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Crown Ether Complexes of Uranyl, Neptunyl, and Plutonyl: Hydration Differentiates Inclusion versus Outer Coordination

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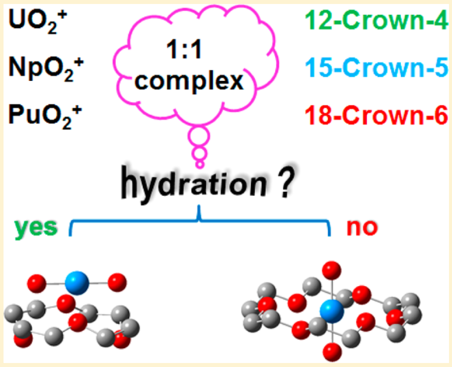
Ⓢ *Supporting Information*



ABSTRACT: The structures of actinyl−crown ether complexes are key to their extraction behavior in actinide partitioning. Only $UO_2(18C6)^{2+}$ and $NpO_2(18C6)^+$ (18C6 = 18-Crown-6) have been structurally characterized. We report a series of complexes of uranyl, neptunyl, and plutonyl with 18-Crown-6, 15-Crown-5 (15C5), and 12-Crown-4 (12C4) produced in the gas phase by electrospray ionization (ESI) of methanol solutions of $AnO_2(ClO_4)_2$ (An = U, Np, or Pu) and crown ethers. The structures of 1:1 actinyl−crown ether complexes were deduced on the basis of their propensities to hydrate. Hydration of a coordinated metal ion requires that it be adequately exposed to allow further coordination by a water molecule; the result is that hydrates form for outer-coordination isomers but not for inclusion isomers. It is demonstrated that all the actinyl 18C6 complexes exhibit fully coordinated inclusion structures, while partially coordinated outer-coordination structures are formed with 12C4. Both inclusion and outer-coordination isomers were observed for actinyl−15C5 complexes, depending on whether they resulted from ESI or from collision-induced dissociation. Evidence for the formation of 1:2 complexes of actinyls with 15C5 and 12C4, which evidently exhibit bis-outer-coordination structures, is presented.

■ INTRODUCTION

Crown ethers are known to form complexes with specific metal cations because of the match between cavity size and metal radii.[1,2] Such molecular recognition renders crown ethers as potentially selective and efficient extractants, which have applications in actinide partitioning[3,4] as a potential alternative to typically used anion exchange chromatography methods.[5−7] Although there have been a number of condensed-phase studies of the extraction behavior of crown ethers, there is limited information about the structures of actinyl−crown ether complexes,[8] which is essential for understanding complexation interactions. Most reported crystal structures are for uranium(VI)−crown ether complexes, which were found to have two types of isomers depending on the experimental conditions. Crystallization from aqueous solutions results in the formation of a fully hydrated UO_2 core with second-shell crown ethers interacting with inner-shell H_2O molecules via hydrogen bonding.[9−12] Anhydrous conditions are required for the formation of inclusion complexes in which uranium(VI) is encapsulated by the crown ether.[13,14] For transuranium elements, only one crown ether complex has been structurally characterized: NpO_2^+ was encapsulated in 18C6 (18C6 = 18-Crown-6) by reaction of NpO_2^{2+}/NpO_2^+ with 18C6 in aqueous solution.[15] The preference for the apparent formation of reduced $NpO_2(18C6)^+$ rather than $NpO_2(18C6)^{2+}$ under aqueous conditions was attributed to solvation effects in polar solvents, as well as the effective screening of charge provided by the crown ether, according to relativistic density functional theory (DFT) studies of the $AnO_2(18C6)^{+/2+}$ (An = U, Np, or Pu) systems.[16] To the best of our knowledge, $UO_2(18C6)^{2+}$ and $NpO_2(18C6)^+$ are the only actinyl−crown ether inclusion complexes that have been experimentally characterized. In this work, several $AnO_2(18C6)^{+/2+}$, $AnO_2(15C5)^+$ (15C5 = 15-Crown-5), and $AnO_2(12C4)^+$ (12C4 = 12-Crown-4) complexes were produced in the gas phase by electrospray ionization (ESI) of solutions containing the actinyls and crown ethers.

Crown ethers can form inclusion or outer-coordination complexes with metal ions, in which the metal center is either encapsulated by the crown ether or partly exposed.[1,17] Although mass spectrometry alone usually cannot distinguish isomers, in combination with gas-phase manipulations structural information can often be derived. Vachet and co-workers, for example, have employed reactions of coordination metal complexes with gases in an ion trap to deduce structural information.[18−22] It has been shown that ligated UO_2^+, NpO_2^+, and PuO_2^+ cations with unsaturated coordination spheres form hydrates with residual background H_2O in a quadrupole ion trap.[23−27] For actinyl inclusion complexes with crown ethers, the equatorial coordination around the actinide metal center is coordinatively saturated such that hydration of the metal center is not feasible. In contrast, outer-coordination actinyl−crown ether complexes can hydrate because coordination of the

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actinide metal center is incomplete (Figure 1). It is demonstrated here that inclusion versus outer-coordination structures of gas-phase actinyl−crown ether complexes can be differentiated on the basis of their hydration properties. Evidence for the formation of gas-phase $AnO_2(15C5)_2^+$ and $AnO_2(12C4)_2^{+/2+}$ bis-outer-coordination complexes is also presented.

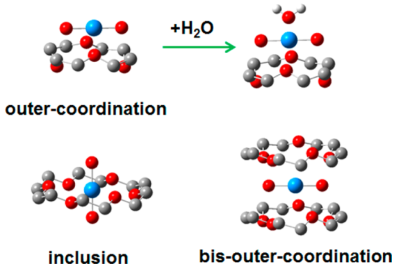


Figure 1. Proposed schematic structures of actinyl−crown ether complexes. Hydration of the outer-coordination actinyl−crown ether complex is shown. The crown ether hydrogens are not shown.

■ EXPERIMENTAL METHODS

The experiments were performed using an Agilent 6340 quadrupole ion trap mass spectrometer (QIT/MS) with the ESI source located inside a radiological containment glovebox.[28] The actinyl−crown ether complexes were produced by ESI of 1:4 $AnO_2(ClO_4)_2$ (200 μM, An = U, Np, or Pu)/crown ether mixtures in methanol with <1% H_2O. 18-Crown-6, 15-Crown-5, and 12-Crown-4 were obtained from Sigma-Aldrich. The Np(VI) and Pu(VI) solutions used for ESI were prepared by oxidation using hot concentrated perchloric acid, with the oxidation state purities established by UV spectroscopy.[29] ^{242}Pu, ^{237}Np, and ^{238}U isotopes were employed and undergo α-decay with half-lives of 3.7×10^5, 2.1×10^6, and 4.5×10^9 years, respectively. The actinyl−crown ether complexes were mass selected after ESI and then reacted with H_2O in the ion trap for 1 s. As discussed previously,[30] the background H_2O and O_2 pressures in the ion trap are estimated to be on the order of 10^{-6} Torr. The helium buffer gas pressure in the trap is constant at $\sim 10^{-4}$ Torr. The MS^n capabilities of the QIT/MS, which designates the ability to perform multiple (n) sequential mass spectrometry stages, allow isolation of ions with a particular mass-to-charge ratio (m/z), followed by collision-induced dissociation (CID), in which ions are excited and undergo energetic collisions with helium. Ions isolated in the trap for thermal (non-CID) reactions are at a temperature of ~300 K.[31] In high-resolution mode, the instrument has a detection range of m/z 20−2200 with a mass width (fwhm) of $m/z \approx 0.3$. Mass spectra were acquired in the positive ion accumulation and detection mode. The intensity distributions of ions in the mass spectra were highly dependent on instrumental parameters, particularly the RF voltage (trap drive) applied to the ion trap; the parameters used for trapping singly and doubly charged cations are similar to those employed in previous experiments.[27,32] Generally, a higher trap drive favors trapping cations with higher m/z values, while efficient trapping of cations with lower m/z values requires a lower trap drive. It has been demonstrated that trapping conditions induced by a lower-voltage trap drive favor retention in the ion trap of doubly charged actinyl cations.[25,26] The high-purity nitrogen gas for nebulization and drying in the ion transfer capillary was the boil-off from a liquid nitrogen Dewar. Several intense peaks attributed to sodium and potassium complexes were evident in the ESI mass spectra; the origins of these contaminants are indeterminate, but they have previously been found to be ubiquitous under similar experimental conditions.[26]

■ RESULTS AND DISCUSSION

The speciation observed upon ESI of the three actinyl/crown ether mixtures is briefly described, followed by the results and discussion of the primary findings, the differentiation of isomeric structures by their hydration behaviors. The ESI mass spectra for the $AnO_2(ClO_4)_2$/crown ether mixtures are provided as Supporting Information; the species discussed below are identified in these spectra. The identified crown ether complexes match the expected m/z ratios and are further established by the ^{13}C isotopomer intensities, and the loss of $(C_2H_4O)_x$ units upon CID, as discussed below. The identified actinyl−crown ether complexes are summarized in Table 1.

Table 1. Actinyl−Crown Ether Complexes Observed in ESI Mass Spectra

crown ether		observed complexes[a]	
18C6	$UO_2(C)^+$, $UO_2(C)^{2+}$	$NpO_2(C)^+$	$PuO_2(C)^+$
15C5	$UO_2(C)_2^{2+}$	$NpO_2(C)^+$, $NpO_2(C)_2^+$	$PuO_2(C)^+$, $PuO_2(C)_2^+$
12C4	$UO_2(C)^+$, $UO_2(C)_2^{2+}$	$NpO_2(C)^+$, $NpO_2(C)_2^+$, $NpO_2(C)_2^{2+}$	$PuO_2(C)^+$, $PuO_2(C)_2^+$, $PuO_2(C)_2^{2+}$

[a] C in parentheses denotes the crown ether shown in the first column. All 18C6 complexes exhibit inclusion structures. $AnO_2(12C4)^+$, $AnO_2(12C4)_2^{+/2+}$, and $AnO_2(15C5)_2^{+/2+}$ complexes exhibit outer-coordination and bis-outer-coordination structures. $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ complexes exhibit inclusion structures when produced by ESI and outer-coordination structures when produced by CID.

18-Crown-6. The $UO_2(18C6)^+$, $NpO_2(18C6)^+$, and $PuO_2(18C6)^+$ complexes were observed at m/z 534.1, 533.1, and 538.1, respectively, along with intense peaks due to bare UO_2^+, NpO_2^+, and PuO_2^+. Complexes such as $Na(18C6)^+$ and $KH(18C6)ClO_4^+$ were present in all spectra; such alkali crown ether complexes have been studied in the gas phase.[33−36] In addition to the pentavalent actinide species, the complex of 18C6 and UO_2^{2+} was observed when a lower trap drive was used (Figure S2 of the Supporting Information). The $UO_2(18C6)^{2+}$ complex at m/z 266.9 exhibited a second peak at 267.4 due to the presence of 12 carbon atoms, which results in an isotopomer peak with one ^{13}C at 13% intensity relative to the fully ^{12}C isotopomer; the m/z splitting of 0.5 is consistent with the $z = +2$ assignment. Protonated 18C6, $H(18C6)^+$, was observed at m/z 265; the m/z 283 peak is likely due to the hydronium−crown ether complex, $H_3O(18C6)^+$, which was recently characterized in the gas phase.[37] No detectable $NpO_2(18C6)^{2+}$ or $PuO_2(18C6)^{2+}$ complex appeared in ESI mass spectra obtained under conditions similar to those used for $UO_2(18C6)^{2+}$. It has been reported that addition of 18C6 to solutions containing NpO_2^{2+} resulted in the formation of reduced $NpO_2(18C6)^+$.[15]

15-Crown-5. The ESI mass spectra of $NpO_2(ClO_4)_2$/$PuO_2(ClO_4)_2$ and 15C5 mixtures revealed the predominance of NpO_2^+, PuO_2^+, and $Na(15C5)^+$. The $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ complexes were observed at m/z 489.1 and 494.1, respectively. In addition to these 1:1 complexes, $NpO_2(15C5)_2^+$ and $PuO_2(15C5)_2^+$ were also present at low intensities. In contrast to the neptunyl and plutonyl ESI spectra, that of $UO_2(ClO_4)_2$ and 15C5 exhibits more product diversity, in part due to the formation of $UO_2(OH)^+$ and $UO_2(CH_3O)^+$ and their hydrates.[24] Although no $UO_2(15C5)^+$ was identified upon ESI of $UO_2(ClO_4)_2$ and 15C5, a peak at m/z 489.1 was observed, which is assigned to $UO_2(15C5\text{-}H)^+$. The weak peak at m/z 490.1, where $UO_2(15C5)^+$ would appear, most likely instead arises primarily from a single ^{13}C substitution in $UO_2(15C5\text{-}H)^+$; the calculated isotopomer relative intensities match the observed values. In an attempt to stabilize dipositive actinyl−15C5 complexes in the gas phase, the trap drive was lowered as in the case of 18C6. However, cations such as $H(15C5)^+$ and $Na(15C5)^+$ dominated all of the resulting spectra. No $UO_2(15C5)^{2+}$, $NpO_2(15C5)^{2+}$, or $PuO_2(15C5)^{2+}$ complexes were identified; $UO_2(15C5)_2{}^{2+}$ was the only observed dipositive 15C5−actinyl complex.

12-Crown-4. Formation of both the 1:1 and 1:2 complexes, $NpO_2(12C4)_n{}^+$ and $PuO_2(12C4)_n{}^+$ ($n = 1$ or 2), was observed upon ESI of $NpO_2(ClO_4)_2/PuO_2(ClO_4)_2$ and 12C4, which is similar to the results for 15C5. In addition, the appearance of an m/z 446 peak indicated the formation of $UO_2(12C4)^+$. Although $UO_2(12C4\text{-}H)^+$ (m/z 445) is also present in the spectra, the intensity of the m/z 446 peak is higher than that expected for the ^{13}C isotopomer of $UO_2(12C4\text{-}H)^+$, which indicates a contribution from $UO_2(12C4)^+$. Experiments with lower trap drive revealed the presence of not only $UO_2(12C4)_2{}^{2+}$ but also $NpO_2(12C4)_2{}^{2+}$ and $PuO_2(12C4)_2{}^{2+}$, presumably bis-outer-coordination complexes absent for 15C5. The yields for the 1:2 complexes of neptunyl and plutonyl were quite low. As observed in the other experiments, bare $AnO_2{}^+$ and $H(12C4)^+$, $Na(12C4)^+$, and $Na(12C4)_2{}^+$ were always present, with intensities dependent on the trap drive.

Structures of Gas-Phase Actinyl−Crown Ether Complexes. The presence of the two capping oxo ligands in actinyls allows differentiation between inclusion and outer-coordination isomers for 1:1 actinyl−crown ether complexes based on their hydration properties. Hydration under the experimental conditions employed in this work occurs via inner-shell coordination of a water molecule directly to the metal center,[24,30] such that the actinyl metal center must be partially uncoordinated and exposed for hydration to occur. Referring to the schematic structures in Figure 1, we predict that hydration should thus occur for outer-coordination $AnO_2(\text{Crown})^{+/2+}$ complexes, but not for inclusion $AnO_2(\text{Crown})^{+/2+}$ complexes. The structures shown in Figure 1 are only approximate representations, not computed structures, and the coordination denticity is not known; such structural details do not affect the interpretations of the experimental observations.

The 1:1 actinyl−crown complexes were mass selected and reacted under thermal conditions with residual water (~10^{-6} Torr) in the ion trap for 1 s. The observed hydration reactions are given in eqs 1−3. In the case of 18C6, none of the four complexes reacted with H_2O to form hydrates during the 1 s reaction time, indicating that all of them exhibit inclusion structures. This is consistent with the reported crystal structures of $NpO_2(18C6)^+$ and $UO_2(18C6)^{2+}$, where the actinide centers are completely encapsulated by 18C6.[13−15] The existence of pentavalent $UO_2(18C6)^+$ and $PuO_2(18C6)^+$ complexes is demonstrated for the first time, and inclusion structures similar to those of $UO_2(18C6)^{2+}$ and $NpO_2(18C6)^+$ were deduced on the basis of the absence of hydration.

$$AnO_2(18C6)^+ + H_2O \rightarrow \text{no reaction } (An = U, Np, Pu) \qquad (1a)$$

$$UO_2(18C6)^{2+} + H_2O \rightarrow \text{no reaction} \qquad (1b)$$

$$AnO_2(15C5)^+ + H_2O \rightarrow \text{no reaction } (An = Np, Pu) \qquad (2a)$$

$AnO_2(15C5)^+$ from ESI

$$AnO_2(15C5)^+ + H_2O \rightarrow AnO_2(15C5)(H_2O)^+ \ (An = Np, Pu) \qquad (2b)$$

$AnO_2(15C5)^+$ from CID

$$AnO_2(12C4)^+ + H_2O \rightarrow AnO_2(12C4)(H_2O)^+ \ (An = U, Np, Pu) \qquad (3)$$

$AnO_2(12C4)^+$ from ESI or CID

15C5 has a cavity size of 1.7−2.2 Å,[38,39] which is ~1 Å smaller than that of 18C6 (2.6−3.2 Å). Neither $NpO_2(15C5)^+$ nor $PuO_2(15C5)^+$ produced by ESI exhibited hydration (Figure 2 and eq 2a), indicating that the inclusion structure is maintained in both cases, similar to their 18C6 analogues [$UO_2(15C5)^+$ not observed]. After actinyl complexes of 12C4 with its smaller cavity size had been produced, a significant change in coordination was indicated by hydration behavior. In contrast to inert $AnO_2(18C6)^+$ and $AnO_2(15C5)^+$, $AnO_2(12C4)^+$ readily hydrated (Figure 3 and eq 3). Approximately 90% of $NpO_2(12C4)^+$ and $PuO_2(12C4)^+$ underwent hydration to form $NpO_2(12C4)(H_2O)^+$ and $PuO_2(12C4)(H_2O)^+$ after a 1 s reaction in the ion trap.

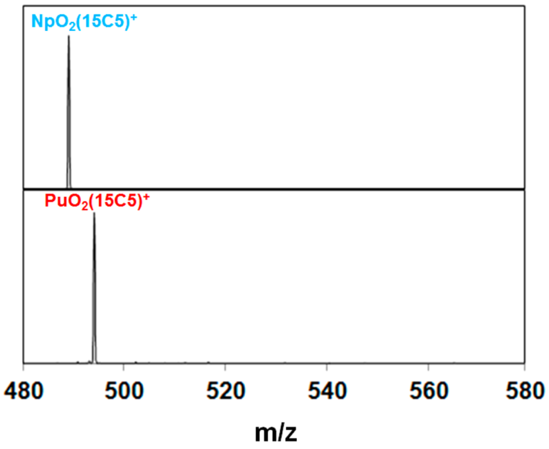


Figure 2. Mass spectra of $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ produced by ESI, after reaction with H_2O for 1 s in the ion trap. There is no indication of hydration.

For $UO_2(12C4)^+$, the formation of $UO_2(12C4)(H_2O)^+$ is accompanied by the formation of $UO_2(12C4)(O_2)^+$, which efficiently hydrates to give $UO_2(12C4)(O_2)(H_2O)^+$ (Figure 3). Oxidation of U(V) to U(VI) by reaction with O_2 to produce superoxide complexes has previously been observed under these experimental conditions.[24,27,40] The formation of $UO_2(12C4)(O_2)^+$ supports the assignment of a major component of the m/z 446 peak as $UO_2(12C4)^+$, rather than the ^{13}C isotopomer of $UO_2(12C4\text{-}H)^+$: the oxidation state would be U(VI) in the latter such that O_2 addition would not be observed. Facile hydration indicates an outer-coordination structure for all three $AnO_2(12C4)^+$ complexes. The switch from inclusion for 15C5 to outer coordination for 12C4 is consistent with the smaller cavity size of 12C4 (1.2−1.5 Å),[39] which is not large enough to accommodate the actinyl cations. Addition of a second H_2O molecule to $AnO_2(12C4)(H_2O)^+$ was also observed during the 1 s reaction period, although the intensities of the $AnO_2(12C4)(H_2O)_2{}^+$ peaks were only ~ 3% of those of $AnO_2(12C4)(H_2O)^+$ (Figure 3). Our previous experiments have shown that multiple hydrates of $UO_2(OH)^+$

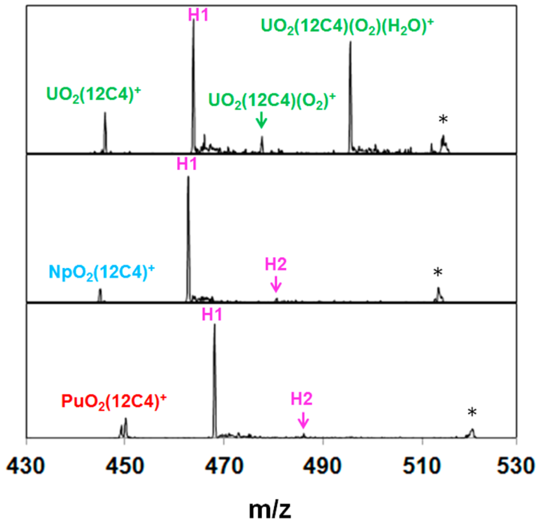


Figure 3. Mass spectra of $AnO_2(12C4)^+$ (An = U, Np, or Pu) after reaction with H_2O for 1 s in the ion trap. H1 and H2 denote the $AnO_2(12C4)(H_2O)^+$ and $AnO_2(12C4)(H_2O)_2{}^+$ hydrate complexes, respectively. The asterisks denote abnormal peaks most likely arising from fragmentation of fragile ions during resonant ejection from the ion trap.[43]

dominated after a reaction time of ~1 s.[24] The slow kinetics for the formation of $AnO_2(12C4)(H_2O)_2{}^+$ is likely due to steric congestion from the polydentate 12C4 ligand in the outer-coordination complex.

All of the 1:2 complexes are expected to exhibit bis-outer-coordination structures; if the actinyl were encapsulated by one of the two crown ethers, there would be no metal coordination site available for coordination by the second crown ether. In the case of 12C4, the inclusion structure is not even exhibited for the 1:1 complexes such that the 1:2 complexes undoubtedly exhibit bis-outer-coordination structures. No hydration was observed for any of the 1:2 actinyl−crown ether complexes produced by ESI (eqs 4−6), suggesting that it is not feasible for H_2O molecules to approach the actinide metal centers, which are coordinated by the two crown ether ligands (Figure 1). Bis-outer-coordination structures have been identified for alkali metal crown ether complexes in the gas phase.[41]

$$UO_2(15C5)_2{}^{2+} + H_2O \rightarrow \text{no reaction} \tag{4}$$

$$AnO_2(C)_2{}^+ + H_2O \rightarrow \text{no reaction}$$
$$(An = Np, Pu; C = 15C5, 12C4) \tag{5}$$

$$AnO_2(12C4)_2{}^{2+} + H_2O \rightarrow \text{no reaction}$$
$$(An = U, Np, Pu) \tag{6}$$

Fragmentation of Actinyl−Crown Ether Complexes. Although the structure of gas-phase 1:1 actinyl−crown ether complexes produced by ESI depends on the cavity size of the crown ether, as revealed by hydration behavior, no definitive structural information could be readily inferred from their gas-phase CID fragmentation patterns. CID of all the 1:1 complexes resulted in a series of fragments, mainly via loss of $(C_2H_4O)_x$, some of which subsequently underwent hydration. Such complex fragmentation patterns due to the contraction of the crown ether ring by the loss of C_2H_4O units have been observed upon CID of magnesium crown ether complexes.[42] Generally, it is more efficient to fragment 12C4 and 15C5 complexes than 18C6 complexes under the same conditions, which is probably related to the higher stability of the actinyl−18C6 complexes arising from the good match between the metal ion and the cavity size. Bare $UO_2{}^+$, $NpO_2{}^+$, and $PuO_2{}^+$ cations always appeared during CID regardless of the structures of the parent complexes.

The fragmentation pathways for singly charged 1:2 complexes are consistent with their proposed bis-outer-coordination structures. CID of $NpO_2(15C5)_2{}^+$, $NpO_2(12C4)_2{}^+$, $PuO_2(15C5)_2{}^+$, and $PuO_2(12C4)_2{}^+$ resulted primarily in the loss of one neutral crown ether (Figure 4). The resulting 1:1 complexes underwent hydration with residual H_2O in the ion trap (eqs 2b and 3). The reaction time for hydration of the $AnO_2(15C5)^+$ complexes produced by CID (Figure 4b,d) was only ~0.07 s because of the low intensities of the CID products; a degree of hydration comparable to that observed for the $AnO_2(12C4)^+$ complexes produced by ESI would be anticipated for the much longer reaction time of 1 s employed there (Figure 3). As discussed above, no hydration was observed when $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ were mass selected from the ESI mass spectra and reacted with background water for 1 s (Figure 2), which distinctly contrasts with the hydration behavior observed for $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ produced by CID (eqs 2a and 2b specify this discrepancy). These observations provide convincing evidence of different structural isomers produced by CID and ESI. As discussed above, both $NpO_2(15C5)_2{}^+$ and $PuO_2(15C5)_2{}^+$ complexes evidently exhibit bis-outer-coordination structures. The hydration of the $AnO_2(15C5)^+$ products from CID-induced elimination of one of the two 15C5 ligands indicates that an outer-coordination structure is maintained, which subsequently hydrates because of the unsaturated coordination sphere (Scheme 1); this is in contrast to the inert behavior of $AnO_2(15C5)^+$ produced by ESI. It is feasible that the

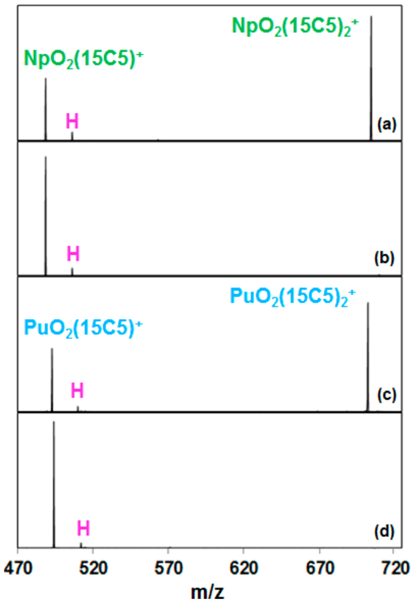
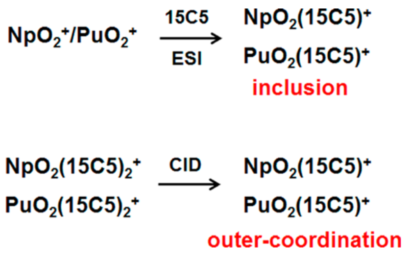


Figure 4. CID spectra of $NpO_2(15C5)_2{}^+$ (a) and $PuO_2(15C5)_2{}^+$ (c) and mass spectra of $NpO_2(15C5)^+$ (b) and $PuO_2(15C5)^+$ (d) isolated from CID spectra a and c, respectively, and reacted with background water in the ion trap for ~0.07 s. H designates hydrates $NpO_2(15C5)(H_2O)^+$ and $PuO_2(15C5)(H_2O)^+$.

Scheme 1



$AnO_2(15C5)^+$ complexes from CID also comprise some inclusion isomers, but the evidence of a second isomer based on its hydration is clear. The observation of inclusion isomers for $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ upon ESI and outer-coordination isomers upon CID indicates that the actinyl moiety does not readily insert into the crown ether upon CID, and that the insertion process is enabled in solution prior to ESI. It may be that there is only a small energy difference between the two isomers, inclusion and outer coordination, for $AnO_2(15C5)^+$.

As the cavity size increases from 12C4 to 18C6, the energy barrier for the conversion between the inclusion and outer-coordination isomers is expected to decrease, while the inclusion complex is expected to become increasingly energetically favorable. Hence, no 1:2 complex was observed for 18C6, and only the outer-coordination isomer was observed for 12C4 complexes. Consistent with this notion, the hydration behaviors of $NpO_2(12C4)^+$ and $PuO_2(12C4)^+$ produced by CID were similar to those of $NpO_2(12C4)^+$ and $PuO_2(12C4)^+$ isolated after ESI. Furthermore, only 1:1 inclusion complexes were observed for 18C6. The structures derived from hydration properties indicate that the crown ether with the cavity size that best accommodates inserted actinyls is 18C6, for which no 1:2 complexes were observed. Note that even 18C6 can form bis-outer-coordination complexes when the size of the metal cation is sufficiently large, such as for Rb^+ and Cs^+.[33,41]

For doubly charged 1:2 complexes, $UO_2(12C4)_2^{2+}$, $NpO_2(12C4)_2^{2+}$, and $PuO_2(12C4)_2^{2+}$, the CID results revealed the formation of both charge reduction and conservation products. Charge reduction mainly occurs via the loss of $H(12C4)^+$, resulting in the formation of $AnO_2(12C4\text{-}H)^+$; both of these cations are observed in the mass spectra. Fragmentation and contraction of the 12C4 moiety are responsible for the appearance of charge conservation products.

CONCLUSIONS

A series of 12-Crown-4, 15-Crown-5, and 18-Crown-6 complexes of uranyl, neptunyl, and plutonyl were observed in the gas phase (Table 1), most of which are reported here for the first time. These complexes were produced by ESI of mixtures of $AnO_2(ClO_4)_2$ and crown ethers in methanol. The 1:1 actinyl−crown ether complexes can exhibit either inclusion or outer-coordination structures, where the metal center is either encapsulated by the crown ether and axial oxo ligands or partly exposed in a side-on coordination mode with the crown ether. Because the actinide coordination sphere in outer-coordination complexes is not saturated, it can hydrate, while hydration cannot occur for inclusion complexes in which the metal center is fully coordinated. It is thus possible to distinguish which isomers are formed for the 1:1 complexes based on hydration behavior. Association reactions between H_2O and actinyl−crown ether complexes produced from ESI revealed inert character and thus the inclusion structure for all of the 1:1 actinyl−18C6 and −15C5 complexes. In contrast, 12C4 preferentially formed outer-coordination structures with the actinyls, as revealed by facile hydration. CID was performed to investigate the fragmentation patterns of the crown ether complexes. No clear structure-specific information was obtained for the 1:1 complexes, with complicated CID fragmentation pathways. However, hydration was observed for both $NpO_2(15C5)^+$ and $PuO_2(15C5)^+$ produced by CID of $NpO_2(15C5)_2^+$ and $PuO_2(15C5)_2^+$, respectively, indicating outer-coordination structures for the 1:1 actinyl−15C5 complexes produced by CID, in contrast to the inclusion structures produced via ESI. The experimental results for the 1:1 complexes demonstrate that the cavity size of 18C6 provides the best fit for actinyls, whereas 12C4 is too small to encapsulate actinyls. 15C5 lies between 12C4 and 18C6 in accommodating actinyl inclusion, as reflected by the formation of both inclusion and outer-coordination isomers depending on the preparative conditions.

In addition to the 1:1 complexes, uranyl, neptunyl, and plutonyl formed some 1:2 complexes with 15C5 and 12C4, which evidently exhibit bis-outer-coordination structures. As expected for such highly coordinated actinide centers, none of the 1:2 complexes exhibited reactivity toward H_2O to form hydrates. CID of singly charged 1:2 complexes mainly resulted in the loss of a single crown ether. More complicated fragmentation patterns were observed for doubly charged 1:2 complexes, which resulted in both charge reduction and charge conservation products.

ASSOCIATED CONTENT

Ⓢ Supporting Information

ESI mass spectra of mixtures of $AnO_2(ClO_4)_2$ (An = U, Np, or Pu) and 18C6, 15C5, and 12C4 in methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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