Ligand NMR Chemical Shift Calculations for Paramagnetic Metal Complexes: 5f$^1$ vs 5f$^2$ Actinides

Frédéric Gendron and Jochen Autschbach*

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14260-3000, United States

Supporting Information

ABSTRACT: Ligand paramagnetic NMR (pNMR) chemical shifts of the 5f complexes UO$_2$(CO$_3$)$_3$$^{5-}$ and NpO$_2$(CO$_3$)$_3$$^{4+}$, and of the 5f complexes PuO$_2$(CO$_3$)$_3$$^{4+}$ and (C$_5$H$_5$)$_3$UCH$_3$ are investigated by wave function theory calculations, using a recently developed sum-over-states approach within complete active space and restricted active space paradigm including spin–orbit (SO) coupling [J. Phys. Chem. Lett. 2015, 20, 2183-2188]. The experimental $^{13}$C pNMR shifts of the actinyl tris-carbonate complexes are well reproduced by the calculations. The results are rationalized by visualizing natural spin orbitals (NSOs) and spin-magnetizations generated from the SO wave functions, in comparison with scalar relativistic spin densities. The analysis reveals a complex balance between spin-polarization, spin and orbital magnetization delocalization, and spin-compensation effects due to SO coupling. This balance creates the magnetization due to the electron paramagnetism around the nucleus of interest, and therefore the pNMR effects. The calculated proton pNMR shifts of the (C$_5$H$_5$)$_3$UCH$_3$ complex are also in good agreement with experimental data. Because of the nonmagnetic ground state of (C$_5$H$_5$)$_3$UCH$_3$, the $^1$H pNMR shifts arise mainly from the magnetic coupling contributions between the ground state and low-energy excited states belonging to the 5f manifold, along with the thermal population of degenerate excited states at ambient temperatures.

1. INTRODUCTION

The theory of NMR chemical shifts for paramagnetic molecular species (pNMR shifts) has taken decades to develop fully. The wave function theory (WFT) and Kohn–Sham (KS) computational methods for pNMR shifts have only become available over the past decade. The theoretical and computational challenges are compounded if the paramagnetic species contains heavy elements, for instance open-shell heavy metal centers. The computations then need to take into account scalar relativistic (SR) effects and spin–orbit (SO) coupling in the determination of the wave function or KS orbitals for the state of interest as well as in the subsequent NMR step. The theoretical methods currently in use for pNMR calculations can roughly be classified by the following categories: (i) Methods expressing the pNMR shift in terms of the parameters of the electron paramagnetic resonance (EPR) pseudospin Hamiltonian such as the $g$-factor and ZFS tensors, or in terms of the magnetic (spin) susceptibility; (ii) Methods where the pNMR shielding tensor is directly calculated as a bilinear energy derivative within a chosen computational method. Direct methods may employ a response theory framework or a sum-over-states (SOS) approach. To our knowledge a direct response theory framework for pNMR shifts is not yet available.

For metal complexes with relatively pure spin multiplets, KS methods have been shown useful for calculating and rationalizing pNMR shifts. Recently, a mixed WFT/KS approach was put forward for the calculation of pNMR shifts in selected, more difficult, transition metal complexes. The EPR parameters ($g$-factors and ZFS tensors) were calculated with WFT, whereas the HyF coupling tensors were obtained from KS calculations. The approach was then improved by taking into account contributions from excited electronic states based on recent theoretical developments by Soncini and Van den Heuvel. However, for most lanthanide or actinide complexes as well as transition metal systems with orbitally degenerate states, KS theory with available approximate functionals has well-known serious difficulties in describing the complexity of the electronic structure, which may limit the accuracy at which the HyF interactions entering the pNMR shift expression are described.

Because of the considerable difficulties with KS calculations to determine the magnetic properties of open-shell heavy element complexes with unquenched orbital angular momentum, we recently developed a direct multi-reference WFT SOS approach for pNMR shifts within a complete active space (CAS) framework. Details are provided in section 2. Pilot calculations of the $^{13}$C NMR shifts of two actinyl 5f$^1$ carbonate complexes, UO$_2$(CO$_3$)$_3$$^{5-}$ and NpO$_2$(CO$_3$)$_3$$^{4+}$, provided good agreement with experimental data and produced a sizable increased carbon shielding in these two compounds relative to...
the isostuctural diamagnetic UVI complex UO2(CO3)4−. The experimental chemical shifts for the U and Np referred to UO2(CO3)4− are −62 and −94 ppm, respectively, at 273 K.25−30 The calculations also reproduced the chemical shift difference between the two paramagnetic species well. This difference is surprisingly large, given that the two complexes are iso-structural and iso-electronic. The calculations indicated that the two main factors driving this difference are (i) the energetic separation of the ground state (GS) doublet and the first electronic excited state (ES) doublet, calculated to be 132 (U) vs 356 (Np) cm−1 and therefore enhancing the magnetic coupling between the two states for the U compound, (ii) a more effective metal-to-ligand transfer of spin magnetization in the ground state of the Np compound.

In the present study, this WFT approach is explored further, by comparing the aforementioned SF systems with actinide complexes having SF configurations, namely PuO2(CO3)3− and (C5H5)3UCH3. Experimental pNMR shift data are available for both. The paramagnetic effects are overall considerably stronger than for the SF species. The experimental 13C shift in PuO2(CO3)3− at 295 K relative to the UVI analogue is −376 ppm.29 The methyl proton shifts in (C5H5)3UCH3 are −195 ppm when referenced to TMS (converted from the reference to benzene given in the original publication).31,32 The experimental cyclopentadienyl (Cp) proton shifts in this compound are −3 ppm and therefore apparently less influenced by the paramagnetic center.

It is shown herein that the large paramagnetic effects on the carbonate 13C and methyl proton shifts on the SF systems are well reproduced by the CAS calculations. For the SF carbonate complexes, we provide additional analyses and date beyond our preliminary results report.15 The demands of the calculations regarding the active spaces are carefully evaluated for all systems. At present, the flexibility of the wave function versus the real-life performance of computing hardware and software need to be balanced on a system-by-system basis. The analysis of the calculated shifts demonstrates the different mechanisms causing pNMR effects and highlight, in particular, the important contributions from the orbital angular momentum magnetization. The GS of PuO2(CO3)3− is a non-Kramers doublet,23,33 and its spin and orbital angular momentum magnetizations are responsible for the large observed pNMR shifts. When SO coupling is included in the wave function calculations, the GS of (C5H5)3UCH3 is nonmagnetic.34 Here, the pNMR shift results predominantly from magnetic coupling with low-energy ESs. The apparently small paramagnetic effects on the Cp proton shifts are to some extent a result of the quasi-free rotations of the Cp ligands. With fixed orientations, the calculated proton NMR shift range in the Cp ligands exceeds 70 ppm. The chemical shifts are also studied as a function of temperature (T), and the influence of Curie magnetism vs thermal populations of low-energy magnetic ESs is discussed.

2. THEORETICAL AND COMPUTATIONAL DETAILS

A SOS equation for the NMR shielding tensor, as a generalization of the Ramsey equation for the ground state of a closed-shell system, was recently derived by SvH.13,14 Our implementation and computational approach is detailed in refs 15 and 35. As mentioned already in refs 15 and 36, a SOS formulation prevents a truly efficient calculation of the full ligand shielding. However, the pNMR ligand chemical shifts of paramagnetic metal complexes in reference to analogous diamagnetic systems are primarily caused by low-energy electronic states related to the metal open shell. The isotropic chemical shift with respect to a diamagnetic reference is then dominated by

\[
\delta_{\text{pNMR}}^N = \sigma_{\text{ref}, \text{dia}}^N - \sigma^N(T) = \frac{1}{3} \sum_i \frac{1}{Q} \sum_j e^{-E_i/k_B T} \times \left[ 2 \text{Re} \sum_{a \neq a'} \langle \lambda a | \tilde{H}_{\text{HyF}} | \lambda a' \rangle \langle \lambda a' \tilde{H}_{\text{HyF}} | \lambda a \rangle + \frac{1}{k_B T} \sum_{a, a'} \langle \lambda a | \tilde{H}_{\text{HyF}} | \lambda a' \rangle \langle \lambda a' \tilde{H}_{\text{HyF}} | \lambda a \rangle \right]
\] (1)

In eq 1, the sum \( \lambda \) runs over the aforementioned low-energy electronic states with energies \( E_\lambda \). Further, \( N \) labels the nucleus of interest, \( i \) counts the components \( \mu^N \) of the nuclear spin magnetic moment and the components \( B_i \) of the external magnetic field of the spectrometer, \( a \) and \( a' \) count the components of a state if it is degenerate, \( k_B \) is the Boltzmann constant, \( T \) the absolute temperature, and \( Q = \sum_{\lambda i} \exp \left( E_i / (k_B T) \right) \) is the partition function. Equation 1 represents the average of the diagonal elements of the pNMR shielding tensor; all individual tensor elements are calculated first via analogous expressions for the components \( i \) and \( j \) of the external and the HyF fields, respectively. A “diamagnetic” shielding term involving the unperturbed wave functions and a bilinear Hamiltonian derivative is not included in eq 1 as it can be assumed to be similar for the reference and the probe, especially when taking the usually large pNMR shift ranges into consideration.

The operators in eq 1 are the external field Zeeman (Z) and HyF interaction operator derivatives with respect to \( B_i \) and \( \mu^N \). As we are concerned with the NMR shifts of light ligand atoms, the operators used for the matrix elements in eq 1 are the familiar nonrelativistic ones (an extension of the code to utilize relativistic magnetic operators is under way). It is illustrative to distinguish between the different shielding mechanisms caused by these operators as they probe the electron spin and the electron orbital angular momentum. The external field couples to the electron spin magnetization (spin density) and the orbital magnetization, giving rise to the spin-Zeeman (SZ) and orbital-Zeeman (OZ) mechanisms caused by \( \tilde{H}_Z \). Likewise, \( \tilde{H}_{\text{HyF}} \) includes electron spin-dependent terms that are commonly separated into a Fermi-contact (FC) and a spin-dipole (SD) contribution, and a spin-independent operator that is often referred to as PSO and responsible for the Paramagnetic interaction of the nuclear Spin with the electron Orbital angular momentum. Explicit expressions for these operators can be found, for example, in refs 35 and 37−39.

Note that the right-hand side of eq 1 has the opposite sign as in ref 15 because of differently chosen sign conventions for the Zeeman operator derivatives.

Like SvH did, we refer to the last term on the right-hand side of eq 1 as the Curie term. It vanishes for a nondegenerate state. We refer to the other contribution, containing the energy differences in the denominator, as the “usual” density (LR) term as it appears as the usual perturbation theory expression for a bilinear perturbation quantity associated with the linear response of the wave function. The LR term couples different electronic states magnetically. For a GS that barely couples with the excited states, the Curie contribution dominates the pNMR
As shown by SvH, Moon, and Patchkovskii, and discussed further in ref 12, the Curie term can then be approximated by

$$\delta_{\text{Curie}}^{\text{pNMR}} = \frac{\beta}{g N \mu_B} \frac{S(S + 1)}{3k_B T} \text{tr}[g A^N]$$

Here, $g$ is the $g$-tensor and $A^N$ the HYF tensor for a system whose paramagnetism can be described by a spin-Hamiltonian for pseudospin $S$, and “tr” indicates a matrix trace. This expression underlies EPR parameter-based pNMR shift calculations. For the Kramers doublets of UO$_2$(CO$_3$)$_3$ and NpO$_2$(CO$_3$)$_3$, we showed in ref 15 that the Curie shifts calculated from eq 1 versus eq 2 were in excellent agreement when the EPR parameters were determined from the same set of ab initio wave functions. There is also a version of eq 2 including a term resembling the LR contribution, which applies when the EPR parameters were determined from the same set of ab initio wave functions. In this case, the following replacement is made in eq 2:

$$S(S + 1)g A^N \rightarrow g Z A^N$$

where $Z$ are the elements of the 3 × 3 matrix $Z$ are given by

$$Z_{kl} = \frac{1}{Q} \sum \epsilon^{-i \lambda / kT} \left[ \sum_{\alpha, \alpha} \langle S|\lambda\delta|S\alpha\rangle \langle S\alpha|\lambda\delta|S\alpha\rangle \right] + 2k_B T \text{Re} \sum_{\alpha, \alpha, \alpha} \langle S|\lambda\delta|S\alpha'\rangle \langle S\alpha'|\lambda\delta|S\alpha\rangle$$

in which $|S\alpha\rangle$ and $E_s$ are the eigenfunctions and eigenvalues of the ZFS Hamiltonian, respectively, in the basis of the pseudospin projection eigenfunctions, and $Q$ is the partition function calculated from its eigenstates. A program “pNMRShift” has been developed in-house to calculate the $Z_{kl}$ and the resulting shielding tensor from the 3 × 3 matrices parametrizing the Zeeman interaction, the HYF interaction, the ZFS interaction, and the orbital shielding. The source code of the program and a compiled 32-bit binary for the Windows operating system is available for download free of charge at the corresponding author’s Web site.

The structures of all complexes investigated in the present study were optimized as part of previous studies using the 2013 release of the Amsterdam Density Functional (ADF) package 40,41 at the all-electron KS level using the scalar relativistic all-electron zeroth-order regular approximation (ZORA) Hamiltonian, and the Conductor-Like Screening Model (COSMO) for solvent effects. The open metal shells were in some cases treated with fractional orbital occupations resembling an average of configurations. For the actinyl tris-carbonate complexes, good agreement was found between the optimized structures and experimental structural data derived from EXAFS measurements. The largest calculated deviation was found for the An-Oeq distances and does not exceed 0.05 Å. For (C$_5$H$_5$)$_3$UCH$_3$, there are no experimental structural data available. The optimized interatomic distances are in good agreement with previous computational studies performed on related complexes.

The wave function-based calculations were carried out with a developer’s version of the Molcas program based on release 8.44 The second-order Douglas-Kroll-Hess scalar relativistic Hamiltonian was employed in SR calculations, along with all-electron ANO-RCC Gaussian-type basis sets contracted to TZP quality (U, Np, Pu = 26s23p17d13f5g3h/9s8p6d4f2g1h; C, O = 14s9p4d3f2g/4s3p2d1f; H = 8s4p3d1f/3s2p1d). For the carbonate complexes, the $s$ functions of carbon were decontracted in order to provide a flexible description of the spin magnetization around the carbon nuclei. The computations used state-averaged complete active space self consistent field (CASSCF) and restricted active space self consistent field (RASSCF) methods. SO coupling was treated by state interaction among the CASSCF/RASSCF wave functions, using the restricted active space state interaction (RASSI) program. For brevity, the SR spin-free and the calculations with SR effects and SO coupling are referred to as SCF-SR and SCF-SO, respectively. As the experimental NMR data were obtained in aqueous solution for the actinyl tris-carbonate complexes, solvent effects were simulated via the equilibrium CPCM model implemented in Molcas, with parameters for water.

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above. For $\text{UO}_2(\text{CO}_3)^{3+}$ and $\text{NPo}_2(\text{CO}_3)^{4+}$, a CAS(1,6) calculation with orbital optimization included the $5f_\alpha, 5f_\delta$, and $5f_\epsilon$ orbitals in the active space; the follow-up RASSCF calculations then used this as the ras2 space. For $\text{PuO}_2(\text{CO}_3)^{4+}$, we used a CAS(2,4) including the $5f_\alpha$ and $5f_\epsilon$ orbitals as a starting point. Two different ras1 spaces, that is, $n = 9$ and $n = 12$, were investigated. For $n = 9$, the ras1 space corresponds to the carbon 1s orbitals and six doubly occupied orbitals with large carbon 2s character. The ras1 space for $n = 12$ corresponds to the same orbitals with large carbon 2s character plus the $\sigma$ and $\pi$-type bonding orbitals of the carbonate ligands. The ras3 space corresponds to unoccupied metal–ligand orbitals which are mainly $s$ and $p$ carbon in character. In the case of the $5f^8$ complexes, the SO state interaction for the RAS$[n,m]$ calculations was performed using the RASSCF wave functions, but the state energies from CAS(7,10) calculations were used for the diagonal elements of the SO Hamiltonian. This approach, labeled “HDIAG” in the following, allows for a more accurate description of the small energy gap between the GS and the lowest ES, which enters the $p$NMR calculations according to eq 1. For the plutonyl system, the GS is sufficiently well separated energetically from the ESs such that the HDIAG procedure has no effect.

Different active spaces were investigated to generate spin polarization in the $\text{Ct}_2\text{H}_2\text{UCl}_3$ complex. For the calculations of the proton $p$NMR shifts of the methyl group and of the hydrogen atoms in the Cp ligands, we used RAS$[n,m]$-CI calculations on top of the ras2 active space CAS(2,7). In the case of the methyl group, a ras1 space $n = 5$ was used and corresponds to the occupied $\sigma$ bonding orbital of the $\text{U}-\text{CH}_3$ bond, and four additional occupied $\text{U}–\text{CH}_3$ orbitals as shown in Supporting Information, Figure S12. In the case of the proton shifts in the Cp ligands, the RASSCF calculations employed a ras1 space $n = 6$. The electronic structure of the $(\text{Ct}_2\text{H}_2)_\text{U}$ moiety was originally rationalized by Strittmatter et al. with the help of Xα molecular orbital calculations. 59–61 In these previous studies it was shown that one set of $\pi$ orbitals of the $\text{Ct}_2\text{H}_2$ ligands is involved in the $\text{U}-\text{Ct}$ bonding. In the $\text{Ct}_2\text{H}_2$ symmetry point group, these $\pi$ orbitals span $a_1 + a_2 + 2e$ irreducible representations and can overlap with the $s$, $d$, and $f$ uranium atomic orbitals of corresponding symmetry. Therefore, these six occupied orbitals, shown in Figure S13, were included in the ras1 space. For both the methyl and Cp proton $p$NMR shift calculations, the ras3 space corresponds to the $m$ first unoccupied orbitals. Similarly to the uranyl- and neptunyl-carbonate complexes, the SO state interaction was performed using the “HDIAG” approach with the state energies taken from the CAS(2,7) calculations.

3. RESULTS AND DISCUSSION

3.1. Electronic States. One of the key components in the calculation of the $p$NMR shifts using eq 1, is the capacity to describe (i) the nature of the ground and low-energy excited states and (ii) the relative state energies. The energies and assignment of the low-lying electronic states of the four complexes were previously studied by our group and others using similar computational strategies as in the present work, and therefore only a brief summary is given here.

The calculated state ordering of the studied complexes at the SCF-SO level is provided in Table 1. The structure of the actinyl tris-carbonate complexes, with the three equatorial $\text{CO}_3^{2-}$ ligands, is of symmetry $D_{3h}$. For simplicity, in the following discussion we use the symmetry notation of the $D_{3h}$.
nondegenerate, nonmagnetic, and of symmetry respect to the diamagnetic U(VI) complex UO$_2$(CO$_3$)$_3$ to the GS level. Accordingly, they therefore be at much higher energies. Accordingly, they therefore − GS by 191 cm$^{-1}$ excited state is a non-Kramers doublet level of the U$^{4+}$ ion by a trigonal crystal-rationalized by considering a perturbation of the SO ground state. The SO GS in (C$_5$H$_5$)$_3$UCH$_3$ is singlet term 1 electrons occupy the 5f$^{-2}$,$^3$ PuO$_2$(CO$_3$)$_3$ is destabilization of the first ES with the increase of the actinide atomic number. For the U and Np carbonate complex, the next set of excited states is of symmetry $E_{1g}$ and calculated to be at much higher energies. Accordingly, they therefore contribute less in the pNMR results using eq. 1. The 5f$^3$ PuO$_2$(CO$_3$)$_3$ is a non-Kramers doublet GS characterized by the quantum number $J = 4$, $M_J = 1$ = 4. $\Omega$ corresponds to the projection of the total angular momentum $J$ onto a molecular axis and is only a proper quantum number for linear molecules, but we can characterize the states of the $D_{3h}$ system in term of the dominant contributions of the plutonyl ion. The GS $\Omega = 4$ arises predominantly from the $3d^6$ term, where the two unpaired electrons occupy the $5f_6$ and $5f_7$ orbitals. Because of the SO coupling, the GS contains also a small contribution from the singlet term $^1$T. The first excited state corresponds to a singlet $\Omega = 0$ and is computed at 3580 cm$^{-1}$ above the GS. The SO electronic structure of (C$_5$H$_5$)$_3$UCH$_3$ is easier rationalized by considering a perturbation of the SO ground level of the U$^{4+}$ ion by a trigonal crystal-field (CF). Following Hund’s rules, the GS $^3$H term of the spherical ion U$^{4+}$ gives rise to the GS level $^3H_4$, upon considering SO coupling, whereas the subscripts indicate the total angular momentum $J$. The 9-fold degeneracy of $^3H_4$ is then split by the trigonal CF into three singlets and three doublets. The SO GS in (C$_5$H$_5$)$_3$UCH$_3$ is nondegenerate, nonmagnetic, and of symmetry $A_1$ in the $C_{3v}$ symmetry group. This assignment is based on a CF model matching the $ab$ initio results for this complex in the basis of $[J] M_J$ total angular momentum eigenfunctions of U$^{4+}$. An $A_2$ state would correspond to a pure linear combination of $M_J = \pm 3$, whereas the $A_1$ states mix $M_J = \pm 3$ and $M_J = 0$. The first excited state is a non-Kramers doublet $E$, separated from the GS by 191 cm$^{-1}$, followed by states of $E$, $A_2$, $E$, and $A_1$ symmetry. The SO coupling mixes states with the same $J = 4$, and therefore the low-energy electronic states contain an important admixture from states deriving from the singlet $^1G_4$ level.

### 3.2. Paramagnetic NMR

#### 3.2.1. Carbon Chemical Shifts of UO$_2$(CO$_3$)$_3$$^{5-}$ and NpO$_2$(CO$_3$)$_3$$^{4-}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta^{pNMR}$</th>
<th>$\delta^{pNMR}_{\text{Curie}}$</th>
<th>FC</th>
<th>SD</th>
<th>PSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO$_2$(CO$_3$)$_3$$^{5-}$</td>
<td>-57.8</td>
<td>-82.0</td>
<td>5.3</td>
<td>-28.0</td>
<td>-58.7</td>
</tr>
<tr>
<td>CAS(1,6)</td>
<td>-57.3</td>
<td>-88.1</td>
<td>16.8</td>
<td>-28.9</td>
<td>-70.3</td>
</tr>
<tr>
<td>CAS(7,10)</td>
<td>-53.2</td>
<td>-89.6</td>
<td>22.3</td>
<td>-30.5</td>
<td>-70.4</td>
</tr>
<tr>
<td>CAS(9,10)</td>
<td>-77.1</td>
<td>-99.0</td>
<td>-2.2</td>
<td>-29.0</td>
<td>-70.1</td>
</tr>
<tr>
<td>CAS(12,10)</td>
<td>-74.6</td>
<td>-99.5</td>
<td>0.1</td>
<td>-27.3</td>
<td>-72.4</td>
</tr>
</tbody>
</table>

Table 2 and compared to the available experimental data. The experimental chemical shifts for these two complexes were obtained at 273 K. To take advantage of the cancellation of some of the shielding contributions between chemically similar species, the carbon shifts are referenced to the diamagnetic complex UO$_2$(CO$_3$)$_3$$^{5-}$ instead of tetramethyl-silane (TMS). The observed $^{13}$C NMR shifts of the $5f^3$ complexes relative to this complex are therefore essentially due to paramagnetic effects associated with the open metal shells. The active space CAS(7,10) qualitatively reproduces the experimental pNMR shifts but is not flexible enough in order to describe the subtle but important differences between the two complexes. The $^{13}$C shifts calculated at this level are $\pm 60$ ppm for UO$_2$(CO$_3$)$_3$$^{5-}$ and NpO$_2$(CO$_3$)$_3$$^{4-}$, respectively, whereas the experimental shifts are $\sim 62$ and $\sim 93$ ppm. The differences between the calculations and experiment are due to the lack of sufficiently strong metal–ligand (M–L) magnetization delocalization and spin polarization in the carbonate ligands. CAS(7,10) was set up to describe properly the ordering delocalization and spin polarization in the carbonate ligands. CAS(7,10) was set up to describe properly the ordering delocalization and spin polarization in the carbonate ligands. RASSCF wave functions with a smaller principal active space but additional orbitals with limited numbers of holes and electrons, as detailed in section 2, were set up such as to allow for M–L magnetization delocalization and spin polarization within the ligands to take place. For UO$_2$(CO$_3$)$_3$$^{5-}$, the RAS calculations slightly overestimate the experiment, with calculated shifts of $\sim 77$ and $\sim 74$ ppm for RAS(9,10) and RAS(12,10), respectively. For NpO$_2$(CO$_3$)$_3$$^{4-}$, the two RAS calculations give similar calculated $^{13}$C shifts of $\sim 92$ ppm, which are very close to the experiment. As already noted previously for these two complexes, the pNMR shifts arise mainly from the Curie terms. For instance, with the largest RAS space, $\delta^{pNMR}_{\text{Curie}}$ terms of $\sim 99$ and $\sim 110$ ppm are calculated for the U and Np complex, respectively. These Curie terms are counterbalanced by positive contributions from the LR terms. Owing to a smaller energetic separation between the GS and the first excited state, the $\delta^{pNMR}$ of the uranyl complex is larger.
in magnitude than that of the neptunyl analogue (25 ppm vs 18 ppm). Overall, the larger magnitude of the Curie and the smaller magnitude of the LR contribution in the neptunyl complex are responsible for its larger pNMR shift.

In Table 2, the Curie and LR contributions are further broken down into the FC, SD, and PSO mechanisms. The main contribution in both Curie and LR arises from the PSO mechanism. This underlines the fact that SO coupling and unquenched orbital angular momenta in the metal open shells can make a strong influence on the magnetic resonance properties of ligand atoms. Furthermore, it is interesting to notice that even though the magnetic moments generated by the metal open shells are strongly anisotropic, the SD contribution originating in the anisotropy of the electron-spin contributions to the magnetic moment is too small to account for the observed shifts. The comparison of the results in Table 2 for the CAS versus RAS wave functions reveals that the extended RAS active spaces affect primarily the FC mechanism, while the PSO and SD contributions remain stable. This behavior is intended and welcome, as the purpose of the RAS calculations is not to change the nature and the ordering of the behavior is intended and welcome, as the purpose of the RAS calculations is not to change the nature and the ordering of the properties of ligand atoms. Furthermore, it is interesting to notice that even though the magnetic moments generated by the metal open shells are strongly anisotropic, the SD contribution originating in the anisotropy of the electron-spin contributions to the magnetic moment is too small to account for the observed shifts. The comparison of the results in Table 2 for the CAS versus RAS wave functions reveals that the extended RAS active spaces affect primarily the FC mechanism, while the PSO and SD contributions remain stable. This behavior is intended and welcome, as the purpose of the RAS calculations is not to change the nature and the ordering of the RAS[12,100] calculations, in order to assess the e2 represent Boltzmann averages of the Curie shifts corresponding to each doublet individually. As already stated, only the FC contribution in both Curie and LR arises from the PSO mechanism. The Curie shifts of Table 2 for the CAS versus RAS wave functions reveals that the extended RAS active spaces affect primarily the FC mechanism, while the PSO and SD contributions remain stable. This behavior is intended and welcome, as the purpose of the RAS calculations is not to change the nature and the ordering of the Curie shifts of the two lowest doublets and their corresponding eigenfunctions, the natural spin orbitals (NSOs). The plots of m∥(r) for the GS and the first ES of NpO2(CO3)4− are shown in Figure 2 for the CAS(1,6) and RAS[12,100] calculations. The corresponding plots for UO2(CO3)4− are qualitatively similar and shown in the Supporting Information, Figure S5. The || direction coincides with the An−O4 and the z axis and was chosen as the quantization axis for the magnetic moment, meaning that linear combinations of the doublet state components were chosen to diagonalize the Zeeman operator for a magnetic field in this direction. In SR calculations, m∥ corresponds to the usual spin density. As explained in refs 44 and 54, in the RASSI calculations the components of the spin magnetization incorporate SO effects and the volume integrals of the magnetization components m∥(r) yield two times the spin component expectation values, that is, 2⟨S∥⟩(u∈{x,y,z}). The corresponding NSO spin populations likewise reflect SO effects. NSO isosurface plots and populations are provided in the Supporting Information, Figures S2 to S8.

For the small active space CAS(1,6), the spin magnetization of the GS E1/2 component shown in Figure 2 exhibits its SR 2Δ parentage (Table 1). We reiterate that the components of the doublet were chosen for a magnetic moment quantization axis in the || direction, that is, the two components of the doublet have nonvanishing orbital angular momentum expectation values in the || direction of opposite sign. Figure 3 displays, for comparison, the spin densities of the six electronic states obtained at the SR level and without diagonalizing the Zeeman operator. Here, the spin densities of the 2Δ components resemble individual real Sf orbitals (their squares, to be precise). These state components do not afford || orbital angular momentum individually, but rather via off-diagonal matrix elements between them. The spin magnetization shown in Figure 2 predominantly represents a SO/50 linear combination of the two SR 2Δ state components of Figure 3, such that the unpaired electron is shared evenly among the two Sf orbitals and the magnitude of the orbital angular momentum is maximized. As seen in Figure S6, the spin populations of the Sf NSOs in NpO2(CO3)4− are +0.48, that is, very close to the idealized 0.5 populations for the corresponding SR case. Since both Sf orbitals have equal spin populations, the corresponding spin density distribution

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**Table 3. Comparison of the Calculated pNMR Curie (δpNMR) Shift Contributions (ppm) for the Two Lowest-Energy Kramers Doublets of UO2(CO3)3\(^{5−}\) and NpO2(CO3)3\(^{4−}\)**

<table>
<thead>
<tr>
<th>state</th>
<th>p (%)</th>
<th>δpNMR (\text{pNMR}^\text{Curie})</th>
<th>FC</th>
<th>SD</th>
<th>PSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO2(CO3)3(^{5−}):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS(1,6)(^a)</td>
<td>E1/2</td>
<td>73</td>
<td>−79.4</td>
<td>0.0</td>
<td>−25.4</td>
</tr>
<tr>
<td></td>
<td>E3/2</td>
<td>27</td>
<td>−111.7</td>
<td>62.2</td>
<td>−33.2</td>
</tr>
<tr>
<td>RAS[12,100](^b)</td>
<td>E1/2</td>
<td>79</td>
<td>−94.0</td>
<td>−12.5</td>
<td>−26.2</td>
</tr>
<tr>
<td></td>
<td>E3/2</td>
<td>21</td>
<td>−121.2</td>
<td>50.0</td>
<td>−31.5</td>
</tr>
<tr>
<td>NpO2(CO3)3(^{4−}):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAS(1,6)(^b)</td>
<td>E1/2</td>
<td>86</td>
<td>−86.5</td>
<td>0.0</td>
<td>−28.2</td>
</tr>
<tr>
<td></td>
<td>E3/2</td>
<td>14</td>
<td>−116.4</td>
<td>61.6</td>
<td>−33.4</td>
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<tr>
<td>RAS[12,100](^b)</td>
<td>E1/2</td>
<td>87</td>
<td>−106.5</td>
<td>−18.0</td>
<td>−28.0</td>
</tr>
<tr>
<td></td>
<td>E3/2</td>
<td>13</td>
<td>−136.6</td>
<td>40.0</td>
<td>−33.4</td>
</tr>
</tbody>
</table>

\(^a\)The Curie terms are also broken down into the FC, SD, and PSO mechanisms. T = 273 K. The state populations p in percent are also listed. \(^b\)HDIAG procedure used (see computational details).
shown in Figure 2 is cylindrically symmetric around the An–Oyl axis.

Because of SO coupling, the $M_z = 1/2$ component of the SR $^2\Delta$ state mixes with the $M_z = -1/2$ component of $^2\Pi$.

Accordingly, small negative spin populations of $S^\circ$ NSOs ($-0.12$) are obtained in the SO calculation. The latter are responsible for the weak negative spin magnetizations of $S^\circ$ NSOs ($-0.12$) in the equatorial plane seen in Figure 2. Indeed, Figure 3 shows that the equatorial plane coincides with a nodal plane of the spin density of the SR $^2\Delta$ state, whereas the $^2\Pi$ state affords spin density in this plane. The negative spin density obtained accordingly in the SO GS reaches out to the metal-coordinating oxygen atoms of the carbonate ligands, but it is negligible at the carbon nuclei. The lack of spin magnetization at the carbon atoms explains the absence of a FC mechanism in the GSs of the two $5f^6$ actinyl carbonate complexes at the CAS(1,6) level (Table 3).

When the active space is increased to RAS[12,100], there is little effect on the appearance of $m^\parallel_S(r)$ around the metal center. However, the spin magnetization in the carbonate ligands is noticeably altered. The changes are clearly visible in the comparison of the contour line plots of $m^\parallel_S(r)$ in the equatorial plane. With RAS[12,100] the negative spin magnetizations increase strongly in magnitude around the oxygen atoms, even the terminal oxygens, and around the carbon centers. The presence of negative spin density around the carbon atoms causes a nonvanishing spin density of the same sign at the carbon nuclei, which is responsible for the negative FC contributions to the pNMR shift listed in Table 3. The comparatively large negative $m^\parallel_S(r)$ in the equatorial plane calculated with RAS[12,100] does not primarily originate from the SO coupling, but from spin polarization at the SR level. (This effect appears to be similar to the known spin polarization in planar organic $\pi$ radicals, in which a nonzero in-plane spin density gives rise to nonzero isotropic carbon and proton hyperfine coupling.) The spin densities of the SR $^2\Delta$ state components, compared between CAS(1,6) and RAS-[12,100] in Figure 3, are very similar to the $m^\parallel_S(r)$ calculated for the $E_{3/2}$ SO case. For the first excited state $E_{1/2}$ of the complexes, the influence from the active space size on $m^\parallel_S(r)$ is less visible due to the larger overall admixture of the SR $^2\Phi$ and $^2\Delta$ states from the SO coupling. The increase of the active space leads to a slight decrease of the positive spin magnetizations around the carbon atoms, likely due to the polarization of the spin density of the SR $^2\Phi$ states visible in Figure 3.
Table 4. Comparison of the Calculated $^{13}$C pNMR Shifts ($\delta_{\text{pNMR}}$) and of Their Curie ($\delta_{\text{Curie}}$) and LR ($\delta_{\text{LR}}$) Terms (ppm) in PuO$_2$(CO$_3$)$_3$$^{4-}$

<table>
<thead>
<tr>
<th>CAS (2,4)</th>
<th>$\delta_{\text{pNMR}}$</th>
<th>$\delta_{\text{Curie}}$</th>
<th>$\delta_{\text{SD}}$</th>
<th>$\delta_{\text{PSO}}$</th>
<th>$\delta_{\text{LR}}$</th>
<th>$\delta_{\text{FC}}$</th>
<th>$\delta_{\text{SD}}$</th>
<th>$\delta_{\text{PSO}}$</th>
</tr>
</thead>
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<td>CAS (8,10)</td>
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<td>-467.7</td>
<td>74.5</td>
<td>-165.6</td>
<td>-376.4</td>
<td>-6.8</td>
<td>-3.4</td>
<td>-3.3</td>
</tr>
<tr>
<td>RAS [9,100]</td>
<td>-475.3</td>
<td>-470.5</td>
<td>78.8</td>
<td>-169.7</td>
<td>-379.7</td>
<td>-4.7</td>
<td>-3.0</td>
<td>-2.5</td>
</tr>
<tr>
<td>RAS [12,100]</td>
<td>-416.0</td>
<td>-409.0</td>
<td>121.7</td>
<td>-159.1</td>
<td>-371.7</td>
<td>-6.9</td>
<td>-4.3</td>
<td>-2.4</td>
</tr>
<tr>
<td>exp$^a$</td>
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<td>-378.5</td>
<td>141.5</td>
<td>-157.4</td>
<td>-362.6</td>
<td>-7.7</td>
<td>-5.0</td>
<td>-2.3</td>
</tr>
</tbody>
</table>

The Curie and LR terms are also broken down into contributions from the FC, SD and PSO mechanism. $T = 295$ K. $^a$The experimental paramagnetic shift from ref 29 is relative to the diamagnetic complex UO$_2$(CO$_3$)$_3$$^{4+}$.

**Figure 4.** Temperature dependence of the $^{13}$C pNMR shift of eq 1 for PuO$_2$(CO$_3$)$_3$$^{4-}$ (left) and of the $^1$H pNMR shift for (C$_5$H$_5$)$_3$UCH$_3$ (right). The experimental shifts of the plutonyl complex at $T = 295$ K ($-376$ ppm)$^{39}$ with respect to diamagnetic uranyl(VI)-tris-carbonate, and of the uranium compound at $T = 298$ K ($-195$ ppm)$^{31}$ with respect to TMS, are indicated by purple squares. "LR" indicates the term with the energy denominators in eq 1, "Curie" is the term with the $1/(k_BT)$ factor, and "pNMR" is their sum.

The noticeable effects on the GS spin magnetization with increasing the active space can be compared to the corresponding NSOs and their spin populations displayed in Figures S2 and S3 for UO$_2$(CO$_3$)$_3$$^{5-}$ and in Figures S6 and S7 for NpO$_2$(CO$_3$)$_3$$^{4-}$, comparing CAS(1,6) with RAS[12,100]. The spin populations of the $S_F^0$ NSOs are hardly affected by the increase of the active space, and these orbitals remain nonbonding. However, there are many additional NSOs that contribute to the spin magnetization in the RAS[12,100] calculations, representing linear combinations of the metal 5f orbitals and actinyl $\sigma$ and $\pi$ orbitals with ligand-centered orbitals. These new NSOs are related to configurations entering the SR wave functions, with very small coefficients, representing an excitation of an electron from a ligand-centered orbital to a metal-centered orbital of the same spin as the nonbonding $S_F^0$ orbitals. This results in a small increase of the Np Mulliken spin population by 0.02 and leaves a small excess of $\downarrow$ over $\uparrow$ density in the ligand plane. The situation is qualitatively similar for UO$_2$(CO$_3$)$_3$$^{5-}$. However, for the GS the spin polarization in the equatorial plane seems to be less important overall. Indeed, the NSO spin populations of the $S_F^0$ orbitals interacting with the ligands for the uranium complex are only about half of those of the neptunium complex (Figure S3). Accordingly, the contribution of the FC mechanism in the pNMR shifts is smaller.

The SR spin densities of electronic configurations representing the $\Delta^0$ and $\Phi^0$ states of the NpO$_2$(CO$_3$)$_3$$^{4-}$ complex were also calculated using spin-unrestricted KS theory. The degenerate $\Delta^0$ state with equal populations of the $S_F^0$ orbitals was in the KS calculations represented according to occupations of 0.5 for the two $\uparrow$ spin orbitals. The $\Phi^0$ actinyl state is split in the presence of the equatorial ligands, and KS calculations with integer occupations of the $\phi_1$ or $\phi_2$ orbital, respectively, converged without difficulties. The spin density plots from the KS calculations are shown in Figure S9. Comparison with their corresponding SR spin densities calculated with Molcas using the largest active space RAS-[12,100] (Figure 3) shows that the wave function calculations are able to reproduce the balance between the spin polarization and the spin delocalization effects which take place at the SR level in the equatorial plane. The magnitude of these effects is overall larger in the KS calculations. In situations where KS calculations are applicable to magnetic properties, it is known that calculated pNMR shifts can be very sensitive to the underlying functional, in particular when the FC mechanism is the dominant one.$^{12,28}$ However, there is certainly also a possibility that the RAS calculations underestimate the resulting spin density around and at the carbon nuclei, as the active spaces remain limited and the dynamic correlation is not explicitly treated. However, this affects mainly the FC mechanism which appears to be less important for our samples than the PSO and SD mechanisms, and moreover the calculations are likely benefiting from cancellations of errors.

### 3.2.3. Carbon Chemical Shifts of PuO$_2$(CO$_3$)$_3$$^{4-}$

The calculated $^{13}$C pNMR shifts of PuO$_2$(CO$_3$)$_3$$^{4-}$ are collected in Table 4 and compared to experiment. The experimental shift$^{29}$ of $-376$ ppm was obtained at 295 K and is given here relative to the diamagnetic complex UO$_2$(CO$_3$)$_3$$^{4+}$. At $-475$ ppm, the pNMR shifts calculated with CAS(2,4) and CAS(8,10) are strongly overestimated in magnitude. It is interesting to note that the CAS space (8,10) versus (2,4) hardly produces any effect on the calculated shifts. As described in section 3.1, the SO GS corresponds principally to the SR $^3$H plutonyl term where the two unpaired electrons occupy the $S_F^0$ and $S_F^0$. 

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$f^a$ DOI: 10.1021/acs.jctc.6b00462

Similar to the $5f_1$ complexes discussed above, the Curie term $S$ for Pseudospin $-5f$ term. The in $RAS[9,100]$ to section 3.2.4.

magnetization on the carbonate ligands, which is discussed in shifts was calculated at the $RAS[12,100]$ level; the results are $5f_1$ to $5f_2$ is rationalized by the larger orbital angular momentum in the ground state, combining those of $5f_0$ and $5f_0$. The spin contribution to the magnetic anisotropy is reinforced via $\text{FC, SD, and PSO mechanisms in Table 4}$. Due to the small $\delta_{\text{LR}}$ terms and the ESs, the LR term remains small and constant over the $\text{considered temperature range}$. Because of the comparatively large energy gap between the GS and the ESs, the contributions of the latter to the pNMR shift are very small. The ES Boltzmann populations are negligible, and therefore only the GS contributes to the Curie term. The temperature dependence of the $^{13}$C pNMR shifts was calculated at the $RAS[12,100]$ level; the results are shown in Figure 4 (left panel). As expected, $\delta_{\text{pNMR}}$ exhibits a $1/T$ dependence corresponding to the Curie shift for the GS. Because of the comparatively large energy gap between the GS and the ESs, the LR term remains small and constant over the considered temperature range.

The Curie and LR terms are further broken down into the FC, SD, and PSO mechanisms in Table 4. Due to the small magnitudes of the LR contributions, we only discuss the Curie term. The influence of PSO and SD is similar to the $S^6_0$ complexes in the sense that PSO is negative and dominant, and SD producing a secondary negative contribution. However, in the $S^6_2$ plutonyl system, the overall magnitudes are much larger. The larger dipolar mechanism in the $S^6_0$ complex is expected, as the spin contribution to the magnetic anisotropy is reinforced by the second unpaired electron. Likewise, the increase in the PSO magnitude upon addition of the electron when going from $S^6_0$ to $S^6_2$ is rationalized by the larger orbital angular momentum in the ground state, combining those of $S^6_0$ and $S^6_0$. The FC mechanisms strongly differ between the $S^6_0$ and $S^6_0$ complexes, being slightly negative in the uranyl and neptunyl complexes but strongly positive in the plutonyl complex. This suggests a very different distribution of the GS spin magnetization on the carbonate ligands, which is discussed in section 3.2.4.

The $^{13}$C pNMR shifts of $\text{PuO}_2(\text{CO}_3)_3^{4+}$ calculated with our implementation of eq 1 can be compared with the pNMR shifts calculated from EPR parameters. Since the ESs hardly contribute to the shifts, this system is a good test case for the validity of eq 2 and eq 3. The electronic g-factors, the hyperfine coupling constants (HyFCCs) for the $^{13}$C atoms, and the carbon pNMR shifts calculated using eq 2 and eq 3 are collected in Table 5. We considered first the SO GS of $\text{PuO}_2(\text{CO}_3)_3^{4+}$ as a pseudospin $\tilde{S} = 1/2$ without any magnetic coupling with electronic ESs. The corresponding electronic g-factors and the HyFCCs are strongly anisotropic, with perpendicular components equal to zero. The resulting $^{13}$C pNMR shifts determined from eq 2 are in excellent agreement with the $\delta_{\text{pNMR}}$ calculated via eq 1 (see Table 4), both in terms of the total as well as in terms of the individual mechanisms FC, SD, and PSO. This agreement confirms that eq 2 is a valid approach for calculating pNMR shifts in the case of complexes where magnetic coupling contributions between the GS and ESs are not important.

The SR GS of $\text{PuO}_2(\text{CO}_3)_3^{4+}$ is a spin triplet. We can therefore also consider the SO GS as a pseudospin $\tilde{S} = 1$ where the 3-fold degeneracy is lifted by a giant zero-field splitting (ZFS). In this case, the pNMR shifts were calculated using eq 3 which takes into account the ZFS and magnetic interactions between the split components of the multiplet. The calculated electronic g-factors and the HyFCCs for the pseudospin $\tilde{S} = 1$ correspond to half of those for the $\tilde{S} = 1/2$ case, with the perpendicular components still equal to zero. Therefore, the large anisotropy of the $\tilde{S} = 1/2$ EPR tensors in the $\tilde{S} = 1$ case modeled to a significant extent via the giant axial ZFS parameter $D$. The coupling contributions in eq 4 turned out to be negligible, and the calculation of $\delta_{\text{pNMR}}$ from EPR parameters corresponding to $\tilde{S} = 1$ leads essentially to the same pNMR shift as in the case of $\tilde{S} = 1/2$. This result also suggests that the calculated small but nonzero LR contribution in Table 4 arises from a magnetic coupling between the GS and ESs other than the lowest one.

We note in passing that the pNMR shifts of $\text{UO}_2(\text{CO}_3)_3^{5-}$ and $\text{NP}_{2}(\text{CO}_3)_3^{4+}$ were also calculated using eq 2 and eq 3. As already observed by us previously, excellent agreement is found between the EPR parameter-based eq 2 and the per-state Curie contributions in the $ab\ initio$ expression in eq 1 when considering the GS and first ES Kramers doublets as pseudospin $\tilde{S} = 1/2$.

* $g$-factors and HyFCCs from CAS/RAS SCF-SO calculations as indicated. || indicates the direction of the 3-fold symmetry axis. In both $S = 1/2$ and $S = 1$ cases, $g_L = 0$ and $A_L = 0$. The Curies terms and HyFCCs are also broken down into the FC, SD and PSO mechanisms. A nuclear g-factor $^{13}$C $g_{13C} = 1.4048$ was employed to convert the calculated HyFCCs from atomic units to MHz. $^b$The rhombic ZFS parameter is zero. The axial ZFS parameters $D$ are 4452, 3580, 4007, and 3974 cm$^{-1}$ for CAS(2,4), CAS(8,10), $RAS[9,100]$, and $RAS[12,100]$, respectively. The pNMR shifts were calculated here with Equation 3 including ZFS as explained in Reference 27.

<table>
<thead>
<tr>
<th>$S$</th>
<th>$g_I$</th>
<th>$A_L^{\text{total}}$</th>
<th>$A_L^{\text{FC}}$</th>
<th>$A_L^{\text{SD}}$</th>
<th>$A_L^{\text{PSO}}$</th>
<th>$\delta_{\text{pNMR}}$</th>
<th>FC</th>
<th>SD</th>
<th>PSO</th>
</tr>
</thead>
<tbody>
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<td>$S = 1/2$</td>
<td>CAS(2,4)</td>
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<td>4.62</td>
<td>−0.73</td>
<td>1.63</td>
<td>3.72</td>
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<td>74.6</td>
<td>−165.8</td>
</tr>
<tr>
<td>$S = 1/2$</td>
<td>CAS(8,10)</td>
<td>−5.802</td>
<td>4.58</td>
<td>−0.77</td>
<td>1.65</td>
<td>3.69</td>
<td>−471.1</td>
<td>78.8</td>
<td>−169.9</td>
</tr>
<tr>
<td>$S = 1/2$</td>
<td>$RAS[9,100]$</td>
<td>−5.711</td>
<td>4.04</td>
<td>−1.20</td>
<td>1.57</td>
<td>3.67</td>
<td>−409.5</td>
<td>121.8</td>
<td>−159.3</td>
</tr>
<tr>
<td>$S = 1/2$</td>
<td>$RAS[12,100]$</td>
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<td>3.76</td>
<td>−1.40</td>
<td>1.56</td>
<td>3.60</td>
<td>−379.0</td>
<td>141.6</td>
<td>−157.6</td>
</tr>
</tbody>
</table>

| $S = 1$ | CAS(2,4) | −2.859 | 2.31 | −0.37 | 0.82 | 1.86 | −468.2 | 74.6 | −165.9 | −376.9 |
| $S = 1$ | CAS(8,10) | −2.901 | 2.29 | −0.38 | 0.82 | 1.85 | −471.1 | 79.0 | −169.9 | −380.1 |
| $S = 1$ | $RAS[9,100]$ | −2.855 | 2.02 | −0.60 | 0.78 | 1.83 | −409.5 | 121.8 | −159.3 | −372.1 |
| $S = 1$ | $RAS[12,100]$ | −2.843 | 1.88 | −0.70 | 0.78 | 1.80 | −379.0 | 141.6 | −157.6 | −363.0 |
3.2.4. Spin Magnetization and Natural Spin Orbitals of PuO$_2$(CO$_3$)$_3^{4-}$. Isosurfaces and contour line plots of the spin magnetization of the GS of PuO$_2$(CO$_3$)$_3^{4-}$, calculated with CAS(2,4) and RAS[12,100], are shown in Figure 5. The spin magnetization around the Pu atom is characteristic of the \( \Omega = 4 \) state, which arises dominantly from a SR spin triplet with occupations of the 5f state, which arises dominantly from a SR spin triplet with magnetization around the Pu atom is characteristic of the RAS[12,100] calculation but it is correctly obtained when the CAS space is extended to include the Pu–O$_4$ bonding and antibonding orbitals.

3.3. Paramagnetic NMR of (C$_5$H$_5$)$_3$UCH$_3$. The proton pNMR shifts for the methyl group in (C$_5$H$_5$)$_3$UCH$_3$ were calculated using RASSCF spaces on top of the small active space CAS(2,7), as detailed in section 2. The main results obtained with the largest active space are collected in Table 6 and compared to experiment. Additional data for the smaller active spaces can be found in Supporting Information, Table S3. Because of the very long computation times, the largest ras3 space was limited to 80 orbitals. The experimental methyl proton shift is given in the present study relative to TMS and was converted from the original experimental data given in refs 31 and 32 for \( T = 298 \) K. Since we are concerned with methyl protons both in the complex and in the TMS reference, the calculated pNMR shift from eq 1 should correspond very closely to the observed shift without the need to invoke a secondary reference. Due to the quasi-free rotation of the methyl group in solution, the calculations were performed on three different structures shown in Figure 6, labeled by a methyl rotation angle \( \theta = 0, 30, \) and 60° with respect to the UC$_3$ fragment, and averaged for comparisons with experiment.

![Figure 5. PuO$_2$(CO$_3$)$_3^{4-}$: Spin magnetization \( m_\uparrow(r) \) for the GS. Doublet component with \( \langle S_y \rangle > 0 \). Isosurfaces at \( \pm 0.001 \) au. Contour lines for cuts within the eq plane. CAS(2,4) (left) and RAS[12,100] (right) calculations.](image)

![Figure 6. Methyl group orientations in (C$_5$H$_5$)$_3$UCH$_3$ used for the methyl $^1$H pNMR shift calculations. View along the U–C(methyl) axis.](image)

### Table 6. (C$_5$H$_5$)$_3$UCH$_3$: Comparison of the Calculated $^1$H pNMR Shifts (ppm) of the Methyl Protons at the RAS[5,80] Level. The Curie ($\delta_{\text{Curie}}^p$) and LR ($\delta_{\text{LR}}^p$) Terms Are Also Broken down into Contributions from the FC, SD, and PSO Mechanism. \( T = 298 \) K

<table>
<thead>
<tr>
<th>( \theta )</th>
<th>$\delta_{\text{Curie}}^p$</th>
<th>( \delta_{\text{Curie}}^p )</th>
<th>( \delta_{\text{LR}}^p )</th>
<th>( \delta_{\text{LR}}^p )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FC</td>
<td>SD</td>
<td>PSO</td>
<td>FC</td>
</tr>
<tr>
<td>( \theta = 0^\circ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_1$</td>
<td>185.4</td>
<td>45.3</td>
<td>3.3</td>
<td>10.6</td>
</tr>
<tr>
<td>H$_2$</td>
<td>185.1</td>
<td>45.3</td>
<td>3.3</td>
<td>10.6</td>
</tr>
<tr>
<td>H$_3$</td>
<td>185.1</td>
<td>45.4</td>
<td>3.3</td>
<td>10.6</td>
</tr>
<tr>
<td>H$_4$</td>
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<td>3.7</td>
<td>11.3</td>
</tr>
<tr>
<td>H$_5$</td>
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<td>47.2</td>
<td>3.7</td>
<td>11.3</td>
</tr>
<tr>
<td>H$_6$</td>
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<td>3.7</td>
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</tr>
<tr>
<td>( \theta = 30^\circ )</td>
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<tr>
<td>H$_1$</td>
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<td>51.0</td>
<td>4.2</td>
<td>12.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>176.1</td>
<td>51.0</td>
<td>4.2</td>
<td>12.5</td>
</tr>
<tr>
<td>H$_3$</td>
<td>175.9</td>
<td>51.1</td>
<td>4.2</td>
<td>12.5</td>
</tr>
<tr>
<td>( \theta = 60^\circ )</td>
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<td></td>
</tr>
<tr>
<td>H$_1$</td>
<td>181.9</td>
<td>47.9</td>
<td>3.7</td>
<td>11.5</td>
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<tr>
<td>avg ext$^a$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$Chemical shift relative to TMS, converted from experimental data in ref 31.

The calculated pNMR shifts of the hydrogen atoms in the Cp groups of \((C_3H_5)_3UCH_3\) are collected in Table 7, with additional data collected in Table S4. Despite our best efforts, none of the calculations produced averaged Cp proton shifts much below 26 ppm; the experimental value from ref 31 is ~3 ppm. It should be noted that the chemical shift range for different Cp protons in Table 7 is over 70 ppm. Averaging individual shifts that differ by large amounts in order to arrive at the experimentally observed average is likely to introduce additional errors. Further, as seen in Table 7, very small FC mechanisms are calculated in the Curie contributions. This small magnitude of the FC mechanism might be a sign that not enough of spin polarization was generated by the RAS calculations. It is likely that the calculation of the proton shifts in the Cp ligands requires a much larger active space. It is also possible that the Cp pNMR shifts require a more elaborate treatment of the rotational dynamics of the Cp rings and—possibly—an explicit treatment of solute–solvent interactions. In general, pNMR shift calculations tend to have larger deviations from experiment, relative to the chemical shift range, than NMR calculations on diamagnetic systems. We note in this context that some authors have considered proton pNMR shifts from KS calculations for metal complexes with large deviations from experimental shifts as predictively useful, as long as the calculations give the correct ordering of the shifts.

### Table 7. \((C_3H_5)_3UCH_3\): Comparison of the Calculated \(^1\)H pNMR Shifts (ppm) of the Hydrogen Atoms of the Cp Groups at the RAS[6,80] Level. The Curie (\(\delta^{pNMR}_{Curie}\)) and LR (\(\delta^{pNMR}_{LR}\)) Terms Are Also Broken down into Contributions from the FC, SD, and PSO Mechanism. \(T = 298\) K

<table>
<thead>
<tr>
<th>H(_a)</th>
<th>(\delta^{pNMR}_{Curie})</th>
<th>FC</th>
<th>SD</th>
<th>PSO</th>
<th>(\delta^{pNMR}_{LR})</th>
<th>FC</th>
<th>SD</th>
<th>PSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_b)</td>
<td>15.2</td>
<td>−3.4</td>
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<td>−0.7</td>
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<td>2.7</td>
<td>6.2</td>
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<tr>
<td>H(_c)</td>
<td>65.1</td>
<td>−19.6</td>
<td>0.8</td>
<td>−4.7</td>
<td>−15.8</td>
<td>84.8</td>
<td>4.4</td>
<td>21.0</td>
</tr>
<tr>
<td>H(_d)</td>
<td>65.6</td>
<td>−19.7</td>
<td>0.8</td>
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<td>−15.8</td>
<td>85.3</td>
<td>4.4</td>
<td>21.2</td>
</tr>
<tr>
<td>H(_e)</td>
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<td>4.2</td>
<td>0.2</td>
<td>0.9</td>
<td>3.0</td>
<td>−12.7</td>
<td>7.4</td>
<td>−4.2</td>
</tr>
<tr>
<td>H(_f)</td>
<td>−8.3</td>
<td>4.4</td>
<td>0.2</td>
<td>1.0</td>
<td>3.2</td>
<td>−12.7</td>
<td>7.5</td>
<td>−4.2</td>
</tr>
<tr>
<td>avg</td>
<td>25.8</td>
<td>−6.8</td>
<td>0.4</td>
<td>−1.6</td>
<td>−5.6</td>
<td>32.6</td>
<td>5.3</td>
<td>8.0</td>
</tr>
<tr>
<td>ext (\text{b}^a)</td>
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</tr>
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</table>

“*The proton shift are averaged over the equivalent positions. Based on the atom numbering of the \(xyz\) coordinates provided in the SI, H\(_a\) corresponds to H21, H26, and H31; H\(_b\) corresponds to H22, H27, H32; H\(_c\) corresponds to H25, H30, H35; H\(_d\) corresponds to H23, H28, H33; H\(_e\) corresponds to H24, H29, H34. Chemical shift relative to TMS, converted from experimental data in."
The breakdown of the Curie and LR contributions in terms of the FC, SD, and PSO mechanisms show that the pNMR shifts are mainly caused by the PSO mechanism. This mechanism is related to the magnetization created by an orbital angular momentum and may arise from unquenched orbital angular momentum at the SR level, SO coupling, or it may be modulated by both as it is the case for the actinyl carbonate complexes. The transmission of the FC mechanism can be rationalized with the help of the NSOs and spin magnetizations calculated from the SO wave functions, in comparison with SR spin densities. For the GSs, in agreement with the calculated negative FC contributions to the pNMR shifts, the spin-magnetization is negative around the carbon atoms and at the carbon nuclei. The origin of these negative magnetizations is predominantly the spin-polarization in the SR wave functions. For the first excited state, a more complex balance between spin-polarization and spin-delocalization effects in the SR wave functions on the one hand, and spin-compensation effects due to SO coupling on the other hand, leads to positive spin density at the carbon nuclei.

For the $^5\text{f}^2\text{PuO}_2(\text{CO}_3)_3^{4+}$ complex, due to the sizable energy gap between the GS and the first ES, the large $^{13}\text{C}$ pNMR shifts are caused by a strongly dominant contribution of the GS Curie term. In contrast to the $^5\text{f}^1$ complexes, the FC mechanism in the GS causes a large positive contribution. Accordingly, the spin-magnetization is positive around and at the ligand carbon nuclei. It has its origin in large positive contributions to the spin density in the SR GS due to the occupations of the $5f$ orbitals. Spin polarization in the ligands increases the spin density at the carbon nuclei and leads to an important reduction of the magnitude of their pNMR shifts toward experiment. The $^{13}\text{C}$ pNMR shifts of the Pu complex were also calculated with the SVH equation expressed in terms of the pseudospin eigenfunctions and parameters of the EPR spin Hamiltonian. The EPR parameters were calculated from the same CAS or RAS wave functions used to determine the pNMR shifts directly, treating the GS either as a pseudospin doublet or as part of a split pseudospin triplet. In both cases, the agreement with the direct results from eq 1 is excellent. For PuO$_2$(CO$_3$)$_3^{4+}$ the magnetic coupling contributions between the GS and the ESs are negligible.

In the case of the $^5\text{f}^1\text{Pu}(\text{C}_5\text{H}_5)_3\text{UCH}_3$ complex, the GS is nondegenerate and nonmagnetic. The large proton chemical shifts arise predominantly from the LR term via magnetic coupling with low-energy excited states that afford large orbital angular momentum magnetizations. At ambient temperatures, we predict the thermal population of low-energy paramagnetic ESs to cause a secondary contribution that brings the calculated methyl proton shift closer to experiment. For the methyl protons, a RAS active space was used to bring the calculated proton pNMR shifts in reasonable agreement with the experimental data. However, the calculated proton pNMR shifts of the Cp groups appear to suffer from the limitation of the active space to agree closely with the experiment.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jctc.6b00462.

Additional data regarding the pNMR shifts calculations, additional plots of natural orbitals, natural spin orbitals, SR spin densities, spin magnetizations, and optimized Cartesian atomic coordinates of the complexes (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*

E-mail: jochen@buffalo.edu.

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**Notes**

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**REFERENCES**