Supporting Information

for

Single-Ion Magnet behaviour in $[U(Tp^{Me2})_2I]$

by

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EXPERIMENTAL

General Preparative Procedures. All manipulations were carried out using vacuum line techniques and a purified nitrogen-filled glove box. THF and *n*-hexane were pre-dried using 4 Å molecular sieves, freshly distilled from sodium-benzophenone under an atmosphere of N_2 and degassed with freeze pump-thaw cycles. Benzene-d_6 was pre-dried over Na and distilled from sodium-benzophenone under an atmosphere of Ar. ^{1}H NMR spectra were recorded at 296 K on a Varian INOVA-300 spectrometer operating at 300 MHz and referenced internally to the residual proton solvent resonances relative to tetramethylsilane (benzene-d_6, δ 7.16 ppm). CHN elemental analyses were performed in-house using an EA110 CE Instruments automatic analyzer.

Synthesis of [U(Tp^{Me2})$_2$I] (1). Compound **1** was prepared according to the method previously reported by Takats and coworkers [1] and crystallized by slow evaporation of a THF solution. The crystals were washing with *n*-hexane and vacuum dried. The formulation and purity of the compound were checked by ^{1}H NMR spectroscopy and CHN elemental analysis. Data are in agreement with those previously reported. Found: C, 37.5; H, 5.0; N, 17.7. $C_{30}H_{44}B_2IN_{12}U$ requires C, 37.7; H, 4.6; N, 17.5 %. δ_H (300.1 MHz; C_6D_6; Me$_4$Si; 296 K): 7.40 (6H, s, 4-*H* of Tp^{Me2}), 0.27 (18H, s, C*H$_3$* of Tp^{Me2}), −11.66 (18H, s, C*H$_3$* of Tp^{Me2}).

Magnetic measurements. Magnetic measurements were performed in polycrystalline powder samples imbedded in hexane and sealed in a 4 mm inner diameter quartz tube. Measurements of **1** were taken using a 6.5 T S700X SQUID magnetometer (Cryogenic Ltd.) in the temperature range 1.8-300 K under several applied magnetic fields from 100 G to 1 kG. For compound **2**, a ^{3}He insert adapted to the SQUID magnetometer was used to measure below 2 K both temperature dependent and field dependent magnetization curves at fixed temperatures. Above 1.8 K field dependent magnetization up to 5 T at different temperatures and AC susceptibility measurements in **1** were taken using a MagLab 2000 system (Oxford Instruments). The paramagnetic data was obtained after a correction for the core diamagnetism estimated, using Pascal's constants, as χ_D= -753.6×10^{-6} and -811.4×10^{-6} emu/mol for **1** and **2** respectively. Temperature dependence of AC magnetic susceptibility was measured using a 5 Oe oscillating field in the 30-10000 Hz frequency

range under zero and 500 Oe static fields. Additional isothermal AC susceptibility measurements, $\chi_{AC} = f(\omega)$, were taken in the 10-10000 Hz frequency range, within 1.7 and 6 K, the temperature range in which the relaxation time reaches a maximum. Cole-Cole plots were fitted using a generalized Debye model [2],

$$\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1+i\omega\tau)^{1-\alpha}$$

which describes both real and imaginary components of AC susceptibility, χ' and χ'' in terms of frequency, isothermal susceptibility (χ_T), adiabatic susceptibility (χ_S), relaxation time (τ), and a variable representing the distribution of relaxation times (α).
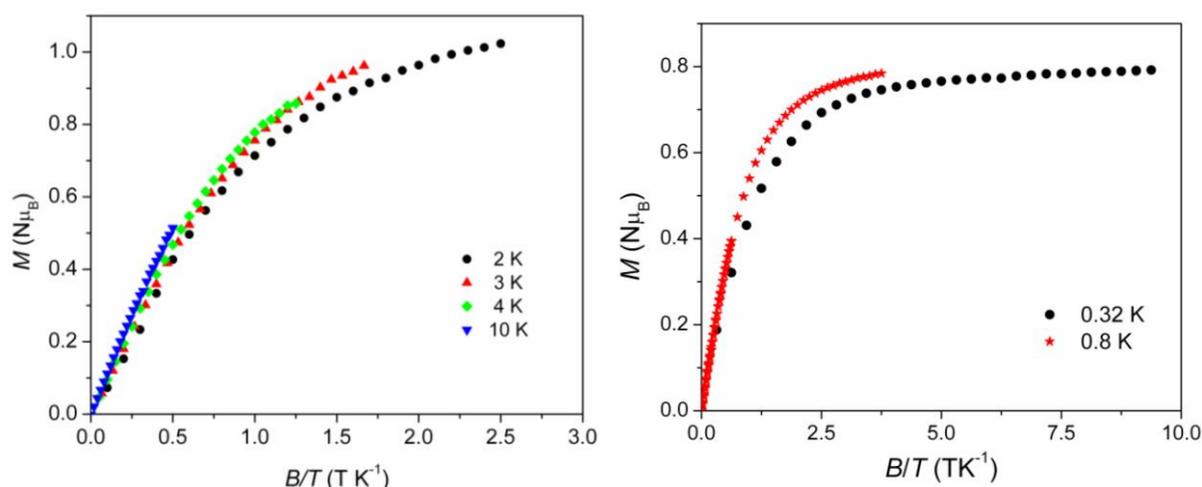
Figure SI1. Reduced magnetisation plots (M vs. B/T) for **1** (left) and **2** (right).

Quantum Chemistry Calculations. The excited states of the complexes have been calculated with the SO-CASPT2 method using the MOLCAS76 suite of programs [3]. A ANO-RCC basis sets of TZP and DZ qualities were used for the Uranium and the other atoms respectively. The active space consists of 3 electrons in the 7 5f orbitals. First, a CASSCF (Complete Active Space Self Consistent Field) calculation was performed [4], then dynamical correlation was included by the CASPT2 (Complete Active Space Perturbation Theory at the 2nd order) method [5] and finally, the spin-orbit coupling was evaluated by a state interaction between the CASPT2 wave functions by the RASSI (Restricted Active Space

State Interaction) method [6]. g factors were calculated according to reference [7]. Expectation values of J are 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).

References:

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Table S1. Experimental effective energy barriers, E_{eff}, and blocking temperatures, T_b, and calculated (CASPT2) energy gaps, ΔE, g-values, angles between the principal magnetic axes of the ground state and the first excited state, θ and expectation values of J, L, S, 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
$[U(H_2Bpz_2)_3]$ *	8.	~3	28	5.1	1.0	0.4	56	4.2	5.4	1.1

* J. D. Rinehart, K. R. Meihaus, and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7572.