Ion association with tetra-\textit{n}-alkylammonium cations stabilizes higher-oxidation-state neptunium dioxocations

Shanna L. Estes\textsuperscript{1,2}, Baofu Qiao\textsuperscript{1,3} & Geng Bang Jin\textsuperscript{1,4}

Extended-coordination sphere interactions between dissolved metals and other ions, including electrolyte cations, are not known to perturb the electrochemical behavior of metal cations in water. Herein, we report the stabilization of higher-oxidation-state Np dioxocations in aqueous chloride solutions by hydrophobic tetra-\textit{n}-alkylammonium (TAA\textsuperscript{+}) cations—an effect not exerted by fully hydrated Li\textsuperscript{+} cations under similar conditions. Experimental and molecular dynamics simulation results indicate that TAA\textsuperscript{+} cations not only drive enhanced coordination of anionic Cl\textsuperscript{−} ligands to Np\textsuperscript{V/VI} but also associate with the resulting Np complexes via non-covalent interactions, which together decrease the electrode potential of the Np\textsuperscript{VI}/Np\textsuperscript{V} couple by up to 220 mV ($\Delta\Delta G = -22.2$ kJ mol\textsuperscript{−1}). Understanding the solvation-dependent interplay between electrolyte cations and metal-oxo species opens an avenue for controlling the formation and redox properties of metal complexes in solution. It also provides valuable mechanistic insights into actinide separation processes that widely use quaternary ammonium cations as extractants or in room temperature ionic liquids.
The electrochemical behavior of redox-active metal cations is inherently dependent on the inner-sphere coordination environment surrounding the metal center\textsuperscript{1,2}. Although this fundamental principle holds true, there is increasing evidence that the chemical environment beyond the first coordination sphere can also influence the observed electrochemical properties\textsuperscript{3–7}. For example, by measuring electrode potentials in organic media and by characterizing solid reaction products, several recent studies have demonstrated that direct second-sphere coordination of strong Lewis acids to oxo groups enhances the redox activity of metal–oxo complexes, including increasing the oxidizing capacity of manganese–oxo clusters in the oxygen-evolving complex of photosystem II\textsuperscript{8,9} and facilitating oxo group functionalization and reduction of the uranyl ion, \(\text{UO}_2^{2+}\)\textsuperscript{10,11}. For aqueous systems, however, the hydration of charged species (e.g., ion–solvent interactions) is expected to inhibit or outcompete any direct ion–ion interactions between molecular metal complexes and other cations\textsuperscript{8}, such that the influence of extended-coordination environments on the redox chemistry of metals dissolved in water has been overlooked.

To address this knowledge gap, we examined the redox behavior of Np\textsuperscript{V} in acidic aqueous chloride solutions as a function of electrolyte cation. The chemical properties of Np\textsuperscript{V} make it an excellent choice for studying the influence of extended-coordination environments on the redox chemistry of aqueous metal ions. First, in aqueous solutions, high-valent early actinides exist as dioxo actinyl cations (An\textsuperscript{V}O\textsubscript{2}+) or An\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+}, where An = U, Np, Pu, and Am), which have a unique and stable nearly linear structure, with two strong An–O covalent bonds. The partial negative character on the yl (yl = actinyl) oxygen atoms facilitates interactions with other cations\textsuperscript{12,13}, including other actinyl cations\textsuperscript{14–16} which is generally termed cation–cation interaction (CCI)\textsuperscript{12}. This property, namely the reactivity of the actinyl oxo group, provides a chemical path for defined second-coordination sphere interactions that do not perturb the inner-coordination sphere (the actinyl unit). Compared to An\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+} complexes, the lower nuclear charge of the An\textsuperscript{V} increases the Lewis basicity of the yl–oxo in An\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+} complexes, enhancing extended-coordination sphere interactions for An\textsuperscript{V} cations\textsuperscript{17}. Additionally, of the An\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+} species, Np\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+} is the most thermodynamically stable\textsuperscript{18}. Second, unlike transition-metal–oxo complexes that readily undergo hydrolysis and oligomerization, of which the latter can compete with second-coordination sphere bonding, hydrolysis and oligomerization of Np\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+} are unlikely under mildly acidic conditions\textsuperscript{19}. In fact, previous studies, including EXAFS, indicate that Np\textsuperscript{V} speciation in acidic chloride solutions (pH = 2, [Cl–] ≤ 6 M) is dominated by a simple monomeric pentahydrate complex, [Np\textsuperscript{V}O\textsubscript{2}(H\textsubscript{2}O)\textsubscript{5}]\textsuperscript{2+}\textsuperscript{20}. Third, in aqueous solutions, the Np\textsuperscript{VI}/Np\textsuperscript{V} redox couple is easily accessible (\(E^{\circ} = +0.959(4)\) V vs. Ag/AgCl)\textsuperscript{18} and generally exhibits reversible or quasi-reversible electron-transfer properties\textsuperscript{21,22}, permitting a quantitative or semiquantitative evaluation of the Np\textsuperscript{VI}/Np\textsuperscript{V} electron-transfer thermodynamics.

In the present work, we combine electroanalytical chemistry, vibrational and electronic spectroscopies, X-ray crystallography, and molecular dynamics simulations to characterize the interactions that electroyte cations (A\textsuperscript{+} = Li\textsuperscript{+} or tetra-n-alkylammonium cations (TAA\textsuperscript{+} = [NMe\textsubscript{4}]\textsuperscript{+}, [NEt\textsubscript{4}]\textsuperscript{+})) have with Np\textsuperscript{V}O\textsubscript{2}\textsuperscript{2+} cations in aqueous systems, and to understand the effect these interactions have on Np\textsuperscript{V} redox behavior, both in solution and during solution evaporation and crystal formation. The two electroyte cations, Li\textsuperscript{+} and TAA\textsuperscript{+}, which are widely used as non-reacting, charge-balancing ions, have significantly different ionic radii and hydration and H-bonding properties, allowing us to investigate how these properties influence interactions between the electroyte and neptunyl cations in aqueous solution. Here, we show that hydrophobic TAA\textsuperscript{+} cations unexpectedly stabilize higher-oxidation-state metal–oxo cations dissolved in aqueous solutions, whereas the strong Lewis acid, Li\textsuperscript{+}, has no effect on the observed redox behavior. Furthermore, we show that TAA\textsuperscript{+} cations, which are not Lewis acids, influence the redox behavior of metal–oxo cations via non-covalent ion association with the metal–oxo complex, not via direct bonding with the oxo group. These findings highlight the underappreciated influence of electroyte cations on the redox chemistry of metal cations and underscore the important role that ion–solvent interactions play in governing extended-coordination sphere interactions between metal cations and other ions in solution.

**Results**

**Redox chemistry of Np\textsuperscript{V} in LiCl and NMe\textsubscript{4}Cl solutions.** We first probed the redox chemistry of Np\textsuperscript{V} in several acidic aqueous chloride solutions as a function of A\textsuperscript{+} using cyclic voltammetry (CV). In 1 M and 5 M LiCl (pH = 1.3), the oxidation of Np\textsuperscript{V} is quasi-reversible (i.e., controlled by both charge transfer and mass transport), with average half-wave potentials (\(E_{1/2}\)) of +0.924(2) V and +0.929(3) V vs. Ag/AgCl, respectively (Supplementary Discussion, Supplementary Figure 2, and Supplementary Table 1). These electrode potentials are equal (within error), indicating that increases in LiCl concentration and ionic strength do not affect the redox behavior of Np\textsuperscript{V} (Supplementary Figure 3). Furthermore, the electrode potentials measured here for the LiCl solutions agree well with the electrode potentials previously reported for the Np\textsuperscript{VI}/Np\textsuperscript{V} couple in 1 M HClO\textsubscript{4}\textsuperscript{21} (Supplementary Table 1). Taken together, these data indicate that the underlying electronic structure and chemical environment of Np\textsuperscript{V} in solutions of 1 or 5 M LiCl and 1 M HClO\textsubscript{4} are the same, and that Np\textsuperscript{V} remains present predominantly as the free, hydrated cation, [NpO\textsubscript{2}(H\textsubscript{2}O)\textsubscript{5}]\textsuperscript{+}, as expected from previous studies\textsuperscript{20,23}.

In contrast, when Li\textsuperscript{+} cations in solution are replaced by TAA\textsuperscript{+} cations, the measured Np\textsuperscript{VI}/Np\textsuperscript{V} electrode potential decreases substantially, by as much as 220 mV, indicating that the presence of TAA\textsuperscript{+} cations in solution increases the thermodynamic stability of Np\textsuperscript{VI} relative to Np\textsuperscript{V} (Fig. 1). Specifically, in 1 M,
The cathodic shifts of the Np VI/NpV electrode potential are vs. Ag/AgCl, respectively. The redox transfer for the NpVI/NpV redox couple is quasi-reversible, with Li/NEt4, magenta line, and 3.5 M NEt4Cl (Np/NEt4, blue line); Raman electrode potentials measured in mixed constant-ionic-strength LiCl/NMe4Cl solutions, as illustrated by the spectra for NpV solutions in various concentrations of NMe4Cl (Fig. 2). This band occurs as a low-frequency shoulder on the NpVO2+ v1 band, indicating that the presence of TAA+ cations induces the formation of NpV species with weaker Np-O bond.

There are two known mechanisms that could cause a red shift of the actinyl v1 vibrational band. First, weakening of the Np–O bond could be due to the inner-sphere coordination of electron-donating chloride ligands in the NpV equatorial plane. Alternatively, the formation of [O=Np=O–M+6] complexes (M+6 = highly charged metal cation) could also weaken the Np–O bond and decrease the v1 frequency, as previously observed in dimeric Np V CCI complexes.

However, in contrast to the spectra of known aqueous [NpO2Cl3(H2O)2(n-1)] or [O=Np–O–M+6] complexes, the Vis–NIR absorption spectra of the NpV–TAACl solutions (Supplementary Figure 6) do not show the ingrowth of peaks at wavelengths higher than the characteristic NpV S = 5f transition at 980.2 nm, suggesting that the interactions between NpVO2+ cations and other constituents in the TAACl solutions, which include Cl– and TAA+ ions and H2O molecules, deviate from any interactions previously reported. Instead, the absorption spectra for 5 mM NpV dissolved in 1, 3, and 5 M NMe4Cl solutions exhibit a small, but significant (up to 2 nm) gradual blue shift of the 980.2 nm band (Supplementary Discussion and Supplementary Figure 6). No noticeable shift of the 980.2 nm band was observed in the absorption spectra for the 5 M LiCl solutions. These results are consistent with findings from the electroanalytical experiments, confirming a negligible impact of LiCl on NpV chemistry in solution.

**Syntheses and structures of representative Np compounds.** How do NpVO2+ cations interact with other solution constituents, particularly TAA+ cations, and how do these interactions stabilize higher-oxidation-state neptunyl species? To answer these questions, we crystallized potential neptunyl solution species by evaporation of acidic chloride solutions containing either Li+ or TAA+ cations. Subsequently, the solid products were characterized using single-crystal X-ray diffraction and Raman spectroscopy. The evaporation experiments reported here were conducted under conditions comparable to previously reported reactions containing only NpVO2+ and HCl. For which open-air evaporation yields a range of products, including the CCl complex, (NpVO2Cl(H2O)2), a mixed-valent NpVI/V compound, and other unidentified green phases.

The open-air evaporation of NpV/HCl solutions containing Li+ yields similar products, confirming that Li+ does not influence the redox behavior of NpV or the formation of CCI complexes in solution. All of the green products that form from the evaporation of NpV/Li/HCl solutions, including the compound, (NpO2Cl3(H2O)2), have Raman signatures matching those of products from Li-free NpV/HCl reactions (Supplementary Discussion and Supplementary Figure 13). Although the disproportionation of NpV to NpIV and NpVI is also possible during evaporative syntheses from acidic solutions, no evidence for the formation of NpVI compounds was observed. The structure of 1 is closely related to that of the dihydrate, (NpO2Cl3(H2O)2), both of which adopt a 3-D CCI network of squares arranged NpO2+ cations with open channels filled by Cl– anions and H2O molecules (Fig. 3a, Supplementary Discussion, Supplementary Figure 9, and Supplementary Figure 10). With a pentagonal bipyramidal geometry, each NpO2+ cation in the dihydrate and in 1 is coordinated by five ligands in the equatorial plane, which include two yl–O atoms, zero to three H2O molecules, and zero to three Cl– anions (Fig. 3b and Supplementary Figure 9). The Np–O bond distances (Supplementary Discussion and Supplementary Table 1) decrease of the electrode potential with increasing NMe4Cl concentration. This change in electrode potential is a weak ligand.

**Comparison of NpV Raman spectra.** Raman spectra of 0.12 M NpV solutions in 3.5 M LiCl (Np/Li, black line), 1.75 M LiCl/1.75 M NEt4Cl (Np/Li/NEt4, white line), and 3.5 M NEt4Cl (Np/NEt4, blue line); Raman spectrum of a 3.5 M NEt4Cl solution (green line) and of the crystalline product [NMe4]Cl[NpO2Cl(H2O)4](3) (orange line). The intensities of all spectra are scaled to facilitate comparison.
\\textbf{Fig. 3} Structure of (NpO}_2)_3Cl_4(H_2O)_7 (1). a) Projection of the three-dimensional network of cation–cation-bonded NpVIO}_2^2+ square nets, with open channels along the [0 0 1] direction. Chloride anions and water molecules that reside inside the channels are omitted for clarity. b) Local coordination environments and connectivities of four crystallographically unique NpVO}_2^+ cations in the structure of 1. Half of the disordered Cl and O\textsubscript{w} positions are omitted for clarity. Green, red, pink, and orange spheres represent Np, O\textsubscript{yl}, O\textsubscript{w}, Cl, N, C, and H atoms, respectively.

Table 3) and \nu_1 stretching frequencies for the dihydrate and 1 are also comparable at approximately 1.845 Å and 672 cm\textsuperscript{-1} (Supplementary Discussion).

In contrast, during solution evaporation in open air, the presence of [NMe\textsubscript{4}]\textsuperscript{+} in the Np\textsuperscript{V}/HCl solutions drastically alters neptunium’s coordination and redox chemistry. Unlike the solid products that formed during the evaporation of solutions containing Li\textsuperscript{+} CCl\textsubscript{4} and no Np\textsuperscript{V} CCl\textsubscript{4} compounds formed during the evaporation of solutions containing [NMe\textsubscript{4}] CCl\textsubscript{4}. Instead, yellow–green crystals of [NMe\textsubscript{4}]\textsubscript{2}[NpVIO}_2Cl\textsubscript{4}] (2) form readily upon solution evaporation in air, indicating that the presence of [NMe\textsubscript{4}]\textsuperscript{+} cations inhibits the formation of CCI compounds and promotes Np\textsuperscript{V} oxidation to Np\textsuperscript{VI}. This finding is consistent with our voltammetry data that clearly demonstrate enhanced stabilization of Np\textsuperscript{VI} relative to Np\textsuperscript{V} in the presence of [NMe\textsubscript{4}]\textsuperscript{+} cations.

The structure of compound 2, which consists of molecular [NpVIO}_2Cl\textsubscript{4}]\textsuperscript{2−} complexes and [NMe\textsubscript{4}]\textsuperscript{+} cations (Fig. 4a, Supplementary Discussion, and Supplementary Figure 11), also provides a possible model for the interplay between oxidized Np cations and other solution constituents in the electrochemical experiments (Fig. 4a). In fact, the NpVIO}_2^2+ unit in the structure of 2 appears to be strongly perturbed by its surrounding environment, which includes Cl\textsuperscript{−} and [NMe\textsubscript{4}]\textsuperscript{+} ions. More specifically, Np–O\textsubscript{Cl} distances within the tetragonal bipyramidal [NpVIO}_2Cl\textsubscript{4}]\textsuperscript{2−} units in 2 are 1.765(3) Å, which are much longer than those for [NpVIO}_2(H_2O)_5]Cl\textsuperscript{−} complexes in the structure of [NpO}_2(H_2O)_5]ClO\textsubscript{4}\textsubscript{2−} (1.7479(9) and 1.740(1) Å\textsuperscript{35}). The \nu_1 symmetric stretching band for O=NP=O moieties in 2 occurs at 797 cm\textsuperscript{-1} (Supplementary Figure 13), which is approximately 60 cm\textsuperscript{-1} less than that for free [NpVIO}_2(H_2O)_5]Cl\textsuperscript{−} complexes in solution (855 cm\textsuperscript{-1}). This finding confirms weakening of the NpV=O\textsubscript{Cl} bond in 2, which has been attributed to the coordination of four chloride (electron-donating) ligands in the NpVIO}_2^2+ equatorial plane in similar compounds. Additional non-covalent interactions between \textsubscript{yl.–}O atoms and [NMe\textsubscript{4}]\textsuperscript{+} cations and between coordinated Cl\textsuperscript{−} anions and [NMe\textsubscript{4}]\textsuperscript{+} cations are apparent, which may also affect the electronic structure of the NpVIO}_2^2+ cations in 2. In total, each discrete [NpVIO}_2Cl\textsubscript{4}]\textsuperscript{2−} anion attracts eight neighboring [NMe\textsubscript{4}]\textsuperscript{+} cations through electrostatic interactions with O\textsubscript{yl} and Cl\textsuperscript{−} moieties with O\textsubscript{yl}–N and Cl–N distances of 4.5417(9) Å and 4.3377(2)–4.5617(3) Å (Fig. 4a, Supplementary Discussion, and Supplementary Table 4). Additionally, each O\textsubscript{yl} and Cl atom potentially
participates in four H-bonds with the methyl group of four neighboring [NMe₄]⁺ cations, with donor–acceptor distances ranging from 3.385(3) Å (C–H⋯Oₐ) to 3.686(2)–3.901(3) Å (C–H⋯Cl–). To isolate potential NpV species present in TAACl solutions, we repeated the above evaporation experiment in the absence of air to exclude the potential oxidizer, O₂. As a result, only teal crystals of [NMe₄][NpO₂Cl₂(H₂O)₄] (3) were obtained. In addition to discrete [NMe₄]⁺ and Cl⁻ ions, compound 3 contains molecular actinyl monochloride complexes, [NpO₂Cl₂(H₂O)₄], which confirms the existence of NpV monochloride species in TAACl solutions (Fig. 4b, Supplementary Discussion and Supplementary Figure 12). No other Np chemistry (i.e., formation of CCl or NpV₅ complexes) was observed during this evaporation experiment, confirming that [NMe₄]⁺ cations inhibit the formation of Np CCl complexes and suggesting that O₂ is the oxidant responsible for the NpV oxidation observed during the evaporation of NMe₄Cl solutions in open air.

In addition, the structure of 3 provides crucial evidence supporting the substantial impact of neptunium-extended coordination environments on NpV-O₃ bonding. This is evidenced by the elongated NpV-O₃ distances (1.839(2) and 1.843(2) Å) and the red-shifted symmetric stretching frequency (ν₁ = 741 cm⁻¹) in 3 (Fig. 2), compared with the distances and symmetric stretching frequencies observed in other non-CCI compounds, such as Naₙ(NpO₂Cl₂SeO₃)(H₂O) (Np–O₃ = 1.813(3) Å and 1.831(3) Å; v₁ = 773 cm⁻¹) [36]. Considering the weaker donating capacity of Cl⁻ anions compared with oxoanions [34,36], such as selenate, the weakened Np–O₃ bonding in 3 results from the non-covalent interactions between NpO₂Cl⁻ cations and [NMe₄]⁺ cations and H₂O ligands. Each [NpO₂Cl₂(H₂O)₄] complex in the structure of the 3 bonds to five [NMe₄]⁺ cations through Oₐ/Cl(2)⋯–[NMe₄]⁺ electrostatic interactions and through potential H-bonds between Cl(2) atoms and methyl groups (Supplementary Discussion and Supplementary Table 5). More specifically, each yl–O atom attracts one [NMe₄]⁺ cation with Oₐ–N distances of 4.062(3) or 4.660(3) Å and each Cl(2)–anion attracts four [NMe₄]⁺ cations with Cl–N distances in the range of 4.184(2)–5.156(2) Å. In addition, each yl–O atom participates in two H-bonds with the H₂O ligands from surrounding [NpO₂Cl₂(H₂O)₄] complexes, with Oₐ–H⋯Oₐ distances of 2.733(3)–2.859(3) Å. Interestingly, the neptunyl ν₁ band for the pentagonal bipyramidal [NpO₂Cl₂(H₂O)₄] complexes in 3 matches the frequency of the shoulder peak observed in the Raman spectrum of the 0.12 M NpV/3.5 M NET₄Cl solution (Fig. 2). This finding indicates that the NpV/NET₄Cl solution contains NpO₂⁺ species that have similar structural properties and that participate in similar non-covalent interactions as the NpVO₂⁺ species in 3.

**Molecular dynamics simulations.** The non-covalent extended-sphere interactions between NpV and TAA⁺ cations and the influence of these interactions on the first coordination sphere of NpV are further supported by all-atom molecular dynamics (MD) simulations. All MD simulations were performed on 0.1 M NpV or NpVI solutions at pH = 2 in the presence of 5 M LiCl or 5 M NMe₄Cl (Supplementary Tables 6 and 7, and Supplementary Figures 14, 15, and 16). Consistent with our experimental results, the MD simulations confirm that neptunyl species in 5 M LiCl solutions are dominated by hydrated neptunyl complexes, with only weak Np–Cl coordination (Table 1). Surrounding these neptunyl hydrates, there are only 0.3 and 0.5 Li⁺ cations, on average, indicating roughly negligible interactions between the neptunyl and Li⁺ cations. In contrast, both NpV and NpVI exhibit enhanced chloride ligation in the presence of 5 M NMe₄Cl. Specifically, substantial quantities of neptunyl mono- and dichlorides and neptunylCl⁺ di- and trichlorides formed under the tested conditions (Table 1). These neptunyl–chloride complexes are embedded inside a cage of six (average) [NMe₄]⁺ cations, each of which is located at approximately 6 Å from the Np centers, indicating significant non-covalent interactions between the [NMe₄]⁺ electrolyte cations and the Np first-coordination sphere. These arrangements are comparable to those observed in the structures of 3 and 2 (Fig. 4), where each neptunyl–chloride complex bonds five or eight [NMe₄]⁺ cations via electrostatic and potential H-bonding interactions with the yl–O atoms or Cl⁻ anions, with Np–N distances of 5.292(4)–7.424(2) Å and 5.3745 (3) Å for NpV and NpVI, respectively.

**Discussion**

On the basis of the experimental and simulation results, we propose that TAA⁺ cations promote the formation of inner-shell NpV–chloride complexes in solution. The formation of such complexes is expected to decrease the measured NpVI/NpV electrode potential because NpO₂Cl⁺ cations form stronger complexes with electron-donating chloride ligands than NpO₂⁻ cations [19–23]. Our combined data, particularly the crystallization of [NMe₄][NpO₂Cl₂(H₂O)₄] (3) and the enhanced neptunyl–chloride complexation observed in the MD simulations for NMe₄Cl solutions, suggest that monochloro–NpV complexes coexist with [NpO₂(H₂O)₃]⁺ complexes in TAACl solutions. However, existing thermodynamic data reveal that the free energy difference expected as a result of the formation of monochloro–neptunyl complexes (ΔΔG = −3.94 kJ mol⁻¹, Supplementary Table 8) is inadequate to account for the large thermodynamic stabilization of NpV observed in 5 M NMe₄Cl (ΔΔE₁/₂ ≈ −220 mV → ΔΔG = −22.2 kJ mol⁻¹, Supplementary Table 8). The formation of higher-order neptunyl–chloride complexes in solution is also possible, as indicated by the structure of 2 and the MD results, and may further decrease the NpVI/NpV electrode potential [37]. The corresponding thermodynamic data for higher-order neptunyl–chloride complexes are unknown, but a decrease of the NpVI/NpV electrode potential less

### Table 1 Average coordination environment surrounding NpV₂O₃²⁺ and NpVI₂O₃²⁺ cations in LiCl or NMe₄Cl solutions determined from all-atom MD simulations

| System       | Oₐ CN | Cl⁻ CN | Li⁺/Cl⁻ CN | εᵣ  |
|--------------|-------|--------|------------|-----|
| NpV/LiCl     | 4.4   | 0.4    | 0.3        | 38.8|
| NpV/NMe₄Cl   | 2.4   | 1.8    | 5.9        | 21.6|
| NpVI/LiCl    | 3.8   | 1.1    | 0.5        | 39.0|
| NpVI/NMe₄Cl  | 2.0   | 2.4    | 5.9        | 21.3|

*Simulation conditions: 0.1 M Np, pH 2, 5 M LiCl or NMe₄Cl
*CN – coordination number
*Relative permittivity
than 220 mV would be expected, considering the weak electron-donating capability of the chloride ligand.\[24,36\]

In addition to the NpVI stabilization conferred upon chloride complexation, the extended-sphere association with TAA+ cations, forming [NpO2Cl6(H2O)4][O4]−...TAACl groups, further decreases the NpV/NpVI electrode potential. For homogeneous 2 and 5 M NMe4Cl solutions, the calculated separation between the centers of [NMe4]+ and Cl− ions is about 7.5 and 5.5 Å, which are close to the N−Cl distances for solvent-separated (7.5 Å) and contact (5.0 Å) [NMe4]+−Cl− ion pairs in aqueous solution.\[38\] As a result, interactions between TAA+ cations and free Cl− anions and between TAA+ cations and the Cl− anions of [NpO2Cl6(H2O)4][O4]− complexes are expected under the solution conditions employed herein. Considering the structure of 3 (Fig. 4) and the MD results (Supplementary Figure 16), we also expect electrostatic and potential H-bonding interactions between TAA+ cations and yl−O atoms in solution. As a whole, it appears that yl−O atoms and coordinated Cl− ligands are both key mediators mediating the association of neptunyl and TAA+ cations. To separate the synergistic effects of yl−O atoms and Cl− ligands, similar experiments with the non-complexing ClO4− ligand were planned but could not be executed because of the much lower aqueous solubility of TAAClO4 compared with TAACL salts.

As a final note, we must also consider the chemical and structural properties of water itself, and the important role that water plays in influencing the electrochemical stabilities of neptunyl complexes. As indicated in the structure of 3 and other reported evidence in the literature,\[37,39\] water can act as a H-bond donor to the yl−O atoms, particularly those of NpO2Cl6−, in a manner competing with TAA+ cations. With increasing concentrations of TAACL, the concentration of water decreases. This effectively decreases the H-bonding interactions between water molecules and neptunyl cations and decreases the relative permittivity of the solutions (Table 1), facilitating stronger interactions between neptunyl cations and Cl− and TAA+ ions.

The divergence in the reactivity of Li+ and TAA+ cations toward the neptunyl first-coordination sphere in aqueous solutions demonstrated in this study can be attributed to the different solution properties of the electrolyte cations. In aqueous solutions, Li+ cations are strongly hydrated (ΔH_hydration = −530 kJ mol−1)\[40\] such that their charge is effectively shielded from the neptunyl−O atoms and Cl− ions. However, TAA+ cations, which are only weakly hydrated in solution (ΔH_hydration = −200 kJ mol−1)\[40\] are expected to more actively engage with the neptunyl−O atoms and Cl− ions via electrostatic interactions. Additionally, potential H-bonding via the alkyl groups may further enhance the association of TAA+ cations and neptunyl complexes in solution. Therefore, despite their lower charge density, compared with Li+ cations, TAA+ cations are expected to associate with NpV oxide cations in aqueous solutions. These phenomena are well illustrated by the structures of 2 and 3 and by the MD simulation results. The observed differences in neptunyl chemistry in LiCl vs. TAACL solutions are consistent with our recent findings that demonstrate a correlation between counterion (A+ = Li+, Na+, K+, Rb+, Cs+, NH4+, or NR4+ (R = Me, Et, and Bu)) hydration enthalpies and the formation of redox-inactive Th−nitrate molecular complexes from aqueous solution, wherein hydrophobic counterions (e.g., TAA+ cations) tend to associate with more anionic Th−nitrate molecular complexes via stronger non-covalent interactions in solid structures.\[41\]

These results highlight the importance of ion hydration properties in regulating the interactions between oxocations and electrolyte cations in solution. The competition between ion solvation and ion association has been well documented for oppositely charged ions such as A+ (A = alkali metal and tetra-n-alkylammonium) and Cl−. Weak ion−solvent interactions also appear to be essential for ion association between neptunyl species and TAA+ cations in aqueous solutions. Related phenomena have been reported for other oxocation and metal ion systems, supporting the fundamental importance of these underlying chemical principles. For example, stronger interactions between NpO2Cl6− and highly charged metal cations, such as Al3+ and Fe3+, are observed in mixed aqueous polar−organic solvents than in aqueous media because ion−solvent interactions are weaker in the mixed solvents.\[42\] Other metal−oxy complexes with similar extended coordination environments, such as those of iron,\[43\] manganese−,\[5,6\] and uranium−oxocations,\[44,45\] have been isolated in organic solvents, where weak ion−solvent interactions are negligible compared to the strong bonding between oxo groups and extended-sphere metal cations.

The influence of hydrophobic, low-charge density TAA+ cations on the electrochemical properties of neptunyl species in aqueous chloride media arises from a mechanism different than that reported previously for studies involving strong Lewis acids, which have a comparatively higher charge density. These previous studies suggest that direct bonding between Lewis acids, such as Ca2+ or Y3+, and oxo groups tends to increase the electrode potentials of oxocations as a function of increasing Lewis acidity.\[6\] In contrast, TAA+ cations associate with neptunyl cations via non-covalent interactions with both the neptunyl oxo groups and equatorial ligands. This association influences ligation within the metal cation’s first coordination sphere, driving enhanced coordination of anionic Cl− ligands to the NpV(VI) centers. The sum of all these interactions, namely the inner-sphere coordination with Cl− anions and the outer-sphere association with TAA+ cations, causes a significant decrease of the NpV(VI)/NpV electrode potential to favor NpV(VI).

Overall, this work opens an avenue of using non-innocent electrolyte cations to control the redox properties and the first-coordination-sphere ligation of metal cations. Furthermore, we highlight that the observed influence of TAA+ cations on the coordination and redox chemistry of neptunyl cations is important in actinide separation processes in which quaternary ammonium cations (e.g., TAA+) are widely employed as anion exchange extractants or in room-temperature ionic liquids (RTILs).\[44−46\] In fact, higher-order (anionic) actinide complexes, including chloride complexes, which would not usually be considered dominant aqueous species based on solution ligand concentrations, are preferentially associated with quaternary ammonium cations in these processes.\[45\] This study provides significant insights into the underlying principles regarding the interactions between actinide species and quaternary ammonium cations, which will aid in optimizing actinide separation processes and tuning the properties of RTILs.

**Methods**

**Caution:** 239Np is an α- and γ-emitting radioisotope and is considered a health risk. Its use requires appropriate infrastructure and personnel trained in the handling of radioactive materials.

**Stock solution preparation.** Solutions of NpV(V) in 1M HClO4 were purified using a cation-exchange column containing Dowex-50-X8 resin. After purification, Np was precipitated using NaOH, washed with water, and redissolved in 1M HCl. The procedure was used to prepare two separate stock solutions, one for solid-product precipitations using NaOH, washed with water, and redissolved in 1M HCl. The procedure was used to prepare two separate stock solutions, one for solid-product synthesizes and Raman spectroscopy and one for electrochemistry experiments. Identification of the characteristic near-infrared absorption band for NpO2− at 980 nm, and the absence of absorption bands characteristic for other Np oxidation states, confirmed that both Np/15Cl solutions contained only Np(V) (Supplementary Figure 1)\[47\]. The purified final stock solutions contained 0.24 M or 0.1 M Np(V), as determined using liquid scintillation counting (LSC). LiCl (Fisher, >99.9%), NMe4Cl, and NEt4Cl (Sigma, >98%) were used as obtained. ACI (A = Li+, [NMe4]+, and [NEt4]+) stock solutions of varying concentrations were prepared by dissolving ACI in deionized H2O.
Voltammetry. Cyclic and differential pulse voltammetry (CV, DPV) data for 5 mM Np(V) solutions in various static electrolytes were collected at room temperature in the absence of oxygen using a BAS 100B electrochemical workstation, a graphite working electrode, a graphite auxiliary electrode, and an Ag/AgCl (3 M NaCl) reference electrode, which has a redox potential of +0.200 V vs. SHE at 25°C. All Np solutions used for the electrochemical experiments were prepared individually by mixing an aliquot of the 0.1 M Np(V) stock solution with appropriate volumes of ACI stock solutions and H₂O to yield the solutions listed in Supplementary Table 1. The Np(V) concentrations of select sample solutions were verified using LSC.

Visible-near-infrared (Vis-NIR) absorption spectroscopy. Vis-NIR spectra (400–1300 nm) were collected for diluted Np(V) stock solutions in standard 1 cm path-length polystyrene cuvettes (Fisher) and for select 5 mM Np(V) electrochemistry solutions in 0.2 cm path-length micro-volume polystyrene cuvettes (Eppendorf, UVette) using an Oliis-modernized Cary 14 spectrophotometer.

Synthesis of (NpO₂)₄Cl₄(H₂O)₇ (1). A 25 μL aliquot of the 0.24 M Np(V) stock solution (in 1 M HCl) and 6 μL of a 1 M LiCl solution were combined in a 2 mL glass vial and covered by paraffin with small pin holes. The solutions were left in a vented hood and allowed to slowly evaporate over three months to complete dryness. Solid products included up to millimeter-sized yellow-green crystals of 1, a green amorphous solid, and colorless salts (Supplementary Figure 7a).

Syntheses of [NMe₄]₂[NpO₂Cl₄] (2) and [NMe₄]Cl[NpO₂Cl(H₂O)₄] (3). A 10 μL aliquot of the 0.24 M Np(V) stock solution and 5 μL of a 1 M NMe₄Cl solution were combined in a 2 mL glass vial and covered by paraffin with small pin holes. The solutions were left in a vented hood and allowed to slowly evaporate to complete dryness. Solid products included up to millimeter-sized yellow-green crystals of 2 and colorless salts (Supplementary Figure 7b). Slowly evaporating the same solution in an apparatus excluding air resulted in teall crystals of 3 and colorless salts (Supplementary Figure 7c).

Structure determinations. Single-crystal X-ray diffraction data for (NpO₂)₄Cl₄(H₂O)₇ (1); [NMe₄]₂[NpO₂Cl₄] (2); and [NMe₄]Cl[NpO₂Cl(H₂O)₄] (3) were collected with the use of graphite-monochromatized MoKα radiation (λ = 0.71073 Å) at 100 K on a Bruker APEXII diffractometer. The crystal-to-detector distance was 5.00 cm. Data were collected by a scan of 0.3° in ω in groups of 600 frames at θ settings of 0°, 90°, 180°, and 270°. The exposure time was 25 s/frame, 15 s/frame, and 20 s/frame for 1, 2, and 3, respectively. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2. Absorption corrections as well as incident beam and decay corrections were performed with the use of the program SADABS.

Molecular dynamics simulations. All-atom explicit-solvent MD simulations were performed using the package GROMACS (5.0.7). Force field parameters for Np²⁺/³⁺ and NpO₂⁻ ions and the recommended SPC/E water model given by Pomogaev et al. were used in all simulations. Additional details and calculated radial distribution functions are given in the Supplementary Methods and in Supplementary Figures 14 and 15.

Data availability. All data supporting this work are available within this manuscript or its associated Supplementary Information, or from the corresponding author upon reasonable request. Additionally, crystallographic data for the compounds reported herein have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CSD 1878175-1878177. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions
G.B.J. and S.L.E. designed the study. S.L.E. performed the voltammetry experiments and collected the Vis–NIR absorption spectra. G.B.J. performed the crystal syntheses, collected the crystallographic data, and collected the Raman spectra. B.Q. performed the MD simulations. All authors analyzed the data. All authors wrote the manuscript.

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