Actinyl-Carboxylate Complexes \([\text{AnO}_2(\text{COOH})_n(\text{H}_2\text{O})_m]^{2-n}\) (An = U, Np, Pu, and Am; \(n = 1–3; m = 0, 2, 4; 2n + m = 6\)): Electronic Structures, Interaction Features, and the Potential to Adsorbents toward Cs Ion

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ABSTRACT: Organic compounds of actinyls and their bonding features have attracted extensive attention in nuclear waste separation due to their characteristics of separating fission products. Herein, detailed studies on the binding sites of \([\text{AnO}_2(\text{COOH})_n(\text{H}_2\text{O})_m]^{2-n}\) (An = U, Np, Pu, and Am; \(n = 1–3; m = 0, 2, 4; 2n + m = 6\)) complexes toward Cs are predicted by calculation, and their electronic excitation characteristics were illustrated, providing theoretical supports for the design of Cs adsorbents. The quantum theory of atom in molecules and electron localization function have been implemented to analyze the chemical bonding characterization. The covalent character of An−Oc bonds become weaker with increasing COOH ligands, and the covalent interaction in An−Oc bonds is more obvious than that in An−OH bonds. Total and partial population density of state suggest that the 2p orbits of O have more significant contribution in the low-energy region atoms and the 6d/5f orbits of An have more significant contribution in the high-energy region. The Cs′ best adsorption site on \([\text{UO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\) and \([\text{UO}_2(\text{COOH})_3]^−\) is the adjacent oxalates, and the \([\text{UO}_2(\text{COOH})_3]^−\) complexes have better adsorption capacity. Besides, the electronic excitation characteristics of Cs′ adsorption on the \([\text{UO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\) complex were analyzed by the UV–vis spectrum and electron–electron distribution.

INTRODUCTION

The management of spent fuel, especially the disposal of new actinides and their fission products (\(^{90}\text{Sr}, ^{137}\text{Cs}, ^{99}\text{Tc}\), etc.) in the nuclear fuel cycle, is one of the main challenges and environmental issues facing sustainable development of nuclear energy.\(^1\)−\(^5\) However, the nuclear waste management especially for actinides and their fission products is still in the stage of scientific and technological exploration up to now.\(^6\)−\(^9\) The improvement of current technologies for waste separation and contamination remediation still depends heavily on sophisticated knowledge of these radioisotopes. Therefore, exploring effective, safe, and economical partitioning technologies for spent fuel is of great importance in nature.

Although the actinide elements have many valence states (+4, +5, +6, and +7),\(^10\)−\(^12\) the hexavalent oxidation state is more accessible in aqueous environment. These hexavalent ions exist as the linear molecular form of actinyls \(\text{AnO}_2\)\(^13\),\(^14\) Actinyl complexes generally coordinate four to six monodentate ligands in their equatorial plane,\(^15\)−\(^18\) often generating tetragonal, pentagonal, and hexagonal-bipyramidal coordination geometries. The rational design of actinide separation has become a popular topic by selecting the befitting atom-donor ligands.

It is well known that actinides have a strong affinity for hard O-donor ligands\(^19\) and have slightly better affinities for soft S-donor ligands.\(^20\) Therefore, these actinyls are easily captured with organic ligands from spent nuclear fuel, which can form metal–organic complexes. Among them, carboxylates have become one of the popular ligands for forming metal–organic framework (MOF) materials based on the good properties that carboxylate groups are not within the same coordination plane, easy to form a layered structure, and have strong ability to gather metal ions into \(M–O–C\) clusters, which can be used as a secondary building unit.\(^21\)−\(^23\)

Uranium-based MOFs have gained wider interest compared to other actinide-based MOFs in view of their potential applications in the post-treatment of spent fuel. Uranyl–organic frameworks (UOFs) also have acquired significant application in chemical sensing,\(^24\) selective detection,
In recent years, a mass of UOF materials have been synthesized in the experiment, which exhibits high potential method for treatment of the adsorption capacity also has been investigated under different ratios, 1:3, 1:2, and 1:1, of uranyl with the HCOO− group. We also have described the microscopic interaction mechanism between Cs+ and uranyl-carboxylate complexes.

Table 1. Selected Average Bond Length (Å) and An−Oy Bond Angle (deg) of the Ground-State [AnO2(COOH)x(H2O)y]2−n (n = 1−3; m = 0, 2, 4; 2n + m = 6) Complexes in Vacuum and in Water Using the Conductor-like Polarizable Continuum Model (C-PCM) Solvation Model (in Parentheses) at PBE-ZORA/def2-TZVPP-SARC

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| An  | 2S + 1 | bond length | bond angle | bond length | bond angle |
|-----|--------|-------------|------------|-------------|------------|
|     | An−Oy  | An−Oc      | An−Oh     | Oy−An−Oy   | An−Oy      |
|     |        |             |            |             |            |
| U   | 1      | 1.78 (1.79) | 2.43 (2.48) | 2.62 (2.56) | 177.4       |
|     |        |             |            |             |            |
| Np  | 2      | 1.77 (1.77) | 2.42 (2.47) | 2.61 (2.56) | 179.4       |
|     |        |             |            |             |            |
| Pu  | 3      | 1.75 (1.76) | 2.42 (2.47) | 2.61 (2.56) | 179.3       |
|     |        |             |            |             |            |
| Am  | 4      | 1.74 (1.75) | 2.44 (2.48) | 2.60 (2.55) | 179.8       |
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Figure 1. Optimized geometries of [AnO2(COOH)x(H2O)y]2−n at the PBE-ZORA/def2-TZVPP-SARC level.

In this study, actinyl carboxylates have been systematically investigated of actinide system. Li et al. have carried out a systematic study of [AnO2(15CS)x]2− and [AnO2(L)y]2− (An = U, Np, Pu, Am, and Cm; n = 1, 2; L = 12TC4, 15TC5, and 18TC6) using DFT with scalar zeroth-order regular approximation (ZORA) and the quality of triple-ζ plus polarization (TZP) functions basis set. Their main conclusion was that the crown ether complexes of actinyls show obvious periodic trends in the actinides chemistry.

In this study, actinyl carboxylates have been systematically evaluated for their geometries, electronic structures, and the information of orbital interactions using density functional theory. They have been designed to gain insight into the chemical bonding characterizations that appear in the actinide–ligand bonding and particularly the change in the bonding features while moving along the HCOO− ligand in the complexes. The change trends of bonding between actinyls and coordinating ligands across the series from U to Am have been explained using various theoretical approaches. The corresponding calculations have been implemented in the gas and solvent phases. In addition, we have predicted the possible adsorption sites of cesium cations with electrostatic potential (ESP) on uranyl-carboxylate molecular van der Waals (vdW) surface. The influence of cesium cations on the adsorption capacity also has been investigated under different ratios, 1:3, 1:2, and 1:1, of uranyl with the HCOO− group. We also have described the microscopic interaction mechanism between Cs+ and uranyl-carboxylate complexes.

**RESULTS AND DISCUSSION**

Structures and Electronic Properties of [AnO2(COOH)x(H2O)y]2−n. To find the reasonable structures, we have considered by three theoretical methods (PBE-ZORA/def2-TZVPP-SARC, PW91-ZORA/def2-TZVPP-SARC, and B3LYP-ZORA/def2-TZVPP-SARC). The ground states of these complexes are singlet, doublet, triplet, and quartet for U, Np, Pu, and Am, respectively. Since one spin state has several low-lying excited states in the case of actinides, time-dependent DFT (TD-DFT) has been performed to check the optimized structures, indicating that the initial state is more stable than excited states by the positive excitation.
energies (Table S1). The corresponding geometries of these ground state are shown in Figure 1, which presents similar structures for the three actinide complexes. AnO$_2^{2-}$ prefers to coordinate six O atoms of COOH$^-$/H$_2$O on the equatorial plane (O$_3$ represents oxygen atoms of AnO$_2^{2-}$, O$_C$ represents oxygen atoms of COOH$^-$, O$_H$ represents oxygen atoms of H$_2$O). The detailed ground-state Cartesian coordinates of [AnO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-}$ complexes can be found in Table S2. The detailed calculation geometric parameters of the ground state at PBE-ZORA/def2-TZVPP-SARC are listed in Table 1, and the related calculation results of other methods are presented in Table S3. It can be seen that solvation has little influence on the geometric parameters, which is also shown in previous studies of similar systems.

Therefore, the following discussion only corresponds to the gas phase.

It can be seen that the average bond lengths of An–O$_C$ bonds decrease from U (1.80; 1.79; 1.78 Å) to Am (1.76; 1.75; 1.74 Å) in the [AnO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-}$ (An = U, Np, Pu and Am; n = 1–3; m = 0, 2, 4; 2n + m = 6) complexes, which is consistent with the change trend of the corresponding bond lengths in the isolated actinyl. This specific phenomenon is mainly attributed to the decrease of the actinide ionic radius. For the cases of U, Pu, and Am, the average An–O$_H$ bond lengths show a decreasing trend as moving along the HCOO$^-$ ligand in the complexes. For the case of [NpO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-}$, the average An–O$_C$ bond lengths display a trend of [NpO$_2$(COOH)$_4$]$^{-}$ > [NpO$_2$(COOH)$_3$(H$_2$O)$_2$] $>$ [NpO$_2$(COOH)$_2$(H$_2$O)$_4$]$^{+}$, which is attributed to the extent of orbital overlap between An and O$_C$. The average bond lengths of An–O$_C$ and An–O$_H$ in [AnO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-}$ exceed the range of An–O single bond covalent radii provided by Pyykkö,

which illustrates that such chemical bonds are primarily coordination interactions. The An–O$_C$ and An–O$_H$ bond lengths present the same variation trend in [AnO$_2$(COOH)(H$_2$O)$_n$]$^+_n$ and [AnO$_2$(COOH)$_2$(H$_2$O)$_n$] complexes, which suggest that An–O$_C$ bond lengths change in the following trend: U > Np > Pu < Am and An–O$_H$ bond lengths change as U > Np > Pu > Am. It is worth noting that the An–O$_C$ bond lengths show plutonium turn phenomenon, which is consistent with the results for [AnO$_2$(15C5)]$^{2+}$ and [AnO$_2$(L)$_n$]$^{2+}$ (An = U, Np, Pu, Am, and Cm; n = 1; 2; L = 12TC4, 15TC5, and 18TC6) complexes. The calculated An–O$_C$ bond lengths of [AnO$_2$(COOH)$_3$]$^{-}$ decrease from uranium, where the U–O$_C$ bond length is 2.526 Å, to americium, where the Am–O$_C$ bond length is 2.52 Å, which depend on the charge–charge interaction. This phenomenon of general decrease in the An–O$_C$ bond length with increasing atomic number also occurred in the [C(NH$_2$)$_3$]$^+_[AnO$_2$(CO$_3$)$_3$]$^-$ system. In the case of the given actinides complexes, as the number of COOH$^-$ ligands in the complexes increases, the An–O$_C$ and An–O$_H$ bond lengths increase, which suggests that the interaction between An and O atoms becomes weak with increasing COOH$^-$ ligands. This is consistent with the decreasing trend of fuzzy bond order (FBO) of An–O bonds. In addition, the bond lengths of An–O$_H$ are longer than An–O$_C$ in the same actinide complexes, indicating a weaker interaction between An and H$_2$O than between An and COOH$^-$ ligands. Table 2 lists the binding energy (BE) and Hirshfeld charges population of [AnO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-}$ (An = U, Np, Pu, and Am; n = 1–3; m = 0, 2, 4; 2n + m = 6) complexes with PBE-ZORA/
def2-TZVPP-SARC. The binding energies present a feature that increases as the COOH\(^-\) ligand increases, which further proves that the interaction between An and COOH\(^-\) is stronger than that between An and H\(_2\)O. The change in the O\(\sim\)An\(\sim\)O bond angle with the trend of \([\text{AnO}_2(\text{COOH})_3]\)^- > \([\text{AnO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\) < \([\text{AnO}_2(\text{COOH})(\text{H}_2\text{O})_4]^+\) is partially due to steric repulsion and electrostatic factors between ligands and actinyl ions.

**Chemical Bonding Characterizations of**

\([\text{AnO}_2(\text{COOH})_n(\text{H}_2\text{O})_m]^{2-n}\) **Clusters Using PBE-ZORA/def2-TZVPP-SARC**

| complexes                     | MBO          | FBO          |
|-------------------------------|--------------|--------------|
|                               | An–O\(_1\)  | An–O\(_C\)  | An–O\(_N\)  | An–O\(_1\)  | An–O\(_C\)  | An–O\(_N\)  |
| \([\text{UO}_2(\text{COOH})(\text{H}_2\text{O})_4]^+\) | 2.039        | 0.481        | 0.253        | 2.904        | 1.139        | 0.807        |
| \([\text{UO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\)  | 2.000        | 0.407        | 0.251        | 2.887        | 1.055        | 0.780        |
| \([\text{UO}_2(\text{COOH})_3]^-\)                       | 1.960        | 0.371        |              | 2.871        | 1.011        |              |
| \([\text{NpO}_2(\text{COOH})(\text{H}_2\text{O})_4]^+\) | 2.004        | 0.483        | 0.250        | 2.904        | 1.147        | 0.807        |
| \([\text{NpO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\)  | 1.984        | 0.413        | 0.250        | 2.895        | 1.063        | 0.786        |
| \([\text{NpO}_2(\text{COOH})_3]^-\)                       | 1.946        | 0.373        |              | 2.879        | 1.014        |              |
| \([\text{PuO}_2(\text{COOH})(\text{H}_2\text{O})_4]^+\) | 1.983        | 0.487        | 0.248        | 2.902        | 1.156        | 0.804        |
| \([\text{PuO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\)  | 1.949        | 0.408        | 0.246        | 2.887        | 1.058        | 0.785        |
| \([\text{PuO}_2(\text{COOH})_3]^-\)                       | 1.914        | 0.370        |              | 2.871        | 1.011        |              |
| \([\text{AmO}_2(\text{COOH})(\text{H}_2\text{O})_4]^+\) | 1.950        | 0.466        | 0.248        | 2.873        | 1.103        | 0.789        |
| \([\text{AmO}_2(\text{COOH})_2(\text{H}_2\text{O})_2]\)  | 1.913        | 0.401        | 0.247        | 2.853        | 1.022        | 0.776        |
| \([\text{AmO}_2(\text{COOH})_3]^-\)                       | 1.876        | 0.368        |              | 2.835        | 0.982        |              |

**Figure 2.** Contour plots of the electron density difference between AnO\(_2\)\(^+\) and ligands fragments. The solid lines (red) represent regions where electron density increases, and the dotted lines (blue) represent the region where the electron density decreases.

**Figure 3.** TDOS and PDOS curves of \([\text{UO}_2(\text{COOH})_n(\text{H}_2\text{O})_m]^{2-n}\) bonding MOs at the PBE-ZORA/def2-TZVPP-SARC level.
respectively). The contour regions are convex from O\textsubscript{c} and O\textsubscript{H} to U in Figure 2, which illustrates charge transfer from ligands toward the metal center AnO\textsubscript{2}\textsuperscript{2+} core. To understand the relative roles of An 5f and 6d orbits and their orbital interaction with O 2p of ligands, we have carried out density of states (DOS) analyses, and the DOS graphics of [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2−} complexes are shown in Figure 3; the corresponding full width at half-maximum (FWHM) is 0.8 eV with Gaussian curves. The curve shapes are similar, in which the partial DOS (PDOS) of O 2p orbits approaches the total DOS (TDOS) at the position of highest occupied molecular orbital (HOMO) energy level (vertical dashed line). This means that most of the contributions to HOMO result from O 2p orbits. On the other hand, the 6d/5f orbits of uranium have more significant contributions in the high-energy region than in the low-energy region, which can be explained by their high valence-electron energy levels. The graphics of other complexes can be found in Figure S2; they show similar results to [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2−} complexes.

We further apply quantum theory of atom in molecules (QTAIM) theory for the (3,−1) bond critical points (BCPs) of the An−O\textsubscript{c} An−O\textsubscript{c} and An−O\textsubscript{c} bonds to explore the chemical bonding nature of these complexes. QTAIM has been proven as a successful method for analyzing the bonding features of metal complexes.\textsuperscript{31} The relevant computed results are collected in Table S4, including density of all electrons \(ρ(r)\), Laplacian of electron density \(\nabla^2 ρ(r)\), Lagrangian kinetic energy \(G(r)\), potential energy density \(V(r)\), total energy density \(H(r)\) (sum of \(G(r)\) and \(V(r)\)), and electron localization function (ELF). According to the QTAIM analytical criteria,\textsuperscript{32} for An−O\textsubscript{c} bonds, the negative \(H(r)\) values become more positive as COOH\textsuperscript{−} ligands increase. Meanwhile, it should be noted that the ratios of \(-V(r)/G(r)\) are more close to 1, which infers that the covalent character becomes weaker with increasing COOH\textsuperscript{−} ligands in An−O\textsubscript{c} bonds. In the same actinide complexes, the value of \(H(r)\) in An−O\textsubscript{c} is more negative than that in An−O\textsubscript{c}, suggesting that the covalent interaction is more obvious in An−O\textsubscript{c} bonds. The larger \(-V(r)/G(r)\) ratios of An−O\textsubscript{c} further prove the above phenomenon. The ELF shaded surface projection maps of actinides complexes can reflect the actual bonding region. The disynaptic valence basins of the ELF map can be qualitatively described by the strength of interatomic interactions.\textsuperscript{33} Figure S3 shows the ELF maps of [AnO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2−} complexes, which show non-obvious disynaptic valence basins between the An and oxygen atoms of ligands. The disynaptic valence basins between An and O\textsubscript{c} are slightly obvious compared to those between An

![Figure 4. ESP-mapped molecular vdW surfaces of [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2−} complexes at the PBE-ZORA/def2-TZVPP-SARC level.](image)

![Figure 5. Optimized geometries of (Cs\textsuperscript{+})[UO\textsubscript{2}(COOH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] and (Cs\textsuperscript{+})[UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{−} at the PBE-ZORA/def2-TZVPP-SARC level.](image)

Table 4. Selected Average Bond Lengths (Å), Hirshfeld Charge (\(e\)), and Fuzzy Bond Order (FBO) of (Cs\textsuperscript{+})[UO\textsubscript{2}(COOH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] and (Cs\textsuperscript{+})[UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{−} Using Different Methods

| species               | methods | \(d(\text{Cs−O})\) (Å) | \(Q(\text{Cs})\) (\(e\)) | \(Q(\text{O})\) (\(e\)) | FBO (\text{Cs−O}) |
|-----------------------|---------|------------------------|---------------------------|------------------------|--------------------|
| (Cs\textsuperscript{+})[UO\textsubscript{2}(COOH)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] | PBE     | 2.95                   | 0.58                      | −0.17                  | 0.30               |
|                       | PW91    | 2.94                   | 0.58                      | −0.17                  | 0.30               |
|                       | B3LYP   | 2.95                   | 0.59                      | −0.21                  | 0.29               |
| (Cs\textsuperscript{+})[UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{−} | PBE     | 2.78                   | 0.50                      | −0.21                  | 0.40               |
|                       | PW91    | 2.78                   | 0.50                      | −0.21                  | 0.40               |
|                       | B3LYP   | 2.80                   | 0.52                      | −0.25                  | 0.39               |
and O\textsubscript{H}, implying that the covalent interaction is more strong in An–O\textsubscript{C} bonds. For An–O\textsubscript{H} bonds, all of the $H(r)$ values are negative and the $-V(r)/G(r)$ ratios are close to 2, which infers that the An–O\textsubscript{H} bonds are typical covalent bonds.

**Cs\textsuperscript{+} Adsorbing Effect in [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2-n}.**

Previous work has shown that Cs\textsuperscript{+} can be extracted from wastewater using UOF\textsubscript{24}. The electrostatic potential (ESP) distribution on van der Waals (vdW) surfaces provides a comprehensive understanding for predicting the adsorption sites of Cs\textsuperscript{+} on these actinide complexes. Since Cs\textsuperscript{+} carries a positive charge, it is easy to attract in the negative ESP sites of [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2-n} complexes. The ESP distribution (Figure 4) of [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2-n} complexes reveals that minimum values occur for the oxygen atoms of uranyl and between adjacent oxalates. Our geometry optimizations (as shown in Figure 5) show that [UO\textsubscript{2}(COOH)\textsubscript{n}(H\textsubscript{2}O)\textsubscript{m}]\textsuperscript{2-n} and [UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{-} can adsorb Cs\textsuperscript{+} between the adjacent oxalates.

Table 4 displays the parameters of different computation methods, which shows good consistency of the changing trend of the Cs–O bond length. The bond length of Cs–O decreases as the ratio of uranyl to HCOO\textsuperscript{-} group changes from 1:2 to 1:3, indicating that the interaction between Cs and O atoms became stronger. It can also be testified by the larger fuzzy bond order and binding energies in (Cs\textsuperscript{+})-[UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{-} complexes. The higher-level calculation method, PWPB95-D3BJ-ZORA/def2-TZVPP-SARC, was used to examine the energy order between (Cs\textsuperscript{+})-[UO\textsubscript{2}(COOH)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}] and (Cs\textsuperscript{+})-[UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{-}. Final results show that energies of (Cs\textsuperscript{+})-[UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{-} are lower than those of (Cs\textsuperscript{+})-[UO\textsubscript{2}(COOH)\textsubscript{3}(H\textsubscript{2}O)\textsubscript{2}]. The results provide evidence that [UO\textsubscript{2}(COOH)\textsubscript{3}]\textsuperscript{-} has stronger binding capacity of Cs\textsuperscript{+}, which is consistent with the experimental conclusion. One important feature in these structures is that they are penta-coordinated, leaving an extra oxygen atom of ligand available to interact with adsorbed Cs\textsuperscript{+}. In general, this type of interaction is much stronger than the
interactions with the coordinate oxygen such as the ones considered in this work. The relevant Cs–O QTAIM parameters are collected in Table S4, which includes positive $\rho(r)$ and $\nabla^2\rho(r)$ values at the BCPs. Hirshfeld charge analysis reveals that Cs carries a positive charge and O carries a negative charge, indicating that Cs–O bonds are mainly electronic interaction. In addition, it is notable that the $H(r)$ values are positive and the values of $-\nabla V(r)$/$G(r)$ are less than 1. Therefore, QTAIM analysis suggests that the Cs–O bond is a typical ionic bond.

Electronic Excitation Characteristics of Cs$^+$ Adsorption on the UO$_2$(COOH)$_2$(H$_2$O)$_2$ Complex. The electronic excitation characteristics of Cs$^+$ adsorption on the UO$_2$(COOH)$_2$(H$_2$O)$_2$ complex were analyzed by UV–vis spectrum and hole–electron distribution within the TD-DFT framework at the PBE0-ZORA/dez2-TZVPP-SARC level. In the simulation of UV–vis spectra, as shown in Figure 6, the Gaussian function was selected for broadening discrete lines as curves with an FWHM of 0.67 eV.

As shown in Figure 6, UV–vis spectra together with the contributions from the transitions whose absolute value of strength is larger than 0.005 are plotted. After Cs$^+$ adsorption, the position of the highest absorption peak is blue-shifted and the corresponding molar absorption coefficient increased from 4046.3 to 5117.1 L/(mol cm). The most contributing transition on the UO$_2$(COOH)$_2$(H$_2$O)$_2$ Complex.

| states    | $D$ (Å) | $S_s$ | $H$ (Å) | $t$ (Å) | $E_{\text{cool}}$ (eV) | HDI | EDI | MLCT (%) |
|-----------|---------|-------|---------|---------|------------------------|-----|-----|----------|
| S0 → S28  | 1.14    | 0.37  | 1.69    | 0.02    | 6.24                   | 11.49 | 24.41 | -84.59   |
| S0 → S34  | 0.27    | 0.37  | 1.49    | -0.59   | 7.99                   | 12.55 | 30.88 | -75.26   |
| S0 → S35  | 0.48    | 0.34  | 1.88    | -0.79   | 6.39                   | 13.29 | 25.93 | -85.06   |
| S0 → S36  | 0.86    | 0.41  | 1.73    | -0.27   | 6.54                   | 10.73 | 22.25 | -85.79   |
| S0 → S70  | 1.93    | 0.34  | 1.93    | -0.66   | 6.33                   | 12.40 | 25.86 | -69.23   |

In conclusion, the geometric and electronic structures of the [AnO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-n}$ (An = U, Np, Pu, and Am; $n = 1–3$; $m = 2, 4$; $2n + m = 6$) compounds have been systematically investigated using different methods. The ground-state structures of the [AnO$_2$(COOH)$_n$(H$_2$O)$_m$]$^{2-n}$ (An = U, Np, Pu, and Am; $n = 1–3$; $m = 0, 2, 4$; $2n + m = 6$) complexes have been constructed, which reveal that AnO$_2$ can coordinate six O atoms of COOH$^-$/H$_2$O on the equatorial plane. A series of analyses suggest that the interaction between An and COOH$^-$ is stronger than that between An and H$_2$O. The chemical bonding properties of An–O$_C$/O$_H$ are mainly electronic interaction, and the covalent character of the An–O$_C$ bonds becomes weaker with increasing COOH$^-$ ligands. The covalent interaction in An–O$_C$ bonds is more obvious than that in An–O$_H$ bonds. [UO$_2$(COOH)$_2$(H$_2$O)$_2$] and [UO$_2$(COOH)$_3$]$^{2-}$ can adsorb Cs$^+$ between the adjacent oxalates. Cs–O bond is a typical ionic bond, and [UO$_2$(COOH)$_3$]$^{2-}$ complexes have better adsorption capacity. The current study of actinide complexes can help us to provide insights into actinides and Cs$^+$ partitioning. The adsorption of cesium atoms will result in a blue shift of the position of the highest absorption peak of the UV–vis spectrum and an increase of the corresponding molar absorption coefficient.

COMPUTATION METHODS

Geometry optimization and frequency calculation have been performed with density functional theory (DFT) using ORCA-4.2.0 package. To obtain reasonable structures, different possible initial structures and different spin multiplicities of each complex have been determined using the PBE, PW91, and B3LYP methods. The geometry optimization has been endowed without symmetry constrains, and the vibrational frequency calculations have been performed to determine the local minima or saddle point of potential surface for all optimized structures. Single-point energies have been calculated using PWPB95 plus the Grimme’s atom-pairwise dispersion correction and Becke–Johnson damping D3(BJ) based on the PBE geometries. The zeroth-order regular approximation (ZORA) has been implemented to consider the scalar relativistic effect.
Segmented all-electron relativistically contracted (SARC)\textsuperscript{41} and triple-\(\zeta\) valence basis sets (def2-TZVPP)\textsuperscript{42} were applied for actinides (U, Np, Pu, Am, and Cs) and light elements (H, O, and C), respectively. We checked the expectation value \(<\hat{S}^Z>\) of each system, and the deviations are found to be very small. The reported energies have taken into account the zero-point vibrational energy and thermal energy corrections. Since one spin state can have plenty of low-lying excited states in the case of actinides, the excited states including 10 transitions have been calculated to check the ground-state structures with time-dependent density functional theory (TD-DFT). In view of the fact that these complexes predominantly exist in the aqueous state, the influence of solvent effect on molecular geometry, electronic energy, and electron distribution was considered using the conductor-like polarizable continuum model (C-PCM).\textsuperscript{43} The solvent is water, and the dielectric constant value is 80.4. We evaluate the effect of spin–orbit coupling (SOC) on geometries and found that SOC has little influence on the geometries of complexes.

The bonding characteristics of the UO\(_2\), NpO\(_2\), PuO\(_2\), and AmO\(_2\) complexes have been explored with MULTIWFN program\textsuperscript{44} based on the all-electron wave functions. The details of charge transfer between AnO\(_2\)\textsuperscript{−} and ligands have been investigated through electron density difference plots and atom population including Hirshfeld atom model (C-PCM).\textsuperscript{45} The solvent is water, and the dielectric constant value is 80.4. We evaluate the effect of spin–orbit coupling (SOC) on geometries and found that SOC has little influence on the geometries of complexes.

The excitation energies of the selected complex were calculated with PBE0\textsuperscript{46} in conjunction with the ZORA-def2-TZVPP basis set. A total of 80 transitions were included in the excited-state calculations. In the analysis of the electronic excitation process, we utilized hole–electron analysis\textsuperscript{53} to comprehensively examines the electron excitation characteristics.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04887.

Excitation energies (eV) of [AnO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\) complexes at the PBE0-ZORA/def2-TZVPP-SARC level; Cartesian coordinates of [AnO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\) complexes at the PBE-ZORA/def2-TZVPP-SARC level of theory; average An−O\(_{An}\), An−O\(_{Oy}\), and An−O\(_{H}\) bond lengths and O\(_{y}\)−An−O\(_{y}\) bond angles of the [AnO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\) complexes at the PW91-ZORA/def2-TZVPP-SARC and B3LYP-ZORA/def2-TZVPP-SARC levels; topological parameters for the bond critical points (BCPs) in [AnO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\); contributions of various major molecular orbital transitions in the selected five excited states of (Cs)+[UO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\); contour plots of the electron density difference between An and ligands fragments; TDOS and PDOS curves of [AnO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\) (An = Np, Pu, and Am; n = 1−3; m = 0, 2, 4; 2n + m = 6) complexes bonding MOs at the PBE-ZORA/def2-TZVPP-SARC level; and two-dimensional color-filled map of ELF for [AnO\(_2\)(COOH)\(_n\)(H\(_2\)O)\(_m\)]\(^{2−}\) (PDF)

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ACKNOWLEDGMENTS
This work was supported by the National Natural Science Foundation of China (NSFC) (grant nos. 11604187, 61725207, 61675121, and 61705123), the Natural Science Young Foundation of Shanxi Province (grant no. 201801D221004), Cooperation projects of Institute of Applied Physics and Computational Mathematics, Open Fund of Key Laboratory of Advanced Reactor Engineering and Safety, Ministry of Education (Tsinghua University, China), and the Program for the Outstanding Innovative Teams of Higher Learning Institutions of Shanxi. The authors are very grateful to Dr. Sobereva for many helpful discussions and providing them with the Multiwf package. They also thank the reviewers for the valuable suggestions on improving this paper.

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