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Single-Molecule Magnets

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Self-Assembly of a 3d–5f Trinuclear Single-Molecule Magnet from a Pentavalent Uranyl Complex**

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Dedicated to Professor Marius Andruh on the occasion of his 60th birthday

Abstract: *Mixed-metal uranium compounds are very attractive candidates in the design of single-molecule magnets (SMMs), but only one 3d–5f hetero-polymetallic SMM containing a uranium center is known. Herein, we report two trimeric heterodimetallic 3d–5f complexes self-assembled by cation–cation interactions between a uranyl(V) complex and a TPA-capped M^{II} complex (M = Mn (**1**), Cd (**2**); TPA = tris(2-pyridylmethyl)amine). The metal centers were strategically chosen to promote the formation of discrete molecules rather than extended chains. Compound **1**, which contains an almost linear {Mn−O=U=O−Mn} core, exhibits SMM behavior with a relaxation barrier of 81 ± 0.5 K—the highest reported for a mono-uranium system—arising from intramolecular Mn–U exchange interactions combined with the high Ising anisotropy of the uranyl(V) moiety. Compound **1** also exhibits an open magnetic hysteresis loop at temperatures less than 3 K, with a significant coercive field of 1.9 T at 1.8 K.*

Uranium compounds have been identified as attractive candidates in the search for new molecules displaying slow magnetic relaxation of a purely molecular origin (i.e. single-molecule magnets, or SMMs).[1] The high magnetic anisotropy of the uranium ion over a range of oxidation states, combined with its ability to engage in strong magnetic exchange interactions with other metal centers, makes it particularly promising for the development of SMMs with barriers to spin reversal of a magnitude sufficient to observe hysteresis at workable temperatures—a crucial prerequisite for the use of SMMs in molecular devices.[2]

Over the last five years, SMM behavior has been observed in mono- and dinuclear compounds containing the highly anisotropic U^{III} ion.[3] Slow magnetic relaxation under applied fields and at low temperatures has been reported for compounds containing mono-oxo and dioxo U^{V} units.[4] These results suggest that the highly anisotropic $5f^1$ UO_2^+ uranyl cation could be used to build improved SMMs by incorporating it into exchange-coupled heterometallic 3d–5f assemblies with high ground-state spin values.

Unfortunately, the rational design of supramolecular multimetallic assemblies of uranium is extremely challenging because of its highly variable coordination number and geometry. As a result, the supramolecular chemistry of uranium is underdeveloped,[5] and there are relatively few polynuclear complexes exhibiting unambiguous magnetic exchange interactions.[6] In particular, strategies to generate polynuclear complexes containing 5f and 3d metal centers remain especially limited.[7]

However, uranyl(V) oxo groups have been shown to bind easily to other metal cations, leading to the formation of homo- and heterometallic supramolecular assemblies.[6e,f,8] Perhaps most importantly, this interaction, commonly referred to as a cation–cation interaction (CCI), has been shown to provide an efficient pathway for magnetic exchange.[6e,f,8a,d,e,9]

To date, only one discrete polymetallic 3d–5f cluster exhibiting exchange-coupled SMM behavior has been established.[8f] This large $\{U_{12}Mn_6\}$ wheel-shaped uranyl(V) cluster exhibits an open magnetic hysteresis loop at low temperatures (below 4 K), and has a non-zero coercive field.[8f] However, the large size and complicated nature of the assembly precludes a programmed modulation of the overall geometry and of the identity of the 3d ion, hampering further investigations into any magneto–structural relationships that might enable us to tune the SMM properties.

Herein, we present the self-assembly of a novel trinuclear 3d–5f $\{UO_2Mn_2\}$ complex that is only the second example of a uranium-based exchange-coupled SMM, and the first to contain only one uranyl ion. The $\{UO_2Mn_2\}$ complex exhibits a large barrier to relaxation of 81 ± 0.5 K, likely as a result of strong intramolecular U–Mn exchange interactions combined with the high Ising anisotropy of the uranyl(V) dioxo group. It

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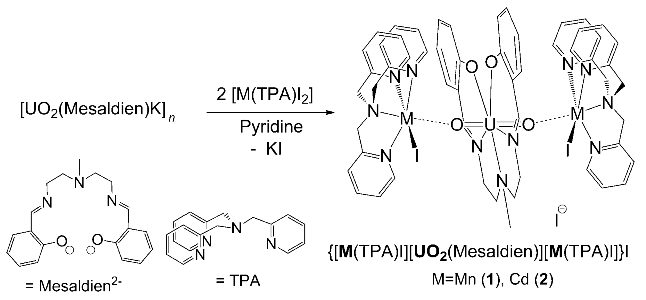
also shows an open magnetic hysteresis loop at temperatures less than 3 K, with a coercive field of 1.9 T at 1.8 K.

Two trinuclear 3d–5f complexes were assembled using a salt metathesis reaction of the polymeric uranyl(V) complex, $[UO_2(Mesaldien)K]_n$[10] (Mesaldien = *N*,*N′*-(2-aminomethyl)diethylenebis(salicylidene imine)), with strategically chosen TPA-capped complexes (TPA = tris(2-pyridylmethyl)amine) of the d-block ions Mn^{II} (**1**) and Cd^{II} (**2**). We anticipated that the association of the high spin of the Mn^{II} ion to the high Ising anisotropy of the uranyl group[8c] would lead to SMM behavior with a high relaxation barrier.[8f] The {M−O=U=O−M} trimers, which maintain their structure in pyridine solution, are formed by the linear cation–cation interaction of the two uranyl(V) oxo groups with the two d-block cations.

The reaction of $[UO_2(Mesaldien)K]_n$[10] with two equivalents of $[M(TPA)I_2]$ (M = Mn,[11] Cd) in pyridine (Scheme 1) leads to the substitution of the oxo-bound potassium cation by a TPA-bound manganese ion, and to the disruption of the polymeric structure of $[UO_2(Mesaldien)K]_n$. The reaction yields the stable trinuclear compounds $[\{[M(TPA)I][UO_2(Mesaldien)][M(TPA)I]\}I]$ (M = Mn (**1**), Cd (**2**)) in 60–65 % yield. Single crystals of **1**.3Py suitable for X-ray diffraction were obtained by slow diffusion of hexane into a pyridine solution of **1**. The two complexes are stable in the solid state and in pyridine or acetonitrile solution for months under an argon atmosphere. Moreover, ^1H and PFGSTE NMR spectroscopy and ESI mass spectrometry studies show that the two complexes retain their trimeric structure in solution (PFGSTE NMR = pulsed field-gradient stimulated echo NMR).



Scheme 1. The synthesis of 3d–5f trinuclear complexes **1** and **2**.

The neutral tripodal tetradentate ligand TPA was used to block the coordination sphere of the Mn^{2+} cations to prevent the formation of 1D coordination polymers.[4b] Indeed, the choice of the capping ligand is crucial to determine the metal nuclearity of the final structure.

The structures of complexes **1** and **2** consist of two $[M(TPA)I]^+$ cations bound to the two oxo groups of the $[UO_2(Mesaldien)]^-$ anion in a linear cation–cation interaction (Figure 1). In both compounds the uranium atoms are heptacoordinate with a slightly distorted pentagonal bipyramid geometry, with the uranium centers coordinated to two uranyl oxygen atoms and the five donor atoms of the $Mesaldien^{2-}$ ligand in the equatorial plane. The transition metal centers are hexacoordinate, with a slightly distorted octahedral geometry defined by the four nitrogen atoms of the TPA ligand, one oxygen atoms from the uranyl(V) group, and a coordinated iodide anion.

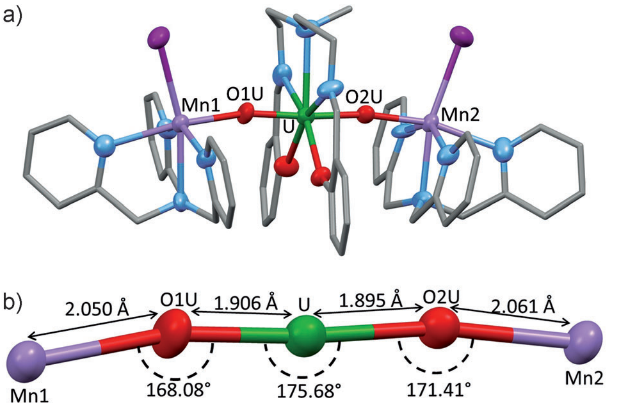


Figure 1. a) Molecular structure of $\{UO_2Mn_2\}$ with hydrogen atoms and cocrystallized solvent molecules omitted for clarity. b) View of the linear core with corresponding bond lengths and angles. Atom colors: C (gray), O (red), Mn (violet), N (light blue), I (purple), U (green.)

In both complexes, the mean U=O bond lengths lie in the range of the values typically observed for uranyl(V) complexes, with the uranyl–metal interaction resulting in a slight lengthening of the bond (1.901 Å in **1**, 1.887 Å in **2**). The mean $Mn-O_{yl}$ (where O_{yl} is the uranyl oxygen atom) bond length in **1** is 2.055(6) Å, significantly shorter than that found in the heteronuclear $\{U_{12}Mn_6\}$ wheel (2.15(2) Å)[8f] and in a heterodimetallic uranyl(VI)–manganese(II) complex (2.163(4) Å).[12] In compound **2**, the $Cd-O_{yl}$ distance (2.201(16) Å) is slightly shorter than that found in a Cd–uranyl(V) polymer complex (2.28(2) Å),[13] and in a heterodimetallic U^{VI}/Cd^{II} system (2.252(4) Å).[13] The mean U-O-M angle measures 169.7(1.7)° in **1** and 168.7(8)° in **2**, whereas the M-U-M angle is 173.77(5)° in **1** and 174.86(6)° in **2**. The deviation from linearity arises from the presence of intramolecular hydrogen bonds between the protons on the TPA ligand and the oxygen atoms of the $Mesaldien^{2-}$ ligand. The mean intramolecular U−M bond lengths are 3.939(5) Å in **1** and 4.072(2) Å in **2**. The Mn−Mn intramolecular distance in **1** is 7.8666(4) Å and the intramolecular distance Cd−Cd in **2** is 8.1354(6) Å. The shortest intermolecular U−U, U−M, and M−M distances are 10.9469(4), 8.7589(4), and 7.6296(4) Å in **1** and 11.0107(7), 8.6904(7), and 7.4179(5) Å in **2**, respectively.

Direct current (dc) magnetic susceptibility measurements were performed on polycrystalline samples of **1** and **2** over the temperature range 1.8–300 K (Figure 2). The measured χT value (χ = molar magnetic susceptibility, T = temperature) of 0.32 $cm^3\,K\,mol^{-1}$ for **2** at room temperature, equating to 1.55 μ_B per uranyl(V) ion (the Cd^{II} ion is diamagnetic), is significantly smaller than anticipated for an isolated $^2F_{5/2}$ uranium(V) ion (0.80 $cm^3\,K\,mol^{-1}$, assuming $g_J = 6/7$ and a fully unquenched orbital momentum). This indicates that not all crystal field components of the ground multiplet state are fully occupied at 300 K, in agreement with previous reports.[8c,14] The χT value decreases on cooling to approximately 0.09 $cm^3\,K\,mol^{-1}$ at 1.8 K (Figure 2) because of depopulation of the U^V excited Stark sublevels.[4b,8c]

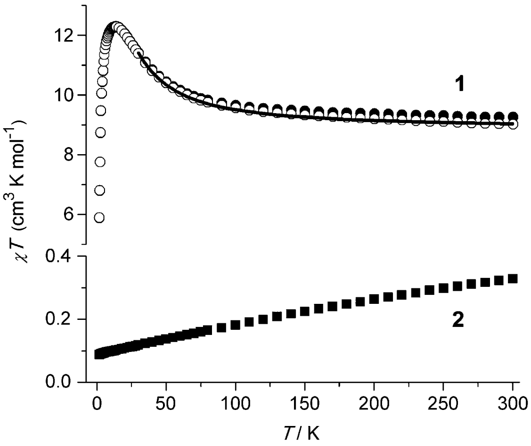


Figure 2. Plots of χT values versus temperature (T) for polycrystalline samples of **1** (●) and **2** (■), measured in a 0.5 T dc field. Open circles (○) correspond to the χT values after subtraction of the $\{UO_2Cd_2\}$ data from the $\{UO_2Mn_2\}$ data, to which a value of 0.094 cm^3 K mol^{-1} has been added as the spin-only contribution of the U^V center. Solid line: the best fit of the data to Equation (1) with $J = +7.5$ cm^{-1}.

For **1**, the χT value is 9.2 cm^3 K mol^{-1} at room temperature, close to the expected value of 9.05 cm^3 K mol^{-1} for two noninteracting Mn^{II} ions ($S = 5/2$, $g_{iso} = 2$, $\chi T = 4.375$ cm^3 K mol^{-1}) and one uranium(V) ion. This χT value increases smoothly with decreasing temperature down to 100 K, and then more rapidly, reaching a maximum of 12.5 cm^3 K mol^{-1} at 12 K, after which it decreases to a value of 6 cm^3 K mol^{-1} at 1.8 K. The increase of χT values with decreasing temperature indicates the occurrence of magnetic exchange coupling between uranium and manganese ions in **1**. The presence of a Mn–Mn interaction is ruled out because the Mn⋯Mn separation is significantly larger (7.912(3) Å) than those reported for compounds presenting magnetic interaction between the Mn ions (3.2–3.4 Å).[15] The downturn in χT values below 12 K is the result of zero-field splitting (zfs) effects associated with the resulting high-spin ground state.

As the $\{UO_2Cd_2\}$ compound **2** is isostructural to **1**, but features two diamagnetic Cd^{II} centers instead of the two $S = 5/2$ Mn^{II} centers in **1**, it can be used as a reasonable model to establish the contribution arising from spin–orbit and ligand field effects associated with the U^V center. Thus, subtraction of the experimental χT values of **2** from the experimental χT values of **1** removes any contribution from the U^V ion to the overall magnetism of **1**, leaving only the magnetic contribution of the two Mn^{II} ions together with any remnants of magnetic exchange coupling. Subsequent addition to the $\Delta\chi T$ data of a temperature-independent value of 0.094 cm^3 K mol^{-1}, to account for the spin-only ($S = 1/2$) contribution of the U^V center (assuming $g_U = 1$), enables the use of the isotropic spin Hamiltonian Equation (1) to model the Mn–U interaction in **1**. A similar procedure was used by Long et al. when modelling the exchange coupling within the trimetallic clusters (cyclam)M[(μ-Cl)U^{IV}(Me$_2$Pz)$_4$]$_2$ (M=Co^{II}, Ni^{II}, Cu^{II}; cyclam = 1,4,8,11-tetraazacyclotetradecane).[2a,7c]

$$H = -2J(S_{Mn1}S_U + S_U S_{Mn2}) \qquad (1)$$

The best fit of the experimental data above 30 K, using Equation (1) in MAGPACK,[16] yielded $J = +7.5$ cm^{-1}, $g_{Mn} = 2$, and $g_U = 1$ (see solid line in Figure 2), where J measures the exchange coupling between adjacent Mn^{II} and U^V centers. The positive sign of J indicates ferromagnetic coupling. This value falls in the range of the values of exchange constants calculated for the few other reported complexes Co^{II}U$_2^{IV}$ and Ni^{II}U$_2^{IV}$ (2.8–49 cm^{-1}) which also present ferromagnetic 3d–5f coupling.[7c,17]

The molar magnetization (M) curves as a function of magnetic field for **1** do not show signs of saturation under magnetic fields up to 7 T, and the $M(H/T)$ curves (where H is the magnetic field strength) cannot be superimposed (see the Supporting Information), indicative of significant magnetic anisotropy and/or low-lying excited states. The magnetization dynamics for **1** were investigated by alternating current (ac) magnetic susceptibility measurements as a function of temperature (1.8–10 K) and frequency ($\nu = 0.1$–1400 Hz), in a zero dc field (Figure 3 and the Supporting Information). Both the in-phase (χ') and out-of-phase (χ'') components of the ac susceptibility show strong frequency dependence below approximately 7.5 K, and maxima are observed in $\chi''(T)$. These observations are indicative of slow relaxation of the molecular magnetization, and thus of single-molecule-magnet (SMM) behavior.

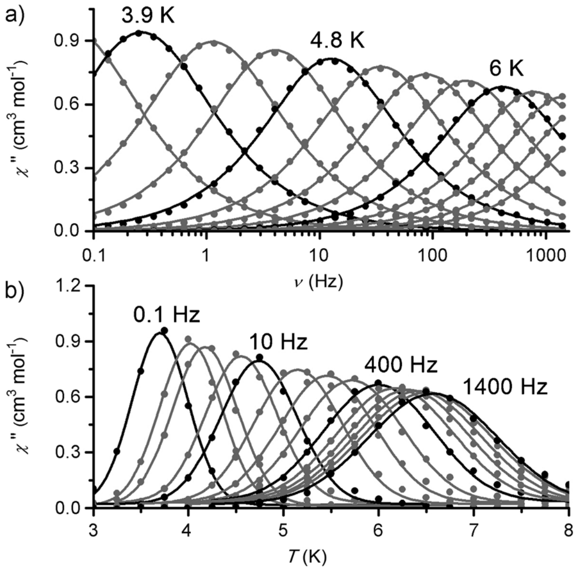


Figure 3. a) Frequency and b) temperature dependence of the out-of-phase ac susceptibility of **1** measured at zero dc field and 1.55 G ac field oscillating at frequencies in the range 0.1–1400 Hz. The solid lines correspond to fits to the Debye (a) and Gaussian (b) models.

The relaxation time (τ) was determined from both $\chi_M''(T)$ values and from Argand (χ_M'' versus χ_M') diagrams. For the Argand diagrams, semicircular Cole–Cole plots were obtained at fixed temperatures between 3.9 and 6.6 K. The plots could be fitted to a generalized Debye model[18] with an α parameter in the range of 0.01–0.15, consistent with a narrow distribution of relaxation times (see the Supporting Information). A plot of the derived relaxation time constants

(τ) as $\ln(\tau)$ versus T^{-1} is linear in this temperature range, and hence can be fitted to the Arrhenius law $\tau = \tau_0\exp(\Delta E/k_B T)$, giving an effective thermal energy barrier to magnetization relaxation $\Delta E = 81 \pm 0.5$ K with a pre-exponential factor of $\tau_0 = 5.02 \times 10^{-10}$ s (Figure S17 in the Supporting Information). This is the highest reported for trinuclear complexes containing 3d ions. Moreover this value remains high compared to the barrier found for the large 3d–5f $\{U_{12}Mn_6\}$ SMM (142 K) despite the presence of only three metal ions. Slow relaxation of the magnetization as a result of anisotropic U^V units is also observed for **2** at low temperatures, under an applied dc field (Supporting Information). SMM behavior arising from monometallic U^V complexes has been previously reported.[4a,14]

Below 3 K, clear hysteresis loops which are due to slow magnetic relaxation are observed in the $M(H)$ data, for both solid-state and solution samples of **1** (Figure 4). The observation of a hysteresis loop for solutions of **1** in pyridine where the complex retains its trinuclear structure confirms the molecular origins of the SMM behavior. Within the same temperature range, a divergence between zero-field-cooled (ZFC) and field-cooled (FC) magnetizations as a function of temperature is observed (Figure S11). The width of the hysteresis increases with increasing the field sweep rate (Figure 4a) and with decreasing temperature (Supporting Information), as would be expected for a single molecule magnet. A remarkable coercive field of 1.9 T is obtained at 1.8 K, and a remnant magnetization of 4.6 μ_B is preserved at 0 T. The larger coercive field observed in solution is probably because of the presence of weaker dipolar interactions compared to the solid state. A partial loss of the magnetization because of quantum tunneling relaxation occurs at very low temperatures, and a sharp step at 0 T is indeed observed. These features are indicative of single-molecule magnetism. The remnant magnetization disappears at approximately 3.1 K, corresponding to the blocking temperature of the material.

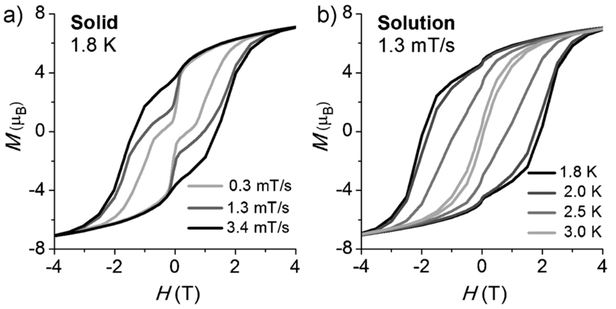


Figure 4. Hysteresis loops for a) the polycrystalline sample of **1** and b) the pyridine solution of **1**, at the indicated temperatures and field sweep rates.

In conclusion, we have identified a versatile route to the programmed assembly of 3d–5f trinuclear heterodimetallic complexes from the pentavalent uranyl ion. An appropriate choice of the ligand which binds to the 3d metal ion allows for a strong cation–cation interaction to take place between the two uranyl(V) oxo groups and the two 3d metal centers, affording the desired trinuclear complex and preventing further oligomerization. Compound **1** is only the second example of a uranium-based polymetallic complex exhibiting SMM behavior and open hysteresis. A comparative study of the magnetic properties of the isostructural cadmium analogue **2** unambiguously demonstrates that the SMM behavior of **1** is a property of the trinuclear entity. The SMM behavior of **1** is associated with its high-spin ground state resulting from ferromagnetic coupling between Mn^{II} and U^V ions, and a large Ising-type anisotropy defined by the O=U=O axis. The effective energy barrier to the reversal of magnetization of 81 ± 0.5 K is significantly larger than any reported for uranium-based SMMs, driving their behavior from single-ion effects. This highlights the importance of using anisotropic UO_2^+ as a bridging component for the construction of SMMs. The role of the 3d metal anisotropy, if any, is yet to be understood. More studies, including EPR measurements, will be necessary to clarify this aspect, and the investigation should be expanded to other mixed uranyl–transition metal complexes. The synthetic approach used in this work should be easily applicable to other metals through the careful tuning of the supporting ligand. We anticipate that a large library of trinuclear 3d–5f complexes will be afforded by this method, and that this will facilitate magneto-structural studies on uranium systems, which might ultimately lead to the design of uranium-based SMMs with vastly improved properties.

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