Gas Phase Computational Studies on the Competition between Nitrile and Water Ligands in Uranyl Complexes

George Schoendorff
Iowa State University

Wibe A. de Jong
Pacific Northwest National Laboratory

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

Theresa Lynn Windus
Iowa State University, twindus@iastate.edu

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Abstract
The gas phase formation of uranyl dicationic complexes containing water and nitrile (acetonitrile, propionitrile, and benzonitrile) ligands, \([\text{UO}_2(\text{H}_2\text{O})_m(\text{RCN})_n]^{2+}\), has been studied using density functional theory with a relativistic effective core potential to account for scalar relativistic effects on uranium. It is shown that nitrile addition is favored over the addition of water ligands. Decomposition of these complexes to \([\text{UO}_2\text{OH}(\text{H}_2\text{O})_m(\text{RCN})_n]^+\) by the loss of either H3O+ or (RCN + H)+ is also examined. It is found that this reaction is competitive with the ligand addition when the coordination sphere of uranyl is unsaturated. Additionally, this reaction is influenced by the size of the nitrile ligand with reactions involving acetonitrile being the most prevalent. Finally, ligand addition to the monocation shows trends similar to that of the dication with energetic differences being smaller for the addition to the monocation.

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Comments
Gas Phase Computational Studies on the Competition between Nitrile and Water Ligands in Uranyl Complexes†

George Schoendorf,§ Wibe A. de Jong,§ Mark S. Gordon,§ and Theresa L. Windus*,§
Department of Chemistry, Iowa State University and Ames Laboratory, Ames Iowa 50011, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352

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The gas phase formation of uranyl dicationic complexes containing water and nitrile (acetonitrile, propionitrile, and benzonitrile) ligands, [UO₂(H₂O)ₙ(RCN)ₙ]²⁺, has been studied using density functional theory with a relativistic effective core potential to account for scalar relativistic effects on uranium. It is shown that nitrile addition is favored over the addition of water ligands. Decomposition of these complexes to [UO₂OH(H₂O)ₙ(RCN)ₙ]⁺ by the loss of either H₃O⁺ or (RCN + H)⁺ is also examined. It is found that this reaction is competitive with the ligand addition when the coordination sphere of uranyl is unsaturated. Additionally, this reaction is influenced by the size of the nitrile ligand with reactions involving acetonitrile being the most prevalent. Finally, ligand addition to the monocation shows trends similar to that of the dication with energetic differences being smaller for the addition to the monocation.

Introduction

Advances in nuclear technology over the last seven decades have alleviated some of the need for fossil fuels. However, nuclear power does come with a significant environmental cost, primarily in the accumulation, treatment, and storage of nuclear waste. Due to the renewed interest in nuclear technology, there has been a resurgence of interest in the chemical reactivity of uranium. In particular, the uranyl dication has received particular attention due to its prevalence in uranium containing species. For these reasons, the chemistry of the uranyl dication, particularly its interaction with water, has been the subject of intense investigation. However, other ligands, such as acetone and acetonitrile derivatives also exhibit a substantial affinity for uranyl and compete with water for coordination sites.

While much of the nuclear waste chemistry happens in the solution or solid phase, gas phase reactions are also being explored to understand the fundamental uranium chemistry. These gas phase studies also provide an excellent source for direct comparison with computation, which can help to validate the computational approach and give insight into the bonding characteristics of these systems. Notably, complexes with both water and acetonitrile derivatives as ligands have been studied experimentally using electrospray ionization mass spectroscopy (ESI-MS) and multiple-stage collision induced dissociation (CID). In the course of the experimental study, two types of reactions were observed. The first of these is a simple ligand addition reaction whereby either water or RCN (acetonitrile, propionitrile, or benzonitrile) is added sequentially to build up a complex with uranyl (e.g., [UO₂(H₂O)ₙ(RCN)ₙ]²⁺). The other reaction involves the decomposition of the aforementioned complex via a charge-exchange (hydrolysis) reaction to produce [UO₂OH(H₂O)ₙ(RCN)ₙ]⁺ and either H₂O⁺ or (H + RCN)⁺. While both reactions occurred in the ion trap before analysis by mass spectrometry, short isolation times (30 ms) yielded only dicationic species and longer isolation times (100–1000 ms) led to the formation of the monocationic species. Due to the long isolation times involved in these experiments, the dominant chemistry occurs under equilibrium conditions.

The present computational work seeks to understand these gas phase experimental results and is an extension of a previous study of the coordination of water, carbonyl ligands (formaldehyde, acetaldehyde, and acetone), and nitrile ligands (acetonitrile, propionitrile, and benzonitrile) to the uranyl dication. In that study, the complexes modeled contained only one type of ligand (e.g., all water ligands, all acetonitrile ligands, etc.). It was found that the ligands’ affinity for uranyl followed the general trend RCN > RCO > H₂O, and larger ligands were shown to bind more strongly to uranyl due to an increased capacity to delocalize charge. The present study proceeds to examine the influence of the coordination of water ligands in competition with the coordination of nitrile ligands in the gas phase, allowing for comparison with the aforementioned gas phase experimental study. By examining a complete set of data as a function of coordination number, number of nitrile ligands, and size of the nitrile ligands, we present general observations of the effects of the coordination of nitrile ligands with uranyl in the presence of water with the aim of elucidating why formation of some of these complexes is favored over the formation of others. First the growth of dicationic uranyl complexes by subsequent ligand additions is examined. The coordination number is varied from 1 to 6 equatorial ligands, and for each equatorial coordination number, N, the numbers of water ligands and nitrile ligands are also allowed to vary from 1 to N while the total equatorial coordination number is kept constant. Finally, the discussion will move on to model the charge-exchange (hydrolysis) reactions that were experimentally observed. These reactions were shown to be thermodynamically competitive with the ligand addition reactions when the coordination sphere of UO₂²⁺ is unsaturated.
All calculations were performed using the NWChem software suite.\textsuperscript{10,11} The choice of functional and basis set for this research was based on a previous systematic study in which fully relativistic coupled cluster theory (specifically, CCSD(T)) benchmark calculations on UO\textsubscript{2}\textsuperscript{2+} were compared to various levels of theory, DFT functionals, and basis set choices.\textsuperscript{12} That study showed that the best agreement was obtained by employing the local density approximation (LDA)\textsuperscript{13,14} to determine optimized geometries and frequencies and the B3LYP\textsuperscript{15,16} functional at the LDA optimized geometries for energetics. Accordingly, all geometry optimizations and Hessians were obtained using LDA, and all energies reported were obtained with the B3LYP functional using the LDA optimized geometry. While DFT energies can introduce some error in calculated energies, the aforementioned benchmark study examined this effect for various functionals and found that in cases with uranyl, the B3LYP functional provided the most consistently accurate energies. All reported energies in this paper include the zero-point energy correction at 0 K. While Gibbs free energies at other temperatures could certainly be calculated to make a more definitive comparison with experiment, many of these molecules have high amplitude/low frequency modes that make a harmonic approach unreasonable. As shown by one of the authors,\textsuperscript{17,18} anharmonic methods are required which are well beyond the scope of this work. Due to this issue, the terms “exoergic” and “exoergicity” are used for the reaction energetics represented in this work.

The small core Stuttgart relativistic effective core potential (RECP) and associated Stuttgart orbital basis set\textsuperscript{19–21} was employed for uranium, while valence triple-ζ plus polarization (TZVP)\textsuperscript{22} DFT optimized basis sets were used for all other atoms (H, C, N, and O). In all cases, spherical primitive Gaussian functions were used. Hessian (energy second derivative) calculations were performed with the LDA functional at the optimized geometries to obtain zero point energies and frequencies and to ensure that the optimized structures are potential energy minima. Molecular images were produced using MacMolPlt.\textsuperscript{23}

**Results and Discussion**

Three types of reactions have been modeled in this study. The first is a ligand addition reaction of the form

$$[\text{UO}_2(\text{H}_2\text{O})_m(\text{RCN})_n]^{2+} + \text{H}_2\text{O} \rightarrow [\text{UO}_2(\text{H}_2\text{O})_{m+1}(\text{RCN})_n]^{2+}$$ (1)

and

$$[\text{UO}_2(\text{H}_2\text{O})_m(\text{RCN})_n]^{2+} + \text{RCN} \rightarrow [\text{UO}_2(\text{H}_2\text{O})_m(\text{RCN})_{n+1}]^{2+}$$ (2)

where the total equatorial coordination number ($n + m + 1$) is constrained to be less than or equal to 6 and RCN is acetonitrile.
(Acn), propionitrile (Pn), or benzonitrile (Bzn). Another type of reaction is a charge-exchange (hydrolysis) reaction that follows either if a protonated water ligand dissociates, or if a protonated nitrile ligand dissociates. Finally, the monocationic complexes can undergo further ligand additions according to the following reactions

\[
[UO_2(H_2O)_m(RCN)_n]^{2+} \rightarrow [UO_2OH(H_2O)_{m-2}(RCN)_n]^+ + H_3O^+ \quad (3)
\]

if a protonated water ligand dissociates, or

\[
[UO_2(H_2O)_m(RCN)_n]^{2+} \rightarrow [UO_2OH(H_2O)_{m-1}(RCN)_{n-1}]^+ + (H + RCN)^+ \quad (4)
\]

if a protonated nitrile ligand dissociates. Finally, the monocationic complexes can undergo further ligand additions according to the following reactions

\[
[UO_2OH(H_2O)_m(RCN)_n]^+ + H_2O \rightarrow [UO_2OH(H_2O)_{m+1}(RCN)_n]^+ \quad (5)
\]

and

\[
[UO_2OH(H_2O)_m(RCN)_n]^+ + RCN \rightarrow [UO_2OH(H_2O)_{m+1}(RCN)_{n+1}]^+ \quad (6)
\]

We first will address the ligand addition reactions involving dicaticonic complexes before moving on to the charge-exchange reactions and ligand additions to monocationic species.

**Ligand Addition Reactions**

The successive addition of nitrile ligands to a uranyl dication was previously examined by this group. The present work builds upon the previous results by allowing water, as well as nitrile ligands, to bind to uranyl.

The trends observed in the ligand addition products are similar to those observed earlier for nitrile ligand addition. Data reflecting this observation can be found in the Supporting Information. In general, when the equatorial coordination number is held constant, there is a red shift in the \( UO_2^{2+} \) symmetric and antisymmetric stretching frequencies as the number of nitrile ligands increases and the number of water ligands decreases. This is accompanied by an increase in both the \( U-O_{\text{axial}} \) bond lengths and the \( U-\text{ligand} \) bond lengths. Additionally, increasing the number of nitrile ligands also causes blue shifts in the \( C-N \) stretching frequencies with concomitant decreases in the \( C-N \) bond lengths. Increasing the total number of ligands results in similar trends. This is accompanied by an increase in both the \( U-O_{\text{axial}} \) bond lengths and the \( U-\text{ligand} \) bond lengths.

Changes in bond lengths and vibrational frequencies caused by ligand addition can be up to an order of magnitude larger than...
changes associated with substituting a water ligand for a nitrile. For example, the U–O$_{\text{axial}}$ bond length increases by approximately 0.01 Å when each successive ligand is added. However, if the coordination number is held fixed and water ligands are substituted with benzonitrile, then the U–O$_{\text{axial}}$ bond length increases by approximately 0.005 Å for each successive substitution.

One limitation of current mass-spectroscopy studies is that one cannot distinguish between isomers; however, a comparison of isomers can be performed straightforwardly using computations. Conformational isomers can occur when the equatorial coordination number exceeds 3. With four ligands, [UO$_2$(RCN)$_2$(H$_2$O)$_2$]$^{2+}$ can take either of the isomeric forms depicted in Figure 1. In this case, the ligand arrangement in isomer 1A (referred to as trans in this paper) always has the lowest energy, regardless of whether the nitrile is acetonitrile, propionitrile, or benzonitrile. The largest energy difference among these isomers occurs when the nitriles are acetonitrile (1.5 kcal/mol). This value decreases as the size of the nitrile ligand increases, so that the energy difference is 0.4 kcal/mol for propionitrile ligands and 0.1 kcal/mol for benzonitrile ligands. Obviously, at this level of theory, the latter two should be considered isoenergetic.

Figure 2 gives examples of the isomers that can occur when five equatorial ligands are present. Structures 2A and 2B are complexes with two nitrile ligands, and structures 2C and 2D are complexes with three nitrile ligands. The energy differences among these isomers are less than 1 kcal/mol, regardless of whether the nitrile is acetonitrile, propionitrile, or benzonitrile. Therefore, all isomers with five equatorial ligands are also nearly isoenergetic.

The isomers associated with six equatorial ligands are not as straightforward as are those for smaller numbers of ligands. As noted in previous work, the sixth ligand can be a direct ligand (although weakly bound), or it can add to the first solvent shell. There are three possibilities when two, three, and four nitrile

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**Figure 4.** Complexes with six equatorial ligands that contain propionitrile. 4C is the only complex found that has three propionitrile ligands bound to uranyl.
ligands are present. Repulsion between adjacent ligands distorts their arrangement around UO$_2^{2+}$ so that the ligands lie above and below the equatorial plane. Nonetheless, some isomers with all six ligands directly bound to uranyl can be found. The isomers of complexes containing acetonitrile are shown in Figure 3, while those that contain propionitrile and benzonitrile are shown in Figures 4 and 5, respectively. The energy difference for the isomers with acetonitrile ligands is only 0.1 kcal/mol. However, energy differences for isomers involving propionitrile ligands and benzonitrile ligands can be as large as 3.8 kcal/mol. In the case of propionitrile, 4A and 4B are isoenergetic while 4D is 3.8 kcal/mol lower in energy than 4E. The energy difference between 5A and 5B is 3.3 kcal/mol, with 5B being lower in energy. In general, the lowest energy structures exhibit the greatest deviation of the ligands from the equatorial plane, indicating that steric effects may contribute to the energy differences.

Figures 6 displays the relative binding energies for acetonitrile and water additions, with water additions associated with arrows pointing toward the right and nitrile additions with those pointing to the left. In those cases where there is a choice of isomers, average values of the isomer energies have been used since these isomers tend to be isoenergetic. Average values were also used in the case of [UO$_2$(Pn)$_2$(H$_2$O)$_2$]$^{2+}$ and [UO$_2$(Bzn)$_3$(H$_2$O)$_4$]$^{2+}$ since the trends are clear even though the binding energies for each isomer vary by up to 2 kcal/mol from the reported values when these complexes are involved. Likewise, Figures 7 and 8 display relative binding energies for the propionitrile and benzonitrile systems, respectively. It is clear that addition of a nitrile ligand is favored over water addition in all cases. Furthermore, as shown previously, large nitrile ligands bind more strongly to uranyl than small nitrile ligands. This trend holds whether or not water ligands are present and is consistent with the experimental observations that complexes with an abundance of nitrile ligands are favored over those with primarily water ligands. For example, the complexes with acetonitrile ligands that have been experimentally observed are [UO$_2$(Acn)$_2$]$_2$$^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)]$_2$$^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)$_2$]$^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)$_3$]$^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)$_4$]$^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)$_5$]$^{2+}$, [UO$_2$(Acn)$_3$(H$_2$O)$_2$]$^{2+}$, [UO$_2$(Acn)$_3$(H$_2$O)$_3$]$^{2+}$, [UO$_2$(Acn)$_3$(H$_2$O)$_4$]$^{2+}$, [UO$_2$(Acn)$_3$(H$_2$O)$_5$]$^{2+}$, [UO$_2$(Acn)$_4$(H$_2$O)$_2$]$^{2+}$, and [UO$_2$(Acn)$_5$]$^{2+}$. Of these eleven complexes, five do not have water ligands and only one of the six remaining complexes has more water than acetonitrile. Similarly, the experimentally observed complexes with propionitrile and benzonitrile ligands are [UO$_2$(Pn)$_2$]$_2$$^{2+}$, [UO$_2$(Pn)$_2$(H$_2$O)$_2$]$^{2+}$, [UO$_2$(Pn)$_2$(H$_2$O)$_3$]$^{2+}$, [UO$_2$(Pn)$_2$(H$_2$O)$_4$]$^{2+}$, [UO$_2$(Pn)$_2$(H$_2$O)$_5$]$^{2+}$, [UO$_2$(Pn)$_3$(H$_2$O)$_2$]$^{2+}$, [UO$_2$(Pn)$_3$(H$_2$O)$_3$]$^{2+}$, [UO$_2$(Pn)$_3$(H$_2$O)$_4$]$^{2+}$, [UO$_2$(Pn)$_3$(H$_2$O)$_5$]$^{2+}$, [UO$_2$(Bzn)$_3$(H$_2$O)$_2$]$^{2+}$, [UO$_2$(Bzn)$_3$(H$_2$O)$_3$]$^{2+}$, [UO$_2$(Bzn)$_3$(H$_2$O)$_4$]$^{2+}$, [UO$_2$(Bzn)$_3$(H$_2$O)$_5$]$^{2+}$, and [UO$_2$(Bzn)$_3$]$^{2+}$. Again, there is only one instance for which the water ligands outnumber the nitrile ligands.

For complexes with four or fewer ligands, it is likely that the ligand addition reactions are primarily driven by thermodynamics. However, the binding energies for successive ligand
additions decrease as the number of ligands increases. This is a result of saturating uranyl with electrons donated from each ligand. When more ligands are present, each ligand donates a smaller amount of electron density to uranyl. Examination of Mulliken charges confirms this. As more ligands are added, the change in the charges on the water ligands’ oxygens and the nitrile ligands’ nitrogens relative to those of the bare ligands are smaller than is observed for the first ligands that are added. Additionally, the binding energies indicate that nitrile addition is always favored over water addition. This is not surprising since water is clearly a weaker electron donor than the nitriles. Even though there is a preference for nitrile addition over water addition, the difference in the binding energy of these two ligands relative to each other decreases as the size of the complex grows. For example, the binding energy of the first ligand addition to UO$_2$ to benzonitrile vs water addition differs by 53.8 kcal/mol for benzonitrile vs water addition. This difference decreases to 29.3 kcal/mol if the parent complex is [UO$_2$(Bzn)$_2$]$_2^{2+}$ and to 41.9 kcal/mol if the parent complex is [UO$_2$(H$_2$O)$_2$]$_2^{2+}$. By the fifth ligand addition, the preference for benzonitrile over water is less than 20 kcal/mol. In all cases, addition of benzonitrile leads to a larger (more negative) binding energy. This trend also can be observed for complexes with acetonitrile and propionitrile, although the difference in the binding energies is less pronounced. Thus, there is greater competition between water and the nitriles when the size of the nitrile ligand is reduced. In general, it can be seen that water addition becomes competitive with nitrile addition when the number of nitrile ligands vs the number of water ligands influences the binding energy of the next ligand addition. As the number of water ligands increases, the difference in the binding energy for the next ligand addition also increases. Generally, the increase in binding energy is greater for addition of a nitrile than for water addition. This observation is true regardless of which nitrile ligand is involved, though it is more pronounced as the size of the nitrile ligands grows. Therefore, if a water does happen to add first, formation of complexes with a mixture of both nitriles and water ligands is favored (i.e., nitriles are favored for subsequent additions). However, this effect can be overshadowed by the relatively large magnitude of the binding energies for the first one to three nitrile additions. Therefore, nitrile addition is favored initially, while water addition becomes more competitive as the size of the complex grows.

Figure 6. Relative binding energies (kcal/mol) with the zero-point energy correction for acetonitrile (left arrow) and water (right arrow) additions according to [UO$_2$(Acn)$_m$(H$_2$O)$_n$]$_2^{2+}$ + Acn $\rightarrow$ [UO$_2$(Acn)$_{m+1}$(H$_2$O)$_n$]$_2^{2+}$ and [UO$_2$(Acn)$_m$(H$_2$O)$_n$]$_2^{2+}$ + H$_2$O $\rightarrow$ [UO$_2$(Acn)$_m$(H$_2$O)$_{n+1}$]$_2^{2+}$. Complexes observed in ESI-MS experiments are UO$_2^{2+}$, [UO$_2$(Acn)]$_2^{2+}$, [UO$_2$(Acn)$_2$]$_2^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)]$_2^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)$_2$]$_2^{2+}$, [UO$_2$(Acn)$_2$(H$_2$O)$_3$]$_2^{2+}$, [UO$_2$(Acn)$_3$]$_2^{2+}$, [UO$_2$(Acn)$_3$(H$_2$O)]$_2^{2+}$, [UO$_2$(Acn)$_3$(H$_2$O)$_2$]$_2^{2+}$, and [UO$_2$(Acn)$_4$]$_2^{2+}$.9
Charge-Exchange Reactions

In addition to ligand additions to dicationic species, it has been observed that some of these complexes can undergo charge-exchange (hydrolysis) reactions of the form given in eqs 3 and 4. Reactions of this type have been experimentally observed in the gas phase for complexes involving all three of the nitrile ligands considered here.9 These observations come from the same ESI-MS experiments that produced the ligand addition products discussed earlier.

The experimentally observed products involving acetonitrile ligands are $[\text{UO}_2\text{OH}(\text{Acn})]^{2+}$, $[\text{UO}_2\text{OH}(\text{Acn})(\text{H}_2\text{O})]^{3+}$, $[\text{UO}_2\text{OH}(\text{Acn})_2]^{2+}$, and $[\text{UO}_2\text{OH}(\text{Acn})(\text{H}_2\text{O})_2]^{3+}$. Likewise, complexes with the same RCN:$\text{H}_2\text{O}$ ratio involving propionitrile and benzonitrile have also been experimentally observed, with the exception of $[\text{UO}_2\text{OH}(\text{Bzn})_2]^{2+}$. As was the case for some of the dicatonic complexes, isomers exist for $[\text{UO}_2\text{OH}(\text{RCN})(\text{H}_2\text{O})]^{2+}$ and $[\text{UO}_2\text{OH}(\text{RCN})_2(\text{H}_2\text{O})]^{+}$. The energy differences ($E_{\text{trans}} - E_{\text{cis}}$) between these isomers are given in Table 1. All energy differences are less than 1 kcal/mol with the exception of $[\text{UO}_2\text{OH}(\text{Pn})_2(\text{H}_2\text{O})]^{2+}$ which has a $\Delta E$ of $-1.2$ kcal/mol (a negative energy means that the trans isomer is lower in energy). While these isomers are essentially isoenergetic, note that when two nitrile ligands are involved, a trans arrangement of the nitriles is favored. Due to the bulky nature of the nitrile ligands, this should be expected. However, when the complex contains two water ligands, the cis arrangement is favored.

Reaction energies for the charge-exchange reactions are given in Table 2. For any of these reactions to proceed, uranyl first must have two ligands bound to it, at least one of which must be water. Thus two ligand additions must occur before a charge-exchange reaction is possible. The reaction energies of the charge-exchange reactions tend to be 10–25 kcal/mol less exoergic than the alternative ligand addition reactions (for example, formation of $[\text{UO}_2\text{OH}]^{2+}$ compared to the third ligand addition). Additionally, the exoergicity of the reaction decreases as the size of the nitrile ligand increases. Thus, observation of these monocationic species requires a longer isolation time as the size of the nitrile ligands is increased, as was noted by van Stipdonk et al.9 Moreover, since the exoergicity of ligand addition reactions increases with the size of the ligand and the exoergicity of charge-exchange reactions decreases with increasing ligand size, there is a preference for the formation of monocationic uranyl complexes from dicationic complexes that contain acetonitrile ligands over dicationic complexes containing propionitrile or benzonitrile.

Charge-exchange reactions can proceed via two likely pathways. When the dicationic precursor contains no nitrile ligands, $\text{H}_3\text{O}^+$ is lost, leading to the monocationic complex (eq 3 is the only possible pathway). When two water ligands are present in the precursor, the charge-exchange reaction can be competitive with the ligand addition reaction. As for ligand additions, an increase in the size of the precursor ion leads to a decrease in the exoergicity of the charge-exchange reaction. When $\text{H}_2\text{O}^+$ is lost in the charge-exchange reaction (eq 3), the reaction energy becomes endoergic when four or more ligands are present in the precursor ion. This endoergicity then increases as the size of the precursor ion grows. A more thermodynamically favorable pathway involves the loss of a protonated nitrile...
The reaction energy of protonated nitrile elimination reactions is more competitive than the pathway with ligand addition reactions. The reaction energy for the loss of \((\text{H}^+ + \text{RCN})^+\) is approximately 15 kcal/mol lower than the reaction energy for the loss of \(\text{H}_3\text{O}^+\). This makes the charge-exchange reaction via loss of \((\text{H}^+ + \text{RCN})^+\) sufficiently exoergic for charge-exchange reactions to be competitive with ligand addition reactions. Despite this, the reaction energy of ligand additions is always more exoergic than the energy of charge-exchange reactions. Additionally, while pathways that lose \(\text{H}_3\text{O}^+\) become endoergic when the precursor ion has four or more ligands, the pathway that loses \((\text{H}^+ + \text{RCN})^+\) is still exoergic even when the precursor ion has five ligands (with the exception of \([\text{UO}_2\text{OH}(\text{Bzn})_5]^+\)).

The fact that hydrated uranyl complexes can undergo hydrolysis reactions should come as no surprise. It is well-known that metal cations are acidic species. Unfortunately, experimental and theoretical data for uranyl induced hydrolysis is scarce. The hydration of one water ligand from uranyl(VI) hydrate has previously been studied with QM/MM simulations, and hydrolysis products with multiple hydroxide ligands have also been examined in both the gas phase and with a polarizable continuum. However, hydrolysis studies of a single uranyl dication with an unsaturated coordination sphere are lacking, though the current results are consistent with trends noted for main group and transition metals. These reactions have been experimentally observed in the gas phase rather than in solution, though hydrolysis of only one water ligand has been observed in these cases. While the reactions modeled here represent gas phase results, microsolvation via inclusion of water ligands can account for some of the solvation effects. Thus, these results can be used to predict general trends in solution, though variation of the pH will also have a substantial influence.

Once a monocationic complex is formed, it can undergo further ligand addition reactions. Binding energies for these reactions can be found in Figures 9–11. In general, ligand additions to monocationic complexes exhibit the same trends as the ligand additions to dicationic complexes. Addition of a nitrile ligand is always thermodynamically favored over water addition, and the exoergicity of the nitrile addition increases with increasing size (\(\text{Acn} < \text{Ph} < \text{Bzn}\)). Unlike the previous ligand addition reactions, though, water is much more competitive with nitrile additions to a monocationic species. The largest difference occurs with the first addition of benzonitrile to \([\text{UO}_2\text{OH}]^+\) compared to the first addition of water. In this case the addition of benzonitrile is favored by 11.4 kcal/mol, whereas the first addition of benzonitrile to \(\text{UO}_2^{2+}\) is 53.8 kcal/mol more exoergic than the first water addition. The difference in binding...
energy between addition of acetonitrile or propionitrile is $\sim 3$ kcal/mol, while the difference in binding energy between the addition of acetonitrile or benzonitrile is up to 6 kcal/mol. As with ligand additions to dicationic complexes, the exoergicity

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<th>Reaction</th>
<th>$[\text{UO}_2(\text{H}_2\text{O})_2]^{2+} \rightarrow [\text{UO}_2\text{OH}]^{+} + \text{H}_2\text{O}^+$</th>
<th>$[\text{UO}_2(\text{H}_2\text{O})_3]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})]^{+} + \text{H}_2\text{O}^+$</th>
<th>$[\text{UO}_2(\text{H}_2\text{O})_4]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})_2]^{+} + \text{H}_2\text{O}^+$</th>
<th>$[\text{UO}_2(\text{H}_2\text{O})_5]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})_3]^{+} + \text{H}_2\text{O}^+$</th>
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<td>Reaction</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})_2(L)]^{2+} \rightarrow [\text{UO}_2\text{OH}(L)]^{+} + \text{H}_2\text{O}^+$</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})_3(L)]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})(L)]^{+} + \text{H}_2\text{O}^+$</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})_4(L)]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})(L)_2]^{+} + \text{H}_2\text{O}^+$</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})_5(L)]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})(L)_3]^{+} + \text{H}_2\text{O}^+$</td>
</tr>
<tr>
<td>Reaction</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})(L)]^{2+} \rightarrow [\text{UO}_2\text{OH}]^{+} + (\text{H} + \text{L})^+$</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})(L)_2]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})(L)]^{+} + (\text{H} + \text{L})^+$</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})(L)_3]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})(L)_2]^{+} + (\text{H} + \text{L})^+$</td>
<td>$[\text{UO}_2(\text{H}_2\text{O})(L)_4]^{2+} \rightarrow [\text{UO}_2\text{OH}(\text{H}_2\text{O})(L)_3]^{+} + (\text{H} + \text{L})^+$</td>
</tr>
</tbody>
</table>

* Reaction energies include the zero-point energy correction.
of the addition increases according to Acn < Pn < Bzn. Since the difference in binding energies of monocationic ligand additions is much smaller than it is with ligand additions to dicationic complexes, the type of nitrile ligand should have a minimal impact on the reactions observed. However, experimental observations show that formation of monocationic complexes with acetonitrile are favored over those with propionitrile and benzonitrile. The reason for this is apparent from the charge-exchange reaction energies. The propensity of a precursor ion to undergo charge exchange is related to the type of nitrile ligands present in the precursor according to Acn > Pn > Bzn; e.g., complexes with smaller nitrile ligands are more likely to undergo charge-exchange reactions. Once the charge-exchange process is completed, ligand addition to the monocationic species can occur just as it does with dicationic complexes. As with the dicationic ligand addition reactions, the ratio of nitrile ligands to water ligands influences the binding energy of subsequent ligand additions. In nearly all cases, more water ligands in the precursor will increase the tendency of the next ligand added to be a nitrile.

**Conclusion**

Reactions involving dicaticionic uranyl complexes with both water and nitrile (acetonitrile, propionitrile, and benzonitrile) ligands have been examined. These include charge-exchange reactions, whereby a dicaticionic complex is reduced to a monocationic complex, addition of ligands to the dicaticionic complexes, and addition of ligands to the monocationic complexes. While many of the complexes presented here have been experimentally observed, the inclusion of all the other possible products has enabled a thorough study of the processes observed experimentally. These results help shed light on some of the possible products of those reactions that have not been observed. Additionally, mass spectrometry studies are unable to distinguish between isomers. In some cases this may be a significant disadvantage. However, the computational results presented here show that, in general, the possible isomers of interest are isoenergetic. Therefore, it is expected that they would be formed in nearly equal proportions.
The predominant reaction pathway in this study is ligand addition. It has been shown that ligand addition reactions are always thermodynamically favored as long as the equatorial coordination number is less than five for dicaticonic complexes and less than four for moncaticonic complexes. Addition of more ligands is generally either endoergic or the exoergicity of the reaction is small enough that thermodynamics alone is not enough to drive the reaction forward. The addition of a water ligand versus a nitrile ligand is influenced by the ratio of nitrile ligands to water ligands in the precursor ion. When there is a predominance of water ligands, the binding energy for the next ligand addition becomes more exoergic than if the precursor ion contains primarily nitrile ligands. This has a greater effect on the binding energies of nitrile additions than it does on water additions. Therefore, the tendency to add a nitrile ligand is enhanced when the precursor ion contains predominantly water ligands. This effect occurs for ligand additions to both the dicaticonic and the moncaticonic species and can explain the large number of dicaticonic complexes with mainly nitrile ligands observed experimentally.9

In addition to ligand addition reactions, charge-exchange or hydrolysis reactions of the form of eqs 3 and 4 have been examined. These reactions involve at least two ligands, and water must be one of them. While it is not clear if both ligands must be bound to UO22+, the energies of the end points of the reactions are unchanged. The reaction energies of the charge-exchange reactions indicate that they are thermodynamically competitive with the third ligand addition to dicaticonic precursor ions, although they are less exoergic than the third ligand addition. Charge-exchange reactions are still exoergic when the precursor ion has many ligands, but only if the reaction proceeds via eq 4 (loss of (H + RCN)+) rather than by eq 3 (loss of H2O2+). Once the complex is reduced to a monocation, it can then proceed with subsequent ligand additions. As with ligand additions to dicaticonic complexes, nitrile addition is favored when ligands are added to monocaticonic complexes. However, the difference in binding energies between a nitrile and water—and even among the nitriles themselves—is diminished when added to monocaticonic species. Thus, water becomes more competitive when added to monocaticonic complexes than it is when added to dicaticonic complexes. This tendency, along with the initial depletion of dicaticonic complexes that contain water through the charge-exchange process, helps explain the tendency of monocaticonic species to be observed with a larger proportion of water ligands than are observed with dicaticonic species.9

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Supporting Information Available: Atomic coordinates for the optimized geometries, complete set of vibrational frequencies (and their descriptions) in the 800–2500 cm−1 range, and raw calculated energies. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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