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Single-Molecule-Magnet Behavior in Mononuclear Homoleptic Tetrahedral Uranium(III) Complexes

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Supporting Information

ABSTRACT: The magnetic properties of the two uranium coordination compounds, $[K(18c6)][U(OSi(O^tBu)_3)_4]$ and $[K(18c6)][U(N(SiMe_3)_2)_4]$, both presenting the U^{III} ion in similar pseudotetrahedral coordination environments but with different O- or N-donor ligands, have been measured. The static magnetic susceptibility measurements and density functional theory studies suggest the presence of different ligand fields in the two compounds. Alternating-current susceptibility studies conducted at frequencies ranging from 95 to 9995 Hz and at temperatures in the 1.7−10 K range revealed for both compounds slow magnetic relaxation already at zero static magnetic field with similar energy barriers U ~24 K.

Actinide-based compounds are attracting increasing interest for the design of molecular magnets[1] with larger relaxation barriers and higher blocking temperatures because of the large single-ion anisotropy and the strong spin−orbit coupling of actinide ions.[2] The larger extension of 5f orbitals compared to that of 4f ones enables stronger metal−ligand interactions, rendering actinide ions attractive for the development of mononuclear[2f,3] and exchange-coupled polynuclear single-molecule magnets (SMMs).[4] Slow relaxation in mononuclear compounds arises from the intrinsic properties of the single ion subject to ligand field. As such, the coordination geometry is an important parameter in determining slow relaxation of magnetization. The nature of ligand donor atoms should also play an important role in determining the magnetic properties of uranium compounds as a result of differences in the ligand field strength and covalent contribution to uranium−ligand bonding. However, besides three structurally unrelated mononuclear uranium(III) SMMs reported by Liddle and co-workers,[5] most of the mononuclear uranium(III) complexes showing single-ion-magnet behavior present high coordination numbers (6−8) and are based on similar scorpionate-type ligands with heterocyclic pyrazolyl N-donor atoms in a trigonal-prismatic geometry.[2f,6,3,5] The first study investigating the effect of donor atoms on slow relaxation for uranium compounds in a similar geometry has just appeared in the literature.[6] The latter study elegantly shows that strongly donating N-heterocyclic carbene ligands lead to higher relaxation barriers compared to heterocyclic N donors as a result of the larger ligand field induced by the carbene atoms.[6]

Here we report two new rare examples of uranium(III)-based single-ion magnets, which are the first ones based on tetrahedral uranium compounds.[7] The two four-coordinated complexes, $[K(18c6)][U(OSi(O^tBu)_3)_4]$ (**1**) and $[K(18c6)][U(N(SiMe_3)_2)_4]$ (**2**), presenting the U^{III} ion in the same geometry but different ligand environments, both show slow relaxation of magnetization at low temperatures and SMM behavior even under zero magnetic field with similar energy barriers.

Complex **2** has been prepared in good yield from reduction of the tetrakis(silylamido) complex $[U\{N(SiMe_3)_2\}_4]$[8] with KC_8 in tetrahydrofuran (THF) in the presence of 18c6. As a result, complex **2** can be easily prepared in an analytically pure form for magnetic studies. X-ray-quality crystals of $[K(18c6)(THF)_2][U(N(SiMe_3)_2)_4]$ (**3**) were obtained from a THF solution at −40 °C. The crystal structure of complex **3** shows the presence of an isolated ion pair similar to the previously reported crystal structure of $\{U[N(SiMe_3)_2]_4\}\{K(THF)_6\}$.[9] The coordination polyhedra of the anion $[U(OSi(O^tBu)_3)_4]^-$ in **1**·toluene[7] and of the anion $[U(N(SiMe_3)_2)_4]^-$ in **3** are presented in Figure 1.

Both anions show distorted tetrahedral geometries, with a more irregular geometry observed for the $[U(N(SiMe_3)_2)_4]^-$ anion (N−U−N angles ranging from 100.4° to 114.9° in **3**

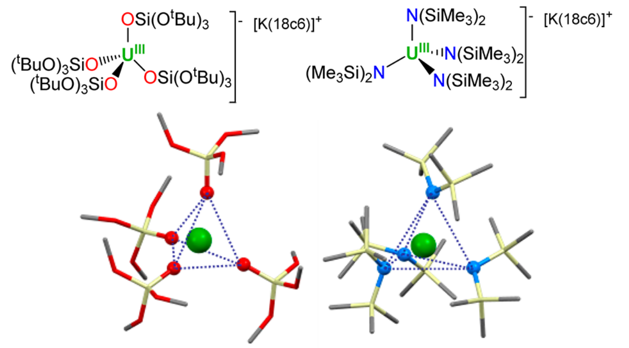

Figure 1. Structure of $[K(18c6)][UL_4]$ complexes (top) and Mercury diagrams (bottom) of the $[U(OSi(O^tBu)_3)_4]^-$ anion in **1**·toluene[7] (left) and of the $[U(N(SiMe_3)_2)_4]^-$ anion in **3** (right).

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compared to O−U−O angles ranging from 108.4° to 111.3° in **1**) probably because of the presence of the bulkier amide ligands. The mean U−O siloxide bond distances in **1** at 2.228(17) Å are similar to those found in uranium(III) triphenoxide[10] or trisiloxide complexes,[11] while the mean U−N distance in **3** [2.434(13) Å] is very close to the one in $\{U[N(SiMe_3)_2]_4\}\{K(THF)_6\}$[9] (2.432 Å). In both cases, the mean U−N distance is significantly longer than that found in the neutral uranium(III) complex $[U(N(SiMe_3)_2)_3]$ [2.320(4) Å].[12] The shortest intermolecular U−U distances are at 12.4 Å for the tetrasiloxide complex **1**·toluene[7] and at 13.3 Å for the tetraamide complex **3**. These U−U distances are significantly longer than those found in the $\{U[N(SiMe_3)_2]_4\}\{K(THF)_6\}$[9] complex (10.1 Å), probably as a result of the presence of the crown ether.

The temperature dependence of the solid-state static magnetic susceptibility of complexes **1** and **2** was measured in the 2−300 K range using a SQUID magnetometer. Compound **2** presents paramagnetic behavior with a χT product dropping monotonically upon cooling, from 1.36 emu K mol^{-1} at 300 K to 0.35 emu K mol^{-1} at 2 K, as shown in Figure 2. Complex **1** shows a significantly smaller temperature dependence of χT versus T at high temperature compared to **2** (Figure 1). The magnetic moment at 300 K for **2** (3.3 μ_B) is higher than that for **1** (2.48 μ_B; see Figures S2 and S3 in the Supporting Information, SI). The different temperature dependence of the χT product and the lower value of the room temperature magnetic moment could be interpreted in terms of a higher covalent contribution to bonding in complex **1** compared to complex **2**.[6,13] In order to elucidate potential differences in the electronic structures of these two complexes, we have performed density functional theory (DFT) calculations with two objectives: (i) gain insight in the ionic/covalent character of the U−ligand bond and (ii) estimate the ligand-field splitting for both ligands. Analysis of the Kohn−Sham orbital composition, of the charges, and of the spin densities on the uranium and ligands clearly shows that both the U^{III}−N and U^{III}−O bonds are mainly ionic in character with a negligible covalent contribution (see the SI for details). The difference observed in the χ_T curves could not therefore originate from covalency effects. Moreover, the computed value of the ligand-field splitting on f orbitals is clearly lower for **2** than for **1**, independent of the type of calculation. This leads to a lower temperature-independent paramagnetism for **1** than for **2**, which may account for the lower slope in χT versus T (Figure 2) for **1** compared to **2**.[9]

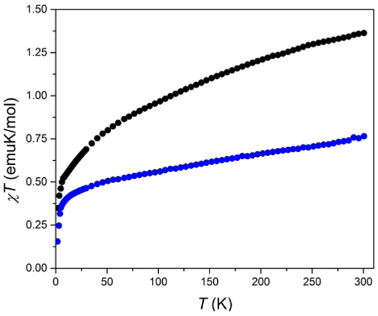

Figure 2. Temperature-dependent χT for **1** (blue) and **2** (black) measured under an applied field of 5000 Oe between 2 and 300 K after being zero-field-cooled.

The field dependence of the magnetization M plotted versus B/T at different temperatures (Figure S8 in the SI) shows for both compounds curves not superimposed. This could be ascribed to the magnetic anisotropy or to the presence of low-lying magnetic states.[14] The magnetization cycling data (inset of Figure S8 in the SI) at several temperatures above 1.6 K, obtained with a sweeping rate of 90 Oe s^{-1}, do not show any coercivity, probably denoting efficient quantum tunneling of the magnetization occurring at zero field. This is probably caused by low-symmetry components of the crystal field, as was already observed in other mononuclear compounds of uranium[3a] and of lanthanides with SMM behavior (i.e., faster than the thermal-activated relaxation).[15]

The magnetization dynamics of both complexes were investigated by alternating-current (ac) susceptibility measurements as a function of the temperature (1.7−10 K) and frequency (ω = 33−9995 Hz), in zero and higher static magnetic fields. In the absence of a static magnetic field, there is already a significant frequency dependence, although more pronounced in complex **1**, with clear maxima in both the in-phase (χ') and out-of-phase (χ'') signals, denoting slow relaxation of magnetization (Figure S7 in the SI). This frequency dependence under zero dc field is in these cases more evident than that in other uranium(III) compounds already classified as SMMs such as the pyrazolyl derivatives $U(Ph_2BPz_2)_3$,[5] $U(H_2BPz_2)_3$,[3c] and $[U(TpMe_2)_2(bipy)]I$,[3a] where χ' was found to be almost frequency-independent. The application of a static field of 500 Oe still clearly slows the relaxation dynamics of **1** and **2** with the occurrence of strong frequency and temperature dependence with well-resolved peaks in both χ' and χ'', as shown in Figure3.

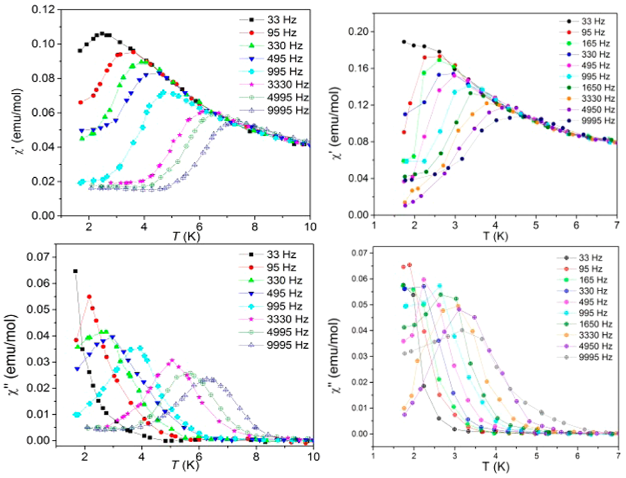

Figure 3. In-phase and out-of-phase components of ac susceptibility at different frequencies in the low-temperature range for **1** (left) and **2** (right) with H_{ac} = 5 Oe and H_{dc} = 500 Oe.

The magnetization relaxation rate was probed in the 1.8−10 K temperature range by measuring χ' and χ'' at fixed temperatures, while the frequency ω of the ac field was varied from 10 Hz to 10 kHz. The Cole−Cole plots at low temperatures (see Figures S9 and S11 in the SI) for both complexes show distorted semicircles and can be fitted to the generalized Debye model.[4a,16] For each complex, the single relaxation time τ extracted from the frequency-dependent ac susceptibility data taken for dc fields at 0 and 500 Oe were fitted to an Arrhenius law, $\tau = \tau_0 \exp(U/k_BT)$, where U is the effective energy barrier and k_B is the Boltzmann constant (Figure 4). The values of the energy barriers [U = 26 (±2) K for **1** and U = 23 (±3) K for **2** at H_{dc} = 0 Oe] and of the preexponential factors ($\tau_0 = 2.6 \times 10^{-7}$ s for **1** and $\tau_0 = 2.20 \times 10^{-8}$ s for **2** at H_{dc} = 0 Oe) are consistent with a slow magnetic

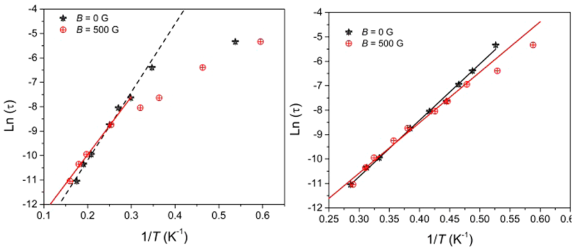

Figure 4. Plots of ln (τ) versus T^{-1} with a fitting to the Arrhenius law for complexes **1** (left) and **2** (right).

relaxation, with energy barriers falling in the high end of the range (5.5−31 K) reported so far for uranium(III) SMM complexes.[2f,3] For both static fields, the U barriers of complexes **1** and **2** are almost identical, slightly higher in the first compound. Also, by a comparison of both plots of ln(τ) versus T^{-1} (Figure 4), it is observable that in the case of **1** the Arrhenius law is only followed in the higher temperature range, although in the lower temperature range, a clear deviation from the activated regime is noticed in both fields, certainly because of the approach of a quantum tunneling regime expected to occur at lower temperatures, as was already observed in other uranium(III) compounds.

In conclusion, we have identified two new examples of uranium-based SMMs. Slow relaxation of magnetization has been reported for a small number of mononuclear complexes of uranium(III), but tetrasiloxide and tetrasilylamide are the first examples of a tetrahedral uranium(III)-based SMM. In spite of the different coordination environments provided by the siloxide ligands compared to the silylamide ligands, which lead to significantly different values of the high-temperature magnetic moment and of its temperature dependence, the two complexes show similar values of the relaxation barriers, which are among the highest reported to date. The difference in the ligand-field splitting shown by DFT studies for these complexes may lead to the very slightly larger value of the relaxation barrier found for the siloxide complex. A significantly higher relaxation barrier was found in isostructural trigonal-prismatic complexes presenting strongly donating carbene donors ($U = 33$ cm^{-1}) compared to N donors ($U = 0$ cm^{-1}).[9] Future studies will be directed to investigate tetrahedral complexes of stronger donating ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, ^{1}H NMR spectra, and XRD, magnetic, and computational data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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