COMMUNICATION

A plutonium-based single-molecule magnet†‡

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The magnetic properties of the 5f^5 [tris-(tri-1-pyrazolylborato)–plutonium(III)] complex have been investigated by ac susceptibility measurements, showing it to be the first plutonium single-molecule magnet; its magnetic relaxation slows down with decreasing temperature through a thermally activated mechanism followed by a quantum tunnelling regime below 5 K.

Actinide (An) based single-molecule magnets (SMMs) are attracting increasing interest, because the presence of unquenched orbital degrees of freedom and the possibility to stabilize different oxidation states provide the ideal compromise between the chemical versatility of 3d-block metals and the strong single-ion anisotropy of rare earth elements.[1] Here, we show that the 5f^5 complex PuTp$_3$ (Tp$^-$ = [κ^3-N-HB(pyrazol-1-yl)$_3$]$^-$) exhibits a slowing down of the magnetic relaxation at low-temperature, and is therefore the first Pu-based SMM to be reported. At about 5 K, the temperature dependence of the characteristic relaxation time, obtained from ac magnetic susceptibility measurements, shows a cross-over between a tunnelling and a thermally activated Orbach relaxation process, with an effective anisotropy barrier about 5 times larger than in the isostructural 5f^3 complex UTp$_3$.[2] The addition of Pu complexes to the families of SMMs is particularly interesting, as the possibility of stabilizing five different oxidation states for one

element introduces an unparalleled flexibility in a synthesis-by-design approach.

After the first report of slow magnetic relaxation in a uranium(III) complex,[3] SMM behavior has been observed in several monometallic uranium and neptunium coordination compounds.[4] In these complexes, as in rare-earth ones,[5] the ligand field splitting of the orbital moment states of An ions, in the presence of strong spin–orbit interaction, generates high energy barriers against magnetic relaxation. On the other hand, superexchange interactions of strength comparable to that observed in transition metal clusters have been measured in the few polymetallic uranium and neptunium complexes investigated so far,[6] suggesting the feasibility of An-based SMMs carrying a large magnetic moment. The PuTp$_3$ complex used in the present work was prepared by the same procedure published for the synthesis of the UTp$_3$ compound[7] after purification in the single-crystalline form (see ESI‡). It crystallizes in the $P6_3/m$ space group, with two molecules of C_{3h} symmetry per unit cell (a = 11.7036(5) Å, c = 13.5561(8) Å), and is therefore isostructural to the PrTp$_3$ complex.[8] The Pu atom is nine-coordinated to N atoms of the three Tp ligands. One N atom of each of the three Tp ligands and the Pu ion are almost coplanar, with a Pu–N distance of 2.761(2) Å. The other six N atoms are at a distance of 2.588(2) Å, in a tricapped trigonal prismatic geometry, corresponding to an effective D_{3h} point group symmetry at the Pu(III) site (Fig. 1).

Temperature-dependent magnetic susceptibility measurements have been performed using a Quantum Design Superconducting Quantum Interference Device (SQUID) in an applied field of 1 tesla. The results, shown as an inset in Fig. 2, are well reproduced by our calculations§ assuming that the ligand-field parameters[9] have the same value as those determined for the isostructural UTp$_3$ complex.[7] The Pu^{3+} $^6H_{5/2}$ lowest energy multiplet is split by the ligand-field potential and the ground state is an almost pure $|J_z = \pm 5/2\rangle$ doublet, with a small (about 1%) $|J_z = \mp 7/2\rangle$ component arising from the high-energy $^6H_{7/2}$ manifold admixed to the ground state. The first excited state (a practically pure $|J_z = \pm 3/2\rangle$ doublet) is located at about 332 cm^{-1} (477 K). This energy gap is expected to determine the barrier against magnetic relaxation through thermally activated processes.

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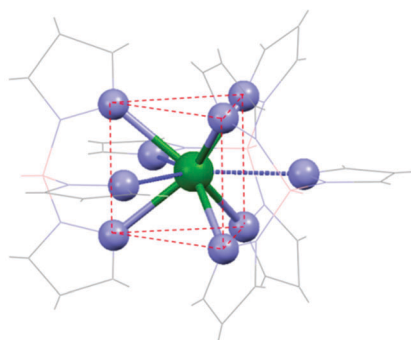*E-mail: nicola.magnani@ec.europa.eu, roberto.caciuffo@ec.europa.eu*

Fig. 1 Molecular structure of PuTp₃, highlighting the tri-capped trigonal prismatic first coordination sphere of the plutonium(III) ion (large sphere). The nine smaller spheres represent the nitrogen atoms coordinated to Pu. The trispyrazolylborate ligands are shown as wireframes.
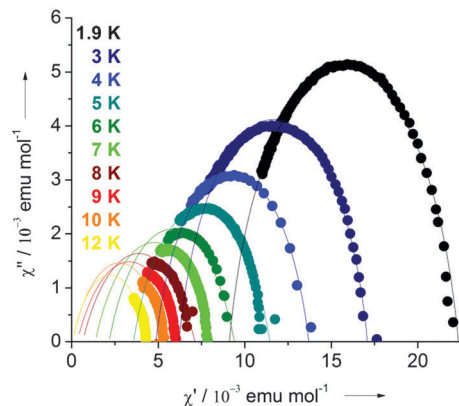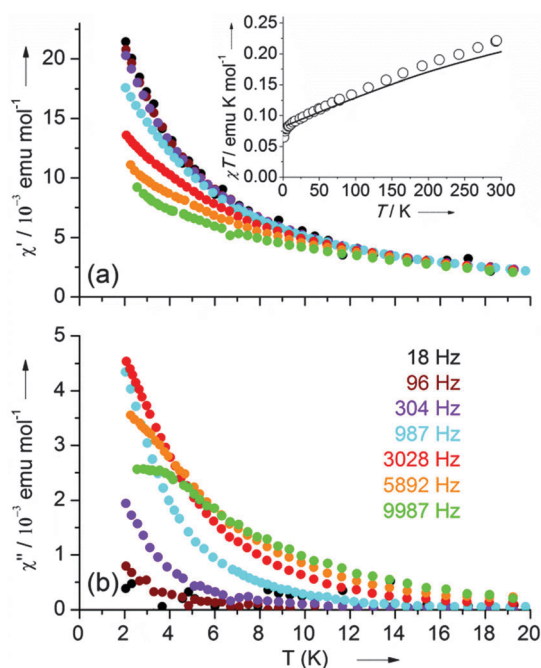

Fig. 2 Temperature dependence of the real (a) and imaginary (b) components of the ac magnetic susceptibility measured in a static magnetic field of 100 Oe, while warming after zero-field cooling to 2 K. The driving ac magnetic field had an amplitude of 10 Oe and oscillation frequencies as indicated in the legend. The inset shows the temperature dependence of the static magnetic susceptibility obtained by SQUID measurements, compared with calculations based on a ligand-field model (solid line).

The magnetization dynamics has been probed by ac magnetic susceptibility measurements, carried out using a Quantum Design PPMS-14 device, spanning the frequency range $f = 10–10^4$ Hz and affording a base temperature of 2 K. The temperature variation of the real (χ') and imaginary (χ'') components of the ac susceptibility has been measured in a static magnetic field of 100 Oe, in order to have the same experimental conditions as in the study of UTp₃.[2] The results obtained reveal a slowing down of the magnetization dynamics with decreasing temperature, although the accessible time-scale is not wide enough to allow observation of a distinct

Fig. 3 Cole–Cole plots for the ac magnetic susceptibility of PuTp₃ measured at different temperatures in a static magnetic field of 100 Oe, with a driving field amplitude of 10 Oe and oscillation frequency varying in the range 10–10⁴ Hz. Solid lines are fits to a modified Debye relaxation model.‡

maximum in χ'' (Fig. 2). However, the temperature dependence of the magnetization relaxation time can be determined from variable frequency measurements at constant temperature, shown in Fig. 3 as Cole–Cole plots. The solid lines in this figure represent the fit of the experimental data to a modified Debye relaxation model providing the average relaxation time τ_c and the width of its distribution function at the measuring temperature T (see ESI‡). The temperature dependence of the relaxation time, τ_c (T), is shown in Fig. 4. Above ~ 7 K, the observed behavior can be fitted by an Arrhenius relation, $\tau_c = \tau_0 \exp(\Delta/k_B T)$, corresponding to a thermally activated regime. The fit provides a pre-exponential factor $\tau_0 = 2.9 \times 10^{-7}$ s and a barrier to relaxation $\Delta = 18.3$ cm^{-1} (26.3 K). However, below ~ 5 K, a tendency towards a temperature-independent relaxation time of roughly 10^{-4} s reveals a cross-over to a tunnelling regime.[10] The efficiency of this fast direct relaxation process was also proved by performing the same frequency-dependent susceptibility measurements at constant temperature with different values of the applied dc field (Fig. S2);‡ for $H_{dc} = 2$ kOe the peaks in the $\chi''(\nu)$ curves shift towards lower frequencies as a result of the longer relaxation time, whereas for $H_{dc} = 0$ the out-of-phase signal becomes very weak and no evident maxima are present in the studied frequency range. This observation can also explain why no clear hysteresis was observed in the magnetic data even at the lowest attainable temperature of our instrument (1.8 K), a situation common to several f-electron SMMs.[4,5] Tunnelling effects on the magnetic relaxation, which reduce the magnetization blocking temperature at a given frequency, have also been reported for the Np(IV) neptunocene complex.[4f] In that case, the origin of tunnelling has been attributed to avoided crossings between hyperfine levels in the coupled electronic-nuclear spectra. For PuTp₃, with a doubly-degenerate electronic ground state weakly coupled to a spin-1/2 ^{239}Pu nucleus, this mechanism is rather unlikely. Quantum tunnelling of the magnetization could be induced by intermolecular magnetic-dipolar interactions, as suggested for several trivalent uranium complexes, where hyperfine interaction is not active as the largely predominant isotope ^{238}U has zero nuclear spin.[4e]
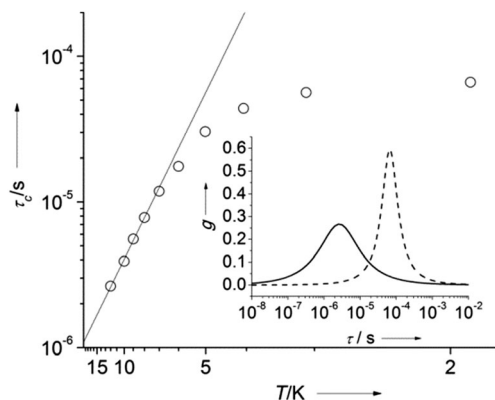
Fig. 4 Log-reciprocal temperature dependence of the magnetization relaxation time τ_c obtained at zero static field. Open circles are derived from variable frequency ac susceptibility isotherms. The straight line is a fit to the Arrhenius relation, giving a thermal energy barrier for the relaxation of $\Delta = 18.3$ cm^{-1}, and a pre-exponential factor $\tau_0 = 2.9 \times 10^{-7}$ s. The inset shows the distribution of relaxation times at 1.9 (dashed line, $\alpha = 0.166$) and 12 K (solid line, $\alpha = 0.341$), characteristic of the two regimes.

However, this mechanism also seems unlikely for PuTp$_3$ since dilution in a nonmagnetic matrix of the isostructural complex NdTp$_3$ (increasing intermolecular distances) has negligible effects on the magnetic relaxation barrier.[2] Thus, the origin of efficient tunneling in An-based SMMs is unclear, and further investigations have to be done in order to gain deeper insight.

In PuTp$_3$, the obtained value of Δ is almost 20 times smaller than the estimated electronic energy gap; a similar discrepancy has been found for many f-electron complexes, in particular for NdTp$_3$ and UTp$_3$,[2] suggesting a relaxation mechanism more complex than for transition metal clusters. In the case of UTp$_3$, the reported value of Δ (3.81 cm^{-1}) is almost one hundred times smaller than the electronic energy gap (267 cm^{-1}); however, as the time window spanned for the latter complex was narrower than in the present study, there is the possibility that the determination of its energy barrier was performed under conditions where quantum tunnelling was still present, as also suggested by the longer prefactor τ_0 (7.0×10^{-5} s).

In conclusion, we have shown slow relaxation of the magnetization in a trivalent plutonium complex, thus expanding the range of elements which exhibit single-molecule-magnet behaviour towards the frontier of the Periodic Table. The possibility to stabilize plutonium in five oxidation states could drastically expand the variety of 5f-block SMMs with different electronic configurations, which will open the way to systematic studies and provide a much needed tool to quantitatively understand the complex relaxation mechanisms in f-electron systems. Finally, we remark that the present Communication is the first reported work on a structurally characterized trivalent plutonium homo-scorpionate complex; a systematic investigation of the structural, electronic and magnetic properties of the whole

AnTp$_3$ family is expected to shed some light on fundamental features such as bonding and covalency, and will be the subject of our future research.

Notes and references

§ The ligand-field Hamiltonian for the plutonium site in PuTp$_3$ (D_{3h} point symmetry) can be written as $H_{LF} = B_0^{(2)}C_0^{(2)} + B_0^{(4)}C_0^{(4)} + B_0^{(6)}C_0^{(6)} + B_6^{(6)}(C_{+6}^{(6)} + C_{-6}^{(6)})$ in terms of the Wybourne operators $C_q^{(k)}$.[9a] The values of the four non-zero $B_q^{(k)}$ ligand-field parameters were assumed to be the same as those determined for the isostructural UTp$_3$ complex,[7] whereas the free-ion Hamiltonian for the 5f^5 electronic configuration of Pu(III) was considered equal to that obtained for PuCl$_3$.[9b] The matrix representing the full f-electron configuration was diagonalized numerically[9c] and the temperature dependence of the magnetic susceptibility was calculated using the obtained eigenvalues and eigenvectors. A good agreement was already obtained with the starting parameters, and in order to improve the fit an orbital reduction factor $k = 0.98$ was assumed (compared to $k = 0.99$ for UTp$_3$).

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