Sequestering Uranium from $UO_2(CO_3)_3^{4-}$ in Seawater with Amine Ligands: Density functional theory calculations

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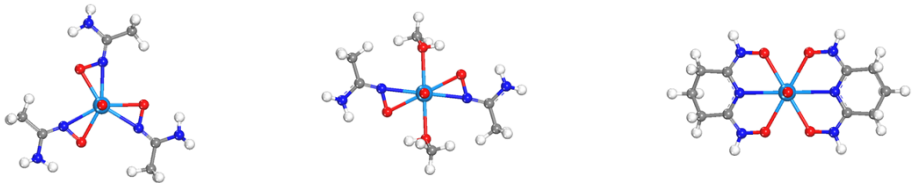

$UO_2(AO)_3^-$ $UO_2(AO)_2(MeOH)_2$ $UO_2(AO)_2(HA)_2$

Figure S1 Optimized structures of $UO_2(AO)_3^-$, $UO_2(AO)_2(MeOH)_2$ and $UO_2(AO)_2(HA)_2$ calculated by the B3LYP method. White, green, red, blue, and light blue spheres represent H, C, O, N, and U, respectively.

Table S1 Selected average bond lengths (Å) for $UO_2(AO)_3^-$,$UO_2(AO)_2(MeOH)_2$and $UO_2(AO)_2(HA)_2$calculated by by the B3LYP method in comparison with previous theoretical and experimental results.

Species	method	U=O	U–O	U–N	U–OH
$UO_2(AO)_3^-$					
	B3LYP, gas	1.799	2.394	2.466	
	B3LYP, gas[(a)]	1.800	2.393	2.466	
	B3LYP, gas[(b)]	1.803	2.381	2.472	
	B3LYP, sol	1.826	2.349	2.441	
$UO_2(AO)_2(MeOH)_2$					
	B3LYP, gas	1.789	2.351	2.438	2.601
	B3LYP, gas[(c)]	1.784	2.349	2.424	2.624
	B3LYP, gas[(d)]	1.793	2.344	2.434	2.602
	X-ray, solid[(e)]	1.789	2.383	2.398	2.458
	B3LYP, sol	1.811	2.315	2.433	2.570
	B3LYP, sol[(f)]	1.817	2.307	2.435	2.557
$UO_2(HA)_2$					
	B3LYP, gas	1.783	2.504	2.652	
	B3LYP, gas[(g)]	1.784	2.503	2.655	
	B3LYP, gas[(h)]	1.798	2.498	2.691	
	X-ray, solid[(i)]	1.785	2.482	2.563	
	B3LYP, sol	1.802	2.487	2.631	
	B3LYP, sol[(j)]	1.810	2.468	2.635	

[a]Theoretical results for $UO_2(AO)_3^-$ from ref 1. [b]Theoretical results for $UO_2(AO)_3^-$ from ref 2. [c]Theoretical results for $UO_2(AO)_2(MeOH)_2$ from ref 1. [d]Theoretical results for $UO_2(AO)_2(MeOH)_2$ from ref 2. [e]X-ray crystallographic results for

$UO_2(AO)_2(MeOH)_2$ from ref 1. [f]Theoretical results for $UO_2(AO)_2(MeOH)_2$ from ref 2. [g]Theoretical results for $UO_2(HA)_2$ from ref 2.[h]Theoretical results for $UO_2(HA)_2$ from ref 3. [i]X-ray crystallographic results for $UO_2(HA)_2$ from ref 3.[j]Theoretical results for $UO_2(HA)_2$ from ref 2.

As shown in Table S1, the predicted U=O and U-O bond distances by B3LYP functional are in good agreement with the X-ray crystallographic results. Though the calculated U-OH distance for $UO_2(AO)_2(MeOH)_2$ and U-N distance for $UO_2(HA)_2$ are in good agreement with other reported theoretical results, they are longer than the X-ray crystallographic results with relatively large differences of 0.143 and 0.089Å. This may be attributed to the crystal packing effects, also as presented in Ref.2 and Ref.3. Compared to other published theoretical results, the calculated U-OH distance for $UO_2(AO)_2(MeOH)_2$ and U-N distance for $UO_2(HA)_2$ are in better agreementwith the X-ray crystallographic results. Thus, the theoretical method we used is reliable in predicting the structures of uranyl complexes. All the calculations were carried out at the B3LYP/6-31++G*/RECP level of theory".

References

[1] S. Vukovic, L. A. Watson, S. O. Kang, R. Custelcean and B. P. Hay, *Inorganic Chemistry*, 2012, **51**, 3855.

[2] C.-Z. Wang, J.-H.Lan, Q.-Y. Wu, Q. Luo, Y.-L.Zhao, X.-K.Wang, Z.-F.Chai and W.-Q.Shi, *Inorganic Chemistry*, 2014, **53**, 9466.

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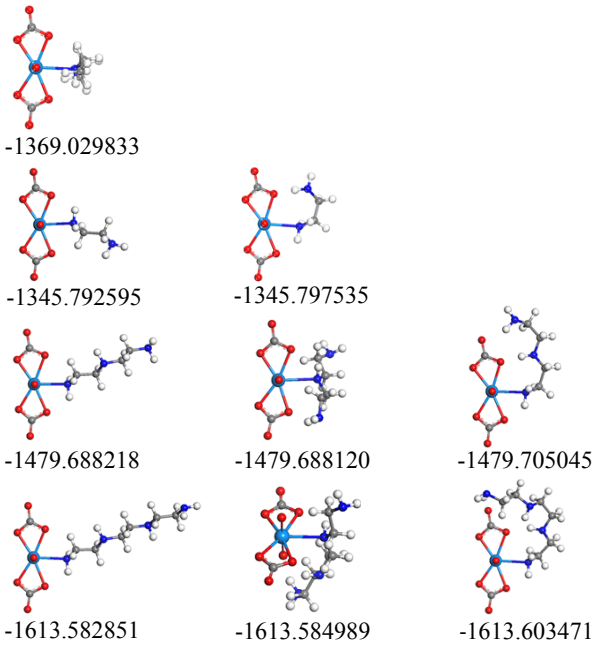

Figure S2. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L(CO_3)_2^{2-}$(L=DEA, EDA, DETA and TETA) in gas phase by the B3LYP method.

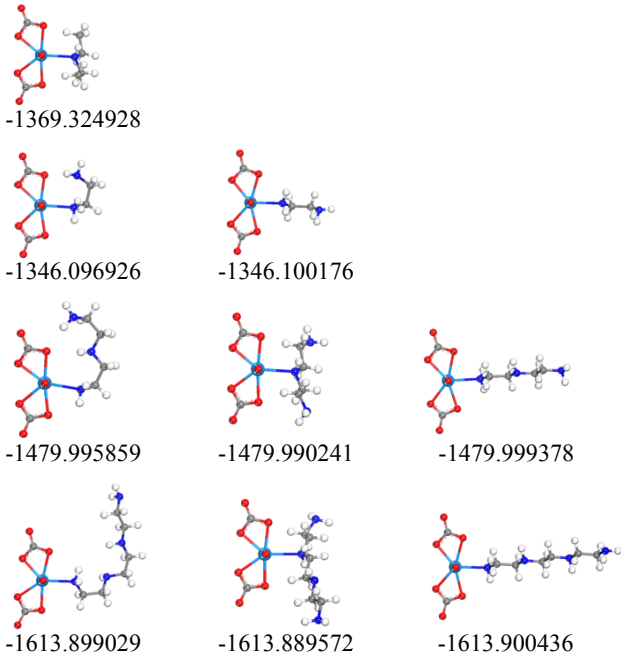

Figure S3. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L(CO_3)_2^{2-}$(L=DEA, EDA, DETA and TETA) in aqueous solution by the B3LYP method.

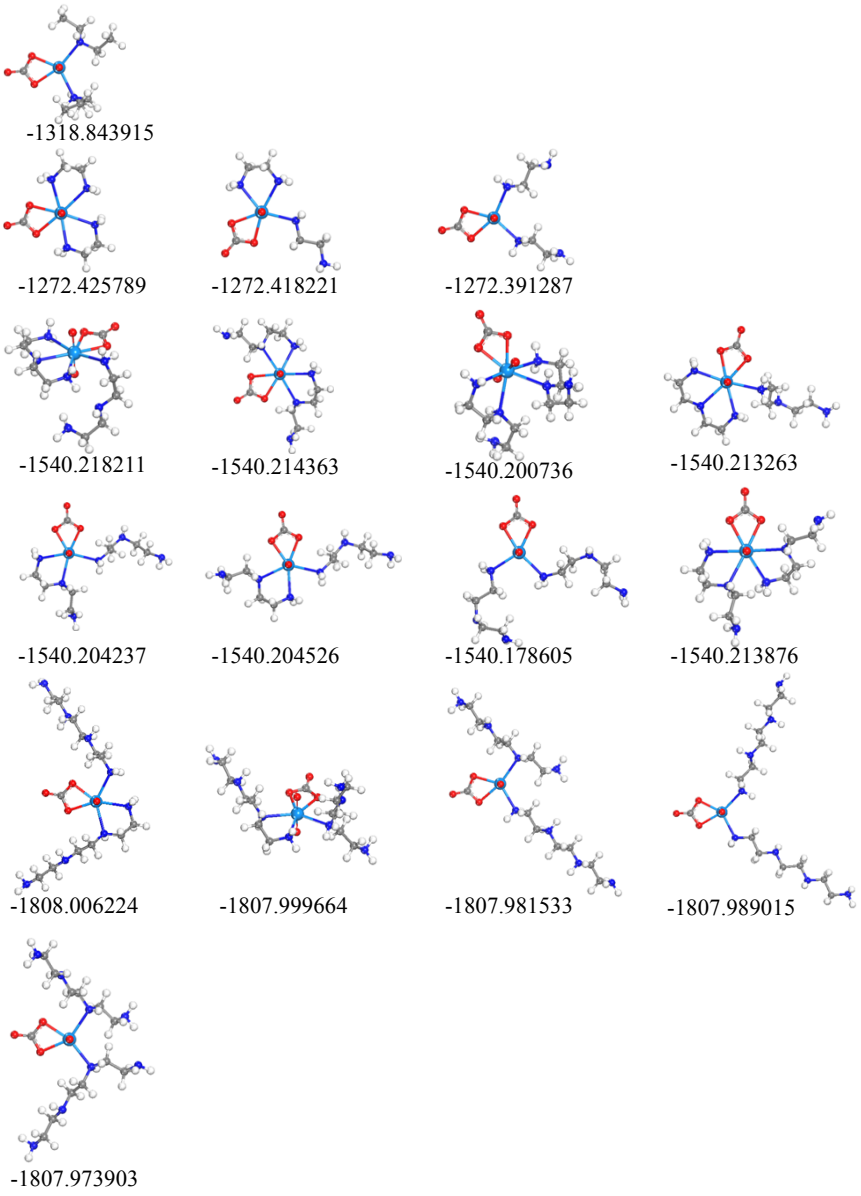

Figure S4. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L_2CO_3$(L=DEA, EDA, DETA and TETA) in aqueous solution by the B3LYP method.

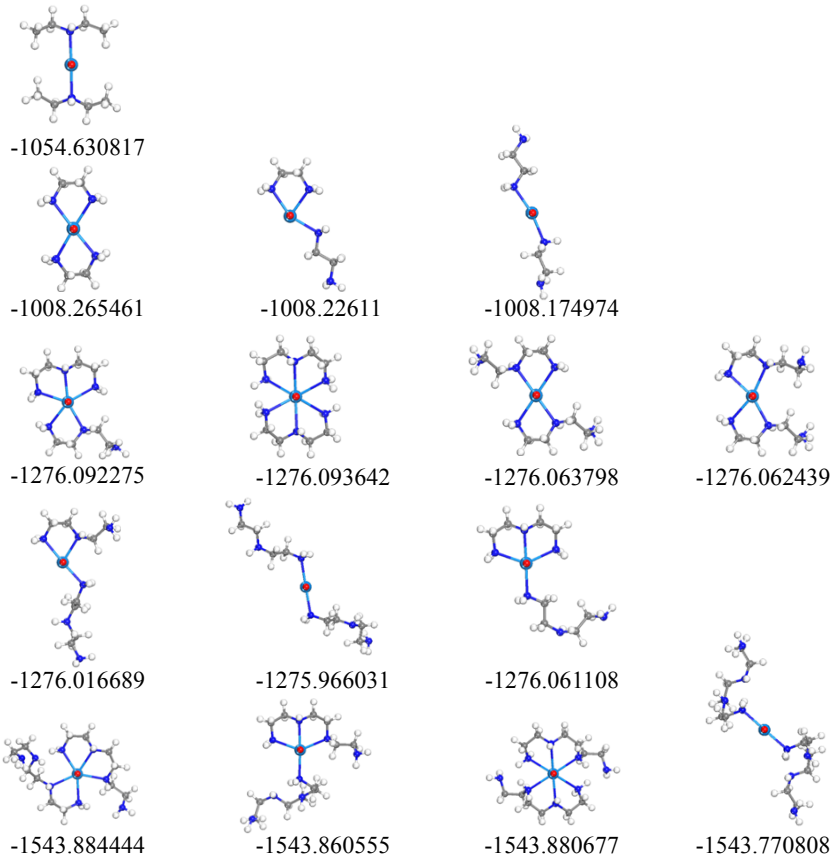

Figure S5. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L_2^{2+}$(L=DEA, EDA, DETA and TETA) in aqueous solution by the B3LYP method.

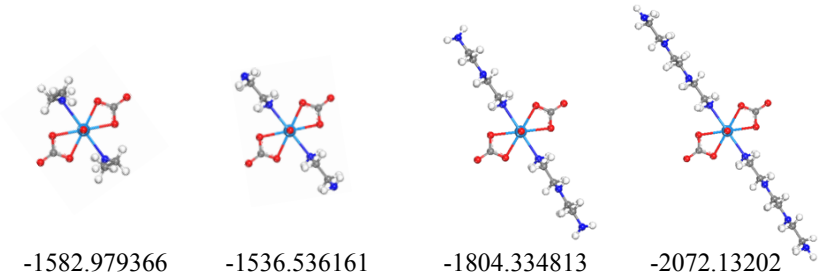

Figure S6. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L_2(CO_3)_2^{2-}$(L=DEA, EDA, DETA and TETA) in aqueous solution by the B3LYP method.

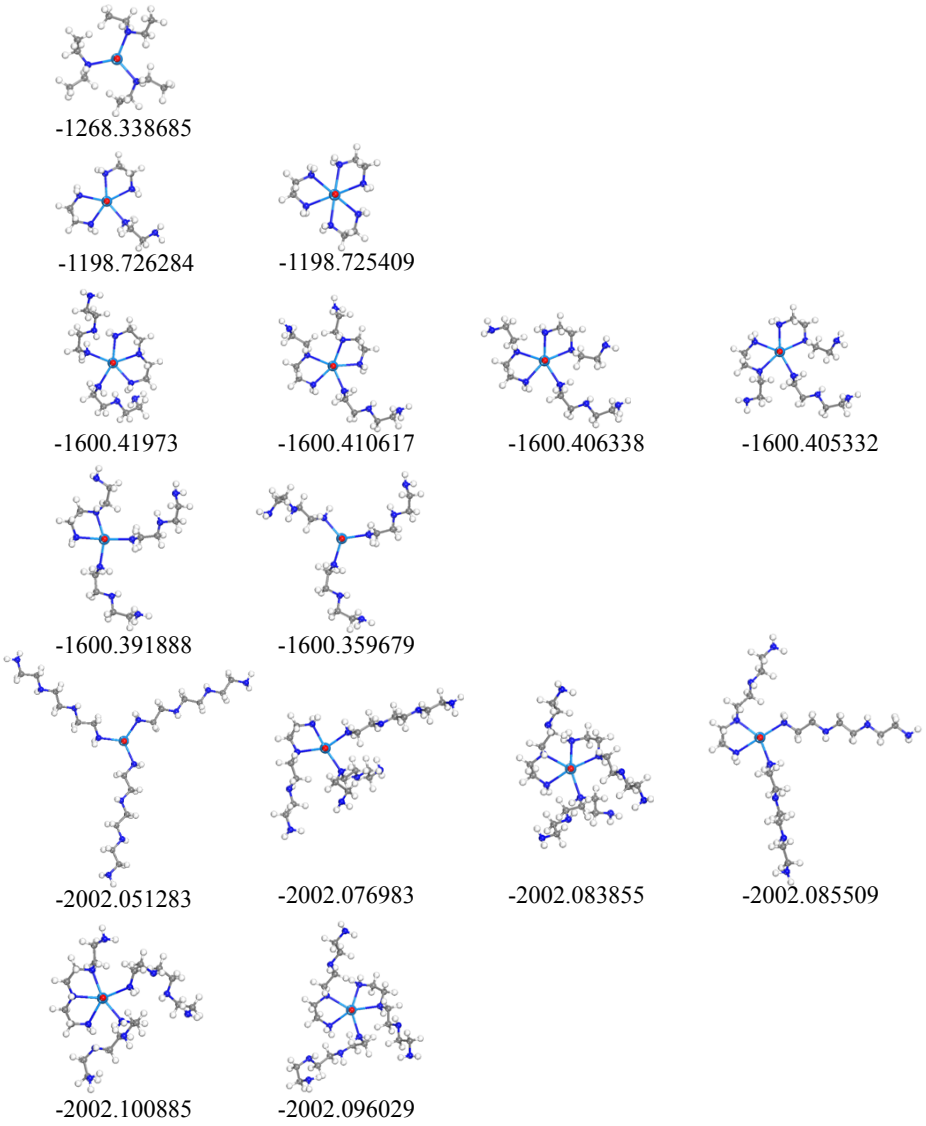

Figure S6. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L_3^{2+}$(L=DEA, EDA, DETA and TETA) in aqueous solution by the B3LYP method.

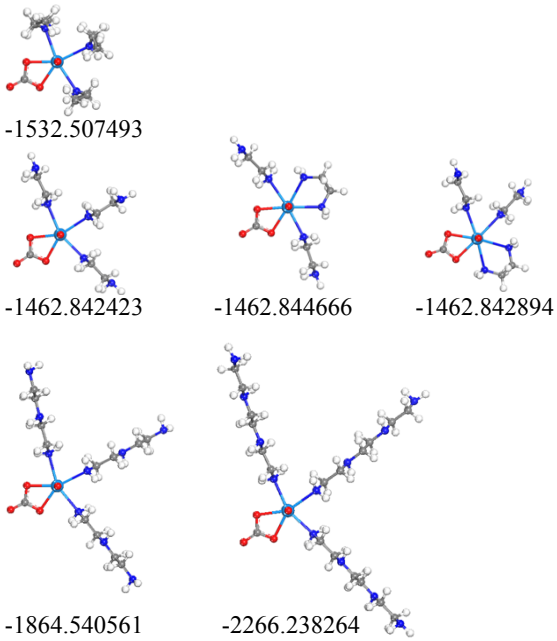

Figure S8. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2L_3CO_3$(L=DEA, EDA, DETA and TETA) in aqueous solution by the B3LYP method.

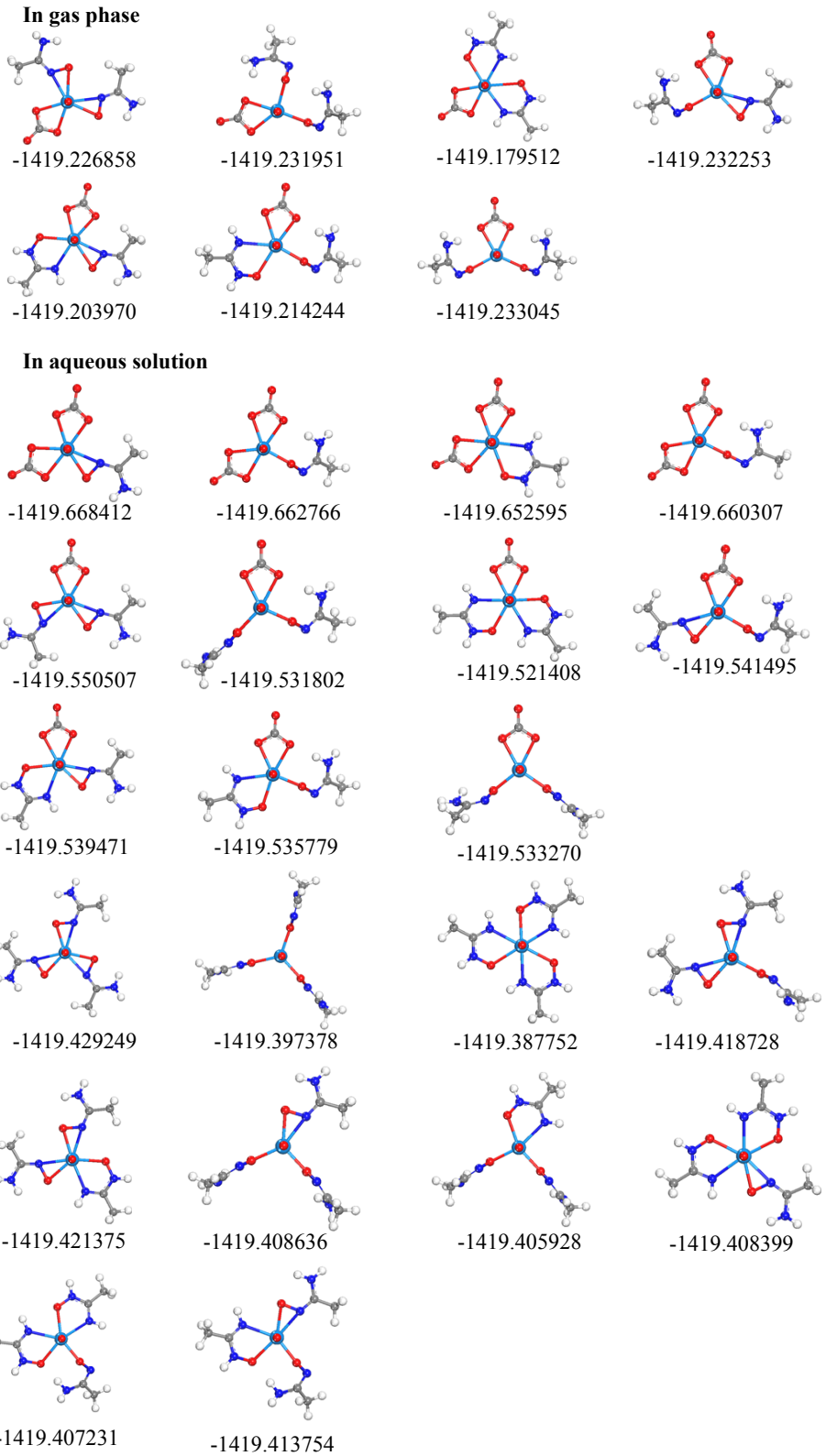

Figure S9. Optimized structures and total energies after zero-point energy correction (in hartrees) of $UO_2(AO)(CO_3)_2^{3-}$, $UO_2(AO)_2(CO_3)^{2-}$, and $UO_2(AO)_3^-$ by the B3LYP method.

Table S2 Wiberg bond indices(WBIs) of U–N bonds and natural charges on the U and O_{axial} atoms for $UO_2L_2CO_3$, $UO_2L_2^{2+}$, $UO_2L_2(CO_3)_2^{2-}$, $UO_2L_3^{2+}$ and $UO_2L_3CO_3$(L=DEA, EDA, DETA and TETA) in aqueous solution.

Species	Q(U)	Q(O_{axial})	U–N	U–N	U–N	U–N	U–N	U–N
$UO_2L_2CO_3$								
L=DEA	1.775	-0.541(-0.542)	0.418	0.386				
L=EDA	1.443	-0.545(-0.544)	0.384	0.411	0.409	0.386		
L=DETA	1.473	-0.552(-0.550)	0.372	0.408	0.427	0.339		
L=TETA	1.607	-0.539(-0.538)	0.396	0.373	0.411			
$UO_2L_2^{2+}$								
L=DEA	2.308	-0.534(-0.534)	0.480	0.484				
L=EDA	1.917	-0.512(-0.512)	0.453	0.452	0.449	0.453		
L=DETA	1.667	-0.545(-0.549)	0.373	0.374	0.371	0.415	0.371	0.415
L=TETA	1.777	-0.537(-0.539)	0.396	0.402	0.450	0.386	0.425	
$UO_2L_2(CO_3)_2^{2-}$								
L=DEA	1.472	-0.583(-0.584)	0.330	0.329				
L=EDA	1.342	-0.560(-0.558)	0.396	0.397				
L=DETA	1.344	-0.560(-0.557)	0.394	0.394				
L=TETA	1.344	-0.560(-0.557)	0.394	0.393				
$UO_2L_3^{2+}$								
L=DEA	2.131	-0.526(-0.527)	0.435	0.425	0.432			
L=EDA	1.693	-0.519(-0.520)	0.437	0.435	0.427	0.425	0.436	
L=DETA	1.699	-0.530(-0.532)	0.426	0.403	0.456	0.460	0.426	
L=TETA	1.788	-0.531(-0.535)	0.401	0.399	0.408	0.426	0.408	
$UO_2L_3CO_3$								
L=DEA	1.789	-0.585(-0.585)	0.355	0.357	0.354			
L=EDA	1.481	-0.548(-0.548)	0.383	0.379	0.395	0.396		
L=DETA	1.583	-0.529(-0.529)	0.405	0.406	0.413			
L=TETA	1.585	-0.530(-0.529)	0.405	0.405	0.414			