Electronic Structure and Chemical Bonding of [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$

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Supporting Information

ABSTRACT: Systematic americyl-hydration cations were investigated theoretically to understand the electronic structures and bonding in [(AmO$_2$)(H$_2$O)$_n$]$^{2+/1+}$ ($n=1$–6). We obtained the binding energy using density functional theory methods with scalar relativistic and spin–orbit coupling effects. The geometric structures of these species have been investigated in aqueous solution via an implicit solvation model. Computational results reveal that the complexes of five equatorial water molecules coordinated to americyl ions are the most stable due to the enhanced ionic interactions between the AmO$_2$:$^{2+/1+}$ cation and multiple oxygen atoms as electron donors. As expected, Am–O$_{\text{water}}$ bonds in such series are electrostatic in nature and contain a generally decreasing covalent character when hydration number increases.

INTRODUCTION

In the past several decades, a rapid increased resurgence of nuclear power in many countries for the goals of ensuring sustainable energy supplies has raised a possible hazard to the environment due to the problems of the radioactive waste and has increased the handling and reprocessing challenge of spent nuclear fuel and high-level nuclear waste.¹–⁵ Especially, the long-term radioactivity of nuclear waste repositories is one of the main issues at stake and is in part determined by the presence of minor actinides, namely, americium (Am) and curium (Cm), with the half-life $t_{1/2} = 3730$ year for $^{244}$Am and $t_{1/2} = 340000$ year for $^{248}$Cm.⁶ During the actinide waste storage, transportation, and separation, water is unavoidable. Therefore, the characterization and identification of the behavior of actinide ions in solution is of particular practical importance in addition to the fundamental actinide chemistry, such as the dynamics between the coordinated water molecules and the bulk solvent and the coordination flexibility of actinyl ions.⁷ So, the solution chemistry of actinide complexes has been considerably explored in experiment and theory; especially, the hydration of actinide ions has been widely investigated.⁸–¹² However, such studies have mostly focused on early actinide ions due to their relatively substantial quantities and extensive applications. The uranyl UO$_2^{2+}$ ion, for example, has received a large amount of interest because of its importance for environmental chemistry of radioactive elements and its role as a benchmark system for heavier actinides.¹³ Experimentally, direct structural information on the coordination of uranyl in aqueous solution has been mainly obtained by extended X-ray absorption fine structure or X-ray absorption near-edge structure measurements.⁹,¹⁴,¹⁵ Theoretically, the structural investigation has been performed via various ab initio studies of uranyl and related molecules, with a number of explicit water molecules or with a polarizable continuum model to mimic the environment over the past years, such as [UO$_2$(CO$_3$)$_3$]$^{4-}$, [Th(H$_2$O)$_n$]$^{3+}$, [U(H$_2$O)$_n$]$^{3+}$, UO$_2$F$_2$(H$_3$O)$_{2-n}$, and [UO$_2$(H$_2$O)$_n$]$^{2+/1+}$.⁶ With the rapid development of quantum chemical methods, the less known transuranium elements have been increasingly studied, i.e., [NpO$_2$(CO$_3$)$_3$]$^{4-}$, [NpO$_2$(CO$_3$)$_n$(H$_2$O)$_m$], [Cm(H$_2$O)$_n$]$^{3+}$, [UO$_2$(H$_2$O)$_n$]$^{3+}$, [NpO$_2$(H$_2$O)$_n$]$^{3+}$, and [PuO$_2$(H$_2$O)$_n$]$^{3+}$,¹⁶–²¹ With the exception of some theoretical report about americyl (AmO$_2^{2+/1+}$) in aqueous solution but one study on the water exchange mechanism in AmO$_2$(H$_2$O)$_n$¹⁵ 15 years ago.²⁹ In addition, the understanding of the coordination chemistry of americyl ions in solution can present the essentials to detect, characterize, and differentiate this metal ion from transition metals or lanthanide metals through the coordination characteristic. Hence, we will focus on speciation of the americyl ions (AmO$_2^{2+}$ and AmO$_2^{1+}$) in this paper, bridging the gap between the wide-established early actinides and the more complicated later actinides. However, an accurate description of solvent effects of the actinide complexes is inherently difficult due to their complicated electronic properties and the challengeable aqueous environment to theoretical chemists. There are two typical quantum
chemistry strategies used to incorporate the solvent effects on the geometry and energy of the actinide complexes in aqueous solution. One is molecular dynamics simulations approach with a discrete model, where a number of explicit solvent molecules are included and treated at the same level of theory as that used for the solute. Although this supermolecule requires a substantial computational expense, the understanding improvement of the structural and chemical behavior of actinyl in solution is inconsequential because this method employs empirical potentials affecting the accuracy significantly, especially for those transplutoniums having few experimental data available. Another approach is the polarizable continuum model, where the solvent is described by a dielectric data available. Another approach is the polarizable continuum manner is longer (0.09 Å) than that for [AmO2(H2O)5]2+ and is significantly shorter (0.13 Å) than that reported for NpO2(H2O)5 having a similar structure largely owing to the actinide contraction of ion radii. A somewhat different structure of [AmO2(H2O)5]1+ is obtained, whereas the sixth water is excluded to the second hydration shell owing to the weak electrostatic interaction between AmO2 and water oxygen. Thus, the hydration number of AmO2 is five in resulting minimum-energy structures of both [AmO2(H2O)6]2+/1+ (n = 1–6) complexes.

Since the solvation effect is significant on the geometry of [AmO2(H2O)6]2+/1+ and also plays a typical role in practical application, we only report the geometry optimization results under the effect of aqueous solvation in text. Table 1 presents the binding energy obtained at SR-B3LYP and CCSD(T) levels of theory for the following reaction of [AmO2(H2O)6]2+/1+ + nH2O → [AmO2(H2O)6]2+/1+ (n = 1–6) in solution. As shown in Table 1, each of these [AmO2(H2O)6]2+ (n = 1–6) complexes is significantly more stable than the corresponding [AmO2(H2O)6]1+ (n = 1–6). At the SR-B3LYP level of theory, the actinyl–water binding energies steadily increase from 34.0 kcal/mol for [AmO2(H2O)5]2+ (19.1 kcal/mol for [AmO2(H2O)4]1+) to 119.0 kcal/mol for [AmO2(H2O)4]2+ (68.2 kcal/mol for [AmO2(H2O)3]1+), whereas at the spin–orbit (SO) level of theory, the binding energies show the same trend by increasing from 45.4 kcal/mol at n = 1 to 135.0 kcal/mol at n = 5 in the series of AmO2(H2O)42+. Overall, the substantial stabilizations of [AmO2(H2O)6]2+/1+ relative to the isolated americyl and free water molecules favors the formation of a maximum of five water ligands in the equatorial plane in the first hydration shell. This five-coordination structure has been commonly observed in other actinyls in water.

### RESULTS AND DISCUSSION

The static structures of hydrated complexes of AmO2 with one to eight water ligands have been regularly investigated via geometry optimizations in gas phase and in aqueous phase at the B3LYP/Ame/ECFP60MBW SEG//O,H/cc-pVTZ level with or without the conductor-like screening solvation model (COSMO) method. First, concerning the water hydrogens lying either in the planes or perpendicular to the planes defined by the O₈AmO₈ two possible gas-phase symmetric arrangements of water molecules for [AmO2(H2O)6]2+/1+ and [AmO2(H2O)6]2+/1+ have been optimized without symmetry constraints. As shown in Figure S1, the one with hydrogens perpendicular to the plane has one imaginary vibrational frequency (428i cm⁻¹) showing the rotation of water ligand, indicating its instability compared with the one with hydrogens lying in the plane. Besides, the starting structure of [AmO2(H2O)5]2+/1+ has been assumed as a first-shell coordination number of seven when seven water molecules are bonded to AmO2, in which the seven equatorial water ligands lie rigorously in the equatorial plane. After optimization within density functional theory (DFT), seven water molecules have been arranged into two coordination shells; there are five water molecules in the first shell with a relatively shorter Am–O₈ distance of <2.5 Å and two water molecules in the second shell at a longer distance of >4.4 Å. Therefore, the hydration number of AmO2 is predicted to be less than seven. In addition, the optimized structural parameters and calculated binding energies of [AmO2(H2O)6]2+/1+ (n = 1–6) in the gas phase and aqueous solution on the basis of different levels of theory are listed in Tables S1–S4. As clearly shown in the Tables S3 and S4, the energy destabilization by roughly 32.0–128.2 kcal/mol for [AmO2(H2O)5]2+/1+ (n = 1–6) complexes is due to the conductor-like polarized continuum model; a similar trend is also observed for [AmO2(H2O)6]2+/1+ (n = 1–6) complexes. Upon inclusion of the surrounding effects, the binding energy decreases drastically to 62.4 kcal/mol for equatorial [AmO2(H2O)5]2+/1+ and to −0.5 kcal/mol for equatorial [AmO2(H2O)4]1+ at scalar relativistic (SR)-B3LYP level of theory, indicating the instability of this structure. In terms of geometries of equatorial [AmO2(H2O)5]2+/1+, the six-water complexes with all six coordinated Ow atoms in the equivalent position are subject to the first-order Jahn–Teller instability and are only saddle points having imaginary frequencies. The C₂ symmetry structure of [AmO2(H2O)5]2+/1+ in which all six ligands are in the first coordination shell, shown in Figure S2, is stable with or without aqueous solution. The distance from the americium center to the water molecules located above and below the equatorial plane in a symmetric manner is longer (0.09 Å) than that for [AmO2(H2O)5]2+/1+ and is significantly shorter (0.13 Å) than that reported for NpO2(H2O)5 having a similar structure largely owing to the actinide contraction of ion radii. A somewhat different structure of [AmO2(H2O)4]1+ is obtained, whereas the sixth water is excluded to the second hydration shell owing to the weak electrostatic interaction between AmO2 and water oxygen. Thus, the hydration number of AmO2 is five in resulting minimum-energy structures of both [AmO2(H2O)6]2+/1+ (n = 1–6) complexes.

| n | [AmO2(H2O)6]2+/1+ | [AmO2(H2O)6]2+/1+ |
|---|------------------|------------------|
| 1 | −34.0            | −19.1            |
| 2 | −64.6            | −36.4            |
| 3 | −88.5            | −52.5            |
| 4 | −110.2           | −63.7            |
| 5 | −119.0           | −68.2            |
| 6 | −113.7           | −65.1            |

Table 1. Binding Energy (kcal/mol) for the Reaction of AmO2 + nH2O → [AmO2(H2O)6]2+/1+ (n = 1–6) in Solution at Different Levels of Theory with COSMO

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ment in the available experimental studies and is in good accord with the published theoretical studies using quantum mechanical method or molecular dynamics approach.

**Geometric Structure of the [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ (n = 1–5)**. Two different density functionals (Perdew–Burke–Ernzerhof (PBE) and B3LYP) were first employed for the geometrical optimization, which gave similar results, so only the results obtained at B3LYP/Am/ECIP60MWB_SEG//O,H/cc-pVTZ level of theory are presented in the text and those obtained at the PBE/TZ2P level are detailed in the Supporting Information (Tables S1 and S2). As noted in the last section, the inclusion of solution therefore and the use of a solvation model are important in modeling the coordination geometries of actinyl. So the calculated ground-state geometries (Table 2) from the COSMO solvation model are listed in Table 2 and shown in Figure 1. In terms of geometry, [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ and [AmO$_2$(H$_2$O)$_n$]$^{3+}$ have similar geometric structures; these are the water molecules coordinating to AmO$_2$ along the equatorial plane of americyl with an increasing hydration number from $n = 1–5$, as expected, with the same hydration number as that of of uranyl, neptunyl, and plutonyl in aqueous solution. The calculated Am–O$_d$ distances in the [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ complexes elongate from 1.669 Å in pure americyl ion to 1.681 Å in [AmO$_2$(H$_2$O)$_1$]$^{2+/1+}$ and increase all through to 1.711 Å in [AmO$_2$(H$_2$O)$_5$]$^{2+/1+}$, whereas the Am–O$_d$ bonds in the [AmO$_2$(H$_2$O)$_n$]$^{3+}$ complexes appear to follow the same trend, consistent with the decrease in the bond order, attributed to the weakening of both ionic and covalent bonding interactions of Am–O$_d$ bond from $n = 1–5$. In all [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ (n = 1–5) complexes, the americyl is coordinated by water O atoms (O$_w$) with bond Am–O$_w$ distances longer than 2.2 Å, which implies weak bonding interactions. In addition, all Am–O$_u$ bond lengths in the complexes are beyond the range of Am–O covalent single-bond lengths estimated by the sum of the self-consistent covalent radii derived by Pyykkö. Expectedly, the Am–O$_u$ bond lengths in the [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ complexes are shorter than the corresponding bond lengths in the [AmO$_2$(H$_2$O)$_n$]$^{3+}$ complexes, owing to the stronger electrostatic interaction in dication complexes. The lengthening of the Am–O$_u$ bond distances in the [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ complexes from 2.260 Å at $n = 1$ to 2.460 Å at $n = 5$ implies the reduction of bond strength and the weakening of bonding interaction of each Am–O$_u$ bond along with increasing hydration numbers. Although each of the Am–O$_u$ bonds is not particularly strong in comparison to Am–O$_d$ multiple bond, the overall bonding interaction is substantial, as indicated by significant binding energies (Table 1) and by the extreme redshift in the americyl asymmetric stretch frequency (Table 3).

For the monoaqua, the ground electronic states of [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ have been confirmed as $^4$B$_1$ and $^3$A$_1$ via a comparison among different multiplicities. Upon the coordination of O$_u$ in [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$, the linear O$_u$AmO$_d$ is broken into a bent O$_u$AmO$_d$ angles of 179.5 and 179.8°, respectively. The water molecule coordinates to americyl on the equatorial plane with the two hydrogen atoms lying symmetrically on both sides of the plane. The shortest Am–O$_u$ bond distance of 2.26 Å among the [AmO$_2$(H$_2$O)$_n$]$^{2+/1+}$ series is within the range of single covalent bond radii of Am–O (2.29 Å), mainly because of the strongest bonding. These distances are consistent with the bonding analysis detailed in the next section. The singly filled highest occupied molecular orbitals of

**Table 2. Selected Optimized Geometrical Structures (Bond Length, Å, Angle, °) and Formation Energy ($E_m$ kcal/mol) for the Reaction of $\phi^2_{\text{AmO}_2(\text{H}_2\text{O})_{n}^{2+/1+}}$ and $\phi_{\text{AmO}_2(\text{H}_2\text{O})_{n}^{2+/1+}}$**

| $\phi$ | $E_m$ ($^{2+}$) | $E_m$ ($^{1+}$) |
|--------|-----------------|-----------------|
| $^{2+}$ | -168.1          | 179.3           |
| $^{1+}$ | -179.6          | 180.0           |
| $^{2+}$ | -179.8          | 180.0           |
| $^{1+}$ | -179.9          | 180.0           |
| $^{2+}$ | -179.4          | 180.0           |

All optimizations are fully relaxed without constraints.
Figure 1. Optimized geometry and binding energy (kcal/mol, in parentheses) of \(\text{AmO}_2(\text{H}_2\text{O})_n^{2+/1+}\) (\(n = 1–5\)) at SR-B3LYP/Am/ECP60MWB\_SEG//O,H/cc-pVTZ levels of theory.

Table 3. Calculated Vibrational Frequencies of \(\text{AmO}_2(\text{H}_2\text{O})_n^{2+/1+}\) (\(n = 1–5\)) at SR-B3LYP/Am/ECP60MWB\_SEG//O,H/cc-pVTZ Levels of Theory with COSMO

| \(n\) | \(v_1\) | \(v_2\) | \(\Delta v_1\) | \(v_3\) | \(v_4\) | \(\Delta v_3\) |
|-------|-------|-------|------------|-------|-------|------------|
| 0     | 1053.7| 925.1 | 128.6      | 925.6 | 828.0 | 117.6      |
| 1     | 1027.6| 904.7 | 232.9      | 904.4 | 810.7 | 233.7      |
| 2     | 1009.1| 891.6 | 117.5      | 882.9 | 792.7 | 210.2      |
| 3     | 994.8 | 880.7 | 143.1      | 866.0 | 777.7 | 188.3      |
| 4     | 980.9 | 868.4 | 122.5      | 849.5 | 764.7 | 184.8      |
| 5     | 970.4 | 855.9 | 14.5       | 839.1 | 754.1 | 105.0      |

Table 4. Average Hirshfeld, Voronoi Deformation Density (VDD) Charges, and Average Mulliken, Multipole Derived Charges (MDC\(_q\)) Spin Density on the B3LYP with COSMO-Optimized Structures of \(\text{AmO}_2(\text{H}_2\text{O})_n^{2+/1+}\) (\(n = 1–5\)) from the PBE/TZ2P Calculations

| \(n\) | \(\text{AmO}_2(\text{H}_2\text{O})_n^{2+}\) | \(\text{AmO}_2(\text{H}_2\text{O})_n^{1+}\) |
|-------|---------------------------------|---------------------------------|
| 0     | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) |
| Am    | \(-0.03\) | \(-0.23\) |
| 1     | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) |
| Am    | \(-0.09\) | \(-0.22\) | \(-0.28\) | \(-0.28\) |
| 2     | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) |
| Am    | \(-0.13\) | \(-0.20\) | \(-0.20\) | \(-0.20\) |
| 3     | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) |
| Am    | \(-0.16\) | \(-0.01\) | \(-0.00\) | \(-0.00\) |
| 4     | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) |
| Am    | \(-0.18\) | \(-0.01\) | \(-0.00\) | \(-0.00\) |
| 5     | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) | \(\text{O}^\text{i}\) |
| Am    | \(-0.23\) | \(-0.01\) | \(-0.00\) | \(-0.00\) |

\(\text{AmO}_2(\text{H}_2\text{O})_n^{2+/1+}\) have roughly 98% Am 5f\(d\) and 90% Am 5f\(f\) character, indicating that the Am 5f orbital is largely unperturbed by the coordination of the ligands. Thus, \(\text{AmO}_2(\text{H}_2\text{O})_n^{2+/1+}\) retain their electron configuration at Am ions in those \(\text{AmO}_2(\text{H}_2\text{O})_n^{2+/1+}\) complexes, namely, \(f^6d^2\) and \(f^6d^2\), respectively.

For the dual aqua, one additional water molecule locates in the equatorial plane with a bent \(\text{O}_\text{am–Am–O}_\text{w}\) angle of 96.8° in \(\text{AmO}_2(\text{H}_2\text{O})_2^{2+}\) and 103.1° in \(\text{AmO}_2(\text{H}_2\text{O})_2^{1+}\), inducing a weakening of both axial and equatorial bond strength, as reflected by the increase of 0.10 and 0.02 Å in the Am–O\(_\text{am}\) and Am–O\(_\text{w}\) bond distances compared to those in \(\text{AmO}_2(\text{H}_2\text{O})_2^{1+}\). The optimized Am–O\(_\text{w}\) bond distance is 2.286 Å in \(\text{AmO}_2(\text{H}_2\text{O})_2^{2+}\) and 2.420 Å in \(\text{AmO}_2(\text{H}_2\text{O})_2^{1+}\); the slightly longer distance in the monoclinic complex is consistent with the small binding energy. Noticeably, the favorable bent versus linear geometries of the \(\text{O}_\text{am–Am–O}_\text{w}\) reveals the covalent characteristic of Am–O bond, which pulls the two O\(_\text{am}\) atoms much closer, leading to an O\(_\text{am–Am}–\text{O}_\text{w}\) distance of 3.420 Å in \(\text{AmO}_2(\text{H}_2\text{O})_2^{2+}\) and 3.790 Å in \(\text{AmO}_2(\text{H}_2\text{O})_2^{1+}\). The electrons singly occupy on Am 5f\(d\) atomic orbital (AO)-based molecular orbitals (MOs) in \(\text{AmO}_2(\text{H}_2\text{O})_2^{2+/1+}\), which provides extensive Am 5f\(d\) O\(_\text{w}\) back-bonding, involving donation from an Am 5f\(d\) orbital into in-plane O\(_\text{w}\) 2p orbitals, thus leading to a three-center interaction. The effectiveness of the O\(_\text{w}\) 2p → Am 5f\(d\) back-bonding and Am 5f → O\(_\text{w}\) 2p back donation is less obvious in \(\text{AmO}_2(\text{H}_2\text{O})_2^{1+}\) due to a longer Am–O\(_\text{w}\) distance, denoted by a relatively large \(\text{O}_\text{am–Am–O}_\text{w}\) angle of 103.1°. In particular, the variety in the average effective charges of the O\(_\text{w}\) ligand, listed in Table 4, is an evidence to this statement. The average Hirshfeld charges on the O\(_\text{w}\) of \(\text{AmO}_2(\text{H}_2\text{O})_2^{2+}\) and \(\text{AmO}_2(\text{H}_2\text{O})_2^{1+}\) are −0.16 lel and −0.20 lel, respectively, slightly greater relative to those of −0.15 lel and −0.20 lel
Table 5. Average Mayer Bond Orders of [AmO2(H2O)4]2+/1+ (n = 1–5) from the PBE/TZ2P Calculations

| n | [AmO2(H2O)4]2+/1+ | [AmO2(H2O)4]1+ | [AmO2(H2O)4]2+ |
|---|------------------|----------------|----------------|
|   | vacuum | COSMO | vacuum | COSMO | vacuum | COSMO | vacuum | COSMO |
| 0 | 2.12 | 2.12 | 2.12 | 2.12 | 1.99 | 2.00 | 1.94 | 1.94 |
| 1 | 2.06 | 2.05 | 0.37 | 0.39 | 0.34 | 0.34 | 0.26 | 0.27 |
| 2 | 2.00 | 2.00 | 0.34 | 0.34 | 0.32 | 0.32 | 0.21 | 0.21 |
| 3 | 1.96 | 1.95 | 0.31 | 0.31 | 0.22 | 0.22 | 0.19 | 0.19 |
| 4 | 1.91 | 1.90 | 0.22 | 0.22 | 0.19 | 0.19 | 0.19 | 0.19 |
| 5 | 1.89 | 1.88 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 | 0.17 |

[AmO2(H2O)n]+, as the consequence of the Am-to-Ow back donation.

For the triaqua, one more water molecule added with the formation of [AmO2(H2O)3]2+/1+ further weakens the Am–O bonds, as identified by the longer Am–Ow and Am–Ow bond distances than those in [AmO2(H2O)2]2+/1+. In gas phase, three coordinated water molecules are equivalent with the $\angle_{\text{OwAmOw}}$ angle of 120.0°, giving a $C_{3v}$ symmetry structure. However, when concerning the presence of aqua solvent, this symmetry has been broken into $C_{3}$ symmetry with the $\angle_{\text{OwAmOw}}$ angles of 127.8, 113.2, and 118.7° in [AmO2(H2O)3]2+ and 117.4, 120.4, and 122.2° in [AmO2(H2O)1−]+ complexes, largely ascribed to the differences responding to the polarization of the hydration upon solvent inclusion. In essence, the solvent polarity is more effective in those complexes with larger polarity. As listed in Table 2, the deviation from the high-symmetry structure of the first shell is in good agreement with the equilibrium structure. In essence, the solvent polarity is more effective in those complexes with larger polarity. As listed in Table 2, the deviation from the high-symmetry structure of the first shell is in good agreement with the equilibrium structure.

From our above discussion of [AmO2(H2O)n]2+/1+ structures, we would expect the additional water molecules to extend the Am–Ow and Am–Ow bond lengths and to decrease the overall degree of dative bonding, consistent with the lower relative binding energy for the [AmO2(H2O)q]2+/1+ compared to that of the [AmO2(H2O)p]2+/1+ ($q \geq p + 1$). The maximum of five hydration number in the first coordination shell is in good agreement with the equilibrium structure having five water coordination of actinyl (UO22+, NpO22+, and PuO22+) in aqueous solution. In the equilibrium structure of [AmO2(H2O)n]2+/1+, four water molecules bonded to the center americyl are perpendicular to the equatorial plane and the fifth coordinated water molecule arranges within the equatorial plane where the dihedral angle between the equatorial water ligands and the equatorial plane is 0° (Figure 1). The bond length of the fifth Am–Ow bond is 2.420 Å in [AmO2(H2O)3]2+ and 2.548 Å in [AmO2(H2O)1−], the shortest one among five Am–Ow bond distances, thus leading to a slight bent of $\angle_{\text{OwAmOw}}$ angles of 179.4°.

Electronic Structure and Chemical Bonding of the [AmO2(H2O)n]2+/1+ (n = 1–5). To provide further insights into the interactions between americyl and the water ligands of [AmO2(H2O)n]2+/1+, several bonding analyses were performed, including the bond order analyses, population partitioning schemes, energy decomposition approach, Kohn–Sham orbital interaction, and electron localization function (ELF) method.

The bond order analyses by three methods give a similar trend that is consistent with the previous detailed bond length trend. Taking the Mayer Am–O bond index as an example, the calculated Mayer bond orders (Table 5) of Am–Ow and Am–Ow for the [AmO2(H2O)4]2+ complexes lie in two ranges, at averaged 1.9 and averaged 0.2, respectively, whereas those for [AmO2(H2O)1−] complexes lie in two ranges, at averaged 1.85 and averaged 0.2, respectively. This result indicates relatively weak Am–Ow bonding interactions compared with the Am–Ow bonding in [AmO2(H2O)n]2+ complexes, which is resulted from not only the ion bonding nature but also the somewhat longer bond distance induced by weaker orbital interaction. The calculated Am–Ow bond order in [AmO2(H2O)n]2+ decreases gradually from 2.05 at n = 1 to 1.88 at n = 5, whereas the Am–Ow bond order decreases from 0.39 at n = 1 further to 0.19 at n = 5, suggesting there is a general decrease in Am–O bond strength with an increasing hydration number. In addition to the bond order, the effective atomic charges on Am and Ow ions can imply the variation of the ionicity of the Am–Ow bond. Several charge analyses were carried out on the B3LYP stationary structure in solution via COSMO. Although the absolute values are different on the basis of different methods used, the trend is the same. As listed in Table 4, the averaged Hirshfeld charges reveal that Am carries a considerable positive charge and the Ow ligands carry substantial negative charges in these [AmO2(H2O)n]2+/1+ complexes, which is in good agreement with the bond order analyses, indicating an ionic Am–Ow bonding interaction. Generally, the Am ions become less charged and both Ow and Ow atoms become more charged along with the increase of the hydration number, i.e., the calculated Hirshfeld charge of Am decreases from +2.06 e [pure AmO2] to +1.77 e in monoaqua and further to +1.11 e in penta-aqua, accompanied by an increased charge of each Ow atom from +0.03 e to –0.21 e; this is due to the charge rearrangement of americyl unit upon inclusion of explicit water in the first shell and implicit water by COSMO, which is in good agreement with the study of [UO2(H2O)4−](OH)n]+.34 The averaged Hirshfeld charges of Ow units becoming greater from –0.15 e to –0.21 e suggests overall increasing of electron back donation into Ow ligand, thus leading to the Am–Ow bond weakening with an increasing hydration number. In addition, the decreased electron density localized on americyl unit listed in Table 4 indicates that the charge transfer is from americyl unit to water ligands, owing to the Am-to-Ow back donation. Furthermore, the formal Am oxidation state of +VI and +V is not apparently affected by the hydration number in these [AmO2(H2O)n]2+/1+ complexes via population analyses.
To better understand the orbital interactions, Figure 2 shows the Kohn–Sham MO energy levels of \([\text{AmO}_2(\text{H}_2\text{O})_n]^{2+}\) at SR-PBE/TZ2P level. In the linear AmO\(_2^{2+}\) moiety due to Am–O\(_2\) bonding, the Am 5f and 6d orbitals transform as 5f\(_n\) and 6d\(_n\) species, respectively. Upon dative coordination with the water oxygen atoms in the equatorial plane, the Am–O\(_w\) orbital interactions cause to 6d\(_n\) level further destabilization. While both \(d\delta_\pi\) and \(d\delta_\sigma\)–\(f\phi\) \(_w\) orbitals lie around the equatorial plane, the Am–O\(_w\) orbital interactions mainly affect the 6d orbitals, indicating that the coordinated water molecules only slightly interact with the “nonbonding” contracted 5f orbitals. This bonding module is in good agreement with the well-known bonding principle proposed for actinides by Bursten, the bonding module is in good agreement with the well-known bonding principle proposed for actinides by Bursten, the bonding module is in good agreement with the well-known bonding principle proposed for actinides by Bursten, the bonding module is in good agreement with the well-known bonding principle proposed for actinides by Bursten, the bonding module is in good agreement with the well-known bonding principle proposed for actinides by Bursten, the bonding module is in good agreement with the well-known bonding principle proposed for actinides by Bursten.

In addition to these chemical bonding analyses based on wave functions and electron densities, the energy decomposition analysis (EDA) based on canonical molecular orbitals and the extended transition state (ETS) method combined with the natural orbitals for chemical valence (ETS–NOCV) theory were further applied to reveal the intrinsic bonding mechanism in terms of the major contributions to the orbital interactions. The computed EDA results for AmO\(_2^{2+}\) + nH\(_2\)O \(\rightarrow\) \([\text{AmO}_2(\text{H}_2\text{O})_n]^{2+}\) (Tables 6 and 7) show that electrostatic ion–molecule (\(\Delta E_{\text{elstat}}\)) accounts for almost 2/3 contribution to the total bonding energy (\(\Delta E_{\text{orb}}\)), playing more significant roles than those of orbital interaction (\(\Delta E_{\text{orb}}\)).

The decreasing trend of both electrostatic interactions and covalent orbital interactions are the same as those of bonding energies, which is, generally increasing with the hydration number from monoaqua toward penta-aqua. The change of \(\Delta E_{\text{elstat}}\) or \(\Delta E_{\text{orb}}\) is not significantly in tetra-aqua and penta-aqua, reflecting that the variation of both ionic and covalent interactions with the increasing number of the water molecules becomes smaller in aqueous solution. In contrast to the monotonous increase of \(\Delta E_{\text{elstat}}\) or \(\Delta E_{\text{orb}}\), the Pauli repulsion increases remarkably from 65.3 kcal/mol in monoaqua to 159.6 kcal/mol in tetra-aqua, then declines to 151.4 kcal/mol in penta-aqua, indicating the formation of the stable penta-aqua. The ETS–NOCV analyses additionally reveal the intrinsic bonding mechanism in terms of the contributions to the orbital interactions. The results of some representative contributions for \([\text{AmO}_2(\text{H}_2\text{O})_n]^{2+}\) are listed in Tables 6 and 7, and their deformation densities describing the density inflow are shown in Figures 3 and 4, respectively. The highest covalent character of each Am–O\(_w\) bond can be observed in monoaqua among these \([\text{AmO}_2(\text{H}_2\text{O})_n]^{2+}\) complexes in terms of the orbital interaction, which is decomposed into two types (\(\pi\)-type and \(\sigma\)-type) with several terms, taking orb1–orb3 as examples, providing energetic stabilizations of \(\Delta E_{\text{orb}}\) = −29.2 kcal/mol, \(\Delta E_{\text{orb}}\) = −14.4 kcal/mol, and \(\Delta E_{\text{orb}}\) = −6.4 kcal/mol, respectively. These natural orbitals denote the typical \(\pi\)–\(\sigma\)-type orbital interactions achieved via two fragments of americyl and water molecules, relating to the Am 5f\(_6\)d\(_6\)-hybridized atomic orbitals and \(\pi\)-MOS of water molecules contributed by O\(_w\) 2p atomic orbitals. Note that consistent with the reduced trend of bonding energy of each Am–O\(_w\) bond across the series, the trend of the donation character is also decreased accompanied by a decrease of major orbital contributions and a slight lengthening of Am–O\(_w\) bonds. The composition of the stabilization energy of each Am–O\(_w\) bond in \([\text{AmO}_2(\text{H}_2\text{O})_n]^{2+}\) complexes is small, but the sum of orbital interactions between the An 5f\(_6\)d hybrid orbitals.

### Table 6. ETS–NOCV Energy Decomposition Analyses between the Interacting Fragments of AmO\(_2^{2+}\) and H\(_2\)O Unit and Their Corresponding Energy \(\Delta E_i^{\text{orb}}\) (kcal/mol) from Open-Shell PBE/TZ2P Calculations

| frag. | 1(A) | 2(A) | 3(A) | 4(A) | 5(A) |
|-------|------|------|------|------|------|
| \(\Delta E_{\text{elstat}}\) | −68.5 | −125.7 | −177.8 | −218.3 | −241.9 |
| \(\Delta E_{\text{Pauli}}\) | 65.3 | 114.6 | 143.9 | 159.6 | 151.4 |
| \(\Delta E_{\text{elstat}}\) | −76.5 | −138.7 | −190.0 | −223.7 | −229.6 |
| \(\Delta E_{\text{orb}}\) | −57.4 | −101.6 | −131.7 | −154.2 | −163.7 |
| \(\alpha\) | −14.5 | −14.6 | −14.2 | −19.3 | −16.6 |
| \(\beta\) | −17.5 | −16.3 | −12.7 | −17.8 | −15.4 |
| \(\Delta E_\phi\) | −7.8 | −6.6 | −10.5 | −10.4 | −14.2 |
| \(\Delta E_\pi\) | −3.1 | −3.2 | −11.4 | −7.4 | −11.5 |
and π-MOs of Ow result in a significant covalent bonding character not only stabilizing [AmO2(H2O)]^{2+1+} complexes beyond electrostatic ionic interaction but also effectively supporting the weak bonding characteristics of 5f orbital, which is consistent with the ELF result shown in Figure 5 and with the NLMO analyses (listed in Table S5).

Considering that the Am–Ow dative bond and back donation were observed from density deformation analyses, NLMO calculations were further explored to describe the extent of this bonding interaction. The localized σ- and π-MOs on Am–Ow are made up of Am 5f6d and O 2s2p hybrid orbitals, which are composed by roughly 95% O 2s2p lone-pair AO and ∼5% Am df hybrid orbitals in [AmO2(H2O)]^{2+} and by ∼98% O 2s2p lone-pair AO and ∼2% Am df hybrid orbitals in [AmO2(H2O)]^{+1+} on the basis of the NLMO analyses. The enhanced stability of [AmO2(H2O)]^{2+1+} complexes across the series can only be explained as a result of the water coordinates inducing the increased electrostatic energy. Noticeably, the Am 6d participating in the dative oxygen bonding plays an important role over Am 5f due to both more

### Table 7. ETS–NOCV Energy Decomposition Analyses between the Interacting Fragments of AmO2^{2+} and H2O units and Their Corresponding Energy ΔE_{orb} (kcal/mol) from an Open-Shell PBE/TZ2P Calculation

| interacting fragments | 1^{(A)} | 2^{(A)} | 3^{(A)} | 4^{(A)} | 5^{(A)} |
|------------------------|---------|---------|---------|---------|---------|
| AmO2^{2+} (5A) | −39.3 | −98.9 | −121.7 | −129.7 | −129.7 |
| H2O (1A) & 8a2 | −69.7 | 92.7 | 101.2 | 100.4 | 100.4 |
| AmO2^{1+} (5A) | −48.1 | −124.9 | −147.9 | −149.9 | −149.9 |
| H2O (1A) & 24a2 | −50.6 | −66.7 | −77.0 | −80.2 | −80.2 |
| AmO2^{1+} (5A) | −29.8 | −6.9 | −9.9 | −8.7 | −8.7 |
| H2O (1A) & 32a2 | −6.7 | −6.7 | −7.7 | −6.9 | −6.9 |
| AmO2^{1+} (5A) | −2.2 | −6.7 | −6.1 | −5.7 | −7.2 |
| H2O (1A) & 40a2 | −5.2 | −6.7 | −6.5 | −6.5 | −6.5 |

**Figure 3.** Contours of representative deformation densities (isovalue = 0.001 au) between the interacting fragments of AmO2^{2+} and H2O unit from ETS–NOCV analysis, describing the density in flow (blue) and outflow (white).

**Figure 4.** Contours of representative deformation densities (isovalue = 0.001 au) between the interacting fragments of AmO2^{+} and H2O unit from ETS–NOCV analysis, describing the density in flow (blue) and outflow (white).
Am\textsuperscript{3+} ions raises several interesting features in the bonding of the Am\textsuperscript{3+} decomposition analysis, and natural orbitals, all agree in that Extensive chemical bonding analyses of the charges, energy Across the series; (3) the small back-bonding donations of Am chemistry. the mission in spent fuel reprocessing of the transplutonium, in represents only the beginning of long-term research relevant to Further quantum mechanics/molecular mechanics molecular approximations using the Gaussian 09 implementation of the potentials and basis sets with this functional (labeled as B3LYP/...ing solvent molecules with the bulk, which is important to some extent in practical application. Further quantum mechanics/molecular mechanics molecular dynamics simulation with explicit solvent molecules is necessary to study statistically the equilibrium between americium and water in different coordination shells. We hope that this investigation represents only the beginning of long-term research relevant to the mission in spent fuel reprocessing of the transplutonium, in addition to enriching our knowledge of actinide coordination chemistry.

**CONCLUSIONS**

Through relativistic quantum chemical calculations, the electronic and geometric structures of the \([\text{AmO}_2(\text{H}_2\text{O})_n]^{2+/1+}\) \((n = 1 - 6)\) complexes have been systematically studied. Full five-coordination binding of water ligands in the first shell is preferred in the aqua solution for \([\text{AmO}_2(\text{H}_2\text{O})_n]^ {2+/1+}\). Extensive chemical bonding analyses of the charges, energy decomposition analysis, and natural orbitals, all agree in that the Am–Ow interaction is predominantly ionic in nature, with a small extent of covalent bonding contribution resulted from the Am 5f\text{6d}-hybridized orbitals and relevant Ow 2p orbitals. The covalent orbital interaction between the equatorial Ow and Am ions raises several interesting features in the bonding of Am–Ow: (1) a bonding interaction between the Am AOs and the Ow 2p orbitals arranges the water ligand deviation from linear in \([\text{AmO}_2(\text{H}_2\text{O})_2]^ {2+/1+}\) into bent; (2) the reduced dative bonding affects the Am–Ow bond length and bond order across the series; (3) the small back-bonding donations of Am Sf → Ow 2p decrease the population of americium ions. As noted, the implicit solvation model is unable to provide the dynamics information of actinide ions in solution or the exchange of ion-influenced solvent molecules with the bulk, which is important to some extent in practical application. The calculations on the open-shell americyl complexes were carried out with unrestricted Kohn–Sham wave functions. As known, the molecular orbital (MO) diagram of pure americyl is similar to that of uranyl: the combinations of the 2p orbitals of the two oxygen with the 6d orbitals of the americium atom form occupied bonding orbitals, whereas the combinations of the O 2p orbitals with the 5f manifold orbitals of the actinide atom result in nonbonding \(\delta_g\) and \(\phi_u\) orbitals and antibonding \(\sigma_u^*\) and \(\pi_u^*\) orbitals; the corresponding bonding \(\sigma_u\) and \(\pi_u\) orbitals are found to have rather small Sf contributions. In \([\text{AmO}_2(\text{H}_2\text{O})_2]^ {2+/1+}\), the americium has the configurations Sf\text{5}\text{f\text{3}} and Sf\text{5}\text{f\text{4}}, respectively, and these electrons are spread in the nonbonding Sf\text{5}\text{d}\text{u} and Sf\text{5}\text{d}\text{u} orbitals. Following Hund’s rule, the ground electronic states of hexavalent and pentavalent Am ions have been found to be of a high-spin character, that is, \(\Delta f^3\phi^1\text{g}\) and \(\Delta f^4\phi^2\text{g}\) configurations and \(\Delta\) and \(\Sigma\) electronic states for \([\text{AmO}_2(\text{H}_2\text{O})_2]^ {2+/1+}\), respectively. The spin–orbit coupling (SOC) effects should be considered during the calculations of the electronic structures of americyl complexes in solution.\textsuperscript{37}

The scalar relativistic DFT calculations were performed with the Gaussian 09 and ADF 2017 softwares\textsuperscript{38–40} for the geometry optimizations and vibrational frequency analyses. First, for geometry optimizations by the Gaussian code, we used the scalar relativistic Stuttgart energy-consistent relativistic 32 valence electron pseudopotential and the associated ECP60MWB SEG valence basis set\textsuperscript{41,42} for the americium atom. The split-valence triple-\(\zeta\) basis sets with polarization functions (cc-pVTZ)\textsuperscript{43,44} were used for the oxygen and hydrogen atoms. The B3LYP hybrid density functional\textsuperscript{45,46} was used in these calculations. The solvent effects were approximated using the Gaussian 09 implementation of the conductor-like screening solvation model (COSMO) solvent model\textsuperscript{47,48} where the solute is embedded in a shape-adapted cavity consisting of interlocking spheres centered on each solute atom or group. The combination of these pseudopotentials and basis sets with this functional (labeled as B3LYP/Am/ECP60MWB SEG/O, H/cc-pVTZ level) has been shown to give accurate predictions of the properties and reaction energies of actinide complexes.\textsuperscript{19,20} At the same B3LYP theory level, vibrational frequency calculations were further performed to ensure that all force constants should be positive and all frequencies should be real. Ultrafine integration grids and very tight optimization were applied. The spin–orbital symmetry restrictions were relaxed, performing spin-unrestricted UDFT calculations. The coupled cluster with singles, doubles, and perturbative triples (CCSD(T)) method\textsuperscript{49–51} in MOLPRO 2012 program\textsuperscript{52} was used for single-point calculations on the optimized aqueous-phase B3LYP geometries to check whether the
systems have multireference character and to acquire more accurate relative energies. The ECP60MBW pseudopotential with ECP60MBW SEG basis set for Am and the cc-pVTZ basis for O and H were applied in the CCSD(T) calculations. However, limited by the computer resources, the nonsymmetry molecules of $[\text{AmO}_2(\text{H}_2\text{O})_6]^{2+}$ or $[\text{AmO}_2(\text{H}_2\text{O})_4]^{2+}$ cannot be handled by CCSD(T) due to the giant basis of those molecules.

Further electronic structure and chemical bonding analyses at the DF level were performed with the ADF 2017. The scalar relativistic (SR) effects were taken into account by the zero-order regular approximation (ZORA). The SOC effects were taken into account by SO-ZORA. The frozen-core Nalewajski analyses based on the Mulliken method, Hirshfeld analysis, Am and the $[1s^2]$ shells of the O atoms. The B3LYP combined with slater basis sets of triple-$\zeta$ valence (NOCV) theory were applied. Single-point calculations were carried out on the B3LYP/Am/ECP60MBW_SEG//O,H/cc-pVTZ optimized aqueous-phase structures to determine the charge distribution and bond order. The bond order analyses based on the Mayer method, Gopinathan charge distribution and bond order. The bond order analyses were performed at the B3LYP/6-31G* level on optimized geometries from B3LYP calculations by using the NBO 5.0 program.

In further geometry optimizations, the generalized gradient approximation with the PBE exchange–correlation functional was used in ADF 2017. Scalar (SR) and SO relativistic effects were accounted by applying the same stratagem as detailed in the above paragraph. The effects of water considered by COSMO were determined using single-point energy calculation on gas-phase structures. The atomic COSMO-default radii 210.0 pm was used.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01324.

Selected optimized geometrical structures (bond length Å and bond angle °) for the $\delta^f_1\delta^f_2$ [AmO$_2$(H$_2$O)$_6$]$^{2+}$ ($n=0$–6) at SR-B3LYP/Am/ECP60MBW_SEG//O,H/cc-pVTZ levels of theory with or without COSMO (in parentheses) (Table S1); selected optimized geometrical structures (bond length Å and bond angle °) for the reaction of $\delta^f_1\delta^f_2$ [AmO$_2$(H$_2$O)$_4$]$^{2+}$ ($n=0$–6) at SR-B3LYP/Am/ECP60MBW_SEG//O,H/cc-pVTZ levels of theory with or without COSMO (in parentheses) (Table S2); binding energy (kcal/mol) for the reaction of AmO$_2^{2+} +$ nH$_2$O $\rightarrow [\text{AmO}_2(\text{H}_2\text{O})_n]^{2+}$ ($n=0$–6) at different levels of theory (Table S3); binding energy (kcal/mol) for the reaction of AmO$_2^{1+} +$ nH$_2$O $\rightarrow [\text{AmO}_2(\text{H}_2\text{O})_n]^{1+}$ ($n=0$–6) at different levels of theory (Table S4); natural localized molecular orbital (NLMO) analyses of [AmO$_2$(H$_2$O)$_{2f}$]$^{2+}$ ($n=1$–6) from open-shell B3LYP/cc-pVTZ/ECP60MBW_SEG calculations (Table S5); average Mayer, Gopinathan–Jug and Nalewajski–Mrozek bond orders for Am−O$_n^+$ and Am−O$_n^-$ on the B3LYP-optimized geometry of AmO$_2$(H$_2$O)$_{2f}$ ($n=0$–6) at the SR–PBE/TZP level with COSMO (Table S6); average Mulliken and MDC charges and spin density on the B3LYP-optimized geometry of AmO$_2$(H$_2$O)$_{2f}$ ($n=0$–6) in solution from the PBE/TZP calculations (Table S7); calculated vibrational frequencies (cm$^{-1}$) of [AmO$_2$(H$_2$O)$_{2f}$]$^{2+}$ ($n=0$–6) in aqueous solution considered by COSMO at SR-B3LYP/Am/ECP60MBW_SEG//O,H/cc-pVTZ 1 level of theory (Table S8); ETS–NOCV energy decomposition analyses between the interacting fragments of AmO$_2^{2+}$ and ligand units and their corresponding energy $\Delta E^{\text{orb}}$ (kcal/mol) on the B3LYP-optimized geometry of AmO$_2$(H$_2$O)$_{2f}$ ($n=1$–5) in solution from an open-shell PBE/TZP2 calculation (Table S9); ETS–NOCV energy decomposition analyses between the interacting fragments of AmO$_2^{2+}$ and ligand units and their corresponding energy $\Delta E^{\text{orb}}$ (kcal/mol) on the B3LYP-optimized geometry of AmO$_2$(H$_2$O)$_{6}$ ($n=0$–5) in solution from an open-shell PBE/TZP2 calculation (Table S10); two isomers (in-plane and perpendicular-to-plane) of water molecules for [AmO$_2$(H$_2$O)$_{2f}$]$^{2+}$ and [AmO$_2$(H$_2$O)$_{2f}$]$^{2+}$ at SR-B3LYP/Am/ECP60MBW_SEG//O,H/cc-pVTZ levels of theory (Figure S1); optimized geometry of $D_{5h}$ C$_5$ symmetry structures of [AmO$_2$(H$_2$O)$_{2f}$]$^{2+}$ and [AmO$_2$(H$_2$O)$_{2f}$]$^{2+}$ at SR-B3LYP/Am/ECP60MBW_SEG//O,H/cc-pVTZ levels of theory (Figure S2) (PDF)

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**Notes**

The authors declare no competing financial interest.

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