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Single-ion magnet behaviour in [U(Tp^{Me2})$_2$I]†

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**[U(Tp^{Me2})$_2$I] exhibits at low temperatures single molecule magnet (SMM) behaviour comparable to its bipyridine derivative and related single ion U(III) complexes recently reported as SMMs. The trend of variation of the energy barrier for the magnetic relaxation in these compounds is well reproduced by quantum chemistry calculations.**

Molecular systems displaying slow relaxation of magnetization at low temperatures and behaving as magnets have been a central topic of interest in contemporary molecular magnetism due to their potential use in high-density information storage, quantum computing and spin-based electronics.[1,2] An important class of materials with such behaviour which have been classified as single-molecule magnets (SMMs) are clusters of magnetic ions with a negative axial magnetic anisotropy on a high-spin ground state, resulting in an energy barrier for reversal of the magnetization.[3] The factors that govern the relaxation process, either through thermal activation or quantum tunnelling across this barrier, remain a central topic of research in this field.[4,5]

More recently slow relaxation of magnetisation has been found to occur not only in clusters of magnetic ions but also in single ions with magnetic anisotropy, namely lanthanides, the so-called single ion magnets (SIMs).[6] In this context, owing to unique characteristics, which can give rise to larger magnetic spin–orbit coupling and enhanced magnetic anisotropy,[7,8] actinide-based molecules appear to be interesting SMM candidates and the study of their magnetic properties is expected to contribute new insights into the field. Nevertheless, only a very few actinide-based SMMs have been reported so far. The first studies were reported by Long and co-workers who observed slow relaxation effects in two mononuclear uranium(III) complexes, [U(Ph$_2$Bpz$_2$)$_3$][9] and [U(H$_2$Bpz$_2$)$_3$][10] (pz = pyrazolyl). In 2011, studies performed on a neptunium-based compound,

[Np(COT)$_2$] (COT = C$_8$H$_8$$^{2-}$),[11] and on a diuranium(III) system featuring an arene bridge[12] also evidenced SMM behaviour and showed clear hysteresis at low temperatures, being the first actinide complexes displaying SMM behaviour. Following our interest in the chemistry of U(III), and motivated by the outstanding challenges in this research field, we have recently reported the synthesis and magnetic properties of the cationic uranium(III) compound [U(Tp^{Me2})$_2$(bipy)]I (**2**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate).[13] The frequency dependence of the out-of-phase AC susceptibility clearly revealed that this compound behaves as an SMM.

At this point it is clearly important to study other uranium based compounds with SIM behaviour in order to establish magnetic–structural correlations. In this paper we describe a single ion magnetic behaviour of the precursor of **2**, [U(Tp^{Me2})$_2$I] (**1**), a compound first prepared and characterized by Takats and co-workers,[14] in comparison with **2** for which we provide additional characterisation data at lower temperatures (down to 0.3 K).
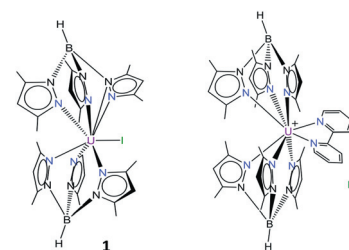
The temperature dependence of the magnetization of complex **1** measured as a polycrystalline powder imbedded in hexane and sealed in a quartz tube (4 mm inner diameter) using a 6.5 T S700X SQUID magnetometer (Cryogenic Ltd) under a field of 1 kG presents paramagnetic behavior with the χT product dropping monotonically on cooling, from 1.13 emu K mol^{-1} at 300 K to 0.5 emu K mol^{-1} at 1.8 K as shown in Fig. 1.

These values correspond to an effective magnetic moment at 300 K of 3.01 μ_B, slightly lower than the calculated moment for a free U(III) ion but still within the range observed for U(III) coordination compounds. Below 5 K there is a minimum in the χT curve with a small upturn. This behaviour is comparable to that of **2** when the magnetization was measured down to 300 mK using a ^{3}He insert (inset of Fig. 1), where a minimum followed by a maximum was found at temperatures close to the blocking temperature, below which the slowing of relaxation

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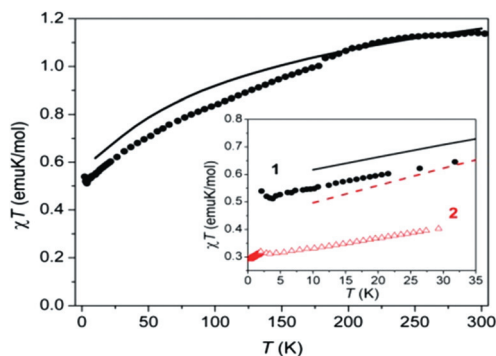
Fig. 1 Temperature dependence of the χT product for **1** at 0.05 T. The inset shows low temperature χT for compounds **1** (circles) and **2** (triangles). The lines are calculated curves.
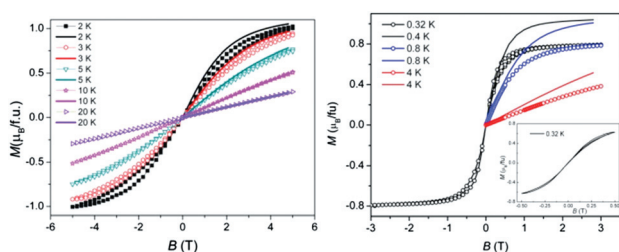

Fig. 2 Magnetic field dependence of the magnetization for **1** (left) and **2** (right) at several temperatures indicated. The solid lines represent the calculated $M(B)$ curves at the corresponding temperatures.

becomes evident probably related with the slow relaxation process.

The magnetic field dependences of magnetization of **1** for several temperatures, measured up to 5 T using a *MagLab 2000* system (Oxford Inst.), are shown in Fig. 2 (left). Below 5 K a clear opening of the magnetic hysteresis is observed as one moves away from zero field, increasing as the temperature is decreasing, which suggests magnet behaviour.

The absence of coercivity can be due to efficient quantum tunnelling of the magnetization occurring at zero field, probably caused by low symmetry components of the crystal field, as was already observed in other uranium compounds with SMM behavior[12] and in some mononuclear lanthanide magnets.[15] Previous measurements for **2** down to 1.5 K did not show any hysteresis and therefore measurements below 2 K using a ^{3}He insert adapted to the SQUID were done, which however did not allow field sweeping rates larger than about 20 Oe s^{-1} while with the *MagLab* system above 1.5 K data were obtained with a larger sweeping rate of 90 Oe s^{-1}. In **2** at 0.32 K, a behaviour with an opening of the hysteresis curve, but no coercivity, is observed (Fig. 2 right) similarly to **1** at 5 K. As can be observed these data are in good agreement with the theoretical modelization of $M(B)$ curves (see details below), taking into account some possible weighting error in compound **2**.

This behaviour occurs in SMMs when the quantum tunnelling of the magnetization at zero field becomes dominant (*i.e.* faster than the thermal-activated relaxation).[16] At the lowest temperature, with a characteristic time of 5.3 ms, although some hysteresis is already observed, it seems that the quantum regime is still

dominant which explains the absence of the typical step on the $M(H)$ curves considering the field sweeping rate.

The field dependence of magnetization M plotted *versus* B/T at different temperatures (Fig. SI1†) shows for both compounds curves not superimposed, suggesting a magnetic anisotropy that appears to be larger in **2**, where a sharper and linear increase of M takes place at low fields. This anisotropy is certainly related to the different coordination environment of the uranium ion.

Clear evidence for slow relaxation of the magnetisation is also given by the AC magnetic susceptibility at low temperatures, which was measured in the range 30–10 000 Hz. In a fashion similar to what was observed in **2**, and in other U(III) complexes U(Ph$_2$BPz$_2$)$_3$[9] and U(H$_2$BPz$_2$)$_3$[10] classified as SMMs, under zero magnetic field the real component of the AC susceptibility, χ', was found to be almost frequency independent as expected for a paramagnetic system, while the imaginary component, χ'', presents a local maximum which shifts to higher temperatures as frequency increases (Fig. 3(a) and (b)). The application of small DC magnetic fields drastically changed the relaxation dynamics with the occurrence of peaks in both χ' and χ'' components, that show strong frequency and temperature dependence, clearly denoting the "freezing" of the spins by an anisotropy barrier (Fig. 3(c) and (d)).

The magnetization relaxation rate was probed in the temperature range 1.8 to 6 K by measuring χ' and χ'' at fixed temperatures while the frequency, ω, of the AC field was varied from 10 Hz to 10 kHz. These data provided Cole–Cole plots (χ'' vs. χ'
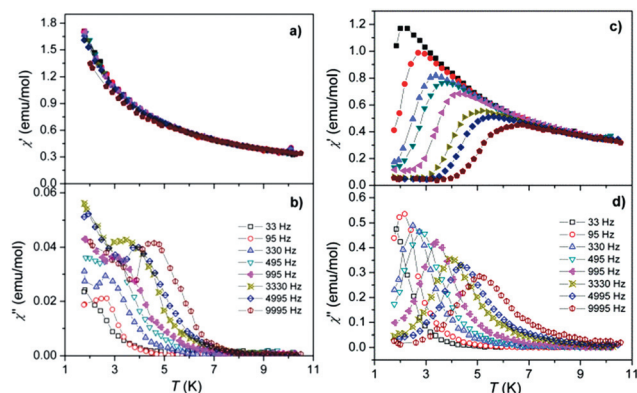

Fig. 3 Temperature dependence of the real (χ') and imaginary (χ'') components of the AC susceptibility of **1** under zero ((a) and (b)) and 0.05 T ((c) and (d)) DC fields, collected at different AC frequencies.
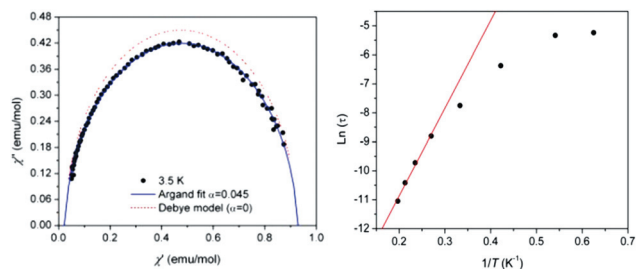

Fig. 4 (Left) Cole–Cole plot for complex **1** at 3.5 K and 0.05 T. (Right) Plot of $\ln(\tau)$ vs. T^{-1} with a fitting to the Arrhenius law.

Table 1 Experimental effective energy barriers, E_{eff}, and blocking temperatures, T_b, and calculated (CASPT2) energy gaps, ΔE, and g-values for mononuclear U compounds

Compound	E_{eff}/cm^{-1}	T_b/K	$\Delta E/cm^{-1}$	g_1	g_2	g_3	θ	J	L	S
1	21.0	3.5	146	4.9	1.1	0.5	77	4.3	5.4	1.1
2	18.2	4.5	138	3.4	1.3	0.7	65	4.2	5.5	1.3
$[U(H_2Bpz_2)_3]$[10]	8.0	~3	28	5.1	1.0	0.4	56	4.2	5.4	1.1

plots) for those different temperatures that were fitted with the generalized Debye model,[17] $\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1 + i\omega\tau)^{1-\alpha}$, where χ_S and χ_T are the adiabatic and isothermal susceptibilities, τ is the average magnetization relaxation time, and α is a parameter ranging from 0 to 1 which quantifies the width of the relaxation time distribution ($\alpha = 0$ corresponds to the ideal Debye model, with a single relaxation time).[17] Fig. 4 (left) shows the Cole–Cole plot obtained at 3.5 K under a field of 0.05 T for which the smallest fitted α value, of 0.045, was obtained (solid line) giving the parameters of $\chi_S = 0.0253$ emu mol^{-1}, $\chi_T = 0.927$ emu mol^{-1}, and $\tau = 1.5 \times 10^{-4}$ s. The small α values obtained along with the nearly semi-circular and symmetrical shape of the Cole–Cole plots are consistent with only one single magnetization relaxation process and a narrow distribution in this relaxation time,[17] in a situation comparable to that previously found for **2**.[13]

This single relaxation time τ extracted from AC susceptibility has an activated temperature dependence (Fig. 4 right) that follows an Arrhenius law, $\tau(T) = \tau_0 \exp(E_{eff}/k_B T)$ in the higher temperature range (solid line), with a pre-exponential factor $\tau_0 = 1.8 \times 10^{-7}$ s which is consistent with slow magnetic relaxation and of the same order of magnitude of **2**[13] and other well-known d-[18] and f-element SMMs.[19] The effective relaxation barrier obtained is $E_{eff} = 30.3$ K (21.0 cm^{-1}), slightly higher than in complex **2**. In the lower temperature range a clear deviation from this activated regime is noticed, likely due to the approaching of a quantum tunnelling regime expected to occur at lower temperatures, as already observed in other U compounds.[9,10,13]

Compound **1** is now the fourth uranium compound where SMM behaviour has been clearly identified, and since all these examples are based on similar pyrazolate ligands the possibility to establish magneto-structural correlations based on theoretical calculations which can guide the design of compounds with larger magnetic relaxation barriers becomes relevant. Therefore the excited states of the complexes have been calculated with the SO-CASPT2 method[20] using the MOLCAS76 suite of programs[21] as well as the g-factors.[22] Expectation values of J were calculated by diagonalizing the matrix of the $\vec{L} + \vec{S}$ operator in the 10 first states (since there is a large energy gap between the 10th and 11th states). In Table 1 the experimental values of the activation energy barriers for the magnetic relaxation and blocking temperatures are listed, with the results of these calculations, including the energy gap ΔE between the ground state and the first excited state, the eigen values for the g-tensor in the ground state and θ the angle between the principal magnetic axes of the ground state and the first excited state.

As can be seen from the calculated values of J, we are quite close to the free ion term $^4I_{9/2}$ and although the theoretical calculations significantly overestimate the experimental energy barrier, the trend of relative variation in different compounds is well reproduced by the calculations. In this respect it is worth referring that dilution experiments in Dy^{III} and U^{III} complexes showed that the energy barrier is sensitive to the separation of the metallic centres.[23] However this is not expected to be significant in these comparisons since U···U shortest distances are similar for all three compounds (9.074 Å,[14] 9.455 Å,[13] and 8.167 Å[10] for **1**, **2**, and $[U(H_2Bpz_2)_3]$ respectively). From the energy levels calculated under this approach it was also possible to model the temperature and field dependence of magnetisation, which as shown in Fig. 1 and 2 are in very good agreement with experimental values.

Conclusions

In summary, $[U(Tp^{Me2})_2I]$ is a compound that exhibits SMM behaviour. It is so far the fourth example of a mononuclear uranium complex based on similar ligands with magnet behaviour, enabling a comparison of the energy barriers for the magnetic relaxation with different ligand field environments. The experimental values of energy barriers and magnetisation are in good agreement with quantum chemistry ligand field theoretical predictions at the CASPT2 level. These calculations are therefore expected to be a useful guide in the future for the design of new SMM compounds with enhanced relaxation energy barriers.

Acknowledgements

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