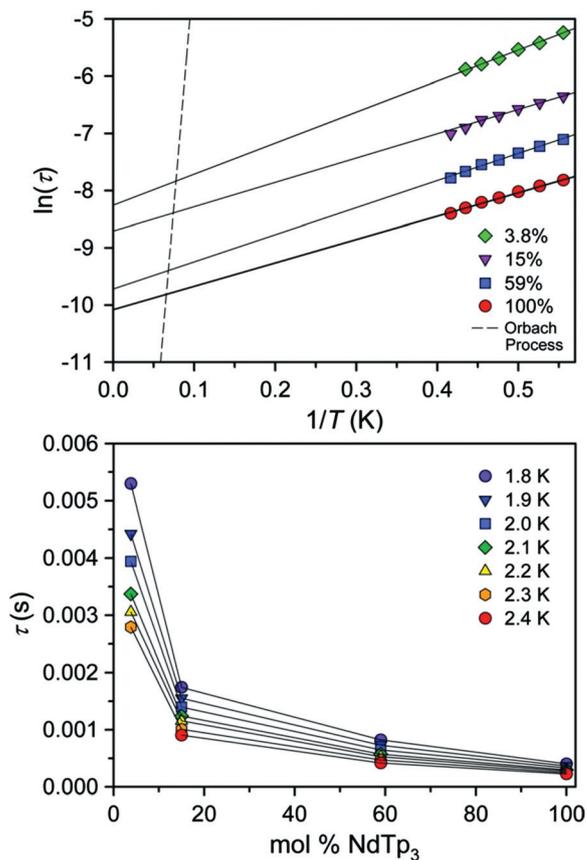


Fig. 3 Upper: Plot of inverse temperature vs. the natural log of the magnetic relaxation time at various molar percentages of NdTp₃ in a LaTp₃ matrix. Solid black lines represent Arrhenius fits with parameters as follows: (100%, $U_{\text{eff}} = 2.84(7)$ cm⁻¹; $\tau_0 = 4.2(2) \times 10^{-5}$ s; 59%, $U_{\text{eff}} = 3.3(1)$ cm⁻¹; $\tau_0 = 6.0(5) \times 10^{-5}$ s; 15%, $U_{\text{eff}} = 3.0(1)$ cm⁻¹; $\tau_0 = 1.7(2) \times 10^{-4}$ s; 3.8%, $U_{\text{eff}} = 3.8(1)$ cm⁻¹; $\tau_0 = 2.6(2) \times 10^{-4}$ s). The dashed line represents theoretical Arrhenius behavior ($U_{\text{eff}} = 119$ cm⁻¹; $\tau_0 = 10^{-9}$ s) predicted by the electronic structure.^{4a} Lower: Plot of molar percentage of NdTp₃ in a LaTp₃ matrix vs. the magnetic relaxation time at various temperatures.

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 NdTp₃, 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 isoelectronic 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

- (a) N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara and Y. Kaizu, *J. Phys. Chem. B*, 2004, **108**, 11265; (b) N. Ishikawa, Y. Mizuno, S. Takamatsu, T. Ishikawa and S.-Y. Koshihara, *Inorg. Chem.*, 2008, **47**, 10217; (c) P.-H. Lin, T. J. Burchell, L. Unger, L. F. Chibotaru, W. Wernsdorfer and M. Murugesu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9489; (d) M. A. AlDamen, S. Cardona-Serra, J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, C. Martí-Gastaldo, F. Luis and O. Montero, *Inorg. Chem.*, 2009, **48**, 3467; (e) Y.-N. Guo, G.-F. Xu, P. Gamez, L. Zhao, S.-Y. Lin, R. Deng, J. Tang and H.-J. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 8538; (f) I. J. Hewitt, J. Tang, N. T. Madhu, C. E. Anson, Y. Lan, J. Luzon, M. Etienne, R. Sessoli and A. K. Powell, *Angew. Chem., Int. Ed.*, 2010, **49**, 6352; (g) M. Gonidec, F. Luis, À. Vilchez, J. Esquena, D. B. Amabilino and J. Veciana, *Angew. Chem., Int. Ed.*, 2010, **49**, 1623; (h) F. Pointillart, K. Bernot, R. Sessoli and D. Gatteschi, *Inorg. Chem.*, 2010, **49**, 4355; (i) S.-D. Jiang, B.-W. Wang, H.-L. Sun, Z.-M. Wang and S. Gao, *J. Am. Chem. Soc.*, 2011, **133**, 4730; (j) J. Long, F. Habib, P.-H. Lin, I. Korobkov, G. Enright, L. Ungur, W. Wernsdorfer, L. F. Chibotaru and M. Murugesu, *J. Am. Chem. Soc.*, 2011, **133**, 5319; (k) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nat. Chem.*, 2011, **3**, 538; (l) A. Watanabe, A. Yamashita, M. Nakano, T. Yamamura and T. Kajiwara, *Chem.-Eur. J.*, 2011, **17**, 7428; (m) M. Gonidec, R. Biagi, V. Corradini, F. Moro, V. De Renzi, U. del Pennino, D. Summa, L. Muccioli, C. Zannoni, D. B. Amabilino and J. Veciana, *J. Am. Chem. Soc.*, 2011, **133**, 6603; (n) H. L. C. Feltham, R. Clérac, A. K. Powell and S. Brooker, *Inorg. Chem.*, 2011, **50**, 4232; (o) R. J. Blagg, C. A. Muryn, E. J. L. McInnes, F. Tuna and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2011, **50**, 6530.
- (a) J. D. Rinehart and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 12558; (b) J. D. Rinehart, K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7572; (c) N. Magnani, E. Colineau, R. Eloiardi, J.-C. Griveau, R. Caciuffo, S. M. Cornet, I. May, C. A. Sharrad, D. Collison and R. E. P. Winpenny, *Phys. Rev. Lett.*, 2010, **104**, 197202; (d) N. Magnani, C. Apostolidis, A. Morgenstern, E. Colineau, J.-C. Griveau, H. Bolvin, O. Walter and R. Caciuffo, *Angew. Chem., Int. Ed.*, 2011, **50**, 1696; (e) D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2011, **3**, 454; (f) K. R. Meihaus, J. D. Rinehart and J. R. Long, *Inorg. Chem.*, 2011, **50**, 8484.
- (a) J. D. Rinehart, T. D. Harris, S. A. Kozimor, B. M. Bartlett and J. R. Long, *Inorg. Chem.*, 2009, **48**, 3382; (b) B. S. Newell, A. K. Rappé and M. P. Shores, *Inorg. Chem.*, 2010, **49**, 1595.
- (a) H. Reddmann, C. Apostolidis, O. Walter and H.-D. Amberger, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1405; (b) C. Apostolidis, A. Morgenstern, J. Rebizant, B. Kanellakopoulos, O. Walter, B. Powietzka, M. Karbowiak, H. Reddmann and H.-D. Amberger, *Z. Anorg. Allg. Chem.*, 2010, **636**, 201.
- C. Apostolidis, J. Rebizant, B. Kanellakopoulos, R. von Ammon, E. Dornberger, J. Mlaller, B. Powietzka and B. Nuber, *Polyhedron*, 1997, **16**, 1057.
- (a) P.-H. Lin, T. J. Burchell, R. Clérac and M. Murugesu, *Angew. Chem., Int. Ed.*, 2008, **47**, 8848; (b) S.-D. Jiang, B.-W. Wang, G. Su, Z.-M. Wang and S. Gao, *Angew. Chem., Int. Ed.*, 2010, **49**, 7448; (c) F. Luis, M. J. Martínez-Pérez, O. Montero, E. Coronado, S. Cardona-Serra, C. Martí-Gastaldo, J. M. Clemente-Juan, J. Sesé, D. Drung and T. Schurig, *Phys. Rev. B: Condens. Matter*, 2010, **82**, 060403; (d) R. A. Layfield, J. J. W. McDouall, S. A. Sulway, F. Tuna, D. Collison and R. E. P. Winpenny, *Chem.-Eur. J.*, 2010, **16**, 4442; (e) P.-E. Car, M. Perfetti, M. Mannini, A. Favre, A. Caneschi and R. Sessoli, *Chem. Commun.*, 2011, **47**, 3751.