

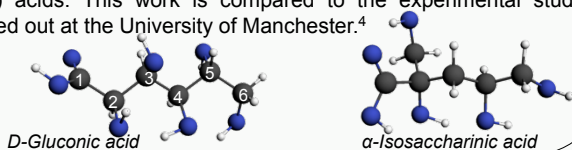
Environmental Speciation of Uranyl with α -Isosaccharinic and D-Gluconic acids

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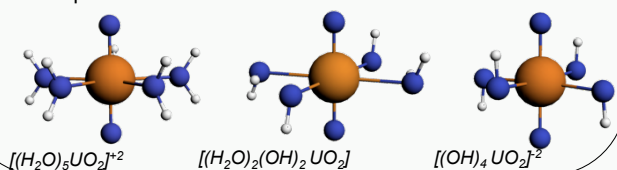
Introduction

There is an environmental concern over the complexation of actinides with organic materials that exist in nuclear waste repositories. It has been found that uranyl (UO_2^{2+}) forms complexes with organic ligands in aqueous environments.¹ This leads to the actinide speciation and behaviour being modified, with altered physicochemical properties, such as migration, solubility, transport, etc. The aim of this project is to use computational modelling techniques to understand and describe the formation of uranyl with both polyhydroxo D-gluconic (GLU) and α -isosaccharinic (ISA) acids. This work is compared to the experimental studies carried out at the University of Manchester.⁴



Aqueous environment and measuring pH

"The principal transport mechanism for migration of transuranic elements away from a repository is expected to be by action of water".² Therefore, modelling the solvation model and the range of pH is a vital part of the research. Firstly, a 1st solvation shell is used to mimic the pH of the species, by adding OH^- and H_2O ligands to the equatorial plane of the uranyl. Two methods of representing the bulk aqueous environment have been employed; the COSMO model and the addition of explicit water molecules to create a 2nd solvation sphere.³

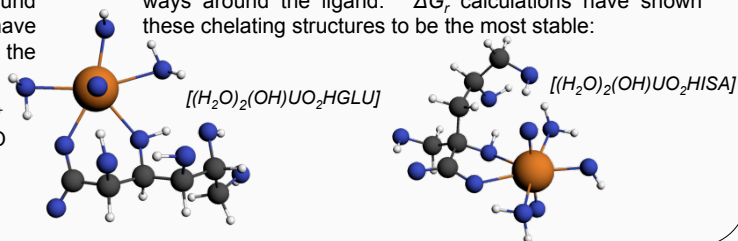


Reactions in the range of pH

So far 6 uranyl ISA and 5 uranyl GLU species have been found experimentally at different pHs,⁴ however, their structures have not yet been identified. The species we are analysing are the products of these reactions:

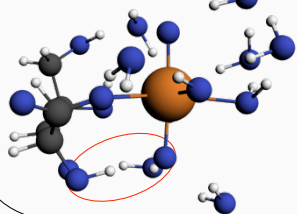
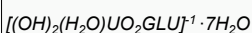
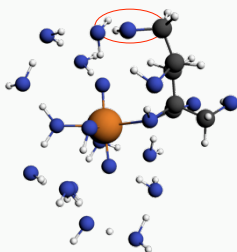
- $[(\text{H}_2\text{O})_5\text{UO}_2]^{+2} + \text{GLU} \rightarrow [(\text{H}_2\text{O})_3\text{UO}_2\text{HGLU}]^{+1} + \text{H}_2\text{O} + \text{H}_3\text{O}^+$
- $[(\text{HO})_2(\text{H}_2\text{O})_2\text{UO}_2]^{-2} + \text{GLU} \rightarrow [(\text{HO})(\text{H}_2\text{O})_2\text{UO}_2\text{HGLU}] + \text{H}_2\text{O}$
- $[(\text{HO})_4\text{UO}_2]^{-2} + \text{GLU} \rightarrow [(\text{HO})_2(\text{H}_2\text{O})\text{UO}_2\text{HGLU}]^{-1} + \text{OH}^-$
- $[(\text{HO})_4\text{UO}_2]^{-2} + \text{GLU} \rightarrow [(\text{HO})_2\text{UO}_2\text{GLU}]^{-2} + 2\text{H}_2\text{O}$
- $[(\text{HO})_4\text{UO}_2]^{-2} + \text{GLU} \rightarrow [(\text{HO})_3\text{UO}_2\text{GLU}]^{-3} + \text{H}_3\text{O}^+$

If one assumes a 1:1 ratio, the uranyl can bind in various ways around the ligand. ΔG_f calculations have shown these chelating structures to be the most stable:



Results - Modelling the 2nd solvation sphere

By including the 2nd solvation shell, the U=O bond lengthens and weakens, leading to a large reduction in the uranyl stretching frequency (see Table 1). Inclusion of explicit 2nd shell waters leads to an improvement for the C_1 chemical shift (Table 2).



Other than the strong chelate bond, OH groups from the ligand can form hydrogen bonds with either the uranyl oxygen or the solvation shell oxygens.

Table 1: Uranyl asymmetric stretching frequency, cm^{-1}

| Species | This work | | Experimental ⁴ |
|--|---------------------------------|--------------------------------|---------------------------|
| | No 2 nd shell waters | 6 2 nd shell waters | |
| $[(\text{H}_2\text{O})_3\text{UO}_2\text{HGLU}]^{+1}$ | 952 | 852 | 942 |
| $[(\text{HO})(\text{H}_2\text{O})\text{UO}_2\text{HGLU}]$ | 927 | 862 | 929 |
| $[(\text{HO})_2(\text{H}_2\text{O})\text{UO}_2\text{HGLU}]^{-1}$ | 891 | 784 | 915 |
| $[(\text{HO})_2(\text{H}_2\text{O})\text{UO}_2\text{GLU}]^{-2}$ | 845 | 795 | 897 |

Table 2: ^{13}C NMR Spectroscopy results

| Chemical shifts, ppm | C_1 | C_2 | C_3 | C_4 | C_5 | C_6 |
|--|--------------|--------------|--------------|--------------|--------------|--------------|
| $[(\text{HO})(\text{H}_2\text{O})_2\text{UO}_2\text{HGLU}]$ | 174 | 85 | 82 | 77 | 80 | 65 |
| $[(\text{HO})(\text{H}_2\text{O})_2\text{UO}_2\text{HGLU}] \cdot 11\text{H}_2\text{O}$ | 181 | 82 | 79 | 81 | 74 | 59 |
| Experimental, at pH 11, ⁴ | 191 | 89 | 86 | 78 | 74 | 65 |

Computational Methods

Calculations were performed using the ADF program,⁵ based on density functional theory. Geometry optimisation calculations were done using the VWN potential, with TZ2P Zero Order Regular Approximations (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. Gas phase and solution phase (COSMO) calculations were performed for all the species. NMR calculations were performed in gas-phase, using the solvent optimised geometry and spin-orbit coupling.

Conclusion

There are many possibilities and coordination modes for the formation of uranyl GLU/ISA species. The most energetically favourable species are the same ones identified experimentally by Kirkham.⁴ These optimised species were used to investigate uranyl properties by adding a 1st and 2nd solvation shell. The 1st solvation shell served as a mimic of pH (varying the number of OH^- present). The 2nd solvation shell has been added in a step-wise manner, and has an evident effect on the U=O bond. The species with the 2nd shell have been compared to the IR and NMR experimental values, with the latter showing better agreement.

References: 1- Wilson, P.D., *The Nuclear Fuel Cycle: From Ore To Waste*. Oxford, 1996. 2- Clark, et al., *Chem. Rev.* 1995, 95, 25-48. 3- Marsden, C.J. et al., *Chem. Phys.*, 2006, 326, 289-296. 4- Kirkham, A.J. Uranyl Coordination to Environmentally Relevant Polyhydroxy Carboxylate Ligands, University of Manchester, 2008. 5- ADF2008.01, S., Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.

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