

Density Functional Studies on the Complexation and Spectroscopy of Uranyl Ligated with Acetonitrile and Acetone Derivatives[†]

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Received: April 27, 2009; Revised Manuscript Received: June 9, 2009

The coordination of nitrile (acetonitrile, propionitrile, and benzonitrile) and carbonyl (formaldehyde, acetaldehyde, and acetone) ligands to the uranyl dication (UO_2^{2+}) has been examined using density functional theory (DFT) utilizing relativistic effective core potentials (RECPs). Complexes containing up to six ligands have been modeled in the gas phase for all ligands except formaldehyde, for which no minimum could be found. A comparison of relative binding energies indicates that 5-coordinate complexes are predominant, while 6-coordinate complexes involving propionitrile and acetone ligands might be possible. Additionally, the relative binding energy and the weakening of the uranyl bond is related to the size of the ligand, and in general, nitriles bind more strongly to uranyl than carbonyls.

Introduction

Understanding the chemical properties of uranium species in the environment is a key issue for the U.S. Department of Energy: to understand speciation in waste tanks at nuclear weapons production sites and to understand the transport of actinides in the subsurface environment. Uranium generally exists as a uranyl dication (UO_2^{2+}) that can readily form complexes with various anions. The uranyl chemistry is dependent on pH and available anions, and multiple species can often exist in equilibrium. Uranyl species can also interact with mineral surfaces and form new species or undergo redox processes. This complex chemistry complicates the interpretation of experimental measurements.

Molecular-scale modeling using computational chemistry methodologies, combined with experimental observations, has been demonstrated to provide a fundamental understanding of the complex chemistry of actinides in the condensed phase. Over the years various computational studies on model systems, with or without the inclusion of an approximate description of the molecule's environment, have been reported in the literature.^{1–7} For example, in our recent computational modeling study of gas-phase uranyl carbonate, nitrate, and acetate complexes⁸ we showed that the calculated structures and vibrational frequencies are in generally good agreement with experimental data obtained in the solution and solid-state environment.

One of the key issues in computational chemistry is the validation of the basic methodologies and calculated results for molecules. For uranyl complexes, we have relied on highly accurate benchmark calculations on the free uranyl in lieu of available experimental data.^{9–11} Over the last couple of years, Groenewold and co-workers published results of measurements on various uranyl complexes in the gas phase.^{12–17} These experiments provide the computational chemistry community with a wealth of experimental benchmark data that can be used

as a proving ground for the current computational methodologies and to improve upon them. In a series of joint experimental and computational papers^{13,18–21} it was shown that vibrational stretching frequencies of the actinide species and the relative energetics calculated with density functional theory (DFT) are in good agreement with experimental data.

This paper reports the results of ab initio calculations on acetonitrile and its derivatives propionitrile and benzonitrile and acetone and its derivatives acetaldehyde and formaldehyde. In their gas-phase experiments of the nitrile series, Van Stipdonk et al.¹² were able to isolate the $[\text{UO}_2(\text{L})_n]^{2+}$ complexes (with $n = 1–5$ for acetonitrile and $n = 2–5$ for propionitrile and benzonitrile), and they studied the intrinsic reactions with water molecules. From acetonitrile to benzonitrile, the ligands have an increased capability to donate electron density to the uranyl. Similarly, by eliminating the methyl groups on acetone, the electron-donating capability is reduced, which should be reflected in the structure and vibrational spectroscopy of uranyl. The vibrational spectra of the uranyl acetone complexes in the gas-phase have been measured, whereas those of the acetaldehyde and formaldehyde complexes have not. The reaction of formaldehyde with uranium has been studied experimentally by Gibson et al.,²² while Senanayake et al. studied the reaction on the surface of UO_2 crystals.²³ We will present the coordination, vibrational frequencies, and the binding and dissociation energetics of the $[\text{UO}_2(\text{L})_n]^{2+}$ ($n = 1–6$, L = formaldehyde (Form), acetaldehyde (Aca), acetone (Ace), acetonitrile (Acn), propionitrile (Pn), and benzonitrile (Bzn)) complexes. These results provide the groundwork for a subsequent study on the reaction of water molecules with these species, which will enable the direct comparison of our calculations with the previous mentioned gas-phase experiments.

Details of the Calculations

All calculations were performed with the NWChem software suite^{24,25} using DFT. The choice of functional and basis sets is based on a previous systematic study where fully relativistic coupled cluster singles and doubles with perturbative triples (CCSD(T)) benchmark calculations on UO_2^{2+} were compared

[†] Part of the "Russell M. Pitzer Festschrift".

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TABLE 1: Calculated Uranyl U=O and C=N Bond Lengths (in Å) and Associated Stretching Frequencies (in cm⁻¹) of the Acetonitrile, Propionitrile, and Benzonitrile Complexes

molecular complex	U=O bond length	UO ₂ symmetric stretch	UO ₂ asymmetric stretch	C=N bond length	C=N stretch
[UO ₂] ²⁺	1.702	1028	1131		
acetonitrile				1.161	2320
1-Acn	1.722	986	1084	1.175	2216
2-Acn	1.735	960	1053	1.168	2253 (a), 2271 (s)
3-Acn	1.745	941	1031	1.164	2284 (a), 2284 (a), 2299 (s)
4-Acn	1.754	923	1011	1.162	2301 (a), 2302 (a), 2302 (a), 2314 (s)
5-Acn	1.759	914	1001	1.160	2319 (a), 2319 (a), 2321 (a), 2321 (a), 2330 (s)
6-Acn	1.761	892	977	1.159	2329 (a), 2330 (a), 2330 (a), 2331 (a), 2331 (a), 2337 (s)
propionitrile				1.161	2309
1-Pn	1.724	974	1078	1.177	2171
2-Pn	1.737	955	1048	1.170	2225 (a), 2244 (s)
3-Pn	1.747	938	1027	1.166	2261 (a), 2261 (a), 2278 (s)
4-Pn	1.756	922	1007	1.163	2281 (a), 2282 (a), 2282 (a), 2295 (s)
5-Pn	1.760	913	997	1.161	2302 (a), 2302 (a), 2304 (a), 2304 (a), 2314 (s)
6-Pn	1.767	891	974	1.160	2315 (a), 2315 (a), 2315 (a), 2316 (a), 2316 (a), 2322 (s)
benzonitrile				1.164	2289
1-Bzn	1.733	958	1058	1.183	2121
2-Bzn	1.747	931	1027	1.177	2182 (a), 2196 (s)
3-Bzn	1.755	916	1010	1.172	2221 (a), 2221 (a), 2241 (s)
4-Bzn	1.763	905	993	1.169	2241 (a), 2245 (a), 2245 (a), 2266 (s)
5-Bzn	1.766	898	984	1.165	2267 (a), 2267 (a), 2272 (a), 2272 (a), 2287 (s)
6-Bzn	1.770	883	968	1.163	2286 (a), 2287 (a), 2287 (a), 2289 (a), 2289 (a), 2297 (s)

to various DFT functionals and basis set choices.¹⁰ The local density approximation (LDA)^{26,27} was used to determine the structures and frequencies, and energies were calculated using the B3LYP^{28,29} functional at the LDA optimized geometry. For uranium the small core Stuttgart relativistic effective core potential (RECP) and associated Stuttgart orbital basis set^{30–32} was employed, whereas for all other atoms (O, C, H, and N) the valence triple- ζ plus polarization (TZVP)³³ DFT optimized basis sets were used. In all cases, spherical functions were employed. Hessian calculations were performed for each optimized structure to verify the structures as minima and to obtain zero point energies and frequencies. Molecular orbital pictures were obtained from canonical orbitals calculated at the LDA optimized geometry using the B3LYP functional. All molecular orbitals were plotted with an isovalue of 0.0178. Molecular and orbital analysis as well as image production was performed using Ecce³⁴ and MacMolPlt.³⁵

Results and Discussion

In this study, complexation of UO₂²⁺ with nitrile and carbonyl ligands was examined with the coordination number ranging from 1 through 6. A few of the key geometrical parameters and frequencies are given in Table 1, and full information is available as Supporting Information. In general, the nitrogens of the nitrile ligands tend to lie in the equatorial plane. When the ligands are not linear, they tend to lie parallel to the O–U–O axis. The smallest of the nitrile ligands studied, acetonitrile, experiences little distortion from this arrangement when multiple ligands are present. When there are five or fewer ligands, the N–U–O bond angle is always nearly 90°, and the N–C–C backbone of acetonitrile lies in the equatorial plane. The

N–U–N angles are always evenly spaced with the 3-coordinate complex having a N–U–N angle of 120°, the 4-coordinate complex 90°, and the 5-coordinate complex 72°. The 2-coordinate complex, however, is an exception with a N–U–N angle of 104°. This arrangement of acetonitrile in the 2-coordinate complexes allows both the p_x and the p_y orbitals on uranium to effectively bind with both N s orbitals (Figure 1).

Like acetonitrile, propionitrile and benzonitrile also form 90° N–U–O bond angles. Likewise, the 2-coordinate complexes also exhibit a N–U–N angle less than 180°. The ethyl groups on propionitrile are free to rotate about the single bond between the nitrogen and the α carbon. This rotation is essentially a free rotor with energy differences of <1 kcal/mol between the ethyl group pointing up or down for each propionitrile. Additionally, while the benzonitriles' nitrogens lie in the equatorial plane, the plane of the phenyl groups lies parallel to UO₂²⁺.

When there are six nitrile ligands present, the structures exhibit significant differences from the smaller complexes. The ligands of these complexes no longer lie in the equatorial plane. Rather, repulsion between adjacent ligands forces acetonitrile and propionitrile to deviate from the equatorial plane by 11°, with ligands lying alternately above and below the equatorial plane. The complex containing six benzonitriles also exhibits a similar distortion. However, the deviation from the equatorial plane is slightly less pronounced and ranges from 9° to 10°.

Since the nitrogen in the ligands has a lone pair of electrons capable of donation to the electron-deficient uranium, it is not surprising that the nitrile ligands have an affinity for uranium, and indeed, electron donation to the metal center does occur. The evidence for this is apparent in the molecular orbitals as well as in the changes in the structure of uranyl. The

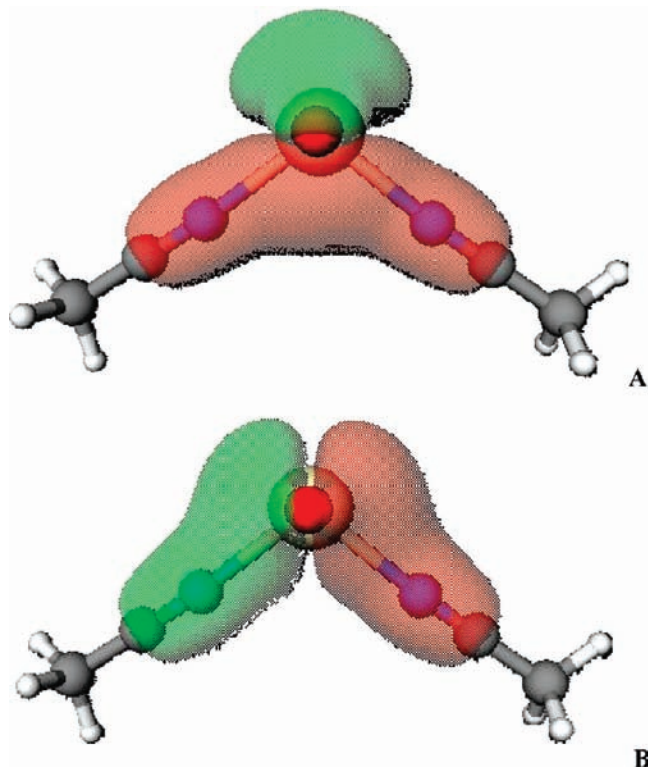


Figure 1. U–N σ bonds in $[\text{UO}_2(\text{Acn})_2]^{2+}$ between U p_x and N s orbitals (HOMO–24) (A) and U p_y and N s orbitals (HOMO–25) (B). Uranium is colored gold, oxygen red, nitrogen blue, carbon gray, and hydrogen white.

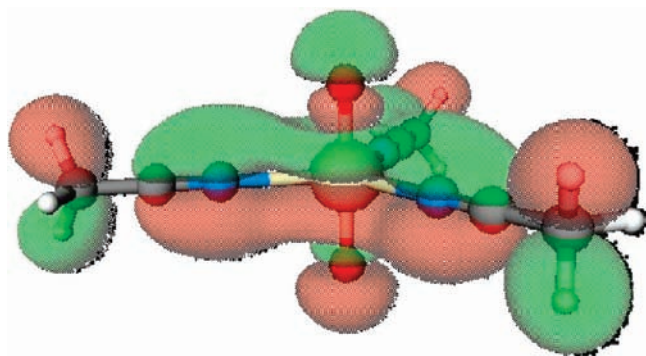


Figure 2. U–N bond in $[\text{UO}_2(\text{Acn})_3]^{2+}$ (HOMO–6) via N p_z donation to U f_z .

3-coordinate acetonitrile complex provides a characteristic example of such a U–N bond (Figure 2). Here, electron density is donated from the C–N π_z to the U $5f_z$ orbital. This bonding scheme recurs with all of the nitrile complexes studied. Addition of ligands to uranyl and the associated electron donation cause an increase in the uranium–oxygen bond length in UO_2^{2+} . It can be seen in Table 1 that the addition of nitrile ligands to uranyl red-shifts both the symmetric and the asymmetric stretching frequencies for UO_2^{2+} by nearly $136\text{--}145\text{ cm}^{-1}$ and by $154\text{--}163\text{ cm}^{-1}$, respectively, by the sixth ligand addition. The red-shift in the UO_2^{2+} stretching frequencies and the increase in the U–O bond lengths are an indication of a weakening of the U–O bond strength, in agreement with the observations of McGlynn et al.³⁶ These effects become more pronounced as the size of the ligand increases. This phenomenon is a result of the nitriles' ability to shift electron density to stabilize donation of electron density from nitrogen to uranium, and the conjugated π system in benzonitrile has the greatest ability to facilitate such a shift in electron density. Additionally,

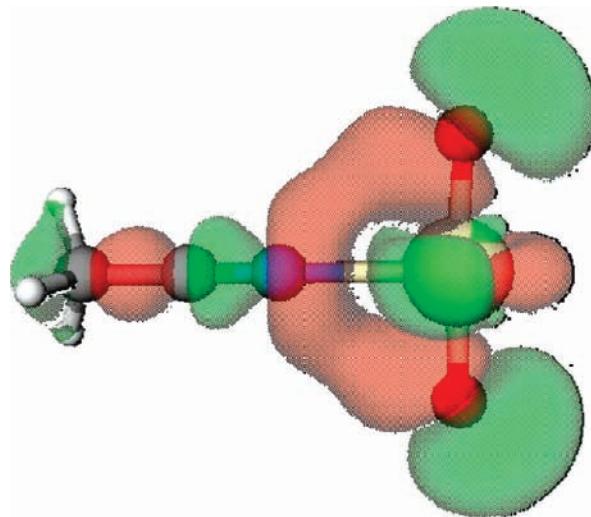


Figure 3. Bond between N p and O p orbitals on uranyl $[\text{UO}_2(\text{Acn})_2]^{2+}$ (HOMO–3).

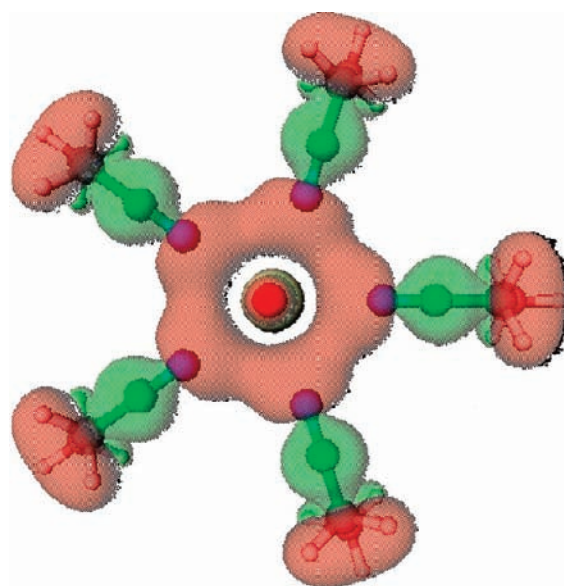


Figure 4. Bonding interaction of adjacent ligands via N s orbitals and antibonding to U s in $[\text{UO}_2(\text{Pn})_5]^{2+}$ (HOMO–45).

the strength of the CN bond in the ligands is reduced upon addition to uranyl. There is a noticeable change in the CN bond length upon the first addition of a ligand (increases by 0.014 \AA for acetonitrile, 0.016 \AA for propionitrile, and 0.019 \AA for benzonitrile). Likewise, the CN stretching frequencies decrease by $104\text{--}168\text{ cm}^{-1}$ upon the first ligand addition. The changes in both the CN bond length and the stretching frequencies reflect the fact that the ligand donates electrons to uranium, thereby diminishing the strength of the CN bonds. As with the UO_2^{2+} stretching frequencies, the change is greater for the larger ligands. This effect diminishes as the number of ligands increases until the sixth addition when the CN bond length recovers to within 0.002 \AA of its bond length in the bare nitrile molecule, indicating a reduction in electron donation per ligand to uranyl from the individual ligands as more ligands are added.

There are also two other notable bonding interactions that frequently occur in these nitrile species. In these cases an additional bonding interaction occurs between a p orbital on the nitrogen and the p orbitals on the uranyl oxygens (Figure 3). Additionally, the p orbitals on adjacent nitrogens exhibit a substantial overlap resulting in a ring of electron density around

TABLE 2: Calculated Uranyl U=O and C=O Bond Lengths (in Å) and Associated Stretching Frequencies (in cm^{-1}) of the Acetone, Acetaldehyde, and Formaldehyde Complexes^a

molecular complex	U=O bond length	UO ₂ symmetric stretch	UO ₂ asymmetric stretch	C=O bond length	C=O stretch
[UO ₂] ²⁺	1.702	1028	1131		
formaldehyde				1.206	1780
1-Form	1.721	988	1087	1.240	1615
2-Form	1.735	960	1054	1.236	1655 (a), 1663 (s)
3-Form	1.746	939	1030	1.232	1683 (a), 1683 (a), 1693 (s)
4-Form	1.755	920	1010	1.227	1706 (a), 1706 (a), 1706 (a), 1721 (s)
5-Form	1.758	915	1004	1.227	1710 (a), 1710 (a), 1710 (a), 1710 (a), 1719 (s)
acetaldehyde				1.212	1790
1-Aca	1.725	980	1077	1.269	1533
2-Aca	1.740	948	1042	1.256	1597 (a), 1614 (s)
3-Aca	1.752	914, 928	1016	1.248	1640 (a), 1640 (a), 1663 (s)
4-Aca	1.762	903, 918	995	1.240	1671 (a), 1675 (a), 1675 (a), 1701 (s)
5-Aca	1.765	898, 915	989	1.239	1682 (a), 1682 (a), 1683 (a), 1683 (a), 1702 (s)
6-Aca	1.784	848	934	1.237	1685 (a), 1685 (a), 1686 (a), 1690 (a), 1690 (a), 1709 (s)
acetone				1.219	1767
1-Ace	1.728	972	1070	1.290	1455
2-Ace	1.745	938	1033	1.271	1536 (a), 1560 (s)
3-Ace	1.757	915	1005	1.259	1593 (a), 1593 (a), 1623 (s)
4-Ace	1.766	899	986	1.252	1626 (a), 1631 (a), 1631 (a), 1660 (s)
5-Ace	1.779	858, 859, 860, 867	948	1.249	1625 (a), 1629 (a), 1638 (a), 1648 (a), 1672 (s)
6-Ace	1.792	823	909	1.247	1641 (a), 1642 (a), 1642 (a), 1649 (a), 1650 (a), 1671 (s)

^a Multiple UO₂ symmetric stretches observed for three to five acetaldehydes and five acetones are the result of coupling to C–C stretches in the acetaldehyde and acetone ligands.

uranium. Generally, this molecular orbital is antibonding with uranium (Figure 4).

The highest occupied molecular orbitals (HOMOs) of the nitrile complexes resemble the HOMOs of the bare ligands. Likewise, most of the other higher energy occupied orbitals are localized on the ligands. Thus, these orbitals are not responsible for bonding between the uranyl and the ligands. The bonding interactions noted above tend to be the result of lower-lying orbitals.

The other class of ligands in this study is carbonyls, in particular, formaldehyde, acetaldehyde, and acetone. These exhibit much the same characteristics as the nitrile ligands with selected information given in Table 2. As with the nitrile complexes, the bonding interactions result from lower-lying orbitals, and the highest energy orbitals tend to be localized on the ligands. In general, the oxygens from the carbonyl ligands lie in the equatorial plane. However, the ligands themselves are oriented perpendicular to UO₂²⁺. This is in contrast to the tendency of the nitriles to lie parallel to the O–U–O axis.

The smallest of the carbonyls studied is formaldehyde. In most cases formaldehyde is oriented such that the U–O–C angle is 180°. The 5-coordinate complex, however, has a U–O–C angle of 141° in the equatorial plane. The Mulliken charge on the hydrogen nearest the adjacent ligand's oxygen is 0.016e⁻ less positive than the other hydrogen. This, together with the structural features, suggests that hydrogen bonding may occur (Figure 5). Unlike the other systems studied, no 6-coordinate complex containing formaldehyde ligands could be found. If a sixth formaldehyde is placed in the equatorial plane with the plane of formaldehyde perpendicular to UO₂²⁺, it is moved outside of the coordination sphere during the geometry opti-

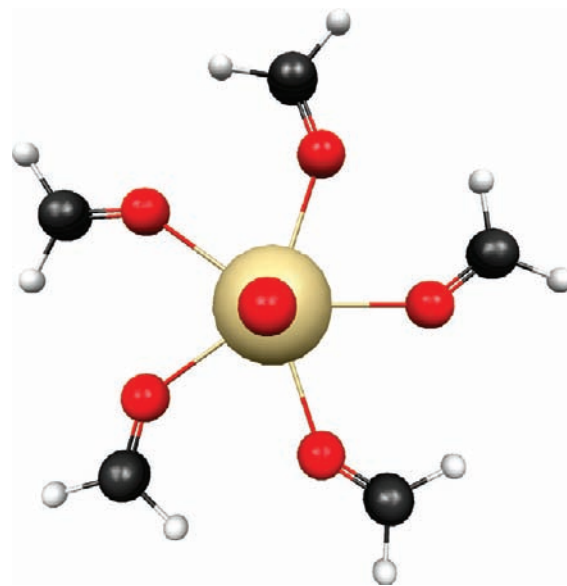


Figure 5. Formaldehydes in [UO₂(CH₂O)₅]²⁺ form 141.1° U–O–C angles. The H–O distance between adjacent formaldehydes is 2.478 Å, and the C–H–O angle is 108.4°, suggesting the possibility of hydrogen bond formation.

mization. Also, if a sixth formaldehyde is added with the plane of formaldehyde parallel to UO₂²⁺, it remains in the coordination sphere. However, a Hessian calculation on this complex produces an imaginary frequency corresponding to the motion of this formaldehyde out of the coordination sphere.

The structures of the acetaldehyde and acetone complexes are similar to those of the formaldehyde complexes. While

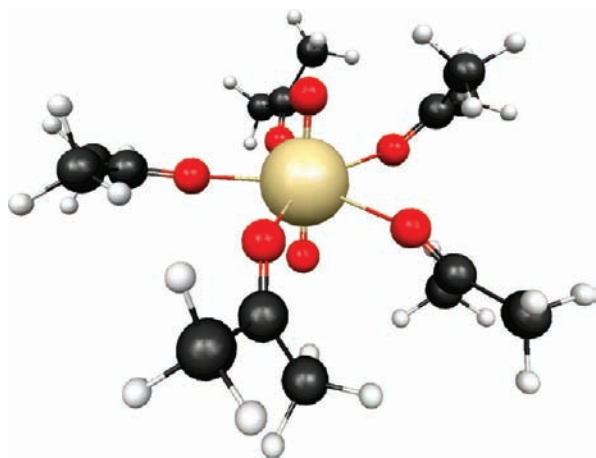
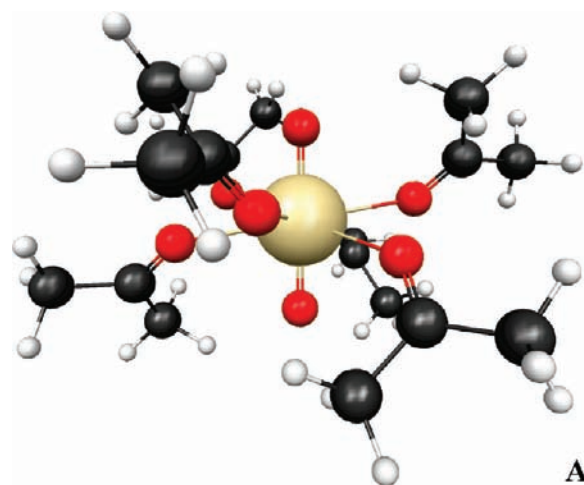


Figure 6. $[\text{UO}_2(\text{Ace})_5]^{2+}$ perspective view. While acetones' oxygens remain in the equatorial plane, the plane of the acetones is rotated $7\text{--}26^\circ$ with respect to the equatorial plane.

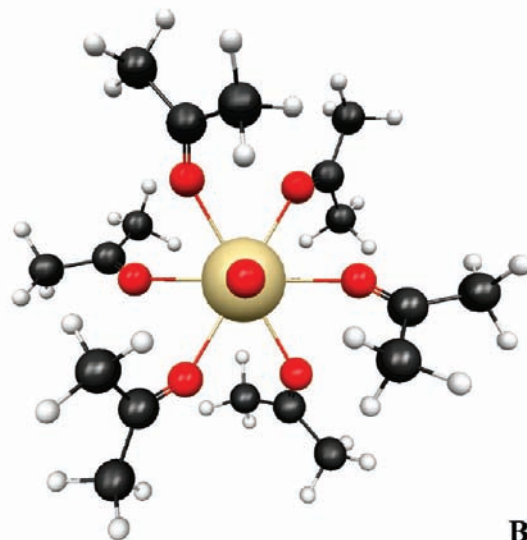
formaldehyde generally is oriented with a $\text{U}\text{--}\text{O}\text{--}\text{C}$ angle of 180° , acetaldehyde and acetone deviate from this angle by up to 5° when there are three or fewer ligands. With four ligands, the $\text{U}\text{--}\text{O}\text{--}\text{C}$ angle decreases to 169° for acetaldehyde and 155° for acetone, and the addition of a fifth ligand decreases this angle further to 139° for acetaldehyde. These ligands tend to arrange such that the oxygens and carbon backbone lie in the equatorial plane and the methyl groups in acetaldehyde point either all clockwise or all counterclockwise. Likewise, acetone's two methyl groups also lie in the equatorial plane.

The remaining complexes are the 5-coordinate acetone complex and the 6-coordinate acetaldehyde and acetone complexes. The proximity of these ligands' methyl groups to the oxygen causes distortions in the geometry due to steric effects. With five acetones, the plane of each ligand is rotated $7\text{--}26^\circ$ from the equatorial plane (Figure 6). The acetones in $[\text{UO}_2(\text{Ace})_6]^{2+}$ cannot all lie in the equatorial plane (Figure 7). The oxygens deviate from this plane by 9° and alternate above and below the equatorial plane. Additionally, the carbon backbone of acetone alternates between 41° and -41° relative to UO_2^{2+} . Another notable feature of this complex is that a methyl group from each acetone is oriented such that one of the hydrogens points toward an axial oxygen on UO_2^{2+} with an $\text{O}\text{--}\text{H}$ distance of 2.245 \AA . Similarly, six acetaldehydes are too bulky to lie in the equatorial plane. Thus, they orient themselves $20.0^\circ \pm 0.6^\circ$ relative to UO_2^{2+} (the $\text{U}\text{--}\text{O}\text{--}\text{C}\text{--}\text{C}$ dihedral angle) and alternate pointing up and down (Figure 8).

The bonding in the carbonyl complexes is akin to the nitriles. For example, all of the 2-coordinate carbonyls, especially formaldehyde and acetaldehyde, bond in a similar manner to that depicted in Figure 1, resulting in an angle of $<120^\circ$ between adjacent ligands. Additionally, when there are four or five ligands, the CO groups on adjacent ligands are sufficiently close that they exhibit a significant overlap, leading to a ring of electron density around uranium. The resulting molecular orbital resembles the one in Figure 4. Primarily, bonding interactions with uranium occur via an electron donation from the CO group to a p orbital on uranium and by overlap of a carbonyl O p orbital with a U s orbital. These two bonding scenarios lead to a decrease in the uranyl $\text{U}\text{--}\text{O}$ bond strength. This can be seen in the increase in $\text{U}\text{--}\text{O}$ bond length and the decrease in the $\text{U}\text{--}\text{O}$ stretching frequencies (Table 2). The changes in the UO_2^{2+} stretching frequencies are more pronounced with carbonyl ligands than with nitriles. Here, the symmetric stretch is red-shifted by $113\text{--}205 \text{ cm}^{-1}$, and the asymmetric stretch is red-



A



B

Figure 7. $[\text{UO}_2(\text{Ace})_6]^{2+}$ perspective view (A) and top view (B). The acetones' oxygens alternate 9° above and below the equatorial plane, and the plane of acetone's carbon backbone is rotated $\pm 40.9^\circ$ relative to the UO_2^{2+} axis. Methyl groups on each acetone are oriented such that one of the hydrogens points toward an axial oxygen in UO_2^{2+} . This $\text{O}\text{--}\text{H}$ distance is 2.245 \AA , suggesting hydrogen bonding.

shifted by $127\text{--}222 \text{ cm}^{-1}$. The largest changes occur with acetone, the largest carbonyl studied. As with the $\text{C}\text{--}\text{N}$ stretches earlier, the $\text{C}\text{--}\text{O}$ stretching frequencies exhibit a substantial red-shift of up to 312 cm^{-1} upon addition of the first ligand. Unlike the nitriles, however, the $\text{C}\text{--}\text{O}$ stretch never fully recovers, even after the addition of a sixth ligand.

Optimized geometries have been obtained for all complexes (both nitrile and carbonyls) with up to six ligands with the exception of formaldehyde complexes. Examination of the relative binding energies, however, indicates that some of these structures are not energetically favorable (Tables 3 and 4). Addition of all ligands is exothermic up to the fifth ligand addition. This is in agreement with other experimental and computational results.^{1,3,4,6} For most ligands, however, the sixth addition is endothermic. The exceptions here are propionitrile and acetone, which have a relative binding energy of 1.8 kcal/mol and 2.7 kcal/mol for the sixth addition, respectively. Additionally, the sixth benzonitrile addition is predicted to be endothermic by 0.8 kcal/mol . This value is quite small and does not necessarily prohibit the formation of $[\text{UO}_2(\text{Bzn})_6]^{2+}$, considering the accuracy of the energetics coming from the DFT methodology used in this work. The process by which these complexes are formed in the experiments is energetic, and

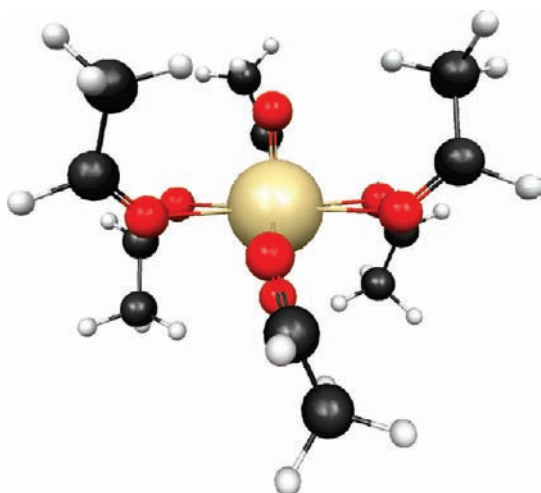


Figure 8. $[\text{UO}_2(\text{Aca})_6]^{2+}$ perspective view. Acetaldehyde ligands alternate pointing up and down. The U—O—C—C dihedral angle is $20.0^\circ \pm 0.6^\circ$.

considering the weak binding energy, it is not surprising that these two complexes were not observed.⁴

The changes in the UO_2^{2+} stretching frequencies for the carbonyl and nitrile ligands seem to indicate that carbonyls are more capable of donating electrons to uranyl. One might expect, then, that they would bind more strongly to uranyl than to the nitrile ligands. This, however, is not the case. Examination of the relative binding energies for the first ligand addition indicates the overall relative strength of the ligands is formaldehyde < acetonitrile < acetaldehyde < propionitrile < acetone < benzonitrile. Thus, the nitrile ligands generally have a greater affinity for uranyl. Additionally, the relative binding energies indicate that a ligand's strength is directly related to its size for both the carbonyl series and the nitrile series. In general, addition of a methyl group to a ligand increases its capacity to donate electrons to uranyl, and

the addition of large delocalized systems, as in benzonitrile, has an even greater effect on the ligand's affinity for uranyl.

Mulliken charges offer additional insight into the changes in electronic structure. Normally, one would expect the charge on uranium to largely decrease as ligands are added. While this reduction in charge occurs, it is not as dramatic as expected. The change in charge on uranium from the bare uranyl ion to a complexed ion with five to six ligands is less than $0.5e^-$. Thus, uranium maintains roughly a +2 charge. The electron density donated from the ligands tends to reside on the axial oxygens, each changing by $-0.2e^-$ to $-0.3e^-$ from the bare uranyl ion to a fully complexed ion. Additionally, while the nitriles' nitrogens and the carbonyls' oxygens conduct this transfer of electron density to uranyl, their Mulliken charges are relatively unaffected. These atom's charges change by $<-0.1e^-$ throughout the additions. The bulk of the donated electron density comes from the carbon backbone of the ligands. While the charge on each carbon changes by about $0.1-0.2e^-$, this adds up to a significant capacity to donate electron density as the number of carbons increases. Thus the role of the uranium and the ligands' nitrogens or oxygens is simply to conduct a shift in electron density from the ligands' carbon backbone to uranyl's axial oxygens.

Some of the complexes with acetone and acetonitrile have been experimentally observed by Groenewold et al., and their vibrational frequencies have been measured.¹³ The trends in the calculated frequencies are in agreement with their results for both the acetone and the acetonitrile series. However, some of the larger complexes presented here have not been observed. Uranyl ligated with up to four acetones and up to five acetonitriles has been observed, while the complexes with five and six acetones and six acetonitriles were not observed in the aforementioned study. This is a result of the weak binding energy of the larger complexes. The binding energy for the fourth addition of acetone is 30.8 kcal/mol, and the binding energy for the fifth addition of acetonitrile is 25.7 kcal/mol, while the binding energy for the next addition drops to 12.7 kcal/mol for acetone and -3.9 kcal/mol for acetonitrile. In another study

TABLE 3: B3LYP Dissociation and Relative Binding Energies (in kcal/mol) for the Uranyl Acetonitrile, Propionitrile, and Benzonitrile Complexes^c

<i>n</i>	acetonitrile		propionitrile		benzonitrile	
	relative binding energy ^a	absolute binding energy ^b	relative binding energy ^a	absolute binding energy ^b	relative binding energy ^a	absolute binding energy ^b
1	92.8	-92.8	98.4	-98.4	119.4	-119.4
2	71.2	-164.1	72.7	-171.0	73.8	-193.2
3	57.9	-221.9	58.6	-229.7	57.6	-250.8
4	41.7	-263.6	41.8	-271.5	40.4	-291.1
5	25.7	-261.8	26.5	-296.7	23.7	-314.8
6	-3.9	-282.1	1.8	-298.5	-0.8	-314.0

^a Relative binding energy: $\text{UO}_2[\text{L}]_n^{2+} \rightarrow \text{UO}_2[\text{L}]_{n-1}^{2+} + [\text{L}]$. ^b Absolute binding energy: $[\text{UO}_2]^{2+} + n[\text{L}] \rightarrow \text{UO}_2[\text{L}]_n^{2+}$. ^c Energies include the zero-point energy correction.

TABLE 4: B3LYP Dissociation and Relative Binding Energies (in kcal/mol) for the Uranyl Acetone, Acetaldehyde, and Formaldehyde Complexes^c

<i>n</i>	formaldehyde		acetaldehyde		acetone	
	relative binding energy ^a	absolute binding energy ^b	relative binding energy ^a	absolute binding energy ^b	relative binding energy ^a	absolute binding energy ^b
1	77.8	-77.8	95.7	-95.7	108.1	-108.1
2	60.2	-137.9	69.5	-165.2	75.0	-183.1
3	39.8	-187.7	55.1	-220.3	57.8	-240.9
4	35.5	-223.2	37.3	-257.7	30.8	-271.7
5	20.8	-241.8	20.8	-278.5	12.7	-280.2
6			-5.4	-273.2	2.7	-282.9

^a Relative binding energy: $\text{UO}_2[\text{L}]_n^{2+} \rightarrow \text{UO}_2[\text{L}]_{n-1}^{2+} + [\text{L}]$. ^b Absolute binding energy: $[\text{UO}_2]^{2+} + n[\text{L}] \rightarrow \text{UO}_2[\text{L}]_n^{2+}$. ^c Energies include the zero-point energy correction.

by Van Stipdonk et al., complexes containing up to five propionitrile ligands and up to five benzonitrile ligands have also been isolated.¹² The binding energies for these complexes are 26.5 and 23.7 kcal/mol, respectively. This suggests that a ligand addition with a binding energy greater than 23.7 kcal/mol should be observable in mass spectroscopic studies. Because of the roughly 10 kcal/mol difference between the fifth and the sixth ligand additions for the complexes studied, a minimum value of the binding energy necessary for experimental observation cannot be exactly determined. However, since the binding energies of the fifth addition of formaldehyde and acetaldehyde are within 3 kcal/mol of that for the fifth addition of benzonitrile, it is possible that these may be isolated in future mass spectrometric studies.

Conclusion

The complexation of gas-phase UO_2^{2+} with nitrile and carbonyl ligands has been examined. Both types of ligands bind to uranyl with the nitrogen or oxygen lying in the equatorial plane. However, complexes containing six ligands as well as the 5-coordinate acetone complex experience distortions because of steric effects that force them to deviate from the equatorial plane. Additionally, the plane of the nitrile ligands is parallel to UO_2^{2+} , while the plane of the carbonyl ligands is generally perpendicular to UO_2^{2+} . The carbonyls, however, have side groups closer to uranium than do the nitriles. This forces the plane of the carbonyl ligands to deviate from a 90° angle with UO_2^{2+} when five or six ligands are present. Additionally, while the nitrile series binds to uranyl with a U–N–C angle of 180° , the carbonyl series binds with a U–O–C angle of less than 180° in the equatorial plane when four or more ligands are present. Notably, formaldehyde is the only ligand studied that does not form a 6-coordinate complex with uranyl.

Both classes of ligands exhibit a strong affinity for uranyl; however, the nitrile ligands tend to bind more strongly than the carbonyls. The strength of the uranyl–ligand bonds are also influenced by the size of the ligands. Larger ligands more easily stabilize a shift in electron density and thus are more capable of donation to the metal center. This effect is most noteworthy for the first ligand addition, and it diminishes as more ligands are added. Complexes containing up to six ligands have been modeled, and the relative binding energies predict all complexes to have five ligands with the exception of complexes containing either propionitrile or acetone ligands. This is similar to the experimental results obtained by Van Stipdonk et al. in their electrospray ionization mass spectrometry study of nitrile containing complexes.⁴ However, in their experimental work, no complexes with six ligands were found.

Acknowledgment. This research was performed in part using the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research, located at the Pacific Northwest National Laboratory, and operated for the Department of Energy by Battelle. Funding has been provided by Iowa State University and an NSF grant in petascale applications to T.L. Windus.

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

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