

Modelling the environmental speciation of uranium at the molecular scale

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ABSTRACT

The formation of uranyl species by the reaction between uranyl (VI) and organic compounds such as α -isosaccharinate and D-gluconate can have important implications for the environment. Most notably, the high mobilities of these soluble uranyl species can contaminate underground geological environments such as the water and soil.

Therefore, an understanding of the formation of these compounds and the reactions which occur have been sought using computational techniques. Density Functional Theory has been used with the PBE functional and relativistic effects have been accounted for with the ZORA method. This work is compared to the experimental research carried out at the University of Manchester. We have identified the most stable molecular structures of these species with particular emphasis on their behaviour in aqueous conditions with variation in pH levels.

Smaller organic ligands, such as 3-hydroxybutyric acid, have also been studied and their complexes with uranyl have been compared to D-Gluconic acid. The molecular structures have been explored through theoretical IR and NMR spectroscopy calculations. The NMR calculations show good agreement with experimental data, whereas the IR results indicate further improvements to the model are required.

INTRODUCTION

Research in actinide chemistry has become increasingly important over the years due to its role in environmental science. The principal applications of actinides are in the nuclear industry; as a source for nuclear power and in weapons. However, the problem of storing and disposing radioactive waste is very significant. Two of the main environmental concerns are: the solubilities of the radionuclides and rate of release (migration) of the radionuclides.¹ In general, actinide complexes have low ionic strengths and low metal ion concentrations and therefore are not likely to be found in natural water systems. However, this has not been found to be the case in water systems near nuclear waste repositories, indicating that many of these sites have suffered leakages and consequently contaminated surrounding natural environments.² "The principal transport mechanism for migration of transuranic elements away from a repository is expected to be by action of water".³ Other than radionuclides being transported by water, it has been found that these metals form complexes with organic ligands which alter the actinide speciation and behaviour, hence changing physiochemical properties, such as

migration, solubility, transport, etc. These are important factors which determine the degree of contamination, and if understood, would allow control of the reaction mechanisms and thereby prevent contamination.

Because the most common way of transporting these species is via water, and because many different species can co-exist in aqueous environments, the medium the studies are carried out in is as important as the species themselves. Factors such as solubility, pH, aqueous conditions and redox equilibria, will determine the reactivity and speciation between actinide ions and various ligands.

The equatorial plane of uranyl can also bind to water and/or hydroxide molecules, depending on the acidity of the solution, leading to different properties and reactivities.⁴ As the pH increases and hydrolysis takes place (OH^- ligands replace coordinated water), the axial uranium oxygen bonds weaken.⁵ It has been shown how 4 or 5 hydroxides can coordinate to the uranyl ion in highly alkaline solutions.^{6, 7} Theoretical studies have found structures with both H_2O and OH^-

molecules arranged around the uranyl ion, such as in Figure 1.⁴

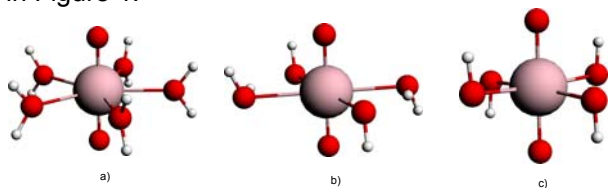


Figure 1 a) $[\text{UO}_2(\text{H}_2\text{O})_6]^{2+}$, b) $[\text{UO}_2(\text{H}_2\text{O})_2(\text{OH})_2]^0$, c) $[\text{UO}_2(\text{OH})_4]^{2-}$ (Pink - uranium, red - oxygen, white - hydrogen)

Intermediate and low level nuclear waste often holds materials such as garments, paper, etc., which contain cellulose. The two ligands studied in this project are the polyhydroxo D-gluconic (HGLU) and α -isosccharinic (HISA) acids, seen in Figure 2, that originate from cellulose decomposition.

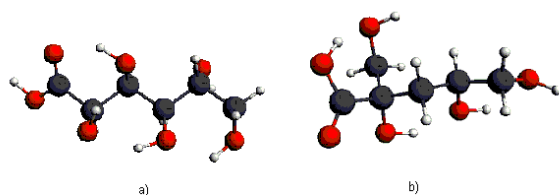


Figure 2 Optimised geometries for a) D-gluconic and b) α -isosccharinic acids (Red - oxygen, white - hydrogen, black - carbon)

In highly acidic conditions (< pH 4) these ligands exist in equilibrium in a lactone form.^{8,9} As the pH increases, the lactone ring breaks and the chain straightens, leading to “zig-zag” shaped molecules (shown in Figure 2). Between pH 3 – 5, the ligands undergo hydrolysis where they are deprotonated,¹⁰ and the first deprotonation corresponds to the most acidic hydrogen, which is that of the carboxylic acid group. Nuclear magnetic resonance techniques demonstrate a second deprotonation takes place with α -isosccharinate at pH > 13.⁹

The aim of this project is to study the interactions between α -isosccharinate (ISA) and D-gluconate (GLU) with uranyl in aqueous environments, considering the range of pH these complexes can co-exist in, using computational techniques. The coordination of multiple ligands to the uranyl will also be investigated.

In order to predict the possible coordination modes one has to assess the possible binding sites of the ligands. It has been demonstrated how coordination will most likely take place with via the carboxy group.^{8, 10} Interactions between uranyl (under different $\text{H}_2\text{O}/\text{OH}^-$ conditions) and ISA and GLU will be studied, and IR and ^{13}C NMR spectroscopic properties will be analysed. The calculated results will be compared to experimental results obtained by Dr Nick Bryan’s research group at the University of Manchester.

Finally, in order to facilitate the synthesis of uranyl-D-gluconate, experimentalists are searching for a simpler and suitable analogue for D-gluconic acid.

Uranyl 3-hydroxybutyric acid and 3-hydroxypropanoic complexes were synthesised and it was found that, unlike Uranyl Gluconate, they precipitate out of solution at high pH (c. pH 13).¹¹ Therefore, calculations on these new ligands and their corresponding uranyl complexes have been performed in order to understand the different reactivity between them and D-gluconic acid.

COMPUTATIONAL METHODS

All the geometry optimisations were performed using the ADF program,¹²⁻¹⁴ based on density functional theory, DFT. Geometry optimisations were performed using the DFT PBE potential, 4.5 integration grid, 0.001 Hartree/Bohr energy gradient convergence, with TZ2P Zero Order Regular Approximation (ZORA) basis set for U, and TZP ZORA basis sets for C, O and H. The Uranium, Oxygen and Carbon atoms had frozen cores up to the 5d, 1s and 1s shells respectively. Frequency calculations were performed, with an integration grid of 6.0, to verify the calculated structures lie at a true energy minimum and to account for thermochemical corrections.

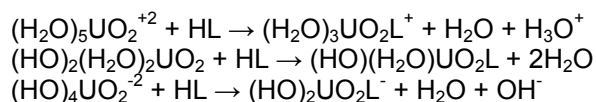
Gas phase and solution phase calculations were performed for all the species. The solution phase was obtained by using the conductor-like screening model, COSMO.

NMR calculations were performed using Gaussian09. The calculations were done in the gas-phase using the ADF solvent optimised geometry. The cc-pVTZ basis set was used for H, O and C atoms, the all electron ANO (Atomic Natural Orbital) basis set for the U, in conjunction with the PBE functional.

RESULTS

Assessing the mode of chelation

The pH of the reaction has been increased by gradually replacing the H_2O ligands on the equatorial plane of the uranyl with OH^- ligands, Figure 1. The following reactions have been studied (in order of increasing pH, HL = acid, L= ligand⁻):



The uranyl can bind to the ligands in various ways. The three main coordination sites (U_4 , U_5 and U_6), are labeled below in Figure 3:

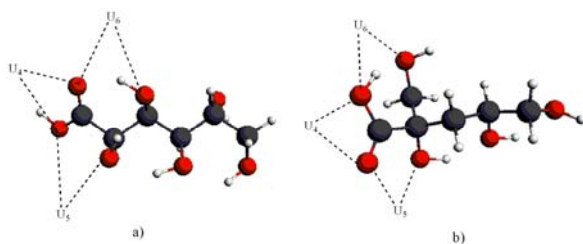


Figure 3 Possible binding sites for Uranyl for optimised a) D-Gluconic acid (HGLU) b) α -Isosaccharinic acid (HISA)

Energetics

The ΔH_f and ΔG_f of the reactions were calculated for all the possible coordination sites in order to find the lowest energy structure.

The most stable geometries for uranyl D-gluconate are with the U_4 and U_6 bonding modes, labeled A and B respectively in Figure 4.

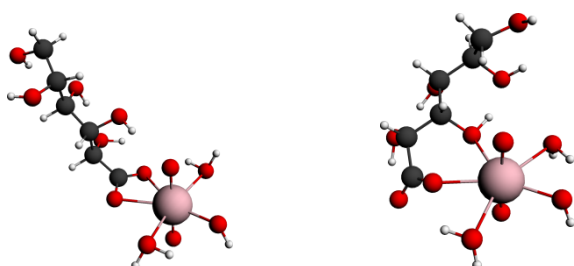


Figure 4 The most stable geometries for uranyl D-gluconate: a) left - A geometry b) right - B geometry

At high pH, the B geometry has been identified by ^{13}C NMR experimental techniques.¹⁰ However, the calculated ΔG_f for the A geometry is $\sim 2\text{kcal/mol}$ more stable than the B geometry. Given this small energy difference, both species are likely to co-exist in solution.

The most stable geometries for Uranyl α -Isosaccharinate are with U_4 and U_5 , forming 4 and 5 membered ring chelating species (Figure 5). The same experimental techniques as above showed the C geometry to be present at high pHs. However, the calculations show the ΔG_f for the A geometry is 4 kcal/mol lower in energy. Again, this is a relatively small difference in energy and both complexes must be considered.

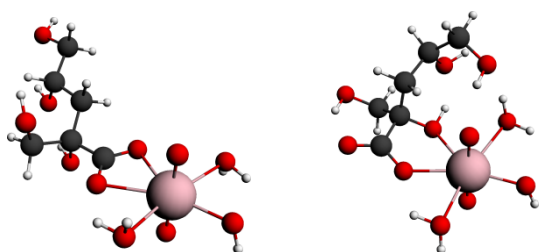


Figure 5 The most stable geometries for Uranyl α -Isosaccharinate: a) left - A geometry b) right - C geometry

IR and ^{13}C NMR Calculations

The vibrational frequency for the uranyl $\text{O}=\text{U}=\text{O}$ asymmetric stretch has been calculated, along with the ^{13}C NMR chemical shielding constants, and

compared to experiment. These results are collected in Tables 1–3.

One can see that as the pH increases, *i.e.* towards $(\text{OH})_2(\text{OH}_2)\text{UO}_2\text{L}^-$, the agreement with experiment decreases. This could be due to the absence of the solvent in the calculated result (experimental IR is taken in solution). Furthermore, the experimental $\nu_{\text{O}=\text{U}=\text{O}}$ does not confirm which of the two geometries is dominant, possibly suggesting they are both present in solution.

Table 1 $\text{O}=\text{U}=\text{O}$ vibrational frequency cm^{-1} for L=D-gluconate

Species (L=D-gluconate)	Calculated, PBE, gas-phase		Experimental ¹⁰
	A Geometry	B Geometry	
$(\text{OH})_3\text{UO}_2\text{L}^+$	929	959	942
$(\text{OH})(\text{OH}_2)_2\text{UO}_2\text{L}$	924	917	929
$(\text{OH})_2(\text{OH}_2)\text{UO}_2\text{L}^-$	889	894	915

Table 2 $\text{O}=\text{U}=\text{O}$ vibrational frequency cm^{-1} for L= α -isosaccharinate

Species (L= α -isosaccharinate)	Calculated, PBE, gas-phase		Experimental ¹⁰
	A Geometry	C Geometry	
$(\text{OH})_3\text{UO}_2\text{L}^+$	956	935	937
$(\text{OH})(\text{OH}_2)_2\text{UO}_2\text{L}$	926	916	926
$(\text{OH})_2(\text{OH}_2)\text{UO}_2\text{L}^-$	869	892	912

Turning to the ^{13}C NMR results (Table 3), one can see the agreement with experiment is not consistent with all the C atoms. The ligand has a relatively good agreement of chemical shifts with experiment, with the exception of the C_4 atom. The computed data for uranyl gluconate do not permit unambiguous assignment of the structure, in that, of the six C atoms, three of them (C_1 , C_2 and C_5) from the A geometry have chemical shifts closer to experiment (at pH 11) than in structure B, for which C_3 , C_4 and C_6 lie closer to experiment than structure A. This again supports the argument of multiple speciation being present.

Table 3 ^{13}C NMR Chemical Shifts, ppm. See Figure 6 below for C atom labeling

	C_1	C_2	C_3	C_4	C_5	C_6
Experimental ¹⁰ D-Gluconic acid pH 7	178.8	74.1	71.0	72.5	71.2	62.6
This work, D-Gluconate	178.4	85.8	79.8	94.3	82.3	72.4
Experimental ¹⁰ Uranyl Gluconate pH 11	191.0	88.5	85.6	77.7	74.4	65.1
This work, A Geometry Uranyl Gluconate-(H_2O)(OH) ²⁻	187.5	86.2	78.2	84.8	77.1	70.6
This work, B Geometry Uranyl Gluconate-(H_2O)(OH) ²⁻	180.4	82.19	83.8	82.1	80.9	64.9

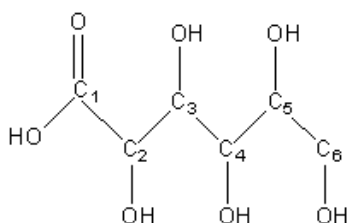


Figure 6 Labelled Carbon atoms on D-Gluconic acid

Metal:ligand ratio

It has been shown that more than one ligand can bind to the uranyl,¹⁵ therefore we calculated the following reactions for uranyl D-gluconate (to model low, neutral and high pH respectively):

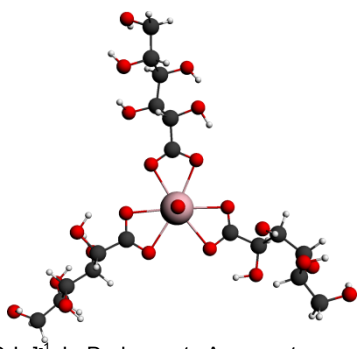
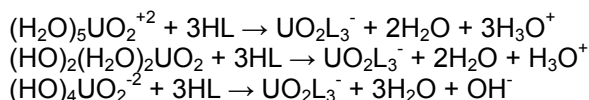


Figure 7 $[\text{UO}_2\text{L}_3]^-$ L=D-gluconate A geometry

The A geometry for UO_2L_3^- is shown in Figure 7. It was not possible to calculate the uranyl complex with three B geometry ligands due to large size of the 6 membered chelate ring. Table 4 shows the ΔH_f for the reactions above. One can see the formation of these species is more favourable at high pH, which is reflected in their high stability in alkaline environments.¹⁶

Table 4 ΔH_f solvent corrected reaction enthalpies (kcal/mol)

pH	ΔH_f kcal/mol
Low	32.4
Neutral	0.22
High	-5.17

Variations to the D-Gluconic ligand

The D-Gluconic acid ligand can be simplified in a number of ways. Here, the following series of ligands were calculated and compared to D-gluconic acid: 3-hydroxyhexanoic acid, 3-hydroxypentanoic acid, 3-hydroxybutanoic acid and 3-hydroxypropionic acid.

Energetics of reactions of formation

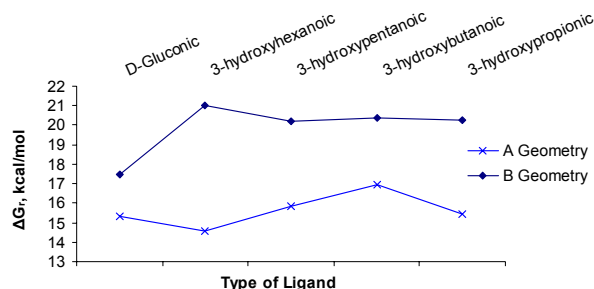


Figure 8 Solvent corrected ΔG_f (kcal/mol) for formation of $(\text{OH})_2(\text{OH}_2)\text{UO}_2\text{L}^-$ for different ligands

One can see from Figure 8 how the shorter chains exhibit larger energy differences between the A and B geometries as compared to the uranyl D-Gluconate. The shorter ligands are ~4-5 kcal/mol more stable as a 4 membered ring chelate (A geometry) than a 6 membered (B geometry). Furthermore, the uranyl D-gluconate lies within the same reaction energy range (~1-2 kcal/mol) as the rest of the ligands, even though experimentally they exhibit different chemical behaviours at high pH.

¹³C NMR

¹³C NMR chemical shifts were calculated for 3-hydroxybutanoic acid and uranyl 3-hydroxybutanoic·3H₂O and compared to experiment.

Table 5 ¹³C NMR Chemical Shifts, ppm. See Figure 9 below for C atom labeling.

	C ₁	C ₂	C ₃	C ₄
Experimental ¹¹				
3-Hydroxybutyric acid pH 4	176.8	43.6	64.6	21.7
This work,				
3-Hydroxybutanoate	177.6	47.7	73.2	25.2
Experimental ¹¹				
Uranyl 3-Hydroxybutyric pH 4	186.5	47.1	65.5	22.1
This work, A Geometry				
Uranyl 3-Hydroxybutanoate·(H ₂ O) ³⁺	207.5	43.1	72.4	21.9
This work, B Geometry				
Uranyl 3-Hydroxybutanoate·(H ₂ O) ₃ ⁺	175.8	43.7	82.5	22.1

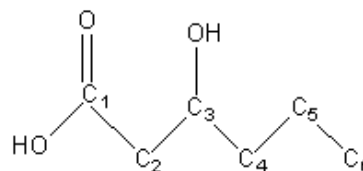


Figure 9 Labelled Carbon atoms for 3-hydroxybutyric acid

One can see that the free ligand has a good agreement with experiment, with a maximum deviation of 7 ppm for the C₃ atom. Again one can see how it is not possible to distinguish between the A or the B type geometry on the basis of NMR calculations.

Metal:Ligand ratio

Uranyl complexes with three 3-hydroxybutyric ligands were calculated and the optimised

geometries are shown in Figure 10. The enthalpy of formation for their respective reactions (same as for the formation of uranyl:3D-gluconate) are shown below in Table 6.

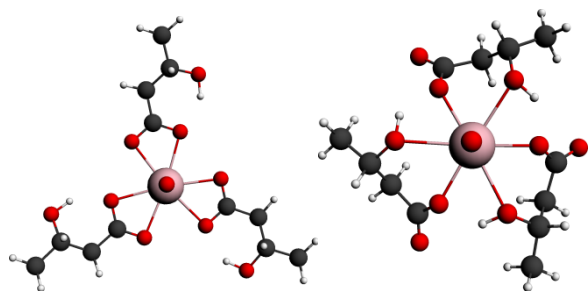


Figure 10 UO_2L_3^- L=3-hydroxybutanoate. Left, A geometry. Right, B geometry

Table 6 ΔH_f solvent corrected reaction enthalpies kcal/mol

pH	ΔH_f kcal/mol	
	A geometry	B Geometry
Low	34.81	57.86
Neutral	2.63	25.68
High	-2.76	20.29

In Table 6 one can see as more ligands are added to the uranyl, the formation of a 4 membered ring chelate (A geometry) is preferred over the 6 membered ring (B geometry). As more ligands are added around the uranyl, the difference in energy between the two geometries becomes more significant, as opposed to the 1:1 species.

CONCLUSION

Stable geometries for uranyl D-gluconate and uranyl α -isosaccharinate have been identified across a range of pH, and compared to experiment where possible. It is suggested that when the metal:ligand ratio is 1:1, there is a case of multiple speciation. Overall, differences in energies of these species are relatively low therefore one would expect them to co-exist in solution. This leads to a more challenging situation in terms of nuclear waste. As the ligand concentration is increased (1:3 ratio), the reactions favour the formation of a 4 membered ring chelate than that of a larger 6 membered ring for the uranyl D-gluconate. When the D-gluconate ligand is replaced by shorter analogues, similar reaction energies are found. These ligands could be considered as a suitable analogue for D-gluconate, except at very high pHs.

Calculations of the uranyl asymmetric stretch show good agreement with experiment (IR) for the cationic and neutral species. In general, NMR calculations are very sensitive to computational parameters but have demonstrated a good agreement overall. However, the results must be interpreted with care as within the same molecule, some carbon shielding constants can deviate significantly more from experiment than others.

FUTURE WORK

^{13}C NMR calculations for the α -isosaccharinate and the uranyl complex are to be performed and compared to experiment and to D-gluconate. Furthermore, the complexation of larger macrocyclic ligands with uranium(IV) will be investigated.

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