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Reference

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A density functional study of plutonyl trifluoroacetone complexes in the gas phase and in solution

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The results of a density functional study on a plutonyl compound with two trifluoroacetone ligands are presented. Several conformations of the complex have been examined, namely the structure in which the two ligands are in a cis conformation one with respect to the other, in a trans conformation one with respect to the other, and the structure in which the two ligands lie on the same plane. The calculations have been carried out at the local density approximation level of theory. The relative energies of the conformers have been determined and their geometries have been optimized in the gas phase and in an organic solution. The liquid-state environmental effects are included via a simple cavity model and by using the self-consistent reaction field method. This study shows that the trends in stability of the different conformers in the gas and liquid phases are similar and that the most stable conformer has a cis structure.

1. Introduction

Actinide extraction is commonly used in the reprocessing of the nuclear fuel and it is also an important component in chelation therapy to remove accidentally incorporated actinides [1–4]. Several multidentate ligands are highly effective for decoporation of actinides in various oxidation states and, among these, the 1,3-diketones are often used [5, 6]. In the enol form they have a hydrogen replaceable by a metal and a ketonic donor. The nature of the alkyl or aryl side groups affects the acidity of the hydrogen. In the case of plutonium, a possible chelating species is the 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione, or thenoyl trifluoroacetone (TTA). TTA can be obtained in a pure state and has a high acidity, which is useful in extraction at low pH. In aqueous solution it forms a keto form which has a low distribution ratio into chloroform and benzene.

Although there has been much experimental work in refining actinide extraction, and plutonium in particular, our theoretical understanding of the chemistry of this process is still limited and little information about the molecular structure and electronic properties of Pu complexes is available in the literature. Two recent experimental papers [7, 8] address some of the typical problems in studying plutonium systems, even if they do not treat the diketonic compounds object of the present study. Reference [7] is an experimental study on a Pu(IV) carbonate system, [Pu(CO3)5]f−, in the solid state and in solution. The authors obtained single crystals of [Na6Pu(CO3)5]2Na2CO3·33H2O and collected XAFS data for Pu(IV) in solution. The study indicates that [Pu(CO3)5]f− is the limiting species in high carbonate solutions. Reference [8] is a theoretical analysis of X-ray absorption near edge structure (XANES) for Pu hydrates with a formal oxidation state of Pu ranging from +3 to +6, using an ab initio multipole scattering code.

On the theoretical side, the review by Schreckenbach et al. [9] presents a survey of recent progress and the application of density functional theory (DFT) calculations to actinide compounds. A theoretical study has been presented by Blaudeau et al. [10] on Pu(H2O)3⁺ clusters, with n = 6, 8, 9, 10 and 12. The results indicate that the first solvation shell of Pu3⁺ is likely to contain 8 or 9 water molecules, with a PuO bond length of 2.51–2.55 Å.

In a previous paper [11] we presented a theoretical study on Pu complexes with TTA and some model ligands related to TTA, in which Pu assumed several oxidation states, namely Pu(II), Pu(IV) and Pu(VI). All the calculations were performed in the gas phase. In line with experimental observations, Pu(IV) and Pu(VI) compounds were found to be more stable than Pu(II) compounds, which can be considered as model compounds.
This contribution represents a continuation of [11]. Our interest is focused on one of the complexes previously studied, namely the plutonyl compound with two trifluoroacetone ligands, $\text{PuO}_2(\text{TA})_2$, in which Pu assumes the formal oxidation state of ‘VI’. We considered three isomeric conformations of $\text{PuO}_2(\text{TA})_2$. In the cis conformer the two trifluoroacetone ligands assume a cis conformation one with respect to the other (Figure 1), in the ‘planar’ conformer the two trifluoroacetone ligands lie on the equatorial plane of the pseudo bipyramid formed by the plutonium and oxygen atoms (Figure 2), and in the trans conformer the two trifluoroacetone ligands assume a trans conformation one with respect to the other (Figure 3). The geometries of the three conformers were optimized and their relative stabilities were determined in both the gas and liquid phase. As a liquid environment we considered a generic organic solvent with dielectric constant $\varepsilon = 5$, since the complex should be more soluble in the organic phase than in the aqueous phase; in the solvent extraction procedure one expects to find it in the organic phase. The aim of this paper is to compare and contrast the relative energies of $\text{PuO}_2(\text{TA})_2$ in gas and organic phases. Any possibility of a structural difference is taken into account by optimizing in both phases.

2. Theoretical approach and computational details

The calculations have been performed by using the newly developed Magic quantum chemistry code, directed at providing a means of performing chemically accurate calculations on systems containing many atoms, some of which are heavy. The Magic code is described elsewhere [12–17] but, in its essentials, it is a code based on the use of Gaussian basis sets that allows density functional calculations within the Kohn–Sham paradigm.

The treatment of complexes containing heavy atoms like plutonium implies the inclusion of relativistic effects [9, 18–20]. The relativistic effects are treated in Magic through an implementation of the relativistic effective core potentials (RECPs) of Hay et al. [21, 22]. Magic includes a simple model for calculating the effects of a liquid environment on the electronic structure of a solute molecule. The model is based on the concept of the reaction field, first introduced by Onsager [23]. The ellipsoidal cavity model developed by Rinaldi et al. [24] is implemented in Magic. The model is extensively described in [17].

In the present study the local density approximation exchange (LDAX) functional [25] plus the Vosko, Wilk and Nusair (VWN) correlation functional [26], commonly called LDA, were used. We are aware of the fact that, in general, LDA is not very good for energetics, and one must go beyond this model to predict bond energies. However, such effects are not so severe when predicting only conformational changes, as in the present study. Moreover, in the previous paper on plutonium compounds [11] and in a study on plutonium and uranium hexafluorides [14] we explored the effect of different functionals on actinide compounds, and LDA results seemed to be in better agreement with experiment, when available, than the results obtained with generalized gradient approach functional, BLYP [27, 28]. In a recent study on thorium tetrahalides [29], we explored the behaviour of several functionals, and it turned out that, for ThI₄, LDA gives better agreement with experiment than other functionals (both gradient corrected and hybrid functionals). This might indicate that the heavier the system, the more it approaches the free electron gas limit. For these reasons, we decided to follow an LDA approach, even if we are aware of the fact that the problem of finding suitable functionals for heavy element systems needs further investigation. For the radial quadrature we followed the scheme by Mura et al. [30], and for the angular quadrature the scheme by Lebedev [31].

The coulomb integrals were evaluated by Rys quadrature [32], and an auxiliary basis set was used, according to the method of Dunlap [33] and Eichkorn et al. [34]. The auxiliary basis sets for the light atoms were those for a split valence plus polarization basis [35]. For Pu, since a specific auxiliary basis set does not exist, we used the rubidium auxiliary basis, reported in [34]. The use of this auxiliary basis set for actinide atoms was tested in our previous studies on uranium and plutonium systems [11, 14]. Moreover, in a general study on the Rys quadrature for evaluating coulomb integrals [16], we proved that the density fit approach gives a result of the same accuracy as if exact Coulomb were used.

The relativistic effects were taken into account implicitly through the use of Hay relativistic effective core potentials (RECPs) on plutonium [36]. The valence basis set used to represent the 6s, 7s, 6p, 7p, 6d and 5f orbitals was a [12s10p2d4f] primitive contracted to a [3s3p2d2f], as reported in Hay’s paper [36]. The all-electron basis used for the light atoms was the Dunning DZ [37].

All the calculations were performed in a spin–orbit approximation. Spin–orbit is known to have a profound influence on the energetics of open shell systems like those studied in this paper. However, in this case it is likely that the effect is approximately constant since the configuration of the Pu 5f electrons should not change between the various conformers, and the lack of spin–orbit coupling should not affect the qualitative and quantitative information of this paper. We have developed a method which takes into account spin–orbit
Figure 1. PuO\(_2\)(TA)\(_2\): cis conformer.

Figure 2. PuO\(_2\)(TA)\(_2\): planar conformer.

Figure 3. PuO\(_2\) (TA)\(_2\): trans conformer.
effects within a DFT framework [38] and this will be used to treat Pu compounds in the future.

The initial geometry of the complexes was optimized by using the force field by Rappe et al. [39] within the package Cerius². Subsequent optimizations were made of the complexes in the gas and organic phase, using Magic, without any symmetry restrictions. The gradient tolerance was set to $10^{-4}$ on the largest component of the Cartesian gradient for the plutonium and oxygen atoms in order to converge the PuO bond lengths to the third decimal and the angles $\angle$OPuO to the first decimal. The largest component of the Cartesian gradient for the carbon atoms was set to to $10^{-3}$, and this allows for convergence of the CC and CO bond lengths to the second decimal.

The calculations were performed in the gas phase and by using the dielectric continuum model with a dielectric constant of $\varepsilon = 5.0$ to mimic an organic solvent. In the following when we refer to the organic phase we imply the simple continuum model.

A Mulliken-type population analysis was performed on the complexes to investigate the electronic properties, effective charges and amount of $d$ and $f$ character of the plutonium atom.

3. Results and discussion

In table 1 the relative energies of the three conformers in the gas and organic phase are reported. The cis conformer is the lowest energy structure in both the gas and organic phase. In the gas phase it is about 22 kcal mol$^{-1}$ lower than the planar structure which in turn, is about 63 kcal mol$^{-1}$ lower than the trans structure. In the organic phase the cis conformer is about 31 kcal mol$^{-1}$ lower than the planar structure, which is about 56 kcal mol$^{-1}$ lower than the trans structure. This indicates that the trends in stability are analogous in the gas and organic phases, with an extra stabilization of the cis structure in the organic phase. The isomerization from cis to trans via planar requires an energy of $\sim 85$ kcal mol$^{-1}$ in the gas phase and $\sim 87$ kcal mol$^{-1}$ in the organic phase. This might be due to the fact that such an isomerization implies an overall rearrangement of the structure of the complex, which will be discussed in the following.

In tables 2 and 3 typical bond distances and angles are reported for the three isomers in the gas and organic phase. The structures were optimized without symmetry constraint and as a consequence they are not strictly cis, planar and trans, and the distances and angles that should be equivalent, if any symmetry were present, are not strictly identical. The two PuO axial bonds are not equivalent in the cis isomer (1.816 Å and 1.806 Å) because of the steric effect of the ligands which lie both above the plane formed by the plutonium atom and the four equatorial oxygens. In the other isomers the two PuO axial distances become almost identical, with average values of 1.817 Å and 1.826 Å for the planar and trans structures, respectively. In our previous paper [17] on the hydration of plutonyl, we obtained a PuO bond distance of $\sim 1.76$ Å. In the present compound the PuO plutonyl bond distance is longer because of the presence of the ligands, which makes the PuO plutonyl interaction weaker. All PuO axial bonds increase upon solvation by $\sim 0.02$ Å. This can be explained in terms of solvent–axial oxygen interactions. The cavity seems to elongate the PuO axial bond and make it more ionic (see below). This is confirmed by an examination of the Kohn–Sham orbitals of the calculations in the gas and organic phases. These orbitals are

| System      | $R_{\text{PuOax}}$ | $R_{\text{PuOS}}$ | $R_{\text{PuO1}}$ | $R_{\text{C2O1}}$ | $R_{\text{C4O5}}$ | $R_{\text{C3C4}}$ | $R_{\text{C2C3}}$
|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------
| Gas cis     | 1.816/1.806       | 2.293             | 2.289             | 1.31              | 1.31              | 1.41              | 1.44              |
| planar      | 1.818/1.815       | 2.258             | 2.216             | 1.30              | 1.30              | 1.40              | 1.41              |
| trans       | 1.825/1.827       | 2.107             | 2.268             | 1.30              | 1.32              | 1.38              | 1.42              |
| Organic cis | 1.822/1.840       | 2.300             | 2.258             | 1.33              | 1.31              | 1.41              | 1.44              |
| planar      | 1.829/1.828       | 2.263             | 2.197             | 1.30              | 1.31              | 1.39              | 1.41              |
| trans       | 1.848/1.847       | 2.108             | 2.249             | 1.30              | 1.33              | 1.38              | 1.42              |
qualitatively identical in both the calculations (i.e. the symmetries and bonding/antibonding characteristics are the same, and there is no swapping of the energetic ordering of the orbitals). Thus the cavity has a quantitative effect, but has no qualitative effect.

We will now comment on the bond distances and angles formed by plutonium and the atoms on the ligands and will refer to the atoms on the ligands as they are numerated on the figures. We will consider O1 equivalent to O6, O5 equivalent to O10, and C2, C3, C4 equivalent to C7, C8, C9, respectively, and the values for the bond distances and angles reported in tables 2 and 3 are the average values. The PuO equatorial distances assume two typical values. The PuO5 bond next to the C4CF3 group is longer than the PuO1 bond next to C2H group in cis and planar. The order of the two PuO bonds is reversed in the trans structure. The electron withdrawing effect of the CF3 group can thus be considered responsible for the lengthening of the corresponding PuO bond in the cis and planar structures. The same trend is maintained in the organic phase. The values of the CO and CC bonds are also reported in table 3. The C2O1 and C4O5 bonds, not strictly equivalent because of the asymmetric effect of the CF3 group, are almost identical in cis and planar in the gas phase, while C4O5 is slightly longer that C2O1 in trans. In the organic phase C2O1 is slightly longer than C4O5 in cis, while the trend for planar and trans is the same as in the gas phase. We can compare these bond distances with experimental results for similar (but not identical) plutonyl systems. In [7] 10 equatorial PuO distances to the carbonate ligands span a relatively narrow range of values, 2.381(6)–2.430(6) Å, with an average value of 2.415(7) Å. Our average PuO equatorial distances are ~2.28, 2.23, and 2.18 Å for cis, planar and trans, respectively, in the organic phase. This leads to some comments. First of all one has to be aware of the structural differences between the systems that are the object of the present study and those reported in [7]. Also the measurements in [7] have been performed in aqueous solution, while in this study we have modelled an organic phase.

In table 3 typical bond angles show the substantial rearrangement that the structure undergoes during the isomerization from cis to trans. The O1PuO5 angle, ~81° degrees in cis, becomes ~101° in trans, with a consequent rearrangement of the O1PuO10 angle, which is ~98° in cis and ~79° in trans. The two ligands thus lie closer to each other in trans than in cis. The C3PuC8 angle of ~130° in cis shows the cis bending of the structure, while in planar and trans it is close to 180°. The two non-equivalent PuO1C2, PuO5C4 angles differ by ~5° in cis and trans, while in planar they are almost identical. The C2C3C4 angle is ~125° in cis and becomes ~131° in planar and trans. Finally, the dihedral angles indicate how far from planarity the three structures are. One can thus say that the complex considerably rearranges, when it changes conformation from cis to trans in both phases, while each isomer maintains a similar structure in going from the gas to the organic phase.

In table 4 the sum of the x, y and z components of the dipole moment for the three structures in the gas and organic phases is reported. The values are expressed in atomic units, $ea_0$. In the gas phase cis has a total dipole moment of 1.08 $ea_0$, planar has a value of 0.01 $ea_0$, and trans has a value of −0.03 $ea_0$. In the organic phase cis has a total dipole moment of 1.78 $ea_0$, planar of

<table>
<thead>
<tr>
<th>System</th>
<th>$\delta$O1PuO5</th>
<th>$\delta$O1PuO10</th>
<th>$\delta$C3PuC8</th>
<th>$\delta$PuO1C2</th>
<th>$\delta$PuO5C4</th>
<th>$\delta$C2C3C4</th>
<th>$\delta$O1PuO10</th>
<th>$\delta$C3C4O5Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>cis</td>
<td>81.1</td>
<td>100.1</td>
<td>125.7</td>
<td>102.3</td>
<td>107.0</td>
<td>125.3</td>
<td>−7.1</td>
</tr>
<tr>
<td></td>
<td>planar</td>
<td>95.6</td>
<td>98.5</td>
<td>103.8</td>
<td>102.3</td>
<td>107.0</td>
<td>117.7</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>101.2</td>
<td>100.1</td>
<td>101.2</td>
<td>107.0</td>
<td>131.3</td>
<td>125.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Organic</td>
<td>cis</td>
<td>79.6</td>
<td>101.0</td>
<td>125.7</td>
<td>103.5</td>
<td>106.4</td>
<td>125.3</td>
<td>−6.1</td>
</tr>
<tr>
<td></td>
<td>planar</td>
<td>95.4</td>
<td>100.1</td>
<td>103.8</td>
<td>103.5</td>
<td>106.4</td>
<td>116.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>101.0</td>
<td>101.0</td>
<td>103.8</td>
<td>103.5</td>
<td>106.4</td>
<td>131.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3. Typical bond angles $\langle\rangle$ and dihedral angles $\delta$ (in deg) for cis, planar and trans in the gas and organic phases. $\delta$O is the dihedral angle formed by the four equatorial oxygens, O1, O5, O6, O10. For the other angles see the numbering of the atoms in the figures.

<table>
<thead>
<tr>
<th>System</th>
<th>cis</th>
<th>planar</th>
<th>trans</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>1.08</td>
<td>0.01</td>
<td>−0.03</td>
</tr>
<tr>
<td>Organic</td>
<td>1.78</td>
<td>−0.15</td>
<td>−0.33</td>
</tr>
</tbody>
</table>
−0.15 e\(\text{a}_0\) and trans of −0.33 e\(\text{a}_0\). The dipole moment of all conformers increases in the presence of the ellipsoidal cavity compared with the gas phase. The cis dipole moment, being one order of magnitude larger than the planar and trans dipole moments, confirms the larger stability of cis compared with the other conformers. This is because the solvent model used in this study is based on electrostatic effects.

The results of the Mulliken analysis are reported in table 5. The effective charge on Pu, \(q_{\text{Pu}}\), is about +0.8, +0.7, +0.5 in cis, planar, trans, respectively. The effective charge borne by the plutonyl oxygens, \(q_{\text{Oax}}\), is \(\sim -0.45\) in the gas complexes and \(\sim -0.60\) in the liquid complexes. The sum of the effective charges on the four oxygen atoms on the ligand, \(q_{\text{Oeq}}\), is \(\sim -1.0\) in all complexes. This shows that the overall bonding is more covalent than the formal oxidation states of Pu and the ligands. The compounds in the organic phase are more ionic than in the gas phase and cis is the most ionic structure. This can be related to the previous observation that the PuO axial bond increases upon solvation. The total number of d and f electrons on Pu has been estimated. The quantity of d electrons varies between 1.20 and 1.38 in the various compounds, and the total quantity of f electrons varies between 4.62 and 4.72. The quantity of d and f electron decreases upon solvation, and this confirms that the compounds become more ionic under solvation.

### 4. Conclusion

In this study three different conformers of PuO\(_2\)(TA)\(_2\) have been examined and their relative stabilities have been determined in the gas and organic phases. The trend in energies cis < planar < trans is maintained from the gas to the organic phase. The isomerization reaction implies a major readjustment of the complex, and this might explain the considerable energy difference between the three conformers in both phases. If a reaction path connecting the three conformers has to be suggested, an analysis of the vibrational frequencies, in order to confirm the nature of the stationary points, is certainly required. At this stage we can only predict a possible reaction in which the cis represents a local minimum and the trans a transition state between the two possible cis forms. The planar structure could be an intermediate point between the local minimum and the transition state on this reaction path. These are preliminary results as long as the structures are not confirmed to be true local minima on the potential energy surface. However, this paper is one of the first studies on plutonium diketones, and it is intended to give general trends and eventually suggest the investigations that are needed for a deeper understanding. A study of the reaction path among the three conformers seems to be of interest and is planned for a forthcoming publication.

One other aspect that has not been considered in the present study is the effect of spin–orbit coupling. This might have some importance in the energetics of open shell systems like plutonium compounds. However, the electronic configuration of Pu should not change between the conformers studied in this paper, and we decided to leave this problem to future studies.

The energy of the cis conformer is lowered within our model of the organic phase compared with the gas phase. The structural differences between the two phases are due mainly to the increase in PuO distances in the organic phase. The real extraction process might imply the inclusion of a few water molecules into the complex when it is extracted from the aqueous phase and goes into the organic phase. In a forthcoming contribution we plan to consider a model which includes some water molecules in the complex, and compare the stability of the hydrated complex to the complex simply surrounded by an ellipsoidal cavity.

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