Angewandte
Communications

DOI: 10.1002/anie.201208015

Single-Molecule Magnets

The Inherent Single-Molecule Magnet Character of Trivalent Uranium**

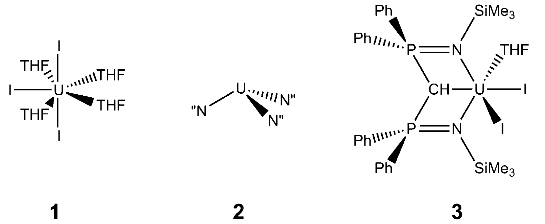
Fabrizio Moro, David P. Mills, Stephen T. Liddle, and Joris van Slageren**

Single-molecule magnets (SMMs) are molecules that exhibit slow relaxation of their magnetization of purely molecular origin.[1] This is because SMMs possess high-spin ground states in which spin–orbit coupling results in zero-field splitting of the $(2S+1)$-fold degenerate ground multiplet, which in turn creates a thermal barrier to relaxation of the magnetization that gives rise to magnetic bistability. SMMs form part of a larger family of molecular nanomagnets which are the subject of intense research because of their potential applications in fields as diverse as molecule-based information storage,[1] quantum information processing,[2] spintronics,[3] and magnetocaloric refrigeration.[4]

SMMs are often based on transition-metal clusters, but significant attention has recently focused on complexes of single and multiple lanthanoid ions, because the crystal-field splitting of the lowest Russell–Saunders multiplet engenders large magnetic anisotropies.[5–11] These anisotropies are responsible for high relaxation barriers and therefore slow magnetic relaxation. However, well isolated high-spin ground states are difficult to achieve within polynuclear lanthanoid SMMs because the valence 4f orbitals have limited radial extension and are usually energetically incompatible with ligand orbitals. These inherent 4f orbital properties give predominantly ionic interactions and results in weak magnetic exchange coupling with neighboring spin centers, with very few exceptions.[7,12]

In principle, actinoids, and in particular uranium, possess properties that render these ions ideal candidates from which to construct SMMs. This is because, compared to the lanthanoids, uranium exhibits enhanced crystal field splitting,[13,14] as well as increased covalency, the latter enabling significant spin couplings in polynuclear systems,[15] and therefore both stronger magnetic exchange and anisotropies can be envisaged. This premise was realized recently with reports of several closely related single-ion pyrazolylborate uranium(III) complexes which were shown to display SMM behavior.[14,16–20] In addition, two neptunium complexes were shown to display slow relaxation of the magnetization.[15,21]

The fact that all uranium(III) SMMs reported to date are closely related to each other raises the question as to how sensitive SMM behavior in trivalent uranium is to the composition of the coordination sphere and its symmetry. SMM behavior in all published examples is much more pronounced in an external field than in zero field, which suggests that quantum tunneling of the magnetization plays a significant role in shortening the relaxation times. However, in principle, low-symmetry crystal field components cannot induce tunneling of the magnetization, because uranium(III) is a Kramers half-integer angular momentum ion. Also the nuclear spin $I=0$ of ^{238}U cannot induce tunneling of the magnetization. The answer to the question of what causes efficient quantum tunneling will have serious implications for the design strategy of novel and improved SMMs based on uranium(III). Therefore, we have investigated in detail the magnetic properties of three simple, but structurally and electronically very diverse, uranium(III) complexes (Scheme 1, Figures S1–3). $[UI_3(THF)_4]$ (**1**)[22,23] bears three weak field iodide ligands, and has approximate C_{2v} symmetry (THF = tetrahydrofuran); UN''_3 [**2**, $N''=N(SiMe_3)_2$][24,25] has approximate axial (C_{3v}) symmetry; and, finally, $[U(BIPM^{TMS})(I)_2(THF)]$ [**3**, $BIPM^{TMS}=CH(PPh_2NSiMe_3)_2$][26] has a heavily distorted C_s symmetry, and is better described as possessing no symmetry at all (C_1). Herein, we report that all complexes **1**–**3** show slow relaxation of the magnetization compatible with SMM behavior, irrespective of the point group symmetry and the nature of the ligands. Importantly, this suggests that trivalent uranium possesses inherent SMM character, in the sense that its complexes show slow relaxation of the magnetization for a much wider range of ligands than previously reported. This observation renders trivalent ura-



N″ = N(SiMe$_3$)$_2$

Scheme 1. Structures of the three investigated complexes.

---

[*] Dr. F. Moro,[+] Dr. D. P. Mills,[+] Dr. S. T. Liddle
School of Chemistry, University of Nottingham
University Park, Nottingham, NG7 2RD (UK)
E-mail: stephen.liddle@nottingham.ac.uk

Prof. Dr. J. van Slageren
Institut für Physikalische Chemie, Universität Stuttgart
Pfaffenwaldring 55, 70569 Stuttgart (Germany)
E-mail: slageren@ipc.uni-stuttgart.de

[+] Current address:
School of Chemistry, The University of Manchester
Oxford Road, Manchester M13 9PL (UK)

[**] We thank the Royal Society, the Engineering and Physical Sciences Research Council, the Deutsche Forschungsgemeinschaft, the European Research Council, the European Union (grant number IEF 253980 to F.M.), the University of Nottingham, COST Action CM1006, and the UK National Nuclear Laboratory for generously funding this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208015.

nium highly promising for the development of novel SMMs with improved energy barriers.

The room-temperature values for the product of the magnetic susceptibility and the temperature (χT, Figure 1 and Figure S4) for immobilized samples of **1**, **2**, and **3** at ambient temperature are similar at $\chi T = 1.03$, 0.91, and $1.14\ \mathrm{cm^3\,K\,mol^{-1}}$, respectively, which are all within the range typically found for uranium(III) compounds (0.78–$1.7\ \mathrm{cm^3\,K\,mol^{-1}}$).[26,27] With decreasing temperature, χT decreases monotonically and reaches values of $\chi T = 0.62$, 0.27, and $0.50\ \mathrm{cm^3\,K\,mol^{-1}}$, at 1.8 K for **1**–**3**, respectively. This decrease in χT is attributed to gradual thermal depopulation of the crystal field levels of the $^4I_{9/2}$ ground multiplet, and is typical for uranium(III) complexes.[16,17,19,26,28] The magnetization as a function of field (Figure S5) displays no significant magnetic hysteresis, and does not reach saturation at the highest employed field (50 kOe). The expected saturation magnetization depends closely on the crystal field splitting and the exact nature of the ground Kramers doublet, but the values of magnetization values of 0.7–1.1 μ_B at the highest employed fields agree with those previously observed for uranium(III) complexes.[18]

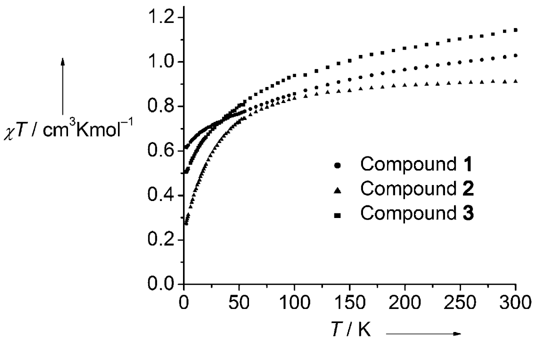


Figure 1. Susceptibility–temperature product χT as a function of temperature recorded on immobilized powder samples of **1** (●), **2** (▲), and **3** (■) in an applied field of 1 kOe for $1.8 < T < 50$ K and 10 kOe for $50 < T < 300$ K.

Alternating current (ac) susceptibility measurements in zero external field show no sign of out-of-phase components of the dynamic susceptibility (Figure S6). However, in small direct current (dc) fields, clear out-of-phase signals (χ'') are observed for all three complexes (Figure 2 and Figures S7–11), concurrent with decreases in the in-phase components. Between $H_{dc} = 0.5$–3 kOe, the dynamic susceptibility is essentially dc-field-independent. The ac susceptibility at $H_{dc} = 2$ kOe is strongly temperature dependent (Figure 2), and clear, frequency-dependent maxima in χ'' are observed, which strongly suggests slow magnetization dynamics because of thermal relaxation over an energy barrier as in single-molecule magnets. The energy barriers $\Delta E/k_B$ were determined from fits to the Arrhenius law $\tau = \tau_0 \exp(\Delta E/k_B T)$ to be 18.6 ± 0.7, 29.0 ± 1.6, and 23.4 ± 0.8 K, for **1**, **2**, and **3**, respectively (Table 1). In these fits (Figure S11–13) no deviation from linearity, indicative of quantum tunneling, was observed. The obtained values are comparable to those obtained for other uranium(III) SMMs. The τ_0 prefactors for **1** and **3** are typical for single-molecule magnets,[1] whereas for **2** it appears to be of the order of 10^{-11} s, which is much shorter than typically found for SMMs, which can hint to intermolecular interactions playing a role. Measurement of the frequency dependence of χ' and χ'' indicate the presence of two distinct relaxation processes for **1** and **2**,[17] but only one for **3** (Figure 3 and Figures S14 and S15). The minor component is due to a slowly relaxing species, whereas the majority component relaxes faster (Table S2). The parameter α of the Cole-Cole formula, which describes the distribution in relaxation times, are in the range $\alpha = 0.04$–0.34 as previously observed for other uranium(III) SMMs.[18]

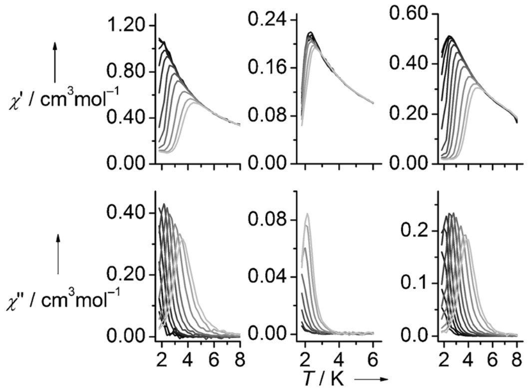


Figure 2. In-phase (top) and out-of phase (bottom) components of the ac susceptibility measured in an applied dc field of 2 kOe and an ac field of 3.5 Oe for powder samples of (left-to-right) **1**, **2**, and **3** at ac frequencies between 1 and 1488 Hz (left to right).

Table 1: Magnetic relaxation parameters for powder and frozen solution samples of **1**–**3** (at 2 kOe), and literature values for other uranium(III) complexes.

Compound	$\Delta E/k_B$ [K]	τ_0 [s]	Reference
1	18.6 ± 0.7	$(6.4 \pm 1.8) \times 10^{-7}$	this work
2	31 ± 3	10^{-11} [b]	this work
3	23.4 ± 0.8	$(2.9 \pm 0.8) \times 10^{-7}$	this work
1 frozen solution	11.5 ± 1.3	$(6 \pm 6) \times 10^{-6}$	this work
2 frozen solution	13.9 ± 0.6	$(1.5 \pm 0.4) \times 10^{-6}$	this work
3 frozen solution	12.2 ± 0.9	$(2.8 \pm 1.0) \times 10^{-6}$	this work
$[U(Ph_2BPz_2)_3]$	29 (at 0 T)[a]	1×10^{-9}	[16]
$[U(H_2BPz_2)_3]$	12 (at 0.01 T)	1.2×10^{-6}	[17,18]
$[U(TpMe_2)_2(bipy)]I$	26.2 (at 0.05 T)	1.4×10^{-7}	[19]
$[UTp_3]$	5.5 (at 0.01 T)	7.0×10^{-5}	[14]
$[U(TpMe_2)_2I]$	30.3	1.8×10^{-7}	[20]

[a] Only a small part of the sample showed an out-of-phase signal in zero external field. [b] Rough estimate, the fit error is larger than the parameter value.

Multiple relaxation processes in f element SMMs have been found previously in a number of cases.[18] Often, these processes are related to intermolecular interactions, for example, quantum tunneling of the magnetization induced by intermolecular magnetic-dipolar interactions. To assess the role of intermolecular interactions, frozen THF solutions of **1**–**3** were investigated using ac susceptibility measurements (Figures 3b and 4). The SMM behavior (in an applied dc magnetic field) is clearly retained in all complexes. The effective energy barriers appear to be somewhat reduced

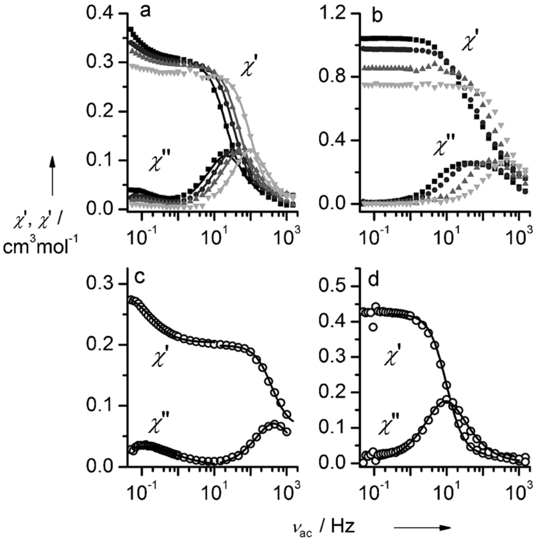


Figure 3. a) In-phase (χ') and out-of phase (χ'') components of the ac susceptibility measured in an applied dc field of 2 kOe and an ac field of 3.5 Oe for a powder sample of **1** at ac frequencies between 0.05 and 1500 Hz at 1.8 (■), 2.0 (●), 2.2 (▲), and 2.4 K (▼). b) The same procedure for a THF frozen solution sample of **1**. c,d) The same procedure for powder samples of **2** (c) and **3** (d).

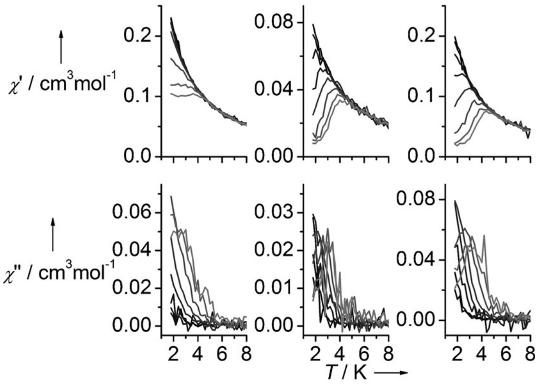


Figure 4. In-phase (top) and out-of phase (bottom) components of the ac susceptibility measured in an applied dc field of 2000 Oe and an ac field of 3.5 Oe for frozen solution samples of (left-to-right) **1**, **2**, and **3** at ac frequencies between 1 and 1488 Hz.

($\Delta E/k_B$ from 11–14 K, Table 1, Figure S16) compared to the solid state. The Arrhenius prefactors τ_0 are all of the order of 10^{-6} s, which is typical for SMMs. Hence, SMM behavior is conclusively proven also for **2**. For **1**, the slower relaxation process is not present in the solution measurements (Figure 3b) proving its intermolecular nature. Interestingly, neither nonzero out-of-phase components of the susceptibility nor magnetic hysteresis were observed in solution in zero external field, where intermolecular magnetic-dipolar interactions should be largely eliminated.

The origin of the apparent fast tunneling is unclear, as all known phenomena that can lead to tunneling should not play a role for diluted frozen solution samples of uranium complexes. At the highest concentration used (47 mM), the average distance between molecules is about 4.1 nm, resulting in a maximum dipolar field at a neighboring molecule of 0.18 mT (of the order of the earth's magnetic field), which is not expected to cause efficient quantum tunneling of the magnetization.

In summary, we have described three structurally unrelated uranium(III) coordination complexes, which all show SMM properties. Hence, the important conclusion from this work is that the SMM behavior of uranium(III) is not closely linked to specific symmetries or ligand surroundings, which greatly increases the potential of this ion for the development of improved SMMs. A fascinating but unsolved question is the origin of efficient tunneling in zero external field, which drastically reduces the magnetization blocking temperature at a given frequency. A promising route to prevent quantum tunneling is the development of strongly coupled polynuclear species,[7] in the direction of which we and others recently have made some progress.[15,26]

Experimental Section

Syntheses: Compounds **1**,[22,23] **2**,[24,25] and **3**[26] were prepared as described previously. Identity and purity were checked by X-ray diffractometry and elemental analysis.

Superconducting quantum interference device (SQUID) magnetometric measurements: All measurements were carried out on a Quantum Design MPMS XL5 SQUID magnetometer, equipped with reciprocating sample option (RSO) and alternating current (ac) measurement capabilities. Samples were either free powders, immobilized powders in hexane or eicosane, or THF solutions. Free powders were inserted into 5 mm NMR tubes fitted with a gas adaptor in a glovebox and subsequently flame sealed under vacuum. For measurements with immobilized powder samples, the powders were inserted into 5 mm NMR tubes and suspended in hexane (m.p. 178 K) for compounds **1** (52.0 mg of **1** and 79.7 mg hexane) and **3** (54.8 mg of **3** and 57.2 hexane) or in melted eicosane (m.p. 310 K, sample dissolves in hexane) in the case of **2** (22.3 mg of **2** and 19.9 mg eicosane) before flame sealing. The solutions were prepared in degassed anhydrous tetrahydrofuran with concentrations of 33.9 mM (5.3 mg) of **1**, 46.5 mM (5.7 mg) of **2**, and 25.8 mM (5.5 mg) of **3**. All temperature-dependent measurements were performed descending in temperature, because initial cooling of the sample to the lowest temperature led to samples that were far from thermal equilibrium with the cryostat. Ac measurements were performed with 3.5 Oe applied ac fields.

Received: October 4, 2012
Revised: January 17, 2013

Keywords: magnetic properties · single-molecule magnets · slow relaxation · uranium

---

[1] D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, **2006**.
[2] J. van Slageren, *Top. Curr. Chem.* **2012**, *321*, 199.
[3] L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179.
[4] M. Evangelisti, E. K. Brechin, *Dalton Trans.* **2010**, *39*, 4672.
[5] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694.
[6] R. J. Blagg, C. A. Muryn, E. J. L. McInnes, F. Tuna, R. E. P. Winpenny, *Angew. Chem.* **2011**, *123*, 6660; *Angew. Chem. Int. Ed.* **2011**, *50*, 6530.
[7] J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *Nat. Chem.* **2011**, *3*, 538.

[8] R. Sessoli, A. K. Powell, *Coord. Chem. Rev.* **2009**, *253*, 2328.
[9] G. J. Chen, Y. N. Guo, J. L. Tian, J. K. Tang, W. Gu, X. Liu, S. P. Yan, P. Cheng, D. Z. Liao, *Chem. Eur. J.* **2012**, *18*, 2484.
[10] A. Watanabe, A. Yamashita, M. Nakano, T. Yamamura, T. Kajiwara, *Chem. Eur. J.* **2011**, *17*, 7428.
[11] F. Habib, J. Long, P. H. Lin, I. Korobkov, L. Ungur, W. Wernsdorfer, L. F. Chibotaru, M. Murugesu, *Chem. Sci.* **2012**, *3*, 2158.
[12] J. D. Rinehart, M. Fang, W. J. Evans, J. R. Long, *J. Am. Chem. Soc.* **2011**, *133*, 14236.
[13] J. D. Rinehart, J. R. Long, *Chem. Sci.* **2011**, *2*, 2078.
[14] J. D. Rinehart, J. R. Long, *Dalton Trans.* **2012**, *41*, 13572.
[15] N. Magnani, E. Colineau, R. Eloirdi, J. C. Griveau, R. Caciuffo, S. M. Cornet, I. May, C. A. Sharrad, D. Collison, R. E. P. Winpenny, *Phys. Rev. Lett.* **2010**, *104*, 197202.
[16] J. D. Rinehart, J. R. Long, *J. Am. Chem. Soc.* **2009**, *131*, 12558.
[17] J. D. Rinehart, K. R. Meihaus, J. R. Long, *J. Am. Chem. Soc.* **2010**, *132*, 7572.
[18] K. R. Meihaus, J. D. Rinehart, J. R. Long, *Inorg. Chem.* **2011**, *50*, 8484.
[19] M. A. Antunes, L. C. J. Pereira, I. C. Santos, M. Mazzanti, J. Marçalo, M. Almeida, *Inorg. Chem.* **2011**, *50*, 9915.
[20] J. T. Coutinho, M. A. Antunes, L. C. J. Pereira, H. Bolvin, J. Marcalo, M. Mazzanti, M. Almeida, *Dalton Trans.* **2012**, *41*, 13568.
[21] N. Magnani, C. Apostolidis, A. Morgenstern, E. Colineau, J. C. Griveau, H. Bolvin, O. Walter, R. Caciuffo, *Angew. Chem.* **2011**, *123*, 1734; *Angew. Chem. Int. Ed.* **2011**, *50*, 1696.
[22] D. L. Clark, A. P. Sattelberger, S. G. Bott, R. N. Vrtis, *Inorg. Chem.* **1989**, *28*, 1771.
[23] L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin, B. D. Zwick, *Inorg. Chem.* **1994**, *33*, 2248.
[24] R. A. Andersen, *Inorg. Chem.* **1979**, *18*, 1507.
[25] J. L. Stewart, R. A. Andersen, *Polyhedron* **1998**, *17*, 953.
[26] D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* **2011**, *3*, 454.
[27] N. M. Edelstein, G. H. Lander in *The Chemistry of the Actinide and Transactinide Elements* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger), Springer, Dordrecht, **2006**.
[28] G. Liu, J. V. Beitz in *The Chemistry of the Actinide and Transactinide Elements* (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger), Springer, Dordrecht, **2006**.