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VIP $[\mathrm{U^{III}}\{\mathrm{N(SiMe_2}t\mathrm{Bu)_2}\}_3]$: A Structurally Authenticated Trigonal Planar Actinide Complex

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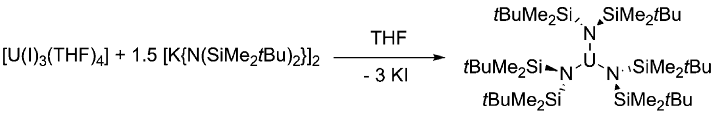
Abstract: We report the synthesis and characterization of the uranium(III) triamide complex $[\mathrm{U^{III}(N^{**})_3}]$ [**1**, $\mathrm{N^{**}=N(SiMe_2}t\mathrm{Bu)_2{}^-}$]. Surprisingly, complex **1** exhibits a trigonal planar geometry in the solid state, which is unprecedented for three-coordinate actinide complexes that have exclusively adopted trigonal pyramidal geometries to date. The characterization data for $[\mathrm{U^{III}(N^{**})_3}]$ were compared with the prototypical trigonal pyramidal uranium(III) triamide complex $[\mathrm{U^{III}(N'')_3}]$ ($\mathrm{N''=N(SiMe_3)_2{}^-}$), and taken together with theoretical calculations it was concluded that pyramidalization results in net stabilization for $[\mathrm{U^{III}(N'')_3}]$, but this can be overcome with very sterically demanding ligands, such as N**. The planarity of **1** leads to favorable magnetic dynamics, which may be considered in the future design of $\mathrm{U^{III}}$ single-molecule magnets.

Investigations into low-coordinate metal complexes (defined herein as coordination number, CN < 4) are legion, because they can exhibit interesting properties,[1] including small-molecule activation chemistry[2] and single-molecule magnet (SMM) behavior.[3] Low CN complexes usually contain sterically demanding ligands to prevent oligomerization,[1] in which bulky monodentate amides are frequently utilized.[4] The bulky silylamide $\{\mathrm{N(SiMe_3)_2}\}^-$ (N″) has provided landmark low CN complexes; for example, three-coordinate $[\mathrm{M^{III}(N'')_3}]$ complexes of Group 13 (M = Al, Ga, In, Tl)[5] and first row d-block (M = Ti–Co)[6] metals are trigonal planar (D_{3h}) in the solid state, but Group 3,[6a,7] lanthanide (Ln),[7] and actinide (An)[8] $[\mathrm{M^{III}(N'')_3}]$ complexes exhibit trigonal pyramidal (C_{3v}) solid-state geometries, although they have zero dipole moment in solution, inferring that they may become planar in this phase.[9] Pyramidal geometries persist for $[\mathrm{Ln^{III}(N'')_3}]$ (Ln = Ce, Pr) in the gas phase,[10] but $[\mathrm{Sc^{III}(N'')_3}]$ vapors are D_{3h}, with crystalline/gas-phase discrepancies for this complex attributed to crystal-packing effects.[11] It is noteworthy that complexes, such as $[\mathrm{Ln^{II}(N'')(\mu\text{-}N'')_2Na}]$ (Ln = Eu, Yb) and $[\mathrm{Sm^{II}(N'')(\mu\text{-}N'')_2M}]$ (M = Na, K), have trigonal planar Ln coordination spheres,[12] but this geometry has not been previously observed in An complexes.

f-Block metal centers favor high CNs, because Ln and An cations have relatively large ionic radii and bonding regimes that are dominated by electrostatic contributions.[13] Low CN $\mathrm{U^{III}}$ chemistry is burgeoning, driven by interesting small molecule activation reactions[14] and intrinsic SMM behavior.[15] Structurally characterized three-coordinate An complexes to date adopt exclusively trigonal pyramidal geometries rather than trigonal planar or T shaped (C_{2v}),[16] although matrix isolation experiments[17] and calculations[18] have shown that monomeric $\mathrm{UO_3}$ is T shaped. Both covalent[19] and electrostatic[10] arguments account for the trigonal pyramidal geometry of $[\mathrm{U^{III}(N'')_3}]$,[8,20] hence, the most influential factor of these two for causing pyramidalization has never been established. Herein, we report the structurally characterized An complex, $[\mathrm{U^{III}(N^{**})_3}]$ (**1**, $\mathrm{N^{**}=N(SiMe_2}t\mathrm{Bu)_2{}^-}$), which adopts an unprecedented trigonal planar geometry for an actinide triamide complex. Complex **1** is closely related to $[\mathrm{U^{III}(N'')_3}]$, allowing the contributions to pyramidalization to be assessed, together with the impact of geometry on magnetic (including dynamic) and electronic properties of $\mathrm{U^{III}}$ complexes, for the future rational design of useful An materials.



Scheme 1. Synthesis of **1**.

Complex **1** was prepared by a modification of the revised synthesis of $[\mathrm{U^{III}(N'')_3}]$.[8c] Compound $[\mathrm{U^{III}(I)_3(THF)_4}]$[8c] was reacted with 1.5 equivalents of $[\mathrm{K\{N(SiMe_2}t\mathrm{Bu)_2\}]_2}$ in THF, followed by work-up and recrystallization from hexane to give **1** as dark purple needles in 62% yield (Scheme 1).[21] Absorbances in the FTIR spectrum of **1** at $\tilde{\upsilon} = 950$, 825, and 761 cm⁻¹ are attributed to the $\mathrm{UNSi_2}$ stretching modes of the silylamide ligand. The asymmetric stretch (950 cm⁻¹) is 40 cm⁻¹ lower than that observed for $[\mathrm{U^{III}(N'')_3}]$ (990 cm⁻¹),[8a] which is of a similar magni-

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tude to the differences between previously reported planar and pyramidal [M(N″)$_3$] MNSi$_2$ asymmetric stretches (ca. 50 cm^{-1}).[5b,6a]

The ^{1}H NMR spectrum of **1** exhibits two resonances at $\delta=3.8$ ($\nu^{1}/_{2}=206$ Hz) and -47.0 ppm ($\nu^{1}/_{2}=4597$ Hz) in a 54:36 ratio that are assigned to the *t*BuSi and Me$_2$Si protons, respectively. The Me$_2$Si resonance of **1** is much broader than the analogous resonance for [U^{III}(N″)$_3$] (δ -11.4, $\nu^{1}/_{2}=15$ Hz),[8] but variable-temperature (VT) studies gave a sharper resonance at 353 K ($\delta=-32.9$ ppm, $\nu^{1}/_{2}=266$ Hz).[21] A wide-scan ^{13}C NMR spectrum of **1** exhibited two resonances for the Me$_2$Si ($\delta=-2.1$ and 1.5 ppm) and *t*BuSi quaternary carbons ($\delta=18.2$ and 32.0 ppm), but only one for the *t*BuSi primary carbons ($\delta=26.4$ ppm). In contrast, in the ^{13}C NMR spectrum of [U^{III}{N(SiPhMe$_2$)$_2$}$_3$], the Me$_2$Si group resonates at $\delta=-57.1$ ppm.[22] A resonance was observed in the ^{29}Si NMR spectrum of **1** at δ -296.0 ppm ($\nu^{1}/_{2}=73$ Hz), which has not been reported for similar systems,[8,22] but is typical for a U^{III} complex.[23]

The electronic absorption spectrum of **1**[21] exhibited 5f$^3\rightarrow$ 5f^{2}6d^1 transitions at 20 000 ($\varepsilon=776$ M^{-1}cm^{-1}) and 22 500 cm^{-1} ($\varepsilon=770$ M^{-1}cm^{-1}) that are typical of U^{III}[24] and comparable to a broad absorption observed for [U^{III}{N(SiPhMe$_2$)$_2$}$_3$] at 21 500 cm^{-1} ($\varepsilon=430$ M^{-1}cm^{-1}).[22] In the 7 000–13 000 cm^{-1} region, weak Laporte forbidden 5f$\rightarrow$5f transitions were observed ($\varepsilon=15$–64 M^{-1}cm^{-1}).[25] Similar weak absorptions were observed for most U^{III} complexes, such as [U(I)$_3$(THF)$_4$][8c,26] and [U^{III}{N(SiPhMe$_2$)$_2$}$_3$],[22] and strong absorptions in this region are very rare.[27]

The crystal structure of **1** was determined and is depicted in Figure 1, with selected metrical parameters.[28] Complex **1** crystallizes in the *C*2/*c* space group, with a twofold axis bisecting the U(1)–N(1) bond. This contrasts to [Fe(N″)$_3$],[9] [Eu^{III}(N″)$_3$],[29] [U^{III}(N″)$_3$],[8d] and [Pu^{III}(N″)$_3$],[8e] which all crystallize exclusively in the *P*3$_1$*c* space group, and [U^{III}{N(SiPhMe$_2$)$_2$}$_3$], which crystallizes in *R*3.[22] The U atom of **1** is almost ideally trigonal planar, with U–N bonds that are statistically identical within experimental uncertainty [U-N range 2.403(3)–2.415(6) Å]. These distances are longer than those observed in [U^{III}(N″)$_3$] [2.320(4) Å][8d] and [U^{III}{N(SiPhMe$_2$)$_2$}$_3$] [2.34(2) Å],[22] which can be attributed to the greater interligand repulsion in **1** arising from the sterically demanding *t*Bu groups. The U centroid/N(1)-N(2)-N(2A) mean plane distance in **1** is 0.008(2) Å, and the N-U-N bond angles (range 119.1(2)–120.47(9)°) sum to 360°; in contrast, [U^{III}(N″)$_3$] and [U^{III}{N(SiPhMe$_2$)$_2$}$_3$] exhibit U centroids 0.456(1) and 0.874 Å from the N$_3$ planes, and the N-U-N angles average 116.24(7) (Σ angles 348.72(7)°) and 106.88° (Σ angles 320.64°), respectively.[8d,22] The UNSi$_2$ fragments of **1** are essentially planar and all bisect the UN$_3$ plane (range 53.23–61.35°) to form a molecular propeller.

The pyramidal geometries of [U^{III}(N″)$_3$] and [U^{III}{N(SiPhMe$_2$)$_2$}$_3$] are predicted by the polarized-ion model, whereby net stabilization was achieved by dipole formation.[8d,22] [U^{III}(N″)$_3$] exhibits unequal U-N-Si angles (108.50(7) and 125.25(7)°), because one Si–C bond for each N″ ligand is relatively close to the U center [U⋯C$_\gamma$ 3.05 Å; U⋯Si 3.29 Å].[8d] These can be attributed to stabilizing agostic M⋯Si–C$_\gamma$ interactions, as have been discussed for [U^{III}{CH(SiMe$_3$)$_2$}$_3$][30] and [Sm^{III}(N″)$_3$].[31] The shortest U⋯C$_\gamma$ and U⋯Si distances in **1** are 3.119–3.301 Å and 3.433–3.510 Å, respectively, and they are not correctly orientated to interact with the U center. Although there is no evidence for agostic U⋯Si–C$_\gamma$ interactions in **1**, stabilizing U⋯C–H contacts cannot be discounted.

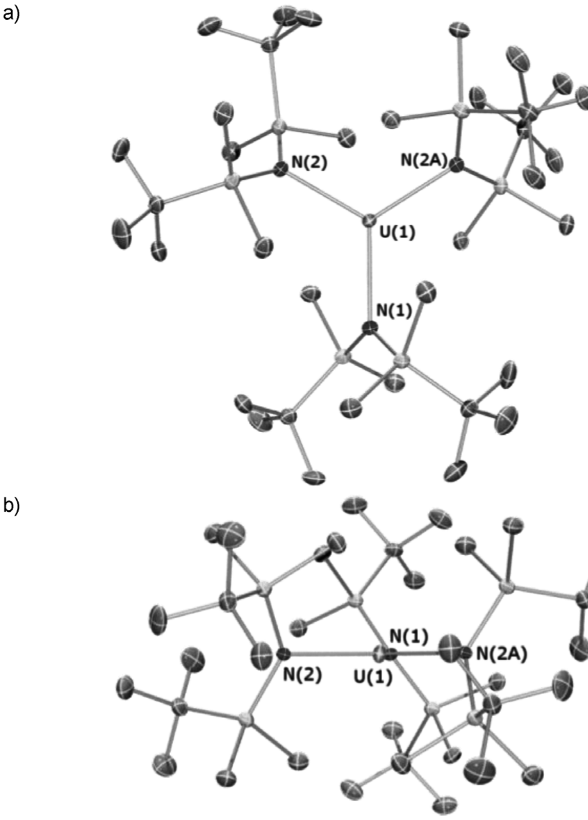

Figure 1. Molecular structures of **1** a) top view and b) along twofold axis, with selected atom labelling. Displacement ellipsoids are set at the 40 % probability level, and hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [°]: U(1)–N(1) 2.403(3), U(1)–N(2) 2.415(6); N(1)-U(1)-N(1′) 119.05(19), N(1)-U(1)-N(2) 120.47(9).

Unrestricted DFT calculations were carried out on full models of **1** and [U^{III}(N″)$_3$].[21] The geometry-optimized structures reproduce the experimental structures with good agreement, despite the slight deviation from planarity for the model of **1** (discrepancies attributed to this being a gas-phase calculation, which does not account for crystal-packing forces), providing qualitative models (bond lengths within 0.05 Å, angles within 1°, U centroid/N$_3$ mean plane distance: **1** 0.132 Å, [U^{III}(N″)$_3$] 0.393 Å). In both models, the HOMO, HOMO-1 and HOMO-2 represent the three unpaired U^{III} 5f electrons (**1**: 93.93, 94.71, 90.09; [U^{III}(N″)$_3$] 86.81, 86.32, 84.17 % U 5f, respectively). Both models exhibit essentially insignificant degrees of U 6d/5f orbital contributions to the U–N bonds, with the HOMO-3, HOMO-4. and HOMO-5, representing the π components (**1**: 5.27/0, 1.57/0, 0/1.31; [U^{III}(N″)$_3$] 4.29/0, 0/2.06, 1.63/1.39 % U 5f/6d, respectively) and the HOMO-6, HOMO-7, and HOMO-8 the σ components (**1**: 0/2.29, 0/2.12, 1.20/0; [U^{III}(N″)$_3$] 0/5.04, 0/5.26, 2.14/0 % U 5f/6d, respectively). This concurs with gas-phase photoelectron spectroscopy (PES) studies of

[U(N″)$_3$], which have shown that π bonding between the ligand and U center is insignificant in this complex.[32] The calculated uranium spin densities (MDC-m α spin, **1** = −3.26; [U^{III}(N″)$_3$] = −3.26) are identical, which also supports similar bonding patterns for **1** and [U^{III}(N″)$_3$].

Ab initio calculations on [An^{III}(CH$_3$)$_3$] (An = U, Np, Pu)[33] and [An^{III}(NH$_2$)$_3$] (An = U, Np)[34] have shown that the involvement of An 6d orbitals in the U–X (X = C, N) σ components may be associated with pyramidalization in the absence of steric contributions. Thus, given the similar bonding within **1** and [U^{III}(N″)$_3$] together with the small U 6d/5f contributions to the U–N σ and π components, we suggest that the experimentally determined trigonal planar geometry of **1** results from steric interactions involving the large N** ligands. These interactions could predominate over crystal packing forces, which are often only approximately 10 kJ mol^{-1}.[35] We conclude that there are minor differences in bonding between **1** and [U^{III}(N″)$_3$], therefore, the planar geometry of **1** derives principally from steric effects involving the ligands.

The solution magnetic moment of **1** was calculated to be 2.59 μ_B in [D$_6$]benzene at 298 K by using the Evans method.[36] Magnetometry measurements on a powdered sample of **1** suspended in eicosane gave a magnetic susceptibility temperature product, χT, of 1.07 cm^3 K mol^{-1} (2.92 μ_B) at 298 K,[21] which corresponds well with the solution measurement considering weighing errors and the difference in phase. These values are lower than for a free-ion 5f^3 $^4I_{9/2}$ ground state (3.69 μ_B), because not all crystal field levels are thermally occupied,[37] but are typical for U^{III} complexes described in the literature (range 2.13–4.63 μ_B).[8,15,22,25,26,30,38] The χT value of **1** decreases to 0.41 cm^3 K mol^{-1} at 2 K; ac measurements give a low-temperature plateau in the in-phase $\chi' T$ at 0.48 cm^3 K mol^{-1}[21] consistent with thermal depopulation into a Kramers doublet ground state.[3,13] Low-temperature EPR spectra of **1** are consistent with U^{III},[27] and simulation gives $g_{\mathrm{eff}} = 3.55$, 2.97, and 0.553 for the ground Kramers doublet (the latter is observed at high field at X-band, but is beyond the magnetic field range at Q band; Figure 2 a).

Compound [U^{III}(N″)$_3$] is an SMM,[15] hence, we have performed low-temperature ac measurements on **1** to probe differences in the dynamic magnetic behavior as a result of the higher symmetry. Compound **1** is also an SMM, with clear frequency-dependent behavior (Figure 2 c and d).[21] Under the optimal dc field of 600 G, the magnetization relaxes much slower than in [U^{III}(N″)$_3$], and maxima in the out-of-phase susceptibility $\chi''(T)$ are seen to significantly higher temperatures for **1** than for [U^{III}(N″)$_3$] at equivalent frequencies (e.g., 3.5 vs. 2.1 K, respectively, for 1.4 kHz). An Arrhenius treatment[21] of the higher-temperature ac data gives an energy barrier of $U_{\mathrm{eff}} = 21.4 \pm 0.2$ K for **1**. Although this is lower than that reported for [U^{III}(N″)$_3$] (31 K), the latter value was derived from an extremely limited temperature range[15] and should be treated with some caution. The relaxation time (τ) at 2 K is 2.6 ms for **1**; from the previously reported data[15] we find 0.3 ms for [U^{III}(N″)$_3$] at 2 K, an order of magnitude quicker. The pre-factor τ_0 for **1** is greater by four orders of magnitude (3.1×10^{-7} cf. 10^{-11} s for [U^{III}(N″)$_3$]).[15] Moreover, the frequency dependence of χ' and χ'' at 1.8 K for **1**[21] reveal a single relaxation process with a narrow distribution in relaxation times ($\alpha = 0.001$–0.03 from Cole–Cole analysis), an order of magnitude lower than in [U^{III}(N″)$_3$] ($\alpha = 0.09$–0.34).[15] In fact, the difference in dynamics is sufficient that magnetization hysteresis is observed for **1** at 1.8 K on a conventional superconducting quantum interference device (SQUID) magnetometer (Figure 2 b), while it is not for [U^{III}(N″)$_3$].

In the trigonal planar geometry of **1**, with no axial ligands, we expect a low J_z state of U^{III} to be stabilized by the crystal field. This is supported by the EPR analysis: if we assume a $^4I_{9/2}$ ground term,[39] with $g_J = 8/11$, the $J_z = \pm 1/2$ doublet is calculated to have $g_{x,y} = 3.65$, $g_z = 0.73$ (all other doublets have $g_{x,y} = 0$), in good agreement with experiment. $|J_z| = 1/2$ is also the ground doublet of the (pyramidal) 4f^3 complex [Nd^{III}(N″)$_3$] from optical studies.[40] Hence, **1** and [U^{III}(N″)$_3$] are SMMs despite their easy-plane anisotropy: this highlights the complexity of interpreting f-block relaxation data,[41] particularly when relatively low (tens of K) energy barriers are involved. At this stage, we can speculate that the "cleaner" and slower relaxation of **1** compared with [U^{III}(N″)$_3$] on flattening the geometry is because of quenched mixing. In D_{3h} $|J_z| = 1/2$ cannot mix with any other doublet within the $^4I_{9/2}$ term, whereas in C_{3v} it can mix with both $|J_z| = 5/2$ and 7/2.

To conclude, we have prepared and fully characterized an unprecedented trigonal planar actinide triamide complex. Differences in the spectroscopic and magnetic data between **1** and [U^{III}(N″)$_3$] can be attributed to differences in symmetry that may be useful to consider in the future design of U^{III} SMMs with greater relaxation times. Computational analyses of **1** and [U^{III}(N″)$_3$] have shown only minor differences in their calculated bonding schemes, therefore, the energy gained by pyramidalization, which leads to favorable agostic M⋯Si–C$_\gamma$ interactions in [U^{III}(N″)$_3$],[8d,32,33] can be overcome by sterically demanding ligands, such as N**.

Experimental Section

Synthesis of 1: THF (20 mL) was added to a precooled (−78 °C) mixture of [K{N(SiMe$_2t$Bu)$_2$}]$_2$ (1.007 g, 1.5 mmol) and [U(I)$_3$(THF)$_4$] (0.907 g, 1 mmol). The reaction mixture was allowed to warm to RT slowly with stirring over 48 h, with precipitation of a pale solid. Volatiles were removed in vacuo, and the dark purple solid was extracted with hexanes (3 × 10 mL). Recrystallization from hexanes (5 mL) at −30 °C gave **1** as dark purple needles (0.605 g, 62 %).^{1}H NMR (400.13 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = -47.04$ (br s, $\nu^1/_2 = 4597$ Hz, 36 H; Si(CH_3)$_2$), 3.79 ppm (br s, $\nu^1/_2 = 206$ Hz, 54 H; SiC(CH_3)$_3$); ^{13}C{^{1}H} NMR (100.61 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = -2.13$ (Si(CH$_3$)$_2$), 1.45 (Si(CH$_3$)$_2$), 18.22 (Si*C*(CH$_3$)$_3$), 26.40 (SiC(CH$_3$)$_3$), 31.98 ppm (Si*C*(CH$_3$)$_3$); ^{29}Si{^{1}H} NMR (79.48 MHz, [D$_6$]benzene, 25 °C, TMS): $\delta = -296.04$ ppm (br. s, $\nu^1/_2 = 73$ Hz); FTIR (Nujol); $\tilde{\nu} = 1259$ (s), 1247 (s), 1002 (s), 950 (m, asym. str., UNSi$_2$), 825 (s, sym. str., UNSi$_2$), 761 (s, sym. str., UNSi$_2$), 655 (m), 604 (s) cm^{-1}; $\mu_{\mathrm{eff}} = 2.59$ μ_B (Evans method); elemental analysis calcd for C$_{36}$H$_{90}$Si$_6$N$_3$U (971.67 g mol^{-1}): C 44.5, H 9.34, N 4.33; found: C 38.29, H 9.10, N 4.22. Low carbon values were obtained upon repeating the analysis multiple times on different batches and is ascribed to **1** being a silicon-rich molecule, as was observed previously.[42]

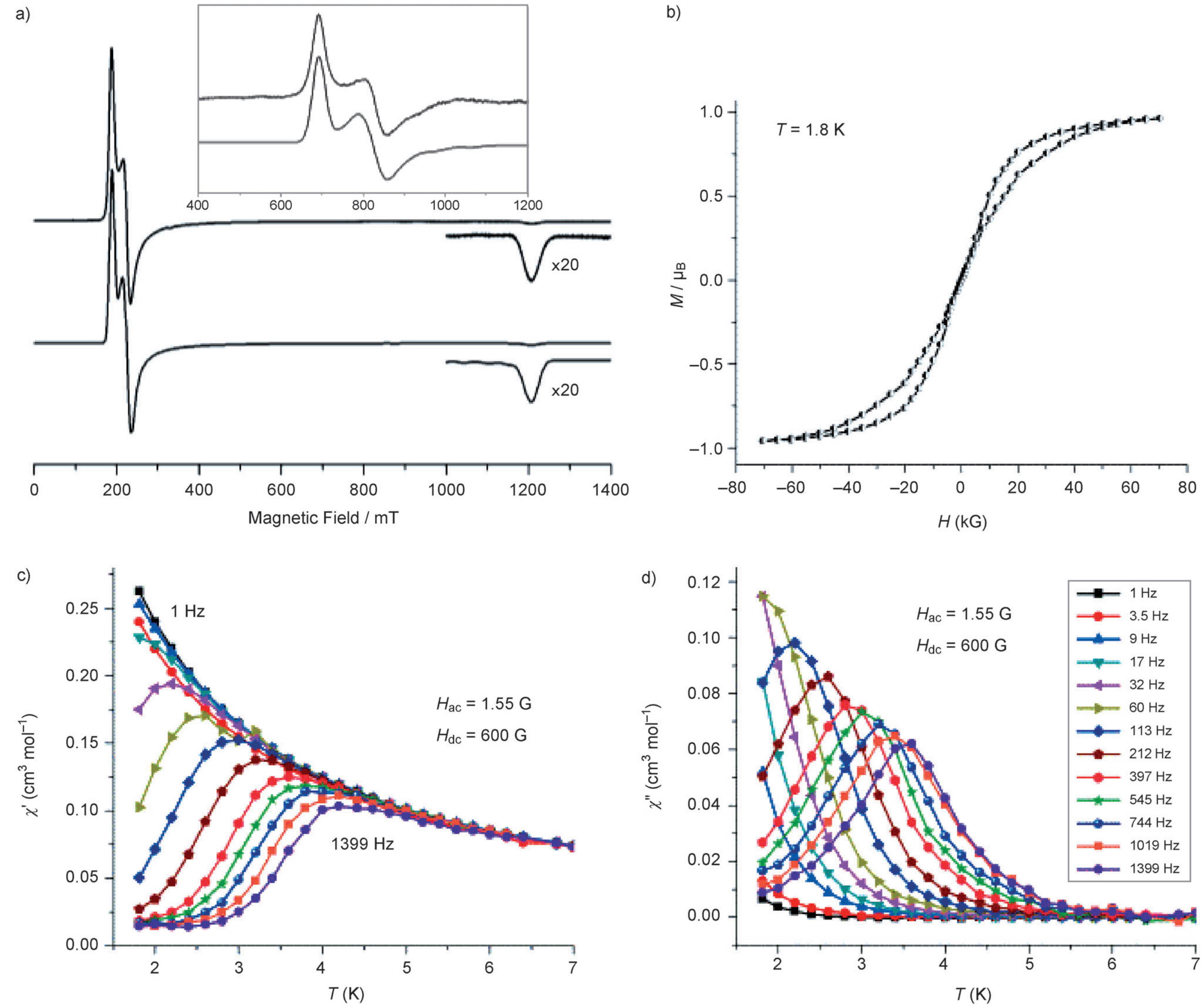

Figure 2. a) X- (9.5 GHz) and Q-band (34 GHz; inset) EPR spectra of **1** at 5 K. Lower spectra are simulations as $S_{\text{eff}} = {}^{1}/_{2}$. Magnetic-susceptibility data for **1**: b) magnetic hysteresis at 1.8 K, sweep rate 13 G s^{-1}; c) in-phase (χ'); and d) out-of-phase (χ'') components of the ac susceptibility measured in an applied dc field of 600 G and an oscillating field of 1.55 G.

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Keywords: actinides · ligand design · ligand effects · single-molecule magnets · uranium

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[28] Crystal data for **1**: $C_{36}H_{90}N_3Si_6U$, $M_r = 971.67$ g mol^{-1}, space group $C2/c$, $a = 21.7732(11)$, $b = 13.2453(8)$, $c = 17.9674(9)$ Å, $\beta = 110.972(6)^\circ$, $V = 4838.4(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.334$ g cm^{-3}; Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 3.529$ mm^{-1}, $T = 150$ K. 11360 points (5457 unique, $R_{int} = 0.0567$, $2\theta < 57.6^\circ$). Data were collected on an Agilent Technologies Supernova diffractometer and were corrected for absorption (transmission 0.926 – 1.000). The structure was solved by direct methods and refined by full-matrix least-squares on all F^2 values to give $wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2} = 0.0678$, conventional $R = 0.0486$ for F values of 5457 with $F_0^2 > 2\sigma(F_0^2)$, $S = 0.986$ for 224 parameters. Residual electron density were 1.240 maximum and -1.355 e Å^{-3} minimum. CCDC-1015959 (**1**) contains the supplementary crystallographic data for this paper. 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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