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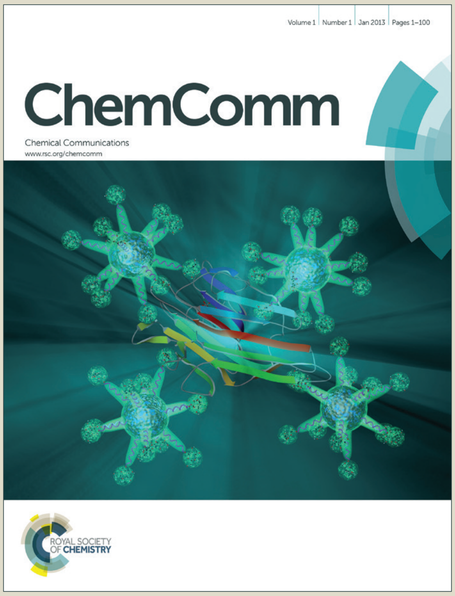

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Zero-field slow magnetic relaxation in a uranium(III) complex with a radical ligand.

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$[U(Tp^{Me2})_2(bipy^{\bullet})]$, a uranium(III) complex with a radical bipyridine ligand which has magnetic properties with contributions from both ligand and metal, presents slow relaxation of the magnetisation at low temperatures, already under zero static magnetic field and energy barriers slightly above the non-radical analogues.

During the last few years a new class of single-molecule-magnets (SMM) based on mononuclear species where, at low temperatures, the magnetisation presents slow relaxation of purely single ion origin, has been identified which are called single-ion magnets (SIM).[1] The first SIMs were based on complexes of lanthanide ions,[2] but recently a few mononuclear systems based on actinides have been identified, in particular, with U(III)[3] where the anisotropic ligand field interacting with the electronic density of the uranium is playing a crucial role in the slow relaxation of the magnetisation[4]. Actinide based compounds have attracted increasing interest in this context since their stronger magnetic anisotropy and larger exchange interactions due to the more extended nature of the 5f orbitals make them better candidates for SIM behaviour and they are regarded as important counterparts in comparison with lanthanide analogues to understand the key parameters determining the features and the mechanisms of the low temperature slow relaxation of magnetisation.[5] However, actinide compounds have been so far only very poorly explored being of obvious interest to study different effects such as variations in ligand field strength, coordination geometry, oxidation state, etc. which so far could be only very partially addressed.[3,6]

Recently we reported the magnetic properties of two uranium(III) complexes based on hydrotris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) ligands, $([U(Tp^{Me2})_2(bipy)]I$ (**2**),[3c] and its precursor, $[U(Tp^{Me2})_2]I$ (**1**)[3d,e] (Figure 1), revealing two new SMMs based on uranium with different coordination geometries. Pursuing our studies within this family of complexes, we present here the magnetic behaviour of the closely related compound $[U(Tp^{Me2})_2(bipy)]$ (**3**), based on a neutral complex containing a radical monoanionic bipyridine ($bipy^{\bullet -}$) as co-ligand[7] (Figure 1), where the extra magnetic moment of the radical ligand can couple to the central ion one. In this work by preserving the coordination geometry and just turning the co-ligand into a radical anion, this effect can be clearly studied. Some examples of lanthanide complexes with radical ligands have been recently reported indicating that the interaction between radical and metal leads to an enhanced anisotropy and energy barriers,[4b,c,5a] but such effect could not be clearly separated from others like coordination geometry.

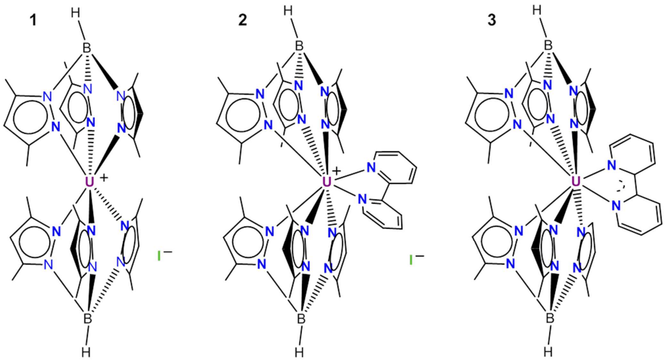

Fig. 1 Diagrams of $[U(Tp^{Me2})_2]I$ **1**, $([U(Tp^{Me2})_2(bipy)]I$ **2** and $[U(Tp^{Me2})_2(bipy)]$ **3**.

Compound **3** was prepared by a procedure similar to the one described previously by Bart and co-workers[7] but using sodium amalgam as reducing agent (see ESI for experimental details). The molecular structure of compound **3** is shown in Figure 2.[7] As previously described[7] the uranium atom in this compound is eight-coordinate by the six nitrogen atoms of the two Tp^{Me2}

ligands and the two nitrogen atoms of the bipy, in a distorted dodecahedral coordination environment in a fashion similar to the non-radical analogue **2**, although with shorter U-N$_{bipy}$ bond lengths. The molecule has approximate C_2 symmetry with the two-fold axis bisecting the N1-U-N2 angle.

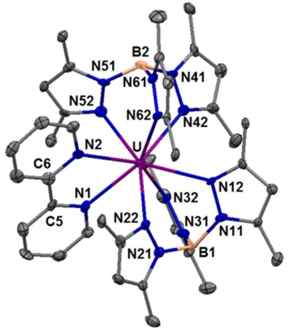

Fig. 2 Molecular Structure of [U(Tp^{Me2})$_2$(bipy)].2THF (ellipsoids are set at 30% probability)[7]. Hydrogen atoms and solvent molecules are not displayed for clarity. Selected bond lengths (Å) and angles (deg): U-N1 2.566(8), U-N2 2.591(8), U-N(Tp^{Me2}) 2.567(7)–2.703(7), C5-C6 1.41(1), N(Tp^{Me2})-U-N(Tp^{Me2}) 67.7(2)–89.1(2), N1-U-N2 63.6(2), B1-U-B2 146.1(2). The shortest intermolecular U···U distance is 10.6670(5) Å.

The temperature dependence of the magnetisation was measured using a 6.5 T S700X SQUID magnetometer (Cryogenic Ltd) in the temperature range 5-300 K under a field of 1 T. As expected this compound shows paramagnetic behaviour and its χT product drops from 1.3 emu K mol^{-1} at 300 K to 0.16 emu K mol^{-1} at 5 K (Fig. 3). At 300 K the effective magnetic moment is 3.27 μ_B, comparatively lower than the calculated moment for a free U(III) (3.58 μ_B) but still within the range observed for U(III) coordination compounds.[3] The effective magnetic moment of **3** at room temperature is significantly higher than those of compound **1** (μ_{eff} = 3.01 μ_B) and the correspondent non radical analogue **2** (μ_{eff} = 2.53 μ_B), as expected from the additional contribution of the extra bipyridine radical spin in the system. On cooling, χT drops monotonically showing a faster decrease below 100 K. At 5 K this moment is lower than the moments of the other two compounds, which may denote antiferromagnetic interactions between the radical ligand and metal moments.

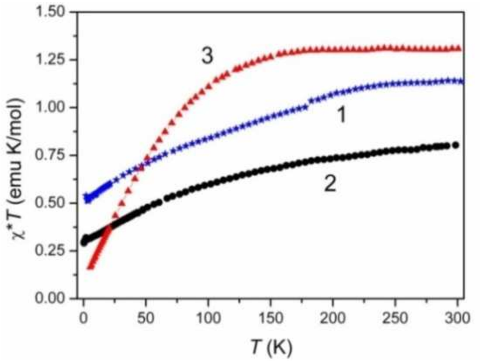

Fig. 3 Temperature dependence of χT for **1**, **2** and **3**.

The magnetic field dependence of magnetisation of **3** was measured at several temperatures above 1.8 K under fields up to 5 T using a MagLab 2000 system (Oxford Instruments) (Fig. SI2). No hysteresis was observed, even with a sweeping rate of 90 Oe s^{-1}. Using an ^{3}He insert adapted to the SQUID magnetometer, it was possible to perform isotherms at lower temperatures although with field sweeping rates not larger than 20 Oe s^{-1}. As shown in Fig. 4, an opening of the hysteresis curves could be observed already at 0.8 K, becoming more pronounced at 0.33 K, although without coercivity at zero fields as usually observed in several other mononuclear uranium[8] and lanthanide complexes.[9] The absence of coercivity can be due to an efficient quantum tunnelling of the magnetisation at zero field and is probably caused by low-symmetry components of the crystal field.

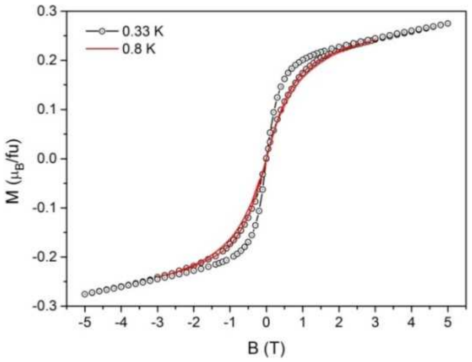

Fig. 4 Magnetic field dependence of the magnetization of compound **3** at 0.8 and 0.33 K.

The low temperature magnetisation dynamics of this complex was probed by using ac susceptibility measurements with an AC field of 5 Oe in the range 30 Hz – 10 kHz, under zero and 0.05 T external magnetic DC fields. Surprisingly, even at zero field, complex **3** shows already some slow magnetic relaxation, with both real, χ´, and imaginary, χ´´, components of susceptibility being frequency dependent, with the appearance of a well resolved local maximum that shifts to higher temperatures as the frequency increases (Fig. 5(a) and 5(b)). This zero-field frequency-dependent behaviour is very clear in an unusual way among uranium compounds. The application of a small static (DC) magnetic field only slightly enhances the frequency and temperature dependence of the peaks, with the maxima becoming better resolved (Fig. 5(c) and (d)) but with no significant increase in the magnitude of the peaks.

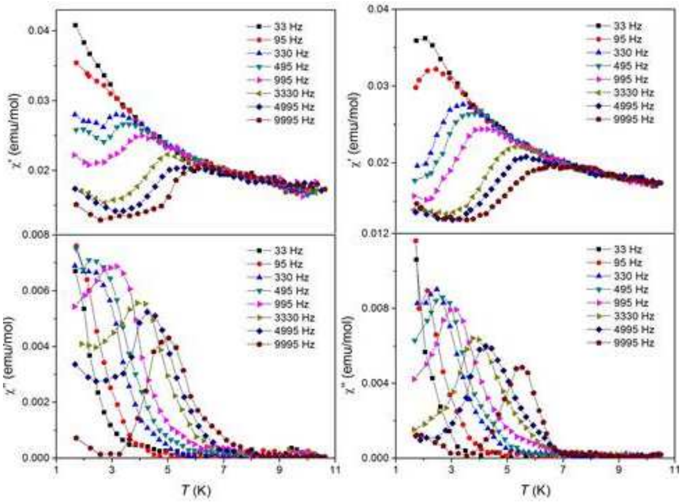

Fig. 5 Temperature dependence of the real (χ´) and imaginary (χ´´) components of the AC susceptibility of **3** under zero (left) and 0.05 T (right) static fields, at various AC frequencies indicated in the range 33-9995 Hz.

The magnetization relaxation rate was determined by measuring the dependence of both χ' and χ'' with the frequency, ω, in the range 10 Hz - 10 kHz, at temperatures between 1.8 and 7 K. These data provided Cole-Cole plots for those fixed temperatures which were fitted with the generalized Debye model, $\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1 + i\omega\tau)^{1-\alpha}$, where χ_S and χ_T are the adiabatic and the isothermal susceptibilities, τ is the average magnetization relaxation time, and α is a parameter ranging from 0 to 1 that quantifies the width of the relaxation time distribution (α = 0 corresponds to the ideal Debye model, with a single relaxation time) (Fig. SI3).[10]

The lowest α was obtained at 4 K (Fig. 6 – left), under a DC field of 0.05 T, giving parameters of $\chi_S = 0.01019$ emu mol^{-1}, $\chi_T = 0.03408$ emu mol^{-1}, $\tau = 6 \times 10^{-5}$ s and $\alpha = 0.05985$.

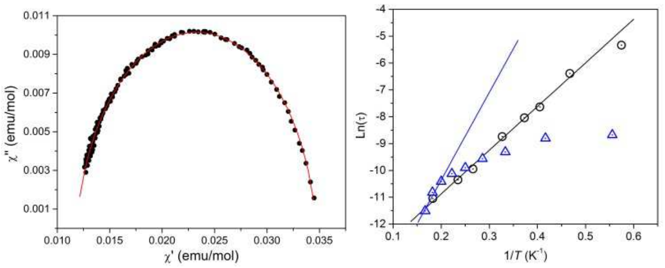

Fig. 6 (Left) Cole-Cole plot for complex **3** at 4 K and 0.05 T (left). The red line represents the least-square fit with a generalized Debye model to a distribution of single relaxation modes. (Right) Plots of ln(τ) vs. T^{-1} with the fits (lines) of the Arrhenius law under static DC fields of zero (black circles) and 0.05 T (blue triangles).

The magnetization relaxation times τ and the correspondent temperatures were fitted using the Arrhenius law, $\tau(T) = \tau_0 exp\left(E_{eff}/k_B T\right)$. In the thermally activated regime (Fig. 6 – right), effective relaxation barriers of $E_{eff}/k_B = 19.8\ cm^{-1}$ and $22.6\ cm^{-1}$ with the correspondent pre-exponential factors of $\tau_0 = 3.28 \times 10^{-7} s$ and $4.68 \times 10^{-8} s$ were obtained for both static magnetic fields of zero and 0.05 T, respectively. These parameters are typical of SMM materials.[1,3] In the case of the applied DC field, a deviation from the Arrhenius law is observed below 4.5 K which can be attributed to a quantum tunnelling mechanism for the magnetic relaxation, in a way similar to that previously found in other actinide based SIMs.[3-6] It is however remarkable that no quantum tunnelling regime is observed under zero field down to 1.7 K at variance with other uranium compounds.

In summary, slow relaxation of the magnetisation was observed in a uranium(III) compound with a radical ligand which brings an additional contribution to the effective magnetic moment, antiferromagnetically coupled to the central metal moment. This compound is closely related to two other uranium(III) complexes based on the same (Tp^{Me2}) ligand, all presenting SIM behaviour with comparable energy barriers for magnetisation relaxation. However the quantum tunnelling mechanism under zero static field is removed, in what appears to be an effect of coupling of the U ion to the radical ligand.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details of preparation and characterisation of **3**, figures S1-S3 of NMR, isothermal magnetisation curves and Cole-Cole plots. See DOI: 10.1039/c000000x/

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