Organic Compounds of Actinyls: Systematic Computational Assessment of Structural and Topological Properties in \([\text{AnO}_2(\text{C}_2\text{O}_4)_n]^{(2n-2)^-}\) (An = U, Np, Pu, Am; n = 1–3) Complexes

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Supporting Information

ABSTRACT: Exploring the bonding features between organics and actinide elements is a fundamental topic in nuclear waste separation. In this work, \([\text{AnO}_2(\text{C}_2\text{O}_4)_n]^{(2n-2)^-}\) (An = U, Np, Pu, and Am; n = 1–3) complexes have been characterized by density functional theory. The actinyl oxalate complexes are found to exhibit the typical An−Oeq bond and Oeq−An−Oeq angles. Interatomic interaction analyzed by electron density difference, charge decomposition analysis, charges population, bond order, electron localization function, and quantum theory of atom in molecules indicates that An−Oeq bonds are ionic (closed-shell) bonding interaction with a small degree of covalent character. The similarities and differences between isomers have been discussed in the actinide coordination chemistry, and the orbital interactions also have been investigated through total, partial, and overlap population density of state diagrams. Besides, the electrostatic potential was used to predict the adsorption sites on the molecular vdW surface.

1. INTRODUCTION

The nuclear energy produced by uranium fission currently may be one of the most perfect replacements for fossil fuel energy, but this task represents a tremendous challenge for further development. Up to now, how to effectively, safely, and economically utilize used spent nuclear fuel is still in the technical exploration stage.1−3 Furthermore, the spent fuel mainly includes \(235\text{U}, 239\text{Pu}\), some minor actinides (Np, Am, Cm) and their fission products (\(^{90}\text{Sr}, ^{137}\text{Cs}, ^{99}\text{Tc}, \text{etc.}\) in the aqueous environment.4 The separation of the spent fuel is also a severe issue in the subsequent waste managing processes.

Due to the complexity of 5f and 6d orbital electrons, actinide elements have more valence states (+4, +5, +6, and +7),7 and the hexavalent oxidation is more accessible. The actinyl oxalate complexes are found to exhibit the typical An−Oeq bond and Oeq−An−Oeq angles. Interatomic interaction analyzed by electron density difference, charge decomposition analysis, charges population, bond order, electron localization function, and quantum theory of atom in molecules indicates that An−Oeq bonds are ionic (closed-shell) bonding interaction with a small degree of covalent character. The similarities and differences between isomers have been discussed in the actinide coordination chemistry, and the orbital interactions also have been investigated through total, partial, and overlap population density of state diagrams. Besides, the electrostatic potential was used to predict the adsorption sites on the molecular vdW surface.
al. have determined the geometries, binding mechanisms, and orbital interactions of the complexes $[\text{AnO}_2\text{L}]^{n+}$ ($\text{An} = \text{U}, \text{Np}, \text{Pu}, \text{Am}, \text{and} \text{Cm}; n = 1, 2; L = 12\text{TC}_4, 15\text{TC}_5,$ and $18\text{TC}_6$) by using density functional theory (DFT). Su et al. showed that the ionic and covalent interactions exist in uranyl and carboxylates ligands. Their results indicated that there are obvious periodic trends in the chemistry of the actinides. Not only that, these theoretical studies have verified that DFT is a universal and successful method for the calculation of actinyl organic complexes.

Figure 1. Optimized geometries of $[\text{AnO}_2\text{L}]^{n+}$ complexes using PW91-ZORA/def2-TZVPP-SARC and B3LYP-ZORA/def-TZVPP-SARC.

In this study, an in-depth exploration of the gas-phase $[\text{AnO}_2\text{L}]^{n+}$ ($n = 1–3$) complexes ($\text{An} = \text{U–Am}$) using DFT has been performed. The main focus lies in detecting the electronic state and microscopic interaction of these complexes. The bonding characteristic and topological properties have been analyzed by the quantum theory of atom in molecules (QTAIM). In addition, the reactivity analysis by using electrostatic potential (ESP) on molecular vdW surface has been performed to predict the adsorption sites of fission product cations.

2. COMPUTATIONAL METHODS

All density functional theory (DFT) calculations of the $[\text{AnO}_2\text{L}]^{n+}$ complexes were performed with the ORCA-4.0.1 package. The geometry optimization and frequency calculations were carried out using the PW91 and B3LYP methods. The geometry optimizations were endowed without symmetry restrictions. The single-point energies were calculated using PW91B95 with the Grimme’s atom-wise dispersion correction and Becke–Johnson damping (D3B) based on PW91 geometries. The segmented all-electron relativistically contracted (SARC) was applied for U, Np, Pu, and Am, and the triple-$\xi$ valence basis sets (def2-TZVPP$^{35}$ and def2-TZVPP$^{36}$) were used for the light C and O atoms. The scalar relativistic effect was examined using the zero-order regular approximation (ZORA)$^{34}$ and Douglas–Kroll–Hess Hamiltonian of second order (DKH2).$^{35,36}$ The binding energy analyses were carried out using the PW91-ZORA/def2-TZVPPD and PW91-DKH2/def2-TZVPPD. The conductor-like screening solvation model (COSMO)$^{40}$ was employed to consider the effects of solvation.

The zero-point vibrational energy and thermal corrections were taken into account. It could be important to research the spin–orbit effects for the actinyl ions due to their open-shell ground state; however, the contributions of the spin–orbit effects are constant with the addition of ligands$^{41,42}$ Therefore, there are no significant effects on the sequential energies, so spin–orbit effects were not treated in this study. Time-dependent density functional theory (TD-DFT) was implemented to calculate the excited states including 10 transitions with the PW91-ZORA/def2-TZVPP-SARC level.

The bonding natures were analyzed with the MULTIWFN program$^{3}$ based on the all-electron wave functions obtained at the PW91-ZORA/def2-TZVPP-SARC level of theory. The electron density difference and charge decomposition analysis (CDA)$^{44}$ were performed to unveil the detail of charge transfer between the $\text{AnO}_2^{2+}$ and $(\text{C}_2\text{O}_4)^{2–}$. The Hirshfeld atom population$^{45}$ and VDPP deformation density (VDD) atom population$^{46}$ were carried out. Bond order analyses were used to reveal the Mayer bond order (MBO)$^{47}$ and Fuzzy bond-order (FBO) methods.$^{48–51}$ The topological properties analyses were conducted by the electron localization function (ELF)$^{52}$ and QTAIM theory.$^{53}$ Total, partial, and overlap population density of state (TDOS, PDOS, and OPDOS)$^{54,55}$ analyses were used to gather the information on orbital interaction. Furthermore, the ESP$^{56}$ on the molecular vdW surface was used to predict the adsorption sites.

3. RESULTS AND DISCUSSION

3.1. Structures and Electronic Properties of the $[\text{AnO}_2\text{C}_2\text{O}_4]^{2n–}$ complexes. In order to find the low-lying energy structures, extensive possible initial conformations of $[\text{AnO}_2\text{C}_2\text{O}_4]^{2n–}$ complexes ($\text{An} = \text{U–Am}; n = 1–3$) were searched, and the different possible spin multiplicities were considered two theoretical levels (PW91-ZORA/def2-TZVPP-SARC and B3LYP-ZORA/def-TZVPP-SARC). These ground state geometries are shown in Figure 1. Since one spin state can have plenty of low-lying excited states in the case of actinides, we have checked all the optimized structures by TD-DFT and the corresponding results have been listed in the Supporting Information (Table S1 and Table S2). As can be seen, all excitation energies are positive indicating that the initial state is more stable than the excited states. The detailed Cartesian coordinates of the ground state $[\text{AnO}_2\text{C}_2\text{O}_4]^{2n–}$ complexes ($\text{An} = \text{U–Am}; n = 1–3$) were given in Table S3.

It can be seen that the three actinide complexes have similar structures. The $\text{AnO}_2^{2+}$ prefers coordination by the O atoms of $\text{C}_2\text{O}_4^{2–}$ on the equatorial plane ($\text{O}_{eq}$ represents the $\text{C}_2\text{O}_4^{2–}$ oxygen atoms, $\text{O}_{eq}$ represents the $\text{AnO}_2^{2+}$ oxygen atoms).
Table 1. Selected Average Bond Length (Å) and Oyl Bond Angle (deg) of the Ground-State AnO$_2$(C$_2$O$_4$), [AnO$_2$(C$_2$O$_4$)$_2$]$^2^-$, [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$, and Isomers in Vacuum and in Water Using the COSMO Solvation Model (in Parentheses) at PW91-ZORA/def2-TZVPP-SARC

<table>
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<th>ISOMERS</th>
<th>Bond length</th>
<th>Bond angle</th>
<th>Bond length</th>
<th>Bond angle</th>
<th>Bond length</th>
<th>Bond angle</th>
<th>Bond length</th>
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<tbody>
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<td>An</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>1.792 (1.784)</td>
<td>2.156 (2.213)</td>
<td>1.792 (1.784)</td>
<td>2.156 (2.213)</td>
<td>1.792 (1.784)</td>
<td>2.156 (2.213)</td>
<td>1.792 (1.784)</td>
<td>2.156 (2.213)</td>
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<tr>
<td>Np</td>
<td>1.772 (1.765)</td>
<td>2.155 (2.207)</td>
<td>1.772 (1.765)</td>
<td>2.155 (2.207)</td>
<td>1.772 (1.765)</td>
<td>2.155 (2.207)</td>
<td>1.772 (1.765)</td>
<td>2.155 (2.207)</td>
</tr>
<tr>
<td>Pu</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
</tr>
<tr>
<td>Am</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
<td>1.768 (1.761)</td>
<td>2.155 (2.207)</td>
</tr>
</tbody>
</table>

These structures can be vividly described as tetrahedron, octahedron, and pentagonal bipyramidal, respectively. In view of the fact that these complexes are predominantly in the form of ions and usually exist in aqueous, the COSMO model was considered in optimization to represent polarizable water solvent.

The detailed geometric parameters of the ground state at PW91-ZORA/def2-TZVPP-SARC are presented in Table 1; the results of other methods are displayed in Table S4. We can see that the solvation has little influence on the geometric parameters; this property also appears in previous studies of similar systems. Therefore, the following discussion only corresponds to the gas phase.

Figure 2 intuitively shows the variation of bonds lengths and bond orders for An–Oeq and An–O$_r$ bonds. The average length of An–O$_r$ bonds decreases from U (1.792 Å, 1.819 and 1.822 Å) to Am (1.768, 1.780, and 1.789 Å); the decreased trend is consistent with the An–O$_r$ bond lengths in isolated actinyl, as expected due to the contraction of the actinide ionic radius. The bond lengths of An–O$_{eq}$ in [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$ exceed the range of An–O single-bond covalent radii provided by Pyykkö, which indicates that such chemical bonds are primarily coordination interactions. The average lengths of the An–O$_{eq}$ increase from U (2.453 Å) to Am (2.507 Å) for [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$, possibly due to contraction of the $f{6d}$ orbitals. Besides, as the number of (C$_2$O$_4$)$_2$ in [AnO$_2$(C$_2$O$_4$)$_2$]$^2^-$ increases, the average distances of the An–O$_{eq}$ bond increased from [AnO$_2$(C$_2$O$_4$)$_3$] (2.156 and 2.155 Å) to [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$ (2.453 and 2.459 Å) for U and Np cases. Based on the increasing An–O$_{eq}$ bond lengths a weaker bonding interaction between the An and O$_{eq}$ might be deceptive; it is notable that the BEs (Table 2) suggest a decreasing trend in bonding between the An–O$_{eq}$ oligomers (U and Np) and (C$_2$O$_4$)$_2$ with the (C$_2$O$_4$)$_2$ ligands increasing. This indicates that the interaction between An and O$_{eq}$ in [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$ is weaker than that in [AnO$_2$(C$_2$O$_4$)$_3$]. This can also be supported by Mayer bond order and Fuzzy bond order analysis (Table S5).

For the case of Pu and Am, the average An–O$_{eq}$ distances change with the trend of AnO$_2$(C$_2$O$_4$) > [AnO$_2$(C$_2$O$_4$)$_2$]$^2^-$ < [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$ By contrast, we find that the change trend of An–O$_{eq}$ length is different for U, Np and Pu, Am. The Pu–O$_{eq}$ and Am–O$_{eq}$ bond lengths in AnO$_2$(C$_2$O$_4$)$_2$ are longer than in [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$ This unique phenomenon is possibly ascribed to their unstable structure and different coordination. In addition, the distances of the An–O$_{eq}$ bond in [AnO$_2$(C$_2$O$_4$)$_3$] and [AnO$_2$(C$_2$O$_4$)$_3$]$^4^-$ complexes decrease from U (2.156 and 2.331 Å) to Np (2.155 and 2.321 Å) and then increase to Pu (2.352 and 2.325 Å). This transition phenomenon also occurred in the [AnO$_2$(15CS)$_2^-$ and [AnO$_2$(L)$_2^-$ (An = U, Np, Pu, Am, and Cm; n = 1, 2; L = 12TC4, 15TCS, and 18TC6) complexes. The change in O with An–O$_{eq}$ bond angles from highly bent for U to linear for Am is partially attributed to steric repulsion and electrostatic factors between ligands and actinyls ions.

3.2. Chemical Bonding Characterizations Analyses of [AnO$_2$(C$_2$O$_4$)$_n$]$^{2n-}$ The Hirshfeld and Voronoi deformation density (VDD) charges were listed in Table 3. As can be seen, the solvation has little effect on charge population. The An (An = U–Am) center carries a high positive charge, and the O$_{eq}$ ligands carry large negative charges in these complexes.

In order to obtain a deep insight into the nature of the charge transformation, we performed the contour plots of electron density difference and charge decomposition analysis.
Using the COSMO Solvation Model (in Parentheses) at PW91-ZORA/def2-TZVPP-SARC for ionic interactions with weak covalence. Figure 3: From Figure 3, the contour regions are convex from Oeq to Oyl. Table 3: Hirshfeld and VDD Charges for An, Oyl, and Oeq in the [AnO2(C2O4)2−] complexes at PW91/def2-TZVPP with ZORA and DKH2.

Table 2: Binding Energy (BE, kcal/mol) Defined as AnO22+ + n(L)2− → [AnO2(L)n]2− (L = (C2O4)2−, n = 1−3) at PW91/def2-TZVPP with ZORA and DKH2.

Figure 3: Contour plots of the electron density difference between UO22+ and n(C2O4)2− (n = 1−3) fragments. Solid lines represent regions where electron density increases, and dotted lines represent the region where the electron density decreases.

Table 3: Hirshfeld and VDD Charges for An, Oyl, and Oeq in the [AnO2(C2O4)2−] and Isomers in Vacuum and in Water Using the COSMO Solvation Model (in Parentheses) at PW91-ZORA/def2-TZVPP-SARC.

(CDA); the results of [UO2(C2O4)2−] complexes were displayed in Figure 3 and Figure 4, respectively. The correlative figures for other complexes are shown in the Supporting Information (Figure S1 and Figure S2). As can be seen from Figure 3, the contour regions are convex from Oeq to U, which represents the charge transfer from Oeq to U. In Figure 4, the HOMOs of [UO2(C2O4)2−] complexes primarily contain the orbitals of (C2O4)2−. Therefore, the electron transitions occurred in the (C2O4)2−. The above charge transfer analysis indicates that for An−Oeq there exists ionic interactions with weak covalence.

Inorganic Chemistry

Figure 2: Left: mean An−Oeq bond distance (solid lines, left axis) and An−Oeq bond order (dotted lines, right axis) of isolated AnO22+ (black squares), AnO2(COOOCOO) (red circles), AnO2(COOOCOO)2− (blue stars), and AnO2(COOOCOO)3− (green triangles). Right: mean An−Oeq bond distance (solid lines, left axis) and An−Oeq bond order (dotted lines, right axis) of AnO2(COOOCOO) (red circles), AnO2(COOOCOO)2− (blue stars), and AnO2(COOOCOO)3− (green triangles).
The ELF shaded-surface-projection maps are displayed in Figure 5. The disynaptic valence basins, corresponding to conventional two-center bonds, can be qualitatively described the strength of interatomic interaction. As can be seen, these are unobvious disynaptic valence basins between the An and Oeq atoms, which reveals that An–Oeq bonds have weak covalent properties. All Mayer bond orders of An–Oeq are less than 1, but the corresponding Fuzzy bond orders are higher. For U and Np, the Mayer bond order of An–Oeq displays a trend of AnO2(C2O4) > [AnO2(C2O4)2]2− > [AnO2(C2O4)3]4+, whereas a trend of AnO2(C2O4) < [AnO2(C2O4)2]2− > [AnO2(C2O4)3]4+ is represented for Pu and Am. It may be attributed to the change of An–Oeq bond distances. What’s more, the trend of An–Oeq bond orders is in parallel with the values of ELF, and all corresponding ELF values appear in Table 4. This phenomenon further confirms that the An–Oeq bonds are dominated by ionic interaction.

Topological analyses of the (3, −1) bond-critical points (BCPs) for the An–Oeq and An–Oyl bonds were listed in Table 3 with the QTAIM theory. Notably, the QTAIM method is a successful strategy to analyze bonding features in actinide complexes.

Previous studies have shown that the criterion of total energy density \( H(r) \) proposed by Cremer and Kraka can correctly describe the properties of chemical bonds for heavy elemental systems. The \( H(r) \) is the sum of the local kinetic energy density \( G(r) \) and the local potential energy density \( V(r) \). Generally, the properties of chemical bonds can be defined as follows: the value of \( H(r) \) is more negative while the covalent interaction is more obvious. Another useful criterion is the \( -V(r)/G(r) \) ratio; \( -V(r)/G(r) < 1 \) is feature of a classical ionic bond, \( -V(r)/G(r) > 2 \) is diagnostic of a typical covalent interaction, and \( 1 < -V(r)/G(r) < 2 \) can be described as partially covalent bonds.

Topological parameters of An–Oeq and An–Oyl are listed in Table 4. All \( H(r) \) values of calculated BCPs in the \([AnO_2(C_2O_4)_n]^{(2n-2)-}\) complexes are negative. For the An–Oeq bond, a low \( \rho(r) \) value and a positive \( \nabla^2 \rho(r) \) value confirm its closed-shell interaction. Meanwhile, it should be noted that the An–Oeq bonds have negative \( H(r) \) values with small absolute quantities and the ratios of \( -V(r)/G(r) \) range from 1.
Table 4. Topological Parameters for the An–O_{yl} and An–O_{eq} Bond Critical Points (BCPs) in the [AnO_{2}(L)_{n}]^{2n−2−} (L = (C_{2}O_{4}), n = 1−3) Complexes

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<th>Species</th>
<th>Bond</th>
<th>ρ(r)</th>
<th>V^{ρ}</th>
<th>G(r)</th>
<th>V(r)</th>
<th>H(r)</th>
<th>−V(r)/G(r)</th>
<th>ELF</th>
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<td>U–O_{yl}</td>
<td>0.299</td>
<td>0.370</td>
<td>0.347</td>
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<td>−0.254</td>
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<td>0.364</td>
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<td>0.076</td>
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<td>AmO_{2}(L)</td>
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<td>0.370</td>
<td>0.347</td>
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<td>−0.255</td>
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<tr>
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<td>Am–O_{eq}</td>
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<td>0.259</td>
<td>0.071</td>
<td>−0.076</td>
<td>−0.006</td>
<td>1.070</td>
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<td>Am–O_{yl}</td>
<td>0.289</td>
<td>0.397</td>
<td>0.335</td>
<td>−0.572</td>
<td>−0.236</td>
<td>1.707</td>
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<td>Am–O_{eq}</td>
<td>0.075</td>
<td>0.257</td>
<td>0.075</td>
<td>−0.066</td>
<td>−0.011</td>
<td>1.146</td>
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<tr>
<td>AmO_{2}(L)_{3}^{4−}</td>
<td>Am–O_{yl}</td>
<td>0.283</td>
<td>0.400</td>
<td>0.326</td>
<td>−0.552</td>
<td>−0.226</td>
<td>1.693</td>
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<td>Am–O_{eq}</td>
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<td>0.172</td>
<td>0.045</td>
<td>−0.048</td>
<td>−0.002</td>
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ISOMERS B

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<tr>
<th>Species</th>
<th>Bond</th>
<th>ρ(r)</th>
<th>V^{ρ}</th>
<th>G(r)</th>
<th>V(r)</th>
<th>H(r)</th>
<th>−V(r)/G(r)</th>
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<td>UO_{2}(L)_{3}^{4−}</td>
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<td>−0.047</td>
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<td>−0.582</td>
<td>−0.243</td>
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<td>1.079</td>
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Figure 6. Computed structures of the [AnO_{2}(C_{2}O_{4})_{3}]^{4−} complexes using PW91-ZORA/def2-TZVPP-SARC.

to 2, which shows that these bonds have a certain degree of
covalent character. This conclusion is consistent with the
results of previous charge and ELF analysis. For the An–O_{yl}
bonds, all the H(r) values are more negative than An–O_{eq} and
the −V(r)/G(r) ratios are closed to 2, which infers that the
An–O_{yl} bonds are typical covalent bonds.

3.3. Comparison of Isomers A and Isomers B.
Geometric optimization results indicate that there are two
specific isomers of [AnO_{2}(C_{2}O_{4})_{3}]^{4−} complexes. Their
energies are extremely close to each other and are lower
than other isomers. In terms of structural characteristics, one is
a pentagonal bipyramidal structure (named isomer A) and the
other is a hexagonal bipyramidal structure with D_{3h} symmetry
(named isomer B). The corresponding structures are depicted
in Figure 6. In order to examine the energy order, the higher
level PWPB95 with D3BJ was used, and the values were
collected in Table S6. The final result shows that the structure of
the lowest energy varies with environmental conditions. In
the gas phase, Isomers B is the lowest energy structure, while in
the solvation model, isomers A is the lowest one. Here, we just
take the compounds of the gas phase into account. In view of
In this particularity, we separately analyze the similarities and differences between these two structures.

In terms of structural parameters (Table 1), the average bond lengths of An–Oeq in isomers B are relatively longer than those in isomers A. The average Hirshfeld charges (Table 3) of An (An = U–Am) and Oeq in isomers B have larger absolute quantities than in the isomers A, and the average Mayer bond orders (Table S5) of An–Oeq display the same trend. Meanwhile, the bond order appears with a trend of U > Np > Pu > Am.

The topological analysis indicates that the An–Oeq bonds of these two structures have the same properties. The values of H(r) are negative, and the results of −V(r)/G(r) ratios are also between 1 and 2. The only difference is that ratios of isomers B are slightly larger than those in the isomers A.

In order to get more in-depth information about orbital interactions in the isomers A and isomers B, the TDOS, PDOS, and OPDOS were calculated and plotted with Gaussian curves. The corresponding full width at half-maximum (fwhm) is 0.05 au. Figure 7 shows the TDOS, PDOS, and OPDOS graphics of the [UO2(C2O4)3]4− complexes. Fragment 1 is defined as (UO2)2+ orbitals, and fragment 2 is defined as (C2O4)2− orbitals. As can be seen, the curve shapes of the DOS are similar in the isomer A and isomer B. At the position of the HOMO energy level (vertical dashed line), the PDOS of (C2O4)2− orbitals approached the TDOS, which means that most of the contributions to HOMO result from the (C2O4)2− orbitals. The OPDOS values of (UO2)2+ and (C2O4)2− are close to zero, which reveals that the interaction between the (UO2)2+ and (C2O4)2− is weak. The orbital interactions analysis to the other actinyls complexes can be found in the Supporting Information (Figure S3–S5).

The electrostatic potential (ESP) values of van der Waals (vdW) surfaces were analyzed in order to evaluate the adsorption sites of fission product cations on these actinide organic complexes. The ESP on the vdW surface has been demonstrated by means of an applicable method for detecting intermolecular interaction.67 Here, we take [UO2(C2O4)3]4− complexes as examples; the results are shown in Figure 8. The more negative the ESP site, the easier it is to attract electrophiles, while the more positive the ESP site, the easier it is to attract nucleophiles.68 It can be seen from Figure 8 that the predominate adsorption sites are located at the most negative ESP value of the [UO2(C2O4)3]4− complex, which occurs between the adjacent oxalates. The adsorption sites of other [AnO2(C2O4)n](2n−2)− complexes are similar to [UO2(C2O4)3]4−; the detailed images are displayed in the Supporting Information. The conclusions of adsorption sites were based solely on the electrostatic potential, and the sterically crowded environment will also influence the adsorption properties (depending on the adsorbing species).

4. CONCLUSIONS

The geometric and electronic structures of the complexes formed by actinyls AnO22+ (An = U–Am) and oxalate ligands have been systematically investigated by using different quantum chemical methods in gas phase. The main conclusions are as follows:

This page contains figures showing the TDOS, PDOS, and OPDOS curves of [UO2(C2O4)3]4− complexes at the PW91-ZORA/def2-TZVPP-SARC. The electrostatic potential (ESP) mapped molecular vdW surfaces of [UO2(C2O4)3]4− complexes are also shown. The images display the adsorption sites of the complexes on actinide organic complexes.
(1) The ground state of [AnO$_2$(C$_2$O$_4$)$_n$]$^{(2n-2)-}$ (An = U, Np, Pu, Am; n = 1–3) was located. Our computational analyses show that all the ground state structures are similar. The O$_{eq}$ atoms prefer to coordinate with the actinyls on the equatorial plane.

(2) The properties of the chemical bonding of [AnO$_2$(C$_2$O$_4$)$_n$]$^{(2n-2)-}$ complexes were evaluated with electron density difference, CDA, population analysis, bond order analysis, ELF, and QTAIM. The An–O$_{eq}$ dative bonding is an ionic bond with the extent of covalent interaction, and An–O$_{di}$ bonds are typical covalent bonds.

(3) The DOS approach was implemented to analyze the orbital interactions in the [AnO$_2$(C$_2$O$_4$)$_3$]$^{4-}$ complexes. The TDOS results show that the HOMO of [AnO$_2$(C$_2$O$_4$)$_3$]$^{4-}$ primarily comes from (C$_2$O$_4$)$^{2-}$ orbitals. The OPDOS analyses suggest that the interaction between the (AnO$_3$)$^{2+}$ and (C$_2$O$_4$)$^3$ is weak. Reactivity analysis of ESP on moleculesvdW surfaces indicates that the adsorption sites of fission product cations appear between the adjacent oxalate molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b03538.

The excitation energies of [AnO$_2$(C$_2$O$_4$)$_n$]$^{(2n-2)-}$ complexes at the PW91-ZORA/def2-TZVPP-SARC level, Cartesian coordinates for the [AnO$_2$(C$_2$O$_4$)$_3$]$^{4-}$ complexes at the PW91-ZORA/def2-TZVPP-SARC level of theory, structural parameters calculated by other methods, Mayer Bond Order (MBO) and Fuzzy Bond Order (FBO) values, relative energies between the isomers A and isomers B, contour plots of the electron density difference, orbital interaction diagram, DOS curves, and ESP mapping molecular vdW surface (PDF)

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Notes
The authors declare no competing financial interest.

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