Puzzling Lack of Temperature Dependence of the PuO$_2$ Magnetic Susceptibility Explained According to Ab Intio Wave Function Calculations

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Supporting Information

**ABSTRACT:** The electronic structure and the magnetic properties of solid PuO$_2$ are investigated by wave function theory calculations, using a relativistic complete active space (CAS) approach including spin–orbit coupling. The experimental magnetic susceptibility is well reproduced by calculations for an embedded PuO$_4$$^{12+}$ cluster model. The calculations indicate that the surprising lack of temperature dependence of the magnetic susceptibility $\chi$ of solid PuO$_2$ can be rationalized based on the properties of a single Pu$^{4+}$ ion in the cubic ligand field of the surrounding oxygen ions. Below $\sim$300 K, the only populated state is the nonmagnetic ground state, leading to standard temperature-independent paramagnetism (TIP). Above 300 K, there is an almost perfect cancellation of temperature-dependent contributions to $\chi$ that depends delicately on the mixing of ion levels in the electronic states, their relative energies, and the magnetic coupling between them.

The PuO$_2$ solid has been well characterized experimentally. It crystallizes in the cubic CaF$_2$ structure with eight-coordinate octahedral plutonium sites and four-coordinate oxygen sites. The Pu$^{4+}$ ion has four valence electrons, with the ability to give rise to a variety of magnetic and nonmagnetic electronic states. Solid PuO$_2$ affords a nonmagnetic electronic ground state (GS), which was characterized both by magnetic susceptibility measurements$^{1,2}$ and by $^{17}$O NMR spectroscopy.$^{3,4}$ $^{239}$Pu NMR measurements also suggested that the magnetic moments of the Pu centers vanish.$^{5}$ A very interesting observation for PuO$_2$ is a temperature-independent paramagnetism (TIP) over a very large range of temperatures, namely, an essentially constant susceptibility $\chi$ of $5.6 \times 10^{-3}$ cm$^3$ mol$^{-1}$ between 1 and 1000 K.$^2$ The surprising TIP up to such high temperatures has since attracted much attention, and its origin remains a subject of debate.

TIP at lower temperatures can be explained with the help of crystal field (CF) theory. The ground level of the Pu$^{4+}$ ion is $^3$I$_4$. The 9-fold degenerate $^3$I$_4$ level is split by the cubic CF into one singlet A$_1$, one doublet E, and two triplets T$_1$ and T$_2$. The GS of PuO$_2$ is expected to be the nonmagnetic singlet A$_1$. If there is no mixing between the ground and excited ion levels, the TIP susceptibility can only arise from a magnetic coupling between A$_1$ and T$_1$, because the magnetic moment matrix elements involving A$_1$ and the other states of the $^3$I$_4$ level are zero. The experimental magnetic susceptibility combined with magnetic transition moments from CF theory lead to the estimate that the T$_1$ excited state (ES) should be 284 meV above the GS.$^2$ (In terms of wavenumbers, 1 meV corresponds to 8.07 cm$^{-1}$). Neutron inelastic scattering (NIS) experiments later measured this energy gap at 123 meV.$^7,8$ The NIS experiment was thought to confirm the localized nature of the Sf states and, therefore, the validity of using a CF model to rationalize the magnetic properties of PuO$_2$. However, an energy gap of 123 meV is inconsistent with TIP at high temperatures. Rather, the magnetic susceptibility should become temperature-dependent at around $\sim$300 K. We also note that with the magnetic transition moment between A$_1$ and T$_1$ obtained from CF theory, the low-temperature TIP susceptibility estimated with a 123 meV energy gap would be more than double the observed value. Clearly, some of the interpretations of the experimental data are at odds with each other.

An explanation of the unexpected magnetic susceptibility of PuO$_2$ by theory has proven challenging. Neither CF$^9$–$^{11}$ nor density functional theory (DFT) calculations were fully satisfactory, and DFT in different flavors tends to produce magnetic GSs.$^{13,18}$ DFT$^{19,20}$ and DFT-based dynamical mean-field theory (DMFT)$^{21,23}$ have predicted Pu–O covalency, which has been used to explain satellite peaks in the core-level photoemission spectra.$^{21}$ In other words, donation bonding would take place between the ligands and the metal. A DFT–impurity model combination with semiempirical parameters was able to produce an only weakly T-dependent susceptibility$^{24}$ due to canceling T-dependent terms, although the susceptibility was sensitive to the model parameters.

As an (often superior) alternative to DFT, many studies of open-shell actinide systems have been carried out successfully with ab inito multiconfigurational wave function methods.$^{25}$ Among these is the Complete Active Space Self-Consistent Field (CASSCF)$^{26}$ approach and its varieties, which allows one (i) to construct all possible configurations within a chosen

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active orbital space and, optionally, a partitioning of the active space with limitations placed on the excitation levels and (ii) to include spin–orbit (SO) coupling via “state interaction” or from the onset. The CAS approach provides a reliable treatment of multiconfigurational character present in open-shell actinide systems, and it can be used with all-electron relativistic Hamiltonians. Furthermore, this computational strategy can be applied to solids as long as a computational model is appropriate. For instance, Ungur et al. were able to describe the electronic structures of several fluoride structures of UO2 by using a UO8 molecular cluster surrounded by four shells of point charges to describe the crystal environment.

Herein, we offer an interpretation of the magnetism of PuO2 that relies only on the electronic structure of the Pu4+ ion surrounded by the nearest-neighbor oxygens. Relativistic CAS wave function results suggest a pseudo-TIP susceptibility of PuO2 at higher temperatures, that is, a near-perfect cancellation of temperature-dependent contributions to χ. The calculations utilize a PuO8 cluster surrounded by an embedding model for the crystal environment, as shown in the graphical abstract. CAS(n,m) and restricted active space (RAS) calculations with n electrons in m orbitals were carried out at the SCF level and with multistate second-order perturbation theory (PT2) for the treatment of dynamic electron correlation, as detailed in the Supporting Information (SI), using the Molcas program. Among the active spaces used in this work are (4,7) = four electrons in the seven 5f orbitals, (4,12) = (4,7) augmented with five 6d orbitals, and (12,16) = (4,12) augmented with four ligand-centered occupied orbitals.

The ab initio results are conveniently analyzed by referring to the levels of the Pu4+ ion from which the various 5f4 states of PuO2 are derived. For illustration, an energy level diagram is shown in Figure 1. According to Hund’s rules, the spin-free (scalar relativistic, SR) ground term of the Pu4+ ion is 5I, that is, L = 6 and S = 2. The cubic CF in the solid splits 5I into three spatially three-fold degenerate spin-quintets (5T2g + 25T2g), one spatially two-fold degenerate spin-quintet (5Eg) and two spatially nondegenerate spin-quintets (5A1g + 5A2g). The SO coupling strongly mixes these states among each other as well as with states derived from excited SR triplet terms of Pu4+. The SO GS of PuO2 is the nondegenerate A1. The GS can also be characterized by considering the SO coupling for the Pu4+ ion first. The 5I term of the spherical ion is split by the SO interaction into 5I levels, with J going from 4 to 8. For a less than half filled f shell, the GS is the nine-fold degenerate J = 4 level. The 5I level is then split by the CF interaction into one singlet A1, one doublet E, and two triplets T1 and T2. The combined CF and SO interaction also mixes 5I with contributions from excited J = 4 levels (5Eg, 5T2g and 5H2g).

Relative calculated electronic energies for the first four electronic states of the PuO8 cluster, without and with embedding, are collected in Table 1 for the different active spaces. The state ordering is A1 (GS), T1, T2, and E. The crystal electrostatic environment in the embedded system leads to a destabilization of the ESs, most notably for E. There are no experimental data for the ordering of the ESs. However, our embedded results are in good agreement with the state ordering calculated using LDA+DMFT, where T1, T2, and E were separated from the GS by 125, 226, and 319 meV, respectively.

Assignments of the low-energy electronic states of PuO2 at the SCF level are provided in Table 2, based on the embedded cluster model. As expected, on the basis of the qualitative discussion of level splitting and mixing, the 5I level contributions are dominant, with about 83–86% weight in the wave functions, with the remaining contributions from excited J = 4 levels. Considering the SO coupling a posteriori, the nondegenerate GS results from an admixture between the lowest SR states 5T2g (1) (49%) and 5Eg (33%) and numerous other small contributions.

Table 1. Relative Calculated Energies (meV) of the Low-Energy Electronic States of an Isolated and Crystal-Embedded PuO8 Cluster of PuO2. CAS/RAS-SCF-SO Results

<table>
<thead>
<tr>
<th>Isolated PuO8 (12−)</th>
<th>Embedded PuO8 (12−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS(4,7)</td>
<td>CAS(4,7)</td>
</tr>
<tr>
<td></td>
<td>CAS(4,12)</td>
</tr>
<tr>
<td></td>
<td>RAS(12,16)</td>
</tr>
<tr>
<td>A1</td>
<td>0</td>
</tr>
<tr>
<td>T1</td>
<td>107</td>
</tr>
<tr>
<td>T2</td>
<td>231</td>
</tr>
<tr>
<td>E</td>
<td>222</td>
</tr>
</tbody>
</table>

Table 2. Assignment of the Low-Energy Electronic States of PuO2 with 5I Parentage

<table>
<thead>
<tr>
<th>State</th>
<th>∆E (meV)</th>
<th>Weight of 5I</th>
<th>Weight of SR</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0</td>
<td>85 5I</td>
<td>49 5T2g, 33 5Eg, 3 5T4g (2)</td>
</tr>
<tr>
<td>T1</td>
<td>134</td>
<td>86 5I</td>
<td>44 5T2g (1), 26 5Eg, 4 5T4g, 8 5T4g (2), 2 5A2g</td>
</tr>
<tr>
<td>T2</td>
<td>262</td>
<td>86 5I</td>
<td>41 5T2g (1), 27 5Eg, 8 5A2g, 9 5T4g (2)</td>
</tr>
<tr>
<td>E</td>
<td>332</td>
<td>83 5I</td>
<td>7 5T2g (1), 24 5Eg, 15 5T4g, 6 5A2g, 23 5T4g (2), 8 5A2g</td>
</tr>
</tbody>
</table>

*RAS(12,16)SCF-SO calculations for the embedded cluster model. Weights are in %. The notations used for the contributions refer to the labels used in Figure 1.
Of particular interest for this study is the energy gap between \( A_1 \) and \( T_1 \). This gap is found to be only weakly dependent on the size of the active space. When the active space includes 5f, 6d, and four formally doubly occupied ligand-centered orbitals of symmetry \( a_{2u} \) and \( t_{2g} \), that is, RAS(12,16), the excited triplet \( T_1 \) is calculated to be 134 meV above the GS. This result is in good agreement with the INS experiment (\( \Delta E = 123 \text{ meV} \)) and at the upper end of the range determined in previous computational studies (97–134 meV).

Natural orbitals (NOs) and occupation numbers for the SO GS of PuO\(_2\) calculated with the RAS(12,16) space are shown in Figure 2 (see Figures S2 and S4 of the SI for the CAS(4,7) and CAS(4,12) active spaces). The occupations of the 5f orbitals do not depend strongly on the size of the active space (see SI). The combined 5f shell occupation of the SO GS obtained from the relativistic \textit{ab initio} calculations is \( n_f = 3.99 \), that is, very close to the idealized Pu\(^{4+}\) 5f occupation. The four unpaired electrons are predominantly distributed over the 5ft\(^{2u}\) and 5ft\(^{1u}\) orbitals, with combined occupations of 3 \( \times \) 0.726 = 2.178 and 3 \( \times \) 0.552 = 1.656, respectively. This occupation pattern arises from mixing of the SR states \( ^5T_2(1) \) and \( ^3E \) (Table 2). The SR \( ^5T_{2g}(1) \) state has a dominant configuration \( (5f_{2u})^3(5f_{1u})^1 \) (72%), while \( ^3E \) has a dominant configuration \( (5f_{2u})^2(5f_{1u})^2 \) (80%). When SO coupling mixes these configurations, the combined 5f\(^{2u}\) occupation ends up between 2 and 3 (closer to 2 in our case), while the 5f\(^{1u}\) occupation is between 1 and 2. At least some of the 5f\(^{2u}\) occupation is also due to this particular state mixing by the SO coupling; the \( ^3E \) state contains a configuration \( (5f_{2u})^1(5f_{1u})^3(5f_{2u}) \) with 17% weight, and there are contributions to the 5f\(^{2u}\) occupation from SR spin-triplets. The 6d shell of the Pu center remains basically unoccupied; the occupation numbers of the corresponding metal-centered NOs do not exceed 0.002, and the metal character of the doubly occupied ligand-centered orbitals of the same symmetry is very small. Indeed, calculations with a (12,11) active space that excludes the 6d shell but includes the four ligand-centered orbitals produces nearly identical state energies and magnetic data (SI). A relatively weak antibonding interaction between the 5f Pu and 2p O orbitals is visible for the Pu 5f\(^{2u}\) NO, with an occupation of 0.158. There is a ligand-centered \( a_{2u} \) NO (occupation \( \approx 1.998 \)) featuring the corresponding bonding interaction, but the contribution from the metal orbital is seen to be small in Figure 2. The fact that SO coupling shifts electron density at the metal center from the formally occupied 5f\(^{2u}\) and 5f\(^{1u}\) also into the 5f\(^{1u}\) orbital, which exhibits some Pu–O antibonding character, means that the covalency involving the 5f shell is quite weak.

The calculated 5f and 6d shell occupations and the weak metal–oxygen hybridization in the SO GS suggest that the GS electronic structure of PuO\(_2\) can be effectively rationalized by using a single-ion picture. Recent LDA+DMFT calculations found strong 5f–2p hybridizations, leading to 5f shell occupation numbers much exceeding four. In this context, it is important to mention that KS DFT-based calculations probably overestimate the orbital mixing due to the KS delocalization error. Our SCF calculations do not include dynamic electron correlation, and therefore, they may inherit an opposite “localization error” from Hartree–Fock theory and underestimate any covalent effects. Consequently, the effect of dynamic correlation was investigated at the PT2 level for CAS(4,7) and CAS(4,12). The resulting relative calculated electronic energies are collected in Table S2 in the SI, and the corresponding NOs are shown in Figures S3 and S5. The introduction of the dynamic correlation leads to a slight energetic destabilization of the ESs when compared to the corresponding SCF-SO results. However, there is also a noticeable symmetry breaking of the PT2 wave functions, which leads to an undesired energetic splitting of the degenerate states. For instance, the three components of the first excited triplet \( T_2 \) are split by more than 13 meV with CAS(4,12)/PT2-SO. Furthermore, the comparison between the NOs obtained from the SCF-SO and PT2-SO calculations reveals that the dynamic correlation only leads to a minor increase of the 5f–2p mixing. For example, with the CAS(4,12) active space, some minor additional 2p oxygen character shows up in the 5f\(^{1u}\) and 6d\(^{2u}\) orbitals. Overall, the introduction of the correlation effects via PT2 does not increase the metal–ligand orbital mixing to a degree that would warrant a reclassification of the system as covalent. Because of the spurious symmetry breaking with PT2, only the magnetic properties calculated at the SCF level are discussed in the following section. We note in this context that CASSCF is usually considered to be suitable for magnetic susceptibility calculations.

The calculated magnetic moment matrix elements \( \mu_{ij} \) for the states of Tables 1 and 2 are given in Table 3. Due to the cubic

\[
\begin{array}{cccc}
\mu_{0} & A_1 & T_1 & T_2 & E \\
A_1 & 0.000 & 0.623 & 0.000 & 0.000 \\
T_1 & 0.623 & 0.928 & 0.270 & 0.694 \\
T_2 & 0.000 & 0.270 & 1.124 & 0.662 \\
E & 0.000 & 0.694 & 0.662 & 0.000 \\
\end{array}
\]

Table 3. Calculated Magnetic Moment Matrix Elements \( \mu_{ij} \) between PuO\(_2\) SO States of \( ^5I_1 \) Parentage

\( ^{12,16}\text{SCF-SO} \) results are in units of \( \mu_B \). For degenerate states, the listed value corresponds to the root-mean-square. The use of these tabulated \( \mu_{ij} \) values in eq 1 leads to curves (a)–(c) of Figure 3.
site symmetry of Pu, the magnetic moment vector components are equivalent, and therefore, only the calculated data for one magnetic axis are discussed in the following section. The GS of PuO$_2$ does not exhibit a magnetic moment as it is not degenerate. The excited non-Kramers doublet E is also calculated to be nonmagnetic (see the SI for further details on the E state). The triplet states T$_1$ and T$_2$ exhibit nonzero magnetic moments with calculated root-mean-square ($\mu$) values of 0.928 and 1.124 $\mu_B$, respectively. We note in passing that SO coupling heavily influences the magnetic moment matrix elements of PuO$_2$, as expected. With the SO GS being nonmagnetic, off-diagonal magnetic moment matrix elements between the GS and the low-energy ESs are predominantly responsible for the TIP of PuO$_2$ for temperatures up to about 300 K. From Table 3, it is seen that for the states with $^3$I$_4$ parentage only the magnetic coupling between A$_1$ and T$_1$ is nonzero, as already mentioned. We also point out that large magnetic moment matrix elements are calculated between T$_1$ and E and between T$_2$ and E, along with a small magnetic coupling between T$_1$ and T$_2$.

The magnetic moment matrix elements $\mu_{ij}$ of Table 3, along with the state energies listed in Table 1, can be used to calculate the magnetic susceptibility $\chi$ of PuO$_2$ from the van Vleck equation

$$\chi = \frac{1}{Q_0} \mu_0 \mu_B^2 \sum_{\lambda} e^{-\beta E_{\lambda}} \left[ \mu \sum_{a,a'} |\langle \psi_{a'} | L_{\alpha} | \psi_{a}\rangle|^2 + 2 \sum_{\lambda \neq \lambda'} \sum_{a,a'} \frac{|\langle \psi_{a'} | L_{\alpha} | \psi_{a}\rangle|^2}{E_{\lambda} - E_{\lambda'}} \right]$$

(1)

Here, $\chi$ is the susceptibility for an applied magnetic field in the direction $\mu$ coinciding with a principal magnetic axis. For PuO$_2$, the susceptibility is isotropic. The summations $\lambda$, $\lambda'$ go over the set of available electronic states. In principle, this should be the complete set of states of the system, but in practice, the sum is restricted to the states that are actually calculated or a subset thereof. Further, $Q_0 = \sum_{\lambda} e^{-\beta E_{\lambda}}$ is the partition function and $\beta = 1/(kT)$. The indices $a$, $a'$ count the components of degenerate states. The factors $\mu_0$, $\mu_B$ are the vacuum permeability and Bohr magneton, respectively. The first “Curie” term inside of the brackets on the right-hand side of eq 1 is proportional to $\beta$ and therefore intrinsically temperature-dependent. This term results from contributions of populated degenerate magnetic states. The second “linear response” (LR) term is not intrinsically temperature-dependent and involves magnetic coupling between different electronic states that describe how state $\lambda$ responds to the presence of the magnetic field. For a system with a nonmagnetic GS, like PuO$_2$, at sufficiently low temperatures where the population of the ESs is negligible, only the coupling between the GS and ESs in the second term contribute to the susceptibility and TIP is observed. At higher temperatures, Curie terms from populated magnetic ESs and LR contributions from magnetic or nonmagnetic ESs may contribute to the susceptibility.

Figure 3 shows several calculated $\chi(T)$ that were obtained from eq 1 and the data in Tables 1 and 3. Curve (a) of Figure 3 was calculated by using only the GS A$_1$ and the first ES T$_1$. The magnetic coupling between A$_1$ and T$_1$ gives a TIP $\chi_{(T)} = 0.562 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$, between 0 K and room temperature. This calculated value of $\chi_{(T)}$ is in excellent agreement with the experiment. We remind the reader that the experimental $\chi$ would be consistent with pure $^3$I$_4$ CF states if the A$_1$/T$_1$ energy gap were 284 meV. However, the $ab$ initio calculations agree well both with the refined experimental A$_1$/T$_1$ energy gap of 123 meV and with the experimental TIP susceptibility. The reason for the excellent agreement in our calculation is that the $ab$ initio calculated magnetic transition moment of 0.623 $\mu_B$ (Table 3) entering the susceptibility is much smaller than the CF estimate of 0.861 determined from the $^3$I$_4$ CF states (further details are provided in the SI). The reduction by a factor of 0.72 is consistent with the reduced weights of the $^3$I$_4$ configurations in the wave functions, around 85% (Table 2), because $0.861^2 = 0.72$. The susceptibility based on all of the calculated states is also influenced by magnetic coupling of the GS with higher ESs (vide infra). However, these couplings do not involve the J = 4 levels that mix into the GS, and therefore, the weights of the $^3$I$_4$ states in A$_1$ and T$_1$ best rationalize the reduction of the magnetic transition moment.

Above 300 K, $\chi_{(T)}$ becomes temperature-dependent because of the thermal population of the T$_1$ state and decreases to 0.362 $\times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ at T = 1000 K. Such a T dependence of the susceptibility was not observed experimentally, but it is consistent with a previous CF analysis performed by Colarieti-Tosti et al. When contributions from the second triplet T$_2$ are included in eq 1, we obtain curve (b) of Figure 3. Because the magnetic moment matrix elements between A$_1$ and T$_2$ vanish (see Table 3), the calculated TIP in $\chi_{(T)}$ at low temperature is the same as in $\chi_{(a)}$. Magnetic coupling between the T$_1$ and the T$_2$ states causes a less pronounced decrease of $\chi_{(T)}$ at higher T when compared to $\chi_{(a)}$.

The influence of the introduction of the excited doublet E in eq 1 is shown by curve (c) in Figure 3. In this case, the Van Vleck equation includes all of the states of Pu$^{4+}$ $^3$I$_4$ parentage. Because the magnetic coupling between A$_1$ and E vanishes, the TIP segment of $\chi_{(a)}$ is not affected by the E state and remains in excellent agreement with the experiment. Just as importantly, however, $\chi_{(a)}$ remains practically constant above 300 K and reaches 0.569 $\times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ at T = 1000 K. The reasons for this behavior are the large magnetic couplings between E and the triplets T$_1$ and T$_2$ (Table 3). The T-dependent Curie contribution from the thermal population of T$_1$ above 300 K is
then counterbalanced in $\chi_T$ by a contribution arising from the magnetic coupling between $T_1$, $T_2$, and $E$. The net result is a \textit{pseudot}-TIP susceptibility up to very high temperature.

The ab initio calculated $\chi(T)$ for all calculated states with the RAS(12,16) active space is also shown in Figure 3 (curve (d)). This calculated $\chi$ is in acceptable agreement with the experimental data. At low temperature, the calculated $\chi$ overestimates the experimental value by $0.17 \times 10^{-3}$ cm$^3$ mol$^{-1}$. Such a deviation from experiment is not unusual for \textit{ab initio} susceptibility calculations for actinide systems.\textsuperscript{36,42,44} The difference between curves (c) and (d) reveals that the calculated TIP of PuO$_2$ is also influenced by magnetic coupling between the GS and ESs derived from other Pu ion levels at higher energies. For instance, nonzero transition magnetic moments were calculated between the SO GS and two triplet states arising from the excited $^1I_3$ ion level. Further, above ~600 K, a minor temperature dependence is caused by magnetic coupling between the populated $^1I_1$ ion level. Above ~600 K, a minor temperature dependence is caused by magnetic coupling between the populated $^1I_1$ state and states derived from excited ion levels. The fact that the TIP susceptibility is overestimated, compared to the experiment, when these states are included suggests (i) that the magnetic coupling between these states and the low-energy electronic states is overestimated, (ii) that the energies of these states are predicted to be too low, or (iii) a combination thereof that may be caused by the various approximations in the calculations. In this case, curve (c) of Figure 3 obtained by including only the $^1I_1$ parentage states in the susceptibility calculation would be the most realistic. Curve (c) is also the one that agrees best with the experiment over the 1000 K temperature range.

To summarize, the calculated energy gap between the GS and the first ES and the magnetic susceptibility are in good agreement with experimental data. The puzzling experimental finding that the susceptibility is essentially constant up to 1000 K has a single-ion interpretation based on the \textit{ab initio} calculations as follows: Up to ~300 K, magnetic coupling between the nonmagnetic GS $A_1$ and the magnetic first ES $T_1$ is responsible for a standard TIP. Compared to a simple CF model, the $A_1/T_1$ magnetic transition moment is significantly reduced due to mixing of states derived from higher-energy ion levels into the low-energy states of $^1I_1$ parentage. Above 300 K, a \textit{pseudot}-TIP is caused by an almost perfect cancellation of $\chi_T$ by a contribution arising from the magnetic coupling between Pu and the oxygens from the ligands that would help facilitate such interactions.

\section*{ASSOCIATED CONTENT}

\subsection*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcl.6b02968.

Additional information and data regarding the embedding calculations and plots of orbitals calculated at the SCF-SO and PT2-SO levels (PDF)

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The authors declare no competing financial interest.

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