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[U\textsuperscript{IV}\{N(SiMe\textsubscript{2}Bu)\textsubscript{3}\}]: A StructurallyAuthenticated Trigonal Planar Actinide Complex

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Abstract: We report the synthesis and characterization of the uranium(III) triamide complex [U\textsuperscript{IV}(N\textsuperscript{**})\textsubscript{3}] \textsuperscript{[1, N\textsuperscript{**}=N-(SiMe\textsubscript{2}Bu)\textsubscript{3}]. 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 [U\textsuperscript{IV}(N\textsuperscript{**})\textsubscript{3}] were compared with the prototypical trigonal pyramidal uranium(III) triamide complex [U\textsuperscript{III}(N\textsuperscript{3})\textsubscript{3}] \textsuperscript{[N\textsuperscript{3}=NiSiMe\textsubscript{3}]} and, taken together with theoretical calculations it was concluded that pyramidalization results in net stabilization for [U\textsuperscript{III}(N\textsuperscript{3})\textsubscript{3}], but this can be overcome with very sterically demanding ligands, such as N\textsuperscript{**}. The planarity of 1 leads to favorable magnetic dynamics, which may be considered in the future design of U\textsuperscript{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,\textsuperscript{[1]} including small-molecule activation chemistry\textsuperscript{[2]} and single-molecule magnet (SMM) behavior.\textsuperscript{[3]} Low CN complexes usually contain sterically demanding ligands to prevent oligomerization,\textsuperscript{[1]} in which bulky monodentate amides are frequently utilized.\textsuperscript{[4]} The bulky silylamide (N(SiMe\textsubscript{3})\textsubscript{2}) \textsuperscript{[N\textsuperscript{3}=N-(SiMe\textsubscript{3})\textsubscript{2}]} has provided landmark low CN complexes; for example, three-coordinate [M\textsuperscript{III}(N\textsuperscript{3})\textsubscript{3}] complexes of Group 13 (M = Al, Ga, In, Tl)\textsuperscript{[5]} and first row d-block (M = Ti–Co)\textsuperscript{[6]} metals are trigonal planar (D\textsubscript{3h}) in the solid state, but Group 3\textsuperscript{[6a, 7]} lanthanide (Ln),\textsuperscript{[7]} and actinide (An)\textsuperscript{[6]} \[M\textsuperscript{VII}(N\textsuperscript{3})\textsubscript{3}] complexes exhibit trigonal pyramidal (C\textsubscript{3v}) solid-state geometries, although they have zero dipole moment in solution, inferring that they may become planar in this phase.\textsuperscript{[9]} Pyramidal geometries persist for [Ln\textsuperscript{III}(N\textsuperscript{3})\textsubscript{3}] (Ln = Ce, Pr) in the gas phase,\textsuperscript{[10]} but [Sc\textsuperscript{II}(N\textsuperscript{3})\textsubscript{3}] vapors are D\textsubscript{3h}, with crystalline/gas-phase discrepancies for this complex attributed to crystal-packing effects.\textsuperscript{[11]} It is noteworthy that complexes, such as [Ln\textsuperscript{III}(N\textsuperscript{3})\textsubscript{3}] (Ln = Eu, Yb) and [Sm\textsuperscript{III}(N\textsuperscript{3})\textsubscript{3}] (M = Na, K), have trigonal planar Ln coordination spheres,\textsuperscript{[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.\textsuperscript{[13]} Low CN U\textsuperscript{IV} chemistry is burgeoning, driven by interesting small molecule activation reactions\textsuperscript{[14]} and intrinsic SMM behavior.\textsuperscript{[15]} Structurally characterized three-coordinate An complexes to date adopt exclusively trigonal pyramidal geometries rather than trigonal planar or T shaped (C\textsubscript{3v}),\textsuperscript{[16]} although matrix isolation experiments\textsuperscript{[17]} and calculations\textsuperscript{[18]} have shown that monomeric UO\textsubscript{3}− has T shape. Both covalent\textsuperscript{[19]} and electrostatic\textsuperscript{[10]} arguments account for the trigonal pyramidal geometry of [U\textsuperscript{IV}(N\textsuperscript{3})\textsubscript{3}],\textsuperscript{[19, 20]} hence, the most influential factor of these two for causing pyramidalization has never been established. Herein, we report the structurally characterized An complex, [U\textsuperscript{IV}(N\textsuperscript{**})\textsubscript{3}] (1, N\textsuperscript{**}=N-(SiMe\textsubscript{2}Bu)\textsubscript{3}, which adopts an unprecedented trigonal planar geometry for an actinide triamide complex. Complex 1 is closely related to [U\textsuperscript{IV}(N\textsuperscript{3})\textsubscript{3}], allowing the contributions to pyramidalization to be assessed, together with the impact of geometry on magnetic (including dynamic) and electronic properties of U\textsuperscript{IV} complexes, for the future rational design of useful An materials.

Complex 1 was prepared by a modification of the revised synthesis of [U\textsuperscript{IV}(N\textsuperscript{3})\textsubscript{3}].\textsuperscript{[24]} Compound [U\textsuperscript{IV}(I\textsubscript{3}(THF))\textsubscript{2}]\textsuperscript{[26]} was reacted with 1.5 equivalents of [K(N(SiMe\textsubscript{2}Bu)\textsubscript{3})] in THF, followed by work-up and recrystallization from hexane to give 1 as dark purple needles in 62 % yield (Scheme 1).\textsuperscript{[21]} Absorbances in the FTIR spectrum of 1 at \(\tilde{\nu}=950, 825,\) and 761 cm\textsuperscript{-1} are attributed to the UNSi\textsubscript{2} stretching modes of the silylamide ligand. The asymmetric stretch (950 cm\textsuperscript{-1}) is 40 cm\textsuperscript{-1} lower than that observed for [U\textsuperscript{IV}(N\textsuperscript{3})\textsubscript{3}] (990 cm\textsuperscript{-1}), which is of a similar magni-
The $^1$H NMR spectrum of 1 exhibits two resonances at $\delta = 3.8$ ($\nu_1/2 = 206$ Hz) and $-47.0$ ppm ($\nu_2/2 = 4597$ Hz) in a 54:36 ratio that are assigned to the $\text{BuSi}$ and $\text{Me}_2\text{Si}$ protons, respectively. The $\text{Me}_2\text{Si}$ resonance of 1 is much broader than the analogous resonance for $[\text{U}^\text{III}(\text{N}^\text{"{N}})^3]_3$ ($\delta = -11.4$, $\nu_1/2 = 15$ Hz),\textsuperscript{26} but variable-temperature (VT) studies gave a sharper resonance at 353 K ($\delta = -32.9$ ppm, $\nu_1/2 = 266$ Hz).\textsuperscript{21} A wide-scan $^{13}$C NMR spectrum of 1 exhibited two resonances for the $\text{Me}_2\text{Si}$ ($\delta = -2.1$ and 1.5 ppm) and $\text{BuSi}$ quaternary carbons ($\delta = 18.2$ and 32.0 ppm), but only one for the $\text{BuSi}$ primary carbons ($\delta = 26.4$ ppm). In contrast, in the $^{13}$C NMR spectrum of $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$, the $\text{Me}_2\text{Si}$ group resonates at $\delta = -57.1$ ppm.\textsuperscript{22} A resonance was observed in the $^{29}$Si NMR spectrum of 1 at $\delta = -296.0$ ppm ($\nu_1/2 = 73$ Hz), which has not been reported for similar systems,\textsuperscript{8,20} but is typical for a $\text{U}^\text{VI}$ complex.\textsuperscript{23}

The electronic absorption spectrum of 1\textsuperscript{21} exhibited $5f^6\rightarrow 5f^56\text{d}^1$ transitions at 20000 ($\epsilon = 776\text{ m}^2\text{ cm}^{-1}$) and 22500 cm$^{-1}$ ($\epsilon = 770\text{ m}^2\text{ cm}^{-1}$) that are typical of $\text{U}^\text{VI}$,\textsuperscript{10} and comparable to a broad absorption observed for $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$ at 21500 cm$^{-1}$ ($\epsilon = 430\text{ m}^2\text{ cm}^{-1}$).\textsuperscript{22} In the 7000–13000 cm$^{-1}$ region, weak Laporte forbidden $5f\rightarrow 5f$ transitions were observed ($\epsilon = 15–64\text{ m}^2\text{ cm}^{-1}$).\textsuperscript{22} Similar weak absorptions were observed for most $\text{U}^\text{VI}$ complexes, such as $[\text{U}^\text{II}(\text{THF})]_3$\textsuperscript{36,26} and $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$, and strong absorptions in this region are very rare.\textsuperscript{27}

The crystal structure of 1 was determined and is depicted in Figure 1, with selected metrical parameters.\textsuperscript{28} Complex 1 crystallizes in the C2/c space group, with a twofold axis bisecting the U(1)–N(1) bond. This contrasts to $[\text{Fe}(\text{N}^\text{"{N}})]_3$,\textsuperscript{9} $[\text{Eu}(\text{N}^\text{"{N}})]_3$,\textsuperscript{29} $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$,\textsuperscript{84} and $[\text{Pu}(\text{N}^\text{"{N}})]_3$,\textsuperscript{86} which all crystallize exclusively in the P3$_1$ space group, and $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$, which crystallizes in R3.\textsuperscript{22} The U atom of 1 is almost ideally trigonal planar, with U–N bonds that are statistically identical within experimental uncertainty ($\text{U–N}$ range 2.403(3)–2.415(6) Å).\textsuperscript{22} These distances are longer than those observed in $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$ [2.320(4) Å],\textsuperscript{84} and $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$ [2.34(2) Å],\textsuperscript{22} which can be attributed to the greater interligand repulsion in 1 arising from the sterically demanding $\text{Bu}$ groups. The U centroid/N(1)–N(2) mean plane distance in 1 is 0.008(2) Å, and the N–U–N bond angles (range 119.1(2)–120.4(9)) sum to 360°; in contrast, $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$ and $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$ 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.\textsuperscript{84,22} The UNSi 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 $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$ and $[\text{U}^\text{IV}(\text{N}^\text{"{N}})^2\text{Si}^\text{Me}_2\text{Ph}]_3$ are predicted by the polarization-ion model, whereby net stabilization was achieved by dipole formation.\textsuperscript{84,22} $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$ exhibits unequal U-N-Si angles (108.50(7) and 125.25(7)°), because one Si–C bond for each N$^\text{"{N}}$ ligand is relatively close to the U center ($\text{U}–\text{C} = 3.05$ Å; $\text{U}–\text{Si} = 3.29$ Å).\textsuperscript{84} These can be attributed to stabilizing agostic $\text{M}^\text{III}–\text{Si}–\text{C}$ interactions, as have been discussed for $[\text{U}^\text{III}(\text{CH}3\text{SiMe}_2\text{Ph})_3]_3$ and $[\text{Sm}(\text{N}^\text{"{N}})]_3$.\textsuperscript{21} The shortest U–C$_\text{t}$ 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, interactions in 1, stabilizing U–C–H contacts cannot be discounted.

Unrestricted DFT calculations were carried out on full models of 1 and $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$.\textsuperscript{31} 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, $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$ 0.393 Å). In both models, the HOMO, HOMO–1 and HOMO–2 represent the three unpaired $\text{U}^\text{IV}$ 5f electrons (1: 93.93, 94.71, 90.09; $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$: 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; $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$: 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; $[\text{U}^\text{IV}(\text{N}^\text{"{N}})]_3$: 0/5.04, 0/5.26, 2.14/0% U 5f/6d, respectively). This concurs with gas-phase photoelectron spectroscopy (PES) studies of
ligand and U center is insignificant in this complex.\cite{32} The calculated uranium spin densities (MDC-m α spin, 1 = −3.26; \(\text{[U}^\text{II}(\text{N})^3]\)) = −3.26) are identical, which also supports similar bonding patterns for 1 and \(\text{[U}^\text{III}(\text{N})^3]\).

Ab initio calculations on [AnIII(CH3)3] (An = U, Np, Pu)\cite{33} and [AnIII(NH3)3] (An = U, Np)\cite{34} have shown that the involvement of An 6d orbitals in the U–X (X = C, N) α 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 α 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\(^{-1}\).\cite{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\text{B} in [D\text{6}]benzene at 298 K by using the Evans method.\cite{36} Magnetometry measurements on a powdered sample of 1 suspended in eicosane gave a magnetic susceptibility temperature product, \(\chi T\) of 1.07 cm\(^3\) K mol\(^{-1}\) at 298 K\cite{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 \(^{1}\) ground term,\cite{39} but are typical for \(\text{U}^\text{III}\) complexes described in the literature (range 2.13–4.63 μ\text{B}).\cite{8d,32,33,11,22,25,26,30,38} The \(\chi T\) 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\(^{-1}\)\cite{21} consistent with thermal depopulation into a Kramers doublet ground state.\cite{13,12} Low-temperature EPR spectra of 1 are consistent with \(\text{U}^\text{III}\)\cite{27} and simulation gives \(g_{\text{eff}} = 3.55, 2.97,\) 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 2a).

Compound \(\text{[U}^\text{I}(\text{N})^3]\) is an SMM,\cite{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).\cite{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\cite{21} of the higher-temperature ac data gives an energy barrier of \(U_{\text{eff}} = 21.4 ± 0.2\) 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\cite{15} and should be treated with some caution. The relaxation time (\(\tau\)) at 2 K is 2.6 ms for 1; from the previously reported data\cite{15} we find 0.3 ms for \(\text{[U}^\text{I}(\text{N})^3]\) at 2 K, an order of magnitude quicker. The pre-factor \(r_0\) for 1 is greater by four orders of magnitude (3.1 × 10\(^{-7}\) cf. 10\(^{-11}\) s for \(\text{[U}^\text{III}(\text{N})^3]\)).\cite{15} Moreover, the frequency dependence of \(\chi'\) and \(\chi''\) 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 \(\text{[U}^\text{III}(\text{N})^3]\) (\(\alpha = 0.09–0.34\)).\cite{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 \(J_{\text{hh}}\) state of \(\text{U}^\text{III}\) to be stabilized by the crystal field. This is supported by the EPR analysis: if we assume a \(^{1}\)\text{hh}\) ground term,\cite{36} with \(g_{\text{eff}} = 8/11\), the \(J_{\text{hh}} = \pm 1/2\) doublet is calculated to have \(g_{\text{hh}} = 3.65, g_{\text{hh}} = 0.73\) (all other doublets have \(g_{\text{hh}} = 0\), in good agreement with experiment. \(J_{\text{hh}} = 1/2\) is also the ground doublet of the (pyramidal) 4f\(^{3}\) complex \([\text{Nd}^\text{III}(\text{N})^3]\) from optical studies.\cite{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,\cite{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 \(D_{3h}\) \(J_{\text{hh}} = 1/2\) cannot mix with any other doublet within the \(^{1}\text{hh}\) term, whereas in \(C_{3v}\), it can mix with both \(J_{\text{hh}} = 5/2\) 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 \(\text{U}^\text{III}\) 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–Si–C interactions in \([\text{U}^\text{III}(\text{N})^3]\)\cite{8d,32,11} 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(\text{SiMe}_2\text{Bu})_2]_2 (1.007 g, 1.5 mmol) and [\(\text{U}^\text{III}(\text{THF})_4\)] (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 (62 %).\(\text{\text{^1}H}\) NMR (400.13 MHz, [D\text{6}]benzene, 25 °C, TMS): \(= -47.04\) (br. s, \(v_{\text{J}}/2\) on 4597 Hz, 36 H; Si(CH\text{\text{3}})\text{3})), 3.79 ppm (br s, \(v_{\text{J}}/2\) = 206 Hz, 54 H; Si(CH\text{\text{3}})\text{3})), 31.9 ppm (Si(CH\text{\text{3}})\text{3})), 31.91 ppm (Si(CH\text{\text{3}})\text{3})), 26.40 (Si(CH\text{\text{3}})\text{3})), 26.30 (Si(CH\text{\text{3}})\text{3})), 26.30 ppm (Si(CH\text{\text{3}})\text{3})), 31.91 ppm (Si(CH\text{\text{3}})\text{3})), 26.40 (Si(CH\text{\text{3}})\text{3})), 26.30 (Si(CH\text{\text{3}})\text{3})), 26.30 ppm (Si(CH\text{\text{3}})\text{3})), 26.40 (Si(CH\text{\text{3}})\text{3})), 26.30 ppm (Si(CH\text{\text{3}})\text{3})), 26.40 (Si(CH\text{\text{3}})\text{3})), 26.30 ppm (Si(CH\text{\text{3}})\text{3})), 26.40 (Si(CH\text{\text{3}})\text{3})).
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Keywords: actinides · ligand design · ligand effects · single-molecule magnets · uranium

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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 ($\chi'$); and d) out-of-phase ($\chi''$) 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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[28] Crystal data for 1: C6H14N3Si3U, M = 971.67 g mol⁻¹, space group C2/c, a = 21.7732(11), b = 13.2453(8), c = 17.9674(9) Å, β = 110.972(6)°, V = 4838.4(5) Å³, Z = 4, µx = 1.334 g cm⁻³, MoKα radiation, λ = 0.71073 Å, μ = 3.529 mm⁻¹, T = 150 K. 11360 points (5457 unique, Rint = 0.0567, 2θ < 75.6°). 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 F² values to give wR2 = Σ[|Fo|² – |Fc|²]|² / Σ|Fo|²|²] = 0.0678, conventional R = 0.0486 for F values of 5457 with Fw > 2σ(Fw), 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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