Computational Tools for Calculating log $\beta$ Values of Geochemically Relevant Uranium Organometallic Complexes

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Supporting Information

ABSTRACT: Uranium (UVI) interacts with organic ligands, subsequently controlling its aqueous chemistry. It is therefore imperative to assess the binding ability of natural organic molecules. We evidence that density functional theory (DFT) can be used as a practical protocol for predicting the stability of UVI organic ligand complexes, allowing for the development of a relative stability series for organic complexes with limited experimental data. Solvation methods and DFT settings were benchmarked to suggest a suitable off-the-shelf solution. The results indicate that the IEFPCM solvation method should be employed. A mixed solvation approach improves the accuracy of the calculated stability constant ($\log \beta$); however, the calculated $\log \beta$ are approximately five times more favorable than experimental data. Different basis sets, functionals, and effective core potentials were tested to check that there were no major changes in molecular geometries and $\Delta G$. The recommended method employed is the B3LYP functional, aug-cc-pVDZ basis set for ligands, MDF60 ECP and basis set for UVI, and the IEFPCM solvation model. Using the fitting approach employed in the literature with these updated DFT settings allows fitting of 1:1 UVI complexes with root-mean-square deviation of 1.38 $\log \beta$ units. Fitting multiple bound carboxylate ligands indicates a second, separate fitting for 1:2 and 1:3 complexes.

INTRODUCTION

The utilization of nuclear energy has resulted in widespread contamination of the environment with uranium. It has generated uranium-containing waste, which, depending on national policy, will likely be disposed of in a near-surface or deep geological repository. Uranium (UVI) can be mobilized from these sites by groundwater as part of an alkaline (pH > 9) or acidic plume (pH 3.5–6). Understanding how the chemical composition of groundwater can influence aqueous UVI chemistry is key to constrain the subsequent mobility of UVI. In particular, it is important to characterize the effect of naturally occurring organic molecules because they are dominant in these environments.

One class of naturally occurring organic molecules is siderophores. These are released by plants, bacteria, and fungi primarily to solubilize FeIII. However, siderophores are known to complex with uranium, leading to uranium leaching and desorption from mineral surfaces. Determining the stability of possible UVI siderophore complexes is not practical because there are 500 known siderophores. Fortunately, there are very few functional groups in siderophores. These are the catecholate (1), hydroxamate (2), $\alpha$-hydroxycarboxylate (3), $\alpha$-aminocarboxylate (4), hydroxyphenyloxazolone (5), and $\alpha$-hydroxyimidazole (6) functional groups, as seen in Figure 1. Characterizing the stability of each functional group across pH 3.5–6 will allow us to begin to understand which class of siderophores form the most stable complexes with UVI in the acidic pH range of interest.

The relative stability of UVI siderophore functional group complexes can be compared by calculating the stability constant, $\log \beta$, of the reaction. The experimental determination of stability constants often requires multiple experimental techniques and is time-consuming and labor-intensive. It can also be difficult to use certain experimental techniques such as potentiometric titrations in high-pH and high-ionic-strength solutions due to the sodium error when using glass electrodes. Density functional theory (DFT) provides a cost-effective and radiation-free way to estimate the $\log \beta$ of UVI complexes because it computes the Gibbs energy ($\Delta G$) directly for each species in metal–ligand complexation reactions, allowing for the subsequent calculation of $\log \beta$ values.

The $\log \beta$ values for UVI ligand reactions were calculated before using DFT. The absolute values, however, were off by...
10 log $\beta$ units ($>60$ kJ/mol)\(^{16,17}\) or $>30$ log $\beta$ units.\(^{18}\) Although absolute values differed from experiment, the relative values estimated chemical trends correctly. The accuracy and computational cost of log $\beta$ calculations under aqueous conditions depend on four different model chemistry aspects in the DFT protocol suggested here. These are the solvation method employed, the effective core potential (ECP), the basis set, and the functional. This is represented by eq 1.

$$
\log \beta = f(\text{solvation method, ECP, basis set, functional})
$$

(1)

The functional employed, ECP (as long as it is a small-core ECP), and the basis set used do not significantly affect the solvation energies for closed-shell, f elements (e.g., U\(^{VI}\)) in solution.\(^{19-21}\) However, previous work suggested that the errors in log $\beta$ are sensitive to the solvation method employed.\(^{19,20,22}\)

Computational methods generally model water molecules that are not directly coordinated with U\(^{VI}\) implicitly to save on computational cost. Calculated stability constants, however, are improved using a mixed implicit–explicit solvation method because it is more successful at incorporating solute–solvent cavity and dispersion terms.\(^{23}\) Nevertheless, this approach has to date only been explored for uranyl in detail for water exchange reactions.\(^{19,22,24}\) A mixed approach was employed for 1:1 U\(^{VI}\) acetate, oxalate, and catecholate complexes.\(^{25}\)

To counter the absolute errors in log $\beta$, a fitting approach is frequently employed. In this case, the computed log $\beta$ of different complexes is plotted against experimental data, and the fitting curve is used to calculate fitted log $\beta$ values. This was successfully applied for a variety of metal centers with ligands including siderophores.\(^{26-28}\) Recently, this approach was also applied to 1:1 U\(^{VI}\) complexes for oxygen donor ligands, allowing for the prediction of log $\beta$ values to within <1 (root-mean-square deviation).\(^{18}\) The protocol developed in ref 18 was used in combination with the SMD implicit solvation model\(^{29}\) in recent uranyl studies.\(^{30,31}\) However, the protocol used a model chemistry with prohibitive computational costs when investigating ligands containing tens of atoms, and establishing a method for large ligands is key for modeling siderophore complexes. Furthermore, the solvation cavity used in the SMD model has not been parametrized for actinides.\(^{29}\)

The aim of the present study was to establish a computationally cost-effective protocol that allows us to estimate the relative stability of functional groups that compromise the reactive components in siderophores. The protocol needs to be sufficiently cost-effective so that it can be applied to full siderophore structures. Initially, we tested different solvation methods because the greatest error in calculated stability is expected to be due to solvation. This was tested for 1:1, 1:2, and 1:3 U\(^{VI}\)/acetate complexes. Two implicit solvation methods were subsequently tested to examine whether a method that better calculates non-electrostatic contributions improved the calculated complex stability. A mixed solvation approach was employed where each aqua ligand was represented as one U\(^{VI}\) bound aqua ligand whose hydrogen atoms form one hydrogen bond to an explicit solvent molecule, [H\(_2\)O\(\cdots\)H\(_2\)O]\(_3\). This was done to investigate if the approach proposed by Gutowski and Dixon\(^{22}\) improves calculated log $\beta$ and whether this outweighs the difficulties associated with applying this method. After this, the effect of changing ECP, basis set size, and functional was tested to establish the magnitude of differences in log $\beta$ for the three U\(^{VI}\) acetate complexes (1:1, 1:2, 1:3). A fitting equation was then established using the seven different ligands presented in Figure 2. These seven ligands were selected because they are similar to or the same as the functional groups that comprise the reactive components of siderophores and have structural and stability data against which the protocol can be validated. Finally, the protocol was used to estimate the log $\beta$ of 1:1, 1:2, and 1:3 uranyl carboxylate complexes, and potential fitting trends were analyzed.

### METHODS

**Computational Details.** Electronic structure calculations were carried out with Gaussian 16, rev. A.03\(^{32}\) using GaussView version 6\(^{33}\) for pre- and postprocessing. All structures were geometrically optimized, and the frequencies were calculated to confirm local minima and determine thermodynamic properties including Gibbs free energy. The PW91\(^{34}\), TPSS\(^{35}\), and M06\(^{36}\) functionals were utilized in addition to B3LYP\(^{37}\) to provide comparisons with a generalized gradient (GGA), meta-GGA, and recent hybrid
The stability of the complex is encapsulated by the equilibrium constant \((K)\). Equilibrium constants are commonly reported as \(-\log K\) (pK) because individual \(K\) values may span many orders of magnitude. Because metal ions have multiple coordination sites, complexion reactions often involve more than one ligand that bind in a series of reactions. The resulting stepwise equilibrium constants are multiplied together and reported as the stability constant, \(\beta\). Stability constants are often reported with the number of metal ions and ligands consumed in the reaction written as subscripts. The reaction of one metal ion with one ligand is denoted \(\beta_{11}\).

The stability constant of the complex is determined by the corresponding Gibbs free energy of reaction, \(\Delta G\). This connection is shown in eq 6, where \(\alpha_{(\text{ML(Sol)},)}\), \(\alpha_{(\text{L})}\), and \(\alpha_{(\text{Sol})}\) are activities for molecules in the reaction. The Gibbs free energy of reaction is calculated by subtracting the sum of the Gibbs free energy (\(G\)) of the reactant species from that of the product species, as shown in eq 7.

\[
\log \beta_{11} = \log K = \log \frac{[\text{ML(Sol)}]_{m-n}}{[\text{ML(Sol)}]_m[\text{L}]} \approx \log \frac{\alpha_{(\text{ML(Sol)},)}}{\alpha_{(\text{ML(Sol)},)}\alpha_{(\text{L})}} = (\log_{10} e) \frac{-\Delta G}{RT} = -\frac{\Delta G}{2.303RT}
\]

\[
\Delta_G = G(\text{ML(Sol)}_{m-n}) + nG(\text{Sol}) - G(\text{ML(Sol)}_m) - G(\text{L})
\]

Organic Molecule Training Set Used for Fitting Calculated Stability Constants. Seven organic molecules were used for the 1:1 fitting and are shown in Figure 2. They were chosen because they are, or are similar to, siderophore chelating groups. The reaction used to calculate \(\Delta G\) is given in eq 7, except for L-glycine, which is given in eq 8. Equation 8 was used based on the reaction used in the experimental literature.

\[
\Delta_G = G(\text{ML(Sol)}_{m-n}) + nG(\text{Sol}) - G(\text{ML(Sol)}_m)
\]

The log \(\beta\) values were calculated using eq 6. For testing the fitting approach for multiple bound ligands, the formation of different 1:1, 1:2, and 1:3 UVI carboxylate complexes was calculated. The ligands were glycolate, acetate, and oxalate. These were chosen to include changes in denticity and difference in charge.

The experimental stability constants (and resulting \(\Delta G\)) used for all comparisons were adjusted to zero ionic strength by using the specific ion theory and the Davies equation, depending on the ionic strength at which the experiments were performed. Further details can be found in the Supporting Information.

RESULTS AND DISCUSSION

When assessing protocol modifications, one must keep in mind that a change of one log \(\beta\) unit requires a \(-5.709\) kJ/mol change in \(\Delta_G\) when \(T = 298.15\) K.

Implicit Solvation Models. For all calculations, the base model chemistry employed the B3LYP functional, aug-cc-pVDZ basis set for ligands, and M06-2X ECP with the corresponding basis set for UVI. The only exception to this rule applied when the UVI ECP and basis set was explored. In this case, the calculations used the cc-pVDZ ligand basis set to be consistent with the cc-pVDZ-PP basis set for UVI. The effects
of using two different implicit solvation methods, IEFPCM and SMD, on $\Delta G$ were studied, and the results are shown in Table 1 and Figure 3a.

The SMD model should provide more accurate $\Delta G$ than IEFPCM. This is because the SMD model is a parametrized version of IEFPCM to better incorporate nonelectrostatic contributions such as cavitation, dispersion, and changes in local solvent structure. Changing the implicit solvation model from IEFPCM to SMD changes $\Delta G$ by +59.4, +125.0, and 155.6 kJ/mol to −59.7, −94.4, and −114.9 kJ/mol for UVI complexation with one to three acetate ligands, respectively, as shown in Table 1 and Figure 3a. SMD is significantly more accurate for calculating $\Delta G$ when compared with the experimental data (−19.4, −29.2, and −42.5 kJ/mol) highlighting the importance of nonelectrostatic contributions.

A downside of using the SMD method with metal-containing systems is that the solvation cavity overexposes metal density to the bulk solvent, as seen in Figure 4a. This effect is the direct result of limited experimental data to calibrate SMD metallic radii for inorganic systems. This is an artifact of the way in which the nonelectrostatic energy contributions were included in SMD. The solvation method was parametrized by adjusting the radii distance used to create the solvation cavity. This has only been applied to nonmetallic contributions. When comparing the results with the experimental data (−19.4, −29.2, and −42.5 kJ/mol) highlighting the importance of nonelectrostatic contributions.

The modified method employed recently in refs 30 and 31 should likely be used cautiously due to the solvation cavity shortcomings of the SMD model, and ideally the IEFPCM model originally employed should be used to predict the relative stabilities of UVI complexes instead.

**Mixed Solvation with IEFPCM.** It has been observed that mixed solvation methods improve the accuracy of solvation energies. This was explored for water exchange reactions between bulk water and UVI bound aqua ligands. Gutowski and Dixon found that for accurate solvation energies, two water molecules are needed to solvate each UVI-bound ligand, $[\text{UO}_2(\text{H}_2\text{O}...(\text{H}_2\text{O})_2)]^{2+}$.

The UVI structures employed in eqs 9 to 11 are shown in Figure 5. They were chosen based on maintaining isodesmic reactions. If reactions are isodesmic, then the number of bonds is preserved. If reactions are nonisodesmic and the resulting UVI–ligand complex contains more or fewer bonds, then the stability of the complex will be higher or lower than it should be. This can significantly affect $\Delta G$.

Using the mixed solvation method should reduce the errors compared with using the implicit method. This is because the explicit solvent molecules position the electron density of UVI further into the solvation cavity. Therefore, electrostatic interactions with the bulk solvent are reduced along with $\Delta G$ dependence on the implicit model employed. Because IEFPCM overpredicts solvation energies, applying the mixed solvation approach seems to shift calculated $\Delta G$ to less negative values and closer to the experimental data. When using the $[\text{UO}_2(\text{H}_2\text{O}...(\text{H}_2\text{O})_2)]^{2+}$ mixed solvation method, $\Delta G$ changes by +30.2, +34.7, and +38.7 kJ/mol to −88.9, −184.7, and −231.8 kJ/mol for one to three acetate ligands, respectively. However, this is still 69.5, 155.5, and 189.3 kJ/mol more negative than the experimental data for one, two, and three acetate ligands, respectively. This is shown in Figure 3a and Table 2.
The calculated $\Delta G$ could be improved by releasing water as a cluster rather than as individual water molecules because it would keep the reaction isodesmic. For reactions 9 and 10, the liberated water molecules are assumed to form a six-ring water structure. This was chosen rather than the three more energetically stable conformers to maintain a consistent number of water molecules. In reaction 11, the final three water molecules were assumed to be released as a trimer. The standard state correction changes from $-17.88$ kJ/mol to $-17.88/n$ kJ/mol for a cluster of $(H_2O)_n$ molecules. The reaction energies changed by $+4.3$, $+8.5$, and $+4.4$ kJ/mol to $-84.6$, $-176.2$, and $-227.4$ kJ/mol, respectively, suggesting that there is little improvement in releasing the water molecules individually.

**Mixed Solvation with SMD.** One interesting idea is to combine the parametrized SMD model with the mixed $[H_2O\cdots(H_2O)_2]$ method. The extra water molecules reduce the $U^{VI}$ atom contribution to the solvation cavity by positioning the $U^{VI}$ atom further into the structure, away from the bulk water. This leads to a better representation of the solvation cavity.

Using the mixed solvation method, $[H_2O\cdots(H_2O)_2]$, in combination with the SMD solvation model results in less accurate $\Delta G$ than modeling solvation implicitly by $-15.9$, $-64.1$, and $-70.0$ kJ/mol for the 1:1, 1:2, and 1:3 uranyl acetate complexes. This is visualized in Figure 3a. This is related to the different errors in solvation. Reference 19 has explored the errors associated with adding increasing numbers of explicit water molecules. The change in free energy of solvation in a reaction, $\Delta G_{solv}$, is the sum of the change in the gas-phase hydration energy, $\Delta G_{hyd}$, and the change in the solvation correction for the reaction $\Delta G_{core}$ ($\Delta G_{solv} = \Delta G_{hyd} + \Delta G_{core}$). Parmar et al. observed that when only aqua ligands

![Figure 3. Comparison of calculated (x axis) and experimental (y axis) Gibbs free energy of reaction (kJ/mol) for the formation of 1:1 (circles), 1:2 (squares), and 1:3 (triangles) uranyl acetate complexes. The effect of changing (a) solvation method, (b) ECP, (c) ligand basis set, and (d) functional. In panel a, the ligand basis set is aug-cc-pVDZ unless otherwise stated. The experimental data are from ref 47, corrected to zero ionic strength using the specific ion theory (ref 58).](image)

![Figure 4. Solvation cavity of $[UO_2(H_2O)_5]^{2+}$. (a) SMD solvation cavity and (b) IEFPCM solvation cavity. The cavity has been colored to represent the contributions of the different elements to the cavity. Red represents oxygen, white represents hydrogen, and blue represents uranium.](image)

![Figure 5. (a) Uranyl water complex and the (b) 1:1, (c) 1:2, and (d) 1:3 uranyl acetate complexes used to work out $\Delta G$ in the mixed solvation methods. The uranyl complex was optimized from ref 22.](image)
are complexed around U^{III} and U^{IV}, a large solvation correction $\Delta G_{\text{corr}}$ is required to counter the errors associated with the gas-phase hydration energy, $\Delta G_{\text{hyd}}$. The $\Delta G_{\text{corr}}$ term is dominated by $\Delta G_{\text{elec}}$, which is sensitive to the volume and surface area of the solvation cavity. Reference 19 observed that the small cavity volume and large surface area of the SMD solvation model led to an overestimated $\Delta G_{\text{solv}}$. This means that the $\Delta G$ from adding aqua ligands to a U^{III} or U^{IV} ion is overpredicted ($\Delta G$ is too negative). In the U^{IV} acetate reactions, water molecules are released rather than added; therefore, the predicted $\Delta G$ is too positive. Addition of the explicit water molecules leads to a reduction in the magnitude of $\Delta G_{\text{corr}}$ required as $\Delta G_{\text{hyd}}$ converges toward $\Delta G_{\text{solv}}$.19 The extra water molecules position the electron density of U^{VI} further into the solvation cavity, reducing $G_{\text{corr}}$ at the edge of the solvation cavity and reducing the overestimation of solvation energies. This leads to a shift of SMD $\Delta G$ to more negative values, as observed in Figure 3a. Conversely, ref 19 observed that the large surface area and volume of the UFF IEFPCM meant that $\Delta G_{\text{solv}}$ is underestimated ($\Delta G$ of adding aqua ligands is too positive); therefore, in the U^{VI} acetate reactions where water molecules are released, $\Delta G$ will be too negative. Adding explicit molecules in this case reduces $\Delta G$, and so IEFPCM

| complex | model chemistry | $U=O$ | $O=U=O$ | $U-O_{\text{H}_{2}O}$ | $U-O_{\text{cor}}$ | $\Delta G$ |
|---------|----------------|-------|---------|-------------------|--------------------|---------|
| [UO_{2}(H_{2}O)_{5}]^{2+} | aug-cc-pVDZ/MDF60/IEFPCM | 1.776 | 177.9 | 2.447 | - | - |
| [UO_{2}(H_{2}O)^{*})_{5}]^{2+} | aug-cc-pVDZ/MDF60/SMD | 1.784 | 179.0 | 2.504 | - | - |
| [UO_{2}(H_{2}O)^{*})_{5}]^{2+} | 6-31g(d,p)/MWB60/SMD | 1.782 | 179.5 | 2.470 | - | - |
| [UO_{2}(H_{2}O)_{5}](Acet)^{+} | aug-cc-pVDZ/MDF60/IEFPCM | 1.791 | 179.1 | 2.489 | 2.495 | 75.6 |
| [UO_{2}(H_{2}O)_{5}](Acet)^{+} | aug-cc-pVDZ/MDF60/SMD | 1.782 | 178.6 | 2.462 | 2.474 | 21.6 |
| [UO_{2}(H_{2}O)_{5}](Acet)^{+} | aug-cc-pVDZ/MDF60/SMD | 1.770 | 179.2 | 2.435 | 2.465 | -19.4 ± 4.81 |
| [UO_{2}(Acet)(H_{2}O)^{*})_{5}]^{+} | aug-cc-pVDZ/MDF60/IEFPCM | 1.786 | 178.4 | 2.425 | 2.461 | 184.7 |
| [UO_{2}(Acet)(H_{2}O)^{*})_{5}]^{+} | aug-cc-pVDZ/MDF60/SMD | 1.791 | 179.0 | 2.415 | 2.508 | 158.5 |
| [UO_{2}(Acet)(H_{2}O)^{*})_{5}]^{+} | aug-cc-pVDZ/MDF60/SMD | 1.787 | 179.2 | 2.421 | 2.471 | 29.6 |
| [UO_{2}(Acet)^{+}]^{-} | aug-cc-pVDZ/MDF60/IEFPCM | 1.794 | 180.0 | 2.500 | 2.498 | -231.8 |
| [UO_{2}(Acet)^{+}]^{-} | aug-cc-pVDZ/MDF60/SMD | 1.796 | 179.9 | 2.535 | 2.509 | -50.0 |

Table 2. Average Bond Lengths (Å), Angles (deg), and $\Delta G$ (kJ/mol) for Acetate (Acet) Complexes Using the Mixed Solvation Approach Where H_{2}O^{*} Represents [H_{2}O(H_{2}O)_{2}]^{+}.

Figure 6. Solvation cavity of U^{VI} with varying amounts of explicitly drawn water molecules. (a,b) Side-on and plan view of [UO_{2}(H_{2}O)_{5}]^{2+}. (c,d) Side-on and plan view of [UO_{2}(H_{2}O)^{*})_{5}](H_{2}O)_{2}^{+}. (e,f) Side-on and plan view of the [UO_{2}(H_{2}O)_{5}](H_{2}O)_{2}^{+} complex (single point energy calculation on coordinates from ref 19).

Figure 6.
reaction energies shift toward more positive values, as observed in Figure 3a.

The addition of the extra water molecules in \([\text{UO}_2\text{(H}_2\text{O}))_5\text{]}^{2+}\) does not sufficiently shield the UVI atom from the implicit solvation model, as can be observed in Figure 6c,d. Only adding a significant amount of water molecules buries the UVI atom enough to prevent interactions with the implicit solvation model \((e.g., \text{[UO}_2(\text{H}_2\text{O}))_5(\text{H}_2\text{O}))_{5}\))\(^{3}\). Keeping reactions isodesmic using such a structure is challenging, and computational cost increases significantly. This would not be a practical approach for exploring a relative stability series.

The results from combining the mixed solvation method with SMD and the 6-31g(d,p) basis set for ligands are worth noting due to the high accuracy of \(\Delta G\) when comparing to the experimental data. The calculated \(\Delta G\) for one to three acetate molecules are \(-21.57, -29.16, \) and \(-21.57\) kJ/mol compared with the experimental values of \(-131.4, -231.4, \) and \(-337.7\) kJ/mol for one to three acetate ligands, respectively, indicating no significant change. Using the MDF60 basis set is adequate in terms of \(\Delta G\).

Table 3 suggests that geometries are very similar, with average \(\text{U}==\text{O}, \text{U}==\text{O}_{\text{water}},\) and \(\text{U}==\text{O}_{\text{acetate}}\) bonds within 1.14, 0.49, and 0.083% of each other, respectively. The \(\text{U}==\text{O}\) length is underpredicted compared with experimental data by \(-0.49, -0.28,\) and \(-0.28\) kJ/mol by MDF60 in the uranyl complex and 1:1 uranyl acetate complex by 1.4 to 0.4%, respectively. The \(\text{U}==\text{O}\) bonds continue to lengthen and are over predicted in the 1:2 and 1:3 uranyl acetate complexes by 0.23 and 0.28%, respectively. The \(\text{U}==\text{O}\) length is over predicted when using MDF60 ECP with and without the cc-pVDZ-PP basis set for all complexes, by up to 1.4%. The \(\text{U}==\text{O}_{\text{acetate}}\) length increases when switching from MDF60 ECP to MDF60 ECP but remains the same when switching to the cc-pVDZ-PP basis set. These bond lengths are up to 2.8% shorter than the experimental data in the 1:1 uranyl acetate complex, with lengths increasing until they are 0.6% longer than the experimental data for the 1:3 uranyl acetate complex. The \(\text{U}==\text{O}_{\text{water}}\) lengths tend to be longer than the experimental data, increasing as acetate molecules are added, and are up to 6.7% longer in the 1:2 uranyl acetate complex. A general trend emerges where \(\text{U}==\text{O}\), and \(\text{U}==\text{O}_{\text{water}}\) bond lengths increase in the order MDF60 (shortest), MDF60, and MDF60 ECP with cc-pVDZ-PP basis set (longest). The opposite trends occur with \(\text{U}==\text{O}\) angle decreasing when switching from MDF60 ECP to MDF60 ECP. The change in \(\text{O}==\text{U}==\text{O}\) decreases as water is removed from the complex, with a decrease in the ECP and basis set being 1.69% for \([\text{UO}_2(\text{H}_2\text{O}))_3\])\(^{3}\) and 0% with 180° \(\text{O}==\text{U}==\text{O}\) angle for \([\text{UO}_2(\text{Acet})_3])\(^{3}\).

Overall, there is little change in the geometries and \(\Delta G\) between the tested UVI ECP and basis sets. Therefore, to reduce computational cost, it is best to use either the MDF60
Basis Set and the B3LYP/MDF60/IEFPCM Model Chemistry (triple), and Q (quadruple). The results presented in Table 4 show faster than molecular energies when increasing basis set size, it is fully relativistic. The MDF60 ECP was used in subsequent calculations because of the MDF60 basis set rather than the cc-pVDZ-PP basis set. The Journal of Physical Chemistry A

Table 4. Average Bond Lengths (Å), Angles (deg), and \( \Delta G \) (kJ/mol) for Acetate (Acet) Complexes with Different Ligand Basis Set and the B3LYP/MDF60/IEFPCM Model Chemistry

| complex                        | ligand basis set | functional | U=O | O=U=O | U–O water | U–O acetate | \( \Delta G \)    |
|--------------------------------|-----------------|------------|-----|-------|-----------|-------------|-----------------|
| \([\text{UO}_2(\text{H}_2\text{O})_6]^{2+}\) | experiment     | 1.764–1.790   | 1.467–1.493   | 2.403–2.420  | –          | –            | –               |
| \([\text{UO}_2(\text{H}_2\text{O})_6](\text{Acet})]^+ | experiment     | 1.771^a     | 1.768–1.790   | 2.350^a     | 2.465^a   | –19.4 ± 4.81^a| –               |
| \([\text{UO}_2(\text{H}_2\text{O})_6](\text{Acet})]^2+ | experiment     | 1.777^a     | 1.768–1.790   | 2.350^a     | 2.465^a   | –29.2 ± 5.02^a| –               |
| \([\text{UO}_2(\text{H}_2\text{O})_6](\text{Acet})]^3+ | experiment     | 1.770^a     | 1.768–1.790   | 2.350^a     | 2.465^a   | –42.5 ± 3.61^a| –               |

Table 5. Average Bond Lengths (Å), Angles (deg), and \( \Delta G \) (kJ/mol) for Acetate (Acet) Complexes with Different Functionals and the aug-cc-pVDZ/MDF60/IEFPCM Model Chemistry

| complex                        | functional | U=O | O=U=O | U–O water | U–O acetate | \( \Delta G \)    |
|--------------------------------|------------|-----|-------|-----------|-------------|-----------------|
| \([\text{UO}_2(\text{H}_2\text{O})_6]^{2+}\) | PW91PW91   | 1.787 | 1.765 | 2.460 | – | – |
| \([\text{UO}_2(\text{H}_2\text{O})_6](\text{Acet})]^+ | PW91PW91   | 1.795 | 1.755 | 2.466 | 2.396 | –126.9 |
| \([\text{UO}_2(\text{H}_2\text{O})_6](\text{Acet})]^2+ | PW91PW91   | 1.793 | 1.758 | 2.464 | 2.391 | –130.3 |
| \([\text{UO}_2(\text{H}_2\text{O})_6](\text{Acet})]^3+ | PW91PW91   | 1.775 | 1.764 | 2.480 | 2.410 | –119.1 |

or the MDF60 basis set rather than the cc-pVDZ-PP basis set. The MDF60 ECP was used in subsequent calculations because it is fully relativistic. **Ligand Basis Set.** Molecular geometries converge much faster than molecular energies when increasing basis set size, and geometries typically converge for double-\( \zeta \) basis sets. To test this hypothesis, the structures were optimized with Dunning’s diffuse augmented correlation-consistent split valence basis sets, aug-cc-pVnZ, where \( n = D \) (double), T (triple), and Q (quadruple). The results presented in Table 4 suggest that there is virtually no change in the geometries of the uranyl complexes as the basis size increases. Typically, the U=O and U–O\(_{\text{water}}\) bond lengths and O=U=O angles vary by <0.1% between the different sized basis sets. The exception is U–O\(_{\text{water}}\) bond distances of the quadruple-\( \zeta \) basis set, which increases by 0.4% compared with the double-\( \zeta \) basis set. The bond distances of U–O\(_{\text{acetate}}\) vary by <0.2% between the three basis sets. Using the aug-cc-pVDZ basis set is adequate when wishing to predict the geometries of uranyl complexes. To understand further the dependence of \( \Delta G \) on basis set size, the structures have been optimized with Dunning’s diffuse augmented correlation-consistent split valence basis sets, aug-
Table 6. Experimental, Calculated, and Fitted (eq 13) log β Values for Different Organic Molecules Representative of Siderophore Functional Groups

| ligand                  | experiment | calculated | difference (calculated – experiment) | fitted       | difference (fitted – experiment) |
|-------------------------|------------|------------|--------------------------------------|--------------|----------------------------------|
| glycolate               | 3.24a      | 15.48      | 12.25                                | 2.14         | −1.10                            |
| acetate                 | 3.39b      | 20.86      | 17.47                                | 4.24         | 0.85                             |
| oxalate                 | 7.44c      | 32.38      | 24.94                                | 8.73         | 1.28                             |
| acetohydroxamate         | 8.03d      | 31.56      | 23.53                                | 8.41         | 0.38                             |
| l-glycine               | 11.08e     | 43.09      | 32.01                                | 12.90        | 1.82                             |
| salicylate              | 13.04f     | 37.35      | 24.31                                | 10.67        | −2.37                            |
| catecholate             | 16.06g     | 51.02      | 34.16                                | 16.00        | −0.86                            |

"Difference between the experimental log K and the calculated and fitted values is also reported. aExperimental stability constant is from ref 48. bExperimental stability constant is from ref 49. cExperimental stability constant is from ref 50. dExperimental stability constant is from ref 51. eCorrected to zero ionic strength using specific ion theory (ref 59). fCorrected to zero ionic strength using the Davies equation (ref 58)."
The experimental log two di

The standard error for the gradient and intercept from our ligand training set after employing eq 13 is 1.38 log β units. The standard error (1.64 log β units) of the equation. To our knowledge, no structural data has not been explored in detail to date. The fitting for 1:2 UVI ligand complexes was studied recently, but this was conducted with the SMD solvation model rather than the IEFPCM solvation model that we employ here. To examine if a fitting can be used for 1:1 to 1:3 UVI ligand complexes on one fitting curve, the stability of UVI glycolate, acetate, and oxalate ligands was explored. All three glycolate ligands bind in a monodentate style via the carboxylate end (at pH <3.5), whereas all three acetate ligands bind in a bidentate fashion.77,68 Oxalate binds in a bidentate fashion in the 1:1 and 1:2 UVI/L complex, while the third oxalate binds in a monodentate fashion.64,65

Figure 8a shows that the experimental log β loosely increases exponentially with respect to calculated log β. The correlation is 0.889 for the nine complexes investigated during this study. Further inspection highlights the complexity of such a fitting.

These test ligands indicate that the fitting curve significantly improves the estimated stability constant for ligands outside the ligand training set.

Sequential Complexation. To our knowledge, using a fitting approach for multiple ligands coordinated around UVI has not been explored in detail to date. The fitting for 1:2 UVI ligand complexes was studied recently,31 however, this was conducted with the SMD solvation model rather than the IEFPCM solvation model that we employ here. To examine if a fitting can be used for 1:1 to 1:3 UVI ligand complexes on one fitting curve, the stability of UVI glycolate, acetate, and oxalate ligands was explored. All three glycolate ligands bind in a monodentate style via the carboxylate end (at pH <3.5), whereas all three acetate ligands bind in a bidentate fashion.64,65 Oxalate binds in a bidentate fashion in the 1:1 and 1:2 UVI/L complex, while the third oxalate binds in a monodentate fashion.64,65

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In Figure 8b, the data have been split by ligand charge, that is, monoanionic charged ligands, glycolate, and acetate (green) and dianionic charged oxalate (black). Both of these curves are linearly correlated ($R^2 = 0.9131$ for $-1$ charge glycolate and acetate and $R^2 = 0.9918$ for $-2$ charged oxalate). The trends and the level of overestimation of the calculated log $\beta$ are similar between glycolate and acetate. Oxalate underpredicts the calculated stability compared with glycolate and acetate and follows a steeper trend. Vukovic et al. split the fitting of 1:1 UVI/L complexes via ligand charge and improved accuracy in the fitted log $\beta$ values. The results in Figure 8b support the evidence that splitting via ligand charge may be important, particularly when exploring multiple bound ligands on one fitting curve.

Figure 8c splits the complexes via the number of ligands complexed with UVI, where blue, green, and black represent one, two, and three ligands complexed around UVI, respectively. The results highlight that 1:2 and 1:3 complexes follow the same trend with similar correlations ($R^2 = 0.9092$ and 0.9056 for 1:2 and 1:3 complexes, respectively). This means that 1:2 and 1:3 complexes can be fitted on the same curve regardless of ligand charge, indicating that if 1:2 or 1:3 experimental data is missing, then it can be inferred from this plot. The trend for 1:1 complexes has a similar correlation ($R^2 = 0.922$); however, the calculated stability constants are underpredicted (shifted to the left) compared with 1:2 and 1:3 complexes. This indicates that the DFT calculations suggest it is more difficult to complex the first ligand, but once the first ligand is in, it becomes easier for the next two ligands to complex with UVI.

# CONCLUSIONS

The first objective of the study presented here was to modify the protocol for estimating the relative stability of UVI complexes proposed by ref 18. This adjusted protocol allows us to estimate the relative stability of functional groups that comprise the reactive components in siderophores while also providing a protocol whose computational cost will not prohibit future exploration of siderophores with tens of atoms. This is important because siderophores complex with UVI, significantly affecting UVI aqueous chemistry and mobility in natural systems. The second objective was to assess whether the difficulties associated with mixed solvation methods are outweighed by improvements in $\Delta G$. The third objective was to explore whether the fitting approach can be expanded to multiple bound ligands, focusing on carboxylate type ligands. The suggested protocol is the B3LYP functional, aug-cc-pVDZ ligand basis set, MDF60 ECP and basis set for UVI, and the IEFFPCM solvation model. The complexes were fully optimized in the solvation model. Mixed solvation models based on previous research22 were tested for UVI acetate complexes. We demonstrate that applying the approach employed in ref 22 significantly improves calculated $\Delta G$; however, a fitting approach would still need to be employed to determine accurate log $\beta$ values. To save on computational cost and to avoid difficulties in keeping reactions isodesmic, all water molecules outside of the uranyl complex [UO$_2$(H$_2$O)$_5$]$^{2+}$ should be modeled implicitly with the IEFFPCM solvation model. Using the protocol outlined above, in combination with a linear regression allows the user to obtained fitted log $\beta$ for 1:1 UVI/L complexes with rmsd of 1.38 log $\beta$ units and a standard error of 1.64 log $\beta$ units. This enables us to develop a relative stability series for organic ligands and to aid future experiments by providing molecular level insight into macroscale experiments.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b06863.

Details of correcting ionic strength using specific ion theory and the Davies equation along with the full Gaussian 16 rev. A03 reference, and structure energies (PDF)

Structure coordinates (PDF)

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### Notes

The authors declare no competing financial interest.

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