Nuclear Magnetic Resonance Measurements and Electronic Structure of Pu(IV) in [(Me₄N)₂PuCl₆]

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ABSTRACT: The synthesis, electronic structure, and characterization via single-crystal X-ray diffraction, nuclear magnetic resonance (NMR) spectroscopy, and magnetic susceptibility of (Me₄N)₂PuCl₆ are reported. NMR measurements were performed to both search for the direct ²³⁹Pu resonance and to obtain local magnetic and electronic information at the Cl site through ³⁵Cl and ³⁷Cl spectra. No signature of ²³⁹Pu NMR was observed. The temperature dependence of the Cl spectra was simulated by diagonalizing the Zeeman and quadrupolar Hamiltonians for ³⁵Cl, ³⁷Cl, and ¹⁴N isotopes. Electronic structure calculations predict a magnetic Γ₃ triplet ground state of Pu(IV) in the crystalline electric field of the undistorted PuCl₆ octahedron. A tetragonal distortion would result in a very small splitting (~20 cm⁻¹) of the triplet ground state into a nonmagnetic singlet and a doublet state. The Cl shifts have an inflection point at T ≈ 15 K, differing from the bulk susceptibility, indicating a nonmagnetic crystal field ground state. The Cl spin–lattice relaxation time is constant to T = 15 K, below which it rapidly increases, also supporting the nonmagnetic crystal field ground state.

INTRODUCTION

The actinide elements mark the emergence of 5f electrons in the valence shell. Whether the 5f electrons in actinide molecules, compounds, metals, and some alloys are involved in bonding has been a central and integrating focus for the fields of actinide chemistry and physics. In the pure elements, actinides to the left of Pu have delocalized (bonding) electrons, while those to the right of Pu are localized (nonbonding). Plutonium is trapped in the middle,† and, for the technologically important δ-phase metal, the electrons seem to be in an exotic state, where they are neither fully bonding nor localized, which leads to novel electronic interactions and unusual physical and chemical behaviors.1–7 The concept of localized or delocalized 5f electrons also pervades the bonding descriptions of many of the actinide molecules and compounds, and whether 5f electrons participate significantly in covalent bonding in molecular compounds has been a topic of considerable interest.8 In the nomenclature of chemistry, the delocalized electrons are those involved in covalent bonding, while the localized electrons give rise to ionic behavior. Despite key experimental breakthroughs and significant advances in theory,9–29 defining relationships between plutonium electronic structure and its physical properties remains a daunting experimental and computational challenge.

The recent installation of modern nuclear magnetic resonance (NMR) instruments in facilities capable of analyzing radioactive elements such as plutonium30–36 offers new and exciting opportunities to better understand the electronic structure and bonding of this complicated element. For example, solid-state NMR spectroscopy provides a powerful tool for characterizing important physical properties that are otherwise difficult to define, that is, electric field gradients (EFGs), magnetic shifts, and hyperfine couplings. Herein, we make use of this spectroscopic technique in studying the highly symmetric PuCl₆²⁻ ion in the (Me₄N)₂PuCl₆ salt (Figure 1). This compound was carefully selected because the octahedral-PuCl₆²⁻ anion has historically provided the foundation upon which much of the current understanding of molecular plutonium’s electronic structure is based. Moreover, because

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(Me₄N)₂PuCl₆ is only weakly magnetic, the salt presents an especially interesting system for the search for ²³⁹Pu NMR signal to both verify the previously determined properties of the plutonium-239 nucleus and to collect new statistics on Pu⁴⁺ local magnetic environments. Furthermore, the presence of the quadrupolar isotopes ³⁵Cl and ³⁷Cl near the central Pu⁴⁺ ion allows the electric fields in the vicinity of the metal site to be characterized through determination of quadrupolar couplings. Hence, we characterized the bulk magnetic susceptibility, local magnetic fields, and electric field gradients of (Me₄N)₂PuCl₆. The NMR shift measurements of the ³⁵Cl and ³⁷Cl nuclei, sensitive to the local electronic and magnetic environments, deviate from the bulk susceptibility at temperatures below 15 K, which is consistent with a splitting of the crystal field triplet ground state expected for a reduction in symmetry of the PuCl₆⁻ octahedron, as predicted by electronic structure calculations. Further evidence of the splitting of the triplet crystal field state comes from the spin–lattice relaxation time, which increases rapidly below 15 K, indicating a slowing of magnetic fluctuations.

**Experimental Methods**

**Synthesis. Caution!** The ²³⁹Pu and ²₄²Pu isotopes are high specific activity α-particle emitting radionuclides, and their use presents extreme hazards to human health. This research was conducted in radiological and nuclear facilities with appropriate analyses of these hazards and implementation of controls for the safe handling and manipulation of these toxic and radioactive materials.

All synthetic manipulations were performed in a certified chemical fume hood. No effort was made to exclude air or moisture. Me₄NCl (Aldrich) was obtained commercially and used as received. Aqueous manipulations were performed with greater than 18 Ω water from a Millipore purification system. Electronic absorption spectra were collected at room temperature using a Varian Cary 6000 UV–vis spectrophotometer with a 0.2 nm spectral bandwidth.

The (Me₄N)₂PuCl₆ compounds were prepared using well-established valence adjustments and anion exchange chromatography that is routinely employed in aqueous plutonium chemistry using the following method. In a fume hood, a tetravalent plutonium stock solution was prepared by adding nitric acid (HNO₃, 16 M, 50 mL) to a Teflon beaker charged with plutonium dioxide (PuO₂, 0.080 g, 0.335 mmol). The suspension was heated, and an aliquot (5 mL) of a 100:1 mixture of hydrochloric (HCl, 12 M) to hydrofluoric (HF, 29 M) acid was added. The solution volume was reduced to 5 mL by heating, and the process was repeated until the PuO₂ dissolved, typically three times. Subsequently, the solution matrix was converted to HCl by repeatedly (3×) heating the solution to a soft dryness and adding HCl (~10 mL). The resulting solution was quantitatively transferred to a disposable centrifuge tube (polypropylene, 50 mL), such that the total volume was ~10 mL and the final HCl concentration was 6 M. Reduction to trivalent plutonium was obtained by adding a buffered aqueous solution of hydroxylamine hydrochloride (NH₂OH.HCl, 1 mL) to the centrifuge tube. After 10 to 30 min the solution began to bubble. The centrifuge tube was placed in a hot block and heated (80 °C for 1 h), and the color changed from burnt orange to blue. Adding HF (29 M, 5 mL) to this solution resulted in precipitation of an insoluble pink solid. After 15 min, the suspension was centrifuged, the supernatant was discarded, and the pellet was washed with water (2×). The solid was dissolved by addition of an aqueous saturated solution of boric acid (H₃BO₃, 2 mL). The pellet was broken up with a glass stir rod and heated at 80 °C in an aluminum hot block for 5 min. Then, HCl (12 M, 1 mL) was added, and the suspension was stirred. With periodic stirring of the suspension, second aliquots of H₃BO₃ (1 mL) and HCl (1 mL) were added, which was followed by final aliquots of H₃BO₃ (1 mL) and HCl (1 mL). After 5 min, the solid had completely dissolved. When the solution cooled to room temperature, ammonium hydroxide (NH₄OH, 15 M) was added until a brown solid precipitated. The suspension was centrifuged, the supernatant was discarded, and the pellet was washed with water (2×). The solid was dissolved by addition of an aqueous saturated solution of boric acid (H₃BO₃, 2 mL). To the solution, an aqueous solution of sodium nitrite (10 M, 1 mL) was added dropwise with stirring, which resulted in a vigorous reaction that produced red fumes and bubbling. The solution was allowed to sit for 20 to 30 min, and the green solution was analyzed by UV–visible spectroscopy to confirm plutonium was in the +4 oxidation state.

During this time an anion-exchange column was prepared by charging a 20 mL BioRad column equipped with an addition funnel with AG MP-1 anion resin (10 mL, 50–100 mesh). The resin was conditioned with water (1 × 25 mL) followed by HNO₃ (7.2 M, 3 × 25 mL). Subsequently, the plutonium solution was loaded onto the column. A stationary green band of PuIV was observed. The column was washed with HNO₃ (7.2 M, 2 × 25 mL) and then HCl (12 M, 3 × 25 mL), until the color of the PuIV band changed from green to red and then yellow. The PuIV was then eluted from the column with slightly acidic H₂O (50 mL of H₂O to five drops of 12 M HCl) and collected in the smallest possible volume (~3 mL). To the blood-orange colored solution, HCl was added, such that the final HCl concentration was ~12 M. An aliquot was added to a quartz cuvette charged with perchloric acid (1 M, 2 mL), and the concentration of the sample was determined by UV–visible spectroscopy (ε₄70 nm = 56.5 and ε₆53 nm = 35 L mol⁻¹ cm⁻¹). This measurement was confirmed by α-spectroscopy of an additional aliquot of the plutonium stock solution that had been stippled on a platinum disk. Using this information, 2.1 equiv of Me₄NCl was dissolved in HCl (6 M, 1 mL), and the resulting solution was added to the plutonium stock solution. Over the course of two weeks, orange single crystals suitable for single-crystal X-ray diffraction of (Me₄N)₂PuCl₆ (0.115 g, 0.191 mmol, 57% from PuO₂) were grown by concentrating the solution volume via slow evaporation over the course of two weeks; however, a drop of HCl (12 M) was added every other day to maintain a high acid concentration.

**Single Crystal X-ray Diffraction.** Crystals of (Me₄N)₂PuCl₆ were prepared with three appropriate layers of containment prior to single-crystal X-ray diffraction studies by following modifications of the published procedures. Single crystal were coated with epoxy and then mounted inside 0.5 mm capillaries. The capillaries were sealed with additional epoxy, and their external surfaces were coated with a thin film of acrylic dissolved in ethyl acetate (Hard as Nails nail polish). The sample was cooled to 140 K in a cold nitrogen gas stream on a Bruker D8 Apex II diffractometer. The data were collected on a Bruker D8 diffractometer equipped with APEX II charge-coupled-device (CCD) detector. The crystal was cooled to 140(1) K by means of an American Cryoindustries low-temperature device. The instru-
had dimensions of 12.864(19) Å with 90° angles, which was consistent with previous powder diffraction data. The unique Pu–Cl bond distance of 2.567(5) Å was consistent with previous distances reported for other plutonium hexachloride salts.4–53

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements from 2.1 to 300 K were made in a Quantum Design MPMS magnetometer. For these measurements, 97 mg of (Me₄N)₂PuCl₆ was tightly packed into a soda drinking straw that was sealed at both ends. Two cylindrical coils of 3 mm diameter and ~7 mm in length. To avoid radioactive contamination, the coil was encapsulated in a 20 mm × 20 mm × 20 mm Stycast 1266 epoxy cube with a hole through the center of the coil and cube. Two different NMR samples were prepared containing a high isotopic abundance of 93%²³⁹Pu (²³⁵Pu sample*) in one sample of approximate mass of 50 mg and 99.93%²³⁹Pu (²³⁹Pu sample*) in another sample of approximate mass of 125 mg. After the sample was inserted in the coil, each end of the coil was capped with 2 μm pore titanium frits, which allowed thermal contact with the ⁴He while simultaneously encapsulating the powder. For all the temperatures measured here, a ⁴He variable-temperature insert was used to regulate temperature.

NMR measurements were performed on (Me₄N)₂PuCl₆ samples by the pulsed spin–echo NMR method with pulse sequence t₁–t₂–t₃–t₄–t₁–t₂–t₃–t₄–t₅–t₆–t₇–t₈–t₉–t₁₀–t₈–t₇–t₆–t₅–t₄–t₃–t₂–t₁–t₈–t₇–t₆–t₅–t₄–t₃–t₂–t₁. NMR spectra were taken by the field sweep technique at constant carrier frequency v₀ = 14.5 MHz. The fast Fourier transforms (FFT) were summed to produce the spectra (FFT Sum). The spin–lattice relaxation time, T₁, was measured at the ³¹Cl central transition by inversion recovery method, t₁–t₂–t₃–t₄–t₅–t₆–t₇–t₈–t₉–t₁₀–t₈–t₇–t₆–t₅–t₄–t₃–t₂–t₁–t₈–t₇–t₆–t₅–t₄–t₃–t₂–t₁. Also, a phase transition was observed at T = 3–35 K. The magnetization recovery was fit to the main exponential function

$$
M(t) = M_0\left(1 - \frac{1}{10}\left(\frac{t}{T_1}\right)^{2/3} + \frac{9}{10}e^{-\frac{t}{T_2}}\right)
$$

appropriate for I = 3/2 and transition (1/2) ↔ (−1/2).5,4

X-RAY CRYSTAL STRUCTURE

The structure was refined in space group Fm̅3m (space group 225), with a = 12.864(2) Å. The PuCl₆⁻ anion occupies a position of m̅3m (O₆, Wyckoff 4a) symmetry, and the tetrachlorammonium cation sits on a site of mmmm (T₄, Wycoff 8c) symmetry. The PuCl₆⁻ anions are well-separated from the (Me₄N)⁺ cations, and there are no indications of contact between them. The one, unique Pu–Cl distance is 5.267(5) Å. The Cl and C temperature factors (Table 2).

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for (Me₄N)₂PuCl₆

| x/a | y/b | z/c | U(eq)¹
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<tr>
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<tr>
<td>Pu(1)</td>
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<td>0</td>
<td>0</td>
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<tr>
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<tr>
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<td>6889(11)</td>
<td>8111(11)</td>
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<tr>
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<td>8005(4)</td>
<td>0</td>
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¹x ×10³, b1 ×10¹ A². U(eq) is defined as one third of the trace of the orthogonalized U tensor.

suggest both anion and cation are disordered, which is consistent with literature bond distances and angles showing distorted octahedra and tetrahedra for the anion and cation, respectively. For example, the tetrabutylammonium (TBA) analogue published by Reilly et al. is monoclinic, and the PuCl₆⁻ anion is sitting in a general position.51 The bond distances range from 2.572(1) to 2.603(1) Å and the angles range from 91.79(4)° to 176.52(4)°. The PuCl₆⁻ anion in the cubic structure reported herein most likely has a similar distorted octahedron bonding geometry. The lattice packing with tetrachlorammonium (TMA) vs TBA is not different in terms of perturbing the PuCl₆⁻ geometry, that is, the C–H…Cl intermolecular interaction is considered to be a very weak hydrogen bond.55 Moreover, the bond distances and angles of the PuCl₆⁻ anion in the recently reported (Ph₄P)₂PuCl₆ crystal structure50 are similar to those of the TBA analogue further demonstrating the weak role of the organic counterions in determining anion structure in these systems.

The structure of (Me₄N)₂PuCl₆ was also recently reported by Wilson.55 In that paper, a room-temperature structure refined in space group Fd̅3c and an a-axis of 26.012(3) Å was reported. Weak reflections in precession images were observed, corresponding to the doubling of the a-axis. Also, a phase

Table 1. Crystal Data and Structural Refinement Parameters for (Me₄N)₂PuCl₆

<table>
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<tr>
<td>R indices (all data)</td>
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transition was reported upon heating \((T > 350 \text{ K})\) to the \(Fm\overline{3}m\) structure reported in this paper. We did not observe the doubling of the \(a\)-axis and the corresponding \(Fd\overline{3}c\) space group symmetry in our structure at 140 K. Previously, the phase transition was attributed to an order-disorder transition, and the Pu–Cl distance of 2.579(2) Å is very similar to what we report for our \(Fm\overline{3}m\) structure and similar structures reported elsewhere (vide supra).\(^{35,50,56}\) The differences in our results probably lie in different synthetic routes and subsequent crystal defects or differing thermal histories of samples from the two laboratories. The X-ray diffractometers used to collect the data are essentially identical. The important point is that this study is largely focused on the PuCl\(_6^{2-}\)-anion and associated properties, and the organic sublattice does not appear to significantly affect the anion structure or its properties in this family of compounds.

### ELECTRONIC STRUCTURE CALCULATIONS

**Crystal Field Analysis of the Octahedral PuCl\(_6^{2-}\)**. The ground-state multiplet of the free Pu(IV) ion is \(^{3}I_{6}\) with \(L = 6\), \(S = 2\), and \(J = L - S = 4\). The ninefold degeneracy is lifted by the metal–ligand interactions, which are dominantly electrostatic (crystal field (CF)) but with some covalency contributions. For f-shells, the CF operator for an octahedral environment and a given \(J\)-manifold can be written as

\[
\mathcal{H}^{\text{CF}} = \beta(J) A_4(\mathbf{r}^4)[\hat{\Omega}_0^0(J) + 5\hat{\Omega}_4^4(J)] + \gamma(J) A_6(\mathbf{r}^6)[\hat{\Omega}_0^0(J) - 21\hat{\Omega}_4^4(J)]
\]

(2)

Here, the \(\hat{\Omega}_l^m\) are the Stevens operators, \(A_4(\mathbf{r}^4)\) the CF parameters, and \(\beta(J)\) and \(\gamma(J)\) are the Stevens coefficients.\(^{57}\) Lea, Leask, and Wolf (LLW) rewrote this operator in the \(O_h\) space group. The diagonalization of \(\mathcal{H}^{\text{CF}}\) leads to four systems where in one the wave function and energy levels of the multiplets arising from the \(^{3}I_{6}\) multiplet of Pu(IV) are collected in Table 3. For the \(O_h\) PuCl\(_6^{2-}\) complex as a function of the CF parameter \(x\) of eq 3 for \(W\) determined by a fit to ab initio state energies. The dashed line indicates the value of \(x\) from the same fit.

The CF parameters \(x\) and \(W\) for an isolated octahedral PuCl\(_6^{2-}\) complex ion were derived from the ab initio energies of the nine lowest electronic states by a least-squares procedure detailed in refs 60 and 61. The wave functions and energies were obtained at the complete active space (CAS) self-consistent field level of theory, with spin-orbit (SO) coupling treated by state interaction, using a developer’s version of the Molcas package.\(^{52}\) For further details, see the Supporting Information. The fit gave \(x = 0.837\) and \(W = 21.15 \text{ cm}^{-1}\). The energy of the multiplets arising from the \(^{3}I_{4}\) term as a function of the CF parameter \(x\) are shown in Figure 2. For small values of \(x\), the ground state of PuCl\(_6^{2-}\) corresponds to the \(\Gamma_1\) singlet and the first excited state corresponds to the \(\Gamma_3\) triplet. As the CF parameter \(x\) increases, the singlet \(\Gamma_1\) is destabilized and the triplet \(\Gamma_3\) becomes stabilized. The state ordering changes at \(x \approx 0.85\), beyond which the triplet \(\Gamma_3\) becomes the ground state (GS). Further crossings appear at \(x \approx 0.85\), where the excited states \(\Gamma_1\), \(\Gamma_4\) and \(\Gamma_3\) reverse their energetic ordering. For the fitted \(x = 0.837\) in the CF model, there is a comparatively large energy gap separating the GS and the excited states. The first excited state is the singlet \(\Gamma_1\) at 751 cm\(^{-1}\) above the GS, and the triplet \(\Gamma_4\) and the doublet \(\Gamma_3\) are at 791 and 819 cm\(^{-1}\), respectively.

**Electronic States of PuCl\(_6^{2-}\)**. The low-energy ab initio electronic states of the PuCl\(_6^{2-}\) complex ion were calculated for five different geometries, namely, \(O_6\), \(T_1\), \(T_2\), \(T_3\), and \(T_4\). These geometries correspond to an octahedral complex with Pu–Cl distances of 256.6 pm, and to four systems where in one of the three sets of trans Cl–Pu–Cl groups the Cl–Cl distances are increased by 1, 2, 3, and 4 pm, respectively, leading to tetragonally distorted complexes of \(D_{4h}\) symmetry. The calculated state energies of these PuCl\(_6^{2-}\) systems deriving from the \(^{3}I_{4}\) multiplet of Pu(IV) are collected in Table 3. For the octahedral complex, the GS corresponds to the triplet \(\Gamma_3\). As seen in Figure 2, in the corresponding CF model derived from the state energies of this system the \(\Gamma_1\) and \(\Gamma_3\) states are close in energy for \(x \approx 0.5\). The \(x\) parameter obtained from the fit is much larger. Only unreasonably large changes of the Pu–Cl distances would lead to \(\Gamma_1\) and \(\Gamma_3\) being close in energy in the ab initio calculations.

The state ordering is not altered in the distorted PuCl\(_6^{2-}\) systems, and the energetic separation of the GS and the excited states is hardly affected by the distortion. Importantly, however, the geometrical distortion leads to a splitting of the GS triplet \(\Gamma_3\) into a singlet and a doublet (see Figure 3). For instance, a
lengthening of 2 pm of the Pu–Cl distances leads to a GS singlet separated from the doublet by 21 cm⁻¹. This energetic splitting is small. However, even a small energetic splitting of the GS triplet has a strong influence on the magnetic susceptibility below 20 K and has a significant effect on the NMR measurements. Without a high-quality single-crystal structure for temperatures below 20 K we cannot reliably assign the reason for an energetic splitting of the GS triplet to either a distortion of the PuCl₆²⁻ octahedra or other crystal packing effects. Irrespective, the NMR data suggest that such an energetic splitting is indeed present in the system as described in section VI.

The influence of the environment on the electronic structure of the PuCl₆²⁻ anion was also investigated by using ab initio embedding calculations as explained in the Supporting Information. The main influence of the environment on the electronic structure of the PuCl₆²⁻ ion in these calculations is a slight energetic destabilization of the excited states without change of the state ordering.

**Electric Field Gradient and Magnetic Susceptibility Calculations for PuCl₆²⁻**. Electric field gradient (EFG) tensors were calculated for the Cl sites for the PuCl₆²⁻ ion without and with embedding, using SO-CAS wave functions and various density functional methods. The magnitude and asymmetry of the calculated EFG is sensitive to the approximations in the calculations. Effects from the embedding and dynamic electron correlation are shown in the Supporting Information to cancel to a large degree, and therefore we are able to use SO-CAS data calculated for the isolated complex ion. The SO-CAS field gradient $V_{zz} = 3.78 \times 10^{21} \text{V/m}^2$ is in reasonable agreement with the measured value determined from the NMR experiments, $V_{zz} = 4.02 \times 10^{21} \text{V/m}^2$.

The magnetic susceptibility was calculated using the different geometries of Table 3 for temperatures down to $T = 1$ K. As shown in Figure S2 in the Supporting Information, the magnetic susceptibility follows a Curie–Weiss law at high temperature for octahedral symmetry. A tetragonal distortion of the PuCl₆²⁻ octahedra causes a splitting of the $\Gamma_2$ magnetic triplet into a nonmagnetic singlet GS and a magnetic doublet. As a result, the magnetic susceptibility becomes constant when the temperature is of order the energy splitting ($\sim 10-20 \text{cm}^{-1}$, 14–29 K). As the magnitude of the tetragonal distortion increases, the onset temperature of this plateau in $\chi(T)$ increases (Figure S2).

### MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility $\chi(T)$ of (Me₄N)₂PuCl₆ is displayed in Figure 4a for this work at $H = 0.1, 5$ T, from Karraker et al., and Burton-Lewis et al. $\chi(T)$ remains paramagnetic down to the lowest measured temperature of 2 K. The overall magnitude of the susceptibility is somewhat smaller than previous reports. A Curie–Weiss fit to the data of the form $\chi = C/(T - \theta_{\text{CW}})$, where $C = N_A \mu_B^2 / 3k_B$ is the Curie constant, for $T > 200$ K as shown in Figure 4b (i.e., a linear fit to $\chi^{-1}(T)$), yields an

![Figure 3. Schematic energy diagram for octahedral ($O_h$) and tetragonal ($D_{4h}$) PuCl₆²⁻ geometries.](image)

![Figure 4. (a) Magnetic susceptibility $\chi$ of (Me₄N)₂PuCl₆ as a function of temperature from the present work in a magnetic field $H = 0.1$ T (black □) and 5 T (red ●), Karraker et al. (blue ▲), and Burton Lewis et al. (green ◆). Inset $\chi(T)$ below 25 K. (b) Inverse magnetic susceptibility $\chi^{-1}$ vs $T$ for the same measurements as the main panel fit. The solid lines are linear fits to the $\chi^{-1}(T)$ data as described in the text.](image)
effective moment \( \mu_{\text{eff}} = 1.60 (1.55) \mu_B \) and a Curie–Weiss temperature \( \theta_{\text{CW}} = -15 (-4) \) K for \( H = 0.1 (5) \) T. These values are somewhat smaller than those reported by Karraker et al. \( (\mu_{\text{eff}} = 1.92 \mu_B \) from a fit between 3 and 50 K) and Lewis et al. \( (\mu_{\text{eff}} = 1.99 \mu_B \) from a fit between 200 and 334 K). As shown in the inset of Figure 4a, the \( \chi(T) \) data in \( H = 5 \) T deviate from the \( \chi(T) \) data in \( H = 0.1 \) T below 15 K, with \( \chi(T, H = 5 \) T) exhibiting a linear temperature dependence with decreasing temperature and perhaps tending toward saturation.

A Curie–Weiss fit to the \( \chi(T, H = 0.1 \) T) data for \( T < 12 \) K yields \( \mu_{\text{eff}} = 1.69 \mu_B \) and \( \theta_{\text{CW}} = -10 \) K. If the upturn at low temperature in \( \chi(T, H = 0.1 \) T) in \((\text{Me}_{2}\text{N})_{2}\text{PuCl}_4\) was due to isolated magnetic impurities, one would expect a significantly smaller Curie constant (proportional to the number of impurities) and also a smaller Curie–Weiss temperature (\( \theta_{\text{CW}} \approx 0 \) K), suggesting that \( \chi(T) \) and the difference between the two data sets in the two different fields below 15 K are intrinsic. The intrinsic nature of the susceptibility is further supported by the lack of scaling of the magnetization with \( H/T \) for data collected at 2.5 and 25 K (not shown), which would be expected for isolated magnetic impurities that follow a Brillouin function \( B_\text{J}(H/T) \) from the Zeeman splitting of the angular momenta states in magnetic field.

**NUCLEAR MAGNETIC RESONANCE MEASUREMENTS**

\(^{35}\text{Cl}\) and \(^{37}\text{Cl}\) Nuclear Magnetic Resonance Spectra. Figure 5 displays spectra measured at \( T = 50 \) K and simulated powder spectra for \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\) resonances. The lower spectrum was taken on the \(^{242}\text{Pu}\) sample, and the upper spectrum was taken on the \(^{239}\text{Pu}\) sample, both at a resonant frequency \( \nu_0 = 14.5 \) MHz and \( T = 50 \) K for \(^{239}\text{Pu}\) (upper) and \(^{242}\text{Pu}\) (lower) samples. The resonant field for unshifted \(^{35}\text{Cl}\) and \(^{37}\text{Cl}\) are also displayed (black, dotted). The \(^{242}\text{Pu}\) spectrum displays significantly better resolution due to a larger sample mass and narrower line widths. All parameters used to simulate the spectra were identical except for a Gaussian broadening function, which indicates distributions of the local magnetic field. The broadening width was \( \Delta \nu = 25 \) and 75 kHz for the \(^{242}\text{Pu}\) and \(^{239}\text{Pu}\) samples, respectively.

![Figure 5. Experimental field swept NMR spectra (red, solid) of \((\text{Me}_{2}\text{N})_{2}\text{PuCl}_4\) and simulated spectra (blue, dashed) at a carrier frequency \( \nu_0 = 14.5 \) MHz and \( T = 50 \) K for \(^{239}\text{Pu}\) (upper) and \(^{242}\text{Pu}\) (lower) samples.](image)

The unperturbed resonant frequencies for \( \nu_\theta \) yields \( \mu_\text{ex} \) exhibiting a linear temperature dependence with decreasing temperature and perhaps tending toward saturation.

The resonant frequencies of these peaks are determined by the Zeeman and the quadrupolar Hamiltonians, which are in turn determined by material properties and physical constants. The Zeeman Hamiltonian is given by

\[
\mathcal{H}_Z = \frac{\hbar}{2\pi} N \gamma I \cdot \vec{B} (1 + K(\theta))
\]

where \( \gamma_N \) is the nuclear gyromagnetic ratio, \( I \) is the nuclear spin, and \( \omega_\theta \) is the angular dependent magnetic shift for the polar angle from the EFG principal axis, \( V_{zz} \) as displayed in Figure 1. Note that due to the tetragonal symmetry of the Cl nucleus, the shift is independent of azimuthal angle. It is easiest to define the shift \( \omega_\theta \) in the basis of \( \{K_{\text{iso}}, K_{\text{aniso}}\} \), which can be expressed in polar coordinates as \( K(\theta) = K_{\text{iso}} + \frac{1}{2} K_{\text{aniso}} (3 \cos^2 \theta - 1) \) where \( K_{\text{iso}} = (K_z + 2K_y)/3 \) and \( K_{\text{aniso}} = K_z - K_y \) in the Cartesian basis.

The quadrupolar Hamiltonian is given by

\[
\mathcal{H}_Q = \frac{\hbar}{2} \eta \left\{ 3I_z^2 - I(I+1) + \frac{\eta}{2} (I^+_z I^-_z + I^-_z I^+_z) \right\}
\]

where \( \nu_Q \) is the quadrupolar splitting, \( \eta \) is the anisotropy parameter, and \( I_\text{n} \) are the corresponding nuclear spin operators. The quadrupolar splitting can be further defined as \( \nu_Q = eQV_{zz}/4I(2I-1)\hbar \) where \( e \) is the electron charge, and \( Q \) is the nuclear quadrupolar moment (a physical property of the nucleus). Again, the tetragonal symmetry of the Cl nucleus suggests that \( \eta = 0 \).

In the limit of high magnetic field (which we are approaching in this experiment), where \( \hbar \omega_\theta \gg \nu_Q \), \( \mathcal{H}_Q \) can be treated as a perturbation of \( \mathcal{H}_Z \). The unperturbed resonant frequencies for a tetragonal system are given by

\[
\omega(\theta) = \frac{\gamma_N}{2\pi} H_0 (1 + K(\theta))
\]

The first order perturbation gives a transition dependent frequency change

\[
\omega^1(\theta) = \frac{\nu_Q}{2} (m-1/2)(3 \cos^2(\theta) - 1)
\]

where \( m = \{3/2, 1/2, -1/2\} \) indicates the transition \( m \), which represents \( \nu_m \leftrightarrow \nu_{-m} \). Note that this term gives \( \omega^1(\theta) = 0 \) for \( m = 1/2 \) and a monotonic angular dependence for the satellite transitions \( m = 3/2, -1/2 \). Thus, to first-order perturbation the powder spectrum gives three peaks.

The highest-order perturbation relevant for this discussion, second order, is significantly more complicated, and the equation can be found in Carter, Bennet, and Kahn.\(^{63}\) The important aspect can be summarized by

\[
\omega^2(\theta) \propto C_0 + C_1 \cos^2 \theta + C_2 \cos^4 \theta
\]

where \( C_0, C_1, \) and \( C_2 \) are constants depending on \( m, I, \) and \( \nu_Q \). Most importantly, this term is nonzero for the central transition, \( m = 1/2 \).
The NMR powder spectrum is the probability distribution of the sum of the above contributions over all θ: 
\[ P(θ) \propto \sin(θ)(ω(θ) + ω(θ) + ω(θ)) \] 
for which the final term has a non-monotonic variation with θ potentially producing two peaks for \( m = 1/2 \) as seen in Figure 5, most clearly for fields 3.4 T ≤ \( H_0 \) ≤ 3.6 T for \(^{35}\)Cl.

With these considerations in mind, the spectrum measured is fully described by a combination of \( H_f \) and \( H_Q \) for \(^{35}\)Cl and \(^{37}\)Cl with no trace of a resonance due to \(^{239}\)Pu. (Note that the nuclear spin \( I = 1 \)) is also present in the spectra at \( H_0 \approx 4.7 \) T and is displayed in Figure 6.) Analysis of the Cl spectra provides detailed microscopic information on the local electronic and magnetic properties of the PuCl\(_6\) octahedron as described in the following sections.

**Nuclear Magnetic Resonance Spectra Simulation: Magnetic Shift and Electric Field Gradient.** In the previous section, the resonant frequencies were described by the quadrupolar perturbation of the Zeeman interaction resonant frequencies under the condition that \( \frac{2Q}{3}H_0 \gg \nu_Q \). This is a more easily understood demonstration of how four resonant peaks appear for each Cl isotope. However, to simulate the powder spectrum accurately, we diagonalize the full NMR Hamiltonian, that is, the sum of Zeeman and quadrupolar interactions, because \( H_Q \) is not sufficiently larger than \( H_f \) to satisfy the conditions of perturbation theory.

The powder spectra were calculated by summing individually calculated spectra with angles \( 0 \leq \theta \leq 90 \). The spectra were parametrized by physical constants \( \{\gamma, Q\} \) and adjustable parameters \( \{K_{aniso}, K_{miso}, \delta \omega\} \), where \( \delta \omega \) is a temperature-dependent Gaussian broadening applied to the spectra. For the different Cl isotopes, \(^{35}\)Cl (\(^{37}\)Cl), \( \gamma/2\pi = 4.171 \) \( 69 \) (3.474 \( 28 \) MHz/T and \( Q = -0.08 \) (0.0632) barns. The physical constants are different for each Cl isotope, but both isotopes are in an identical crystal environment; thus, the adjustable parameters are identical when calculating the spectrum for each isotope, except for \( \nu_Q \) which scales with the ratio of Qs.

To fit the spectra, initial parameters were obtained from the peak positions between 3.4 and 4.4 T. A least-squares fit to the data of the probability distribution of eigenvalue solutions to the sum of eqs 4 and 5 broadened by a Gaussian function for the \(^{239}\)Pu and \(^{241}\)Pu samples at \( \omega_0 = 14.5 \) MHz and \( T = 50 \) K was performed. For the \(^{241}\)Pu sample spectrum, the optimized parameters are \( K_{iso} = 0.75 \)%, \( K_{aniso} = 21 \)%, \( \delta \omega = 25 \) kHz, and \( V_0 = 4.02 \times 10^{21} \) \( \text{V/m}^2 \), giving \( \nu_Q = 4.125 \) (3.239) MHz for \(^{37}\)Cl (\(^{35}\)Cl; Figure 5). Additionally, the spectral weight of the \(^{35}\)Cl spectrum was found to be 74.2% of the total spectral weight, and the \(^{37}\)Cl contribution accounted for 25.8%, consistent with the natural abundances of each isotope. The fit for the \(^{239}\)Pu sample was the same, within error bars, with the exception of a larger \( \delta \omega = 75 \) kHz, indicating a larger amount of magnetic and electronic disorder in the \(^{239}\)Pu sample.

The \(^{239}\)Pu sample spectra were fit with the same fashion as a function temperature, with the results shown in Figure 6. The fits were performed with both variable and fixed \( \nu_Q \) but no temperature dependence was observed within error bars, allowing us to extract the shifts as a function of temperature, as plotted in Figure 7.

**Magnetic Shift.** The temperature dependence of the shifts found from fitting the spectra are shown in Figure 7a. \( K_{iso} \) decreases from \( T = 50 \) to 15 K, below which it is approximately

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**Figure 6.** Field swept NMR spectra of the \(^{239}\)Pu sample from \( T = 1.6 \)–50 K at carrier frequency of \( \omega_0 = 14.5 \) MHz (red, solid) and simulated spectra (blue, dashed). The resonant field for unshifted \(^{35}\)Cl, \(^{37}\)Cl, and \(^{14}\)N nuclei are also displayed (black, dotted).

**Figure 7.** (a) Shift parameters used in the simulation of spectra shown in Figure 6. (b) \( K_{iso}(T) \) vs the experimentally measured susceptibility \( \chi_{iso}(T) \) (red ●) and the calculated susceptibility for a 0.020 Å tetragonal distortion \( \chi_{calc}(T) \) (green ▲) with \( T \) as an implicit parameter demonstrating scaling between the two parameters at higher temperatures allowing the extraction of a hyperfine field \( A \) by a linear fit to both sets of data. Arrows on both figures indicate deviations from Curie–Weiss behavior and the behavior of the bulk susceptibility. As indicated from calculations, the plateau of the shift below this temperature becomes the sole occupation of the nonmagnetic ground state, as temperature fluctuations have frozen out.
constant to the lowest temperatures. $K_{\text{aniso}}$ has similar behavior, where it increases from $T = 50$ to 15 K and becomes constant at low temperatures. The larger error bars for $K_{\text{aniso}}(T)$ come from the uncertainty separating the contributions from $K_{\text{aniso}}$ and the quadrupolar shift. To understand the behavior of the shifts, the following analysis is performed.

For nuclear magnetic resonance, the shift is described as

$$K(T) = K_c(T) + K_0$$

where $K_c(T)$ is the temperature-dependent spin shift, described below, and $K_0$ is the temperature-independent Van Vleck orbital susceptibility. The spin component of the shift is a measure of the the static electronic spin susceptibility scaled by the hyperfine field detected by the nucleus. Therefore, the spin shift is defined by

$$K_c(T) = \frac{A}{\mu_0 N_A} \chi_f(T)$$

where $A$ is the hyperfine coupling, $\mu_0$ is the Bohr magneton, and $N_A$ is Avogadro’s number.

By plotting $K(T)$ as a function of susceptibility $\chi_f(T)$ with $T$ as an implicit parameter, we may extract $A$ and $K_0$ from a linear fit to the data. For $K_{\text{aniso}}(T)$ and the measured $\chi_{\text{bulk}}(T)$, this plot is displayed in Figure 7b. For temperatures $15 \leq T \leq 50$ K a linear fit is performed to find $A = 8.26 \pm 0.81$ kOe/$\mu_B$ and $K_0 = -0.09 \pm 0.13$. However, it is evident that the linear relationship between $K_{\text{aniso}}(T)$ and $\chi_{\text{bulk}}(T)$ for $15 \leq T \leq 50$ K abruptly changes below $T = 15$ K, where $\chi_{\text{bulk}}(T)$ continues to increase, while $K_{\text{aniso}}(T)$ levels off to a constant value, within error bars. This indicates that the local susceptibility, as detected by the Cl nucleus, is not the same as the bulk susceptibility.

The temperature dependence of the susceptibility calculated for a symmetric PuCl$_2$O$_2$ octahedron is similar to the measured bulk susceptibility; however, the magnitude is larger than the measured values (see Figure S5 in Supporting Information). Furthermore, at low temperatures, $T < 20$ K, the functional form is quite different from $\chi_{\text{bulk}}(T)$. With increasing tetragonal distortion, the magnitude of the calculated susceptibility decreases over all temperatures and becomes constant at low temperatures with an increasing onset temperature. The decreasing magnitude comes closer to matching the experimental measurement of $\chi_f$, even though the temperature dependence disparity increases. Nevertheless, with increasing tetragonal deformation, the temperature dependence of $\chi_{\text{calc}}$ approaches that of $K(T)$.

The $K-\chi$ plot for $K_{\text{aniso}}$ versus $\chi_{\text{calc}}(T)$ for 0.020 Å tetragonal distortion is also displayed in Figure 7b. The linear fit for $15 \leq T \leq 50$ K results in $A = 6.03 \pm 0.54$ and $K_0 = -0.09 \pm 0.13$. The main difference between this fit and $K_{\text{aniso}}$ versus $\chi_{\text{bulk}}$ is that for the lowest temperatures $T < 15$ K, the deviation has decreased. Perhaps, with further distortion of the Z bond, the temperature dependence of $\chi_{\text{calc}}$ would match that of $K(T)$.

Spin–Lattice Relaxation. The nuclear spin–lattice relaxation rate $T_1$ is the characteristic time scale for which the nucleus gives its energy to the lattice in the form of phonons or via the electrons through the momentum-dependent hyperfine interaction. $T_1$ was measured in the range of $1.5 \leq T \leq 35$ K, Figure 8. Above $T = 15$ K, $T_1$ is temperature-independent, typical of a magnetic insulator. However, below $T = 15$ K, the relaxation time rapidly increases indicating the freezing of some relaxation channel(s).

Figure 8. Experimentally measured $T_1$ and $T_1$ calculated using eq 13 and scaled to the data for cubic symmetry and tetragonal distortions of $z = 0.010$ and 0.020 Å as described in the text. The arrow indicates the point at which $T_1$ begins slowing coinciding with the calculation for thermal fluctuations freezing out relaxation channels. (Inset) The magnetization recovery for $T = 25$ K at the central transition of $^{35}$Cl fit the multieponential form given in eq 1.

The relaxation rate is generally expressed using the fluctuation dissipation theorem$^{63-67}$ as

$$\frac{1}{T_1} = \frac{\gamma^2 k_B T}{\mu_B^2 \sum_{\vec{q} \Delta} A^2(q) \chi_f''(\vec{q}, \omega)}$$

where the sum is over directions $\vec{q}$ perpendicular to the external magnetic field and all wave vectors $\vec{q}$, $A(q)$ is the Fourier transform of the hyperfine coupling, and $\chi_f''(\vec{q}, \omega)$ is the imaginary component of the dynamic susceptibility. Therefore, $1/T_1$ is sensitive to the fluctuations perpendicular to the external magnetic field, at NMR frequencies.

When crystal-field splittings become relevant for nuclei with a large spin–orbit coupling, thermal fluctuations allow for channels of relaxation from the ground state to excited states when the fluctuations are larger than the crystal-field splitting. However, as the temperature decreases below the crystal-field energy-level splitting, the thermal fluctuations are frozen out, and relaxation becomes much longer with decreasing temperature.

The spin–lattice relaxation for fluctuations between crystalline electric field (CEF) levels may be calculated by$^{63-67}$

$$\left( \frac{1}{T_1} \right)_{\text{CEF}} = \frac{2 \gamma^2 A^2}{\omega_{\text{ex}} Z} \sum_j \frac{\langle J_j \rangle^2 \exp(-E_j/k_B T)}{Z}$$

where $\omega_{\text{ex}}$ is a constant exchange energy, $\langle J_j \rangle$ is the expectation value of the total spin for the $j$th CEF level, $E_j$ is the energy of the $j$th CEF level, and $Z$ is the partition function. The energy levels used to calculate $T_1$ are listed in Table 2 for different local symmetries. On the one hand, for the octahedral symmetry, the three $\Gamma_5$ wave functions are degenerate. Therefore, the next closest energy levels are 1000 K above the ground state and thus are irrelevant for our temperature range. $T_1$ is then temperature-independent. On the other hand, for tetragonal distortions, the $\Gamma_5$ ground state splits of order 10 K with an increasing splitting for increasing distortion length. For the cubic CF levels, the only nonzero $\langle J_j \rangle^2$ values come from the double components of $\Gamma_5$ and $\Gamma_4$, for which $\langle J_j \rangle^2 = 25/4$ and 1/4, respectively. Because the distortion causes a small splitting, to first order, these values are a reasonable estimate for the tetragonal case and $1/T_1 \approx \exp(-E/k_B T)/Z$, where $E$ is the energy of
The doublet excited state. The calculated relaxation is then scaled to the high-temperature constant measured value to avoid a selection of hyperfine field and exchange energy. The best agreement between the measured and calculated $T_1$ comes from the energy levels for the 0.010 Å tetragonal distortion, as displayed in Figure 8.

**DISCUSSION**

The formation of (Me$_4$N)$_2$PuCl$_6$ apparently depends sensitively on synthesis conditions. Specifically, in one case, the existence of at least one structural transition from Fd3c (the room-temperature structure) to Fm3m occurs at 360 K, with significant changes with temperature of the Pu–Cl$_6$ octahedra rotation and likely another structural transition present below 120 K. Another study reports the existence of a tetragonal phase at room temperature. The structure determined at 140 K in the present study reveals that (Me$_4$N)$_2$PuCl$_6$ has the space group Fm3m. The $^{35}$Cl and $^{37}$Cl NMR measurements indicate, through comparison with theory, a change in the local electronic ground state of the PuCl$_6^{2-}$ octahedron below ~15 K, reflected in the isotropic and anisotropic shifts and spin–lattice relaxation (Figures 7 and 8). A likely scenario for this change in electronic configuration of Cl is a splitting of the crystal-field $\Gamma_1$ ground state of Pu(IV) (in octahedral symmetry) in this compound, which is supported by the electronic structure calculations (Section IV). The origin of this CEF splitting is not known, but a distortion of the Pu–Cl$_6$ octahedra changes in the surrounding electrostatic environment of the octahedra (e.g., a change in the torsion angle of the octahedra), or a structural transition may cause the $\Gamma_1$ ground state to split into a nonmagnetic singlet and a doublet for a tetragonal distortion or three singlets for an orthorhombic distortion. The electronic structure calculations indicate that the energy separation of these levels is very small, of order 5–10 cm$^{-1}$ (6–12 K). The depopulation of these nonmagnetic singlets and magnetic doublets with decreasing temperature would lead to a plateau in the bulk magnetic susceptibility (Supporting Information) at the lowest temperature. It is not understood why the magnetic susceptibility does not show such a plateau (Figure 4), although if the distortion/structural transition of the octahedra were small, then the saturation of $\chi(T)$ may only appear at temperatures well below the energy of the split CEF levels (i.e., below 2 K) in the present sample. A small plateau in $\chi(T)$ was observed by Karkare et al. pointing to sensitivity of the properties on growth conditions or external factors (e.g., cooling rate). In any case, the NMR measurements clearly reveal that the Cl atoms in (Me$_4$N)$_2$PuCl$_6$ are sensitive to these changes in electronic structure. Further structural refinements or local structure measurements, such as X-ray absorption fine structure and X-ray diffraction of (Me$_4$N)$_2$PuCl$_6$ at low temperature to investigate the nature of the possible distortions and/or structural transition, would be particularly useful.

**CONCLUSION**

The synthesis of high-purity single crystals of (Me$_4$N)$_2$PuCl$_6$ and characterization via single-crystal X-ray diffraction and NMR measurements are reported. By comparison to NMR spectra of samples prepared by NMR-active $^{239}$Pu or nonactive $^{24}$Pu isotopes, no signature of the direct $^{239}$Pu NMR resonance was observed. Instead, the magnetic shift and spin–lattice relaxation were measured for the ligand $^{35}$Cl and $^{37}$Cl isotopes. The principal component of the electric field gradient at the Cl site was found to be $V_{zz} = 4.02 \times 10^{21}$ V/m$^2$. Electronic structure calculations predict that a tetragonal distortion of PuCl$_6^{2-}$ octahedron would result in a very small splitting (~20 cm$^{-1}$) of the $\Gamma_1$ triplet ground state into a nonmagnetic singlet and doublet state. Changes in the NMR spectra, including the magnetic shift and spin–lattice relaxation below 15 K, are indicative of a splitting of the Pu(IV) triplet crystal field ground state.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00735.

CIF file for (Me$_4$N)$_2$PuCl$_6$ (CIF)

NMR measurements and electronic structure of Pu(IV) in [(Me)$_2$N]$_2$PuCl$_6$ calculation results and details (PDF)

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