# Role of the Uranyl Oxo Group as a Hydrogen Bond Acceptor

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S *Supporting Information*

ABSTRACT: Density functional theory calculations have been used to evaluate the geometries and energetics of interactions between a number of uranyl complexes and hydrogen bond donor groups. The results reveal that although traditional hydrogen bond donors are repelled by the oxo group in the $[UO_2(OH_2)_5]^{2+}$ species, they are attracted to the oxo groups in $[UO_2(OH_2)_2(NO_3)_2]^0$, $[UO_2(NO_3)_3]^-$, and $[UO_2Cl_4]^{2-}$ species. Hydrogen bond strength depends on the equatorial ligation and can exceed 15 kcal mol^{-1}. The results also reveal the existence of directionality at the uranyl oxo acceptor, with a weak preference for linear U=O—H angles.
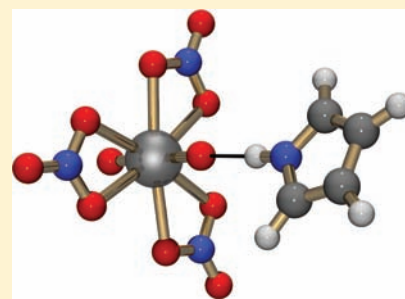
INTRODUCTION

The development of ligands capable of selective and effective binding of the uranyl ion (UO_2^{2+}) has been motivated by a diverse range of applications including uranium mining and purification,[1] uranium sequestration from seawater,[2] nuclear fuel cycle process chemistry,[3] and chelation therapy for metal poisoning.[4] Ligand design strategies for uranyl ion complexation have largely been based on traditional coordination chemistry concepts.[5] These concepts include (i) matching the electronic character of the donor groups with that of the metal ion (e.g., HSAB principle)[6] and (ii) matching the spatial array of donor groups enforced by the ligand's architecture to the coordination sites on the metal ion.[7] The uranyl ion is classified as a hard metal ion, and as such, it has an enhanced affinity for oxygen donor atoms.[8] Given the linear *trans* O=U=O geometry, the ideal ligand architecture will position 4 to 6 metal-binding donor groups in an ideally coplanar arrangement, perpendicular to the oxo groups and at an optimal distance from the metal center. Prior studies provide examples of ligands designed with the intent of meeting the above criteria—placing multiple oxygen donor groups in the equatorial plane of the uranyl ion.[2,9,10]

An augmented design strategy emerged in the early 1990s when it was noted that the uranyl oxo groups might represent more than blocked coordination sites on the metal ion.[11] It was proposed that uranyl oxo groups could function as hydrogen bond acceptors and that enhancements to both the stability and selectivity of complexation could result if hydrogen bond donors able to contact the oxo group were included within the ligand. This strategy motivated the preparation of several tripodal ligands containing three carboxylate groups for chelation in the equatorial plane and one R_3NH^+ donor group to form the hydrogen bond with the oxo group (see Figure 1, A and B).[11,12] A third recent example, again engaging the uranyl ion via three carboxylate groups (Figure 1C), directs three amide N—H

donors toward an oxo group.[13] In this instance, single crystal X-ray diffraction confirmed the expected binding motif, but revealed that the hydrogen bonds to the oxo group were quite long, with N---O distances of 3.56 Å (average H---O of 2.85 Å).

As illustrated in Figure 1, all of these ligands are able to adopt conformations that allow the three carboxylates to chelate the uranium metal and put at least one hydrogen bond donor in the vicinity of a uranyl oxo group. Moreover, all three ligands have been shown to extract the uranyl ion from aqueous phase into chloroform, forming 1:1 uranyl:ligand complexes in the organic phase.[11−13] However, in the absence of control experiments, it is impossible to conclude (i) whether these tripodal architectures actually exhibit any enhanced affinity or recognition for the uranyl ion and (ii) whether the hydrogen bonding interactions play any significant role in the binding.

It has long been known that simple hydrophobic carboxylic acids function as metal ion extractants with an intrinsic selectivity order of $Fe^{3+} > UO_2^{2+}$ > trivalent lanthanides > Al^{3+} > divalent transition metals > divalent alkaline earths > monovalent alkali metals.[15] Given this behavior, any hydrophobic ligand containing carboxylate groups would be expected to function as a "selective" extractant for the uranyl ion over most other metal ions. The extent to which uranyl binding and recognition is enhanced by incorporating three carboxylate donors within a given molecular scaffold requires comparison to some baseline behavior, for example, that exhibited by ligands containing a single carboxylate donor. Evidence of whether enhanced recognition is attained by the presence of one or more H---O=U hydrogen bonds would require comparison against structurally similar ligands lacking the hydrogen bonding functionality. Although there is reason to expect that the incorporation of three carboxylate donors within a single ligand could result in enhanced binding,[5] literature
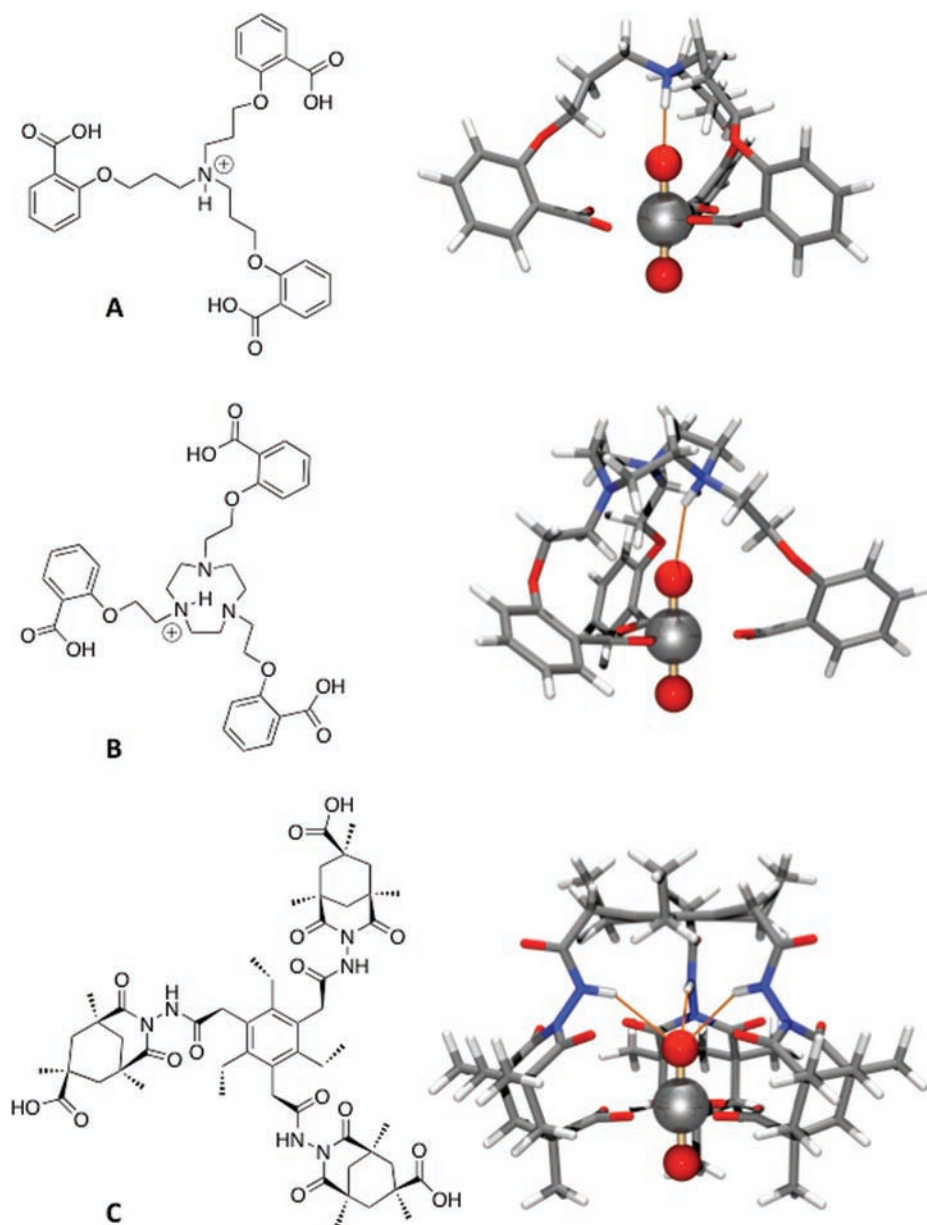
Figure 1. Structures of tripodal tris-carboxylate ligands containing hydrogen bonding groups.[11−13] Optimized geometries for uranyl complexes (extended MM3 force field model)[14] illustrate how the hydrogen bond donors contact one of the oxo groups.

precedent for anticipating significant stabilization from H---O=U hydrogen bonds is lacking.

It is a widely held tenet that actinyl oxo groups are much weaker Lewis bases than transition metal oxo groups.[16,17] This is because they are generally much less reactive and rarely exhibit interactions with Lewis acids. As a result, the uranyl oxo group would be expected to be a poor hydrogen bond acceptor. Evidence regarding the hydrogen bonding ability of the uranyl oxo group appears at first glance to be conflicting. There have been numerous computational studies conducted to evaluate the outer-sphere solvation of $[UO_2(OH_2)_5]^{2+}$ in aqueous solution. Electronic structure calculations,[18] ab initio MD simulations,[19] and QM/MM calculations[20] indicate that the oxo group of the uranyl aqua ion either does not form hydrogen bonds or else engages in very weak hydrogen bonding when water is the donor. However, in at least one instance, hydrogen bonding between water and

uranyl oxo groups was observed in optimized water clusters containing the $[UO_2Cl_4]^{2-}$ complex.[18e] In contrast to the results of theoretical studies, there have been numerous observations of close H---O=U contacts in crystal structures of small molecules[11,17] and proteins[21] suggesting that hydrogen bonding with the uranyl oxo group does occur in the solid-state.

To achieve a more complete understanding of the role of the uranyl oxo group as a hydrogen bond acceptor, we have used electronic structure theory to evaluate the geometries and energetics of interactions between a number of uranyl complexes and hydrogen bond donor groups. The results presented herein reveal that although traditional hydrogen bond donors are repelled by the oxo group in the $[UO_2(OH_2)_5]^{2+}$ species, they are attracted to the oxo groups in $[UO_2(OH_2)_2(NO_3)_2]^0$, $[UO_2(NO_3)_3]^-$, and $[UO_2Cl_4]^{2-}$ species. Hydrogen bond strength depends on the equatorial ligation and can exceed 15 kcal mol^{-1}.

The results also reveal the existence of directionality at the uranyl oxo acceptor, with a weak preference for linear H---O$=$U angles.

■ COMPUTATIONAL DETAILS

All calculations were performed with the Gaussian 09 package[22] using density functional theory (DFT) at the B3LYP[23] level of theory. The Stuttgart RSC 1997 effective core potential (ECP) was used for uranium, replacing 60 core electrons to account for scalar relativistic effects.[24] The valence electrons in this basis set are represented by a contracted [8s/7p/6d/4f] basis; 6-31+G(d,p) basis sets were used for carbon, nitrogen, oxygen, chlorine, and hydrogen atoms. The most diffuse function on uranium (having an exponent of 0.005) in all calculated structures was removed from the basis to improve SCF convergence, particularly of $[UO_2(H_2O)_2(NO_3)_2]^0$. Spin$-$orbit interactions were not considered explicitly. All reported structures were converged with the default SCF convergence cutoffs (SCF = tight), with a quadratically convergent SCF procedure used where needed to obtain SCF convergence.[25] All geometry optimizations were performed in C_1 symmetry, and frequency calculations were performed to verify whether geometries were minima. Resolution of small negative frequencies often required tightened convergence criteria (opt = tight) and a finer DFT grid (int = ultrafine). Unless otherwise indicated, all reported geometries are minima. Binding enthalpies were calculated as follows: $\Delta H = E(\text{adduct}) - E(\text{donor}) - E(\text{acceptor}) + \Delta E_{ZPE} + \Delta E_{thermal} + \Delta(PV)$, where $\Delta(PV) = nRT = -0.593$ kcal mol^{-1} at 298.15 K ($n = -1$). Data for reported uranyl complexes (optimized atomic coordinates, absolute energies, zero point energies, enthalpies, and free energies) are provided as Supporting Information.

■ RESULTS AND DISCUSSION

To explore the role of the uranyl oxo group as a hydrogen bond acceptor, geometry optimizations were performed on a series of adducts between hydrogen bond donor groups and uranyl complexes. Representative hydrogen bond donors included traditional N$-$H donors (pyrrole, formamide) and O$-$H donors (methanol, water), as well as one example of the less traditional C$-$H donor (nitrobenzene).[26] The uranyl complexes included $[UO_2(OH_2)_5]^{2+}$, $[UO_2(OH_2)_2(NO_3)_2]^0$, $[UO_2(NO_3)_3]^-$, and $[UO_2Cl_4]^{2-}$. After preliminary geometry optimization of the individual donors and acceptors, initial adduct geometries containing X$-$H---O$=$U hydrogen bond contacts (X = N, O, C) were generated by placing the hydrogen bond donor with respect to the uranyl complex to yield H---O distances near 1.8 Å and X$-$H---O angles near 180°. Within these constraints, a number of initial orientations were built for each donor$-$acceptor pair through variation of the U$=$O---H angle, as well as rotation of the donor group about the U$=$O and O---H axes.

Following geometry optimization, these starting geometries yielded multiple minima for each adduct. The majority of the starting geometries led to stable structures whose primary feature was interaction of the hydrogen bond donor with one or more of the equatorial ligands in the uranyl complex. As shown by **1**$-$**6** in Figure 2, the equatorial ligands can serve either as hydrogen bond donors or hydrogen bond acceptors. Although some of these structures also show a hydrogen bonding contact with the uranyl oxo, for example **5** and **6**, such structures do not allow an unambiguous assessment of the strength and geometric features of an isolated H---O$=$U interaction because of the presence of the additional binding interactions.

All attempts to locate an adduct containing a hydrogen bond with the oxo group of the cationic aqua complex, $[UO_2(OH_2)_5]^{2+}$,
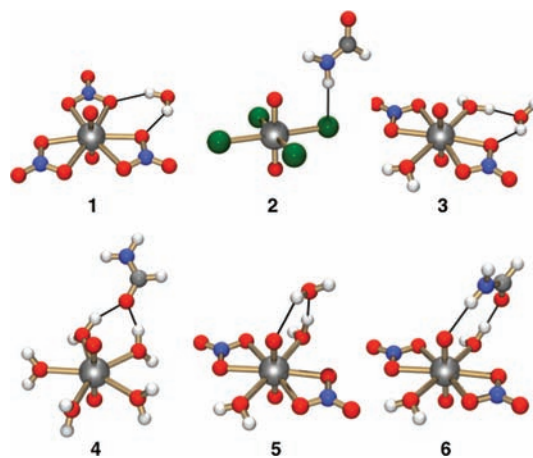

Figure 2. Examples of hydrogen bonding interactions involving equatorial ligands.

were unsuccessful. Regardless of the identity of the donor group or initial geometry, optimization either led to an ever lengthening H---O distance or gave adducts that only involved interaction with the equatorial ligands. The behavior indicates that the nature of the interaction between a hydrogen bond donor and the oxo group in this complex is repulsive rather than attractive. This observation is consistent with prior computational studies showing that the oxo group in this species does not hydrogen bond with water.[18−20]

In contrast to the behavior exhibited by the uranyl aqua ion, the other uranyl complexes that were investigated all exhibit adducts containing clear examples of hydrogen bonding with the oxo group. Optimized geometries **7**$-$**21**, which represent the best example of an isolated H---O$=$U bonding interaction found for each adduct, are shown in Figure 3. All of these geometries represent stationary points and, with few exceptions, each represents a local minimum on the potential surface. The exceptions **9**, **10**, **15**, and **18**, each exhibit a single, very small (-2.8 to -8.7 cm^{-1}), negative frequency indicating a very flat potential surface in the vicinity of the geometry. Binding enthalpies and selected geometric parameters for these adducts are summarized in Table 1.

Focusing on the cases where the H---O$=$U bond is least contaminated by secondary interactions, ΔH values for hydrogen bonding with the oxo group range from a low of -0.1 kcal mol^{-1} for the nitrobenzene-$[UO_2(OH_2)_2(NO_3)_2]^0$ adduct to a high of -15.5 kcal mol^{-1} for the pyrrole-$[UO_2Cl_4]^{2-}$ adduct. The hydrogen bond strength depends on the identity of the equatorial ligands. In general, as the overall charge on the uranyl complex becomes more negative after replacing water with nitrate or chloride ligands, the hydrogen bond strength increases. Thus, the $[UO_2(OH_2)_2(NO_3)_2]^0$ oxo group forms weak hydrogen bonds ranging from -0.1 to -2.1 kcal mol^{-1}, the $[UO_2(NO_3)_3]^-$ oxo group forms moderate hydrogen bonds ranging from -4.8 to -7.1 kcal mol^{-1}, and the $[UO_2Cl_4]^{2-}$ oxo group can form strong hydrogen bonds, in excess of -15 kcal mol^{-1}. In the latter case, interference from secondary interactions with equatorial chloride ligands clouds the assessment of hydrogen bonding strength in **17**, **20**, and **21**.

Such gas-phase ΔH values provide a useful scale for ranking the intrinsic ability of the oxo group to function as a hydrogen bond acceptor. To place these values within the context of the strength of other hydrogen bonds, ΔH values for hydrogen

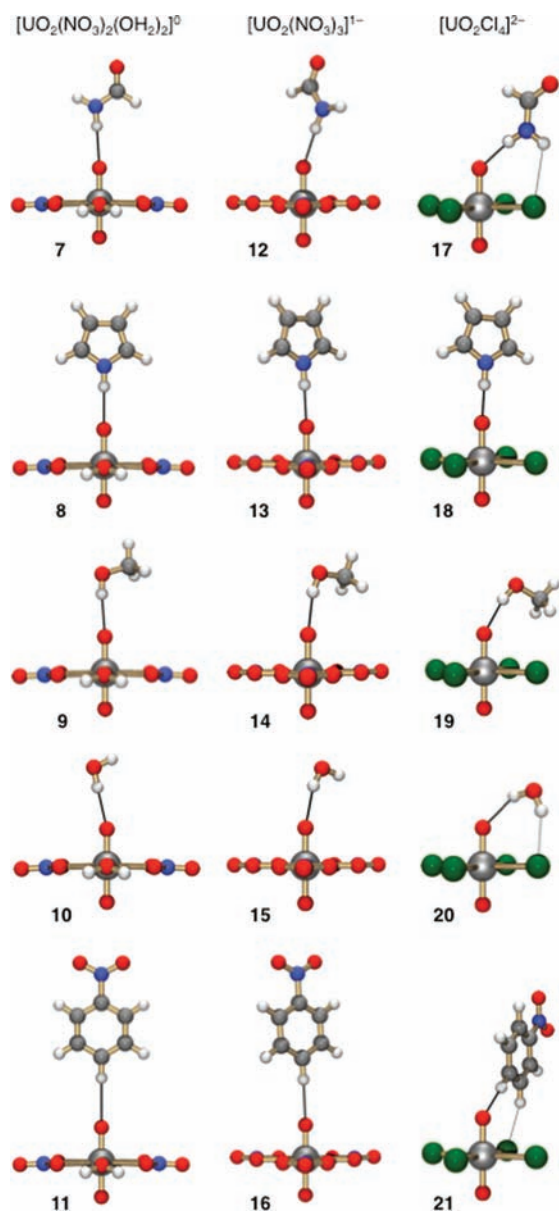$[UO_2(NO_3)_2(OH_2)_2]^0$ $[UO_2(NO_3)_3]^{1-}$ $[UO_2Cl_4]^{2-}$

Figure 3. Optimized adduct geometries showing H---O=U hydrogen bonding and the least contamination from secondary equatorial ligand interactions.

Table 1. ΔH of Formation and Selected Geometric Parameters for Uranyl Oxo Hydrogen Bonded Adducts Shown in Figure 3

ID	adduct	ΔH, kcal mol^{-1}	X−H---O, deg	H---O=U, deg	H---O, Å
		$[UO_2(NO_3)_2(OH_2)_2]^0$			
7	formamide	−1.7	175.8	163.4	2.166
8	pyrrole	−1.7	179.9	179.9	2.146
9	methanol	−2.0	174.3	176.0	2.103
10	water	−2.1	177.5	167.0	2.088
11	p-nitrobenzene	−0.1	179.9	179.8	2.518
		$[UO_2(NO_3)_3]^-$			
12	formamide	−7.1	176.8	158.6	2.031
13	pyrrole	−5.6	179.5	176.8	2.019
14	methanol	−4.3	165.3	172.4	2.032
15	water	−5.1	162.6	168.1	2.054
16	p-nitrobenzene	−4.8	179.1	176.6	2.303
		$[UO_2Cl_4]^{2-}$			
17	formamide	−19.3	168.9	130.0	1.944
18	pyrrole	−15.5	179.6	176.6	1.827
19	methanol	−10.8	165.7	150.8	1.948
20	water	−13.2	149.3	132.3	2.153
21	p-nitrobenzene	−17.1	178.4	132.3	2.170

Table 2. Comparison of ΔH Values (kcal mol^{-1}) for Hydrogen Bond Formation with the Uranyl Oxo Acceptor versus Selected Traditional Acceptors

	$[UO_2(NO_3)_2(OH_2)_2]^0$	O=CH$_2$	H$_2$O	$[UO_2(NO_3)_3]^{1-}$	Cl$^-$	$[UO_2Cl_4]^{2-}$
formamide	−1.7	−2.7	−4.3	−7.1	−21.0	c^a
pyrrole	−1.7	−2.6	−4.2	−5.6	−19.3	−15.5
methanol	−2.0	−3.2	−4.1	−4.3	−14.9	−10.8
water	−2.1	−3.4	−4.2	−5.1	−14.4	c^a
p-nitrobenzene	−0.1	−0.6	−1.4	−4.8	−14.9	c^a

^{a} c = contaminated by secondary interactions with equatorial ligands.

bonds between the same donors and selected traditional acceptors were computed at the same level of theory. Comparison of the results, summarized in Table 2, reveals that the oxo group in $[UO_2(OH_2)_2(NO_3)_2]^0$ has an acceptor strength similar to that of the formaldehyde oxygen atom, the oxo group in $[UO_2(NO_3)_3]^-$ has an acceptor strength similar to that of the water oxygen atom, and the oxo group in $[UO_2Cl_4]^{2-}$ has an acceptor strength similar to that of the chloride anion.

The results demonstrate that the oxo acceptor strength is tuned though the identity of the equatorial ligands and that the effect is significant. For example, the −15.5 kcal mol^{-1} hydrogen bond formed between pyrrole and $[UO_2Cl_4]^{2-}$, **18**, is nearly three times as strong as the interaction in $[UO_2(NO_3)_3]^-$, **13**, nine times as strong as the interaction in $[UO_2(OH_2)_2(NO_3)_2]^0$, **8**, and not detectable in $[UO_2(OH_2)_5]^{2+}$. This behavior can be rationalized in terms of the degree of electron donation to the metal. The more the equatorial ligands are able to donate charge to uranium, the less electron density is taken from the oxo groups. This effect, which is believed to increase the Lewis basicity of the oxo groups, has provided a rationalization for the formation of U=O interactions with metal cations and other Lewis acids.[17]

Given that equatorial ligand donation results in a weakening and lengthening of the U=O bonds, it has been suggested that the symmetric O=U=O stretching frequency can provide a measure of the oxo ligand basicity.[16,17,27] In addition, it was anticipated that the partial atomic charge on the uranyl oxo atom might also serve as an indicator of basicity. Calculated values of these parameters for the complexes evaluated in this study are given in Table 3. Comparison of the symmetric O=U=O stretching frequency for the non-hydrogen bonded complex with hydrogen bond strength, again using pyrrole as the example, reveals a clear trend suggesting this metric can be used to assess the hydrogen bond acceptor ability of other uranyl complexes. While the ΔH values clearly become more favorable with the increasing net negative charge on the uranyl complex, Mulliken

Table 3. Comparison of Pyrrole-Oxo Hydrogen Bond Strength (ΔH) with Theoretical U=O Bond Lengths, O=U=O Symmetric Stretching Frequencies, and Oxo Atom Mulliken charges (q_M) Calculated for the Uranyl Complexes Prior to Hydrogen Bond Formation

complex	ΔH, kcal mol^{-1}	U=O length, Å	O=U=O sym ν, cm^{-1}	q_M
$[UO_2(OH_2)_5]^{2+}$	nd^a	1.748	949.0	−0.358
$[UO_2(OH_2)_2(NO_3)_2]^0$	−1.7	1.766	905.6	−0.769
$[UO_2(NO_3)_3]^-$	−5.6	1.773	889.7	−0.890
$[UO_2(acetate)_3]^-$	−9.6	1.782	869.0	−0.751
$[UO_2(CN)_4]^{2-}$	−11.5	1.778	878.7	−0.619
$[UO_2Cl_4]^{2-}$	−15.5	1.779	864.7	−0.613
$[UO_2(CN)_5]^{3-}$	−19.1	1.784	860.1	−0.641

^{a} nd = not detected.

Figure 5. Plot of ΔH versus H---O distance for N—H and OH donors (data from Table 1).
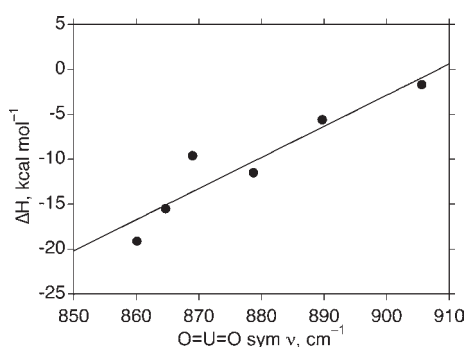
Figure 4. Plot of ΔH for pyrrole-adduct formation versus O=U=O symmetric stretching frequency (data from Table 3).

Figure 6. Distortion of the H---O=U angle in pyrrole adducts **8**, **13**, and **18**.

charges calculated for the oxo atoms fail to correlate with hydrogen bond strength.

To further evaluate possible trends, calculations were performed on three additional uranyl complexes, $[UO_2(acetate)_3]^-$, $[UO_2(CN)_4]^{2-}$, and $[UO_2[CN]_5]^{3-}$. Data for these complexes, which form pyrrole adducts with geometries similar to those observed with **8**, **13**, and **18**, are also summarized in Table 3. The correlation of ΔH with the O=U=O symmetric stretching frequency (Figure 4) establishes that this metric provides a predictive indicator of the hydrogen bond acceptor strength for the uranyl oxo group in any given complex. The behavior of $[UO_2(acetate)_3]^-$ suggests that the uranyl oxo group in tris-carboxylate coordinated complexes (Figure 1, A−C) are capable of forming strong hydrogen bonds.

Geometric parameters generally associated with hydrogen bonding interactions, the H---O distance, the X—H---O angle, and the H---O=U angle, are tabulated for **7**−**21** in Table 1. The X—H---O angles, which exhibit a mean value of $173 \pm 9°$ over all structures, act as expected showing a preference for aligning the X—H vector with the oxo atom. Consistent with observed behavior of other oxygen atom acceptors,[28] hydrogen bonding distances to the uranyl oxo acceptor range from 1.83 to 2.17 Å for the N—H and O—H donors and exhibit somewhat longer values, 2.17 to 2.52 Å, for the C—H donor. A plot of ΔH versus H---O distance for the N—H and O—H donors, Figure 5, shows the anticipated trend that stronger hydrogen bonding is associated with shorter hydrogen bond distance.

Whereas the behavior exhibited by H---O distances and X—H---O angles is anticipated based on the behavior of other
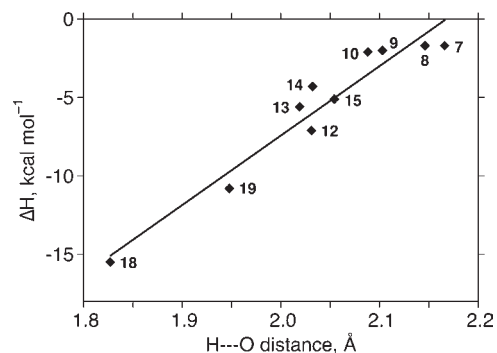
hydrogen bonds,[28] the nature of the directionality at the uranyl oxo acceptor is not. A simple organic analogue, the C=O group in a ketone, exhibits a distinct hydrogen bonding directionality in which the X—H vector lies in the plane of the ketone with a H---O=C angular preference of $120 \pm 10°$.[29] The oxygen atoms in anionic tetrahedral oxoanions such as molybdate and chromate exhibit a similar H---O=M angular preference of $122 \pm 12°$.[30] In contrast, the data in Table 1 show that over half of the structures exhibit H---O=U angles $>175°$ suggesting a preference for the H donor atom to approach along the O=U=O axis. Distortions from this ideal angle can be attributed to secondary interactions with equatorial ligands. This effect is most pronounced with $[UO_2Cl_4]^{2-}$ adducts where four of the five H---O=U angles are $<150°$.

To further investigate hydrogen bonding directionality at the uranyl oxo acceptor, the potential energy surface for distortion of the H---O=U angle was investigated through a series of single-point energy calculations. Holding all other geometric parameters constant, energies were calculated for the pyrrole adducts **8**, **13**, and **18** as the H---O=U angle was varied from 180° to 110° as shown in Figure 6. Plots of the relative energy versus H---O=U angle, Figure 7, confirm a weak 180° preference in all cases. Adduct **8**, with a ΔH of only −1.8 kcal mol^{-1}, exhibits an
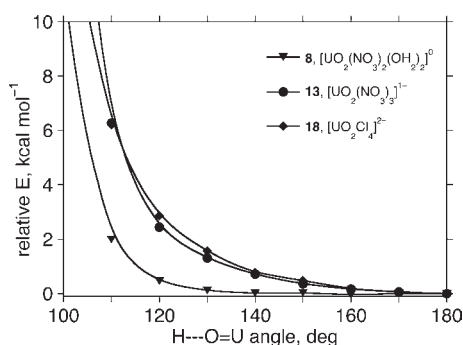
Figure 7. Potential energy surfaces for H---O=U angle distortion (see Figure 6).
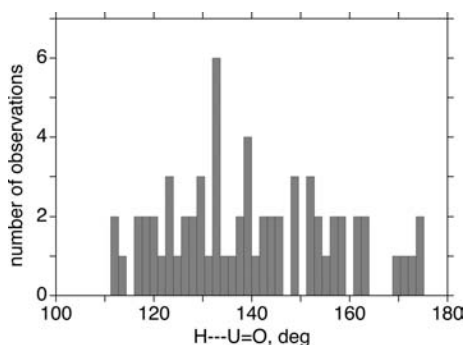

Figure 8. Distribution of H---O=U angles in the CSD.

extremely flat potential energy surface, where distortions of up to 60° from linearity result in decrease of <0.5 kcal mol^{-1} in interaction energy. Adducts **13** and **18** show a somewhat stronger directionality, with a 0.5 kcal mol^{-1} destabilization occurring at a distortion of 30° from linearity.

An analysis of structures in the Cambridge Structural Database (CSD)[31] yields results in full agreement with all theoretical results presented above. A search for examples of hydrogen bonding between N—H, O—H, and C—H donors yielded a total of 65 examples when using the following constraints: normalized X—H distances, H---O distance ≤2.2 Å, X—H---O angle ≥150°, R-factor ≤0.10, no error, no disorder. These examples all exhibit H---O distances well within the $\sum$vdw (sum of the van der Waals) radii (the default value used by the CSD is 2.90 Å) and exhibit X—H---O angles that fall within the range of those observed in Figure 3.

A histogram of the observed H---O=U angle distribution, Figure 8, shows values ranging from 115 to 175° and fails to exhibit any clear acceptor directionality. This behavior is fully consistent with the potential energy surfaces shown Figure 6. The lack of a significant geometric preference in the gas phase suggests that the H---O=U angles observed in the solid-state are likely dictated by secondary interactions with equatorial ligands, steric effects, and packing forces.

■ CONCLUSION

The role of the uranyl oxo group as a hydrogen bond acceptor has been evaluated through a series of electronic structure calculations on adducts formed between a variety of hydrogen bond donors and uranyl complexes. The results confirm the U=O group in $[UO_2(OH_2)_5]^{2+}$ to be a very poor hydrogen

bond acceptor. However, when the aqua ligands are replaced with equatorial ligands that are better able to donate electron density to the metal center, the U=O group becomes a hydrogen bond acceptor. This study provides the first report of the intrinsic strength of these interactions, which range from −0.1 to −2.1 kcal mol^{-1} with $[UO_2(NO_3)_2(OH_2)_2]^0$, −4.8 to −7.1 kcal mol^{-1} with $[UO_2(NO_3)_3]^-$, and can exceed −10 kcal mol^{-1} in $[UO_2Cl_4]^{2-}$, $[UO_2(CN)_4]^{2-}$, and $[UO_2[CN]_5]^{3-}$. The results reveal that the bonding strength of the oxo group can be tuned through the selection of the equatorial donor groups and that the symmetric O=U=O stretch of the parent uranyl complex provides a predictive indicator of the hydrogen acceptor strength.

With respect to uranophile design, it can be concluded that the incorporation of hydrogen bonding groups within the host is a strategy that could certainly lead to enhanced binding affinity and recognition. Structural criteria for maximizing such interactions involve achieving close X—H contact distances, X—H---O angles that are near linear, and H---U=O angles ideally in the range of 150 to 180°. Models of the three uranophiles that contain one or more hydrogen bonding groups (Figure 1), predict that whereas A is able to achieve the desired hydrogen bond placement (H---O, 1.99 Å, N—H---O, 166°; H---O=U, 177°), hydrogen bond distances are too long to make a significant contribution in B (H---O, 2.57 Å) and C (H---O, 2.89 Å calc, 2.85 Å X-ray). The correlation between ΔH and H---O distance (Figure 5) predicts that H---O distances >2.5 Å would have intrinsic hydrogen bond strengths well below 1 kcal mol^{-1}. Although A, B, and C have been experimentally shown to complex the uranyl ion, it has not yet been established whether hydrogen bonding interactions play any significant role in the observed binding. Demonstrating enhanced recognition for the uranyl ion through the exploitation of H---O=U hydrogen bonding is a task that remains to be accomplished.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Optimized atomic coordinates, absolute energies, zero point energies, enthalpies, and free energies for **1**−**21** and additional pyrrole adducts; additional parameters used to model uranyl complexes with the PCModel. This material is available free of charge via the Internet at http://pubs.acs.org.

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