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Theoretical Investigations of Uranyl–Ligand Bonding: Four- and Five-Coordinate Uranyl Cyanide, Isocyanide, Carbonyl, and Hydroxide Complexes

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The coordination and bonding of equatorial hydroxide, carbonyl, cyanide (CN^-), and isocyanide (NC^-) ligands with uranyl dication, $[UO_2]^{2+}$, has been studied using density functional theory with relativistic effective core potentials. Good agreement is seen between experimental and calculated geometries of $[UO_2(OH)_4]^{2-}$. Newly predicted ground-state structures of $[UO_2(OH)_5]^{3-}$, $[UO_2(CO)_4]^{2+}$, $[UO_2(CO)_5]^{2+}$, $[UO_2(CN)_4]^{2-}$, $[UO_2(CN)_5]^{3-}$, $[UO_2(NC)_4]^{2-}$, and $[UO_2(NC)_5]^{3-}$ are reported. Four-coordinate uranyl isocyanide complexes are the predicted gas-phase species while five-coordinate uranyl cyanide complexes are energetically favorable in aqueous solution. Small energy differences between cyanide and isocyanide complexes indicate the energetic feasibility of mixed cyanide and isocyanide complexes. A D_{2d} uranyl tetrahydroxide is the dominant gas-phase and aqueous species, but formation of uranyl carbonyl complexes is seen to be exothermic in the gas-phase and endothermic in aqueous solution.

1. Introduction

Throughout the development of actinide chemistry over the last six decades, a detailed understanding of the electronic structure of actinide complexes has been, and continues to be, a challenge for experimental and theoretical chemists. The theoretical description of actinide-containing compounds is complicated by the sheer number of electrons present, the participation of 5f, 6d, and 7s orbitals possessing different spatial extent and relative energies, and the importance of relativistic effects including spin–orbit coupling.[1−4] One of the fundamental questions addressed by theoretical studies of actinide complexes is the nature of actinide–ligand interactions. In this contribution, we address some aspects of metal–ligand interactions in the widely studied actinide system uranyl dication, $[UO_2]^{2+}$.

The uranyl dication is ubiquitous in aqueous uranium chemistry. With the two axial coordination sites occupied by oxo groups, the interaction of uranyl ion with ligands is dominated by coordination in the equatorial plane, which can typically accommodate four, five, or six coordination sites. Experimental studies of uranyl coordination have included a variety of ligands, including chloride,[5] hydroxide,[6,7] carbonate,[8] iodate,[9] and crown ethers.[10] Since U in the uranyl dication is in the U(VI) oxidation state, the U electron configuration is closed-shell f^0d^0 and facilitates single-configuration descriptions without the need to consider metal-based spin–orbit multiplets. The relative ease with which experimental uranyl complexes can be probed provides important data to test the efficacy of various theoretical models.[4]

Recent theoretical investigations of uranyl coordination have focused on primarily σ-donor ligands.[11−18] Continuing

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Table 1. Optimized Bond Length (Å) and Vibrational Frequencies (cm^{-1}) for the Uranyl Dication Using Various Uranium and Oxygen Basis Sets with the Stuttgart 1997 RECP

property	U, Stuttgart 1997 RSC; O, 6-311+G(d)	U, [7s 6p 5d 3f] basis; O, 6-311+G(d)	U, Stuttgart 1997 RSC;[a] O, TZVP DFT basis	U, [7s 6p 5d 3f] basis; O, aug-cc-pVDZ
r_e	1.701	1.701	1.701	1.700
$\nu_{\mathrm{symmetric}}$	1035	1035	1048	1029
$\nu_{\mathrm{asymmetric}}$	1134	1134	1147	1129
ν_{bend}	174	174	158	166

[a] References 28 and 29.

experimental work suggests uranyl can form aqueous complexes with cyano ligands,[19] but such complexes have been absent from theoretical uranyl−ligand bonding investigations until just recently. Clavaguéra-Sarrio et al.[20] investigated $UO_2(CN)_2$ and $UO_2(NC)_2$ utilizing density functional theory (DFT) and found a preference for N-bound isocyanide ligands (NC^-) over C-bound cyanide ligands (CN^-). This is an intriguing result since there are no known transition metal complexes containing monodentate isocyanide ligands.[21] One lingering question is the nature of uranyl cyanide complexes formed in aqueous solution by reaction of uranyl with free cyanide. Although dicyanide systems provide useful insights into uranyl cyanide and isocyanide bonding, the uranyl dication is more likely to fill all available equatorial coordination sites in solution.

To understand solution phase uranyl cyanide structure and bonding, we use scalar relativistic DFT to examine four- and five-coordinate complexes of $[UO_2]^{2+}$ ion with CN^- and NC^- ligands, both of which may serve as π-donors and π-acceptors as well as σ-donors. Comparative calculations employing the predominantly σ-donor ligand OH^- and the classic π-acceptor ligand CO are also presented. The conductor-like screening model is utilized to mimic the effects of hydrating these uranyl compounds.

2. Theoretical Methods and Computational Details

All calculations were performed using the Gaussian03 suite of programs[22] and employed the B3LYP functional.[23,24] Scalar relativistic effects were taken into account via the relativistic effective core potential (RECP) of Küchle et al. for the uranium center,[25] while spin−orbit effects have been ignored. This RECP places 60 electrons in the uranium core leaving the 5s, 5p, 5d, 6s, 6p, 5f, 6d, and 7s electrons for explicit treatment. The most diffuse s, p, d, and f Gaussian functions of the associated uranium basis set were removed to generate the [7s 6p 5d 3f] basis, which has been used previously.[26,27] No 5g-polarization functions have been included in the uranium basis due to the formal f^0 nature of uranyl complexes. This modified basis was benchmarked against previous uranyl dication calculations.[28,29] Table 1 shows that our modification of the Stuttgart 1997 relativistic small core uranium basis[25] has no effect on uranyl bond lengths or vibrational frequencies in DFT and is in good agreement with existing literature values.[28,29] The choice of oxygen basis set produced only minor changes when the U basis was kept constant. To properly describe weak uranyl−ligand interactions, ligand orbitals were described by Dunning's aug-cc-pVDZ basis set[30] unless otherwise noted.

All complexes were optimized using the Berny algorithm.[31] Analytic harmonic vibrational frequencies were computed to ensure that optimized structures were minima on the potential energy surface and to provide zero point energy (ZPE) corrections. Basis set superposition error (BSSE) corrections were ignored throughout this work: the counterpoise BSSE correction for $[UO_2(CN)_4]^{2-}$ was found to be 2.551 millihartrees, which is 1 order of magnitude smaller than ZPE corrections. To address aqueous solvation effects, the conductor-like screening model as developed in the polarizable continuum model[32] (CPCM), utilizing $\epsilon = 78.39$, has been applied with united atom topological model atomic radii optimized at the Hartree−Fock 6-31G(d) level.[33] Single point CPCM calculations of all complexes were performed using gas-phase optimized geometries. Natural population analysis (NPA) analysis[34] was applied to resulting gas-phase structures employing the partitioning scheme developed in our companion paper.[35]

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Table 2. Calculated Gas-Phase Bond Lengths (Å) and Vibrational Frequencies (cm^{-1}) for the Uranyl Dication and Ligands in This Work

molecule	r_e	ν_{sym}	ν_{asym}	ν_{bend}
OH^-	0.970	3736		
CN^-	1.183	2113		
CO	1.134	2185		
$[UO_2]^{2+}$	1.700	1029	1129	166

3. Results and Discussion

We begin the discussion with calculated results for the bare $[UO_2]^{2+}$ ion, which has been extensively studied. Before comparing CN^- and NC^- as ligands, we present results using the OH^- ligand, which serves as a strong σ-donor, and CO, which is expected to function as only a weak σ-donor to $[UO_2]^{2+}$. The primary species of interest are the four- and five-coordinate complexes $[UO_2L_4]^{(2+4q)}$ and $[UO_2L_5]^{(2+5q)}$ ($L = OH^-$, CO, CN^-, NC^-; q = the charge on L), which are formed primarily via σ-donation from the ligand into vacant 6d- and 5f-based orbitals in the equatorial plane of uranyl.

The preferred ligand coordination number is inferred from energy changes for the complex formation reaction in eq 1. Complex formation energies were determined for the isolated $[UO_2(L)_n]^{(2+nq)}$ ions and for the ions modeled in the aqueous phase via the polarized-continuum model. Neither set of reaction energies includes ZPE corrections, thermal corrections, or entropic contributions necessary for free energies at 298 K. Unscaled, harmonic zero-point vibrational energy corrections for gas-phase compounds are listed in the Supporting Information.

$$UO_2^{\ 2+} + nL^q \rightarrow [UO_2(L)_n]^{(2+nq)} \qquad (1)$$

3.1. Uranyl Dication. The electronic structure of bare uranyl dication has been reviewed extensively.[1,5] Table 2 presents our calculated results for the $[UO_2]^{2+}$ ion, which agree well with previous investigations.[14,28,29] The principal interactions involve electron donation from O σ and π lone pairs of the formal O^{2-} ligands into vacant d and f orbitals on the formal U^{6+} ion. Due to the centrosymmetry of uranyl, the interactions partition into those involving U 6d orbitals (σ_g and π_g) and those involving U 5f orbitals (σ_u and π_u). From the partial $[UO_2]^{2+}$ molecular orbital (MO) diagram in Figure 1, the highest occupied MOs are the predominantly oxygen-based π_g, π_u, σ_g, and σ_u described in Table 3. In this simple one-electron picture, the U 5fδ, 5fφ, and 6dδ orbitals are nonbonding and energetically accessible to serve as equatorial ligand-acceptor orbitals. On the basis of our previous work exploring the competition between actinide 5f and 6d orbitals to act as acceptor orbitals,[36] we expect the dominant equatorial ligand donation will involve U 6d orbitals, except when the interaction symmetry permits only 5f orbitals to be involved.

3.2. Hydroxide Complexes. A bent hydroxide ligand presents both σ- and π-donor orbitals, with the π-donor orbital oriented perpendicular to the U−O−H plane, which may engage the uranium center.[37] Thus, in the absence of large steric effects, the orientation of the hydrogen atoms is largely dependent on the arrangement of the π-donor orbitals to maximize the ligand-to-metal π donation. Previous work in our group showed that the D_{2d} isomer of uranyl tetrahydroxide (**I**) is the lowest energy conformer.[38] As seen in Table 4, our current work is in better agreement with U−OH bond lengths determined from crystallographic studies.[39] This improvement validates our present computational method and is a result of the small core RECP[25] uranium basis utilized currently rather than the large core RECP[40] used previously. As seen in Figure 2, the hydroxides are arranged with hydrogen pointing up or down in an alternating fashion with a UOH bond angle of 106.4° maximizing hydroxide π-donor ability to the 6d$_{x^2-y^2}$ uranium orbital. The strong π-donor ability of hydroxide is also evident in the perturbed uranium−oxo bonds and natural charge of U, which have lengthened by 0.141 Å and decreased by 1.12 electrons, respectively.

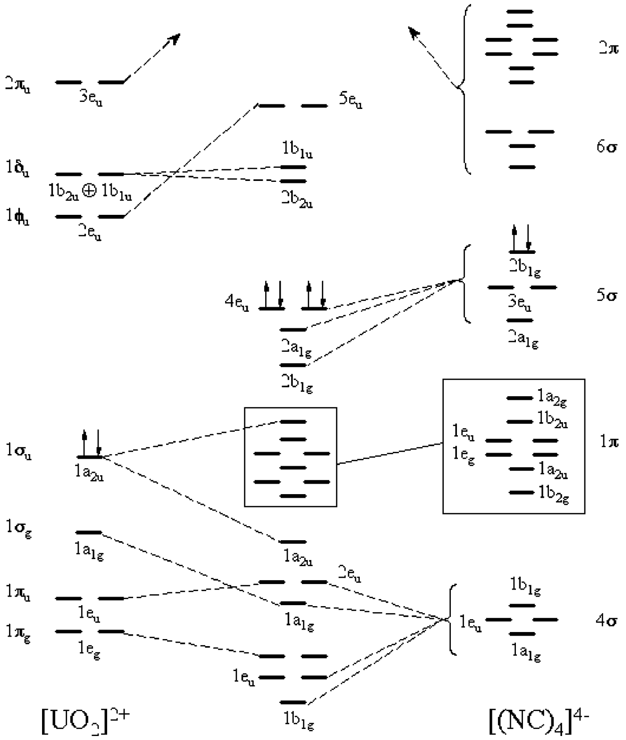

Figure 1. Qualitative canonical MO diagram showing the interaction of $[UO_2]^{2+}$ and four isocyanide ligands under single-group D_{4h} symmetry to form $[UO_2(NC)_4]^{2-}$. Symmetry labels for the free ions are also given. Spin−orbit coupling effects are not included.

The odd number of ligands in uranyl pentahydroxide prevents the complex from adopting a similar alternating arrangement of its hydroxides, although it is nearly achieved if the fifth ligand is placed in the equatorial plane. All endeavors to locate a minimum corresponding to this

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Table 3. Energy (eV) and Mulliken % Character for Selected $[UO_2]^{2+}$ Molecular Orbitals

MO	energy	U s	U p	U d	U f	oxo s	oxo p
$2\pi_u$	−15.49		2.0		66.8		31.2
$1\delta_u$	−17.95				99.7		
$1\phi_u$	−18.38				100.0		
$1\sigma_u$ HOMO	−23.63		9.1		58.1	1.4	31.4
$1\sigma_g$	−24.27	8.4		15.1		−2.4	78.8
$1\pi_u$	−24.56		1.4		31.0		67.0
$1\pi_g$	−24.91			19.8			78.6

Table 4. Calculated Bond Lengths (Å), OUO Bond Angles (deg), and Vibrational Frequencies (cm^{-1}) for Uranyl Tetraligand Complexes with Vibrational Mode Symmetries in Parentheses

molecule	sym	U−O	OUO	U−L	ligand r_e	uranyl ν_{sym}	uranyl ν_{asym}	ligand ν
OH^-								
I	D_{2d}	1.841	180.0	2.309	0.965	762 (A_1)	833 (B_2)	3824 (A_1, B_2, E)
I[a]	D_{2d}	1.842	180.0	2.334		739 (A_1)	823 (B_2)	
expt[b]		1.82(1) (av) [1.801(6)−1.835(5)]	180.0	2.26(2) (av) [2.229(5)−2.275(5)]		796		
CO								
VI	C_{2v}	1.727	179.9	2.760 2 × 2.757 2.765	1.121	983 (A_1)	1069 (B_1)	2301 (A_1) 2303 (A_1, B_2) 2304 (A_1)
CN^-								
VIII	D_{4h}	1.777	180.0	2.575	1.174	875 (A_{1g})	957 (A_{2u})	2190 (E_u) 2191 (A_{1g}, B_{1g})
IX	D_{4h}	1.778	180.0	2.443	1.181	873 (A_{1g})	956 (A_{2u})	2131 (E_u, B_{1g}) 2141 (A_{1g})

[a] Reference 38. [b] Crystal structure of $[Co(NH_3)_6]_2[UO_2(OH)_4]_3 \cdot H_2O$ in reference 39.

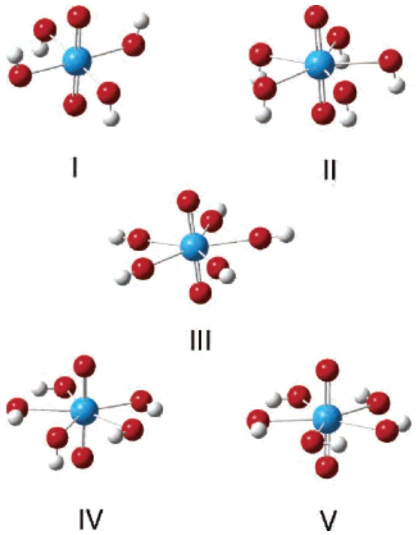

Figure 2. Uranyl hydroxide complexes with U, O, and H atoms denoted in turquoise, red, and white, respectively.

structure resulted in a D_{2d} uranyl tetrahydroxide plus hydroxide anion. Optimization of uranyl pentahydroxide under C_{5v} symmetry resulted in convergence to a seventh-order saddle point (**II**). Similarly, all attempts to optimize the structure under D_{5h} symmetry resulted in convergence to a tenth-order saddle point (**III**). Removing all symmetry constraints located the previously unreported C_s uranyl pentahydroxide minimum (**IV**) pictured in Figure 2, which is only 1.1 kcal/mol higher in energy than the confirmed uranyl pentahydroxide C_{5h} ground-state miminum (**V**) previously reported.[41,42] Structural characteristics for all uranyl pentahydroxide isomers are presented in Table 5.

The C_s and C_{5h} geometries were initially puzzling since the ligand arrangement does not maximize π donation as anticipated. Larger natural charges on the hydroxide oxygens seen in Table 6 and the near 90° UOH bond angles in these complexes indicate a decreased π donation to uranium when compared to **I**. This smaller hydroxide π donation is counterbalanced by improved intramolecular hydrogen bonding between hydroxide groups in the equatorial plane of the uranyl moiety, which gives rise to the stability of the these geometries.

3.3. Carbonyl Complexes. Before presenting the CN^- and NC^- binding results, it is instructive to examine the bonding of CO ligands to uranyl dication. CO is isoelectronic with CN^- and NC^- and will therefore present the same types of orbitals for interaction with the uranyl ion. Since CO is a weaker σ-donor and stronger π-acceptor than CN^-, the opportunity arises to study how $[UO_2]^{2+}$ responds to changes in ligand σ-basicity and π-acidity. Although CO is a strong π-acceptor, the uranyl dication is a formally d^0f^0 ion so we do not anticipate predominantly metal-based electrons to engage in back-bonding to the CO ligands. As a comparison to the tetracyano and pentacyano complexes discussed later, we examine uranyl tetracarbonyl and pentacarbonyl complexes. All of the carbonyl complexes examined involved conventional C-bonded carbonyls; the possibility of O-bonded isocarbonyl complexes was not investigated as their existence is unexpected based upon the previous theoretical work of Clavaguéra-Sarrio et al.[20]

The bonding of four CO ligands with $[UO_2]^{2+}$ to form $[UO_2(CO)_4]^{2+}$ might be expected to produce a D_{4h} complex with octahedral coordination about the U atom. Under D_{4h} single-group symmetry, the 5σ highest occupied molecular orbital (HOMO) orbitals of CO, which serve as σ-donor

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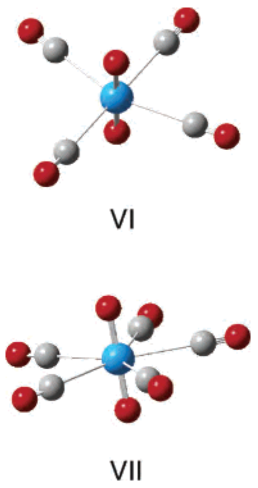
Table 5. Calculated Bond Lengths (Å), OUO Bond Angles (deg), and Vibrational Frequencies (cm^{-1}) for Uranyl Pentaligand Complexes with Vibrational Mode Symmetries in Parentheses

complex	sym	U−O	OUO	U−L	UOH	ligand r_e	uranyl ν_{sym}	uranyl ν_{asym}	ligand ν
OH^-									
II[a]	C_{5v}	1.831 1.856	180.0	2.457	100.9	0.966	735 (A_1)	826 (A_1)	3795 (E_2) 3796 (E_1) 3797 (A_1)
III[b]	D_{5h}	1.819	180.0	2.422	180.0	0.959	767 (A_1')	841 (A_2'')	3881 (E_1', E_2') *3883 (A_1')*
IV	C_s	1.832 1.838	175.1	2 × 2.371 2 × 2.492 2.584	2 × 95.0 2 × 92.3 96.0	2 × 0.970 2 × 0.971 0.967	750 (A')	822 (A')	3718 (A'') 3720 (A') 3748 (A', A'') *3790 (A')*
V	C_{5h}	1.830	180.0	2.455	95.0	0.969	755 (A')	827 (A'')	3765 (A') 3767 (E_1') *3771 (E_2')*
CO									
VII	D_{5h}	1.732	180.0	2.763		1.121	973 (A_1')	1058 (A_2'')	2296 (E_2') 2297 (E_1') 2299 (A_1')
CN^-									
X	D_{5h}	1.784	180.0	2.653		1.177	857 (A_1')	937 (A_2'')	2165 (E_2') 2166 (E_1') *2168 (A_1')*
XI	D_{5h}	1.781	180.0	2.543		1.179	862 (A_1')	946 (A_2'')	2142 (E_2') 2144 (E_1') 2150 (A_1')

[a] Seventh-order saddle point. [b] Tenth-order saddle point.

Table 6. Natural Charges

molecule	U	oxo	O	H	C	N
$[UO_2]^{2+}$	2.84	−0.42				
OH^-			−1.39	0.39		
I	1.72	−0.69	−1.03	0.44		
II	1.82	−0.75 −0.68	−1.09	0.41		
III	1.80	−0.64	−1.11	0.41		
IV	1.79	−0.69 −0.68	2 × −1.09 2 × −1.17 −1.18	4 × 0.46 0.43		
V	1.80	−0.67	−1.15	0.46		
CO			−0.52		0.52	
VI	1.92	−0.42	−0.28		0.51	
VII	1.59	−0.42	−0.29		0.54	
CN^-					−0.21	−0.79
VIII	1.61	−0.56			−0.05	−0.57
IX	1.90	−0.54			0.06	−0.77
X	1.34	−0.57			0.02	−0.66
XI	1.81	−0.56			−0.03	−0.71


VI

VII

Figure 3. Uranyl carbonyl complexes with U, C, and O atoms denoted in turquoise, gray, and red, respectively.

orbitals to the metal, generate group orbitals of $a_{1g} \oplus b_{1g} \oplus e_u$ symmetry. The b_{1g} interaction is expected to dominate inasmuch as it involves donation into a vacant U 6d $_{x^2-y^2}$ orbital, the lobes of which lie in the equatorial plane and point directly at the CO ligands. The principal π-acceptor mode is expected to involve the e_g interaction of out-of-plane CO 2π orbitals with U 6dπ orbitals. Those metal-based orbitals, although formally empty, also serve as π-acceptors for the oxo ligands, thereby acquiring some electron density.

Our results suggest that, despite these potential interactions, the bonding of CO to $[UO_2]^{2+}$ is very weak and generates a very soft potential surface for motion of the carbonyl ligand in the equatorial plane. Four CO ligands do not sterically saturate the equatorial plane, and our calculations predict $[UO_2(CO)_4]^{2+}$ is unlikely to adopt a D_{4h} geometry. All attempts to optimize a D_{4h} uranyl tetracarbonyl ground state produced a second-order saddle point. Relaxing all symmetry constraints produced a C_{2v} ground-state structure (**VI**) in which all the carbonyls lie in the equatorial plane. See Figure 3. Two of the CO ligands are rigorously trans to one another (C−U−C = 180.0°) as seen in Table 4. The other two CO ligands distort toward one of the trans CO ligands, reducing the corresponding C−U−C angle from 90 to 79.9°. This distortion suggests that one more equatorial CO ligand will be favored; however, a simple orbital explanation is unavailable. We shall see that the tetraligand complexation changes dramatically when CN^- is used as a consequence of the greater donor ability of that ligand. The calculated U−CO bond lengths are nearly 0.43 Å longer than the U−OH bond lengths calculated for $[UO_2(OH)_4]^{2-}$, which reflects the differences in uranium−ligand bonding character between π-acceptor and π-donor ligands and the charge of the ligand.

Uranyl pentacarbonyl (**VII**) has a calculated D_{5h} ground-state structure possessing U−C bond lengths of 2.763 Å and U−O bond lengths of 1.732 Å as presented in Table 5. With five CO ligands, the equatorial plane is sufficiently crowded such that pentagonal bipyramidal coordination about U is achieved as shown in Figure 3. The calculated U−CO bond lengths and natural charges in $[UO_2(CO)_5]^{2+}$ are nearly identical with those of the tetracarbonyl compound, which underscores the notion of unsaturation in uranyl tetracarbonyl.

In both carbonyl complexes, **VI** and **VII**, the U−O bond lengths are essentially the same as in the isolated $[UO_2]^{2+}$ ion. This observation implies that the U−CO interactions are sufficiently weak to leave the U−O bonding largely unperturbed, which is not unexpected given the weak σ-basicity of CO. It is likewise not surprising that calculated C−O stretching frequencies in **VI** and **VII** are both higher than that of free CO as seen in nonclassical carbonyls.[43] The inability of the d^0f^0 metal center to π-back-bond to CO, coupled with the polarization caused by the positive ion interaction with CO, was expected to produce an increase in ν_{CO}.[44]

3.4. Cyanide Complexes. The calculations on carbonyl complexes **VI** and **VII** suggest uranium-to-ligand π-donation is insignificant even in the presence of a strong π-acid. To further investigate this result, we now examine the bonding of CN^- and NC^- to $[UO_2]^{2+}$. Both of these anionic ligands are expected to be stronger σ-donors than CO, via donation from either the C-localized 5σ orbital of CN^- or the N-localized 4σ orbital of NC^-. Based on the spatial extent and energetic closeness to vacant U-based orbitals, the 5σ orbital is a much more effective donor than the 4σ. See Figure 1. The more effective σ-donation by CN^- coupled with the greater π-acceptor capability of the C-bonded ligand helps explain why CN^- is the preferred ligand over NC^- for non-d^0 metals capable of back-bonding.

In the case of the uranyl dication, however, π-donation is much more important than π-acceptance. The filled cyano 1π orbital, which has greater N than C character, can be a more effective π-donor orbital for NC^- than for CN^-. Thus, examining the bonding capability of these ligands provides a comparison of σ- and π-donation importance for the uranyl ion. In their study of diligand adducts to uranyl ion, Clavaguéra-Sarrio et al.[20] found NC^- to be a more effective ligand than CN^-. Those studies are extended here to four- and five-coordinate uranyl cyanide (CN^-) and isocyanide (NC^-) complexes to determine whether the observations of Clavaguéra-Sarrio et al.[20] are also seen at larger, solution-phase coordination numbers.

The binding of four CN^- or four NC^- ligands produces six-coordinate complexes predicted to have D_{4h} symmetry. The U−O bond lengths are virtually identical in $[UO_2(CN)_4]^{2-}$ (**VIII**) and $[UO_2(NC)_4]^{2-}$ (**IX**). The calculated U−C bond lengths in **VIII** are almost 0.2 Å shorter and the U natural charge nearly 0.3 electrons smaller than those in $[UO_2(CO)_4]^{2+}$, indicating significantly stronger interactions due to the greater σ-donor ability of the CN^- ligand. The natural charges on U are consistent with a bonding model in which the C-bonded CN^- acts as a significantly stronger σ-donor and slightly weaker π-donor than N-bonded NC^-. The fact that the two isomeric forms are so close in energy is indeed curious and unexpected. The binding of CN^- or NC^- to uranyl also has a significant effect on the vibrational properties of the $[UO_2]^{2+}$ moiety; the symmetric and antisymmetric U−O stretches in **VIII** and **IX** are each more than 100 cm^{-1} lower than the vibrations in $[UO_2(CO)_4]^{2+}$. The subtle differences in bonding between uranyl tetracyanide and uranyl tetraisocyanide, which influence the 3.0 kcal/mol energy difference in **VIII** and **IX**, are evident in their respective MO diagrams.

Both the 4σ and 5σ orbitals of CN^- and NC^- generate D_{4h} symmetry-adapted orbitals of $a_{1g} \oplus b_{1g} \oplus e_u$ symmetry as seen in Figure 1. The interaction diagram in Figure 1 does not include spin−orbit coupling effects, which will cause further splittings of the levels according to the double-group symmetry. However, for a complex comprised of closed-shell uranyl and cyanide ligands, we do not expect any significant differential effect in the nature of the interactions depicted in the figure. The HOMO $4e_u$ and $2a_{1g}$ and $2b_{1g}$ are primarily ligand-based MOs resulting from the 5σ cyano symmetry-adapted orbitals. The $4e_u$, $2a_{1g}$, and $2b_{1g}$ MOs are more stabilized in the CN^- complex since the C-localized 5σ orbitals are pointing toward U whereas they are pointing away from U in the NC^- complex. The $1a_{2u}$ and $2a_{2u}$ MOs are bonding and antibonding interactions, respectively, between the σ_u HOMO of uranyl and the $1a_{2u}$ 1π symmetry-adapted orbital as pictured in Figure 6. The admixture of U f character is particularly large for this interaction in **VIII** (Figure 5) as seen in U f Mulliken percent characters of 43.9% and 7.8% for the $1a_{2u}$ and $2a_{2u}$ MOs, respectively. Mulliken percent character for selected MOs in **VIII** and **IX** are given in the Supporting Information. As expected, the 1π cyano orbitals are more effective π-donors for NC^- than for CN^- as denoted by the box of π-block MOs in Figure 4. From the Mulliken percent character analysis, it is clear that the $2e_u$, $1a_{1g}$, and $1e_g$ MOs are essentially the π_u, σ_g, and π_g orbitals, respectively, of $[UO_2]^{2+}$. In a manner similar to that for the 5σ symmetry-adapted orbitals, the $1e_u$ and and $1b_{1g}$ MOs arising from the N-localized 4σ cyano symmetry-adapted orbitals are nonbonding in **VIII** but bonding in **IX**.

For both cyanide (**X**) and isocyanide (**XI**) seven-coordinate complexes, the ground state possesses D_{5h} symmetry with U−O bond lengths of 1.784 and 1.781 Å, respectively. The change in U−O bond length in **X** and **XI** is smaller than in the uranyl carbonyl complexes, indicating cyanide and isocyanide ligands are more π donating than π accepting when bonded to uranyl compounds. The unusually positive natural charge of carbon in **IX**, which has been previously observed in $UF_4(NC)_2$,[45] prompted us to investigate the natural charge on carbon in a series of uranyl isocyanide compounds of the form $[UO_2(NC)_n]^{(2-n)}$ ($n = 1-5$). Our results (see Supporting Information) demonstrate that the

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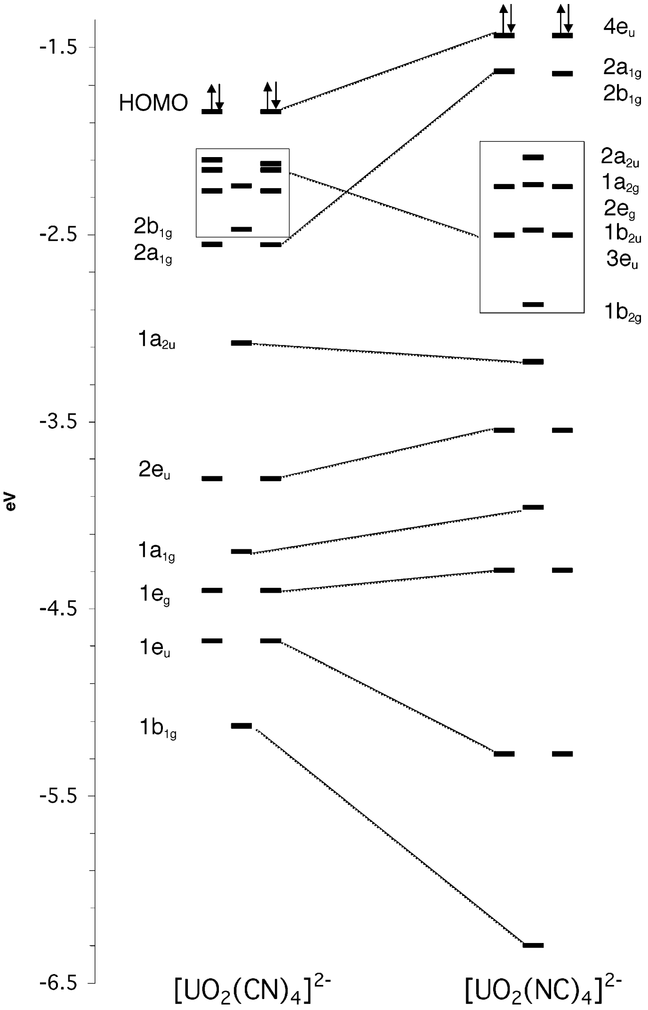

Figure 4. Uranyl tetracyanide versus tetraisocyanide quantitative MO diagrams. $2a_{1g}$ and $2b_{1g}$ are energetically degenerate in $[UO_2(CN)_4]^{2-}$. The ordering of $2a_{1g}$ and $2b_{1g}$ along with $2a_{2u}$ and $1a_{2g}$ switch in $[UO_2(CN)_4]^{2-}$. Primarily π-bonding MOs are enclosed in the squares.

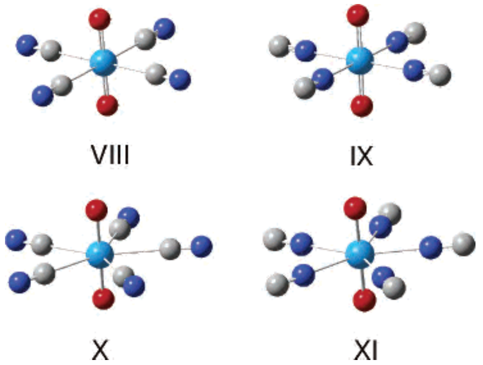

Figure 5. Uranyl cyanide complexes with U, C, and N atoms denoted in turquoise, gray, and blue, respectively.

positive natural charge on carbon is not artificial and tracks very well with the trends in Mulliken atomic charges. Although the bonding characteristics of uranyl cyanides tell us a great deal about their chemistry, we turn to reaction energetics to discern relative stabilities of six- and seven-coordinate complexes.

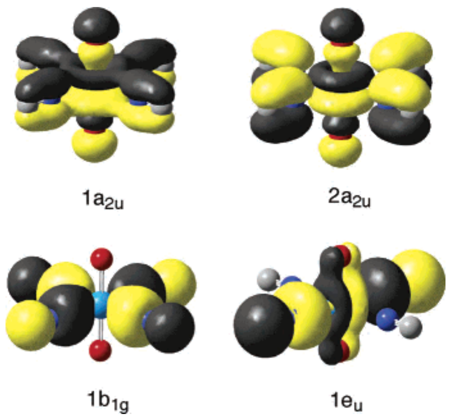

Figure 6. Selected $[UO_2(NC)_4]^{2-}$ molecular orbitals plotted at an isovalue of 0.025.

Table 7. $UO_2^{2+} + nL^q \rightarrow [UO_2(L)_n]^{(2+nq)}$ Reaction Energies (kcal/mol)

product	gas-phase ΔE_{elec}	aq ΔE_{elec}
$[UO_2(OH)_4]^{2-}$ (**I**)	−665.6	−139.0
$[UO_2(OH)_5]^{3-}$ (**V**)	−531.0	−113.5
$[UO_2(CO)_4]^{2+}$ (**VI**)	−117.4	42.9
$[UO_2(CO)_5]^{2+}$ (**VII**)	−138.2	31.8
$[UO_2(CN)_4]^{2-}$ (**VIII**)	−558.5	−90.2
$[UO_2(NC)_4]^{2-}$ (**IX**)	−561.5	−93.1
$[UO_2(CN)_5]^{3-}$ (**X**)	−463.4	−105.2
$[UO_2(NC)_5]^{3-}$ (**XI**)	−457.7	−99.4

3.5. Coordination Preferences. To establish equatorial coordination preferences of uranyl complexes, the electronic reaction energies of forming the four- and five-coordinate uranyl complexes discussed above were computed relative to the free ions utilizing the reaction given in eq 1. Table 7 lists gas-phase and aqueous results where solvation effects were addressed via CPCM single-point DFT calculations at gas-phase optimized geometries.[46]

In first considering overall stability of the four-coordinate uranyl complexes with negatively charged ligands, we note the overall gas-phase stabilities in Table 7 decrease in the order $OH^- < NC^- < CN^-$ with large complexation energies for eq 1 of approximately −600 kcal/mol. The presence of aqueous solvent is expected to favor formation of highly charged species. When these effects are included with CPCM, the same ordering is observed but with smaller exothermicities: OH^- (−139.0 kcal/mol) < NC^- (−93.1) < CN^- (−90.2). The greater stability of the tetrahydroxo complex illustrates the importance of hydroxide π-donor ability over the weak σ-donor and π-acceptor character in the cyanide and isocyanide ligands. While CO ligand results are not directly comparable with those of the anionic ligands because of differing charge effects, it is interesting to note that the calculated gas-phase complexation energy for neutral CO ligands is less exothermic (−117.4 kcal/mol), and solution formation of the uranyl tetracarbonyl species is actually predicted to be endothermic (+42.9 kcal/mol).

For the five-coordinate uranyl complexes the overall stability relative to initial fragments has a slightly different ordering, both in gas phase and in solution. The calculated formation values in solution are as follows: OH^- (−113.5 kcal/mol) < CN^- (−105.2) <NC^- (−99.4). A more germane quantity is the relative energy of the four- and five-coordinate

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[46] Benchmark calculations in which the geometries are reoptimized including CPCM effects show that reoptimization will have minimal effect on presented conclusions.

complexes for the following process:

$$[UO_2(L)_4]^{2-} + L^- \rightarrow [UO_2(L)_5]^{3-} \qquad (2)$$

For the anionic ligands the same ordering is obtained in both gas phase and solution, with the latter calculated energies in the order CN^- (−15.0 kcal/mol) < NC^- (−6.3) < OH^- (+25.5). While we saw above that the tetrahydroxide complex had the greatest stability of the three ligands, addition of the fifth hydroxide is endothermic by 25.5 kcal/mol. It was suggested that uranyl tetrahydroxide is in equilibrium with uranyl pentahydroxide in aqueous solution with uranyl pentahydroxide the dominant species;[39] however, this disagrees with this work and that of others.[41,42,47,48]

In contrast, for cyanide and isocyanide ligands addition of the fifth ligand (**X**) is exothermic by −15.0 and −6.3 kcal/mol, respectively. The 2.9 kcal/mol preference for NC^- ligands in four-coordinate uranyl complexes and 5.8 kcal/mol preference for CN^- ligands in five-coordinate uranyl complexes accentuates the subtle differences in U bonding with the 5σ and 4σ cyano orbitals.

While addition of a fifth carbonyl ligand is favorable by −11.1 kcal/mol, the overall uranyl tetracarbonyl and pentacarbonyl formation is endothermic when solvent effects are included. This may explain the lack of uranyl carbonyl complexes in the literature.

4. Conclusions

The gas-phase structures and equatorial coordination trends in four- and five-coordinate uranyl hydroxide, carbonyl, cyanide, and isocyanide complexes have been investigated using scalar relativistic DFT. Uranyl hydroxide formation energetics clearly suggest a D_{2d} complex containing four equatorial hydroxide ligands is the dominant species in the gas phase and aqueous solution. The ground-state four- and five-coordinate uranyl carbonyl complexes were reported for the first time and shown to be energetically accessible, although weakly bound, as gaseous molecules. The usually strong π-acceptor carbonyl ligands showed only weak σ-donor character when bonded to uranyl as manifested in the increased ν_{CO} of **VI** and **VII**. Formation of these same complexes was found to be endothermic in solution, partially explaining the complete lack of solution-phase experimental data on these systems.

Gaseous uranyl cyanide complexes are predicted to exist with the uranium bound to four isocyanide ligands. As seen previously,[20] uranyl prefers NC^- over CN^- ligands except for five-coordinate aqueous complexes. The variation in isoelectronic cyanide and isocyanide ligand binding to uranyl dication results from different dominant σ and π interactions occurring when the ligand is bound through C versus N**.** The low energy differences between cyanide and isocyanide complexes hint at the energetic feasibility of mixed cyanide and isocyanide complexes. Mixed-ligand complexes and complexes containing solvato ligands will be addressed in future work.

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Supporting Information Available: Gas-phase and aqueous electronic energies, unscaled, harmonic, zero-point vibrational energy corrections for gas-phase compounds, and Cartesian coordinates for each molecule and Mulliken percent character for selected MOs in **VIII** and **IX**. This material is available free of charge via the Internet at http://pubs.acs.org.

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