

Ligand Effects | *Very Important Paper*
VIP $[\text{U}^{\text{III}}\{\text{N}(\text{SiMe}_2\text{tBu})_2\}_3]$: A Structurally Authenticated Trigonal Planar Actinide Complex

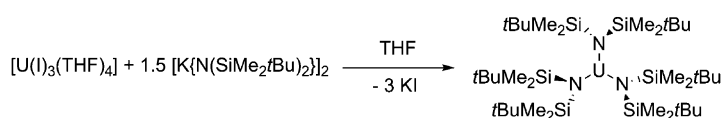
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Abstract: We report the synthesis and characterization of the uranium(III) triamide complex $[\text{U}^{\text{III}}(\text{N}^{**})_3]$ (**1**, $\text{N}^{**} = \text{N}(\text{SiMe}_2\text{tBu})_2^-$). Surprisingly, complex **1** exhibits a trigonal 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 $[\text{U}^{\text{III}}(\text{N}^{**})_3]$ were compared with the prototypical trigonal pyramidal uranium(III) triamide complex $[\text{U}^{\text{III}}(\text{N}^{\text{r}})_3]$ ($\text{N}^{\text{r}} = \text{N}(\text{SiMe}_3)_2^-$), and taken together with theoretical calculations it was concluded that pyramidalization results in net stabilization for $[\text{U}^{\text{III}}(\text{N}^{\text{r}})_3]$, 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 U^{III} single-molecule magnets.

Investigations into low-coordinate metal complexes (defined herein as coordination number, $\text{CN} < 4$) 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 $\{\text{N}(\text{SiMe}_3)_2\}^-$ (N^{r}) has provided landmark low CN complexes; for example, three-coordinate $[\text{M}^{\text{III}}(\text{N}^{\text{r}})_3]$ complexes of Group 13 ($\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{Tl}$)^[5] and first row d-block ($\text{M} = \text{Ti} - \text{Co}$)^[6] metals are trigonal planar (D_{3h}) in the solid state, but Group 3,^[6a,7] lanthanide (Ln),^[7] and actinide (An)^[8] $[\text{M}^{\text{III}}(\text{N}^{\text{r}})_3]$ 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 $[\text{Ln}^{\text{III}}(\text{N}^{\text{r}})_3]$ ($\text{Ln} = \text{Ce}, \text{Pr}$) in the gas phase,^[10] but $[\text{Sc}^{\text{III}}(\text{N}^{\text{r}})_3]$ 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 $[\text{Ln}^{\text{II}}(\text{N}^{\text{r}})(\mu\text{-N}^{\text{r}})_2\text{Na}]$ ($\text{Ln} = \text{Eu}, \text{Yb}$) and $[\text{Sm}^{\text{II}}(\text{N}^{\text{r}})(\mu\text{-N}^{\text{r}})_2\text{M}]$ ($\text{M} = \text{Na}, \text{K}$), 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 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 UO_3 is T shaped. Both covalent^[19] and electrostatic^[10] arguments account for the trigonal pyramidal geometry of $[\text{U}^{\text{III}}(\text{N}^{\text{r}})_3]$,^[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, $[\text{U}^{\text{III}}(\text{N}^{**})_3]$ (**1**, $\text{N}^{**} = \text{N}(\text{SiMe}_2\text{tBu})_2^-$), which adopts an unprecedented trigonal planar geometry for an actinide triamide complex. Complex **1** is closely related to $[\text{U}^{\text{III}}(\text{N}^{\text{r}})_3]$, allowing the contributions to pyramidalization to be assessed, together with the impact of geometry


 Scheme 1. Synthesis of **1**.

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on magnetic (including dynamic) and electronic properties of U^{III} complexes, for the future rational design of useful An materials.

Complex **1** was prepared by a modification of the revised synthesis of $[\text{U}^{\text{III}}(\text{N}^{\text{r}})_3]$.^[8c] Compound $[\text{U}^{\text{III}}(\text{I})_3(\text{THF})_4]$ ^[8c] was reacted with 1.5 equivalents of $[\text{K}\{\text{N}(\text{SiMe}_2\text{tBu})_2\}_2]$ 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 $\tilde{\nu} = 950, 825,$ and 761 cm^{-1} are attributed to the UNSi_2 stretching modes of the silylamide ligand. The asymmetric stretch (950 cm^{-1}) is 40 cm^{-1} lower than that observed for $[\text{U}^{\text{III}}(\text{N}^{\text{r}})_3]$ (990 cm^{-1}),^[8a] which is of a similar magni-

tude to the differences between previously reported planar and pyramidal $[M(N^{\nu})_3]$ $MNSi_2$ asymmetric stretches (ca. 50 cm^{-1}).^[5b,6a]

The ^1H NMR spectrum of **1** exhibits two resonances at $\delta = 3.8$ ($\nu^{1/2} = 206\text{ Hz}$) and -47.0 ppm ($\nu^{1/2} = 4597\text{ Hz}$) in a 54:36 ratio that are assigned to the *t*BuSi and Me_2Si protons, respectively. The Me_2Si resonance of **1** is much broader than the analogous resonance for $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ ($\delta = -11.4$, $\nu^{1/2} = 15\text{ Hz}$),^[8] but variable-temperature (VT) studies gave a sharper resonance at 353 K ($\delta = -32.9\text{ ppm}$, $\nu^{1/2} = 266\text{ Hz}$).^[21] A wide-scan ^{13}C NMR spectrum of **1** exhibited two resonances for the Me_2Si ($\delta = -2.1$ 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 ($\delta = 26.4\text{ ppm}$). In contrast, in the ^{13}C NMR spectrum of $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$, the Me_2Si group resonates at $\delta = -57.1\text{ ppm}$.^[22] A resonance was observed in the ^{29}Si NMR spectrum of **1** at $\delta = -296.0\text{ ppm}$ ($\nu^{1/2} = 73\text{ Hz}$), 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 $5f^2 \rightarrow 5f^2 6d^1$ transitions at 20000 ($\epsilon = 776\text{ M}^{-1}\text{ cm}^{-1}$) and 22500 cm^{-1} ($\epsilon = 770\text{ M}^{-1}\text{ cm}^{-1}$) that are typical of U^{III} ^[24] and comparable to a broad absorption observed for $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$ at 21500 cm^{-1} ($\epsilon = 430\text{ M}^{-1}\text{ cm}^{-1}$).^[22] In the $7000\text{--}13000\text{ cm}^{-1}$ region, weak Laporte forbidden $5f \rightarrow 5f$ transitions were observed ($\epsilon = 15\text{--}64\text{ M}^{-1}\text{ cm}^{-1}$).^[25] Similar weak absorptions were observed for most U^{III} complexes, such as $[\text{U}(\text{I})_3(\text{THF})_4]$ ^[8c,26] and $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$,^[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 $C2/c$ space group, with a twofold axis bisecting the $\text{U}(1)\text{--N}(1)$ bond. This contrasts to $[\text{Fe}(\text{N}^{\nu})_3]$,^[9] $[\text{Eu}^{\text{III}}(\text{N}^{\nu})_3]$,^[29] $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$,^[8d] and $[\text{Pu}^{\text{III}}(\text{N}^{\nu})_3]$,^[8e] which all crystallize exclusively in the $P3_1c$ space group, and $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$, which crystallizes in $R3$.^[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 $2.403(3)\text{--}2.415(6)\text{ \AA}$]. These distances are longer than those observed in $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ [$2.320(4)\text{ \AA}$]^[8d] and $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$ [$2.34(2)\text{ \AA}$],^[22] which can be attributed to the greater interligand repulsion in **1** arising from the sterically demanding *t*Bu groups. The U centroid/ $\text{N}(1)\text{--N}(2)\text{--N}(2A)$ mean plane distance in **1** is $0.008(2)\text{ \AA}$, and the N–U–N bond angles (range $119.1(2)\text{--}120.47(9)^\circ$) sum to 360° ; in contrast, $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ and $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$ exhibit U centroids $0.456(1)$ and 0.874 \AA from the N_3 planes, and the N–U–N angles average $116.24(7)$ (Σ angles $348.72(7)^\circ$) 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 $53.23\text{--}61.35^\circ$) to form a molecular propeller.

The pyramidal geometries of $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ and $[\text{U}^{\text{III}}\{\text{N}(\text{SiPhMe}_2)_2\}_3]$ are predicted by the polarized-ion model, whereby net stabilization was achieved by dipole formation.^[8d,22] $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ exhibits unequal U–N–Si angles ($108.50(7)$ and $125.25(7)^\circ$), because one Si–C bond for each N^{ν} ligand is relatively close to the U center [U...C $_{\gamma}$ 3.05 \AA ; U...Si 3.29 \AA].^[8d] These can be attributed to stabilizing agostic M...Si–C $_{\gamma}$ interactions, as have been discussed for $[\text{U}^{\text{III}}\{\text{CH}(\text{SiMe}_3)_2\}_3]$ ^[30] and $[\text{Sm}^{\text{III}}(\text{N}^{\nu})_3]$.^[31] The shortest U...C $_{\gamma}$ and

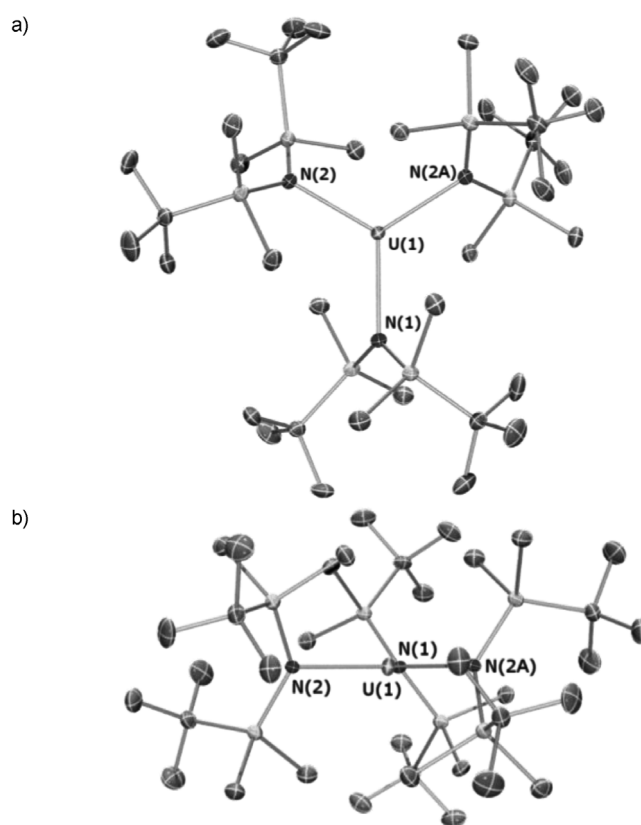


Figure 1. Molecular structures of **1** a) top view and b) along twofold axis, with selected atom labelling. Displacement ellipsoids are set at the 40% probability level, and hydrogen atoms are removed for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: U(1)–N(1) $2.403(3)$, U(1)–N(2) $2.415(6)$;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

U...Si distances in **1** are $3.119\text{--}3.301\text{ \AA}$ and $3.433\text{--}3.510\text{ \AA}$, 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.

Unrestricted DFT calculations were carried out on full models of **1** and $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$.^[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 \AA , angles within 1° , U centroid/ N_3 mean plane distance: **1** 0.132 \AA , $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ 0.393 \AA). 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; $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ 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; $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ 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; $[\text{U}^{\text{III}}(\text{N}^{\nu})_3]$ 0/5.04, 0/5.26, 2.14/0% U 5f/6d, respectively). This concurs with gas-phase photoelectron spectroscopy (PES) studies of

$[\text{U}(\text{N}^*)_3]$, 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, $1 = -3.26$; $[\text{U}^{\text{III}}(\text{N}^*)_3] = -3.26$) are identical, which also supports similar bonding patterns for **1** and $[\text{U}^{\text{III}}(\text{N}^*)_3]$.

Ab initio calculations on $[\text{An}^{\text{III}}(\text{CH}_3)_3]$ (An = U, Np, Pu)^[33] and $[\text{An}^{\text{III}}(\text{NH}_2)_3]$ (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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$, 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 $[\text{D}_6]$ 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 cm³ 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 5f³ $^4I_{9/2}$ 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 cm³ K mol⁻¹ at 2 K; ac measurements give a low-temperature plateau in the in-phase χ'/T at 0.48 cm³ 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 $g_{\text{eff}} = 3.55, 2.97, \text{ and } 0.553$ 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 2a).

Compound $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 2c and d).^[21] Under the optimal dc field of 600 G, the magnetization relaxes much slower than in $[\text{U}^{\text{III}}(\text{N}^*)_3]$, and maxima in the out-of-phase susceptibility $\chi''(T)$ are seen to significantly higher temperatures for **1** than for $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 $U_{\text{eff}} = 21.4 \pm 0.2$ K for **1**. Although this is lower than that reported for $[\text{U}^{\text{III}}(\text{N}^*)_3]$ (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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$).^[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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$ ($\alpha = 0.09$ –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 2b), while it is not for $[\text{U}^{\text{III}}(\text{N}^*)_3]$.

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 $g_{xy} = 3.65, g_z = 0.73$ (all other doublets have $g_{xy} = 0$), in good agreement with experiment. $|J_z| = 1/2$ is also the ground doublet of the (pyramidal) 4f³ complex $[\text{Nd}^{\text{III}}(\text{N}^*)_3]$ from optical studies.^[40] Hence, **1** and $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$ 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 $[\text{U}^{\text{III}}(\text{N}^*)_3]$ have shown only minor differences in their calculated bonding schemes, therefore, the energy gained by pyramidalization, which leads to favorable agostic M^{III}–Si–C_i interactions in $[\text{U}^{\text{III}}(\text{N}^*)_3]$,^[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 $[\text{K}(\text{N}(\text{SiMe}_2\text{tBu})_2)_2]$ (1.007 g, 1.5 mmol) and $[\text{U}(\text{I}_3)(\text{THF})_4]$ (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%). ¹H NMR (400.13 MHz, $[\text{D}_6]$ benzene, 25 °C, TMS): $\delta = -47.04$ (br s, $\nu^{1/2} = 4597$ Hz, 36 H; Si(CH₃)₂), 3.79 ppm (br s, $\nu^{1/2} = 206$ Hz, 54 H; SiC(CH₃)₃); ¹³C{¹H} NMR (100.61 MHz, $[\text{D}_6]$ benzene, 25 °C, TMS): $\delta = -2.13$ (Si(CH₃)₂), 1.45 (Si(CH₃)₂), 18.22 (SiC(CH₃)₃), 26.40 (SiC(CH₃)₃), 31.98 ppm (SiC(CH₃)₃); ²⁹Si{¹H} NMR (79.48 MHz, $[\text{D}_6]$ 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., UNSi₂), 825 (s, sym. str., UNSi₂), 761 (s, sym. str., UNSi₂), 655 (m), 604 (s) cm⁻¹; $\mu_{\text{eff}} = 2.59 \mu_B$ (Evans method); elemental analysis calcd for C₃₆H₉₀Si₆N₃U (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]

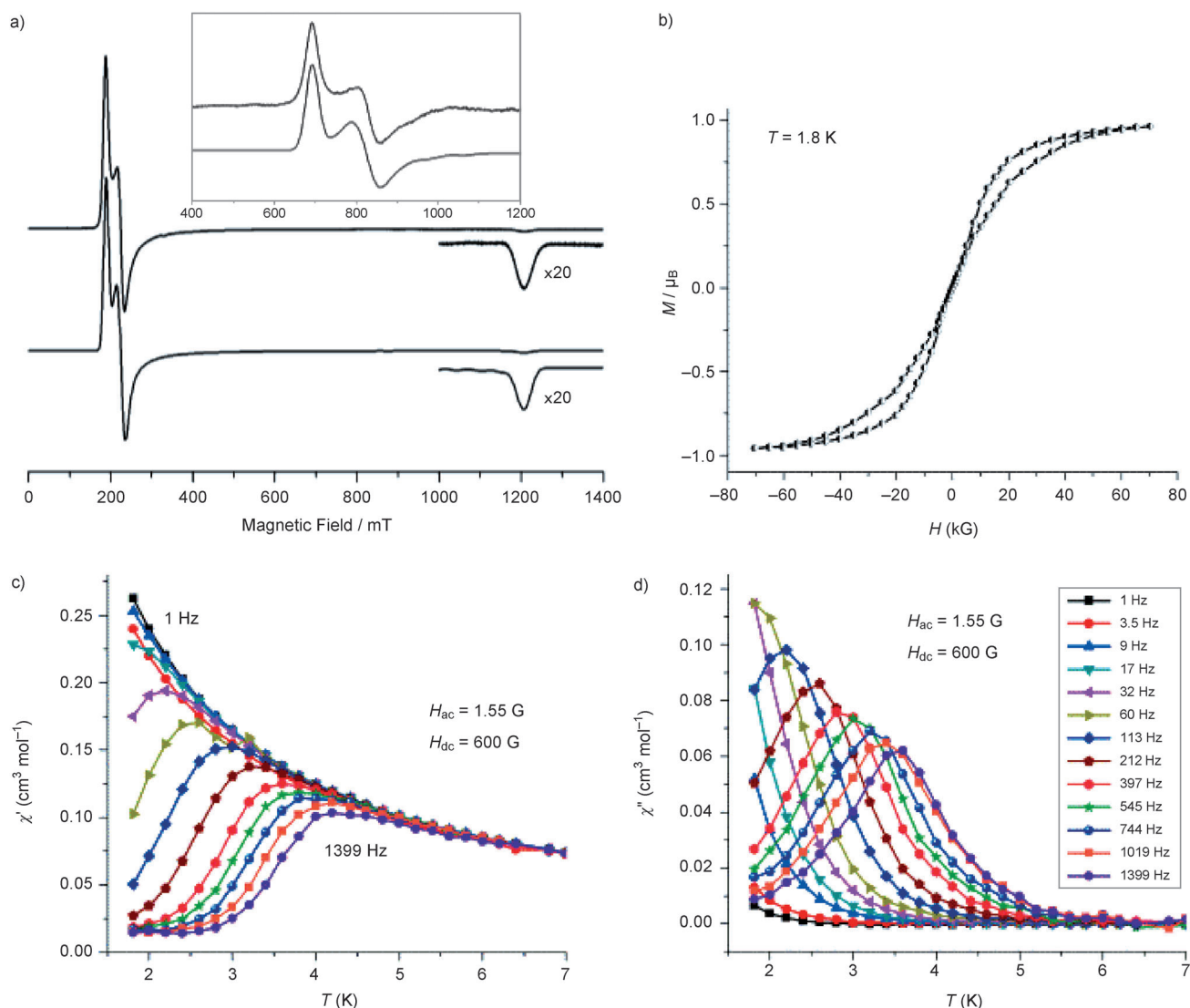


Figure 2. a) X- (9.5 GHz) and Q-band (34 GHz; inset) EPR spectra of **1** at 5 K. Lower spectra are simulations as $S_{\text{eff}} = 1/2$. Magnetic-susceptibility data for **1**: b) magnetic hysteresis at 1.8 K, sweep rate 13 G s^{-1} ; c) in-phase (χ'); and d) out-of-phase (χ'') components of the ac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