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Single-Molecule Magnets

Single-Molecule Magnetism in a Single-Ion Triamidoamine Uranium(V) Terminal Mono-Oxo Complex**

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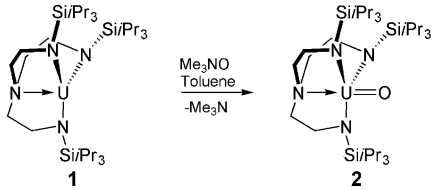
Single-molecule magnets (SMMs) are defined as molecules that exhibit slow relaxation of magnetization of purely molecular origin.[1] SMMs are intensively researched not only for their important fundamental physics, but also because of potential applications in high-density data storage,[2] quantum information processing,[3] and spintronics.[4] These applications are conceivable because SMMs generally possess well-isolated high-spin ground states in which spin–orbit coupling results in zero-field splitting of the $(2S+1)$-fold degenerate ground multiplet.[5,6] This phenomenon creates a thermal barrier to the relaxation of the magnetization which gives rise to slow magnetic relaxation and magnetic bistability.[6] Great advances have been made with lanthanide SMMs[7] arising from the huge magnetic anisotropies that can result from the crystal field splitting of the total angular momentum (J) ground states. Very recently, there has been great interest in actinide[8] and especially uranium SMMs.[9,10] This stems from the same phenomena, but with the potential advantage that uranium can engage in covalent bonding which can enable stronger magnetic interactions.[11] However, only a handful of uranium-based SMMs have been isolated, and the ground rules for maximizing their blocking temperatures are not clear. Furthermore, when we initiated this study all uranium SMMs exploited the highly anisotropic ($5f^3$) Kramers ion uranium(III) which has an $^4I_{9/2}$ ground state.[10] We reasoned that a highly anisotropic, strongly axially coordinated ligand environment at a uranium(V) Kramers ion should engender increased magnetic anisotropy and thus SMM behavior, despite the smaller total angular momentum ($^2F_{5/2}$) of uranium(V) compared to uranium(III). Here we report the first monometallic uranium(V), $5f^1$ SMM, where the physical properties result from imposing a strongly axial ligand field with C_{3v} symmetry.

Recently, a uranyl(V)/manganese(II) $(UO_2)_{12}Mn_6$ *N,N′*-ethylenebis(salicylimine) cluster was demonstrated to exhibit SMM behavior.[12] In this cluster the authors speculate that there is significant exchange coupling between the uranyl(V) and Mn^{II} ions, hence the relative importance of the ligand field and exchange coupling to the SMM behavior was unclear. We now report a triamidoamine uranium(V) terminal-oxo complex which is a SMM. This monometallic uranium(V) SMM provides the first unambiguous confirmation that uranium(V) complexes can indeed exhibit SMM behavior.

We previously reported the trivalent uranium complex [U(Tren^{TIPS})] [**1**, Tren^{TIPS} = {N(CH$_2$CH$_2$NSi*i*Pr$_3$)$_3$}$^{3-}$] and its use in the preparation of a terminal uranium(V)-nitride by a two-electron oxidation with sodium azide and the abstraction of the sodium ion with [12]crown-4 ether.[13] Similarly, two-electron oxidation of **1** with trimethyl-*N*-oxide in toluene afforded the terminal mono-oxo uranium(V) complex [U(O)(Tren^{TIPS})] (**2**; Scheme 1 and Figure 1) as red crystals in 52% yield following work-up and recrystallization from hexane.[14]



1 **2**

Scheme 1. Synthesis of **2**.

The ^{1}H NMR spectrum of **2** spans the range from +16 to −3 ppm and exhibits four resonances consistent with C_{3v} symmetry on the NMR time scale. The FTIR spectrum of **2** exhibits an absorption at 910 cm^{-1} which we attribute to a terminal U=O stretch. The UV/Vis/NIR electronic absorption spectrum of **2** exhibits strong charge-transfer bands in the region from 25000 to 10000 cm^{-1} and an absorption at 5890 cm^{-1} ($\varepsilon = 40\ M^{-1}cm^{-1}$) that is characteristic of a $^2\Gamma_4$ ($^2F_{5/2}$) to $^2\Gamma_4$ ($^2F_{7/2}$) transition for uranium(V).[14] The solution magnetic moment of **2** in C_6D_6 at 298 K is 1.79 μ_B. The solid-state magnetic moment of **2** at 298 K measured by superconducting quantum interference device (SQUID) magnetometry is 1.76 μ_B, which is consistent with the solution-phase magnetic data. The magnetic moment decreases only slowly with decreasing temperature down to about 50 K (about 1.5 μ_B), below which it decreases more rapidly as low-

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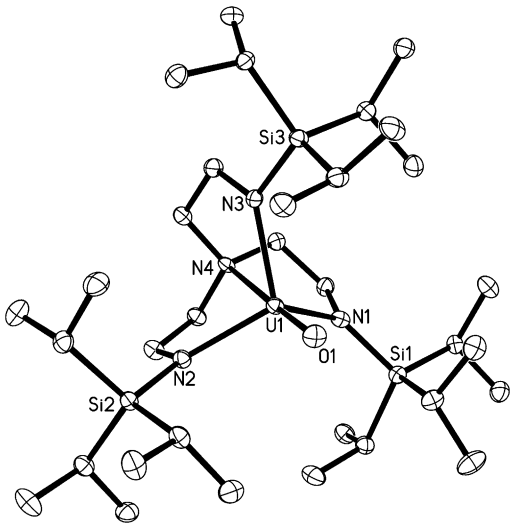

Figure 1. Molecular Structure of [U(O)(Tren^{TIPS})] (**2**). Displacement ellipsoids set at 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: U(1)–N(1) 2.299(5), U(1)–N(2) 2.292(4), U(1)–N(3) 2.280(4), U(1)–N(4) 2.482(6), U(1)–O(1) 1.856(6); N(4)–U(1)–O(1) 177.4(2).

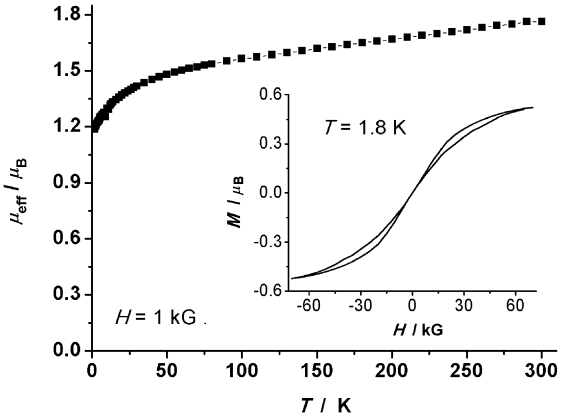

Figure 2. Effective magnetic moment of solid-state complex **2**, measured in 1 kG static field. Inset: Molar magnetization at 1.8 K.

lying excited states are depopulated, reaching 1.2 μ_B at 1.8 K (Figure 2). These data are all self-consistent with the pentavalent assignment of **2**.[15]

To confirm the identity of **2** we determined the structure by X-ray diffraction[16] and this is shown in Figure 1 with selected bond lengths and angles. The uranium center adopts a distorted trigonal bipyramidal geometry enforced principally by the quadridentate nature of Tren^{TIPS} where the tertiary amine and oxo groups adopt axial positions and are thus mutually trans with respect to each other. The U=O bond distance is 1.856(6) Å which is comparable to the U=O bond distances of 1.859(6), 1.85 (av.), and 1.847(2) Å for [U(O)(Cp*)$_2$(O-2,6-*i*Pr$_2$C$_6$H$_3$)] [U(O){tacn(OAr^R)$_3$}] (R = *t*Bu, Ad), and [Ph$_3$PMe] [U(O)(CH$_2$SiMe$_2$NSiMe$_3$){N(SiMe$_3$)$_2$}$_2$], respectively, which all contain structurally characterized uranium(V) terminal mono-oxo groups.[17]

The U–N$_{amide}$ bond lengths in neutral **2** average 2.290 Å which are only slightly shorter than the corresponding U–N$_{amide}$ average of 2.353 Å (av.) in anionic [U(N)(Tren^{TIPS})]$^-$.[13] Notably, the U–N$_{amine}$ bond length [2.482(6) Å] is very short; U–N$_{amine}$ distances in uranium–Tren complexes over oxidation states III–VI are usually about 2.6 Å.[18] We suggest this may be a result of an inverse-trans-influence (ITI)[19] which has previously usually been observed in oxo, aryloxide, and imide σ/π-donor ligands.[20] Thus, the ITI in **2** represents an unusual example involving a pure σ-donor ligand, but this is reasonable since the ITI stems principally from a σ interaction between uranium and a donor atom. Further support for an ITI in **2** can be gathered from the fact that the U–N$_{amine}$ bond length is short despite the uranium center being displaced 0.753(4) Å above the plane defined by the three amide nitrogen atoms; in [{U(μ-N)(μ-Na)(Tren^{TIPS})}$_2$] the displacement of uranium from the amide plane is 0.791 Å but the U–N$_{amine}$ distance is 2.654(4) Å.[13] Lastly, we examined the structure of **2** with DFT and NBO methods to support its formulation. These calculations suggest a highly polarized U=O linkage in **2** and details can be found in the Supporting Information.[14]

We have studied the dynamic and static magnetization behavior of **2** in detail. The low-temperature (1.8 K) molar magnetization as a function of the applied magnetic field reaches 0.52 μ_B at 7 T, and is still rising with the applied field (Figure 2, inset, and Supporting Information). If we assume pure $\pm M_J$ Kramers doublets in the $^2F_{5/2}$ ground state ($g_J = 6/7$) then we would expect effective g values ($g_\parallel$, $g_\perp$) of: (6/7, 18/7), (18/7, 0) and (30/7, 0) for $M_J = \pm 1/2$, $\pm 3/2$, and $\pm 5/2$, respectively. Such isolated doublets would give powder saturation magnetizations of about 1, 0.6, and 1 μ_B, respectively.[21] Although these values can be altered by the mixing of the $M_J = \pm 1/2$, $\pm 5/2$ doublets under C_{3v} symmetry, and/or the mixing with the $^2F_{7/2}$ excited state and/or covalency effects, they still suggest that $M_J = \pm 3/2$ is the ground doublet in **2**. This is also consistent with the low-temperature plateau in $\chi' T(T)$ (see the Supporting Information), where χ' is the in-phase component of the AC molar magnetic susceptibility, at ca. 0.18 cm^3 K mol^{-1} below about 5 K (calculated powder values of 0.44, 0.21, and 0.57 cm^3 K mol^{-1} for $M_J = \pm 1/2$, $\pm 3/2$, and $\pm 5/2$, respectively). Under C_{3v} symmetry, the $M_J = \pm 3/2$ state must be pure and hence is expected to be EPR silent; indeed we do not find any EPR signal for **2** in the solid or solution state (measured at X- and Q-band down to 4 K). This is also true of [U(N)(Tren^{TIPS})]$^-$.[13]

Alternating current (ac) susceptibility measurements in zero static field show no response in the out-of-phase component of the susceptibility, χ''. However, in a small static field of 1 kG there are strong frequency- (ν) dependent peaks in the in-phase and out-of-phase components as a function of T and ν (Figure 3 and the Supporting Information). For our maximum available ν of 1.2 kHz, we see a maximum in $\chi''(T)$ at 3.5 K (Figure 3, bottom); while at our base temperature (1.8 K) we see a peak in $\chi''(\upsilon)$ at frequencies as low as 10 Hz (see SI). This behaviour is consistent with SMM behavior, that is, slow relaxation of the molecular magnetization. Well-defined semi-circular Cole–Cole plots (χ'' vs. χ') are obtained for temperatures below 3.2 K, which can be fitted to a generalized Debye model with the α parameter in the range 0.07–0.11 indicating a very narrow

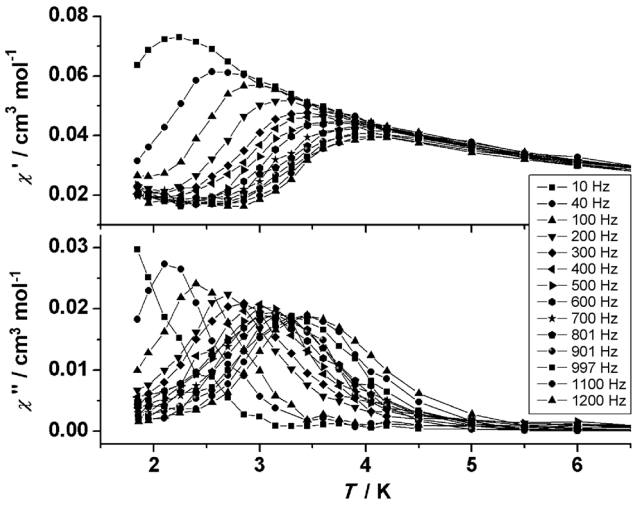

Figure 3. Temperature dependence of (top) χ' and (bottom) χ'' for solid state **2** under a static applied field of 1 kG and a 1.55 G alternating field at various frequencies.

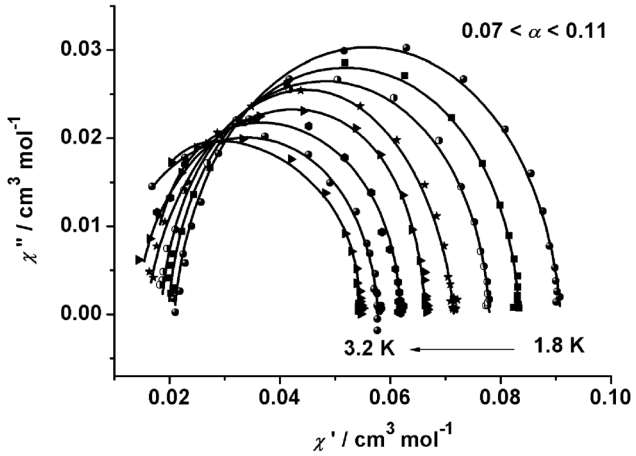

Figure 4. Cole–Cole plots for **2**, with best fits (solid lines).

distribution of relaxation times (Figure 4). A plot of the derived relaxation time constants (τ) as $\ln(\tau)$ versus T^{-1} is linear above 2.2 K (Figure 5), and fitting to the Arrhenius law $\tau = \tau_0 \exp(\Delta E/kT)$ gives an effective thermal energy barrier to magnetization relaxation of $\Delta E/k = 21.5$ K with a pre-exponential factor of $\tau_0 = 2.6 \times 10^{-7}$ s. This barrier is within the range reported for uranium(III) SMMs reported to date (about 5–30 K),[10] and is presumably the result of the energy gap between the $M_J = \pm 3/2$ ground Kramers doublet and the lowest-lying excited Kramers doublet: the nature of the latter is not determined by our measurements. The relaxation is slow enough that hysteresis is observed in $M(H)$ below 3 K using a commercial SQUID magnetometer (Figure 2, inset), although even down to 1.8 K the width of the hysteresis loop collapses on approach to zero-field. This is consistent with efficient quantum tunneling in zero-field and the need to apply a small direct current (dc) field to suppress these effects and to observe the out-of-phase behavior (Figure 3). This is the case with most of the uranium(III) SMMs measured to date,[10] despite their Kramers nature.

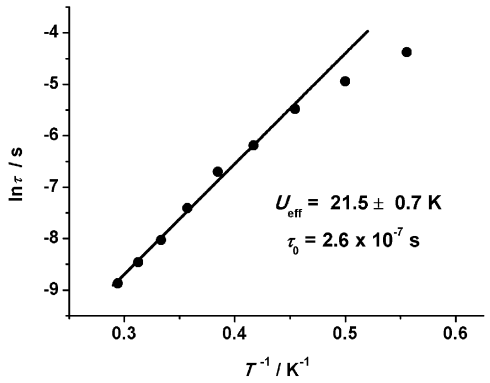

Figure 5. Magnetization relaxation time constant as $\ln(\tau)$ versus T^{-1} for solid-state **2** in a 1 kG static field, from fitting to the data in Figure 4, and best fit to the Arrhenius law of the thermally activated regime (solid line).

Complex **2** is the first monometallic uranium(V) SMM, and the first monometallic f^1 SMM of any description.[22] These results show unambiguously that uranium(V) represents as promising route to 5f SMMs as lower-valent species. Indeed, the wide and growing range of terminal uranim(V) mono-oxo complexes and uranium(V) in strongly axially coordinated environments suggests that uranium(V) has significant potential to play a far more substantial role in SMM chemistry than has been anticipated previously, particularly because the symmetry at uranium can be controlled.

Experimental Section

Complex **2**: Toluene (10 mL) was added slowly to a stirred mixture of [U(Tren^{TIPS})] (0.85 g, 1.00 mmol,) and Me_3NO (1.06 mmol, 0.08 g) at −78 °C. The red mixture was allowed to warm to room temperature with stirring over 16 h. Volatiles were removed in vacuo and the product was extracted into hot hexane (10 mL). The mixture was filtered, concentrated, and stored at 4 °C to yield red crystals of **2**. Yield: 0.45 g, 52 %. Anal. Calcd for $C_{33}H_{75}N_4OSi_3U$: C, 45.76; H, 8.73; N, 6.47. Found: C, 44.17; H, 8.62; N, 5.90. Note. Elemental analyses were repeated five times with independently prepared batches and all gave the same results. The ^{1}H NMR spectra are free of impurities so we attribute the low carbon value to the fact that this is a silicon rich molecule as reported previously.[23] ^{1}H NMR (C_6D_6, 298 K): $\delta = 15.42$ (s, 6H, CH_2), 12.85 (s, 6H, CH_2), −1.34 (s, 54H, $CH(CH_3)_2$), −2.15 ppm (s, 9H, $CH(CH_3)_2$). ^{29}Si NMR (C_6D_6, 298 K): $\delta = -71.00$ (bs). FTIR (Nujol): $\tilde{\nu}$ =2955 (vs), 2925 (vs), 2855 (vs), 1461 (s), 1401 (w), 1378 (m), 1261 (m), 1106 (m), 1069 (m), 1013 (m), 995 (w), 926 (w), 910 (m), 884 (m), 838 (m), 800 (m), 764 (s), 725 (m), 674 (m), 634 (m), 594 cm^{-1} (w). μ_{eff} (Evans method, C_6D_6 solution, 298 K): 1.79 μ_B.

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[16] Crystal data for **2**: $C_{33}H_{75}N_4OSi_3U$, $M_r = 866.27$, space group $P2_1/c$, $a = 12.4268(12)$, $b = 20.692(2)$, $c = 16.5987(16)$, $\beta = 109.041(1)$, $V = 4034.5(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.426$ g cm^{-3}; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 4.141$ mm^{-1}, $T = 90$ K. 34704 points (9955 unique, $R_{int} = 0.048$, $\theta < 58.3°$). Data were collected on a Bruker SMART APEX CCD diffractometer and were corrected for absorption (transmission 0.28–0.43). The structure was solved by direct methods and refined by full-matrix least-squares on all F^2 values to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.2174$, conventional $R = 0.0612$ for F values of 7126 with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.141$ for 398 parameters. Residual electron density extrema were 4.46 and -5.04 e Å^{-3}. CCDC 922773 (**2**) contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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