Aqueous Speciation of the Actinides with Organic Ligands Relevant to Nuclear Waste

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Jennifer Dawn Rochford

School of Chemistry
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9
<table>
<thead>
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<td>δ</td>
<td>Chemical shift</td>
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<td>(2-hydroxy-5-methyl-1,3-phenylene)bis(methylene)bis(azanitriyl)tetraacetate</td>
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<td>Acetonitrile</td>
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<tr>
<td>An</td>
<td>Actinide</td>
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<tr>
<td>AWE</td>
<td>Atomic Weapons Establishment</td>
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<td>BTBP</td>
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<td>D₂O</td>
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<td>EMF</td>
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<td>Sodium hydroxide</td>
</tr>
<tr>
<td>NEA</td>
<td>Nuclear Energy Agency</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>ppt</td>
<td>Precipitate</td>
</tr>
<tr>
<td>Saldien((\text{Et}_2\text{N})_2)H₂</td>
<td>N,N′-Bis((4-diethylamino)salicylidene)diethylenetriamine</td>
</tr>
<tr>
<td>SalterpyH₂</td>
<td>6,6″-Bis(2-hydroxyphenyl)-2,2′:6′,2″-terpyridine</td>
</tr>
<tr>
<td>SIT</td>
<td>Specific ion Interaction Theory</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>THF</td>
<td>TetraHydroFuran</td>
</tr>
<tr>
<td>TM</td>
<td>Transition Metal</td>
</tr>
<tr>
<td>UV-Vis(-nIR)</td>
<td>UltraViolet-Visible(-near-InfraRed)</td>
</tr>
<tr>
<td>v/v</td>
<td>Percentage composition by volume</td>
</tr>
<tr>
<td>WIPP</td>
<td>Waste Isolation Pilot Plant</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
</tbody>
</table>
Abstract

Aqueous Speciation of the Actinides with Organic Ligands Relevant to Nuclear Waste

The University of Manchester, Jennifer Dawn Rochford, 2014, Doctor of Philosophy

The aqueous speciation and hydrolysis of actinides in both the presence and absence of organic ligands has been investigated in the pH range 1 - 13.

The speciation and hydrolysis of Th^{4+}, U^{4+} and UO_2^{2+} with H_3thme, H_3tea, H_3bic, H_3heidi, H_3NTA, H_2ADA and H_3cit have been investigated using various analytical techniques (\textsuperscript{1}H NMR, \textsuperscript{13}C NMR, IR, UV-Vis(-nIR) spectroscopy and potentiometric titrations). The PHREEQC interactive software suite was used to predict speciation with the formation constants for various complexes calculated in the Hyperquad software suite.

Formation constants of Th^{4+}, U^{4+} and UO_2^{2+} hydroxide species have been calculated showing the formation of polymeric complexes. Experiments showed no complexation of actinides by H_3thme and H_3tea in aqueous solutions. However, 1:3 (M:L) complexation of Th^{4+} and U^{4+} was observed with H_3bic along with 1:2 (M:L) complexation of UO_2^{2+}. A variety of 1:1 and 1:2 (M:L) complexes were observed with H_3heidi, H_3NTA, H_2ADA and H_3cit for the actinides. Formation constants for complexes of H_3NTA with Th^{4+} and UO_2^{2+}, H_2ADA with Th^{4+} and H_3cit with UO_2^{2+} were calculated in Hyperquad. Studies of Pu^{3+} with H_3heidi showed little complexation but 5Me-HXTAH\textsubscript{4} showed 1:3 (M:L) speciation. Complexation of PuO_2^{2+} by saldien\textsubscript{(Et,N)}\textsubscript{2}H\textsubscript{2} and salterpyH\textsubscript{2} was shown and a secondary band was observed at \textasciitilde 944 nm after multiple days. The functionalities of organic ligands have been shown to have a profound effect on the (partial) hydrolysis of the actinides.
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1 Introduction

The actinides have found multiple applications since their discovery in 1789. Their ability to release a large quantity of energy through nuclear fission is of great use to power generation (i.e. nuclear power stations) whilst their long lifetimes find use in more long-term operations, such as power sources for space exploration and in hospitals for radiotherapy treatment.\(^1\)

In 1789 pitchblende was found to contain uranium through work by Klaproth, followed by the discovery of thorium in 1828 and protactinium in 1913.\(^2\) The remaining actinides (transuranium elements) are not naturally occurring so have been synthesised through nuclear reactions, therefore evidence of their existence came decades later (1940 – 1971).\(^2\)

1.1 The Chemistry of the f-elements

The f-block consists of two series of metals; the 4f lanthanides (Ln) and the 5f actinides (An). Lanthanum and actinium are group 3 metals and strictly speaking are part of the d-block, but their properties fit the patterns of the f-block so are commonly referred to as part of the lanthanide and actinide series respectively.\(^3,4\)

1.2 The f-orbitals

The f-orbitals are seven-fold degenerate with more than one way for them to be represented.\(^5\) There are two common sets of f-orbitals; the general set and the cubic set (Figure 1-1).\(^2\) Orbitals lie within distinct planes along specific axes, therefore bonding is deemed to be highly directional.\(^6\) The cubic set is appropriate to molecules with geometries of high symmetry, whereas the general set is used when referring to molecules of non-cubic geometry.\(^2\) There are only three orbitals which are common to both sets (5\(f_\alpha^2\), 5\(f_{xyz}\), 5\(f_{z(x^2-y^2)}\)).
The contracted nature of the 4f-orbitals results in limited radial extension; electrons are core-like hence not involved in bonding. As such, they are unaffected by the ligand environment to a large degree with bonds considered to be ionic in nature. The 5f-orbitals have greater radial extension with respect to 7s/7p-orbitals compared to the 4f- relative to the 6s/6p-orbitals. Figure 1-2 shows the comparison of radial probability between Sm$^{3+}$ (4f) and Pu$^{3+}$ (5f), in essence displaying the probability of where an electron can be found as a function of distance from the centre of the nucleus. With a radius of approximately 2 Å, the 5f-orbitals of Pu$^{3+}$ are noticeably larger than the analogous 4f-orbitals of Sm$^{3+}$, which have a radius of approximately 1.5 Å. The larger radius results in the 5f-orbitals being less shielded from the influence of ligands, therefore, early members of the actinide series (Ac - Am) possess a more covalent character when bonding to ligands. As the actinide series progresses (Cm - Lr), the 5f-orbitals become increasingly stabilised and more core-like in character, similar to that of the lanthanides.\textsuperscript{2,7}

The lanthanides are hard Lewis acidic ions as the valence elections are tightly held and bonding has a high degree of ionic character. Consequently, the most stable complexes will be when the lanthanides are bound to hard donor ligands such as N and O atoms. As the actinide display radial extension they display an intermediate character between hard and soft metal ions with more covalent character noticed.\textsuperscript{5,7}
Relativity has an effect on atomic structures, especially that of large elements. Einstein’s Theory of Relativity states ‘velocities greater than that of light have no possibility of existence’.

The average velocity of an electron in the 1s shell is approximately equal to the element’s atomic number. As the electron reaches speeds near to the speed of light the average relativistic mass of the electron increases slightly. For example, for thorium the mass of a 1s electron is increased by 1.33 times compared to the mass of a typical 1s electron (Equation 1-1).

\[
\text{mass} = \frac{m_0}{\sqrt{1 - \left(\frac{V_{\text{rad}}}{c}\right)^2}} = \frac{m_0}{\sqrt{1 - \left(\frac{90}{137}\right)^2}} = 1.33m_0
\]

Equation 1-1: Relativistic mass increase of an electron in the 1s-orbital of thorium. Where \(m_0\) = mass of electron, \(V_{\text{rad}}\) = radial velocity, \(c\) = speed of light.
The mass increase has an effect on the radial distribution of electrons as the Bohr radius of an atomic orbital can be described as \( 1/m \). Therefore the \( 1s \)-orbital of thorium has an average radial contraction of \( ca. 25 \% \) in comparison to one that has no relativistic effects.\(^9\) This contraction of the \( 1s \) orbit has a knock-on effect on the radial distribution of subsequent atomic orbitals as they too contract. Figure 1-2 displays this comparison between relativistic and non-relativistic effects which are especially evident in the \( 7s \)-orbital of \( \text{Pu}^{3+} \), where the most probable radius decreases from 1.8 Å to 1.6 Å when relativistic effects are taken into account.

For the most part, lanthanide electrons fill the \( f \)-orbitals in a regular sequence with only a few exceptions (Table 1-1). In the early part of the lanthanide series the \( 5d \)-orbitals are slightly lower in energy than the \( 4f \) orbitals,\(^4,5\) hence lanthanum and cerium both have an electron situated in the \( 5d \)-orbital. The other exception is gadolinium which incurs an increase of stability due to having a half-filled (\( 4f \)) electron shell.

The electron configurations of the actinide series are slightly more complicated (Table 1-1). Initially the \( 6d \)-orbitals are much lower in energy than the \( 5f \)-orbitals in comparison to the \( 5d/4f \)-orbitals of the lanthanides, hence thorium is more stable without utilising its \( 5f \)-orbitals. Elements up to neptunium are then able to benefit from extra stability by placing an electron in the \( 6d \)-orbital. After this point, the actinides are analogous to the lanthanides with curium gaining stability with half-filled \( f \)-orbitals.\(^4\)
1.3 Oxidation states of the f-elements

Lanthanide chemistry is dominated by the +3 oxidation state with the sum of the first three ionisation energies being less than the fourth. For the majority of lanthanides, once three electrons are removed the 4f-orbitals become stabilised causing the electrons to be held so tightly they are no longer available for bonding. A +2 oxidation state is available for Sm, Eu and Yb as they incur extra stability arising from the orbitals being nearly half-filled, half-filled and filled respectively. Cerium is the only lanthanide which shows extensive chemistry in the +4 oxidation state. As Ce is at the beginning of the series the 4f-orbitals are higher in energy and as such are not sufficiently stable to prevent the loss of the fourth electron. The common oxidation states of the f-block are shown in Table 1-2.
The metallic and ionic radii of $4f$ elements show a gradual reduction with increase in atomic number, known as the lanthanide contraction. It arises from the poor ability of the $4f$-electrons to screen other valence electrons from an increasing nuclear charge. The metallic radii of Eu and Yb are higher than expected but can be rationalised in terms of oxidation states, as both prefer a +2 oxidation state rather than the common lanthanide state of +3. Actinides also show a reduction in radii with an increase in atomic number, an effect known as the Actinide Contraction.

In contrast to the lanthanides, the early (Ac-Pa) and mid (U-Am) actinides have a wider range of stable oxidation states as the $5f$, $6d$ and $7s$-orbitals are of comparable energy. Subsequently there is greater orbital mixing and the $6d$-orbitals are available for bonding unlike the $5d$-orbitals of the lanthanides. Oxidation states between +3 and +7 have been isolated for some actinides such as plutonium and neptunium. Low oxidation states (II - IV) are present as metal cations or in species derived from the ions, but higher oxidation states (V - VII) require the metal to be in the form of oxygenated cations e.g. $\text{AnO}_2^+$ and $\text{AnO}_2^{2+}$ or halides e.g. $\text{MF}_6$. However, beyond americium the stabilisation of the $5f$-orbitals results in the +3 oxidation state dominating the series just as in the lanthanides. The discrepancy of nobelium for which the +2 oxidation state is accessible resides from the loss of two $7s$-electrons which is stable due to the full $5f$ shell.

### 1.4 The Bonding of the Actinides

The number of coordinated ions is dependent on the oxidation state and radius of the metal cation. As the oxidation state increases the number of coordinated ions decreases due to the presence of linear actinyl units (Table 1-3).
<table>
<thead>
<tr>
<th>Ox. state</th>
<th>Ac</th>
<th>Th</th>
<th>Pa</th>
<th>U</th>
<th>Np</th>
<th>Pu</th>
<th>Am</th>
<th>Cm</th>
<th>Bk</th>
<th>Cf</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 (AnO$_2$$^{2+}$)</td>
<td>5</td>
<td>5</td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 (AnO$_4^-$)</td>
<td>5</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 (An$^{4+}$)</td>
<td>10</td>
<td>9 or 10</td>
<td>11.2</td>
<td>8 or 9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 (An$^{4+}$)</td>
<td>9 or 10</td>
<td>9 or 10</td>
<td>10.2</td>
<td>10.3</td>
<td>10.2</td>
<td>8.5 ± 1.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1-3: Number of bound water molecules in actinide aqua ions.$^2$

Tetravalent ions of thorium and uranium have an ionic radius of 1.05 and 1.00 Å respectively with high coordination numbers common. Since the ions are similar in size the geometry is found to be similar also. As a result steric and electrostatic principles of ligands dominate geometry.$^7$ An$^{4+}$ have the highest effective charge of possible oxidation states forming the most stable precipitates with the lowest solubility in aqueous solutions.$^{14}$

High oxidation states (above IV) of uranium, neptunium and plutonium form actinyl complexes AnO$_2$$^{n+}$ (where $n = 1, 2$). These actinyl entities are linear, inflexible O=An=O units containing short, strong actinide to oxygen double bonds with a formal bond order of 3.$^6$ Similar dioxo complexes are well known in d$^0$ transition metals such as V(V), Mo(VI) and W(VI);$^{13}$ although in these cases the O=M=O units are not linear with angles typically around 110°, bond distances of 1.7-1.9 Å and a formal bond order of 2.$^{2,4,13}$ The most closely related dioxo complex is that of OsO$_2$$^{2+}$ in which the Os=O unit is linear with bond distances of around 1.75 Å.$^2$ The use of the $f$-orbitals enables actinyls to have stable linear entities unlike their transition metal counterparts. The distinct $f$-orbital geometries of uranium are able to successfully overlap with the $p$-orbitals of oxygen with the optimum overlap being in the linear plane (Figure 1-3).

![Figure 1-3: Actinyl bonding combinations of uranium 5f- and oxygen 2p-orbitals.$^6$](image-url)
The $\text{AnO}_2^{+2+}$ unit is stable due to the strong M=O bonds present so does not hydrolyse as readily as actinide(III)/(IV), allowing the formation of complexes rather than hydrolysed species over a wider pH range.$^{6,7,13}$ This can be explained through the Molecular Orbital (MO) diagram, as shown for $\text{UO}_2^{2+}$ in Figure 1-4.

A mixture of theoretical and spectroscopic techniques have been utilised over the years to generate the MO diagrams of the actinyls. An unusual feature of actinyl units relates to the energy of bonding orbitals with the $\pi$-orbitals being lower in energy than the $\sigma$-orbitals. This is rationalised by the short length of the U=O bonds in $\text{UO}_2^{+2+}$ units generating antibonding overlap of oxygen $2p$-orbitals and uranium 5$f$-orbitals.$^2$ In the case of $\text{UO}_2^{2+}$, the dioxo cation possesses no $f$-electrons ($f^0$) and has 12 electrons donated by the two axially bonded oxygen atoms. These electrons fill the oxygen centred bonding orbitals resulting in a formal bond order of 3.$^{14,15}$ This bond order can be rationalised by looking at the shape of the 5$f$-orbitals, where are six uranium $f$-orbital combinations which have symmetries which complement oxygen $p$-orbitals (Figure 1-4).
Transuranium actinyls, e.g. NpO$_2^{n+}$ (where $n = 1, 2$), have additional electrons in the non-bonding 5f-orbitals leading to a reduction in stability of these species, as electrons can readily be lost resulting in reduction of the metal to a lower oxidation state. However, reactions that involve the breakage of the stable O=An bonds in trans-dioxo cations are kinetically slow, so generating oxidation states below five via reduction is unlikely unless under certain conditions or radiolysis occurs.$^2$ High oxidation states such as Pu(VII) in [PuO$_2$(OH)$_4$(OH$_2$)]$^+$ exist only in strongly alkaline solutions (e.g. the oxy/hydroxyl species PuO$_2$(OH)$_3^-$ is stable when pH < 10)$^{3,4}$ and low oxidation states such as Pu(IV) require...
strongly acidic media (> 6 M) to prevent polymerisation (colloid production) and disproportionation (e.g. PuF₄ is stable in 0.5 M hydrofluoric acid).⁵⁻⁷

Due to the linear nature of the actinyl units, remaining bonding to auxiliary ligands occurs in the equatorial plane, with the radius of the actinide ion determining the number of valence sites and hence coordination sites. The number of bound ligands however, is determined by the steric and electronic properties of the ligands usually with 4 - 6 saturating this plane (Figure 1-5). The most common coordination number around the equatorial plane being 5, leading to a complex with a distorted (flattened) pentagonal bipyramid shape.²⁻⁹

\[
\text{PuO}_2\text{Cl}_4^{2-} \quad \text{PuO}_2\text{F}_5^{3-} \quad \text{PuO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2
\]

Figure 1-5: Geometry of AnO₅²⁺ complexes. a) octahedral b) pentagonal bipyramidal c) hexagonal bipyramidal.²

1.5 Hydrolysis

In aqueous solutions the f-block elements are highly charged cations which undergo hydrolysis, polarising O-H bonds in water to form hydroxides and complexes (Equation 1-2).¹⁶ The reactivity of an element towards hydrolysis is defined by \( z/r \) during which the electronegativity of each atom is equalised by electron transfer. Hence, hydrolysis is dependent upon electronegativity, ionic radius (\( r \)), charge (\( z \)) and pH.¹⁶,¹⁷

\[
[M(\text{OH}_2)_n]^z^+ + \text{H}_2\text{O} \rightleftharpoons [M(\text{OH})_h(\text{OH}_2)^{n-h}]^{(z-h)^+} + \text{hH}^+
\]

Equation 1-2: Hydrolysis equilibrium. \( M = \text{metal}, z = \text{charge and h} = \text{hydrolysis rate} \).¹⁶

The hydrolysis equilibrium is a delicate balance. If the pH is too low then H⁺ ions are in abundance and are able to compete with the metal for the ligand but if the pH is too high the metal is precipitated out of solution as a hydroxide salt.¹⁰ Figure 1-6 demonstrates how the nature of water alters with radius and charge of the metal ion. Hydrolysis reactions are
fundamental to aqueous chemistry and affect various properties vital to reactions such as solubility, formation of colloidal suspensions and the extent of complexation.\textsuperscript{12-14}

![Figure 1-6: The dependency of ionic charge ($z$) and ionic radius ($r$) on the nature of water as a ligand.\textsuperscript{17}}](image)

Hydrolysis is enhanced at high pH, higher metal ion concentration and with increasing charge/size ratio. Tetravalent actinides have a high charge ratio and consequently show extensive hydrolysis chemistry\textsuperscript{12} that can often result in the formation of oligomers and clusters that usually have low solubility.\textsuperscript{16} The major factors determining the formation of these species are pH, charge, concentration, temperature and presence of other materials e.g. counterions.\textsuperscript{16}

1.6 Polymerisation

The characteristics described so far show the complexities of aqueous actinide chemistry, so it is understandable that there has been relatively slow development within this area despite great interest.\textsuperscript{18} The understanding of aqueous uranium species is the most advanced as it is at the heart of the nuclear fuel cycle and as such has received the most interest.\textsuperscript{18,19} Proton loss in hydroxide species is generally accompanied by the formation of dinuclear or polynuclear species through intermolecular condensation reactions (olation). An increase in hydroxide concentration can promote olation whereby water is displaced to develop bridging hydroxyl groups. As pH is increased further, the hydroxide bridging
group can again become ionised, promote condensation leading to the production of an oxo-bridge (oxolation).\textsuperscript{10,20}

Wilson \textit{et al.} demonstrated this with the isolation of a dimeric thorium complex when 1 M HCl was added to thorium hydroxide (Figure 1-7).\textsuperscript{21} A more complex structure demonstrating the effect of increased hydroxide concentration was isolated by Knope and Soderholm, containing six Pu\textsuperscript{4+} cations bridged by four $\mu_3$-OH and four $\mu_3$-O groups. The core of the cluster is displayed in Figure 1-7 but the full structure also contained water and glycine substituents demonstrating hydrolysis occurs with the inclusion of organic ligands to a complex.\textsuperscript{22}

![Figure 1-7: Crystal structure of [Th$_2$(μ$_2$-OH)$_2$Cl$_2$(H$_2$O)$_{12}$]Cl$_4$ (left), illustration of the hexanuclear [Pu$_6$(μ$_3$-OH)$_4$(μ$_3$-O)$_4$(H$_2$O)$_6$]$^{12+}$ core of the Pu$^{4+}$ cluster (right). Pu = green, O = red, C = black, N = blue, shaded area = Pu$_6$ core.\textsuperscript{21,22}]

A larger plutonium (IV) oxide cluster has been isolated and characterised by Soderholm \textit{et al.} (Figure 1-8). Diffraction studies on the isolated solid found it to be nanometer-sized revealing the possible scope of hydrolysis. Plutonium in the tetravalent state is unstable in natural waters and as such is insoluble. This instability is thought to be a factor in the production of colloidal species.\textsuperscript{23}
However, hydrolysis is not the only phenomenon which occurs in natural waters. Many ions are found in appreciable concentrations in ground waters, such as, sulphate, fluoride, phosphates and carbonates. Carbonate ions in particular are found in reasonably high concentrations and form strong metal complexes so can overcome the effect of hydrolysis.\(^2\)

1.7 Databases and Thermodynamics.

The PHREEQC software suite is commonly used to estimate what species are present in radionuclide solutions. Calculated speciation data can then be used to determine soluble species, reference pore waters, sorption coefficients and solubility limits in genuine systems.\(^2\) Nevertheless, to enable reliable estimations accurate thermodynamic constants are required. There are many thermodynamic databases available but only a few include data which relate to radionuclide species. The SIT (Specific ion Interaction Theory, European), LLNL (Lawrence Livermore National Laboratory, American) and Hatches-20 (UK) databases are frequently utilised around the world to estimate radionuclide speciation in PHREEQC.

However, there is still a lack of certain chemical knowledge owing to relatively few places able to undertake radioactive experiments and with fundamentals of radionuclide chemistry unlike any other experienced in the periodic table. The uncertainties and voids in
thermodynamic constants along with equilibria and redox conditions could produce an inaccurate view on species. Experimental data is highly dependent on concentration, solubility, temperature (T) and ionic strength (I) thus this is where differences arise and is especially common for tetravalent radionuclides. The most recent updates for databases contain hydrolysis constants which have been independently determined with missing constants adjusted to fit experimental measurements.\(^{24}\)

### 1.8 Relevance

The safety of projects employing radioactive materials is one of the most debated topics in the field of environmental hazards.\(^{25}\) Not only is there waste from nuclear reactors and submarines to consider, there are also unpredictable natural hazards such as earthquakes and flooding witnessed in Fukushima in 2011 and equipment malfunctions such as the Chernobyl disaster of 1986.

Much work has been done on the speciation of radionuclides within reactors and in subsequent steps, \textit{e.g.} reprocessing.\(^{26-28}\) Despite this, little is known about speciation in other areas and it is prerequisite to determine speciation with the possibility of contamination. Potential contamination ranges from contact with non-radioactive contaminants (\textit{e.g.} mercury and beryllium) in a localised area and contaminated land (near field) to remediation issues in ground water (far field). All sites investigated have different characteristics, chemistry and geology and so a wide range of species are expected.

In UK nuclear sites such as Sellafield and disposal sites such as the LLWR (Low Level Waste Repository) there are various contaminants to consider which may come in contact with radionuclides. In certain areas of site there is the existence of hydrocarbons (\textit{e.g.} from past fire training exercises or un-bunded storage tanks) and the presence of asbestos (from original plant construction). There are also areas on site which contain residue from explosives from former munitions manufacturing and storage.

Several countries (such as US) prefer to dispose of all waste nuclear fuel material as reprocessing is not deemed feasible.\(^9\) The UK currently has reprocessing plants in operation to chemically separate and recover fissionable from irradiated nuclear fuel.\(^{29-31}\) However Sellafield site houses legacy waste from first generation Magnox reactors, pile ponds and wet silos. After reprocessing of spent nuclear fuel there are waste streams that require disposal. These waste streams, along with legacy waste first require storage in large
water cooled pools at interim storage facilities above ground (Figure 1-9). \( ^{32} \) The storage pools are large water filled basins containing a lattice of stainless steel racks on which the spent fuel rods are laid. In order to keep the pools cool the water is continually circulated allowing heat removal. \( ^{33,34} \) When removed from the reactor, spent fuel rods release large amounts of energy as heat and as such are allowed to cool in the ponds. This also allows time for the shorter-lived radioactive fission products to decay. \( ^{30} \) The spent fuel rods are stored in the fuel ponds for a few decades for the level of radioactivity and generation of heat to reduce to less than a thousandth of the original level. \( ^{35} \)

Once the spent fuel has cooled to an adequate temperature it can be relocated to an underground geological repository where nuclear waste is immobilised and decay of the long lived highly radioactive daughter species, \( e.g. \) \( ^{237} \text{Np}, ^{239,240} \text{Pu} \) and \( ^{241,243} \text{Am} \), can continue. \( ^{5,19} \) To prevent the release of actinides, multiple barrier systems would be in place aiming to retard the migration of radionuclides from High Level Waste (HLW) in nuclear disposal facilities through rock by a series of engineering and natural barriers, with differing chemical and physical properties. \( ^{34,36} \)

There are however few repositories in operation; the UK has not decided upon a location and the US President, Barack Obama, halted work on the American underground facility in Yucca Mountain, fearing not enough is known about the consequences of radioactive leaks and containment in the long-term. \( ^{37} \) Figure 1-9 shows the final disposal repository for low and intermediate-level waste in Olkiluoto. \( ^{38} \) The US has a Waste Isolation Pilot Plant (WIPP) in operation in New Mexico but to date, only repositories for low and intermediate level waste are in use within Europe with applications on-going for safety purposes.

If geological disposal becomes the future of nuclear waste disposal then it is essential that actinide complexation is understood. Radioactive lifetimes of minor actinides and FPs can be extremely long (\( ^{237} \text{Np} \) half life is \( 2.14 \times 10^6 \) years). \( ^{36} \) Any long-term solution to waste storage needs to take into consideration that the waste cannot be isolated from the external environment for thousands of years to come and if the barriers containing waste were to fail, then water would come into contact with the waste materials and actinides would migrate into the environment.
As long-term storage options have not been agreed upon, spent fuel has been contained within storage ponds for much longer than anticipated and longer than they were designed for. Consequently the Magnox cladding of spent fuel rods have corroded creating a brucite sludge ($\text{Mg(OH)}_2$) at the bottom. This is not the only repercussion, as the corrosion of cladding has led to the degradation of fuel and the release of radionuclides into surrounding cooling water. In an effort to control the radionuclides, fuel ponds are treated to adjust the water to $\text{pH} \geq 10$ to induce hydrolysis. But speciation is not as clear cut as radionuclide interactions with surrounding water; many other ions are present in the ponds. These range from natural debris (e.g. atmospheric carbonate, organics from leaves, birds and algae) and unnatural components (chemicals and polyelectrolytes) which in theory can complex radionuclides altering their composition. If radionuclides are not prevented from becoming part of the sludge they are suspended in the circulating water ultimately leading to increased radiation levels. Due to the high activity in the pools the sludge and pool water is very difficult to sample and characterise. Safe clean-up requires full knowledge of the physical and chemical properties of evolved waste to develop suitable waste forms, and make accurate predictions of radionuclides both in the short term (during retrieval) and in the long term (behaviour within storage environments).
In these basic aqueous conditions the actinides can cluster through hydroxyl/oxy bonds and form colloids.\textsuperscript{2,21} The presence of organic molecules can produce unanticipated radionuclide complexes and change the chemical characteristics allowing, in some cases, the prevention of hydrolysis, the existence of soluble species and the failure of effluent treatments. Organic molecules can also stabilise colloids, inhibit flocculation and hence prevent precipitation.\textsuperscript{39,40} As such, radionuclides, especially plutonium, are in higher concentrations than originally thought with a massive potential for migration issues. All of these reasons indicate that nuclear storage ponds are of particular concern as speciation within is sophistication, unpredictable and unlike any other. Concern over colloid-facilitated transport was raised upon observation of plutonium in groundwater at the underground weapons testing facility in Nevada, USA. Over 20 years after initial tests, plutonium had been discovered over a mile away from the site.\textsuperscript{40}

The mechanism of colloid formation is not fully understood but their presence is significant to the long-term performance and safety of spent nuclear fuel repositories.\textsuperscript{34,40,41} Colloid formation can dramatically increase the apparent solubility of actinides,\textsuperscript{42} but is dependent on the chemical environment and interactions.\textsuperscript{39} A colloid consists of particles \(\sim 10-10000 \text{ Å} \) in size dispersed evenly throughout another substance.\textsuperscript{43} Some forms of colloids are naturally occurring in ground water and can allow sorption of charged radionuclides, for example from degraded engineered barrier systems, onto their surfaces (pseudo colloids).\textsuperscript{39,41} Others are formed by the hydrolysis of radionuclides themselves these are intrinsic colloids.\textsuperscript{2,42} Radiocolloidal species can form irreversibly and their migration has been found to be faster than the velocity of water.\textsuperscript{43} The size and composition of colloids significantly affect the rate and direction of radioactive contamination zones.\textsuperscript{44}

Once operations at nuclear facilities cease, the plants and fixtures need to undergo decontamination and remediation. Legacy waste will eventually be treated, radioactive material moved into long term storage with cement and steel fixtures undergoing decontamination and possible long-term storage. There is also the ongoing clean-up from historic leaks arising from effluent discharge pipes and from surface water collectors, which flooded draining surplus water into groundwater (surface run-off). As most sub surface groundwater in the UK has \( \text{pH} \) between 5-10 the speciation and solubility of the actinides within this \( \text{pH} \) range must be understood in order to effectively treat these areas.\textsuperscript{44}
Nuclear power sites are not the only locations where information and basic understanding of radionuclides is necessary. Worldwide facilities such as the Atomic Weapons Establishment (AWE) which design, build and maintain nuclear deterrents also need information in order to understand consequences and to aid in nuclear proliferation monitoring.

Thus there is a need for basic information including species, sorption and migration data at a wide range of pH in order to ensure thorough decontamination and fully understand possible environmental consequences and how to counteract them.

1.9 Ligands

Naturally occurring ligands are found in ground water, storage ponds and soil. They are known to coordinate to radionuclides and in some cases are key to the formation of soluble radionuclide colloids, including humic and fulvic acids. Although the exact chemical structure has not be determined, analysis using molecular weight, IR and electron microscopy have reported hypothetical models (Figure 1-10) which are widely accepted.\textsuperscript{35,46} They contain multiple functional groups with fulvic acid displaying higher density of functional groups and a higher acidity compared to humic acid leading to a larger uptake of radionuclides. As they are capable of binding to numerous radionuclides organic ligands can enable sorption or migration to take place depending on conditions.\textsuperscript{7}
In addition to naturally occurring organic materials, there are many chemicals used in the nuclear fuel process which can have an impact environmentally if their chemical and physical properties are not fully understood.

Waste fuel can undergo a separation process whereby the actinides are separated from the lanthanides which have similar properties when in the $+3$ oxidation state. Here ligand design is important to generate binding to specific radionuclides of a particular oxidation state. As the actinides have greater radial extension they show a more covalent character in bonding and as such are able to bind through softer donor ligands compared to oxygen.

There have been many generations of separating agents including oxygen donating ligands (e.g. N,N'-Dimethyl-N,N'-dibutyl-tetradecylmalonamide, DMDBTDMA), sulphur donating ligands (e.g. bis(2,4,4-trimethylpentyl)dithiophosphinic acid, Cyanex 301) and nitrogen donating ligands (e.g. bis-triazinyl bipyridines, BTBPs), see Figure 1-11 for examples. To yield the best separations it has become apparent that ligand architecture is important. A cavity containing donor atoms can encapsulate radionuclides to product stable complexes utilising the chelate effect. Encapsulation also allows all coordinated water molecules to be replaced creating a lipophilic exterior facilitating phase transfer.
Other chemicals which are used in nuclear facilities include detergents and extractants. Decon90 is a commonly used decontaminating agent in laboratories and at nuclear sites. It is an emulsion containing a mixture of anionic and ionic surface active agents and sequestering agents in an aqueous base. Although citric acid is a naturally occurring organic ligand it is in high concentrations in Magnox tanks at Sellafield. Chelates such as Tiron and citric acid are of use as extraction agents to remove uranium from soil. Although much work has been completed to understand speciation during the separations process and in decontaminants, over time changes in conditions cause organic ligands to break down into smaller organic particles with differing chemical and physical characteristics; hence altering the speciation of radionuclides.

Ligands investigated here are simplified versions of organics found in the nuclear process and in nature. They have multi-donor functionality (hydroxide, amine, amide, carboxylic acid) and are theoretically able to bind through multiple sites (Figure 1-12). The use of relatively small organics should allow the study of binding through specific functional groups which, once understood will lead to an increased comprehension of binding in more complex ligand systems such as humic acids and the behaviour of actinides in the aqueous environment including hydrolysis products.
Experiments will employ controlled hydrolysis methods in which auxiliary ligands are used to occupy part of metal coordination sphere, thus preventing excessive hydrolysis by reducing number of coordination sites available for H$_2$O. The multiple binding sites should help fill the coordination sphere of the actinide whilst leaving a small number of vacant coordination sites to form extended frameworks (clusters). Nanoparticles (particles $< 100$ nm in dimension) created in this manner are important as they can occur at low temperatures and in alkaline environments like those found in nuclear waste storage pools and could have a large impact on the transport of radionuclides in the environment.$^{33,49}$

Pentadentate ligands should be able to saturate the equatorial plane of actinyls preventing solvent exchange from occurring. By altering the size of the N$_3$O$_2$ cavity selectivity of actinides may be achieved allowing for the selective extraction or capture of radionuclides.
The two pentadentate ligands containing a $N_3O_2$ to be investigated with plutonium are 6,6’-Bis(2-hydroxyphenyl)-2,2’-6’,2’-terpyridine (salterpyH$_2$) and N,N’-Bis((4-diethylamino)salicylidene)diethylenetriamine (saldien$^{(Et_2N)_2}$H$_2$) shown in Figure 1-13. As these ligands lie near planar there should be little obstruction of the axial oxo ligands of plutonyl.

![Figure 1-13: Pentadentate $N_3O_2$ ligands investigated. Saldien$^{(Et_2N)_2}$H$_2$ (left) and salterpyH$_2$ (right).](image)

Previous investigations have established the complexation of saldien$^{(Et_2N)_2}$H$_2$ and salterpyH$_2$ to uranyl in alcoholic solutions. The deprotonation of phenol groups occurs without the requirement of base allowing solution state and solid state characterisation of the complexes (Figure 1-14).

![Figure 1-14: Crystal structures of UO$_2^{2+}$ pentadentate complexes. UO$_2^{VI}$(saldien$^{(Et_2N)_2}$) (left) and UO$_2^{V}$ (salterpy) (right).](image)

However, reactions of NpO$_2^{2+}$ with saldien$^{(Et_2N)_2}$H$_2$ and salterpyH$_2$ revealed there was instantaneous reduction of neptunium to NpO$_2^{+}$ upon ligand addition in organic solvents. A crystal of salterpyH$_2$ with NpO$_2^{+}$ was isolated (Figure 1-15) but the solid state structure of the saldien$^{(Et_2N)_2}$H$_2$ complex was unable to be isolated but was identified using NMR spectroscopy.
1.10 Aims

This work aims to characterise the solution state behaviour of actinides over a wide pH range in the presence of organic ligands. The ligands to be investigated are H$_3$thme, H$_3$tea, H$_3$bic, H$_3$heidi, H$_3$NTA, H$_2$ADA and H$_3$cit, and pK$_a$ values will be calculated for each.

The solution state complexation of the organic ligands listed will be characterised with Th$^{4+}$, U$^{4+}$ and UO$_2^{2+}$ in the absence of CO$_2$ between over a wide pH and formation constants for the complexes will be determined. The LLNL, SIT and Hatches-20 databases will be used with the PHREEQC software suite to predict species formed in the aqueous solutions for comparison with experimental results.

The complexation of H$_3$heidi and H$_4$HXTA with Pu$^{3+}$ in aqueous solutions in the absence of CO$_2$ will be characterised along with the complexation of Pu$^{3+}$, Pu$^{4+}$ and PuO$_2^{2+}$ with salterpyH$_2$ and saldiene$^{(Et_2N)_2}$H$_2$ in THF.

1.11 References


2 Experimental Techniques

2.1 Chemicals

Deionised 18 MΩ water was obtained using an Elix Millipore purifier for the preparation of aqueous solutions. This was freshly acquired for each experiment and nitrogen gas was bubbled through the water for 30 minutes before it was placed in a carbonate free glove box. All solutions were pH calibrated using a Mettler Toledo pH meter and with pH 4.01 (±0.01), 7.00 (±0.01) and 10.01 (±0.02) Fisher Scientific standard buffer solutions.

HNO₃ (laboratory reagent grade, 70 %, Fisher Scientific), HCl (ACS reagent, 37 %, Sigma Aldrich), NaOH (pellets, 99.99 % trace metal, Sigma Aldrich), HClO₄ (70 %, 99.999 % trace metal, Sigma Aldrich), Et₃N (≥ 99 %, Sigma Aldrich), HONH₃Cl (99.999 % trace metal, Sigma Aldrich), methanol (puriss, ACS reagent, ≥ 99.8 %, Sigma Aldrich), THF (anhydrous, ≥ 99.9 %, Sigma Aldrich), ethanol (ACS reagent, ≥ 99.5 %, Sigma Aldrich), diethyl ether (anhydrous ACS reagent, ≥ 99.0 %, Sigma Aldrich) and ACN (anhydrous, 99.8 %, Sigma Aldrich) were used as supplied.

Pro-ligands, 1,1,1-Tris(hydroxymethyl)ethane (H₃thme, Sigma Aldrich, 99 %), Triethanolamine (H₃tea, Sigma Aldrich, 99 %), N,N-bis(2-hydroxyethyl)glycine (H₂bic, Sigma Aldrich, ≥ 99 %), N-(2-Hydroxyethyl)iminodiacetic acid (H₂heidi, Sigma Aldrich, ≥ 98.0 %), Nitrilotriacetic Acid (H₃NTA, Sigma Aldrich, 99 %), Citric Acid (H₃cit, Sigma Aldrich, ACS reagent, ≥ 99.5 %) and N-(2-acetamido)-2-iminodiacetic Acid (H₂ADA, Sigma Aldrich, 98 %) were used as received. N,N’-Bis((4-diethylamino)salicylidene)diethylenetriamine (saldien(Et₂N)₂H₂), (2-hydroxy-5-methyl-1,3-phenylene)bis(methylene)bis(azanitriyl)tetraacetate (5Me-HXTAH₄) and 6,6’’-Bis(2-hydroxyphenyl)-2,2’:6’,2’’-terpyridine (SalterpyH₂) were synthesised using previously detailed methods.¹²

Thorium nitrate pentahydrate, {Th(NO₃)₄.5H₂O}, uranyl nitrate hexahydrate, {UO₂(NO₃)₂.6H₂O} and uranium trioxide, UO₃, were obtained from the Centre of Radiochemistry Research (CRR) isotopes store. Caution! Thorium-232 and Uranium-238/235 are radioactive with half-lifes of 1.41x10¹⁰ years, 4.47x10⁹ years and 2.45x10⁵ years respectively.³⁴ ²³²Th and ²³⁵/²³⁸U are α-emitters which present internal hazards. Care must be taken and suitable precautions must be in place in order to handle these materials.
Plutonium experiments were conducted at the Joint Research Centre-Institute for Transuranium Elements (JRC-ITU) in both nitrogen and argon glove boxes. Plutonium (Pu(IV) in HNO₃, 0.28 M) was acquired from JRC-ITU. Caution! Pu²³⁹ is a strong α-emitter with a half-life of 24,100 years. It has severe radiological effects and must be handled with extreme care.

2.2 NMR Spectroscopy

NMR experiments were performed on a Bruker Avance Ultrashield™ Spectrometer of frequency 400 MHz (¹H) and 101 MHz (¹³C). The NMR was controlled using Bruker Topspin 2.1 Software and spectra analysed using MestReNova software.

Solutions for analysis by ¹H NMR spectroscopy were prepared using 5 mM metal solutions, varying the concentration of pro-ligand accordingly; I was not controlled. All solutions used deuterium oxide (D₂O, 99.92 atom % D, Sigma Aldrich) with pD altered using 0.1/1 M sodium deuteroxide (NaOD, 40 wt % solution in D₂O, 99.5 atom % D) and 0.1/1 M deuterium chloride (DCl, 35 wt % solution in D₂O, 99 % atom D) solutions in D₂O. Aliquots of 0.5 mL were taken from the experimental solution at regular pD intervals and placed in a 5 mm glass NMR tube for analysis.

¹H NMR spectra were recorded for 128 scans and referenced to the sodium salt of 3-(trimethylsilyl)-1-propanesulfonic acid (DSS, 97 %, Sigma Aldrich) which was added as internal reference (one drop 0.1 M) using the methyl signal (δH 0.00 ppm). Spectra included in this thesis exclude DSS, but D₂O signals are altered accordingly so the two spectra can be superimposed.

¹³C NMR spectra were recorded for 1024 scans with 1,4-dioxane (anhydrous, ≥ 99.8 %, Sigma Aldrich) used as a ¹³C peak position reference (δC 67.19 ppm). pKₐ values were determined by ¹³C NMR spectra using the Henderson-Hasselbalch equation (Equation 2-1).⁵

\[
\delta_{\text{obs}} = \frac{\delta_{A^-} \times 10^{(pH-pK_a)} + \delta_{AH}}{1 + 10^{(pH-pK_a)}}
\]

Equation 2-1: The Henderson-Hasselbalch equation. δ₀bs = observed chemical shift, HA = protonated form of ligand, A⁻ = deprotonated form of ligand. δAH and δA⁻ are the chemical shifts at low and highest pH respectively.
### 2.3 UV-Vis Spectroscopy

Solution UV-Vis spectra of uranium samples were recorded on a Shimadzu UV-2600 UV-Vis spectrophotometer. Spectra were recorded with a resolution of 0.5 nm over the wavelength range 200 - 1400 nm. All solutions were kept at constant I of 0.5 with NaNO₃ (Sigma Aldrich) using Equation 2-2.⁶

\[ I = \frac{1}{2} \sum c z^2 \]

Equation 2-2: The ionic strength equation. \( I \) = ionic strength, \( c \) = molar concentration, \( z \) = charge of ion.

Samples were prepared with an initial uranium concentration of 10 mmol. Pro-ligand concentration was altered depending on the desired ratio. pH was altered using 0.1/0.5 M NaOH and 0.1/0.5 M HNO₃ solutions in deionised water. A 1 mL aliquot of solution was taken at each pH for analysis; volumes of NaOH and HNO₃ were recorded to ensure accurate calculation of the extinction coefficient using the Beer-Lambert Law.

UV-Vis-nIR spectra of plutonium samples were recorded on solution samples using an Ocean Optics mini spectrometer, DH-2000-BAL deuterium - tungsten halogen light source and either an Ocean Optics CUV-UV cuvette holder (nitrogen glovebox) or an Ocean Optics TP300 dip probe fitted with fibre optic connections (argon glovebox) displayed in Figure 2-1. Spectra were recorded in the 300 - 1200 nm range and are displayed relative to plutonium concentration.
2.4 Infra-red Spectroscopy

Infra-red spectroscopy was carried out on solid samples using a Shimadzu IRAffinity-1 spectrometer with a “Golden Gate” Attenuated Total Reflectance (ATR) attachment. The resolution of the IR spectra was 4 cm\(^{-1}\) and data was collected for 32 scans.

2.5 Elemental Analysis

Elemental analysis was completed by the analytical department in the department of chemistry at the University of Manchester. A Carlo Erbra Instruments CHNS-O EA1108 Elemental analyser was used to determine carbon, hydrogen, nitrogen and sulphur composition. Metal and halide analysis were completed using a Fisons Horizon elemental analysis ICP-OES spectrometer.

2.5.1 ICP-OES

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) measurements on plutonium samples were conducted by Rafael Álvarez Sarandés at ITU on a Horiba Ultima 2 machine. Plutonium stock solutions underwent ICP-OES to identify plutonium concentration.
2.6 Potentiometry

Potentiometric titrations were conducted on a Mettler Toledo automated burette. Electromotive force (EMF) in mVs was measured with a Metrohm pH meter (Model 713) and a Ross combination pH electrode (Orion Model 8102). Apparatus consists of a water-jacketed glass cell with temperature maintained at 298 K using water in constant circulation from a temperature bath. A pH probe and the burette outlet were inserted into the solution through holes in the lid of the glass cell. A Mettler Toledo stirring attachment was used to allow stirring throughout titrations. The apparatus (Figure 2-2) is controlled remotely using Mettler Toledo LabX software with data interpreted using Hyperquad 2008 software.

Solutions for potentiometric titrations had an initial concentration of 5 mM pro-ligand (metal concentration was altered for varying ratios accordingly), total volume of 20 mL and I of 0.5 (NaNO₃). Solutions were degassed with N₂ and titrations were completed under an N₂ atmosphere to reduce carbonate concentration. Solutions were titrated from an acidic pH to an alkaline pH with standardised 0.1/0.01 M NaOH as titrant. Titrant was added at a rate of 0.01 mL min⁻¹.

Figure 2-2: Aqueous potentiometric titration set-up.
2.6.1 Standardised Solution of Sodium Hydroxide

A 0.1/0.01 M sodium hydroxide solution (500 mL) was made up from NaOH pellets and deionised water. I was adjusted to 0.5 (NaNO$_3$) and standardised by titration with potassium hydrogen phthalate (BioXtra, ≥ 99.5 %, Sigma Aldrich).

2.6.2 Speciation Diagrams

Speciation simulations of actinides were completed in PHREEQC using condition parameters obtained by potentiometric titrations.

Data obtained from potentiometric titrations were fitted using Hyperquad 2008 software to generate formation constants which were then placed in the Hyperquad Simulation and Speciation 2009 programme to generate speciation diagrams.

2.7 Preparation of Uranium tetrachloride, UCl$_4$

The preparation of UCl$_4$ was achieved in a nitrogen glovebox using previously reported procedures.$^7$ UO$_3$ (10 g, 35 mmol) was dissolved in hexachloropropene (44 mL) and the solution heated to 158 °C under inert atmosphere; an exothermic reaction was observed. Once this reaction had subsided the solution was refluxed for 7 hours with a heating mantle. The by-product, trichloroacryloyl chloride, was removed by distillation. The remaining green solid was filtered using a dry filter stick, washed with CCl$_4$ (dried over CaH$_2$) and dried under vacuum for 6 hours.

2.8 Preparation of Plutonium Samples

Before any manipulation of plutonium was performed, the oxidation state of the plutonium starting material was verified by UV-Vis-nIR spectroscopy using the major absorption bands stated in Table 7-1.
2.8.1 PuO$_2^{2+}$ Stock Solution

The preparation of PuO$_2^{2+}$ stock solution in THF was achieved in a nitrogen glovebox using previously reported procedures.$^5$ A stock solution of Pu$^{4+}$ (300 μL, 0.28 M) in conc. HNO$_3$ was heated to dryness using a hotplate. The resulting green residue was oxidised upon heating to PuO$_2^{2+}$ by the addition of HClO$_4$ (70 %, 0.2 mL). The mixture was dissolved in HCl (1 M, 0.3 mL) and heated to dryness using a hotplate; this procedure was repeated two further times. The resulting solid was dissolved in THF (2 mL). A UV-Vis-nIR spectrum was recorded to confirm the oxidation of Pu$^{4+}$ to PuO$_2^{2+}$. An aliquot was taken for ICP-OES to confirm Pu content.

2.8.2 Pu$^{3+}$ Stock Solution

The preparation of Pu$^{3+}$ stock solution in H$_2$O was achieved in a nitrogen glovebox using methods previously reported procedures.$^9,10$ A Pu$^{4+}$ solution (300 μL, 0.28 M) was heated to dryness, 0.1 M HCl (0.5 mL) was added to the residue and was heated until fuming on a hotplate. Solid HONH$_3$Cl (~10 mg) was added causing the solution to immediately change colour from brown to purple. The solution was diluted to 1 mL with DI H$_2$O. A UV-Vis-nIR spectrum was recorded to confirm the reduction of Pu$^{4+}$ to Pu$^{3+}$. An aliquot was taken for ICP-OES to confirm Pu content.

2.8.3 Pu$^{3+}$ Titrations

2.8.3.1 Pu$^{3+}$

A solution of Pu$^{3+}$ (1.4 mM) in HCl (0.0125 mM, 4 mL) was placed in small beaker. Aqueous NaOH (0.1 M) was added to the Pu$^{3+}$ solution in 10 μL aliquots to increase pH. UV-Vis-nIR spectra and pH were recorded after each aliquot addition.

2.8.3.2 Pu$^{3+}$ and H$_3$heidi/5Me-HXTAH$_4$

To a solution of Pu$^{3+}$ (1.4 mM) in DI H$_2$O (4 mL) a pro-ligand solution (H$_3$heidi or 5Me-HXTAH$_4$, 5.6 mM) in DI H$_2$O was added in 20 μL aliquots (0.2 equivalents, 0.28 mM) until four equivalents had been added. UV-Vis-nIR spectra and pH were recorded after each aliquot addition.
2.8.3.3 Pu$^{3+}$ and salterpyH$_2$/saldien$^{(Et_2N)_2}H_2$

To a solution of Pu$^{3+}$ (1.4 mM) in 1M HCl (2 mL) a pro-ligand solution (salterpyH$_2$ or saldien$^{(Et_2N)_2}H_2$, 1.4 mM) in THF (100 μL) was added in 10 μL aliquots (0.1 equivalents, 0.14 mM) until one equivalent had been added. UV-Vis-nIR spectra were recorded after each addition.

2.8.4 Pu$^{4+}$ Reaction with saldien$^{(Et_2N)_2}H_2$

A sample of Pu$^{4+}$ (2.8 mM) in conc. HNO$_3$ (10 μL) was heated to dryness and dissolved in 1 M HClO$_4$ (20 μL). This was added to a solution of saldien$^{(Et_2N)_2}H_2$ (6.35 mg, 1.4 mM) in THF (2 mL) and a UV-Vis-nIR spectrum recorded.

2.8.5 PuO$_2^{2+}$ Titrations with salterpyH$_2$/saldien$^{(Et_2N)_2}H_2$

To a solution of PuO$_2^{2+}$ (1.4 mM) in THF (2 mL) a pro-ligand solution (salterpyH$_2$ or saldien$^{(Et_2N)_2}H_2$, 1.4 mM) in THF (0.2 mL) was added in 20 μL aliquots (0.2 equivalents, 0.28 mM) until one equivalent had been added. UV-Vis-nIR spectra were recorded after each addition and for 24 hours after complete addition.

2.9 Working with Radioactive materials

Research within the University of Manchester was done in accordance to radiological safety precautions put in place by the Radiation Protection Supervisor. Use of radioisotopes was subject to accountancy procedures along with an extensive protocol in a controlled area. Radiation was monitored with a film badge with all work carried out in well ventilated fumehoods or in nitrogen glove boxes.

Research within JRC-ITU was undertaken in accordance with Section 34 of the Radiation Protection Ordinance (Strahlenschutzverordnung) and the regulations in place in the Institute for Transuranium Elements (ITU) and the German Regulations. Disposal of radioactive material undergoes rigorous accounting and measurement procedures to allow waste to be transported to an interim storage facility.
Access to controlled areas is through full body contamination monitors with admission granted with card keys and retina scanner. Whilst working in the controlled areas, the Institutes’ protective clothing and shoes must be worn with entry to the laboratories only allowed between 8.00 to 12.00 hrs and 13.00 to 16.00 (Friday: 15.00) hrs. Whilst in the institute an official dosimeter must be worn, electronic dosimeters are also worn giving an instant readout so workers are aware if they need to move away or work quickly with a source with the alarm threshold being 10 μSvhr⁻¹. Work with plutonium was carried out in a negative pressure glove box wearing cotton and rubber gloves to reduce the risk of skin contamination. A respirator mask is worn when removing or placing items into the glove boxes to filter against the inhalation of radioactive materials.

2.10 References


3 Ligand Characterisation

All ligands used in this thesis have been fully characterised. The data obtained has been compared to literature values where applicable, to enable suitable and reliable comparisons to be made when analysing the complexation behaviour with actinides.

3.1 1,1,1-Tris(hydroxymethyl)ethane (H₃thme)

H₃thme is an example of a tripodal ligand containing terminal alcohol functional groups from which multiple modes of complexation are permitted. Alcohol moieties are a significant functional group in natural organics. They are found everywhere from humic acids and solvents to sugars such as glucose and are often bound to other organic fragments such as phenyl rings and alkenes.¹⁻³ Consequently, alcohol moieties are likely to be an important group for the complexation to actinides.

H₃thme alkoxide chemistry has historically been successful in the formation of complexes with transition metals in organic solvents under both atmospheric temperatures and pressures and using solvothermal techniques.⁴⁻⁵ In all cases H₃thme remains protonated at all alcohol moieties upon complexation. An insoluble cluster (thme)₂M₄(OCHMe₂)₁₀, where M is Ti or Zn, can be isolated when refluxed in a mixture of toluene/THF (Figure 3-1).⁶ Multiple Fe³⁺ clusters have also been synthesised in acetonitrile and MeCN including [Fe₉O₄(O₂CCMe₃)₁₃(thme)₂] and [Fe₈(O₂CR)₁₂(thme)₄].⁴ There are many other reports showing the ability of H₃thme to bind to TM including manganese,⁷ vanadium² and multinuclear transition metal-lanthanide complexes.⁸

![Figure 3-1: Structure of H₃thme (left), crystal structure of [Fe₉O₄(O₂CCMe₃)₁₃(thme)₂] (center) and crystal structure of [Fe₈(O₂CPh)₁₂(thme)₄] (right).⁴](image-url)
The $^1$H NMR spectrum of H$_3$thme shows two proton environments displayed in Figure 3-2. The electronegativity of the oxygen atoms causes the signal of neighbouring protons ($H_1$) to be shifted downfield (3.44 ppm) in comparison to the methyl protons (0.8 ppm). Integration confirms this assignment. The lack of variance with increased pD demonstrates that the alcohol moieties are not deprotonated within the pD range 2 - 12. This is expected as the pK$_a$ of the alcohol groups is around 14. However, the presence of a highly charge dense species e.g. Th$^{4+}$ may enable deprotonation of the alcohol at a lower pD.$^{10,11}$

![Figure 3-2: Stacked $^1$H NMR spectra of H$_3$thme at pD 2 - 12.](image)

The lack of deprotonation is also observed in $^{13}$C NMR spectra with no transformation of signals upon increasing pD (Figure 3-3). There are three distinct carbon environments with three signals in the $^{13}$C NMR spectrum. The most deshielded (due to the neighbouring OH) is furthest downfield at 65.01 ppm.
3.2 Triethanolamine (H$_3$tea)

The use of N-donor ligands in chemical procedures has been intensively researched over the past decade, especially within separations chemistry and in particular as complexing agents containing bipridyl and phenanthroline units. Amines and their derivatives are also found naturally, for example as alkaloids in certain plants and fungi, and as serotonin and histamine in animal tissues.

H$_3$tea is closely related to H$_3$thme, but it incorporates a central nitrogen atom (amine). Consequently, it is possible for H$_3$tea to have tetridentate coordination to metal ions compared to tripodal (H$_3$thme). If coordinated through both alcohol and amine moieties to a metal ion a 5 membered chelate ring would be achieved. This should create a more stable complex than with the 6-membered chelate ring that H$_3$thme forms.

Reactions of H$_3$tea with TM$_2$s are known to produce cluster species in solvents. H$_3$tea usually acts as a tridentate ligand in TM complexes with complexation via the central amine and two alcohol moieties with structures obtained where one, two or all three alcohol moieties are protonated. Tetradentate coordination via the central amine and alcohol moieties has also been observed especially towards metals with large ionic radii. The [Cd(H$_3$thme)$_2$](C$_4$O$_4$)$_2$.H$_2$O complex was isolated after the methanoic solution
was heated for 12 hours at 323 K and contains a tridentate and tetradeutate ligand, both of which remain fully protonated (Figure 3-4).

Lanthanide wheel structures containing six metal ions and six Htea\(^{2-}\) have been published demonstrating the ability of this ligand to stabilise clusters by bridging to multiple lanthanide (Dy and Gd) atoms in methanoic media (Figure 3-4). In the wheel, Htea\(^{2-}\) is tetradeutate with two oxygen arms bridging Ln\(^{\text{III}}\) ions and the protonated arm chelating an Ln\(^{\text{III}}\) ion.\(^{24}\) Polymeric [Ln(H\(_3\)tea)]\(_n\) complexes have been identified for all lanthanide metals using mass spectrometry with Plaziak et al. proposing that the lone pair localised on the nitrogen may be involved in bonding to the metal.\(^{25}\)

As previously discussed, although the Lns are part of the f-block, their chemical properties differ from those of the early actinides. Work by Joshi et al. has shown that tea can be used as a buffer in uranyl systems enhancing complexation to chromaphores but not to H\(_3\)tea.\(^{26}\) However, Riaz et al. contradict this stating that the presence of tea instead interferes with uranyl concentration analysis by High-Performance Liquid Chromatography (HPLC) suggesting uranyl complexation with H\(_3\)tea.\(^{27}\)

![Figure 3-4: Structure of H\(_3\)tea (left), crystal structure of [Cd(H\(_3\)thme)\(_2\)](C\(_6\)O\(_4\))\(_2\).H\(_2\)O with H atoms shown as small circles (centre) and representation of [Dy\(_6\)(teaH)(NO\(_3\))\(_6\)].8MeOH (right). Dy\(^{\text{III}}\) (purple), O (red), N (blue), C (grey) with H atoms omitted.\(^{23,24}\)]

Two proton environments are observed in the \(^1\)H spectrum of H\(_3\)tea (Figure 3-5) demonstrating its symmetry. Protons adjacent to the alcohol group are furthest downfield (3.93 ppm at pD 2) with both proton signals split into triplets. H\(_3\)tea is a weak base and as such is protonated at the amine in acidic conditions forming H\(_4\)tea\(^+\). Both proton signals incur a downfield shift between pH 2 - 6 caused by deprotonation of the central nitrogen. The proton groups nearest to the central nitrogen (H\(_2\)) undergo a larger shift of ~0.8 ppm
compared to ~ 0.3 ppm for H₁ as the deprotonation of nitrogen has a larger impact on H₂ than on H₁.

The nitrogen deprotonation is also observed in the $^{13}$C NMR spectrum with both carbon environments exhibiting chemical shifts as an effect of the deprotonation. The pKₐ can be determined by measuring the chemical shift of carbon atoms as a function of pH using the Henderson-Hasselbalch equation (Equation 2-1). This is a least-squared fit of the experimental results assuming that the observed signal is weighted average between the protonated and deprotonated species. The equation is solved using trial and error for pKₐ until the best fit is achieved. The pKₐ was determined to be 8.62 (+0.09/-0.05). The model fit generated for both carbon environments is shown in Figure 3-6.
However, pH electrodes react differently to H⁺ (H₂O) and D⁺ (D₂O). Glasoe et al. reported the following relationship which allows comparison to literature values.³¹-³³

\[
pD = pH + 0.41
\]

**Equation 3-1: The pD to pH conversion equation.**

The modified pKₐ is 8.21 (+0.09/-0.05) which is comparable to literature values displayed in Table 3-1. This is however, only an approximation of the pKₐ as I was not kept constant. Hence, potentiometric titrations were done to generate a more conclusive result in a non-deuteronated system with constant I. Experimental data was fitted with Hyperquad software and included model values for alcohol deprotonation at I = 0.5 (NaNO₃). The hyperquad model along with the resulting speciation diagram for H₃tea is shown in Figure 3-7.
The modelled potentiometric data correlates well with pKₐ values obtained from $^{13}$C NMR analysis, both of which are within range of the literature values, shown in Table 3-1. The results show that the techniques utilized are accurate and so further studies incorporating different metal species ought to generate reliable formation constants.

<table>
<thead>
<tr>
<th>Calc. $^{13}$C pKₐ, 25 °C</th>
<th>Calc. potentiometric pKₐ, I = 0.5 (NaNO₃), 25 °C</th>
<th>Lit. pKₐ, I = 0.5 (unknown), 25 °C</th>
<th>Lit. pKₐ, I = 1.0 (NaNO₃), 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.21 (+0.09/-0.05)</td>
<td>8.27 (±0.1)</td>
<td>7.9 (-0.01)</td>
<td>8.05 (±0.01)</td>
</tr>
</tbody>
</table>

Table 3-1: Calculated and literature pKₐ values for H₃tea.

3.3 **N,N-bis(2-hydroxyethyl)glycine (H₃bic)**

Through the substitution of a terminal alcohol group with a carboxylic acid group H₃tea can be converted to H₃bicine (known as H₃bic hereafter) enabling assessment of the carboxylate binding capacity. Investigations into coordination with TM ions have established that H₃bic is a tetradeutate ligand capable of bridging and chelating (forming 5 membered rings) TM ions. When complexed the carboxylate and amine are deprotonated but the alcohol moieties are protonated. Coordination modes of bicine that have been identified are displayed in Figure 3-8.
An assemblage of lanthanide work has been conducted with bicine in aqueous conditions. Determination of formation constants of lanthanide bicine complexes along with corresponding hydroxide complexes using NMR and potentiometric techniques has been reported by Calderón et al.,\textsuperscript{39} with ternary complexes also being investigated by Orabi et al.\textsuperscript{40} and Taha et al.\textsuperscript{41} to name a few. Calderón et al. proposed structures for the tetradentate Ln-H$_2$bic complexes using solution state data with protonated alcohol moieties (Figure 3-9). The crystal structure of a gadolinium complex incorporating a tetradentate bicine protonated at the alcohol moieties and a bidentate phenanthroline group is shown in Figure 3-9.\textsuperscript{38}

Both the $^1$H and $^{13}$C NMR show that bicine is symmetrical with the $^1$H spectrum displaying the alcohol terminated alkane chains as two distinct triplets and the carboxylate terminated alkane chain as a singlet (Figure 3-10). In acidic solutions bicine is protonated at the amine forming an H$_4$bic$^+$ species. The deprotonation of carboxylate between pD 2 - 3 is displayed by the upfield shift of H$_3$ from 4.04 to 3.89 ppm with deprotonation of the amine illustrated
by the upfield shift of all peaks between pD 7 - 10. As H₂ and H₃ are closer to the amino nitrogen they incur greater shifts and broadening. The upfield shift at pD > 12 is due to deprotonation of the alcohol groups.

Figure 3-10: Stacked ¹H NMR spectra of H₃bic at pD 2 - 13.6.

In acidic solutions (pH < 1.5), H₃bic is protonated at the amine to form H₄bic⁺, as pH increases the carboxylate is deprotonated to form a zwitterion, further increase in pH results in nitrogen deprotonation. As such the Henderson-Hasselbalch equation is expanded (Equation 3-2) to incorporate two deprotonating groups within the pH range studied.²⁸,⁴² Calculated pKₐ values are shown in Table 3-2 with values modified for pH.

\[ \text{HOOC} - C - N^+ - R_2 \leftrightarrow \text{⁻OOC} - C - \text{⁻NH} - R_2 \quad (\text{pK}_{a1}) \]

\[ \text{⁻OOC} - C - \text{⁺NH} - R_2 \leftrightarrow \text{⁻OOC} - C - N - R_2 \quad (\text{pK}_{a2}) \]

\[ \delta_{\text{obs}} = \frac{\delta_{AH_4^+} + \delta_{AH_3} \times 10^{(p\text{H} - \text{pK}_{a1})} + \delta_{AH_2^-} \times 10^{(2 \times p\text{H} - \text{pK}_{a1} - \text{pK}_{a2})}}{1 + 10^{(p\text{H} - \text{pK}_{a1})} + 10^{(2 \times p\text{H} - \text{pK}_{a1} - \text{pK}_{a2})}} \]

Equation 3-2: The Henderson-Hasselbach equation expanded for two pKₐ terms. \( \delta_{\text{obs}} \) = observed chemical shift, \( AH_4^+ \) = protonated form of ligand, \( AH_3 \) = first ligand deprotonation, \( AH_2^- \) = second ligand deprotonation. \( \delta_{AH_4^+}, \delta_{AH_3} \) and \( \delta_{A^-} \) are the chemical shifts at low, intermediate and highest pH respectively.
$^{13}$C NMR data showing the downfield shifts of signals upon pD increase is presented in graphical form in Figure 3-11. The carboxylate peak ($C_4$)\textsuperscript{30,43} incurs an initial downfield shift between pD 2 - 3 from 170.31 to 170.87 ppm due to deprotonation of the carboxylate and another more dramatic shift from 170.87 to 180.71 ppm between pD 8 - 10 due to deprotonation of the amine. The shift of $C_3$ from 56.28 ppm at pD 2 to 56.98 at pD 3.5 coincides with the initial deprotonation of $C_4$ determining that $C_3$ neighbours the carboxylate group. The ethyl groups ($C_{1/2}$) are in the region 55 - 57 ppm at pD < 3. They are not directly affected by the deprotonation of the carboxylate hence incur only a minor shift at pD < 7.

Figure 3-11: Graphs showing the $^{13}$C chemical shift of H$_3$bic as a function of pD with Henderson-Hasselbalch model fits.
A potentiometric titration was conducted with I maintained at 0.5 (NaNO₃) at 25 °C in order to generate more accurate pKₐ values. The model incorporated pKₐ values of carboxylate and amine groups attaining a low sigma value of 9 verifying the good fit of the model values to the experimental data (Figure 3-12). That the first deprotonation of H₄bic⁺ occurs above pH 2 (carboxylate) with the second deprotonation (amine) commencing at pH > 7 as H₂bic⁻ becomes the dominant species in solution at pH > 9. Alcohol moieties remain protonated in the pH range investigated. Calculated and literature pKₐ values are shown in Table 3-2.

![Figure 3-12: Potentiometric titration of H₃bic modelled in Hyperquad (left) and speciation diagram of H₃bic (right). T = 25 °C; I = 0.5 (NaNO₃); Vₒ = 20.02 mL; [H₃bic]₀ = 5 mM; Titrant = 0.1 M NaOH.](image)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pKₐ₁</td>
<td>2.35 (+0.12/−0.04)</td>
<td>2.458 (±0.23)</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>pKₐ₂</td>
<td>8.29 (+0.031/−0.036)</td>
<td>8.357 (±0.23)</td>
<td>8.11</td>
<td>8.33 (±0.0024)</td>
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</table>

Table 3-2: Calculated and literature pKₐ values for H₃bic.

### 3.4 N-(2-Hydroxyethyl)iminodiacetic acid (H₃heidi)

H₃heidi is a symmetrical potentially tetradeinate ligand containing two carboxylic acid moieties, a hydroxyl group and a donating nitrogen atom (Figure 3-13). Similar to H₃bic, H₃heidi can bridge and chelate (forming 5 membered rings) metal ions. Carboxylates and aminocarboxylates are used widely in spent fuel processing, clean-up/decontamination processes and are important in waste processing.⁴⁶
H$_3$heidi already has extensive chemistry with the $d$-block$^{47,48}$ and with several lanthanide ions$^{49-51}$ so it is natural that it should be considered for the production of actinide complexes. Tetradeptate Ln(H$_3$heidi)$_2^+$ complexes with protonated alcohol moieties have been reported with elemental, thermal and IR analysis to confirm these structures.$^{49,50}$ Hnatejko et al. were able to undertake solution state spectroscopic studies to corroborate the 1:1 and 1:2 complexation of heidi to lanthanide metals.$^{51}$

Recently, Thakur et al. have reported formation constants of 1:1 (M:L) complexes with Am$^{3+}$, Cm$^{3+}$ and Eu$^{3+}$ using potentiometric titrations and luminescence lifetimes, which indicate the presence of 1:1 and 1:2 (M:L) complexes with tetradeptate H$_2$heidi$^-$ (Figure 3-13).$^{46}$ In 1968 Bogucki et al. investigated the interaction between Th$^{4+}$ and heidi with potentiometry able to establish the formation of a complex. Unfortunately the exact speciation was unable to be obtained but it was suggested that the hydroxymethyl group was involved in bonding.$^{52}$

<table>
<thead>
<tr>
<th></th>
<th>Log $K$, Thakur et al.$^{46}$</th>
<th>Log $K$, Martel et al.$^{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I = 0.1 (NaClO$_4$); 25 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Am$^{3+}$</td>
<td>10.30 ± 0.06</td>
<td>9.14</td>
</tr>
<tr>
<td>Cm$^{3+}$</td>
<td>9.98 ± 0.07</td>
<td>9.14</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>9.69 ± 0.05</td>
<td>9.10</td>
</tr>
</tbody>
</table>

Figure 3-13: Structure of H$_3$heidi (left). Stability constants of the 1:1 species of Am$^{3+}$, Cm$^{3+}$ and Eu$^{3+}$ with H$_2$heidi$^-$ (right).$^{44,46}$

H$_3$heidi displays the same proton assignments as H$_3$bic and is also protonated at the amine in acidic conditions forming a H$_4$heidi$^+$ species. The initial inflection in the $^1$H NMR spectrum (Figure 3-14) is due to deprotonation of the carboxylate groups. This is most likely done in quick succession rather than simultaneously with both deprotonated by pH 4. The second inflection between pH 7 - 11, together with substantial broadening of signals indicates nitrogen deprotonation.
H₃heidi is a zwitterion akin to H₃bic, with two carboxylate groups and the central nitrogen atom all capable of deprotonating at pD < 12. As such, the Henderson-Hasselbach equation requires an expansion to three pKₐ terms (Equation 3-3).

\[
\delta_{\text{obs}} = \frac{\delta_{AH_4^+} + \delta_{AH_3} \times 10^{(pH-pK_{a1})} + \delta_{AH_2^-} \times 10^{(2 \times pH-pK_{a1}-pK_{a2})} + \delta_{AH_2^-} \times 10^{(3 \times pH-pK_{a1}-pK_{a2}-pK_{a3})}}{1 + 10^{(pH-pK_{a1})} + 10^{(2 \times pH-pK_{a1}-pK_{a2})} + 10^{(3 \times pH-pK_{a1}-pK_{a2}-pK_{a3})}}
\]

Equation 3-3: The Henderson-Hasselbalch equation expanded for three pKₐ terms. AH₄⁺ = protonated form of ligand, AH₃⁻ = first ligand deprotonation, AH₂⁻ = second ligand deprotonation, AH⁻²⁻ = third ligand deprotonation. \(\delta_{AH_4^+}, \delta_{AH_3}, \delta_{AH_2^-}\) and \(\delta_{AH_2^-}\) are the chemical shifts at lowest to highest pH respectively.

Figure 3-15 shows the model fitted with experimental results. The model is not unflawed as the C₃ model is imprecise at low pD however the equation does hold up at higher pD values and for other carbon signals. The adjusted pKₐ values are shown in Table 3-3.
A potentiometric titration was conducted to determine $pK_a$ values of $H_3$heidi at $I = 0.5$ (NaNO$_3$). The resulting Hyperquad model fit and speciation diagram (Figure 3-16) show deprotonation of both carboxylates at $pH < 2$ with nitrogen deprotonation commencing at $pH 8$. The $pK_a$ values obtained for both $^{13}$C and Hyperquad determination method are similar to that obtained in literature suggesting reliable results (Table 3-3).
Figure 3-16: Potentiometric titration of $H_3$heidi modelled in Hyperquad (left) and speciation diagram of $H_3$heidi (right). $T = 25 \, ^{\circ}C$; $I = 0.5 \text{ (NaNO}_3\text{)}$; $V_0 = 20.05 \text{ mL}$; $[H_3\text{heidi}] = 5 \text{ mM}$; Titrant = 0.1 M NaOH.

<table>
<thead>
<tr>
<th></th>
<th>Calc. $^{13}$C pK$_a$, 25 $^\circ$C</th>
<th>Calc. potentiometric pK$_a$</th>
<th>Lit. pK$_a^{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK$_{a1}$</td>
<td>1.8 (+0.35/-0.16)</td>
<td>2.22 (±0.9)</td>
<td>2.20 (±0.05)</td>
</tr>
<tr>
<td>pK$_{a2}$</td>
<td>2.2 (+0.34/-0.16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pK$_{a3}$</td>
<td>8.5 (+0.55/-0.11)</td>
<td>8.53 (±0.9)</td>
<td>8.66 (±0.02)</td>
</tr>
</tbody>
</table>

Table 3-3: Calculated and literature pK$_a$ values for $H_3$heidi.

3.5 Nitrilotriacetic Acid ($H_3$NTA)

$H_3$NTA is a well-developed, potentially tetradentate ligand with both solution and solid state research previously undertaken not only with transition metals and Lns but also with actinides.$^{52,54}$ The stability of uranyl-NTA complexes within the pH range 2 – 7 has been reported using potentiometric studies by De Stefano et al. who proposed the formation of a neutral $\text{UO}_2$(HNTA) species with protonation of the amine.$^{55}$ Other studies carried out under hydrothermal conditions have led to the isolation of a $[(\text{UO}_2)\text{(HNTA)}(\text{H}_2\text{O})_2].3\text{H}_2\text{O}$ species in which HNTA$^{2-}$ is protonated at the nitrogen site and is tridentate with carboxylate moieties bridging three metal atoms (Figure 3-17).$^{56}$
Aqueous 1:1 and 1:2 (M:L) complexes of H$_3$NTA with An$^{4+}$ cations (An = Th, U, Np, Pu) have been established using spectroscopic methods with the 1:2 complexes also studied using EXAFS in concentrated nitric and hydrochloric acid. A solid state structure of (Hpy)$_2$[U(NTA)$_2$].H$_2$O was obtained through reaction in refluxing pyridine in which NTA$^{3-}$ is tetradentate and fully deprotonated. Complexations of H$_3$NTA with neptunyl and plutonyl have been investigated by various research groups with the work of Sinkov et al. indicating the formation of 1:1 complexes in a mixed methanoic-aqueous medium. Nitsche et al. provided further evidence for this, forming NpO$_2$NTA$^{2-}$, Pu$^{IV}$(NTA)$^+$ and PuO$_2$NTA$^-$ complexes in aqueous conditions at pH < 5. In these complexes, NTA$^{3-}$ is fully deprotonated however it is unclear whether it is acting as a tri or tetradeinate ligand through potentiometric and spectroscopic methods used.

With one signal, the $^1$H NMR spectrum identifies H$_3$NTA as a symmetrical molecule (Figure 3-18). The initial shift between pD 2 - 4 represents the deprotonation of the carboxylate groups and the second inflection between pD 8.5 - 11, along with peak broadening, is reminiscent of amine deprotonation. Deprotonation actually commences at pH < 2 but H$_3$NTA is only sparingly soluble at pH < 4 so minimal data can be obtained.
Due to the poor solubility of H$_3$NTA in water at highly acidic pH, $^{13}$C NMR were not conducted at pH < 2, consequently deprotonation of the three carboxylate groups cannot be separated. However, there are three deprotonating groups with pK$_a$'s above 2, the expanded Henderson-Hasselbalch in Equation 3-3 was used. This was found to generate three pK$_a$ values consistent with literature values (Table 3-4).
Figure 3-19: Graphs showing the $^{13}$C chemical shift of H$_3$NTA as a function of pD with Henderson-Hasselbalch model fit.

Potentiometric titrations cannot determine the first carboxylate deprotonation with three pK$_a$ values refined. It is assumed that deprotonation of the first carboxylate group is at pH $< 1.5$, all three carboxylates are deprotonated by pH 4 and amine by pH 8 facilitating the concept that NTA is able to bind to actinides in a tetradentate fashion at acidic pH and delay/prevent hydrolysis. At very acidic pH ($< 1.5$) it is possible for all three carboxylates to be protonated as well as the basic amine producing a H$_4$NTA$^+$ species. Calculated pK$_{a1-3}$ values are displayed in Table 3-4 and are within range of the literature values so reliable
Speciation data should be obtained from metal-ligand experiments. The Hyperquad model fit and speciation diagram for the deprotonation of H$_3$NTA is shown in Figure 3-20.

![Figure 3-20: Potentiometric titration of H$_3$NTA modelled in Hyperquad (left) and speciation diagram of H$_3$NTA (right). T = 25 °C; I = 0.5 (NaNO$_3$); V$_0$ = 20.04 mL; [H$_3$NTA]$^-$ = 5 mM; Titrant = 0.1 M NaOH.](image)

<table>
<thead>
<tr>
<th></th>
<th>Calc. $^{13}$C pK$_{a}$, 25 °C</th>
<th>Calc. potentiometric pK$_{a}$ I=0.5 (NaNO$_3$), 25 °C</th>
<th>Lit. pK$_{a}$, I=0.5, 25 °C</th>
<th>Lit. pK$_{a}$, I=0.1, 20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pK$_{a1}$</td>
<td>1.9 (±2.02)</td>
<td>1.90 (± 0.2)</td>
<td>1.7 (±0.1)</td>
<td>1.8</td>
</tr>
<tr>
<td>pK$_{a2}$</td>
<td>2.35 (±2.02)</td>
<td>2.37 (± 0.2)</td>
<td>2.30 (±0.03)</td>
<td>2.48</td>
</tr>
<tr>
<td>pK$_{a3}$</td>
<td>9.02 (±2.02)</td>
<td>9.19 (± 0.2)</td>
<td>8.96 (±0.02)</td>
<td>9.71</td>
</tr>
</tbody>
</table>

Table 3-4: Calculates and literature pK$_{a}$ values of H$_3$NTA.

3.6 N-(2-acetamido)-2-iminodiacetic Acid (H$_2$ADA)

Amides are found in the natural world as peptides and proteins among many other organic compounds and industrially as solvents and bases. As such, knowledge of their speciation with the actinides is essential.

H$_2$ADA has been widely investigated with transition metals in 1:1 and 1:2 (M:L) complexes. In general, stable chelates of 1:1 complexes were shown to form at acidic pH (< 4) whilst 1:2 (M:L) complexes were formed at more neutral pH (~7). Tridentate complexation was observed through carboxylic acid and amine moieties with a protonated amine.$^{61}$ Ternary transition metal complexes with histidine and H$_2$ADA have also been studied demonstrating complexation to metals through the two carboxylate groups and the
amine with no indication of binding through the amide moiety. The structure of Cu\textsuperscript{II} and Co\textsuperscript{II} complexes are shown in Figure 3-21 with the amine protonated.\textsuperscript{62}

Lanthanide complexes have also been examined with Orabi \textit{et al.} performing potentiometry to determine speciation of ternary complexations, such as Ln\textsuperscript{III}+H\textsubscript{3}AMP+H\textsubscript{2}ADA (AMP = adenosine 5\textsuperscript{'}-monophosphate) in which ligands were monoprotonated\textsuperscript{40} and Azab \textit{et al.} determining 1:1 speciation of lanthanides with H\textsubscript{2}ADA, also through potentiometry in which the ligand, HADA\textsuperscript{-} is protonated at the amine.\textsuperscript{63}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3-21.png}
\caption{Structure of H\textsubscript{2}ADA (left). Structure of Na\textsubscript{2}[M(HADA)(Histidine)]. (M = Cu\textsuperscript{II} or Co\textsuperscript{II}) (right).\textsuperscript{62}}
\end{figure}

The subtle upfield shift of signals in the \textsuperscript{1}H NMR spectra as pD is increased to pD 4 is due to deprotonation of carboxylates. The deprotonation of the amine moiety is observed in the second inflection between pD 5 - 9. This suggests that in highly acidic conditions (pD < 1.5) the amine is protonated and H\textsubscript{3}ADA\textsuperscript{+}. The amido group is relatively stable to deprotonation although in strongly acidic solutions they can undergo acid catalyst hydrolysis to be reduced to carboxylate groups.\textsuperscript{56} As the NMR shows two distinctive proton environments at each pH, amide reduction has not occurred in solutions studied.
The Henderson-Hasselbalch equation containing two $pK_a$ terms (Equation 3-2) was used to determine $pK_a$ values through examination of the $^{13}$C NMR as the first deprotonation occurs below pH examined where H$_2$ADA is sparingly soluble. The signals in the $^{13}$C NMR shift as deprotonation of the carboxylates and amine moieties occurs. The graphs in Figure 3-23 show these chemical shifts along with the Hyperquad model fit. Calculated $pK_a$ values are shown in Table 3-5.
Potentiometric titrations established pKₐ values which were in line with those determined by ¹³C NMR and reported in literature. One carboxylate moiety is deprotonated at pH < 1.5 so has already occurred before the potentiometric titration began, hence H₂ADA is a zwitterion at pH 2 and the first pKₐ cannot be calculated. The close relationship between the results and literature suggests that respectable metal-ligand data will be obtained using
this method. The Hyperquad model fit and the resulting speciation diagram are displayed in Figure 3-24.

![Figure 3-24: Potentiometric titration of H₂ADA modelled in Hyperquad (left) and speciation diagram of H₂ADA (right). T = 25 °C; I = 0.5 (NaNO₃); V₀ = 20.02 mL; [H₂ADA]ᵢ = 5 mM; Titrant = 0.1 M NaOH.](image)

<table>
<thead>
<tr>
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<th>Calc. pKᵦ, 25 °C</th>
<th>Calc. potentiometric pKᵦ, I = 0.5 (NaNO₃), 25 °C</th>
<th>Lit. pKᵦ, I = 0.1 (unknown), 25 °C</th>
<th>Lit. pKᵦ, I = 0.1 (unknown), 20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKᵦ₁</td>
<td>2.2 (± 0.4)</td>
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<tr>
<td>pKᵦ₂</td>
<td>6.6 (± 0.4)</td>
<td>6.59 (± 0.3)</td>
<td>6.67 (± 0.01)</td>
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Table 3-5: Calculated and literature pKᵦ values of H₂ADA.

### 3.7 2-Hydroxy-1,2,3-propanetricarboxylic acid (H₃cit)

Citric acid (henceforth known as H₃cit) plays a large role in the metabolism of various organisms,⁶⁴ it has been shown to increase the accumulation of uranyl in plants.⁶⁵,⁶⁶ As such it has become a significant reagent in remediation. An advantage of using citric acid over synthesised chemicals is it is cost effective with compounds formed being photodegradable and biodegrade in alkaline conditions but not in acidic-neutral conditions; therefore mobility can be controlled.⁶⁷

Lanthanide coordination polymers have been well reported with [La(cit)(H₂O)]ₙ prepared at pH ranging from 2.2 to 2.5. In this compound cit³⁻ is monoprotonated at the alcohol group and shows tridentate binding to La through the α-carboxylate, one β-carboxylate and the protonated alcohol, cit³⁻ bridges three La ions creating a polymeric structure.⁶⁸ This structure along with analogous lanthanide complexes are reported to form in solutions where pH is not monitored under hydrothermal conditions at temperatures above 130 °C.
for multiple days.\textsuperscript{69,70} Lanthanide ternary complexes with citric acid and EDTA have also been formed at 70 °C and pH between 5 and 7, with structures involving tridentate \textit{cit}\textsuperscript{3-} and fast exchange of the β-carboxylate moieties (Figure 3-25).\textsuperscript{71} Thorium complexation from amorphous ThO\textsubscript{2} at pH 5 has been monitored using \textsuperscript{13}C NMR spectroscopy and EXAFS (Extended X-ray Absorption Fine Structure) suggesting the existence of Th(OH)\textsubscript{3}(cit)\textsubscript{8-} and Th(OH)\textsubscript{3}(cit)\textsubscript{5-}.\textsuperscript{72}

Citric acid speciation with uranyl has been extensively studied with multiple analytical techniques employed. As early as 1965 potentiometric studies carried out between pH 2 - 8 proposed the formation of (UO\textsubscript{2})\textsubscript{2}(cit)\textsuperscript{3-} and (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}\textsuperscript{2-} both with protonated alcohol moieties and multiple structures proposed for the dimeric species (Figure 3-25).\textsuperscript{73} These findings have been corroborated by \textsuperscript{1}H, \textsuperscript{13}C NMR and IR spectroscopy\textsuperscript{74} along with luminescence.\textsuperscript{64} More recently EXAFS studies have proven the presence of (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}\textsuperscript{2-} at pH 3.8\textsuperscript{75} with Berto \textit{et al.} including potential hydrolysis products using potentiometric titrations between pH 2 - 7.\textsuperscript{67}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Structure of H\textsubscript{3}cit (top left), (NH\textsubscript{4})\textsubscript{8}[La\textsubscript{2}(cit)\textsubscript{2}(EDTA)\textsubscript{2}].9H\textsubscript{2}O (bottom left) and proposed structures of a) [(UO\textsubscript{2})\textsubscript{2}(Hcit)(OH)\textsubscript{2}]\textsuperscript{2-} b) [(UO\textsubscript{2})\textsubscript{2}(cit)(H\textsubscript{2}O)\textsubscript{2}]\textsuperscript{2-} and c) [(UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}]\textsuperscript{2-} (right).\textsuperscript{71}}
\end{figure}

Citric acid speciation with uranyl has been extensively studied with multiple analytical techniques employed. As early as 1965 potentiometric studies carried out between pH 2 - 8 proposed the formation of (UO\textsubscript{2})\textsubscript{2}(cit)\textsuperscript{3-} and (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}\textsuperscript{2-} both with protonated alcohol moieties and multiple structures proposed for the dimeric species (Figure 3-25).\textsuperscript{73} These findings have been corroborated by \textsuperscript{1}H, \textsuperscript{13}C NMR and IR spectroscopy\textsuperscript{74} along with luminescence.\textsuperscript{64} More recently EXAFS studies have proven the presence of (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}\textsuperscript{2-} at pH 3.8\textsuperscript{75} with Berto \textit{et al.} including potential hydrolysis products using potentiometric titrations between pH 2 - 7.\textsuperscript{67}

Citric acid is a prochiral molecule containing enantiotropic protons; the two protons on the methylenic group are chemically inequivalent and adjacent to a stereogenic centre.\textsuperscript{76} The protons have a small chemical shift difference in comparison to their coupling constant so
do not satisfy the first order approximation used previously to assign NMR spectra. Accordingly, second order effects have to be considered. Splitting no longer corresponds to a coupling constant and several signal intensities are common. The splitting pattern observed is termed AB splitting with Figure 3-26 demonstrating the common roofing effect whereby the intensities in the multiplet tilt upwards towards one another.\textsuperscript{76,77} The upfield shift of the signals correlates to the systematic deprotonation of the three carboxylate groups. The alcoholic proton is not deprotonated.

\textbf{Figure 3-26: Stacked }\textsuperscript{1}H NMR spectra of H\textsubscript{3}cit at pD 2 – 13.

\textsuperscript{13}C NMR spectroscopy of citric acid displays four distinct carbon environments, with chemical shifts displayed in Figure 3-27. The three carboxylate pK\textsubscript{a} values were determined using Equation 3-3 with values shown in Table 3-6.
Potentiometric titrations and resulting Hyperquad models are shown in Figure 3-28 along with the speciation diagram. The potentiometric curve displays the carboxylate moieties deprotonating successively with all deprotonated by pH 5.5. The Hyperquad model pK$_a$ values correlate with those calculated using the Henderson-Hasselbalch model and with values reported in literature (Table 3-6).
Figure 3-28: Potentiometric titration of $\text{H}_3\text{cit}$ modelled in Hyperquad (left) and speciation diagram of $\text{H}_3\text{cit}$ (right). $T = 25 \degree C$; $I = 0.5$ (NaNO$_3$); $V_0 = 20.02$ mL; $[\text{H}_3\text{cit}] = 5$ mM; Titrant = 0.1 M NaOH.

Table 3-6: Calculated and literature $pK_a$ values of $\text{H}_3\text{cit}$.

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<th>Lit. $pK_a^{13}$</th>
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<tbody>
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<td>(unknown), $25 \degree C$</td>
<td>(unknown), $25 \degree C$</td>
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<td>5.29 ($\pm$ 0.2)</td>
<td>5.83</td>
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</tbody>
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3.8 References


4 Thorium (IV)

4.1 Introduction

Aqueous thorium chemistry is dominated by the tetravalent oxidation state;\(^1\) with no electrons in the \(f\)-orbitals the electronic configuration is closed shell, resembling a noble gas [Rn]\(^{f0}\). Hydrolysis of Th\(^{4+}\) occurs in the pH range 1.5 - 3.5 but is very dependent on concentration, at higher concentrations the rate of hydrolysis increases and thus initiates at lower pH.\(^2\)\(^3\) Many hydrolysis products are possible including aquo-hydroxo, hydroxo and oxo complexes, with the formation of each dependent on pH and concentration. The hydrolysed products can then undergo polymerisation to form polymetallic species (see section 1.6).\(^1\)\(^2\) Thorium is a cheaper element and carries reduced radioactive hazards in comparison to heavier An\(^{4+}\) elements. For this reason it is often used as an analogue in actinide investigations\(^4\) and is under study for use as a possible fuel source in next generation nuclear reactors.\(^5\)

A downside to the use of Th\(^{4+}\) is that it has an electronic configuration of [Rn]\(^{f0}\). As such \(f-f\) transitions do not occur and optical spectroscopy is largely uninformative.\(^6\) However, Th\(^{4+}\) is diamagnetic so does not interfere with NMR spectroscopic measurements, allowing complexation to be observed through the shifting of ligand signals in NMR spectroscopy. Potentiometric titrations indicate the release of protons in a solution as a buffer region is observed revealing complexation and hydrolysis points from which species can be determined. IR spectroscopy displays the change of ligand environment upon complexation as bonds may be broken or formed. Therefore these techniques are often used for species identification.

4.2 Speciation of Th\(^{4+}\)

As thorium nitrate is not optically or NMR active, potentiometric titrations were used to distinguish species present in the aqueous system under investigation.

The acid dissociation constant (\(K_w\)) was determined for the system by titration of standardised NaOH solution against 0.016 M HNO\(_3\) solution under N\(_2\) as to eliminate CO\(_2\) from experiments (20 μl conc. HNO\(_3\) was added to 20 mL DI D\(_2\)O to induce acidity). I of 0.5 was maintained in both the NaOH solution and the experimental solution with NaNO\(_3\). The Hyperquad software suite was used to model the experimental data. This calculated \(K_w\)
to be 13.74 for the system, which correlates to values utilised by Boukhalfa et al. and Mateescu et al. in aqueous potentiometric models.\textsuperscript{7,8} The experimental $K_w$ titration curve is shown in Figure 4-1. The vertical portion of the profile between pH 3 and 11 signifies an acid-base reaction; which will be apparent in all titrations.

A potentiometric experiment was completed in which a solution of Th(NO$_3$)$_4$.5H$_2$O was titrated against 0.1 M NaOH (both I = 0.5 (NaNO$_3$)) from acidic to alkaline pH (Figure 4-1). Concentrated HNO$_3$ (50 μL) was added to generate an initial pH < 2. Initially, the pH remains constant upon addition of NaOH as protons are released to neutralise added HNO$_3$. Between pH 2 - 4 an acid base titration occurs with the protuberance at pH 4 due to the release of H$^+$ ions into the solution and hence a change of solution species (hydrolysis of coordinated water leaving hydroxide ions complexed to thorium releasing H$^+$ ions into solution), forming thorium hydroxide species. Data obtained at pH > 5 are no longer accurate for the aqueous speciation of Th$^{4+}$ as the precipitation of hydroxide species interferes with data, hence the trace becomes erratic.

There are various reports investigating thorium hydrolysis and the consequence thereof, with multiple hydrolysis species suggested. Ekberg et al. investigated thorium speciation in highly acidic solution (pH 1.8 - 3.1) suggesting the presence of Th(OH)$_2$$^{2+}$, Th$_4$(OH)$_8$$^{8+}$ and Th$_6$(OH)$_{18}$$^{9+}$ under conditions similar to those used here. The monomeric Th(OH)$_3$$^{3+}$ species is only apparent at thorium concentrations above 0.25 mM.\textsuperscript{9} Milic et al. also studied the pH

![Figure 4-1: Potentiometric titration of standard aqueous solution (black trace) and Th(NO$_3$)$_4$.5H$_2$O (red trace). T = 25 °C; [Th$^{4+}$]$_i$ = 5 mM, I = 0.5 (NaNO$_3$); $V_0$ = 20 mL; Titrant = 0.1 M NaOH.]
range 1.5 - 3.5 and provide contradictory species to those of Ekberg et al. using NaNO₃ instead of NaClO₄ to adjust pH.³ Their work resulted in the apparent existence of four thorium species, three of which are polymeric and result from hydrolysis with the fourth being “free” Th⁴⁺, which is dominant at pH < 3.5. The dimetallic species Th₂(OH)₄⁶⁺ is present in solution at pH > 2 displaying maximum speciation of 40 % at pH 3, the trimetallic Th₃(OH)₆⁹⁺ incurs its maximum of 25 % at pH 3.2 with the Th₆(OH)₁₅⁹⁺ species becoming the principal complex at pH > 4.5. Both reports demonstrate the dominance of Th₆(OH)₁₅⁹⁺ at pH > 4.5, however disagree in respect to thorium species at lower pH.³ Kraus and Holmberg concluded that Th(OH)₂²⁺ and Th₂(OH)₂⁶⁺ formed in their experiments linking the work by Milic and Ekberg.¹⁰ They were also able to demonstrate the unstable nature of Th(OH)³⁺ along with the additional polymeric hydrolysis products, which they could not assign with any confidence.

Bentouhami et al. investigated the pH range 3.5 - 10 and observed the presence of five major thorium hydroxide species. At pH 4, 30 % of total thorium is in the “free” Th⁴⁺ state with 60 % hydrolysed to Th(OH)₃⁺ and 10 % in the form of Th(OH)₂²⁺. Th(OH)₃⁺ reaches a maximum of 70 % speciation relative to Th⁴⁺ concentration between pH 4 - 5 with thorium predominantly converting to the bimetallic Th₂(OH)₇⁺ species between pH 5 – 8, at pH > 8 thorium reaches the fully hydrolysed state of Th(OH)₄⁻.² Interestingly the work does not mention the hexametallic Th₆(OH)₁₅⁹⁺ species otherwise reported by Ekberg and Milic.³,⁹ However, Baes et al. undertook an extensive investigation into thorium hydrolysis with species reported encompassing those from the previous studies discussed with the exception of Th₃(OH)₅⁹⁺ as reported by Milic.¹,³,⁹,¹⁰

The considerable differences in reported thorium speciation is most likely due to the formation of Th⁴⁺ colloidal species, which have been detected at pH 3 - 10 by laser-induced breakdown detection methods.¹⁰ Therefore, the slightest difference in reaction conditions can lead to drastically different thorium species being formed and deciding which set of species and hydrolysis constants are to be used is a major challenge.

Because of the extensive hydroxide formation and thus the presence of multiple Th⁴⁺ species,¹,² the PHREEQC software suite was used to suggest species likely to exist in aqueous solution. PHREEQC calculations were run at multiple pH’s using data obtained in the potentiometric titration. This should allow, through the combination of computational and experimental data, the determination of solution speciation. In order to generate the most dependable computational model reliable formation constants must be utilised. The
most up to date and recognised work on radionuclide formation constants are provided in Nuclear Energy Agency (NEA) reports. These are not available as an online database for modelling work and so various companies and countries have developed individual databases.

There are three databases in contention for use with respect to the actinides and hence in this work, the LLNL database, the SIT database and Hatches-20 database, from America, Europe and UK respectively. All of these use multiple literature resources with various techniques to obtain hydrolysis constants as detailed in section 1.7. Examining the formation constants within each database, it can be observed that predicted formation constants are identical in the SIT and Hatches-20 databases for all aqueous thorium hydroxide and nitrate species, the only exception is the presence of a Th(OH)$_3^+$ species in the SIT database. However, this does not exist above 0.3 % relative to total Th$^{4+}$ in the model so can be ignored in the Hyperquad modelling. Due to the similarities of the SIT and Hatches-20 databases only the Hatches-20 database will be discussed for Th$^{4+}$ speciation. The predicted thorium speciation from each database are displayed in Figure 4-2.
There are noticeable discrepancies between American (LLNL) and European databases (Hatches-20). The LLNL database proposes there are three major (and two minor) species present in aqueous solution (Th^{4+}, Th_{6}(OH)_{15}^{9+} and Th(OH)_{4}^{+}) with clearly defined pH ranges at which each species is prominent. Hatches-20 describes a more complicated
picture of hydrolysis with three potential species in existence at pH 1 - 3 and the proposition of an alternative dominant cluster of Th$_4$(OH)$_{12}^{4+}$ between pH 3 - 8. The tetrahydroxyl thorium complex (Th(OH)$_4$) dominates at pH > 6 in the LLNL prediction but not until pH > 9 in the Hatches-20 predictions. Work by Bentouhami et al. suggests the tetra-hydroxide complex is the major species at pH > 8 implying that the use of the Hatches-20 database may provide more reliable speciation parameters. However, neither database accounts for the existence of Th$_4$(OH)$_8^{8+}$ or Th$_3$(OH)$_5^{9+}$ in appreciable amounts as displayed by previous experimental work reported by Milic et al. and Ekberg et al.$^{3,9}$

Proposed species from PHREEQC simulations along with parameters from the appropriate database were used with the Hyperquad software suite coupled with potentiometric data to establish a correlation between simulated speciation and the experimentally obtained data.

The Hyperquad model obtained using the LLNL database contains the five thorium species which PHREEQC predicated were present in appreciable amounts (Figure 4-3). Limited species (Th$^{4+}$, Th(OH)$^{3+}$, Th$_2$(OH)$_2^{6+}$, Th(OH)$_4$ and Th$_6$(OH)$_{15}^{9+}$) were selected as Hyperquad is unable to model data with an excessive number of unknown variables. These omissions could explain the errors of the model to the experimental data. At pH > 5, data are inaccurate due to the formation of a precipitate and lack of solid state species in the model. Therefore, these points have been ignored from the model fit (denoted by red markers).

Figure 4-3: Potentiometric titration of Th$^{4+}$ modelled in Hyperquad using the LLNL database.
The Hyperquad models obtained using the Hatches-20 database included seven thorium hydrolysis species, as predicted by PHREEQC (Th$^{4+}$, Th(NO$_3$)$_3^{3+}$, Th(NO$_3$)$_2^{2+}$, Th$_2$(OH)$_3^{5+}$, Th(OH)$_2^{2+}$, Th(OH)$_4$ and Th$_4$(OH)$_{12}^{4+}$). The inclusion of Th(OH)$_3^{+}$ does not affect the model, hence it was been removed from the model, in line with results of Milic and Ekberg.\textsuperscript{10} The model contained two thorium nitrate species, which dominate speciation at pH $< 8$. However, this behaviour has not been reported under any conditions during thorium hydrolysis, as such there is little probability these species are truly formed and it is likely the identification is wrongly assigned. The model fit is shown in Figure 4-4.

![Figure 4-4: Potentiometric titration of Th$^{4+}$ modelled in Hyperquad using the Hatches-20 database.](image)

The Hyperquad model using the LLNL database displays a better fit to the experimental data observed using Hatches-20 although, Hatches-20 has formation constants closer to those reported by NEA. This could be because the model using the LLNL database includes more extensive experimental work in a low pH region (0 - 4) as is being studied here whereas the Hatches-20 database compromises of formation constants generated from experimentation at neutral pH range (6 - 9).

A final model was attempted through the amalgamation of thorium species which have been previously reported to exist in acidic conditions (Figure 4-5). Formation constants were refined based on the experimental data and are shown in Table 4-1. The model obtained shows a better fit to experimental data than those produced using the LLNL and
Hatches-20 databases and so is identified as the best model to use in subsequent thorium investigations.

Figure 4-5: Potentiometric titration of Th⁴⁺ modelled in Hyperquad using the using literature speciation data. \( T = 25 \, ^\circ \text{C}; \, I = 0.5 \, (\text{NaNO}_3); \, V_0 = 20.05 \, \text{mL}; \, [\text{Th}^{4+}]_1 = 5 \, \text{mM}; \, \text{Titrant} = 0.1 \, \text{M NaOH.}\)

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<tr>
<th>Th⁴⁺:H⁺</th>
<th>Calc. log β, Potentiometry, I=0, (NaNO₃)</th>
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<th>Lit. Bentouhami et al., log β, I=0.1 (NaClO₄)</th>
<th>Lit. Milic et al., log β, I=0.5 (NaNO₃)</th>
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Table 4-1: Calculated and literature formation constants for Th⁴⁺ hydrolysis. The ratio of Th⁴⁺:H⁺ is denoted as 1,1 and 1,-1 etc.

The formation constants calculated from experimental data and in Table 4-1 are within the range of reported literature values. As the model converged to generate a good fit, the
refined formation constants in Table 4-1 will be used for thorium hydrolysis in subsequent thorium speciation experiments. A speciation graph was produced using the resulting formation constants (Figure 4-6).

At the end of the potentiometric titration a white suspension was observed. When the white suspension was allowed to settle, the mother liquor decanted off and the solid washed a clear white gel remained. Elemental analysis was performed on the gel and the results show it contained no carbon or nitrogen atoms and only thorium, hydrogen and oxygen. The results could not be fitted to any thorium hydrolysis product in the literature and is likely to contain a mixture of species.

4.3 Speciation of Th$^{4+}$ with H$_3$thme

$^1$H NMR spectroscopy was used to determine parameters for the complexation of Th$^{4+}$ by H$_3$thme in solutions containing various concentrations of H$_3$thme. A plot of chemical shift Vs pD was produced to enable observations of chemical shifts. (Figure 4-7). The two proton signals do not shift in solutions containing thorium compared to H$_3$thme alone at any pH or stoichiometry indicating that complexation is negligible. All spectra are shown in Appendix 1.1.
Figure 4-7: Observed $^1$H chemical shifts at various pD as a function of Th$^{4+}$ to H$_3$thme ratio. T = 25 °C; I = not controlled; [Th$^{4+}$] = 5 mM; [H$_3$thme] = 5n mM (where n = ratio).

The $^{13}$C NMR spectra are shown in Appendix 1.1 with chemical shifts displayed in Figure 4-8 and results corroborate $^1$H NMR spectral data. The three carbon environments are the same with no shift upon addition of H$_3$thme therefore there is very little interaction between the ions. Complexation to Th$^{4+}$ is minimal at any ratio of H$_3$thme and precipitation was observed at pD 5. NMR spectroscopy demonstrates the inability of terminal alcohol moieties to bind to thorium under the conditions studied.
Figure 4-8: Observed $^{13}$C chemical shifts at various pD as a function of Th$^{4+}$ to H$_3$thme ratio. T = 25 °C; I = not controlled; [Th$^{4+}$] = 10 mM; [H$_3$thme]$_i$ = 10n mM (where n = ratio).

At pD 5, a white suspension was observed which when filtered, washed and dried produced a white gelatinous material. This is the same pD at which hydrolysis of Th$^{4+}$ occurs without the presence of organic ligands. The gel was examined by elemental analysis and an absence of organic material was found. This suggests thorium hydrolysis and demonstrates the inability of H$_3$thme to bind to Th$^{4+}$. IR spectroscopy of the white gel shows no C=O or C-C bands confirming the lack of binding of H$_3$thme to Th$^{4+}$ in this solid. The composition of the gel could not be fit to any individual species suggesting multiple species are present.

To ascertain whether complexation occurs if H$_3$thme is deprotonated in solution before it is added to thorium solution, a solution of H$_3$thme at pH 13.5 was added to a Th$^{4+}$ solution at pH 1 (to inhibit hydrolysis). Upon addition precipitation was immediate. The resultant gel was examined with elemental analysis and IR spectroscopy complementing analysis discussed previously, the gel was found to contain no carbon, again demonstrating a lack of complexation.

The presence of this highly charged actinide cation in solution did not allow deprotonation of the alcohol groups at a lower pH than the pK$_a$ as is the case for $d$-transition metals and
No evidence of complexation was observed and so no further analysis was undertaken.

4.4 Speciation of Th$^{4+}$ with H$_3$tea

$^1$H NMR spectroscopy was performed on solutions containing various ratios of Th$^{4+}$:H$_3$tea at multiple pD to examine the potential for complexation. The $^1$H NMR spectra (Appendix 1.2) do not show any change in chemical shift for either proton environment of H$_3$tea when in solution with Th$^{4+}$ compared to that of “free” ligand spectrum shown in Figure 3-5 suggesting complexation is minimal. A graph showing chemical shift vs. pD is shown in Figure 4-9. Experiments detailed in section 4.3 showed that terminal alcohol groups on alkyl chains do not bind to Th$^{4+}$, but the inability of the amine to complex to Th$^{4+}$ is rather surprising given previous work on N-donor molecules ability to bind to actinide ions.\textsuperscript{17-19} The $^{13}$C NMR spectra (Appendix 1.2) also display the same behaviour with no shift of ligand signals when thorium solutions are added to H$_3$tea substantiating the observation that no complexation occurs. Figure 4-9 shows the change in chemical shift of H$_3$tea in solution with Th$^{4+}$. 

lanthanide ions.\textsuperscript{11-16}
The NMR experiments yielded a white gelatinous material, which was washed and dried in air. IR spectra displayed no C-C or C-O stretches and elemental analysis identified no organic constituents present (no carbon). Therefore, confirming H₃tea does not complex Th⁴⁺ under the conditions studied, with the precipitate being made up of multiple Th⁴⁺ hydrolysis products. Due to this no further analysis was undertaken.
4.5 Speciation of Th⁴⁺ with H₃bic

¹H NMR spectroscopic analysis was conducted on samples containing various ratios of Th⁴⁺ and H₃bic at multiple pD. The labelled structure is displayed in Figure 4-10. Selected stacked spectra are shown in Figure 4-11 with all spectra being displayed in Appendix 1.3.

Figure 4-10: Structure of H₃bic with ¹H atom labels.

![Structure of H₃bic with ¹H atom labels.](image)

Figure 4-11: Stacked ¹H NMR spectra of Th⁴⁺ and H₃bic solutions at pD 3. T = 25 °C; I = not controlled; [Th⁴⁺] = 5 mM; [H₃bic] = 5n mM (where n = ratio).

![Stacked ¹H NMR spectra of Th⁴⁺ and H₃bic solutions at pD 3.](image)

At pD 3, there is a downfield shift of the H₃ signal of H₃bic when in solution with Th⁴⁺ compared to “free” H₃bic from 3.86 to 3.96 ppm (Figure 4-11). This shows binding of H₃bic to Th⁴⁺ through the carboxylate moiety. There is also a slight shift relating to the proton environments on the terminal alcohol chain, H₁ and H₂. The maximum shift observed at pD 3 is ~0.05 ppm and implies the binding of carboxylate alters the chemical nature of the ligand. If binding occurred through the amine or alcohol moieties a more substantial shift for all proton environments would be expected, such as those described in Figure 4-28 upon complexation of Th⁴⁺ with H₂ADA (see section 4.8).

The same shifts are observed in all spectra between pD 2 – 5. H₃bic is highly labile and it can be seen to be bound and unbound in roughly an equal proportion. Due to this the different environments cannot be separated; consequently an averaging of signals occurs
and the signals resonance broadens.\textsuperscript{20} This trait is characteristic when the lifetime of the bonding is shorter than the timecode of the NMR experiment (fast exchange).

There are no further changes observed in the spectra when more than three equivalents of H\textsubscript{3}bic are in solution suggesting three bicine ligands coordinate to the Th\textsuperscript{4+} centre forming a complex of 1:3 (M:L) stoichiometry.

The labelled carbon structure is shown in Figure 4-12 with selected \textsuperscript{13}C NMR spectra displayed in Figure 4-13. At pD 2, carboxylate signals at 170.9 ppm disappear with 1 - 3 equivalents of H\textsubscript{3}bic in solution. When bound to thorium, the carboxylate carbon signal is broadened to such an extent it coalesces fades into the baseline. The signals reappear once a fourth equivalent of H\textsubscript{3}bic is added implying the presence of unbound ligand and confirming a 1:3 (M:L) speciation. There is a corresponding shift for the C\textsubscript{3} signal from 56.28 to 56.74 ppm upon complexation at pD 2, with the signal shifting back to 56.3 ppm when four equivalents of H\textsubscript{3}bic are in solution suggesting the presence of unbound ligand.

![Figure 4-12: Structure of H\textsubscript{3}bic with \textsuperscript{13}C atom labels.](image)

![Figure 4-13: Stacked \textsuperscript{13}C NMR spectra of Th\textsuperscript{4+} and H\textsubscript{3}bic solutions at pD 2. T = 25 °C; I = not controlled; [Th\textsuperscript{4+}] = 10 mM; [H\textsubscript{3}bic] = 10n mM (where n = ratio).](image)
As with the $^1$H NMR spectrum, the lack of chemical shift observed for signals C$_1$ and C$_2$ at 55.8 and 56.8 ppm related to the alcohol terminated alkyl chain demonstrates no binding through the alcohol or amine moieties. This suggests a monomeric complex is formed.

A precipitate was observed at pD 6.2 with the $^1$H NMR spectrum of the supernatant displaying characteristic “free” ligand signals (Figure 4-14). As the concentration of OH$^-$ is further increased it competes with water and H$_2$bic$^-$ molecules for coordination sites around Th$^{4+}$. As “free” ligand signals are observed the hydrolysis of Th$^{4+}$ must outcompete some H$_2$bic$^-$ molecules releasing them into solution whilst creating an insoluble thorium hydrolysis product.

![Figure 4-14: Stacked $^1$H NMR spectra of Th$^{4+}$ and H$_3$bic solutions at pD 6. T = 25 °C; I = not controlled; [Th$^{4+}$]$_i$ = 5 mM; [H$_3$bic]$_i$ = 5n mM (where n = ratio).](image)

Aqueous solutions containing varying ratios of Th$^{4+}$:H$_3$bic were titrated against 0.1 M NaOH from an acidic to alkaline pH (1 - 12) with I constant at 0.5 with NaNO$_3$ (Figure 4-15) to determine speciation.
Initially binary solutions are at a lower pH than their individual counterparts implying interaction of H₃bic with Th⁴⁺. The binary solutions display an inflection at pH 4 with the pH buffered due to the release of protons from hydrolysis, analogous to the Th⁴⁺ profile. As the concentration of H₃bic approaches three times that of the Th⁴⁺ ion, fewer protons are released as the zwitterion H₃bic blocks the coordination sites around the metal ion when bound at which hydrolysis can occur. The inflection between pH 8 - 10 is due to the deprotonation of the amine group; at acidic pH the amine remains protonated in the complex. All solutions form precipitate once pH is increased to 6.0, profiles above this are jagged with pH measurements affected by the precipitate hence accurate solution speciation cannot be interpreted in this region.

Elemental analysis was conducted on the gelatinous material from potentiometric titrations with results containing carbon and nitrogen atoms suggesting complexation of U⁴⁺ by H₃bic. The samples contain various amounts of ligand an average of three H₂bic⁻ ligands per U⁴⁺ ion correlating with ⁱH NMR data (Figure 4-11). The production of a gelatinous material suggests a polymeric species, as experimental data shows monodentate complexation through the carboxylate moiety, bridging for polymeric species must be through hydroxide/oxide formed by hydrolysis. Diffusion-Ordered Spectroscopy (DOSY) was conducted on ¹H NMR samples but no cross-peak was observed for the complex also.
suggesting that hydrolysis of Th$^{4+}$ created an oligomeric species. The absolute speciation of the precipitate was unable to be calculated successfully.

### 4.6 Speciation of Th$^{4+}$ with H$_3$heidi

$^1$H NMR spectroscopy was conducted on solutions containing various ratios of Th$^{4+}$ and H$_3$heidi at multiple pD to determine complexation. The labelled structure of H$_3$bic is displayed in Figure 4-16 with selected spectra in Figure 4-17. Additional spectra can be found in Appendix 1.4.

![Figure 4-16: Structure of H$_3$heidi with $^1$H atom labels.](image)

![Figure 4-17: Stacked $^1$H NMR spectra of Th$^{4+}$ and H$_3$heidi at pH 4 (left) and pH 11 (right). T = 25 °C; I = not controlled; [Th$^{4+}$]$_i$ = 5 mM; [H$_3$bic]$_i$ = 5n mM (where n = ratio).](image)

At pD 4 three distinct proton environments are observed in the $^1$H NMR spectra of H$_3$heidi. In solution with Th$^{4+}$ a shift in the H$_1$ singlet from 3.84 to 3.5 - 3.8 ppm indicates complexation to Th$^{4+}$ through the carboxylate functional group. As a consequence of
complexation, the carboxylate arms are no longer equivalent and so the signal is split from a singlet into a multiplet. As there are no “free” H$_3$ signals in 1:1 and 1:2 (M:L) solutions it can be assumed carboxylates to Th$^{4+}$ ions is via carboxylate moieties.

The 1:1 and 1:2 (M:L) solutions display a shift and broadening of the H$_2$ triplet from 3.4 to 2.86 ppm. This is suggestive of binding through the amine moiety to Th$^{4+}$. The H$_1$ triplet does not experience a shift of the resonance implying there is no complexation through the alcohol functionalities similar to results discussed in sections 4.3, 4.4 and 4.5; the broadening of the signal is a result of the amine bonding to the Th$^{4+}$ ion in solution.

As tridentate complexation occurs through two carboxylates and the amine, it is possible to have chelation of a carboxylate with an amine creating a relatively stable 5-membered ring whilst the second carboxylate bridges to another Th$^{4+}$ ion causing H$_3$ environments to be different. This possibility is shown in Figure 4-18.

![Figure 4-18: Possible binding mode of H$_2$heidi$^-$ to Th$^{4+}$.](image)

When the concentration of H$_3$heidi is increased to three equivalents, signals relating to unbound H$_3$heidi are observed implying that two H$_2$heidi$^-$ anions bind to one Th$^{4+}$ ion. The complex can be observed at pH < 11 when a precipitate forms and NMR spectra of the remaining solution display unbound ligand signals with minor contributions of complex signals. Thorium solutions containing no H$_3$heidi formed a precipitate at pH 6.2 so the addition of this molecule increases the solubility of Th$^{4+}$, substantially impeding hydrolysis.

Potentiometric titrations were conducted on solutions containing various ratios of Th$^{4+}$ and H$_3$heidi and the plots are shown in Figure 4-19.
Figure 4-19: Potentiometric titrations of Th$^{4+}$ and H$_3$heidi solutions in varying ratios. T = 25 °C; I = 0.5 (NaNO$_3$); V$_0$ = 20 mL; [H$_3$heidi]$_i$ = 5 mM; [Th$^{4+}$]$_i$ = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.

The 1:1 (M:L) solution displays a step between pH 3 - 4 due to the release of protons into solution. As this feature required the addition of approximately half the number of moles of NaOH compared to Th$^{4+}$ to continue the pH increase, it can be assumed that complexation to H$_2$heidi$^-$ blocks coordination sites at which hydrolysis would occur in the absence of H$_3$heidi. The 1:2 and 1:3 (M:L) solutions display an even smaller buffer region at pH 5 - 6 where protons are released, suggesting the second equivalent of H$_2$heidi$^-$ complexes to Th$^{4+}$ and prevents hydrolysis to an even greater extent. As the profile is not vertical like the curve for H$_3$heidi alone it can be assumed that a degree of hydrolysis is occurring at the Th$^{4+}$ centre. In all binary solutions, amine deprotonation is observed between pH 8 - 10 suggesting that the amine is protonated when complexed at pH < 8 to Th$^{4+}$. Potentiometric titrations corroborates the conclusions of $^1$H NMR experiments implying that a 1:2 (M:L) complex is being formed in aqueous solution.

Elemental analysis of the white solid obtained at the end of the titration is in agreement with the $^1$H NMR assignment with a 1:2 (M:L) complex being observed. The absolute speciation was unable to be identified due to the capability of H$_2$heidi$^-$ to complex via multiple functional groups leading to the possibility of bridging structures.

Previous work reported the isolation of the dithorium compound, Na$_4$[Th$_2$(heidi)$_4$]18H$_2$O at pH 9.7 with tetrabutylammonium hydroxide (TBAOH) and NaOH acting as base.$^{22}$ $^1$H NMR investigations in this work complement the 2:4 (Th$^{4+}$:H$_3$heidi) ratio of the isolated complex. However, the structure demonstrates tetradentate bonding of Hheidi$^{2-}$, which has
not been observed in this work. The structure does not account for hydroxide molecules bound to Th$^{4+}$, which can be identified as the product of hydrolysis in potentiometric titrations (Figure 4-17). The difference in experimental conditions could influence the stability of the different compounds.

4.7 Speciation of Th$^{4+}$ with H$_3$NTA

$^1$H NMR spectroscopy was conducted on solutions containing various ratios of Th$^{4+}$ and H$_3$NTA at multiple pD. Stacked spectra at pD 3, 5 and 10 are displayed in Figure 4-20 with the remaining spectra located in Appendix 1.5.

![Figure 4-20: Stacked $^1$H NMR spectra of Th$^{4+}$ and NTA at pD 2 (left), pD 5 (centre), pD 10 (right). T = 25 °C; I = not controlled; [Th$^{4+}$] = 5 mM; [H$_3$NTA] = 5n mM (where n = ratio).](image)

A single signal is observed at 3.87 ppm in the spectra of H$_3$NTA at pD 2 implying a symmetrical molecule. In the presence of Th$^{4+}$ and in a ratio of 1:1 and 1:2 (M:L) the signal is shifted upfield to 3.63 ppm at pD 2 with no “free” ligand signal observed indicating complexation; a sequence which is repeated though to pD 6.3 in the 1:1 and pD 9 in the 1:2 (M:L) solutions. As this signal is not split, the ligand remains in equivalent environments after complexation with tridentate binding to Th$^{4+}$ through all carboxylate moieties. $^1$H NMR spectroscopy cannot determine whether there is also binding through
the amine group so binding could also be tetridentate. The use of $^{15}$N NMR would help to
determine denticity.

The complex signal in the 1:2 (M:L) solution lies downfield of the “free” ligand signal at
3.45 ppm compared to 3.59 ppm at pD 10. The complex signal has not shifted upfield with
increasing pD as seen with the “free” ligand signal. Therefore it can be postulated that
either the amine is deprotonated when H$_3$NTA is bound to Th$^{4+}$ or it does not deprotonate
at any pH examined. Potentiometric titrations should aid in determining whether the amine
remains protonated.

In solutions containing three or more equivalents of H$_3$NTA, the signal relating to the
“free” ligand is observed at all pD implying a 1:2 (M:L) stoichiometry. The complex is
able to inhibit the onset of hydrolysis with the precipitation of the 1:1 (M:L) species
occurring at pD 6.3 and precipitation at pD 10.5 for solutions containing two or more
equivalents of H$_3$NTA. This confirms earlier observations of a 1:2 Th$^{4+}$:H$_3$NTA
stoichiometry.

As precipitation of the 1:1 (M:L) solution occurs at pD 6.3 rather than pD 10.5 as observed
in solutions containing more than two equivalents of H$_3$NTA it can be deduced that one
NTA$^{3-}$ is not able to block enough coordination sites around the Th$^{4+}$ centre in order to
hinder hydrolysis. However, when two ligands (at least six coordination sites occupied)
bind to Th$^{4+}$, their shape encapsulates the metal leaving little space in which OH$^-$ groups
can attack and bind, thereby preventing hydrolysis and precipitation. It is possible that the
ligands do not entirely encapsulate one metal centre, but bridge multiple metals forming
oligomeric species but this cannot be proven here.

The structure of [Th(NTA)$_2$]$^{2-}$ has been previously studied by EXAFS spectroscopy
revealing that NTA$^{3-}$ can bind to Th$^{4+}$ through three carboxylate moieties and the amine
functional groups, all of which are deprotonated (Figure 4-21). Subsequent quantum
calculations also demonstrated that the NTA$^{3-}$ molecules encapsulate Th$^{4+}$ cations in a
monomeric structure rather than bridge to other cations in oligomeric arrays.$^{23}$ These
observations complement the data presented in this work.
In the 1:1 (M:L) solution, precipitation commenced at pD 5.7. An IR spectrum (Figure 4-22) of the solid resulting from potentiometric titrations was recorded and compared against the starting materials for the experiment. There are some significant differences in the spectrum of the precipitate (blue trace) compared to NaNO₃ (red trace) and H₃NTA (black trace). The differences include the asymmetric C=O stretch, which has shifted from 1708 cm⁻¹ in H₃NTA to 1565 cm⁻¹ indicating complexation. There is a N-O stretch at 1295 cm⁻¹ indicating that the complex also contains one (possibly more) NO₃⁻ ions. Lastly, there is a strong, broad O-H stretch, which could be due to hydroxide and/or water incorporation. These characteristic features are all expected to be present in the species identified through ¹H NMR.
The IR spectrum of the homogeneous precipitate acquired from the 1:2 (M:L) experiment at pH 10.5 was also recorded (Figure 4-23) obtaining a similar spectrum to that from the 1:1 precipitate. The band correlated to OH stretching modes indicates its presence in the solid as H$_2$O/OH$^\cdot$. The C=O stretch is located at 1511 cm$^{-1}$ compared to 1565 cm$^{-1}$ in the sample recorded at the end of the 1:1 (M:L) experiment. This additional shift of $\sim$ 54 cm$^{-1}$ indicates that there is a stronger bond between the Th$^{4+}$ ion and the anionic carboxylate moiety, which is likely due to the increased chelation as two NTA$^{3-}$ molecules binding to the metal produces a more stable complex.$^{25}$

![Figure 4-23: IR spectrum of the precipitate from a 1:2 Th:H$_3$NTA solution (blue), NaNO$_3$ (red) and H$_3$NTA (black).](image)

Elemental analysis conducted on the solid precipitates from the 1:1 -1:4 (M:L) experiments suggest a 1:1 and 1:2 (M:L) ratio in the solids when comparing Th:C ratios, this compliments the solution data analysis. Multiple species must be present in the powder which was shown to include other elements (e.g. N and Na) as the absolute speciation of the solid was unable to be successfully calculated.

Potentiometric titrations (Figure 4-24) were conducted, titrating solutions containing various molar ratios of Th$^{4+}$ and H$_3$NTA against 0.1 M NaOH in which all solutions had I = 0.5 (NaNO$_3$). The resulting experimental traces are displayed in Figure 4-22. Initially, the pH of binary solutions was lower than their individual counterparts, indicating complexation of H$_3$NTA to Th$^{4+}$.  

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The profile of the 1:1 (M:L) solution (blue trace) displays a protuberance between pH 4 - 5 owing to the release of protons from the hydrolysis of complexed water. The buffer region is smaller than in the Th⁴⁺ profile as fewer protons are released, consequently, less hydrolysis occurs when NTA⁻³ is complexed to Th⁴⁺.

The potentiometric titration curve of the 1:2 (M:L) solution (pink trace) has no inflection at pH < 8 signifying that hydrolysis is prevented and hydroxide species are not formed. This demonstrates the increased stability of Th⁴⁺ when a second NTA⁻³ is coordinated. In both the 1:1 and 1:2 (M:L) solution profiles, the curvature between pH 8 - 12 is due to the release of protons indicating the onset of hydrolysis and deprotonation of the amine. This corresponds with the ¹H NMR experiments in which precipitation was observed at pD 10.5 (as hydroxide inclusion destabilises the solution species).

Hyperquad models were fitted to experimental potentiometric data and included pKₐ values for H₃NTA (Table 3-4) and the Th⁴⁺ formation constants (Table 4-1) calculated previously. The models are displayed in Figure 4-25 and Figure 4-26 for the 1:1 and 1:2 (M:L) titration respectively. Formation constant values for 1:1 and 1:2 (M:L) speciation were refined for both data sets and are displayed in Table 4-2. Calculations containing other species were
attempted (e.g. $\text{Th}_2(\text{NTA})_2^{2+}$, $\text{Th}_2(\text{NTA})_4^{4-}$, $\text{Th}(\text{NTA})(\text{OH})_2$) with refinements failing to converging or producing a poor fit.

Figure 4-25: Potentiometric titration of a 1:1 $\text{Th}^{4+}$:$\text{H}_3\text{NTA}$ solution modelled in Hyperquad. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); $V_0 = 20.05$ mL; $[\text{Th}^{4+}] = 5$ mM; $[\text{H}_3\text{NTA}] = 5$ mM; Titrant = 0.1 M NaOH.

Figure 4-26: Potentiometric titration of a 1:2 $\text{Th}^{4+}$:$\text{H}_3\text{NTA}$ solution modelled in Hyperquad. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); $V_0 = 20.05$ mL; $[\text{Th}^{4+}] = 2.5$ mM; $[\text{H}_3\text{NTA}] = 5$ mM; Titrant = 0.1 M NaOH.
<table>
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<tr>
<th>Th$^{4+}$:H$_3$NTA:H$^+$</th>
<th>Calc. log β, 1:1 soln, I=0.5 (NaNO$_3$), 25 °C</th>
<th>Calc. log β, 1:2 soln, I=0.5 (NaNO$_3$), 25 °C</th>
<th>Lit.$^{25}$ log K, I=0.05 (NH$_4$OAc), 25 °C</th>
<th>Lit.$^{24}$ log K, I=0 (unknown), 25 °C</th>
<th>Lit.$^{24}$ log K, I=0.1 (KNO$_3$), 25 °C</th>
<th>Lit.$^{24}$ log K, I=0.1 (KNO$_3$), 25 °C</th>
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<td>15.88 ± 0.3</td>
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<td>14.6 ± 0.3</td>
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<td>15.20 ± 0.3</td>
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<td>-8.6</td>
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Table 4-2: Calculated and literature formation constants of Th$^{4+}$-H$_3$NTA species. The ratio of Th$^{4+}$:H$_3$NTA:H$^+$ is denoted as 1,1,0 and 1,1,-1 etc. $a$ = MINTEQ database and $b$ = HYDRA database.

The literature range of 12.4 - 16.9 for the log K of Th(NTA)$^+$ is quite wide and shows the difference that changes in conditions can make. The value determined in this work is 15.88 so it within the literature range and similar to values reported in similar conditions. Literature reports have focused on the Th(NTA)$^+$ and Th(NTA)(OH) species with only a few reporting formation constants for 1:2 (M:L) species. The resulting speciation diagrams for the 1:1 and 1:2 (M:L) solutions are displayed in Figure 4-27 and Figure 4-28 respectively.

![Figure 4-27: Speciation diagram for Th$^{4+}$-H$_3$NTA species in a 1:1 Th$^{4+}$:H$_3$NTA ratio in aqueous solution. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); [H$_3$NTA] = 5 mM; [Th$^{4+}$] = 5 mM; The ratio of Th$^{4+}$:H$_3$NTA:H$^+$ is denoted as 1,1,0 and 1,1,-1 etc.](image-url)
Figure 4-28: Speciation diagram for $\text{Th}^{4+}$-$H_3\text{NTA}$ species in a 1:2 $\text{Th}^{4+}$:$H_3\text{NTA}$ ratio in aqueous solution. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); $[H_3\text{NTA}]_i = 5$ mM; $[\text{Th}^{4+}]_i = 5$ mM; The ratio of $\text{Th}^{4+}$:$H_3\text{NTA}$:$H^+$ is denoted as 1,1,0 and 1,1,-1 etc.

In both solutions $\text{Th(NTA)}^+$ is the dominant species at pH < 3 and $\text{Th}_2(\text{OH})_7^+$ is dominant at pH > 9 and 10 for 1:1 and 1:2 (M:L) solutions respectively. Differences are observed between pH 3 - 9 with $\text{Th(NTA)}(\text{OH})$ being the major species in the 1:1 (M:L) solution with a contribution of $\text{Th(NTA)}_2^{2-}$ at pH 8.2 with a maximum of 18 %. Species are reversed in the 1:2 (M:L) solution with $\text{Th(NTA)}_2^{2-}$ being the major species with $\text{Th(NTA)}(\text{OH})$ being present at a maximum of 3.5 % between pH 2 - 10. The monohydroxy $\text{Th(NTA)}_2(\text{OH})^{3-}$ species present between pH 8 - 11 reaches a maximum of 24 % relative to $\text{Th}^{4+}$.

The potentiometric data were input into the PHREEQC software suite to illustrate the differences between current models and those produced in this work. The subsequent speciation models demonstrated no complexation between $\text{Th}^{4+}$ and $H_3\text{NTA}$ with the predicted models identical to the $\text{Th}^{4+}$ models displayed in Figure 4-2. As complexation has been demonstrated in this work and in the literature using multiple analytical techniques, it is clear that current databases are lacking with speciation models not capable of calculating the experimentally observed speciation.
4.8 Speciation of Th$^{4+}$ with H$_2$ADA

$^1$H NMR spectroscopy was conducted on solutions of Th$^{4+}$ and H$_2$ADA in various ratios and at multiple pD. The labelled structure of H$_2$ADA is displayed in Figure 4-29 with selected spectra in Figure 4-30. Additional spectra are located in Appendix 1.6.

![Structure of H$_2$ADA with $^1$H atom labels.](image)

Solutions of H$_2$ADA at pD 2 display two signals related to the two proton environments. When H$_2$ADA is in a 1:1 ratio with Th$^{4+}$ the signals shift upfield with the H$_2$ signal shifting from 3.99 to 3.63 ppm and the H$_1$ signal from 4.15 to 3.86 ppm. This implies tridentate coordination of H$_2$ADA to Th$^{4+}$ through the amine and carboxylate moieties. The splitting of the H$_2$ when complexed to Th$^{4+}$ implies that the ligand is no longer symmetrical. Previous reports of H$_2$ADA complexation with TM and lanthanide ions (including Co$^{II}$, Ni$^{II}$, Zn$^{II}$, Eu$^{II}$, Dy$^{II}$ and Pr$^{II}$) also show tridentate binding of HADA$^-$ through the carboxylate and amine moieties.$^{31-34}$
At pD 3 both the H₁ and H₂ signals incur shifts from the “free” ligand with the H₂ signal between 3.62 and 3.65 ppm splitting into a doublet. This suggests the ligand is no longer symmetrical and the complex is either a diastereomer or an oligomeric species. Coordination of HADA⁻ to Th⁴⁺ is tridentate through one amine and two carboxylate moieties. The lack of broadening at this pD suggests that there is little exchange and the complex is relatively stable as seen with previous complexes (e.g. Th⁴⁺-bicine, section 4.5). These observations hold until pD > 7.

When more than two equivalents of H₂ADA are in solution with Th⁴⁺ at pD < 8, “free” ligand signals are observed implying that two HADA⁻ ligands complex to Th⁴⁺ with the third existing as “free” ligand, as confirmed by integration of the signals. With excess H₂ADA in solution, all signals broaden suggesting that there is a mixture of bound and unbound functional groups within the ligands.

In solutions containing 1 - 4 equivalents of H₂ADA there are proton signals which can be assigned to the “free” ligand and an additional peak at 3.71 ppm at pD 8. Integration of the signals shows that there are an equal number of protons for all three signals, indicating that the peak at 3.71 ppm is due to one bound carboxylate moiety. The bound carboxylate signal incurs an upfield shift of ~0.8 ppm compared to spectra at lower pD. This shift could be due to the inclusion of a hydroxide in the complex.

Precipitation is observed at pD 8.8 in the 1:1 (M:L) solution and at pD 9.5 in 1:2 - 1:4 (M:L) solutions implying that two HADA⁻ ligands bind to and stabilise Th⁴⁺ ions in solution and thus hindering the hydrolysis of Th⁴⁺.

Potentiometric titration studies on solutions containing various ratios of Th⁴⁺ and H₂ADA are displayed in Figure 4-31. In all binary solutions, there is no release of protons into the solution until pH 6 suggesting that hydrolysis of Th⁴⁺ is prevented when complexed to HADA⁻ (cf. pD 5.2 without H₂ADA). The 1:1 (M:L) solution has an inflection at a lower pH than solutions containing larger equivalents of ligand to metal suggesting hydrolysis of the 1:1 species at a lower pH. Solutions containing two or more equivalents of H₂ADA to Th⁴⁺ have an inflection commencing at pH 7, this is higher than when H₂ADA is alone implying that deprotonation of the amine moiety does not occur with the release of protons being due to hydrolysis of Th⁴⁺ bound H₂O.
Figure 4-31: Potentiometric titrations of Th$^{4+}$ with varying ratios of H$_2$ADA. T = 25 °C; I = 0.5 (NaNO$_3$); $V_0 = 20$ mL; [$H_2$ADA]$_i$ = 5 mM; [Th$^{4+}$]$_i$ = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.

Potentiometric data obtained from solution titrations of Th$^{4+}$ and H$_2$ADA were modelled in Hyperquad. The model included the thorium hydrolysis species (Table 4-1) and H$_2$ADA pK$_a$ values (Table 3-5) previously calculated. The Hyperquad models are displayed in Figure 4-32 and Figure 4-33 for the 1:1 and 1:2 (M:L) titrations respectively. Log β values (Table 4-3) were calculated using trial and error with multiple oligomeric and hydroxide species being included (e.g. Th$_2$(ADA)$_2$$^{4+}$, Th$_2$(ADA)(OH)$_2$$^{4+}$ and Th(ADA)(OH)$_3^-$), however, their inclusion produced a worse fit and in some cases the model did not converge.
Figure 4-32: Potentiometric titration of 1:1 Th⁴⁺:H₂ADA solution modelled in Hyperquad. \( T = 25 \, ^\circ\text{C} \); \( I = 0.5 \, (\text{NaNO}_3) \); \( V_0 = 20.05 \, \text{mL} \); \([\text{Th}^{4+}]_i = 5 \, \text{mM} \); \([\text{H}_2\text{ADA}]_i = 5 \, \text{mM} \); Titrant = 0.1 M NaOH.

Figure 4-33: Potentiometric titration of 1:2 Th⁴⁺:H₂ADA solution modelled in Hyperquad. \( T = 25 \, ^\circ\text{C} \); \( I = 0.5 \, (\text{NaNO}_3) \); \( V_0 = 20.05 \, \text{mL} \); \([\text{Th}^{4+}]_i = 2.5 \, \text{mM} \); \([\text{H}_2\text{ADA}]_i = 5 \, \text{mM} \); Titrant = 0.1 M NaOH.
<table>
<thead>
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<th>Th$^{4+}$:H$_3$NTA:H$^+$</th>
<th>Calc. log β 1:1 sol$^a$, I=0.5 (NaNO$_3$), 25 °C</th>
<th>Log β 1:2 sol$^a$, I=0.5 (NaNO$_3$), 25 °C</th>
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Table 4-3: Calculated and literature formation constants of Th$^{4+}$:H$_2$ADA species. The ratio of Th$^{4+}$:H$_2$ADA:H$^+$ is denoted as 1,1,0 and 1,2,-1 etc.

The fitting converged with each system and returned reasonable values of Th(HADA)$_{3+}$, Th(ADA)$_{2+}$ and other species present in solution. The errors as determined as part of the fitting procedure are all similar and show the variability of the determined values. For the 1:1 (M:L) solution the inclusion of 1:2 (M:L) species led to a model that was unable to converge. Log β values produced are within the same magnitude as those reported for other actinide systems e.g. UO$_2$-cit species (Table 6-3), suggesting the results are reliable. Speciation diagrams derived for the 1:1 and 1:2 (M:L) solutions are shown in Figure 4-34 and Figure 4-35.
Figure 4-34: Speciation diagram for Th$^{4+}$-H$_2$ADA species in a 1:1 Th$^{4+}$:H$_2$ADA aqueous solution. The ratio of Th$^{4+}$:H$_2$NTA:H$^+$ is denoted as 1,1,0 and 1,1,-1 etc. T = 25 °C; I = 0.5 (NaNO$_3$); [H$_2$ADA]$_i$ = 5 mM; [Th$^{4+}$]$_i$ = 5 mM.

Figure 4-35: Speciation diagram for Th$^{4+}$-H$_2$ADA species in a 1:2 Th$^{4+}$:H$_2$ADA aqueous solution. The ratio of Th$^{4+}$:H$_2$NTA:H$^+$ is denoted as 1,1,0 and 1,1,-1 etc. T = 25 °C; I = 0.5 (NaNO$_3$); [H$_2$ADA]$_i$ = 5 mM; [Th$^{4+}$]$_i$ = 2.5 mM.

The major species between pH 4 - 10 is Th(ADA)(OH)$^+$ with the neutral dihydroxide Th(ADA)(OH)$_2$ species dominant at pH > 10. Complexation of TM and lanthanide ions by HADA$^-$ have been reported whereby HADA$^-$ is deprotonated at both carboxylate moieties but protonated at the amine and amido moieties.$^{33,34}$ Therefore suggesting the plausibility of this occurring with thorium.
The speciation diagram of the 1:2 (M:L) solution shows that Th(ADA)_2 is the dominant species at pH < 7 corroborating the interpretation of the ^1H NMR spectral data (Figure 4-30). A 1:2 (M:L) speciation with tridentate ADA^{2-} are predicted in high concentrations increasing the solubility of Th^{4+} by blocking six coordination sites of Th^{4+} compared to three in the 1:1 (M:L) species hindering hydrolysis to a greater extent. The increased solubility and hence stability is substantiated by the 1:1 (M:L) solution producing precipitate at pH 9 and the 1:2 solution at pH 10.6.

Precipitates produced in potentiometric titrations were filtered and washed for solid state analysis. The IR spectrum of the 1:1 (M:L) precipitate is shown in Figure 4-36 along with spectra of starting materials. The spectrum shows a shift of the C=O stretch (carboxylate) from 1669 cm\(^{-1}\) in H\(_2\)ADA to 1548 cm\(^{-1}\) and the C-N stretch from 1357 to 1392 cm\(^{-1}\) indicating complexation of Th^{4+} by H\(_2\)ADA. The absence of N-O stretch imply there are no NO\(_3^-\) groups in the complex.

Figure 4-36: IR spectrum of the precipitate from a 1:1 Th^{4+}:H\(_2\)ADA solution (blue), NaNO\(_3\) (black) and H\(_2\)ADA (red).

The IR spectrum of the 1:2 (M:L) precipitate is shown in Figure 4-37 with C=O bands at 1675 and 1548 cm\(^{-1}\) suggesting that there are bound and unbound carboxylate groups in the precipitate correlating with the ^1H NMR spectral data at pH 8 (Figure 4-30). This is
confirmed by the C-N stretch observed at both bound (1357 cm\(^{-1}\)) and unbound (1392 cm\(^{-1}\)) positions.

Elemental analysis of the precipitate calculated ratios of between 1:0.7 - 1:2.1 (M:L) from the Th:C results correlating to solution state data. Other elements were found to be present in the precipitates (e.g. Na and N) suggesting their incorporation in the solid but the absolute speciation of the precipitates were unable to be calculated.

### 4.9 Speciation of Th\(^{4+}\) with H\(_3\)cit

\(^1\)H NMR spectroscopy was conducted on solutions containing Th\(^{4+}\) and H\(_3\)cit in various concentrations and at multiple pD. Spectra at pD 3 and 7 are shown in Figure 4-38 with other spectra located in Appendix 1.7.
AB splitting is observed in $^1$H spectra of H$_3$cit in aqueous solutions at each pH. When solutions of Th$^{4+}$ and H$_3$cit are combined at pD < 2 a white suspension is observed, as individual components are soluble complexation is implied. At pD 3 the spectrum of the 1:1 (M:L) supernatant displays no signals suggesting complexation of H$_3$cit to Th$^{4+}$ withdraws H$_3$cit from solution so proton signals are not observed. The 1:2 (M:L) spectrum shows signals at 2.5 - 3 ppm broadened in comparison to H$_3$cit suggesting a combination of bound and unbound signals. At pD 7 the spectrum of the 1:1 (M:L) solution displays weak but broadened signals suggesting complexation. The 1:2 – 1:4 (M:L) spectra display signals in the “free” ligand region, AB splitting is not observed however signals are broadened in comparison to the H$_3$cit spectrum again suggesting both bound and unbound signals.

The complex becomes soluble at pD 8 in the 1:1 (M:L) solution and pD 6 in the 1:2 (M:L) solutions possibly due to the hydrolysis of Th$^{4+}$ when complexed to cit$^3^-$ increasing solubility. Precipitate is once again observed at pH 11.8 along with sharp “free” ligand signals in all solutions.

Potentiometric titrations of solutions containing various ratios of Th$^{4+}$ and H$_3$cit are shown in Figure 4-39. All binary solutions had initial pH lower than solutions of their individual counterparts suggesting the release of protons upon complexation. At pH < 6 a white suspension is visible, consequently potentiometric titrations cannot be used to calculate
formation constants, they can only be used qualitatively to determine what is happening in solution.

The 1:1 (M:L) solution (blue trace) shows an inflection between pH 3 - 6 due to the release of protons upon hydrolysis. This is a higher pH than that observed for Th⁴⁺ as the complexation of cit³⁻ hinders the onset of hydrolysis by blocking sites of Th⁴⁺. The 1:2 (M:L) solution (pink trace) does not have such an intense step between pH 3 - 5 where protons are released suggesting a second equivalent of cit³⁻ interacts with Th⁴⁺ further hindering hydrolysis. The profile of the 1:3 (M:L) solution resembles that of H₃cit implying the presence of free ligand in solution.

Literature reports of complexation using macroscopic thermodynamic data (e.g. solvent extraction and EMF techniques) suggest that at pH < 6 Th⁴⁺ complexes are monomeric identifying Th(cit)⁺, Th(cit)₂⁻ and Th(cit)₃⁻⁻ complexes; the latter two were identified in solutions where the concentration of H₃cit was 10 times higher than Th⁴⁺. Bonnin et al. used spectroscopic competition techniques with Th⁴⁺ competing with Np⁴⁺ suggesting 1:1 (M:L) speciation with a small concentration of 1:2 (M:L) complexation. This correlates with ¹H NMR spectral data provided in this work (Figure 4-38) in which a second equivalent of H₃cit in solution broadens spectra at pD < 7. Other literature sources have
identified the formation of a Th$_3$(cit)$_4$ complex which would explain broadened ligand signals in spectra of 1:2 (M:L) solutions. As it is a neutral species it would most likely be insoluble explaining the precipitate observed in $^1$H NMR experiments.$^{37,38}$

The potentiometric data was input into the PHREEQC interactive software and using the Hatches-20 database the dominance of the Th(cit)$_2^{2-}$ species was established in both the 1:1 and 1:2 (M:L) solutions with hydrolysis of the 1:1 species also producing Th$_4$(OH)$_{12}^{4+}$ in an approximately equal proportion (Figure 4-40 and Figure 4-41). This concurs with solution analysis in this work. However, the PHREEQC speciation does not contain any hydrolysis species relating to the thorium citrate complex which have been shown to form in potentiometric titrations. The species predicted in PHREEQC did not converge a Hyperquad fit and neither did the addition of other species such as Th(cit)(OH) or Th$_3$(cit)$_4$ hence formation constants were unable to be calculated. Neither the LLNL or the SIT databases show complexation between Th$_4^{4+}$ and H$_3$cit identifying gaps in the databases.

Figure 4-40: Speciation diagram for Th$_4^{4+}$-H$_3$cit species in a 1:1 Th$_4^{4+}$:H$_3$cit aqueous solution generated in PHREEQC using the Hatches-20 database. The ratio of Th$_4^{4+}$:H$_3$cit:NO$_3^{-}$:H$^+$ is denoted as 1,1,0,1 and 1,2,0,-1 etc. T = 25 °C; I = 0.5 (NaNO$_3$); [H$_3$cit]$_i$ = 5 mM; [Th$_4^{4+}$]$_i$ = 5 mM.
Figure 4-41: Speciation diagram for Th\textsuperscript{4+}:H\textsubscript{3}cit species in a 1:1 Th\textsuperscript{4+}:H\textsubscript{3}cit aqueous solution generated in PHREEQC using the Hatches-20 database. The ratio of Th\textsuperscript{4+}:H\textsubscript{3}cit:NO\textsubscript{3}⁻:H\textsuperscript{+} is denoted as 1,1,0,1 and 1,2,0,-1 etc. T = 25 °C; I = 0.5 (NaNO\textsubscript{3}); [H\textsubscript{3}cit]\textsubscript{i} = 5 mM; [Th\textsuperscript{4+}]\textsubscript{i} = 2.5 mM.

Precipitates formed in potentiometric titrations were filtered and washed. Elemental analysis of the precipitates show varied M:L ratios between 1:0.79 - 1:4.83 suggesting multiple complexes are present. The absolute speciation could not be calculated.

### 4.10 Summary

Formation constants of thorium hydrolysis species have been obtained using a combination of experimental (potentiometric) and computational (Hyperquad) techniques. Results are within range of values calculated in literature (Table 4-1) but species derived are different to those predicted using PHREEQC software indicating that formation constant databases require continual updates as improved data is available.

Experiments with H\textsubscript{3}thme and H\textsubscript{3}tea determined no complexation to Th\textsuperscript{4+} under the conditions investigated demonstrating that alcohol groups on straight chain alkyls do not contribute to bonding to Th\textsuperscript{4+} in aqueous solutions.

Analysis on aqueous solutions containing H\textsubscript{3}bic and Th\textsuperscript{4+} characterised a 1:3 (Th\textsuperscript{4+}:H\textsubscript{3}bic) complex in which binding was through the carboxylate moiety. No binding of the amine or
alcohol moieties was evident suggesting a monomeric species. However, DOSY spectra display no cross-peaks suggesting polymerisation of the species. As H₃bic is not capable of bridging of two metal ions, polymerisation must be a result of hydrolysis with oxy/hydroxyl bridges creating a more stable molecule. Elemental analysis also suggests polymerisation with gels produced containing multiple ratios of Th⁴⁺:H₃bic.

¹H NMR spectroscopy and potentiometry suggest the formation of a 1:2 (Th⁴⁺:H₃heidi) complex in aqueous solutions in the pH range 2 - 10. The H₃heidi⁺ zwitterion is a tridentate ligand binding to Th⁴⁺ through two carboxylate and an amine moiety. This enables the formation of a stable 5-membered chelate rings and allows bridging of multiple metal ions. Potentiometric curves show that complexation of two H₃heidi molecules does not prevent hydrolysis but does reduce the extent at which hydrolysis occurs as few coordination sites around the Th⁴⁺ ion are available. Elemental analysis demonstrated the complexities of hydrolysis with multiple species proposed.

Complexation of H₃NTA to Th⁴⁺ was confirmed by various analysis techniques with precipitates with 1:1 and 1:2 complexes identified. Spectroscopic data has shown that NTA³⁻ is a tetradentate ligand with the protonation of amine dependent upon pH. Formation constants have been calculated (Table 4-2) and are consistent with those identified in literature. Experiments have also shown that complex formation is independent of kinetic and thermodynamic parameters with a probable monomeric species formed in each solution.

Two HADA⁻ molecules have been identified to complex to Th⁴⁺ in a tridentate manner in acidic solutions. Complexation is through carboxylate and amine moieties at pD < 7 with monodentate complexation through one carboxylate observed in ¹H NMR spectra at pD 8. Tridentate complexation of the ligand forms an unsymmetrical molecule with carboxylate moieties in different environments. This could be due to hydrolysis or how the ligand is coordinated around Th⁴⁺ with respect to other coordinated ligands. Formation constants were calculated with resulting speciation diagrams relating well with other solution experiments. Values obtained are the same magnitude of formation constants for similar actinide complexes implying they are reliable.

Analysis of Th⁴⁺ with H₃cit shows that an insoluble precipitate is formed at acidic pH upon formation of a 1:1 (M:L) complex. Analysis of the precipitate showed the Th:C ratio was different in each sample implying multiple species were present in the precipitate.
Potentiometric titrations show that hydrolysis of the Th$^{4+}$ complex begins at $\sim$ pH 5, simultaneous to the onset of “free” ligand signals in the NMR suggesting hydrolysis forms a polymeric structure and is able to displace ligand molecules to create a more stable complex.

4.11 References

5 Uranium (IV)

5.1 Introduction

Tetravalent uranium undergoes extensive hydrolysis chemistry analogous to tetravalent thorium (see section 4.1), with hydrolysis commencing at pH < 1.\(^1\)\(^2\) Not only is there the possibility of monometallic U(IV) hydroxides, polymetallic species can also form with oxy/hydoxy bridges between metal ions.\(^1\) As the solubility of U(IV) hydroxides is low and U(IV) is easily oxidised, experimental investigations are complicated.\(^2\)

Tetravalent uranium has an ionic radius comparable to tetravalent plutonium and neptunium (U\(^{4+}\) = 89 pm, Pu\(^{4+}\) = 86 pm, Np\(^{4+}\) = 87 pm) with all metals primarily adopting an octahedral geometry.\(^3\) Therefore, it is considered a good aid in determining adequate conditions and possible reactions which can occur for more toxic actinides like plutonium and neptunium.\(^4\) The NMR spectrum of U\(^{4+}\) has two unpaired 5\(^f\)-electrons therefore exhibits isotropic shifts may also be broadened due to the paramagnetic ion.\(^5\)^\(^6\) The optical spectra of U\(^{4+}\) display characteristic absorptions as a result from coupling of electronic transitions of the 5\(^f^2\) electrons so is a valuable tool for analysis.

5.2 Speciation of U\(^{4+}\)

The UV-Vis absorption spectra of uranium (IV) in acidic conditions (pH 1 - 3) are shown in Figure 5-1. Precipitation was observed at pH 3.3 so analysis was stopped.
The UV-Vis spectra of aqueous U$^{4+}$ shows an increase of absorption with increasing pH. Even at pH 1 the UV absorption bands of U$^{4+}$ are very broad due to hydrolysis. The bands used to determine complexation in this study have a maxima at 646 (+) and 466 (*) nm respectively at pH 1 and 653 (+) and 470 (*) nm at pH 3.6,7 There have been various reports investigating the assignments of the absorption bands to energy levels. Kirishima et al. used luminescence to assign individual electronic transitions in the UV-Vis region8 and E. Hashem et al. combined luminescence with computational modelling to determine mean ground and excited state energy levels and assignments of U$^{4+}$ in water and UCl$_4$ in THF.9 These show the absorption maxima at 466 and 646 nm are due to the $^3F_2$ and $^3H_5$ energy levels respectively. The absence of a band at 414 nm indicates that oxidation to uranyl in the solution state has not occurred during hydrolysis. A precipitate was observed at pH 3.1 with no U$^{4+}$ trace observed in solution, hence spectroscopic titrations were terminated.

The potentiometric titration of an aqueous solution of U$^{4+}$ at 5 mM and I = 0.5 is shown in Figure 5-2. The inflection between pH 2 - 6 is due to the release of protons as hydrolysis of U$^{4+}$ occurs and coincides with precipitation.
Figure 5-2: Potentiometric titration of standard aqueous solution (black trace) and $\text{U}^{4+}$ (red trace). 
$T = 25 \, ^{\circ}\text{C}; I = 0.5 \, (\text{NaNO}_3); \, V_0 = 20.05 \, \text{mL}; \, \text{Titrant} = 0.1 \, \text{M NaOH}; \, \lbrack \text{U}^{4+} \rbrack_i = 5 \, \text{mM}.$

The PHREEQC interactive software suite was used to predict the speciation of $\text{U}^{4+}$ at multiple pH using data obtained in the potentiometric titration. The predicted speciation diagrams are shown in Figure 5-3. Interestingly, all three databases (Hatches-20, SIT and LLNL) predict different major species.
Figure 5-3: Speciation diagrams of U⁴⁺ hydrolysis generated in PHREEQC from potentiometric titrations. Hatches-20 (top), SIT (middle) and LLNL databases (bottom). The ratio of U⁴⁺:NO₃⁻:H⁺ is denoted as 1,1,1 and 1,0,-2 etc.
Hatches-20 predicts that U(OH)\(^{3+}\) is dominant at pH < 2.7 proceeding the increase in the polymetallic U\(_6\)(OH)\(_{15}\)\(^{9+}\) species which exceeds 90 % at pH 3. The SIT database predicts that U(OH)\(_2\)\(^{2+}\) is at the highest concentration throughout and LLNL predicts the major species is U(OH)\(_4\) at pH > 2. The volume of published work relating to U\(^{4+}\) hydrolysis is smaller in comparison to Th\(^{4+}\) and UO\(_2\)\(^{2+}\) leading to the possibility of greater errors and poor reliability.\(^2,4\)

Numerous authors have investigated the formation of U(OH)\(^{3+}\) and U(OH)\(_4\) species with formation constants calculated by spectroscopy and potentiometric titrations.\(^1,2,10\) Formation constants for secondary and ternary hydrolysis species (U(OH)\(_2\)\(^{2+}\) and U(OH)\(^{3+}\)) have been determined by spectroscopy, but attempts to calculate them from solubility data include uncertainties originating from their solubility and probable colloid formation. As such they are often omitted from formation constant calculations or produce values which are not considered reliable.\(^2,4\) Polymetallic species such as U\(_2\)(OH)\(_2\)\(^{6+}\), U\(_4\)(OH)\(_8\)\(^{8+}\) and U\(_6\)(OH)\(_{15}\)\(^{9+}\) are considered probable in various reports although none are convincingly identified.\(^1\) The uncertainty suggests that polymeric aggregates of over 100 An\(^{4+}\) could be present (i.e. colloids) which may lead to misinterpretation of the data.\(^1,4\)

Proposed species from PHREEQC simulations along with parameters from the appropriate database (SIT, Hatches-20 or LLNL) were used with the Hyperquad software suite and potentiometric data with models displayed in Figure 5-4. There are multiple errors with each fit with none of the models fitting the experimental data highlighting differences between the databases. The models potentially omit species or require more complex species to be included in order to satisfy experimental results.
Figure 5-4: Potentiometric titration of $\text{U}^{4+}$ modelled in Hyperquad. Hatches-20 database (top), SIT database (centre) and LLNL database (bottom).
Taking these points into consideration, a new Hyperquad model was attempted including the polymeric $\text{U}_6(\text{OH})_{15}^{9+}$ species reported in literature and log $\beta$ values were refined to fit experimental data (Figure 5-5). The model shows a good fit to experimental data however with the strong tendency of $\text{U}^{4+}$ to hydrolysis it is likely that other polymeric and colloidal species are present in solution and have not been accounted for in this model. The calculated formation constants are shown in Table 5-1.

![Figure 5-5: Potentiometric titration of $\text{U}^{4+}$ modelled in Hyperquad using the using literature speciation data. $T = 25 \, ^\circ\text{C}; I = 0.5$ (NaNO$_3$); $V_0 = 20.02$ mL; $[\text{U}^{4+}]_i = 5$ mM; Titrant = 0.1 M NaOH.](image)

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<th>Lit. Baes et al.$^{13}$ I=0, (unknown)</th>
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Table 5-1: Calculated and literature formation constants for $\text{U}^{4+}$ hydrolysis. The ratio of $\text{U}^{4+} : \text{H}^+$ is denoted as 1,-1 etc.
Precipitates produced in the potentiometric and UV-Vis titrations were filtered and washed for solid state analysis. PHREEQC predicted that uranite (U\text{IV}O_2) is supersaturated by pH 2 but this did not fit elemental analysis results. Each solid provided different experimental analysis results, even when repeated suggesting a mixture of complexes. Hence the speciation of the solid could not be calculated. U\textsuperscript{4+} is highly instable in both aqueous and atmospheric conditions with decomposition/oxidation of the metal species is likely,\textsuperscript{10} this may have occurred on samples whilst analysis was completed.

5.3 Speciation of U\textsuperscript{4+} with H\textsubscript{3}bic

Solutions of U\textsuperscript{4+} and H\textsubscript{3}bic in various concentrations and multiple pD were analysed by \textsuperscript{1}H NMR spectroscopy. The labelled structure is shown in Figure 5-6, selected spectra in Figure 5-7 and remaining spectra located in Appendix 2.1.

![Figure 5-6: Structure of H\textsubscript{3}bic with \textsuperscript{1}H atom labels.](image)

![Figure 5-7: Stacked \textsuperscript{1}H NMR spectra of U\textsuperscript{4+} and H\textsubscript{3}bic pD 1 (left) and pD 6 (right). T = 25 °C; I = not controlled; [U\textsuperscript{4+}] = 5 mM; [H\textsubscript{3}bic] = 5n mM (where n = ratio).](image)
At pD 1 binary solutions of U^{4+} and H_{3}bic display a downfield shift together with a merging of signals into one broad signal suggestive of complexation. The broadened signals are reminiscent of labile H_{2}bic as a result of averaging between complexed and uncomplexed H_{2}bic −. As pD < 4 the broad signal splits with H_{2} located in the “free” ligand position implying it is not involved in complexation. The signal of H_{1} and H_{3} remains broadened until pD 7 at which point the H_{3} singlet is observed upfield to the H_{1} signal indicating complexation through the carboxylate moiety.

The monodentate coordination of H_{2}bic − to Th^{4+} (section 4.5) and UO_{2}^{2+} (section 6.5) through the carboxylate moiety has been observed with broadened ^{1}H NMR spectra. As tetravalent uranium and thorium have a similar radius (1.00 and 1.05 Å respectively) and coordination numbers between 7 - 9 depending upon conditions, analogous complexes are expected.\textsuperscript{14,15} Such similarities between Th^{4+} and U^{4+} complexes are reported for malonato complexes with the shorted M-O distance for the U^{4+} complex compared to Th^{4+} a result of the smaller radius.\textsuperscript{16} Similarly, An^{4+} complexes with DTPA (diethylenetriaminepentaacetic acid) display the same coordination modes but show an increase of stability as the actinide series is traversed.\textsuperscript{17}

A precipitate was observed at pD 10.2 in the 1:1 (M:L) solution, pH 10.8 in the 1:2 (M:L) solution and pD 11.8 in both 1:3 and 1:4 (M:L) solutions. This shows the solubility of U^{4+} is significantly increased by the inclusion of H_{3}bic in solution as precipitate of U^{4+} was observed at pH 3.1 implying complexation of H_{2}bic − to U^{4+} hindered hydrolysis. As the solubility is increased with increasing equivalents of H_{3}bic and the H_{3} signal incurs a shift until 3 equivalents of H_{3}bic are in solution, it can be assumed that at least 3 equivalents if H_{2}bic − are complexed to U^{4+}.

UV-Vis titrations on solutions containing U^{4+} and H_{3}bic in multiple ratios were performed at various pH. Spectra at pH 2 and 7 are shown in Figure 5-8 with remaining spectra displayed in Appendix 2.1. Binary solutions show enhanced absorption bands associated with U^{4+} suggesting complexation.\textsuperscript{17,18}
Figure 5-8: UV-Vis spectra of U$^{4+}$ and H$_3$bic at pH 2 (top) and pH 7 (bottom). T = 25 °C; I = 0.5 (NaNO$_3$); [H$_3$bic]$_i$ = 10n mM, [U$^{4+}$]$_i$ = 10 mM (n = ratio); Titrant = 0.1/0.5 M NaOH.

At pH < 6, the characteristic U$^{4+}$ profile is observed in all binary solutions. At pH 2, the 1:1 (M:L) solution has maximum absorptions at 481 (*) and 662 (+) nm and the 1:2 (M:L) solution has similar absorptions at 505 and 662 nm with a splitting of the 662 nm band implying a slightly different species is present. In the 1:3 and 1:4 (M:L) solutions the band
at lower frequency remains at 506 nm with the other band splitting with maxima at 652 and 662 nm suggesting a 1:3 (M:L) speciation correlating to $^1$H NMR spectral data.

At pH 7 spectra of 1:1 - 1:4 (M:L) solutions display a splitting of the 662 nm (+) band with $\lambda_{\text{max}}$ blue shifted to 472 and 644 nm indicating a change in species from that observed at pH 2. This is most likely due to the onset of hydrolysis, the shoulder at 496 nm in the 1:3 and 1:4 (M:L) spectra being due to the complex which has yet to undergo hydrolysis. Solutions which contain three and four equivalents of H$_3$bic do not show the broadening and loss of U$^{4+}$ bands observed in the 1:1 and 1:2 (M:L) spectra suggesting a reduction in the extent of hydrolysis and a 1:3 (M:L) speciation in aqueous solutions analogous to that reported for Th$^{4+}$ (section 4.5).

Potentiometric titrations of solutions containing various ratios of U$^{4+}$ and H$_3$bic were performed with results shown in Figure 5-9.

![Figure 5-9: Potentiometric titrations of U$^{4+}$ and H$_3$bic solutions in varying ratios. T = 25 °C; $I = 0.5$ (NaNO$_3$); $V_0 = 20$ mL; [H$_3$bic]$_i = 5$ mM; [U$^{4+}$]$_i = 5/n$ mM (n = ratio); Titrant = 0.1 M NaOH.](image)

Binary solutions of U$^{4+}$ and H$_3$bic have an initial pH below that of the separate counterparts implying complexation. The profile of the 1:1 (M:L) solution (blue trace) displays an inflection at pH 3 - 6 similar to that observed for U$^{4+}$, due to the release of protons as hydrolysis occurs with the second inflection between pH 8 - 10 due to deprotonation of the amine.
The gradual increase of pH between 3 - 4 in the 1:3 (M:L) solution suggests hydrolysis is occurring but is greatly reduced compared to the 1:1 (M:L) solution. The third equivalent is able to block more coordination sites around the U⁴⁺ centre and therefore less hydroxide molecules bind corroborating ¹H NMR spectral data of 1:3 (M:L) speciation in aqueous solution.

Precipitates obtained in the UV-Vis experiments were filtered and washed. The IR spectrum of the 1:1 and 1:2 (M:L) solids in are shown Figure 5-10 along with the starting materials so comparisons can be made.

![IR spectra](Image)

**Figure 5-10:** IR spectra of precipitates from a 1:1 (red) and 1:3 (blue) U⁴⁺:H₃bic solution, NaNO₃ (green) and H₂bic (black).

The blue shift of the C=O band from 1636 cm⁻¹ in H₃bic to 1614 and 1506 cm⁻¹ in the 1:1 (M:L) precipitate and to 1564 cm⁻¹ in the 1:3 (M:L) precipitate indicates complexation. The appearance of two C=O stretching bands in the 1:1 (M:L) precipitate suggests that H₂bic⁻ molecules are in different environments when the U⁴⁺ complex has undergone hydrolysis forming polymeric species. As binding of H₂bic⁻ is monodentate through the carboxylate moiety, the polymeric structure must be comprised of oxy or hydroxyl bridges. Potentiometric titrations showed that the 1:3 (M:L) complex undergoes hydrolysis to a lesser degree than the 1:1 (M:L) complex, thus less hydroxide groups will bind to U⁴⁺,
polymerisation will be less and a more symmetrical species is likely; only one C=O environment is observed.

Elemental analysis suggest a mixture of complexes are present in the solids with M:L ratios varying from 1:0.6 to 1:2.2 calculated from the M:C ratio. This could be due to hydrolysis forming polymeric structures which can incorporate varying amounts of ligand as a periphery to a polymeric array.

5.4 Speciation of U⁴⁺ with H₃heidi

Solutions containing U⁴⁺ and H₃heidi in various ratios have been characterised with ¹H NMR spectroscopy at multiple pD. The labelled structure of H₃heidi is shown in Figure 5-11 with spectra at pD 2, 3 and 11 shown in Figure 5-12, Figure 5-13 and Figure 5-14 respectively. Additional spectra are located in Appendix 2.2.

![Figure 5-11: Structure of H₃heidi with ¹H atom labels.](image-url)
Figure 5-12: Stacked $^1$H NMR spectra of $U^{4+}$ and $H_3$heidi at pD 2. Full spectrum (left) and enlarged 0-13 ppm region (right). $T = 25 \degree C$; $I$ = not controlled; $[U^{n+}] = 5$ mM; $[H_3$heidi] = 5n mM (where n = ratio).

The 1:1 (M:L) solution at pD 2 shows the broadening of the $H_1$ signal 3.3 ppm with a shift of the $H_2$ and $H_3$ signals to 11.31 and 9.79 ppm indicating complexation. As both the $H_2$ and $H_3$ signals incur a shift complexation, binding of $H_2$heidi$^-$ is tridentate through the carboxylate and the amine moieties. Potentiometric experiments suggests the amine is protonated at pH 2 (Figure 5-16).

The spectra of the 1:2 (M:L) solution is more complex with six broad signals observed at 49.59, 45.80, 30.69, 7.15, 6.94 and -11.42 ppm. The large shifts illustrate the paramagnetism of $U^{4+}$ and complexation of $H_2$heidi$^-$ to $U^{4+}$. Three signals in the “free” ligand range are also observed suggesting the presence of uncomplexed ligand. The number of observed signals suggests the ligand is in multiple environments perhaps in a polymetallic complex.
At pD 3, the 1:1 (M:L) solution displays broad paramagnetic signals at 30.8 and 10.7 ppm with sharp signals at 3.6, 3.3, 1.2 and 0.1 ppm indicating complexation. In the 1:2 (M:L) solution, the broad signals at 30.8 and 12.5 increase in intensity whilst the sharp signals decrease suggesting the downfield species is more favourable. Broadened signals at 3.9 and 3.45 ppm are also observed suggesting the presence of unbound ligand.

In spectra at pH 2 and 3 and the 1:2 (M:L) solution, complex signals at 30.8 and 12.5 ppm become more defined whilst “free” ligand are also observed implying that a second equivalent of H$_3$heidi is required to obtain a 1:1 (M:L) complex.
As pD increases from 4 to 11, signals at 3.75, 3.54, 3.07, 1.2 and 0.1 ppm become more intense implying this complex becomes more concentrated and is therefore likely to be a hydrolysis product. The shifts of the H₃heidi signals indicate complexation through the amine and carboxylate moieties (NOO donor ligand). The number of signals observed suggests the presence of multiple environments of Hheidi²⁻ most likely due to the formation of polymetallic and hydroxide species.

UV-Vis spectra of solutions containing various ratios of U⁴⁺ and H₃heidi between pH 1 - 8 are displayed in Figure 5-15 with additional spectra located in Appendix 2.2.
Figure 5-15: UV-Vis spectra of U⁴⁺ and H₃heidi at pH 1 (top) and pH 8 (bottom). T = 25 °C; I = 0.5 (NaNO₃); [U⁴⁺]ᵢ = 5 mM; [H₃heidi]ᵢ = 5n mM (where n = ratio).

All solutions containing H₃heidi display characteristic U⁴⁺ bands and remain in solution until pH 10 indicating complexation. At pH 1, $\lambda_{\text{max}}$ shifts from 465 (*) and 641 (+) nm for aqueous U⁴⁺ to 479 and 651 nm in the 1:1 (M:L) solution indicating complexation. Solutions containing two or more equivalents of H₃heidi have a maxima at 480 and 655 nm but with increased $\varepsilon_{\text{max}}$ compared to U⁴⁺ suggesting excess ligand is required to form a 1:1
(M:L) complex as observed in the $^1$H NMR spectral data. This pattern continues until precipitation is observed at pH 10.8 in the 1:1 (M:L) solution and pH 11.6 for 1:2 – 1:4 (M:L) solutions. The solubility of U$^{4+}$ suggests that a second H$_3$heidi molecule is required to stabilise U$^{4+}$ over a wider pH range corroborating previous analysis that an excess of H$_3$heidi is required to form a 1:1 (M:L) complex.

The potentiometric titrations of solutions containing U$^{4+}$ and H$_3$heidi in various ratios are displayed in Figure 5-16.

![Figure 5-16: Potentiometric titrations of U$^{4+}$ and H$_3$heidi solutions in varying ratios. T = 25 °C; I = 0.5 (NaNO$_3$); $V_0 = 20$ mL; [H$_3$heidi]$_i$ = 5 mM, [U$^{4+}$]$_i$ = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.](image)

Binary solutions of U$^{4+}$ and H$_3$heidi display a potentiometric curve with no clear inflection representing hydrolysis of U$^{4+}$, however there is a gradual increase in pH between 2 – 4. Fewer protons are released as H$_3$heidi block coordination sites around U$^{4+}$ hindering the extent of hydrolysis.

The 1:1 (M:L) solution curve (blue trace) has an inflection between pH 7 - 11 due to deprotonation of the zwitterion at the amine. This inflection is larger than for H$_3$heidi so protons must also be released from hydrolysis. The 1:2 (M:L) curve (pink trace) shows a gradual increase in pH until pH 4 similar to the 1:1 (M:L) curve suggesting hydrolysis. There are no other inflections at pH > 5 implying that there is no further hydrolysis as pH increases nor does the amine deprotonate.
Solution state analysis has shown a second equivalent of H$_3$heidi is required to stabilise U$^{4+}$ in solution in a 1:1 (M:L) speciation. The reduction in the number of complex signals in the 1:2 (M:L) $^1$H NMR spectra shows a reduced number of complexes in solution. This, along with the increased solubility when two equivalents of H$_3$heidi are in solution with U$^{4+}$ suggests the formation of a 2:2 complex or a large polymeric array blocking coordination sites around U$^{4+}$ in which hydrolysis can occur.

The precipitates generated in potentiometric experiments were filtered and washed. IR spectroscopy was performed with spectra shown in Figure 5-17 along with starting materials for comparison.

![IR spectrum](image)

**Figure 5-17:** IR spectra of precipitates from a 1:1 (red) and 1:2 (blue) U$^{4+}$:H$_3$heidi solution, NaNO$_3$ (green) and H$_3$heidi (black).

A shift of the C=O signal of ~ 130 cm$^{-1}$ to lower frequencies in 1:1 and 1:2 (M:L) precipitates. The C=O stretch in the 1:1 (M:L) precipitate is broad suggesting overlapping peaks from multiple environments. This correlates with solution data previously discussed. Both binary solids contained a N-O stretch identifying its presence in the solid.

Elemental analysis performed on the solids found multiple ratios of M:L in the solids (between 0.18 and 1.62 equivalents of ligand) by calculating results of the U:C ratio. This suggests there was not isolation of a single product, but the solids contain multiple species.
implying polymeric structures. These results show the complexities of hydrolysis with calculation of the absolute speciation of the solid unsuccessful.

5.5 Speciation of U^{4+} with H\textsubscript{3}NTA

Solutions of U^{4+} and H\textsubscript{3}NTA in various ratios were characterised by \textsuperscript{1}H NMR spectroscopy at multiple pD with spectra at pD 2, 3 and 9 shown in Figure 5-18 and Figure 5-19. The remaining spectra are located in Appendix 2.3.

![Figure 5-18: Stacked \textsuperscript{1}H NMR spectra of U^{4+} and H\textsubscript{3}NTA at pD 2. T = 25 ºC; I = not controlled; [U^{4+}] = 5 mM; [H\textsubscript{3}NTA] = 5n mM (where n = ratio).](image)

At pD 2, a single signal is observed in the spectrum of H\textsubscript{3}NTA at 4.19 ppm. The spectrum of the 1:1 (M:L) solution displays a shift and splitting of the signal to 11.71 and 3.43 ppm, the integration of the signals shows the protons are in a 4:2 ratio respectively. The weaker signal at 3.43 ppm could be due to protons neighbouring an unbound carboxylate group with the signal at 11.71 due to bound carboxylates displaying a paramagnetic shift upon complexation with U^{4+}. The upfield shift of the unbound signal to 3.43 ppm at pD 2 suggests complexation through the amine moiety. The complexation of U^{4+} by H\textsubscript{3}NTA at pD 2 is tridentate through two carboxylate and an amine group (NOO). The spectrum of the 1:2 (ML) solution displayed weak complex signals with a signal at 4.08 ppm due to “free” ligand visible suggesting a 1:1 (M:L) speciation.
As pD increases to 3, broad signals are observed at 3.60-3.33, 1.22 and 0.13 ppm in a 4:1:1 ratio in the 1:1 (M:L) solution suggesting a change of species compared the complex suggested at pD 2. The splitting of signals imply two ‘arms’ of NTA$^{3-}$ are in a different environment to the third, implying polymerisation and bridging of one of the ‘arms’ to a second uranium metal. This possibility is shown in Figure 5-20. The “free” ligand signal at 3.74 ppm gradually increases from pD 5 - 10 implying polymerisation of U$^{4+}$ releases NTA$^{3-}$ from the complex as a result of hydrolysis.

![Figure 5-20: Example of a possible tridentate polymerisation mode at pD 3.](image)
UV-Vis titrations were performed on solutions containing various ratios of $\text{U}^{4+}$ and $\text{H}_3\text{NTA}$ at multiple pH. Spectra at pH 2 and 7 are shown in Figure 5-21 with remaining spectra found in Appendix 5.3.

![Figure 5-21: UV-Vis spectra of $\text{U}^{4+}$ and $\text{H}_3\text{NTA}$ at pH 3 (top) and pH 7 (bottom). $T = 25^\circ\text{C}$; $I = 0.5$ (NaNO$_3$); $[\text{H}_3\text{NTA}] = 10\text{nM}$; $[\text{U}^{4+}] = 10\text{mM}$ (n = ratio); Titrant = 0.1/0.5 M NaOH.](image)

The UV-Vis spectrum of the 1:1 (M:L) solution at pH 3 shows a shifting of $\lambda_{\text{max}}$ from 467 (*) and 628 (+) nm in aqueous $\text{U}^{4+}$ to 472 and 655 nm respectively. The spectra of binary solutions display more defined bands compared with aqueous $\text{U}^{4+}$ suggesting
complexation. Spectra between pD 3 - 7 show no further shift in $\lambda_{\text{max}}$ implying the same uranium complex is formed in each. This corroborates results from $^1$H NMR spectral data and the formation of a 1:1 (M:L) complex. Therefore, the bands at 543 and 655 nm correlate to a U(NTA)$^+$ complex. The formation of a U(NTA)$^+$ complex has been reported previously in 0.5 M HNO$_3$ ([U$^{IV}$] = 4.8 mM) with $\lambda_{\text{max}}$ of 652 to 664 nm upon complexation.$^{19}$ The difference in $\lambda_{\text{max}}$ between literature and this work is due to the pH differences in the experimental work.

Precipitation of a green solid was observed within half an hour of performing the UV-Vis titration (Figure 5-24), it is highly likely that precipitation begins during the UV-Vis titration and as such the calculation of extinction coefficients are not accurate.

![Figure 5-22: UV-Vis samples of U$^{IV}$-H$_3$NTA 1:1 experiment at pH 1-12 (left to right)](image)

Potentiometric titrations were performed on aqueous solutions of U$^{IV}$ and H$_3$NTA in various molar ratios with the profiles shown in Figure 5-22.
Initially the 1:1 (M:L) solution has a lower pH than the individual counterparts indicating complexation. The inflection between pH 4 - 6 in the 1:1 (M:L) solution is due to the release of protons upon hydrolysis of U^{4+}. This inflection is approximately a quarter of the size of that observed for U^{4+} implying fewer protons are released and complexation of NTA^{3-} hinders hydrolysis of U^{4+}. The inflection between pH 9 - 12 originates from deprotonation of the amine. Once more, this requires more NaOH than H$_3$NTA suggesting further hydrolysis of U^{4+}.

The potentiometric data were input into the PHREEQC interactive software suite to predict the speciation of U^{4+} with H$_3$NTA in aqueous solution. The results using the SIT database are displayed in Figure 5-23.
Figure 5-24: Speciation diagram for $\text{U}^{4+}$-$\text{H}_3\text{NTA}$ species in a 1:1 $\text{U}^{4+}$:$\text{H}_3\text{NTA}$ aqueous solution predicted by PHREEQC using the SIT database. The ratio of $\text{U}^{4+}$:NTA$^{3-}$:NO$_3^{-}$:H$^+$ is denoted as 1,1,0,0 and 1,0,0,1 etc.

The speciation diagram shows the SIT database predicts a U(NTA)$^+$ complex at pH < 5 consistent with experimental observations. However, the prediction excludes hydroxide species of $\text{U}^{4+}$ and NTA$^{3-}$ which have been suggested in potentiometric titrations at pH < 4. The Hatches-20 and LLNL databases did not predict the complexation of $\text{U}^{4+}$ by $\text{H}_3\text{NTA}$ although it has been observed experimentally therefore presenting flaws within the databases.

Precipitates produced in UV-Vis experiments were filtered and washed. IR spectroscopy was performed on with selected precipitates in Figure 5-25 along with starting materials for comparison.
Figure 5-25: IR spectra of precipitates from a 1:1 (red) and 1:2 (green) U⁴⁺:H₃NTA solution at pH 7, NaNO₃ (blue) and H₃NTA (black).

The spectrum of the precipitates show a shift of the C=O stretch to lower frequencies indicating complexation. The band in the 1:1 (M:L) precipitate is broad with maximum transmittance at 1550 cm⁻¹ shifted from 1714 cm⁻¹ in H₃NTA. The spectrum of the 1:2 (M:L) precipitate contains two bands related to the C=O stretch at 1608 and 1506 cm⁻¹ suggesting the carboxylates are in different environments possibly a result of polymerisation.

Elemental analysis was conducted on the precipitates and results show a varied speciation of solids with calculations of U:C showing the complexes contain NTA⁻³ bound to three or four U⁴⁺ atoms suggesting a polymeric array. This correlates with ¹H NMR spectral data in which “free” ligand signals are observed in spectra at pH < 3. PHREEQC simulations do not predict the supersaturation of U-NTA species, only uranium hydrolysis products locating a gap in the database.
5.6 Speciation of U⁴⁺ with H₂ADA

When solution of U⁴⁺ and H₂ADA were combined, a precipitate formed immediately (Figure 5-26). Precipitation was independent of uranium and H₃NTA concentrations, the rate of addition or the sequence of addition.

![Figure 5-26: UV-Vis samples of U⁴⁺-H₂ADA 1:1 (top) and 1:3 (bottom) (M:L) experiments at pH 1 - 12 (left to right). T = 25 °C; I = 0.5 (NaNO₃); [UO₂²⁺]ᵢ = 10 mM; [H₃bic]ᵢ = 10n mM (where n = ratio); Titrant = 0.1/0.5 M NaOH.](image)

The solids were filtered and washed for IR spectroscopy and elemental analysis to be performed. The C=O stretch blue shifts from 1674 cm⁻¹ in H₂ADA to 1533 cm⁻¹ in the precipitates indicating complexation. IR spectra display the same bands and shifts in all precipitates suggesting the same complex is formed in each.
Elemental analyses conducted on the precipitates indicate multiple species are present in the solid. The absolute composition of the solid could not be solved with U:L ratios between 1:0.22 and 1:0.29 calculated indicating that less than one equivalent of ligand is bound to U\(^{4+}\) suggesting that a polymeric species is present.

\(^1\)H NMR spectroscopy of the supernatant was performed allowing the solution species to be observed (Figure 5-28). The 1:1 (M:L) spectra shows complex signals at 25.59 and 17.27 ppm with “free” ligand signals between 421 - 346 ppm. The spectra of the 1:2 (M:L) solution shows “free” ligand signals are more defined with simultaneous reduction of the complex signals. These observations in conjunction with solid state analysis suggests the presence of polymeric species when ADA\(^2-\) complexes to U\(^{4+}\) ions.
Figure 5-28: Stacked $^1$H NMR spectra of $U^{4+}$ and H$_2$ADA at pH 3. $T = 25$ °C; $I$ = not controlled; $[U^{4+}] = 5$ mM; $[H_2ADA] = 5n$ mM (where $n$ = ratio).

The UV-Vis of the supernatant (Figure 5-29) was also performed with bands at 470 and 660 nm observed in binary solutions compared to broadened signals and no distinction of bands in the aqueous $U^{4+}$ spectrum. Extinction coefficients are not reliable as exact concentration in solution was unknown due to precipitation.

Figure 5-29: UV-Vis spectra of UO$_2$$^{2+}$ and H$_2$ADA solutions at pH 2. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); $[H_2ADA] = 10n$ mM, $[U^{4+}] = 10$ mM ($n$ = ratio); Titrant = 0.1/0.5 M NaOH.
5.7 Speciation of U⁴⁺ with H₃cit

¹H NMR spectroscopy was performed on solutions containing various ratios of U⁴⁺ and H₃cit at multiple pD. Spectra at pD 2, 4 and 11 are shown in Figure 5-30 with remaining spectra displayed in Appendix 2.5.

Figure 5-30: Stacked ¹H NMR spectra of U⁴⁺ and H₃cit at pD 2 (top left), pD 4 (top right), pD 11 (bottom). T = 25 °C; I = not controlled; [U⁴⁺] = 5 mM; [H₃cit] = 5n mM (where n = ratio).
At pH 2, the AB splitting of citric acid is not observed with a broad signal between 3.59 - 3.25 ppm in its place. The downfield shift from 2.81 - 3.03 ppm indicates binding with the broadness suggesting the fluxional behaviour of citric acid to U⁴⁺. At pH 4, the broad signal is still apparent alongside sharp signals at 3.58, 3.35, 1.22 and 0.11 ppm also suggestive of complexation and asymmetry of the complex with protons in different environments. At pH < 9 unbound H₃cit signals are observed in the 1:1 (M:L) solution with the simultaneous decrease of complex signals. Despite the evolution of “free” ligand signals 1:1 (M:L) spectrum, a precipitate is not observed until pH > 13 implying polymerisation of U⁴⁺ complexes with oxy/hydroxyl bridges increasing the solubility of U⁴⁺.

UV-Vis spectroscopic titrations were performed on solutions of U⁴⁺ and H₃cit in various molar ratios and multiple pH. Spectra at pH 3 and 10 are shown in Figure 5-31 with additional spectra located in Appendix 3.5.

At pH > 5, the λ_{max} of 1:1 (M:L) solutions are shifted from 465 and 654 nm in aqueous U⁴⁺ to 488 and 666 nm indicating complexation of U⁴⁺ by cit⁻. This does not shift upon increasing the complexation of H₃cit suggesting 1:1 (M:L) speciation. The increase in absorption suggests the interaction of a second equivalent of H₃cit to U⁴⁺. This phenomenon has been previously observed by Bonin et al. who report that excess H₃cit are required to form a 1:1 (M:L) speciation in 1 M HNO₃. When pH > 5, the absorptions do not shift between all solutions suggesting a 1:1 (M:L) speciation with λ_{max} at 490 (*) and 665 (+) nm. At pH > 5 a shift in maxima from the 1:1 (M:L) spectrum at 470 and 665 nm to 496 and 661 nm in 1:2 - 1:4 solutions suggests the formation of a second species such as the inclusion of a hydroxide in the complex or a second citrate molecule. Bonin et al. reported a λ_{max} of 550 and 654 nm for the U(cit)⁺ complex and 560 and 662 nm for the U(cit)₂⁻ complex ([U⁴⁺] = 4.8 mM, I = 0.5 (N₂H₅) in 0.5 M HNO₃] corresponding to absorptions at 556 and 665 nm in the 1:2 (M:L) spectrum above.
Figure 5-31: UV-Vis spectra of $\text{U}^{4+}$ and $\text{H}_3\text{cit}$ solutions at pH 3 (top) and pH 10 (bottom). $T = 25 ^\circ\text{C}$; $I = 0.5 (\text{NaNO}_3)$; $[\text{UO}_2^{2+}] = 10 \text{ mM}$; $[\text{H}_3\text{bic}] = 10n \text{ mM (n = ratio)}$; Titrant = 0.1/0.5 M NaOH.

The potentiometric titration of a 1:1 (M:L) solution of $\text{U}^{4+}$ and $\text{H}_3\text{cit}$ is shown in Figure 5-32. The initial pH of the 1:1 (M:L) solution is lower than that of the individual counterparts indicating the release of protons upon complexation. The absence of an inflection at pH < 6 demonstrates the lack of hydrolysis when $\text{U}^{4+}$ is complexed by $\text{H}_3\text{cit}$ with the inflection between pH 8 – 11 is due to hydrolysis of the complex, this is at a much
higher pH than $U^{4+}$ suggesting complexation of $U^{4+}$ by $H_3\text{cit}$ hinders hydrolysis to a great extent.

![Figure 5-32: Potentiometric titrations of a 1:1 $U^{4+}$ and $H_3\text{cit}$ solution. $T = 25 \, ^\circC$; $I = 0.5$ (NaNO$_3$); $V_0 = 20 \, \text{mL}$; $[H_3\text{cit}]_i = 5 \, \text{mM}; [U^{4+}]_i = 5 \, \text{mM}; \text{Titrant} = 0.1 \, \text{M NaOH}.\]

Potentiometric titration data were input into the PHREEQC software suite to predict the solution speciation of $U^{4+}$ with $H_3\text{cit}$. The LLNL and SIT databases predict no complexation between $U^{4+}$ and $H_3\text{cit}$ conflicting experimental results. Therefore the Hatches-20 database was used for the prediction with the speciation graphs displayed in Figure 5-33.
Figure 5-33: Speciation diagram for $U^{4+}$-H$_3$cit species in a 1:1 Th$^{4+}$:H$_3$cit aqueous solution generated in PHREEQC using the Hatches-20 database.

The predicted speciation diagram suggests that a 1:1 (M:L) species is dominant at pH < 4, with the 1:2 (M:L) complex formed between pH 4 - 7 beyond which U(OH)$_4$ is the main species. Experimentally, the 1:2 (M:L) complex was not evident showing a small difference between the prediction and work presented here. The model predicts that the U(OH)$_4$ species increases in concentration at pH < 3, the gradual increase in “free” ligand signals in the $^1$H NMR spectral data could be due to the formation of U(OH)$_4$ although a polymeric species is more likely with H$_3$cit forming initial bridging structures between $U^{4+}$.

Solutions of $U^{4+}$ and H$_3$cit containing more than 1 equivalent of citric acid are soluble within the pH range 1-12 (Figure 5-34). However in 1:1 (M:L) solutions a suspension is observed at pH < 2.5 and a precipitate at pH 12 indicating that a second H$_3$cit is involved in stabilising $U^{4+}$ in solution.
The precipitate at pH 12 was analysed by IR spectroscopy (Figure 5-35). The shift in the C=O stretches from 1742 and 1684 cm\(^{-1}\) in H\(_3\)cit to a broad signal with a maxima at 1558 cm\(^{-1}\) in both precipitates. The similarity of the signal in 1:1 and 1:2 (M:L) precipitates suggest the carbonyls are in the same environments and therefore same species is isolated in both accounts.

Figure 5-35: IR spectra of precipitates from a 1:1 (blue) and 1:2 (green) U\(^{4+}\):H\(_3\)cit solution at pH 12, NaNO\(_3\) (red) and H\(_3\)cit (black).
Elemental analysis was conducted on the precipitates with M:L ratios of 1:0.7 and 1:0.62 calculated from the U:C ratio. As “free” ligand signals are observed in the \(^{1}H\) NMR spectra at pD > 9 and elemental analysis calculates that cit\(^{3-}\) complexes to multiple U\(^{4+}\) atoms a polymeric structure is likely. PHREEQC simulations conducted on potentiometric data do not predict the supersaturation of any species containing both U\(^{4+}\) and cit\(^{3-}\) locating a gap in the database which needs to be reviewed.

### 5.8 Summary

The hydrolysis of U\(^{4+}\) was investigated in aqueous solutions between pH 1 - 3 with precipitation observed at pH 3.2. UV-Vis spectroscopy identified two bands at 465 and 646 nm at pH 1 to allow comparisons to solutions containing organic ligands. Speciation predictions using the PHREEQC software suite highlighted vast differences between aqueous U\(^{4+}\) species predictions by the Hatches-20, SIT and LLNL databases. Literature reports also demonstrated discrepancies between potential speciation and their formation constants. Hyperquad software was used to model potentiometric data and calculate formation constants of multiple U\(^{4+}\) hydroxide species. Values calculated are within range of literature data.

Solution state experiments showed H\(_{3}\)bic complexed to U\(^{4+}\) in a monodentate manner through the carboxylate moiety. As U\(^{4+}\) remained soluble pH 10.4, polymerisation through oxy/hydroxyl bonds resulting from hydrolysis must complete the coordination sphere to stabilise the U\(^{4+}\). Solid state analysis confirms complexation.

H\(_{3}\)heidi complexes to U\(^{4+}\) in a 1:1 (M:L) complex but a second equivalent of H\(_{3}\)heidi is required to obtain full 1:1 (M:L) speciation of U\(^{4+}\). Solid state analysis confirms complexation.

H\(_{3}\)NTA complexes to U\(^{4+}\) in 1:1 (M:L) ratio at pH 2 with tridentate (NOO) binding. At pH > 2 splitting and broadening of \(^{1}H\) NMR signals implies hydrolysis occurs forming an unsymmetrical species and possibly polymerisation. PHREEQC predictions suggest the formation of U(NTA)\(^+\) at pH < 5 complimenting experimental data. At pH > 5 predictions suggest the presence of uranium hydroxide complexes which contain no NTA\(^{3-}\) conflicting with experimental data and presenting gaps within the databases.
In the presence of H$_2$ADA, U$^{4+}$ is sparingly soluble in aqueous solutions between pH 1 - 12. Analysis of the supernatant and precipitate showed complexation but speciation could not be determined.

A 1:1 (M:L) speciation of U$^{4+}$ and H$_3$cit at pH < 5 requires excess H$_3$cit. When pH > 5 hydrolysis occurs and “free” ligand signals are observed in the $^1$H NMR spectra implying polymerisation of U$^{4+}$ through oxy/hydroxyl bonds; ligands are released to allow further polymerisation. PHREEQC simulations predict 1:1 (M:L) complexation at pH < 5 correlating to experimental data but excludes hydroxide complexes of U$^{4+}$ and H$_3$cit observed experimentally.

5.9 References

6 Uranium (VI)

6.1 Introduction

Uranium dioxide is one of the most common forms of uranium as it is used as fuel in the majority of nuclear reactors. However, once uranium dioxide has been removed from the reactor, it is relocated into storage ponds. Here, many environmental conditions determine the oxidation state and speciation, such as temperature and pH. In aqueous solutions the most stable oxidation state of uranium is +6 (as the uranyl cation, UO$_2^{2+}$), but U$^{4+}$ and to a lesser extent U$^{3+}$ can also be present.$^{1,2}$

The optical spectra of uranium compounds display characteristic absorptions of $f$-$f$ transitions for U$^{3+}$ ($5f^3$), U$^{4+}$ ($5f^2$) and UO$_2^{+}$ ($5f^1$). However, in the ground state electronic configuration for UO$_2^{2+}$ compounds, the $5f$ electron shell is empty and the optical properties observed originate from charge transfer from filled molecular orbitals on the ligand to the empty $5f$-orbitals of the uranium.$^3$

Uranyl consists of a linear UO$_2$ backbone with strong double bonds to oxygen enforcing the attachment of auxiliary ligands in the equatorial plane (see section 1.4). The presence of the uranyl unit is detected by IR spectroscopy with an asymmetric stretching vibration ($\nu_3$) between 920-980 cm$^{-1}$ and a corresponding symmetric vibration ($\nu_1$) at 860 cm$^{-1}$ in the Raman Spectrum.$^4$ Shifts in the signals therefore signify a change in the actinyl unit, and complexation can be characterised in this way. Other techniques useful to the characterisation of uranium compounds include NMR, elemental analysis, potentiometric titrations and XRD crystallography.

6.2 Speciation of UO$_2^{2+}$

Initially UV-Vis spectroscopy was used to show the change in UO$_2^{2+}$ species as pH was increased from 2. At pH 6.2, precipitation occurred so no further experiments were undertaken. The UV-Vis absorption spectra of uranyl in acidic conditions (pH 2 - 6) is shown in Figure 6-1.
The UV-Vis spectra of uranyl show an increase in absorption with increasing pH. In acidic conditions (pH < 4), uranyl displays a well-defined fine structure consisting of a nearly regular sequence of nine absorptions. These result from coupling of electronic transitions with the symmetric stretching vibration of the UO$_2^{2+}$ group. The main absorption band of uranyl at pH 2 has $\lambda_{\text{max}}$ at 414 nm, which is consistent with those reported in the literature.$^5$ As pH is increased, not only does the absorption increase, there is also loss of uranyl fine structure, with only one broad band observed, and a red shift of $\lambda_{\text{max}}$ to 420 nm at pH 4. The loss of fine structure is in accordance with published data and is due to the formation of polynuclear species as a result of hydrolysis.$^5$ It has been proposed that the major uranyl species at pH 4 is the binuclear (UO$_2$)$_2$(OH)$_2^{2+}$ with a minor contribution of the trinuclear (UO$_2$)$_3$(OH)$_4^{2+}$ species (where [UO$_2^{2+}$]$_T$ = 0.0031 - 0.647 M).$^5$ Other investigations have reported the absorption maxima for (UO$_2$)$_2$(OH)$_2^{2+}$ to be 422 nm ([UO$_2^{2+}$]$_T$ = < 20 mM),$^8$ close to the maxima for this experiment.

When the pH of the uranyl solution increases to 5, a shoulder to the right of the main uranyl band appears. This has previously been assigned by Lubal et al. to a polynuclear hydroxide species, (UO$_2$)$_3$(OH)$_5^+$, with minor quantities of (UO$_2$)$_3$(OH)$_4^{2+}$ ([UO$_2^{2+}$]$_T$ = 0.031 M).$^5$ Other reports defend this assignment showing the absorption

**Figure 6-1:** UV-Vis spectra of UO$_2^{2+}$ at a pH 2 - 6. $T = 25^\circ$C, $I = 0.5$ (NaNO$_3$); [UO$_2^{2+}$]$_T$ = 10 mM.
maxima for \((\text{UO}_2)_3(\text{OH})_5^+\) to be 429 nm \([\text{UO}_2^{2+}]_\text{T} < 20 \text{ mmol}\).\(^8\) This is close to the maxima of 427.8 nm observed in this study suggesting the same species is formed.

At pH 6, the band again experiences an increase in intensity, along with the shoulder between 466 and 500 nm becoming more prominent. It has been suggested that this is due to the formation of a \((\text{UO}_2)_3(\text{OH})_7^-\) species.\(^7,9\)

The PHREEQC software suite was used to predict the speciation of uranyl using the SIT, the LLNL and the Hatches-20 databases. Molarities and volumes used were obtained in potentiometric titrations. The resulting speciation diagrams for uranyl hydrolysis from each database are very similar (Figure 6-2). Upon further inspection, the log K values in the SIT and Hatches-20 databases are identical (so only Hatches-20 will be discussed here) with the LLNL database having only minor differences between formation constants.

One noticeable difference between the predicted speciations is the high percentage of \(\text{UO}_2(\text{OH})_4^{2-}\) predicted by the Hatches-20 database at pH 12, compared to the dominance of \(\text{UO}_2(\text{OH})_5^-\) in predictions using the LLNL database. Previous studies at pH < 12 report the presence of \(\text{UO}_2(\text{OH})_4^{2-}\) and \((\text{UO}_2)_3(\text{OH})_{11}^{5-}\) \([\text{U}]_\text{T} < 10 \text{ mM}\), but these are not included in the Hatches-20, LLNL or NEA databases.\(^10,11\)
Figure 6-2: Speciation diagrams of UO$_2$$^{2+}$ hydrolysis generated in PHREEQC from potentiometric titrations. LLNL database (top), Hatches-20 database (bottom). The ratio of UO$_2$$^{2+}$:NO$_3$$^-$:H$^+$ is denoted as 1,1,0 and 2,0,-2 etc.

The predicted uranyl speciation obtained through PHREEQC is different to that reported in literature. Calculations from all databases suggest a mononuclear uranyl nitrate species (UO$_2$)(NO$_3$)$_2^+$ along with a tetranuclear (UO$_2$)$_4$(OH)$_7^+$ species at pH < 9, which experimental data suggests are only present in inconsequential quantities (where
[U]_T = 0.01 M and I = 0.5 (tetramethylammonium hydroxide)). PHREEQC simulations also suggest the binuclear (UO₂₂⁺(OH)²⁺ species is present in insignificant quantities and neglects to incorporate the trinuclear (UO₂⁻(OH)₄⁻²⁺ species contradicting experimental results observed in literature under a range of conditions ([U]_T = 0.008 - 0.0331 M, I = 0.3 (NaClO₄) and [U]_T = 4.75 x 10⁻⁴ M, I = 0.1 (tetramethylammonium trifluoromethanesulfonate)). The variation of species could be due to the difference of uranyl concentration, I or electrolyte.

Proposed species from PHREEQC simulations along with parameters from the appropriate database were used with the Hyperquad software suite coupled with experimental potentiometric titration data. The resulting model fits for UO₂²⁺ in aqueous solution using the Hatches-20 and the LLNL databases are shown in Figure 6-3.
The steep inflections in the potentiometric data represent a strong acid-strong base titration (HNO$_3$-NaOH). The release of H$^+$ ions into the solution is represented by the horizontal portions of the data; this is where the UO$_2^{2+}$ ion undergoes hydrolysis to the greatest extent. Precipitation is observed at pH 6.2, as this interferes with the pH measurement data above this pH was disregarded. Consequently, only uranyl speciation predicted in
appreciable amounts below or at this pH were be incorporated into the model. The Hatches-20 model included the $\text{UO}_2^{2+}$, $\text{UO}_2(\text{NO}_3)^+$, $(\text{UO}_2)_3(\text{OH})_5^+$, $(\text{UO}_2)_4(\text{OH})_7^+$, $(\text{UO}_2)_3(\text{OH})_7^-$ and $\text{UO}_2(\text{OH})^+$ species and the LLNL model also incorporated the $(\text{UO}_2)_2(\text{OH})_2^{2+}$ species. Neither model fits the experimental data within the pH of 2 - 6.

A third model was attempted, incorporating species that have been assigned in literature. The reported formation constants were refined to generate a suitable model fit, errors were determined during the fitting process. Figure 6-4 shows the results of this fitting incorporating $\text{UO}_2^{2+}$, $(\text{UO}_2)(\text{OH})^{2+}$, $(\text{UO}_2)_3(\text{OH})_4^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$ and $(\text{UO}_2)_3(\text{OH})_7^-$. It can be observed that the model (dotted line) fits the experimental data (blue diamonds) more closely using species derived from literature sources and allowing their equilibrium constants to float compared to using the PHREEQC databases.

![Figure 6-4: Potentiometric titration of $\text{UO}_2^{2+}$ modelled in Hyperquad using the using literature speciation data. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); $V_0 = 20.02$ mL; $[\text{UO}_2^{2+}] = 5$ mM; Titrant = 0.1 M NaOH.](image)

The formation constants calculated from the data are presented in Table 6-1 and are within range of literature values. As the model converged to a good fit, the refined formation constants in Table 6-1 are reliable and will be used for uranyl hydrolysis in subsequent uranyl speciation experiments. A speciation diagram was produced using the resulting formation constants and is shown in Figure 6-5. There is a possibility that uranyl hydroxide species can undergo oxolation to form oxide bridges (section 1.5) although such structures
were omitted from the model, as calculations that included them would not converge and could not be fitted.

<table>
<thead>
<tr>
<th>UO$_2$$^{2+}$:H$^+$</th>
<th>Calc. log $\beta$</th>
<th>Lit. NEA</th>
<th>Lit. Palmer et al.$^1$</th>
<th>Lit. Lubal et al.$^2$</th>
<th>Lit. Zanonato et al.$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I = 0.5 (NaNO$_3$)</td>
<td>I = 0.1 (TMATFMS)</td>
<td>I = 3 (NaClO$_4$)</td>
<td>I = 0 (TMANO$_3$)</td>
</tr>
<tr>
<td>1.0</td>
<td>0 ± 0.05</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.2</td>
<td>-5.301 ± 0.05</td>
<td>-5.620</td>
<td>5.74 ± 0.01</td>
<td>-6.098 ± 0.066</td>
<td>-5.94 ± 0.03</td>
</tr>
<tr>
<td>3.4</td>
<td>-12.13 ± 0.05</td>
<td>-11.9</td>
<td>-12.57 ± 0.02</td>
<td>-12.25 ± 0.08</td>
<td>-16.43 ± 0.02</td>
</tr>
<tr>
<td>3.5</td>
<td>-15.91 ± 0.05</td>
<td>-15.55</td>
<td>16.09 ± 0.01</td>
<td>-16.62 ± 0.01</td>
<td>-16.43 ± 0.02</td>
</tr>
<tr>
<td>3.7</td>
<td>-26.25 ± 0.05</td>
<td>-31.00</td>
<td>28.59 ± 0.05</td>
<td>-28.97 ± 0.07</td>
<td>-12.25 ± 0.08</td>
</tr>
</tbody>
</table>

Table 6-1: Calculated and literature formation constants of uranyl hydrolysis species in acidic conditions. The ratio of UO$_2$$^{2+}$:H$^+$ is denoted as 1,1 and 1,-1 etc. (TMATFMS = tetramethylammonium trifluoromethanesulfonate. TMANO$_3$ = tetramethyl ammonium nitrate)

Precipitation is observed at pH 6.2. At the end of the titration it was allowed to settle, the mother liquor decanted off and the solid washed with DI H$_2$O. PHREEQC simulations in both Hatches-20 and LLNL databases predict that Na$_2$U$_2$O$_7$, U$_3$O$_8$, UO$_2$(OH)$_2$ and UO$_3$.2H$_2$O are all supersaturated at pH 6 implying the precipitate contains these species. Elemental analysis was performed on the solid and the results showed it did not contain carbon and nitrogen, only thorium and hydrogen. The results could not be fitted to any
individual uranyl hydrolysis product suggesting it contains a mixture of species demonstrating the complex nature of uranyl hydrolysis. The gelatinous nature of the material could also indicate that polymerisation of uranyl has occurred through the formation of hydroxide (or oxide) bridges, although such species are not included in PHREEQC databases as data is unreliable.

6.3 Speciation of UO$_2^{2+}$ with H$_3$thme

$^1$H NMR spectroscopy was used to determine the parameters for the complexation of UO$_2^{2+}$ by H$_3$thme in solutions containing various concentrations of H$_3$thme at multiple pD values. The chemical shifts in each solution are shown in Figure 6-6 resembling observations of H$_3$thme with Th$^{4+}$. Solutions of H$_3$thme with UO$_2^{2+}$ show no shift in proton signals compared to “free” ligand suggesting complexation is negligible.

The chemical shifts for the $^{13}$C environments are shown in Figure 6-7 showing no shift of signals upon addition of UO$_2^{2+}$ corroborating $^1$H NMR results. Complexation of H$_3$thme to UO$_2^{2+}$ is insignificant at any ratio of H$_3$thme or pD investigated.
At pH 6.3, a yellow suspension was observed which, when filtered and washed produced a yellow gelatinous material. This is the same pD at which hydrolysis of UO$_{2}^{2+}$ occurs without the presence of organic ligands. The gel was examined by microanalysis and an absence of organic material was found. This suggests hydrolysis of UO$_{2}^{2+}$ has occurred and demonstrates the inability of H$_{3}$thme to bind to UO$_{2}^{2+}$.

### 6.4 Speciation of UO$_{2}^{2+}$ with H$_{3}$tea

$^1$H NMR spectroscopy was performed on uranyl solutions that contained various concentrations of H$_{3}$tea within a pH range 2 - 6 to examine the potential for complexation (Figure 6-8). Neither signal of H$_{3}$tea shows any change in chemical shift compared to the spectra of “free” H$_{3}$tea spectrum implying that there is minimal complexation to uranyl; consistent with results observed for thorium (section 4.4).
The $^1$H NMR experiments produced yellow precipitates at pH 6.4 which was filtered and washed. Elemental analysis of the solid and dried before elemental analysis of the precipitates found no carbon or nitrogen contribution to the solid confirming that H$_3$tea has negligible complexation properties to UO$_2$$^{2+}$ under conditions studied.

Complexation of UO$_2$$^{2+}$ with H$_3$tea was insignificant with the hydrolysis of uranyl not prevented by the presence of H$_3$tea. This is consistent with experiments conducted by Joshi.
et al. with uranium concentrations of 0.02 M. As no complexation was evident no further analysis was attempted.

6.5 Speciation of UO$_2^{2+}$ with H$_3$bic

NMR spectroscopic analysis was performed on uranyl solutions containing various concentrations of H$_3$bic within a pD range 2 - 6 to determine the parameters of complexation. The labelled structure of H$_3$bic is shown in Figure 6-9 with selected spectra in Figure 6-10, additional spectra can be found in Appendix 3.1.

![Figure 6-9: Structure of H$_3$bic with $^1$H atom labels.](image)

![Figure 6-10: Stacked $^1$H NMR spectra of UO$_2^{2+}$ and H$_3$bic at pD 3 (left) and pD 5 (right). T = 25 °C; I = not controlled; [UO$_2^{2+}$]$_i$ = 5 mM; [H$_3$bic]$_i$ = 5n mM (where n = ratio).](image)
In solution with $\text{UO}_2^{2+}$ at pH 2, a downfield shift of 0.05 ppm is observed for $\text{H}_3$ compared to the “free” ligand spectrum implying complexation. No shift is observed for $\text{H}_1$ or $\text{H}_2$ in the presence of $\text{UO}_2^{2+}$ implying the terminal alcohol groups of $\text{H}_3\text{bic}$ do not complex to $\text{UO}_2^{2+}$. Therefore complexation of $\text{H}_2\text{bic}^-$ to $\text{UO}_2^{2+}$ is monodentate through the carboxylate moieties. The $\text{H}_3$ signal of $\text{H}_2\text{bic}^-$ undergoes no further chemical shift when more than two equivalents of $\text{H}_3\text{bic}$ are in solution with $\text{UO}_2^{2+}$ suggesting a 1:2 (M:L) speciation. At pH 5, signals in M:L solutions are broadened in comparison to “free” ligand due to hydroxide formation altering the structure of the uranyl complex. An averaging of ligand environments is observed. At pH 5.7 a yellow precipitate is observed in all solutions.

$^{13}\text{C}$ NMR spectra (Figure 6-12) display a downfield shift and broadening of the carboxylate signal between pH 3 – 6 indicating complexation. The carboxylate signal reappears once the third equivalent of $\text{H}_3\text{bic}$ is added confirming 1:2 (M:L) speciation. Carbon assignments are shown in Figure 6-11, spectra at pH 4 are displayed in Figure 6-12 with other spectra presented in Appendix 3.1.
Figure 6-11: Structure of H₃bic with ¹³C atom labels.

Figure 6-12: Stacked ¹³C NMR spectra of UO₂²⁺ and H₃bic at pH 4. T = 25 °C; I = not controlled, [UO₂²⁺]ᵢ = 5 mM; [H₃bic]ᵢ = 5n mM (where n = ratio).

In a 1:1 (M:L) solution, signals assigned to C₁ and C₂ display shifts of ~0.005 ppm compared to “free” H₃bic implying no binding of H₂bic⁻ occurs through the terminal alcohol or anime moieties. The shift of ~0.25 ppm for the C₃ signal suggests binding to UO₂²⁺ through the carboxylate moiety of H₂bic⁻. This shift is observed until two equivalents of H₃bic are added to UO₂²⁺ solution confirming a 1:2 (M:L) speciation.

UV-Vis spectroscopy was used to study the effect that the presence of H₃bic on the uranyl ion. The spectrum of H₃bic in aqueous solution (protonated or deprotonated) has no absorbance, hence there is no interference within the wavelengths of interest for uranyl absorption. Selected spectra are displayed in Figure 6-13, with all other spectra found in Appendix 3.1.
The characteristic fine structure of uranyl is visible at pH 2 in all solutions with a slight red shift in $\lambda_{\text{max}}$ from 414 nm in the UO$_2^{2+}$ solution to 416 nm in solutions containing H$_3$bic. There is also an increase in extinction coefficient upon addition of one equivalent of H$_3$bic suggesting complexation. The relatively low absorbance at low pH favours the existence of a monomeric species,$^6$ a conclusion that agrees with NMR spectroscopy which suggests monodentate complexation through the carboxylate group.

At pH 3, the fine structure begins to degrade, and by pH 4 it is no longer visible with a broad absorbance detected. At pH 5, the uranyl solution a shoulder is observed to the right

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Figure 6.13: UV-Vis spectra of UO$_2^{2+}$ and H$_3$bic at pH 2 and 5 (top) and pH 6 (bottom). T = 25 °C; $I = 0.5$ (NaNO$_3$); [H$_3$bic]$_i$ = 10n mM, [UO$_2^{2+}$]$_i$ = 10 mM (n = ratio); Titrant = 0.1/0.5 M NaOH.
of the major UO$_2^{2+}$ signal. This shoulder has previously been identified as a polynuclear hydroxide species, (UO$_2$)$_3$(OH)$_5^{2+}$. The UV-Vis spectra of the 1:1 (M:L) solution displays a shoulder similar to that observed for UO$_2^{2+}$ implying uranyl in these solutions has undergone hydrolysis to form a similar hydroxide species. The shoulder is not as distinct as that seen for pure uranyl solutions suggesting H$_2$bic$^-$ is complexed to UO$_2^{2+}$, but there are coordination sites available for hydroxide ions to bind. The shoulder is not evident in solutions containing more than two equivalents of H$_3$bic suggesting hydrolysis of UO$_2^{2+}$ is hindered by the complexation of two H$_2$bic ions.

Precipitation was observed at pH 5.7 in all UO$_2^{2+}$:H$_3$bic solutions, this is below pH 6.4 at which precipitation in UO$_2^{2+}$ solutions in the absence of organic ligands is observed. This implies that uranyl-H$_2$bic$^-$ species formed is less stable in solution than uranyl hydroxides.

Aqueous solutions containing varying ratios of UO$_2^{2+}$ and H$_3$bic were titrated against 0.1 M NaOH from acidic to alkaline pH keeping I constant at 0.5 with NaNO$_3$ (Figure 6-14). Concentrated HNO$_3$ was added before the experiment to ensure pH was initially below 2.

![Figure 6-14: Potentiometric titrations of UO$_2^{2+}$ and H$_3$bic solutions in varying ratios. T = 25 °C; I = 0.5 (NaNO$_3$); V$_o$ = 20.02 mL; [H$_3$bic]$_i$ = 5 mM, [UO$_2^{2+}$]$_i$ = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.](image)
The inflection between pH 2 - 6 in uranyl solution is due to hydrolysis and the formation of uranyl hydroxide species including \((\text{UO}_2)_3(\text{OH})_5^+\) and \((\text{UO}_2)_3(\text{OH})_7^-\) (see section 6.2).\(^9,13\) At pH > 6, the majority of the hydroxide species precipitate, resulting in a standard acid-base titration shape for the remaining portion of the curve.

As the ratio of \(\text{UO}_2^{2+}:\text{H}_3\text{bic}\) is increased from one to three equivalents of ligand, there is a steady reduction of the uranyl hydroxide feature between pH 2 - 6. This supports \(^1\text{H NMR}\) and UV-Vis data that suggest that, as the concentration of bicine increases, complexation hinders hydrolysis, reducing the number of protons released.

Precipitates formed from UV-Vis spectrometric experiments were filtered and washed to facilitate solid state analysis. The IR spectra of the solids obtained in 1:1 and 1:3 (M:L) experiments are shown in Figure 6-15; the spectra of \(\text{H}_3\text{bic}\) and \(\text{NaNO}_3\) are also shown for reference.

![Figure 6-15: IR spectra of precipitates from 1:1 (blue) and 1:3 (red) \(\text{UO}_2^{2+}:\text{H}_3\text{bic}\) solutions, \(\text{NaNO}_3\) (green) and \(\text{H}_3\text{bic}\) (black).](image)

The differences between the 1:1 and 1:3 (M:L) precipitates and starting materials include the signature broad curve of an O-H stretch and the shift of the N-O stretch of \(\sim 9\ \text{cm}^{-1}\) compared to \(\text{NaNO}_3\) signifying the presence of OH/H\(_2\)O and at least one NO\(_3^-\) group bound to uranyl. The asymmetric carboxylate stretch is shifted to lower frequencies from 1636 cm\(^{-1}\) in \(\text{H}_3\text{bic}\) to 1613 cm\(^{-1}\) in the 1:1 (M:L) precipitate indicating complexation. The
The spectrum of the 1:3 (M:L) precipitate is more complex in this region, with a main peak shifted by ~80 cm$^{-1}$ to 1512 cm$^{-1}$ and two less prominent peaks at 1574 and 1615 cm$^{-1}$. These all suggest complexation of UO$_2^{2+}$ by H$_3$bic with the presence of multiple peaks explained by the high probability that there are multiple species present, both monomeric and polymeric. The symmetric uranyl stretch is also observed in both shifted from 810 cm$^{-1}$ in hydrated UO$_2^{2+}$ to 834 and 815 cm$^{-1}$ in 1:1 and 1:3 (M:L) spectra respectively.$^{14,15}$

Elemental analysis performed on the solid precipitates illustrate the complex nature of hydrolysis, with various ratios of U:C found in each precipitate and in repeats. In some cases, four H$_3$bic$^-$ ions are calculated to be complexed to UO$_2^{2+}$ whilst others contain less than one H$_3$bic$^-$ complexed to uranyl, indicating the presence of dimeric and possibly polymeric species. The absolute speciation of the solid was unable to be successfully calculated.

### 6.6 Speciation of UO$_2^{2+}$ with H$_3$heidi

$^1$H NMR spectroscopy was performed on solutions containing various ratios of UO$_2^{2+}$ and H$_3$heidi at multiple pD. The labelled structure of H$_3$heidi is shown in Figure 6-16 and the $^1$H NMR spectrum at pD 3 and 6 is shown in Figure 6-17. Other spectra can be found in Appendix 3.2.

![Figure 6-16: Structure of H$_3$heidi with $^1$H atom labels.](image)
Figure 6-17: Stacked $^1$H NMR spectra of UO$_2^{2+}$ and H$_3$heidi at pD 3 (left) and pD 6 (right). T = 25 °C; I = not controlled; [UO$_2^{2+}$] = 5 mM; [H$_3$heidi] = 5n mM (where n = ratio).

The $^1$H NMR of H$_3$heidi shows three distinct environments at each pD studied. When H$_3$heidi is added to UO$_2^{2+}$ solution in a 1:1 ratio the spectra at pD 2 shows broadening but no change in chemical shift of signals suggesting only weak interactions between the ions. However, at pD 3, two new peaks are observed at 3.83, 4.13 ppm along with a broadened peak between 4.60 and 4.42 ppm suggesting complexation of Hheidi$^-$ to UO$_2^{2+}$. The shifting of all three signals implies tridentate coordination of Hheidi$^-$ to UO$_2^{2+}$ through the carboxylate and amine moieties with three signals suggesting that the carboxylate moieties are in different environments upon complexation.

As pD is increased to 6, the complex peaks at 4.13 and 4.5 ppm in the 1:1 (M:L) solution become larger and more defined with an increase in complexation compared to pD 3. Complexation though terminal alcohol groups is not observed, analogous to similar ligands e.g. H$_3$tea (section 6.4) and H$_3$bic (section 6.5). At all pD investigated, “free” ligand signals are observed implying that an excess of H$_3$heidi is required to produce a 1:1 (M:L) speciation.
The pattern of spectra containing both complexed and uncomplexed H$_2$heidi$^-$ is observed until a precipitate is observed at pD 7.6 for the 1:1 (M:L) solution and pH 10 for 1:2 - 1:4 (M:L) solutions suggesting that two equivalents of H$_2$heidi$^-$ hinder hydrolysis to a greater extent than one. Uranyl becomes more soluble in solution when complexes to H$_2$heidi$^-$ as H$_2$heidi$^-$ has three atoms able to bind to uranyl introducing the chelate effect into complexes.

Potentiometric titrations were conducted on solutions containing various ratios of UO$_2^{2+}$ and H$_3$heidi (Figure 6-16).

![Diagram](image_url)

**Figure 6-18:** Potentiometric titrations of UO$_2^{2+}$ and H$_3$heidi solutions in varying ratios. T = 25 °C; I = 0.5 (NaNO$_3$); $V_s$ = 20 mL; $[H_3heidi]_i$ = 5 mM; $[UO_2^{2+}]_i$ = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.

Initially, the pH of binary solutions was lower than their individual counterparts, indicating complexation of H$_3$heidi to UO$_2^{2+}$. Between pH 3 - 6 the 1:1 (M:L) trace displays an inflection akin to that observed in the UO$_2^{2+}$ solution due to the release of protons upon hydrolysis. The inflection for the 1:1 (M:L) curve is narrower than for UO$_2^{2+}$, as fewer moles of NaOH are required to increase pH and the complexation of H$_3$heidi$^-$ to UO$_2^{2+}$ blocks a number of coordination sites around the uranyl ion hindering hydrolysis. Precipitation is observed at pH 7.8. Solutions containing a 1:2 and 1:3 (M:L) ratio show a lesser inflection within the pH 3 - 6 region. $^1$H NMR spectral data show that two
equivalents of $H_3$heidi are required to produce a 1:1 (M:L) complex. The increased coordination of HHeidi$^{2-}$ molecules reduces the number of coordination sites at which hydrolysis can occur, so fewer protons are released than the 1:1 (M:L) and $UO_2^{2+}$ profiles. The inflection between pH 8 - 9 is due to the deprotonation of the amine.

UV-Vis spectra of $UO_2^{2+}$ and $H_3$heidi solutions at selected pH are shown in Figure 6-19, remaining spectra are located in Appendix 3.2.

Figure 6-19: UV-Vis spectra of $UO_2^{2+}$ and $H_3$heidi at pH 3 and 6 (left) and pH 7 and 8 (bottom). $T = 25 \ ^\circ C$; $I = 0.5$ (NaNO$_3$); $[H_3$heidi$]_i = 10n$ mM, $[UO_2^{2+}]_i = 10$ mM (n = ratio); Titrant = 0.1/0.5 M NaOH.
At pH 3 the characteristic uranyl vibrational pattern is visible in the UV-Vis spectrum of 1:1 - 1:4 (M:L) solutions. The $\lambda_{\text{max}}$ is red shifted from 414 to 418 nm in the presence of H$_3$heidi suggesting complexation. There is a minor shift of 1 nm with the second equivalent of H$_3$heidi, but with no additional shift in the UV-Vis spectra, no further complexation takes place. A similar pattern is shown through to pH 5, with broadening of the uranyl signal.

At pH 6 the 1:1 (M:L) solution displays less of a broadening along with a blue shift from 427 to 420 nm in relation to the uranyl band. The 1:1 (M:L) band does not display a shoulder between 465-500 nm present in the uranyl spectra, suggesting that heidi has prevented hydrolysis to (UO$_2$)$_3$(OH)$_4^{+}$ and (UO$_2$)$_3$(OH)$_7^{-}$\textsuperscript{6,7,9} The UV-Vis bands do not alter when two or more equivalents of H$_3$heidi are in solution with UO$_2^{2+}$ meaning the second equivalent does not interact with UO$_2^{2+}$.

At pH 7, vibrational modes of uranyl are observed in the binary solutions with the $\lambda_{\text{max}}$ remaining at 420 nm as observed at lower pH. However, there is a broadening of the band with an increase in intensity. The $\varepsilon_{\text{max}}$ of the 1:1 (M:L) solution at a lower intensity in comparison to the higher equivalent solutions. Precipitation of the 1:1 (M:L) solution occurs at pH 7.4 with precipitation of the 1:2-1:4 (M:L) solutions occurring at pH 10.1 suggesting the 1:1 (M:L) it is not as stable to hydrolysis and precipitation as the 1:2 system. The increase in solubility of uranyl in solution with two equivalents of H$_3$heidi correlates with $^1$H NMR spectral data implying that an excess of H$_3$heidi is required to form a 1:1 (M:L) species. A polymeric species is likely with H$_3$heidi$^-$ bridging metal ions and inhibiting the onset of hydrolysis.

The precipitates produced in the UV-Vis experiments were filtered and washed with the resulting solid was analysed by IR spectroscopy (Figure 6-20). All solids contain an O-H stretch, an N-O stretch and a C=O stretch. The C=O stretch is red shifted by 83 cm$^{-1}$ in all three uranyl solids insinuating that H$_2$heidi$^-$ is bound to uranyl in all three. The N-O stretch is shifted by 3 cm$^{-1}$ in the 1:1 (M:L) precipitate and 6 cm$^{-1}$ in the 1:2 and 1:3 (M:L) precipitates. Although the shift is small, it suggests complexation of NO$_3^-$ to uranyl. Finally the UO$_2$ symmetric stretch is located at 989 cm$^{-1}$ in the 1:1 (M:L) precipitate and 884 cm$^{-1}$ in the 1:2 and 1:3 (M:L) precipitates suggesting two different complexes.
Figure 6-20: IR spectra of precipitates from 1:1 (red), 1:2 (blue) and 1:3 (green) UO$_2^{2+}$:H$_3$heidi solutions, NaNO$_3$ (purple) and H$_3$heidi (black).

Elemental analysis of the precipitates suggests that organic material is present in the solid with ligand equivalents of 0.8 - 2.4 calculated from the U:C ratio found. Hydroxides and nitrate groups are also incorporated into the solid but the absolute speciation could not be calculated. The wide range of results for samples suggests that there is a mixture of hydrolysis species present in the precipitates.

### 6.7 Speciation of UO$_2^{2+}$ with H$_3$NTA

Figure 6-21 shows potentiometric titration data of UO$_2^{2+}$ with various quantities of H$_3$NTA when titrated with 0.1 M NaOH. The UO$_2^{2+}$ solutions containing H$_3$NTA were initially at a lower pH in comparison to the individual counterparts due to the release of protons upon complexation.
The pronounced inflection between pH 5 - 6 in the 1:1 and 1:2 (M:L) solutions is due to the release of protons from hydrolysis reactions. This commences at a higher pH when NTA$^{3-}$ is a complexant in uranyl solution then when uranyl is alone in solution (pH 4 – 5) as the complex formed is more stable to hydrolysis in comparison to a pentaaqua uranyl complex.

When the concentration of H$_3$NTA doubles the inflection at pH 5 halves with fewer protons released suggesting complexation of a second equivalent of H$_3$NTA and fewer sites available for hydrolysis on the uranyl ion. The second inflection between pH 9 - d 12 is due to the deprotonation at the amine of the zwitterion forming the NTA$^{3-}$ anion. This suggests that at pH < 8, the uranyl complex with HNTA$^{2-}$ is protonated at the central nitrogen. Precipitation was observed at pH 5.2 and 9.5 in the 1:1 and 1:2 (M:L) solutions respectively.

This data were fitted into a model with Hyperquad software including pK$_a$ values determined previously for H$_3$NTA (Table 3-4) and uranyl (Table 6-1). The fits for the 1:1 and 1:2 (M:L) systems are displayed in Figure 6-22 and Figure 6-23 with calculated formation constant values displayed in Table 6-2.
**Figure 6-22:** Potentiometric titration of a 1:1 $\text{UO}_2^{2+}:\text{H}_3\text{NTA}$ solution modelled in Hyperquad. $T = 25\ ^\circ\text{C}; I = 0.5$ (NaNO$_3$); $[\text{H}_3\text{NTA}]_i = 5$ mM; $[\text{UO}_2^{2+}]_i = 5$ mM.

**Figure 6-23:** Potentiometric titration of a 1:2 $\text{UO}_2^{2+}:\text{H}_3\text{NTA}$ solution modelled in Hyperquad. $T = 25\ ^\circ\text{C}; I = 0.5$ (NaNO$_3$); $[\text{H}_3\text{NTA}]_i = 5$ mM; $[\text{UO}_2^{2+}]_i = 2.5$ mM.
Table 6-2: Calculated and literature formation constants of $\text{UO}_2^{2+}$–$\text{H}_3\text{NTA}$ species. The ratio of $\text{UO}_2^{2+}$–$\text{H}_3\text{NTA}$–$\text{H}^+$ is denoted as 1,1,0 and 1,1,1 etc.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Calc. log $\beta$, 1:1 sol, $I = 0.5$ (NaNO$_3$), 25 °C</th>
<th>Calc. log $\beta$, 1:2 sol, $I = 0.5$ (NaNO$_3$), 25 °C</th>
<th>Lit$^4 I = 0.7$ (NaCl), 25 °C</th>
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<td>2.620 ± 0.4</td>
<td>2.510 ± 0.5</td>
<td>2.390 ± 0.04</td>
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</tbody>
</table>

The model fits are good with formation constants calculated in this work in agreement with those reported in literature suggesting their reliability. Other hydrolysis species such as $(\text{UO}_2)(\text{NTA})(\text{OH})_2^{3-}$, $(\text{UO}_2)(\text{HNTA})_2^{2-}$ and $(\text{UO}_2)_2(\text{HNTA})_2$ did not improve the model with refinements unable to converge with their incorporation.

The speciation diagrams of $\text{H}_3\text{NTA}$-uranyl species in the presence of $\text{H}_3\text{NTA}$ using the calculated formation constants in Table 6-2 are displayed in Figure 6-24 and Figure 6-25 for 1:1 and 1:2 (M:L) ratios respectively and are similar to those reported by De Stefano et al.$^{16}$

Figure 6-24: Speciation diagram for uranyl-NTA species in a 1:1 $\text{UO}_2^{2+}$–$\text{H}_3\text{NTA}$ aqueous solution. The ratio of $\text{UO}_2^{2+}$–$\text{H}_3\text{NTA}$–$\text{H}^+$ is denoted as 1,1,1 and 1,1,0 etc. $T = 25$ °C; $I = 0.5$ (NaNO$_3$); [H$_3$NTA] = 5 mM; [UO$_2^{2+}$] = 5 mM.
Figure 6-25: Speciation diagram for uranyl-NTA species in a 1:2 \(\text{UO}_2^{2+}:\text{H}_3\text{NTA} \) aqueous solution. The ratio of \(\text{UO}_2^{2+}:\text{H}_3\text{NTA} : \text{H}^+\) is denoted as 1,1,1 and 1,1,-1 etc. \(T = 25 \, ^\circ\text{C}; I = 0.5 \, (\text{NaNO}_3)\); \([\text{H}_3\text{NTA}] = 5 \, \text{mM}; [\text{UO}_2^{2+}] = 2.5 \, \text{mM}\).

The 1,1,1 and 1,1,-1 (M, L, H) species are in appreciable amounts in both speciation diagrams. As precipitation is observed at a higher pH in the 1:2 (M:L) solution, it is implied that excess \(\text{H}_3\text{NTA}\) is required to form 1:1 (M:L) speciation corroborating \(^1\text{H}\) NMR spectral data. This trait has previously been observed previously by De Stefano et al. however potentiometric titrations and subsequent models predicted the formation of \((\text{UO}_2)_2(\text{OH})_2^{2+}\) rather than the \((\text{UO}_2)_3(\text{OH})_5^{4-}\) species predicted in this work.\(^6\) This is most likely due to differences in uranyl concentrations ([\(\text{U}\)]\(_T\) = 0.5 mM compared to 2.5 - 5 mM in this work).

Data from the 1:1 and 1:2 (M:L) potentiometric titrations were input into PHREEQC to compare the results obtained above to those predicted by the SIT database. The speciation profile was the same for both solutions and is displayed in Figure 6-26. Only the results using the SIT database are shown as both LLNL and Hatches-20 databases did not predict complexation with \(\text{H}_3\text{NTA}\).
Figure 6-26: Speciation diagram of 1:1 and 1:2 $\text{UO}_2^{2+}$:$\text{H}_2\text{NTA}$ solutions generated using PHREEQC and the SIT database. The ratio of $\text{UO}_2^{2+}$:$\text{H}_2\text{NTA}$:$\text{H}^+$ is denoted as 1,1,1 and 1,2,-1 etc.

At pH 4 - 6, the SIT database predicts a $(\text{UO}_2)(\text{NTA})^-$ species whereas in experiments the protonated form $(\text{UO}_2)(\text{HNTA})$ is observed. Thuéry et al. studied single crystal XRD data obtained on a sample that grew under hydrothermal conditions and detected tridentate complexation of the ligand with the amine in the protonated form, $(\text{UO}_2)(\text{HNTA})$. This implies that this could occur in this work. At pH > 6 the SIT database does not include any hydroxide species of the uranyl-NTA complex. This absence shows that there are a number of missing species within the SIT database which needs to be resolved. Predictions using Hatches-20 and LLNL databases yielded no evidence of complexation to $\text{H}_2\text{NTA}$ with the ligand remaining unbound in solution. This does not match experimental data in this work or in literature reports and shows the gaps within the databases which need addressing.

$^1\text{H}$ NMR spectroscopy was performed on deuterated aqueous uranyl solutions with various quantities of $\text{H}_2\text{NTA}$ over a pH range 2 - 10. Selected spectra are shown in Figure 6-28 with remaining spectra found in Appendix 3.5.
Figure 6-27: Structure of H$_3$NTA with $^1$H atom labels.

Figure 6-28: Stacked $^1$H NMR spectra of UO$_2^{2+}$ and H$_3$NTA at pD 2 (top left), pD 5 (top right), pD 7 (bottom left) and pD 8 (bottom right). T = 25 °C; I = not controlled; [UO$_2^{2+}$] = 5 mM; [H$_3$NTA] = 5n mM (where n = ratio).
The $^1$H NMR spectra of the 1:1 (M:L) solution at pH 2 shows a downfield shift in the “free” signal of H$_3$NTA from 3.8 ppm to 3.34 ppm suggesting complexation. At pH 5, the spectrum displays a signal at 4.6 ppm again implying complexation of HNTA$^{2-}$ to UO$_2^{2+}$. When the concentration of H$_3$NTA doubles (the 1:2 M:L solution) the signal is broadened hugely due to averaging of bound and unbound ligand signals. As the concentration of H$_3$NTA is increased further (in the 1:3 and 1:4 M:L solutions) the signal shifts to 3.8 ppm with a weak broadened signal detected between 4.7 and 4.3 ppm suggesting that “free” ligand is at a much higher concentration than complexed ligand when there are greater than two equivalents in solution and the presence of a 1:1 (M:L) speciation of UO$_2^{2+}$ and HNTA$^{2-}$ as predicted in Hyperquad models.

At pH 7, the averaging of the signals ceases with a distinct species at 4.4 ppm observed along with unbound ligand at 3.7 ppm. Increasing the pH to 7 also increases the complexation of hydroxide. As both bound and unbound signals are observed it is likely that hydroxide outcompetes the HNTA$^{2-}$ for binding resulting in two bound carboxylate arms and an unbound arm. $^1$H NMR spectroscopy has failed to identify whether binding occurs through the amine as well as the carboxylate moieties, further investigations with $^{15}$N NMR spectroscopy would clarify this.

The UV-Vis spectra of uranyl and H$_3$NTA solutions (Figure 6-29) correlate to the $^1$H NMR spectra. At pH 2, a shift in the $\lambda_{\text{max}}$ from 414 nm in the UO$_2^{2+}$ solution to 416 nm in the 1:1 (M:L) solution suggests complexation. As pH is increased to 6, complex formation is again evident as spectra of binary solutions a distinct uranyl vibrational pattern. The absence of the band between 466 - 500 nm observed in uranyl spectra suggests a less hydrolysis when NTA$^{3-}$ is complexed to UO$_2^{2+}$ in comparison to that of uranyl. The spectra of binary solutions so not change upon increasing concentrations of H$_3$NTA suggesting 1:1 (M:L) speciation.
When pH is increased to 7, a shoulder at 480 nm is observed to the right of the major UO$_2^{2+}$ band in the 1:1 (M:L) spectrum due to the complexation of hydroxide to the uranyl complex. This correlates to the calculated formation constant values (Table 6-2) and
subsequent speciation diagrams (Figure 6-24 and Figure 6-25) in this work. As the \( \lambda_{\text{max}} \) does not shift from 421 nm at higher pH values it is therefore associated with the \( \text{UO}_2(\text{NTA})(\text{OH})^{2-} \) species.

The precipitates formed in UV-Vis spectroscopic experiments were washed and dried for solid state characterisation. The IR spectra of precipitates from the 1:1 and 1:2 (M:L) experiments (Figure 6-30) display an OH stretch implying the incorporation of hydroxide groups and/or water molecules in the solid and there is no evidence of an N-O stretch for uranyl precipitate implying the species does not contain nitrates. The C=O stretch of the carboxylate moiety is shifted from 1706 cm\(^{-1}\) for \( \text{H}_3\text{NTA} \) to 1625 cm\(^{-1}\) in the precipitates suggesting complexation to uranyl. Both precipitates show a uranyl stretch at 920 cm\(^{-1}\) shifted from 833 cm\(^{-1}\) in a uranyl hydroxide solid due to complexation of \( \text{UO}_2^{2+} \) to \( \text{H}_3\text{NTA} \).

It was not possible to crystallise precipitates as they were insoluble in organic solvents. This has been reported previously by Thuéry et al. who was ultimately able to generate crystals suitable for XRD analysis by the hydrolysis of ADA in uranyl solutions under hydrothermal conditions.\(^{17}\) Solid samples produced in this work underwent elemental analysis confirming complexation of \( \text{NTA}^{3-} \) to \( \text{UO}_2^{2+} \). Results showed various ratios of M:C which calculated M:L ratios of \( 1:0.9 - 1:1.2 \) equivalents of ligand along with excess
nitrogen and sodium suggesting multiple species are present in the precipitate. Calculations to predict solution species of a solution of uranyl and H₂NTA were calculated using PHREEQC software and the SIT database (Figure 6-26). The absolute speciation of the precipitates was unable to be calculated. Saturation indices were also calculated with precipitation of U₂O₇Na₂ and UO₂(OH)₂ predicted at pH 6.3. There is no predicted solid which contains NTA at any pH contrasting solid state data and presenting a gap in the databases.

### 6.8 Speciation of UO₂²⁺ with H₂ADA

Potentiometric titrations were performed whereby solutions of uranyl and H₂ADA at various ratios were titrated against 0.1 M NaOH solution, all at I = 0.5. The curves are shown in Figure 6-31.

![Figure 6-31: Potentiometric titrations of UO₂²⁺ and H₂ADA solutions in varying ratios. T = 25 °C; I = 0.5 (NaNO₃); V₀ = 20.0 mL; [H₂ADA] = 5 mM, [UO₂²⁺] = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.](image)

Initially, the pH of 1:1 and 1:2 (M:L) solutions were lower than the individual counterparts implying complexation. The 1:1 (M:L) trace displays an inflection between pH 3 - 8 due to the release of protons. This overlaps with the regions of hydrolysis in the uranyl curve and amine deprotonation in the H₂ADA curve suggesting that both of these process cause the inflection. Complexation of H₂ADA to UO₂²⁺ leaves fewer sites for hydrolysis to occur,
hence fewer protons are released. The 1:2 (M:L) curve shows no such hydrolysis step implying that with two ADA\(^2^-\) anions complexed to the UO\(^{2+}\) metal centre hydrolysis is hindered in acidic conditions. The step between pH 6 - 8 represents the loss of protons from the deprotonation of the amine and hydrolysis of the complex.

Deuterated aqueous solutions containing various ratios of UO\(^{2+}\) and H\(_2\)ADA were analysed by \(^1\)H NMR spectroscopy at multiple pD. The labelled structure of H\(_2\)ADA is shown in Figure 6-32, selected spectra in Figure 6-33 and remaining spectra can be found in Appendix 3.4.

![Figure 6-32: Structure of H\(_2\)ADA with \(^1\)H atom labels.](image)
Figure 6-33: Stacked $^1$H NMR spectra of $\text{UO}_2^{2+}$ and $\text{H}_2\text{ADA}$ at pD 2 (top left), pD 4 (top right), pD 7 (bottom left) and pD 10 (bottom right). $T = 25 \, ^\circ\text{C}$; $I$ not controlled, $[\text{UO}_2^{2+}] = 5 \, \text{mM}$; $[\text{H}_2\text{ADA}] = 5n \, \text{mM (where n = ratio)}$. 

$\text{UO}_2^{2+}: \text{H}_2\text{ADA}$ 1:5

$\text{UO}_2^{2+}: \text{H}_2\text{ADA}$ 1:4

$\text{UO}_2^{2+}: \text{H}_2\text{ADA}$ 1:3

$\text{UO}_2^{2+}: \text{H}_2\text{ADA}$ 1:2

$\text{UO}_2^{2+}: \text{H}_2\text{ADA}$ 1:1

$\text{H}_2\text{ADA}$

$\text{H}_2\text{ADA}$
The spectra of 1:1 (M:L) solutions display broadened compared to that of the free ligand. At pH 2 the H2 signal shifts downfield by 0.3 ppm but the H1 signal does not incur a shift indicating that binding is through the carboxylate moieties only. As pH increases to pH 4 both signals incur a shift to 4.43 and 4.52 from 3.82 and 4.13 in H2ADA for H2 and H1 respectively. This suggests tridentate complexation through the carboxylate and amine moieties (NOO complexation) which has been reported for numerous TM and lanthanide ions (including CoII, NiII, ZnII, EuII, DyII and PrII).\textsuperscript{18-21} Potentiometric data shows deprotonation of the amine occurs between pH 6 and 7 in uranyl solution implying that at pH 4 the amine remains protonated as a zwitterion (HADA\textsuperscript{−}). The downfield shift of both signals when in solution with uranyl continues until pH 8 when precipitation commences.

At each pH there is a broadening of signals in the 1:2 (M:L) solution due to an averaging between bound and unbound ligands. When the concentration of H2ADA is increased further, “free” ligand signals increase suggesting excess ligand is present. It is acknowledged that five water molecules coordinate to uranyl (Table 1-3). As HADA\textsuperscript{−} is tridentate then two coordinated molecules will be 6-coordinate, with broadened signals in the spectra it is more likely that the complex contains one bound and one partially bound HADA\textsuperscript{−} molecule which has the potential to bridge to another uranyl ion forming polymeric arrays with some functional groups remaining unbound. DOSY experiments were conducted on solutions at multiple pH and various ligand concentration. For the 1:1 and 1:2 (M:L) solutions, no cross peaks were observed at any pH suggesting the species are polymeric.

The increased stability when two ligands are in solution with uranyl is observed when precipitation of a yellow solid commences at pH 8.4 in the 1:1 (M:L) system and pH 10.2 in systems containing higher concentrations of ligand.

Selected UV-Vis spectra of solutions of uranyl and H2ADA at multiple ratios are shown in Figure 6-34 with remaining spectra displayed in Appendix 3.4.
At pH 2, there is a shift in $\lambda_{\text{max}}$ from 413.2 nm to 415.8 nm in the 1:1 (M:L) solution and to 148.6 nm in 1:2 - 1:4 (M:L) solutions implying complexation of HADA$^-$ to UO$_2^{2+}$. At pH 6 the $\lambda_{\text{max}}$ shifts from 427.8 nm for UO$_2^{2+}$ to 420.8 nm in the 1:1 (M:L) solution and to 433.8 nm in the 1:2 – 1:4 (M:L) solutions. These shifts show the difference in speciation upon the addition of H$_2$ADA to UO$_2^{2+}$ and implies the interaction of a second ligand with UO$_2^{2+}$ corroborating $^1$H NMR results.
As pH increases to 8 the spectra of all binary solutions containing more than two equivalents of H$_2$ADA show the vibrational pattern of uranyl as hydrolysis is hindered. In the 1:1 (M:L) solution a precipitate is observed at pH 7.6, consequently the spectrum at pH 8 is not shown. When two or more equivalents of H$_2$ADA are in solution, the profile of the spectra do not alter as pH increases; the same vibrational modes of uranyl are evident for all. Precipitation is observed at pH 8.3 for solutions containing two or more equivalents of H$_2$ADA displaying the increase in solubility compared to UO$_2$$^{2+}$ and the 1:1 (M:L) solution. These observations imply that 2 equivalents of H$_2$ADA complex to uranyl.

Solids resulting from potentiometric titrations were filtered and washed for solid state characterisation. IR spectroscopy show weak bands at 1530, 1600 and 1650 cm$^{-1}$ corresponding to a C=O (COO$^-$) stretch, N-H (amide) bend and C=O (amide) stretch respectively (Figure 6-35). The carboxylate stretch is shifted to lower frequencies than in the “free” ligand indicating complexation to uranyl ions with the N-O stretch insinuating the presence of nitrate groups. The uranyl stretch is located at 933 cm$^{-1}$ in the precipitate, shifted from 833 cm$^{-1}$ in uranyl hydroxide precipitate also suggesting complexation.

**Figure 6-35:** IR spectrum of the precipitate from a 1:1 UO$_2$$^{2+}$:H$_2$ADA solution (blue),NaNO$_3$ (red) and H$_2$ADA (black).

Elemental analysis conducted on solid precipitates containing various molar ratios of UO$_2$$^{2+}$ and H$_2$ADA suggest multiple species are present. Results were varied with some
precipitates calculate two HADA\textsuperscript{−} molecules binding to uranyl ions whereas other calculate 1.3 and 1.5 equivalents of HADA\textsuperscript{−} from the U:C ratio. This suggests that between 1 and 2 molecules of HADA\textsuperscript{−} complex to UO\textsubscript{2}\textsuperscript{2+} with the possibility of bridging HADA\textsuperscript{−} molecules and hence the formation of polymeric species.

6.9 Speciation of UO\textsubscript{2}\textsuperscript{2+} with H\textsubscript{3}cit

There have been many reports investigating the complexation of citric acid with uranyl ions. The majority have characterised UO\textsubscript{2}(cit)\textsuperscript{−} and (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}\textsuperscript{2−}, both in the solution and solid state at ~ pH 1 and 1.8 respectively. The same species have been identified in solutions containing 0.005 - 0.1 M uranyl with I = 0 - 1 using multiple electolytes.\textsuperscript{22-26} The (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}\textsuperscript{2−} species in particular has been extensively studied with bonding through the alcohol and carboxylate moieties of citric acid.\textsuperscript{22,27,28} At higher pH many trimeric and hexameric species have been proposed including a 3,3,\textsuperscript{26,29} a 3,2\textsuperscript{30} and a 6,6 UO\textsubscript{2}\textsuperscript{2+}:Hscit species.\textsuperscript{26} Single crystals of [(UO\textsubscript{2})(cit)]\textsubscript{n} stabilised by bipy (4,4’-bipyridine) and DABCO (1,4-diazabicyclo[2.2.2]octane) which were suitable for X-ray Diffraction (XRD) spectroscopy were produced using hydrothermal techniques showing the extended H-bonded network of citric acid.\textsuperscript{28}

Hydrolysis of uranyl also leads to the formation of uranyl-citrate-hydroxides. Many hydrolysis species have been identified in multiple literature sources which use various techniques. Proposed hydroxide species which have been suggested in numerous literature sources include UO\textsubscript{2}(cit)(OH)\textsuperscript{2−}, (UO\textsubscript{2})\textsubscript{2}(cit)(OH)\textsubscript{2}\textsuperscript{4−} and (UO\textsubscript{2})(Hcit)(OH)\textsubscript{2}\textsuperscript{3−} in solutions with uranyl ion concentrations ranging from 1 - 200 mM and I = 0.1 - 1 with NaCl and NaClO\textsubscript{4}.\textsuperscript{30-33} Other species such as (UO\textsubscript{2})\textsubscript{3}(cit)\textsubscript{3}\textsuperscript{−} and (UO\textsubscript{2})\textsubscript{6}(cit)\textsubscript{6}(OH)\textsubscript{10}\textsuperscript{16−} have been reported on fewer occasions (uranyl concentrations of 0.2 - 1 mM and I = 0.1 - 1 NaClO\textsubscript{4} and NaCl) but their presence cannot be overlooked.\textsuperscript{26,34} It is reasonable to assume that under different conditions other species may be present due to the complexities of hydrolysis. Therefore other possible trinuclear and polynuclear species may also be present.

Potentiometric titrations were performed on solutions containing various molar ratios of UO\textsubscript{2}\textsuperscript{2+} and H\textsubscript{3}cit with results shown in Figure 6-36 alongside comparisons to uranyl and NaNO\textsubscript{3}.
Figure 6-36: Potentiometric titrations of UO$_2^{2+}$ and H$_3$cit solutions in varying ratios. T = 25 °C; I = 0.5 (NaNO$_3$); V$_0$ = 20.0 mL; [H$_3$cit]$_i$ = 5 mM; [UO$_2^{2+}$]$_i$ = 5/n mM (n = ratio); Titrant = 0.1 M NaOH.

Both the 1:1 and 1:2 (M:L) solutions have a lower pH than their individual counterparts due to the release of protons upon complexation. The inflection between pH 3 - 5 is lessened compared to that of uranyl as fewer hydroxides bind to uranyl when it is complexed to H$_3$cit. The stability of the complex is evident by the absence of precipitate at pH < 6 as observed in UO$_2^{2+}$ solution.

Hyperquad models were fitted to experimental 1:1 and 1:2 (M:L) potentiometric data and included the calculated uranyl formation constants (Table 6-1) and pK$_a$ values for citric acid (Table 3-6). Once these values had refined, species which have been reported in literature were added and refinement attempted, these include (UO$_2$)$_2$(cit)$_2$$_2^-$, (UO$_2$)$_2$(cit)(OH) and (UO$_2$)$_3$(cit)$_2$(OH)$_5$$. The Hyperquad model fits are shown in Figure 6-37 and Figure 6-38 with calculated formation constant values in Table 6-3.
Figure 6-37: Potentiometric titration of a 1:1 UO$_2$$^{2+}$:H$_3$cit solution modelled in Hyperquad. T = 25 °C; I = 0.5 (NaNO$_3$); $V_0$ = 20.05 mL; [UO$_2$$^{2+}$]$_i$ = 5 mM; [H$_3$cit]$_i$ = 5 mM; Titrant = 0.1 M NaOH.

Figure 6-38: Potentiometric titration of a 1:2 UO$_2$$^{2+}$:H$_3$cit solution modelled in Hyperquad. T = 25 °C; I = 0.5 (NaNO$_3$); $V_0$ = 20.05 mL; [UO$_2$$^{2+}$]$_i$ = 2.5 mM; [H$_3$cit]$_i$ = 5 mM; Titrant = 0.1 M NaOH.
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<td>6.917 ± 1.5</td>
<td></td>
<td>3.62 ± 0.06</td>
<td>5.30 ± 0.011</td>
<td></td>
</tr>
<tr>
<td>2,2,-1</td>
<td>17.14 ± 1.1</td>
<td></td>
<td>14.05 ± 0.03</td>
<td>16.04 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>2,2,-2</td>
<td>11.31 ± 1.1</td>
<td></td>
<td>8.87 ± 0.01</td>
<td>9.29 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>3,2,-5</td>
<td>-2.198 ± 1.5</td>
<td>-2.201 ± 1.1</td>
<td>-0.92 ± 0.03</td>
<td>-1.53 ± 0.06</td>
<td></td>
</tr>
</tbody>
</table>

Table 6-3: Calculated and literature formation constants of \( \text{UO}_2^{2+} \)-citric acid species. The ratio of \( \text{UO}_2^{2+}:\text{H}_3\text{cit}:+\text{H}^+ \) is denoted is 1,1,1 and 1,2,-2 etc.

The model for the 1:1 (M:L) experiment did not include the \((\text{UO}_2)_2(\text{cit})_2(\text{OH})_3^3^\) or \((\text{UO}_2)_2(\text{cit})_2(\text{OH})_2^{4+}\) species as their inclusion worsened the model fit and the 1:2 (M:L) model excluded the \((\text{UO}_2)_2(\text{cit})(\text{OH})\) and \((\text{UO}_2)_2(\text{cit})(\text{OH})_2^-\) species as they did refine in the model. As the only difference in the solutions is the ratio, the difference in species must be due to a concentration effect. The incorporation of any additional species (e.g. \((\text{UO}_2)_3(\text{cit})_3^{3+}\), \((\text{UO}_2)_6(\text{cit})_6^{6+}\), \((\text{UO}_2)(\text{Hcit})\) and \((\text{UO}_2)(\text{H}_2\text{cit})^+\) to name a few) did not improve the statistical parameters of either model with a convergence of values not achieved. This is due to the possibly that there are much larger polymeric species in solution with models described here being idealised. Values reported here are slightly higher than those in literature; this could be due to the use of different ions for the electrolyte having a different stabilising effect upon the species formed.

The speciation diagrams for the 1:1 and 1:2 (M:L) systems are shown in Figure 6-39 and Figure 6-40 respectively. Species maxima correlate well with those reported by Bailey et al. at pH 0 - 2 ([U]_T = 0.05 - 0.1 M, I = not controlled),\(^25\) Berto et al. at pH 2 - 7 ([U]_T = 0.04 - 0.1 M, I = 0.1 KNO\(_3\))\(^30\) and Pasilis et al. at pH 4 - 12 ([U]_T = 0.1 M, I = not controlled).\(^32\)
Speciation diagrams were predicted in PHREEQC using conditions obtained in potentiometric experiments to allow comparisons with this work. However, neither the LLNL nor SIT databases predict complexation of $\text{UO}_2^{2+}$ with $\text{H}_3\text{cit}$. The predicted species using the Hatches-20 database are shown in Figure 6-41 and are the same for the 1:1 and 1:2, 1:3, etc.
1:2 (M:L) solutions. At pH < 7, most uranyl is complexed as \((\text{UO}_2)^2_2(\text{cit})^2_2\) similar to the experimental data. However, at pH > 7 complexation of \(\text{UO}_2^{2+}\) with \(\text{H}_3\text{cit}\) is not predicted with no prediction of uranyl hydrolysis species either. Experimentally, complexes containing uranyl, citrate and hydroxides were modelled and this difference highlights the need for further investigations and updates to databases.

![Figure 6-41: Speciation diagram for \(\text{UO}_2^{2+}\):\text{H}_3\text{cit}\) species in 1:1 and 1:2 \(\text{UO}_2^{2+}:\text{H}_3\text{cit}\) aqueous solutions generated in PHREEQC using the Hatches-20 database. The ratio of \(\text{UO}_2^{2+}:\text{H}_3\text{cit}:\text{NO}_3^-:\text{H}^+\) is denoted as 1,1,0,1 and 1,2,0,-1 etc.](image)

\(^1\text{H}\) NMR spectroscopy was performed on deuterated solutions of \(\text{UO}_2^{2+}\) and \(\text{H}_3\text{cit}\) at multiple pD. Spectra at pD 3 and 10 are shown in Figure 6-42 with other spectra found in Appendix 3.7.
Figure 6-42: Stacked $^1$H NMR spectra of UO$_2^{2+}$ and H$_3$cit at pH 3 (top) and pH 10 (bottom). T = 25 °C; I = not controlled; [UO$_2^{2+}$] = 5 mM; [H$_3$cit] = 5n mM (where n = ratio).

The $^1$H NMR spectrum of the 1:1 (M:L) solution at pH 3 shows a shift in all proton signals to 2.36, 3.24 - 3.87 and 5.58 ppm. The absence of “free” ligand signals implies that all H$_3$cit in solution is complexed to UO$_2^{2+}$. The signals are much broader than those in the “free” ligand NMR spectrum suggesting the possibility of multiple species in which citric acid has similar symmetry, i.e. the ligands are bound to metal in the same manner (e.g. cit$_3^-$ bound to one or more metal centres). In spectra of 1:2 (M:L) solutions “free” ligand
signals are observed suggesting a 1:1 speciation of UO$_2^{2+}$ and cit$^{3-}$. This correlates with model data previously fitted (Table 6-3).

At pH 9 the “free” ligand signals are displayed along with complex signals shifted at around 3.5 ppm. Both speciation diagrams from Hyperquad calculations (Figure 6-39 and Figure 6-40) imply that the (UO$_2$)$_2$(cit)$_2$(OH)$_5^{5-}$ is the dominant species between pH 9 - 13, therefore for every two complexed citric acid ligands there will be one uncomplexed ligand. The $^1$H NMR spectral data resembles the speciation diagrams. There have been few literature reports of NMR spectroscopy with uranyl-citric acid systems but to date the signals relating to individual complexes identified by potentiometric titrations have not been resolved.$^{29}$

UV-Vis spectroscopy was conducted on solutions containing various ratios of UO$_2^{2+}$ and H$_3$cit. Selected UV-Vis spectra are shown in Figure 6-43 with remaining spectra displayed in Appendix 3.7.

At pH 3 there is a shift in the $\lambda_{\text{max}}$ of the uranyl band from 414 nm in the UO$_2^{2+}$ solution to 434 nm in the 1:1 (M:L) solution. The increase of intensity ($\varepsilon_{\text{max}}$) in the presence of citric acid confirms complexation of cit$^{3-}$ to UO$_2^{2+}$ and relates to species predicted in the Hyperquad model (Table 6-3). There is no further shift for $\lambda_{\text{max}}$ or $\varepsilon_{\text{max}}$ upon the addition of more than one equivalent of citric acid implying a 1:1 speciation of UO$_2^{2+}$ and H$_3$cit.
The distinct uranyl vibration spectrum is visible in spectra of binary solutions up to pH 5 compared to pH 3 for uranyl suggesting complexation hinders hydrolysis. At pH > 6 the spectra of binary solutions show a loss of the vibrational structure with a broad band observed. This is characteristic of hydrolysis and the presence of hydroxide in the uranyl-
citrate complex. The UV-Vis spectra of UO\(_2^{2+}\) and H\(_3\)cit have been reported on a few occasions but the deconvolution of bands in relation to individual species is still largely unknown with the majority of reports excluding hydroxide species.\(^{26,30,33}\) Table 6-4 lists the literature \(\lambda_{\text{max}}\) of predicted solution species with multiple species producing very similar values making their identification problematical. The reported species are the same as the species modelling in potentiometric data in Hyperquad advocating their use.

<table>
<thead>
<tr>
<th>UO(_2^{2+}):H(_3)cit:H(^+)</th>
<th>1,1,0</th>
<th>2,2,0</th>
<th>2,2,-1</th>
<th>2,2,-2</th>
<th>3,2,-5</th>
<th>2,1,-1</th>
<th>2,1,-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\lambda_{\text{max}}) (nm)</td>
<td>436</td>
<td>435</td>
<td>436</td>
<td>440</td>
<td>440</td>
<td>426</td>
<td>441</td>
</tr>
</tbody>
</table>

Table 6-4: Literature \(\lambda_{\text{max}}\) values with their corresponding UO\(_2^{2+}\)-cit species.\(T = 25\) °C; \(I = 0.1 - 1\) \((\text{NaClO}_4)\); \([\text{H}_3\text{cit}]_i = 0.5\) - 50 mM, \([\text{UO}_2^{2+}]_i = 0.5\) - 20 mM. The ratio of UO\(_2^{2+}\):H\(_3\)cit:H\(^+\) is denoted as 1,1,1 and 1,2,-1 etc.\(^{26,30}\)

The \(\lambda_{\text{max}}\) of UV-Vis spectra recorded in this work are displayed in Table 6-5. Identification of species was done comparing the formation of uranyl species predicted in the Hyperquad model (Table 6-3) to those reported in literature for UV-Vis investigations (Table 6-4).

<table>
<thead>
<tr>
<th>pH</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>433.2</td>
<td>434.4</td>
<td>434.4</td>
<td>435.8</td>
<td>437.4</td>
<td>434.2</td>
<td>434.4</td>
<td>433.2</td>
<td>433.2</td>
<td>434.8</td>
</tr>
<tr>
<td>(\lambda_{\text{max}}) (nm)</td>
<td>434</td>
<td>434.4</td>
<td>434.6</td>
<td>435.8</td>
<td>338.2</td>
<td>439</td>
<td>439.2</td>
<td>439.2</td>
<td>439.2</td>
<td>432.4</td>
</tr>
</tbody>
</table>

Table 6-5: \(\lambda_{\text{max}}\) values obtained from the UV-Vis spectra of UO\(_2^{2+}\)-H\(_3\)cit solutions at various pH.\(T = 25\) °C; \(I = 0.5\) (NaNO\(_3\)); \([\text{H}_3\text{bic}]_i = 10n\) mM, \([\text{UO}_2^{2+}]_i = 10\) mM (n = ratio); Titrant \(= 0.1/0.5\) M NaOH

Between pH 2 - 6 the \(\lambda_{\text{max}}\) remains constant for 1:1 and 1:2 (M:L) solutions but at pH 2 the \(\varepsilon_{\text{max}}\) of the 1:1 (M:L) species is 2/3\(^{rd}\)s the value of the 1:2 – 1:4 (M:L) suggesting different complexes are present. These species correspond to the (UO\(_2\))\(_2\)(cit)(OH)\(^-\) species predicted for the 1:1 (M:L) solution and the (UO\(_2\))\(_2\)(cit)\(_2\)\(^2-\) species predicted for the 1:2 (M:L) solution in speciation diagrams to the species observed in UV-Vis spectroscopy. Between pH 3 - 5 both the \(\lambda_{\text{max}}\) and \(\varepsilon_{\text{max}}\) are constant for the 1:1 and 1:2 (M:L) solutions. In both cases hydrolysis has commenced with the formation of (UO\(_2\))\(_2\)(cit)\(_2\)\(^2-\) and related hydroxide species. This work supports that reported by Berto et al..\(^{30}\) The (UO\(_2\))\(_2\)(cit)\(_2\)\(^2-\) species has
been identified as the most stable form of uranyl citrate at pH < 5 so may have a stronger influence in the UV-Vis spectrum.\textsuperscript{31,32} The absence of a shoulder between 475 - 500 nm in binary solutions compared to uranyl solutions in the absence of organic ligands indicates the absence of uranyl hydrolysis species determined in Table 6-1.

The difference in the UV-Vis spectra between pH 6 - 9 is due to different species present in 1:1 and 1:2 (M:L) solutions. Again these can be attributed to the (UO\textsubscript{2})\textsubscript{2}(cit)\textsubscript{2}(OH)\textsubscript{2}\textsuperscript{3-} and (UO\textsubscript{2})\textsubscript{3}(cit)\textsubscript{2}(OH)\textsubscript{5}\textsuperscript{5-} species respectively which have been suggested in potentiometric studies (Table 6-3) and in literature (Table 6-4).

Precipitation in all binary solutions was observed at pH 12.7 suggesting a large concentration of hydroxide ions are required to initiate hydrolysis and destabilise the uranyl-citrate complex inducing precipitation. The precipitates were filtered and washed for solid state analysis. The IR spectrum on solid samples (Figure 6-44) exhibit large O-H stretches (hydroxides) along with a shift from 1690 to 1578 - 1510 cm\textsuperscript{-1} for the C=O stretch of the carboxylate moieties in comparison to “free” citric acid confirming complexation of cit\textsuperscript{3-} to UO\textsubscript{2}\textsuperscript{2+} though carboxylate moieties. The COO\textsuperscript{-} stretches are not sharp nor are they as strong as those observed in the citric acid spectrum suggesting that carboxylate moieties are in different environments.

![Figure 6-44: IR spectra of precipitates from 1:1 (blue) and 1:3 (green) UO\textsubscript{2}\textsuperscript{2+}:H\textsubscript{3}cit solutions, NaNO\textsubscript{3} (red) and H\textsubscript{3}cit (black).](image-url)
Elemental analysis on the same solid samples found high sodium and nitrate percentages with M:L ratios ranging from 1:0.4 – 1:1.2. Calculations could not fit the speciation of the solid with any species observed in solution state experiments with it most likely containing multiple species including be a polymeric array of uranyl-citrate in which citric acid and hydroxides bridge to multiple uranyl moieties.\textsuperscript{27,28} PHREEQC simulations did not predict the supersaturation of solid complexes containing citrate at any pH conflicting experimental results presenting holes in the databases.

6.10 Summary

Computational models use idealised systems to fit the experimental data. Clusters and hydrolysis have not been taken into account as this system is too complicated to model with this software at this time. Multiple experiments have demonstrated voids within the databases with well-developed ligands showing complexation to uranyl experimentally but not through PHREEQC predictions. This something which needs to be addressed as accurate speciation predictions are required by the nuclear industry.

Formation constants for uranyl hydrolysis products were calculated (Table 6-1) through potentiometric titrations and Hyperquad modelling generating values within range of literature values demonstrating reliable results can be obtained. However, these models are idealised.

Experiments with H\textsubscript{3}thme and H\textsubscript{3}tea showed no complexation to UO\textsubscript{2}\textsuperscript{2+} under conditions studied. Neither alcohol nor amine moieties were able to bind to the metal centre and hydrolysis of the uranyl was not hindered by the ligand presence.

Analysis on aqueous solutions containing H\textsubscript{3}bic and UO\textsubscript{2}\textsuperscript{2+} characterised a 1:2 (M:L) complex in which binding was through the carboxylate moiety analogous to thorium. No binding of the amine or alcohol moieties was evident suggesting a monomeric species. However, DOSY spectra display no cross-peaks suggesting polymerisation of the species whereby polymerisation is a result of hydrolysis with oxy/hydroxyl bridges. Elemental analysis also suggests polymerisation with gels produced containing multiple ratios of UO\textsubscript{2}\textsuperscript{2+}:H\textsubscript{3}bic.

\textsuperscript{1}H NMR spectroscopy shows that H\textsubscript{2}heidi\textsuperscript{−} is a tridentate ligand binding to UO\textsubscript{2}\textsuperscript{2+} through two carboxylate and one amine moieties. Potentiometric titrations reveal that the amine is
protonated in the complex and that hydrolysis commences at pH 5. The presence of a second equivalent of $\text{H}_2\text{heidi}$ stabilises $\text{UO}_2^{2+}$ in solution for a wider pH range suggesting interaction with the metal. As “free” ligand signals are displayed at all ratios in the $^1\text{H}$ NMR spectra is it assumed that an excess of $\text{H}_2\text{heidi}$ is required to form a 1:1 (M:L) complex.

Complexation of $\text{H}_3\text{NTA}$ to $\text{UO}_2^{2+}$ was confirmed by various analysis techniques with 1:1 (M:L) speciation identified. Spectroscopic data identified NTA$^{3-}$ as a tetradeutate ligand with the protonation of amine dependent upon pH. Formation constants for the 1:1 (M:L) complex and the resulting $^1\text{H}$ NMR and UV-Vis spectroscopy show the major complex is solution is a 1:1 (M:L) species which is characterised to be $(\text{UO}_2)_2(\text{cit})_2^{2-}$ by potentiometry and comparisons to literature. Hydrolysis species have been calculated (Table 6-2) and are consistent with those identified in literature.

Complexation between $\text{UO}_2^{2+}$ and $\text{H}_2\text{ADA}$ is tridentate with two carboxylate and one amine moiety involved in bonding. UV-Vis spectrometry demonstrated that two ADA$^{2-}$ ligands interact with $\text{UO}_2^{2+}$ with $^1\text{H}$ NMR spectroscopy showing “free” ligand signals when double the concentration of ligand is in solution identifying that ligands are partially bound to the metal centre. Formation constants could not be deduced.

Potentiometry showed that hydrolysis has been hindered by the complexation of $\text{UO}_2^{2+}$ to $\text{H}_3\text{cit}$ with fewer protons released compared to $\text{UO}_2^{2+}$ solutions. Formation constants of 1:1 and 1:2 (M:L) complexes were calculated and are within range of those in literature. $^1\text{H}$ NMR and UV-Vis spectroscopy show the major complex is solution is the 1:1 (M:L) species which is characterised to be $(\text{UO}_2)_2(\text{cit})_2^{2-}$ by pH experiments and comparisons to literature.

### 6.11 References


7 Plutonium

7.1 Introduction

The oxidation state of plutonium has important consequences in relation to environmental conditions. In general, Pu$^{3+}$ and Pu$^{4+}$ are relatively insoluble whereas PuO$_2^+$ and PuO$_2^{2+}$ are more soluble impacting migration to a greater extent. The insolubility of Pu$^{3+/4+}$ is largely due to their tendency to hydrolyse to form insoluble hydroxides (Pu(OH)$_3^+$ and Pu(OH)$_4$) and colloids.$^1$ However all oxidation states of plutonium exist as highly charged ions, and as such, undergo hydrolysis. The order of increasing tendency to hydrolyse is Pu$^{4+}$ > Pu$^{3+}$ > PuO$_2^{2+}$ > PuO$_2^+$. The tetravalent oxidation state in particular has the ability to be stabilised through hydrolysis, the formation of stable polymers (by formation of oxy/hydroxyl bonds) and eventually the formation of colloidal plutonium species.$^{2,3}$ This is a major problem as colloidal species can remain soluble in aqueous environments and thus can migrate long distances contaminating large areas of water and land.

The hydrolysis of plutonium is complex and commences at pH < 1 for Pu$^{4+}$.\textsuperscript{1,4} There are many possible hydrolysis species of Pu$^{4+}$ (Figure 7-1), and speciation diagrams for other oxidation states have been reported by Allard \textit{et al.}\textsuperscript{5}
As displayed in Figure 7-1 monometallics are not the only hydroxide species formed. The hydrolysis processes can form hydroxyl/oxy bridges leading to metal oligomers, clusters and aggregates of colloidal sizes depending on concentration and other constituents present (metals or organics). Relatively little is known about the structure of possible plutonium oligomers/complexes in solution compared to that of the lighter actinides and transition metals. There are however a few structures reported with recent evidence of a Pu\(^{4+}\) cluster (Figure 1-8) assembled from an aqueous solution containing glycine, the simplest amino acid.

Plutonium is unique among the actinides in the fact that it is capable of attaining multiple oxidation states (+3 to +6) in appreciable amounts simultaneously under suitable conditions. This is due to the redox potentials for the four oxidation states being very similar (< 0.1 V difference) so interconversion though disproportionation and reproportionation can readily occur. The presence of an aqueous septivalent plutonium has been reported by Krot and Gel’man but only under highly oxidising conditions, electrochemically or through radiation. The reduction of PuO\(_2\)\(^{2+}\) to Pu\(^{3+}\) with acetaldoxime (CH\(_3\)CHNOH) and hydroxyethylhydrazine (HOC\(_2\)H\(_4\)N\(_2\)H\(_3\)) in nitric acid
media has been reported along with the reduction of Pu$^{4+}$ by hyroxamic acids with the general structure (RCONHOR’). The reduction was monitored by UV-Vis-nIR spectroscopy with the production of a Pu$^{3+}$ absorption band at ~ 905 nm.$^{17}$

Each oxidation state of plutonium has a characteristic colour in solution dependant on type and number of ligands. As such, electronic absorption spectroscopy can be used to determine the oxidation state of plutonium in solution, as absorbance of the $f$-$f$ transitions is characteristic of the oxidation state. The absorption spectra of plutonium aqua ions are displayed in Figure 7-2 along with their distinctive colours.

\[ \text{Figure 7-2: Oxidation states of plutonium in aqueous solutions (left). Electronic spectra of plutonium in aqueous solutions (right). 1 M HClO}_4 \text{ except Pu(V) in NaClO}_4 \text{ at pH 7 and Pu(III) in 2.5 M NaOH.}^{1} \]

The major absorption bands associated with each plutonium oxidation state in perchloric acid medium are shown in Table 7-1.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu$^{3+}$</td>
<td>557</td>
</tr>
<tr>
<td></td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>664</td>
</tr>
<tr>
<td></td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>Pu$^{4+}$</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td>505</td>
</tr>
<tr>
<td></td>
<td>555</td>
</tr>
<tr>
<td></td>
<td>652</td>
</tr>
<tr>
<td></td>
<td>726</td>
</tr>
<tr>
<td></td>
<td>811</td>
</tr>
<tr>
<td></td>
<td>1100</td>
</tr>
<tr>
<td>PuO$_2$$^{2+}$</td>
<td>517</td>
</tr>
<tr>
<td></td>
<td>568</td>
</tr>
<tr>
<td>PuO$_2$$^{2+}$</td>
<td>831</td>
</tr>
</tbody>
</table>

Table 7-1: The characteristic absorption bands associated with each plutonium oxidation state. Pu$^{3+}$, Pu$^{4+}$ and PuO$_2$$^{2+}$ in 0.1 M HClO$_4$, PuO$_2$$^{3+}$ in 0.001 M HClO$_4$. $^{18}$
Many groups have attempted to characterise the energy states of plutonium but the $5f$
 electronic structure is still under debate.$^{19-21}$ So far, calculations using PuCl$_3$ have
 established the signature peaks of $^4L_{13/2}$ and $^4M_{15/2}$ energy levels at around 600 nm with
 $^6H_{13/2}$ at around 900 nm. Only the signal at around 1100 nm has been assigned to be $^5F_2$
 and $^5I_6$ in the absorbance spectrum of PuF$_4$ with transitions of wavelengths below 900 nm
due to multiple J states which have yet to be deconvoluted.$^{22,23}$ Most observable transitions
are likely to be from one $f$-electron energy state to another ($f$-$f$ transitions)$^{24}$ although there
may also be some $d$-$f$ transitions which are displayed in the UV-Vis spectrum. As each
oxidation state requires differing energies to excite valence electrons a unique spectrum is
produced for each.$^{1,25,26}$

## 7.2 Characterisation of Pu$^{3+}$

A pH titration of Pu$^{3+}$ was completed to demonstrate changes in the spectrum as pH is
increased (Figure 7-3). The bands observed concur with those determined previously in the
literature with characteristic bands at 557, 600 and 664 nm (see Table 7-1).$^{1,18,27}$ As pH
increases above 2, there is an increase in absorption, with the largest changes occurring at
wavelengths below 550 nm. This could be due to the presence of colloidal plutonium
species which have been shown to display large absorptions in the blue range of the
spectrum, most likely due to Rayleigh scattering of suspended particles which obstruct
bands at low wavenumbers.$^{26,28}$ The Pu$^{3+}$ spectra in Figure 7-3 are affirmed by similar
experiments which modify the concentration of nitric acid solutions.$^{29,30}$
7.2.1 Speciation of Pu$^{3+}$ with H$_3$heidi

The addition of four equivalents of H$_3$heidi (0.2 equivalents sequentially) to Pu$^{3+}$ in H$_2$O was monitored with UV-Vis-nIR spectroscopy and pH. Addition of H$_3$heidi was monitored by UV-Vis-nIR with the pH remaining constant at 1.8/9. UV-Vis-nIR spectra of the solution after the addition of each equivalent of H$_3$heidi is shown in Figure 7-4 with the general profile of Pu$^{3+}$ evident in all spectra. The UV-Vis-nIR spectra for H$_3$heidi at pH 1.03 and Hheidi$^{2-}$ at pH 7.99 are also displayed in Figure 7-4, neither show absorption at the investigated wavelengths.

There is only a minor variation in the spectra (Figure 7-4) where a shoulder appears at 675 - 698 nm on the Pu$^{3+}$ peak of 664 nm (see Table 7-1). This change is only small suggesting that H$_3$heidi does not form a Pu$^{3+}$ complex under these conditions. As the first pK$_a$ of H$_3$heidi is 1.8 (see Table 3-3) it is likely that one of the carboxylate moieties is deprotonated; therefore the shoulder formation could be due to a slight interaction with the anionic carboxylate. The observed change in the band is so small the interactions are not strong with fluxional ligands observed for thorium and uranium also a possibility (see Figure 4-15 and Figure 6-18). Complexation through strong bonds would most likely alter
the spectrum profile more severely than what is observed, such as the reported shift from 557 to 540 nm upon Pu$^{3+}$ complexation with acetohydroxamic acid. After three weeks a precipitate which was insoluble in THF, H$_2$O and ACN had formed. This was unable to be further analysed.

![UV-Vis-nIR spectra of Pu$^{3+}$ and H$_3$heidi in H$_2$O](image)

**Figure 7-4:** UV-Vis-nIR spectra of Pu$^{3+}$ and H$_3$heidi in H$_2$O. T = 25 °C; I = not controlled; [Pu$^{3+}$]$_i$ = 1.4 mM; [H$_3$heidi]$_i$ = 1.4n mM (where n = ratio); Titrant = 0.1/0.5 M NaOH.

7.2.2 Speciation of Pu$^{3+}$ with 5Me-HXTAH$_4$

The addition of four equivalents of 5Me-HXTAH$_4$ (0.2 equivalents sequentially) to Pu$^{3+}$ in H$_2$O was monitored with UV-Vis-nIR spectroscopy and pH measurement. Upon addition of colourless 5Me-HXTAH$_4$ solution there was an immediate colour change from violet to brown. This is an initial indication that a reaction/complexation has occurred and is depicted in Figure 7-5. Contrary to reactions with H$_3$heidi, 5Me-HXTAH$_4$ does not act as a pH buffer with pH increasing steadily upon ligand addition from 1.65 to 2.58. 5Me-HXTAH$_4$ is not fully deprotonated until pH 4 however two carboxylate groups are deprotonated by pH 2.5 leaving the possibility of binding to Pu$^{3+}$ though the deprotonated carboxylate groups.
The extent of complexation is indicated further through observation of UV-Vis-nIR spectra (Figure 7-6) where there are multiple alterations from the spectrum of Pu$^{3+}$ upon addition of 5Me-HXTAH$_4$. The most apparent difference is the increase in absorption at wavelengths below 700 nm as ligand is added resulting in the progressive loss of the Pu(III) peaks at 557 and 600 nm. 5Me-HXTA$_4^+$ has no absorbances within the region studied (5Me-HXTAH$_4$ at pH 1.01 and 5Me-HXTA$_4^+$ at pH 10 are shown in Figure 7-6) and work discussed previously demonstrates that pH does not alter the spectrum to such an extent (Figure 7-3). The increase in absorption at wavelengths below 700 nm can be a consequence of charge transfer between the ligand and metal upon complexation as observed for uranyl complexation. A similar charge transfer band has been reported for the iron complex [Fe(5-5Me-HXTA)(H$_2$O)$_2$] with the peak maxima incurring a red shift upon increasing pH. Other signals relevant to complexation are those at wavelengths between 664 and 747 - 831 nm (see Table 7-1).

The decrease of the Pu$^{3+}$ peak at 664 nm and the formation of a peak at 680 nm (*) are observed in the UV-Vis-nIR spectral profile after the addition of two equivalents of 5Me-HXTAH$_2^{2-}$. At three equivalents of 5Me-HXTAH$_2^{2-}$ the peak at 680 nm becomes more defined with the addition of more ligand not altering the signals. Other clear observations are the appearance of a peak at 729 nm (#) and the apparent splitting of the very broad signal between 747 - 831 nm (+).

After the addition of three equivalents of ligand, the UV-Vis-nIR spectral changes are greatly reduced in comparison to the unmistakable changes at lower ligand concentrations. The only change being the relatively small elevation of absorbance from three to four equivalents of ligand. This is most likely due to an increase in pH from 2.16 to 2.58 as...
similar attributes were observed in the Pu$^{3+}$ titration shown in Figure 7-4. Pu$^{3+}$ has been observed to have 10 coordination water molecules (see Table 1-3) and 10 coordination sites to n-C$_3$H$_7$-BTP (Figure 7-9). As three molecules of 5Me-HXTAH$_2^2$ have six coordination sites available it is likely the deprotonated carboxylate moieties are complexed to Pu$^{3+}$ creating a Pu$^{III}$(5Me-HXTAH$_2$)$_3^-$ complex with other coordination sides complexed to water molecules. Within two weeks, a precipitate had formed; however, further analysis was not obtained.

7.2.3 Speciation of Pu$^{3+}$ with salterpyH$_2$

A THF solution of salterpyH$_2$ was added to a Pu$^{3+}$ THF solution in aliquots (0.1 equivalents) until one equivalent had been reached with UV-Vis-nIR spectra recorded after each addition. The spectrum of Pu$^{4+}$ does not alter with the presence of salterpyH$_2$ in THF solution: the violet colour does not change nor does the profile of the UV-Vis-nIR spectrum indicating no complexation (Figure 7-7 - only 0.2 equivalent additions shown). The spectra of salterpyH$_2$ and salterpy$^2^-$ show absorbances below 350 nm with ε$_{\text{max}}$ reaching 30200 M$^{-1}$cm$^{-1}$. Therefore, the presence of “free” ligand is not observed in the region of
interest for Pu$^{3+}$ ions. If bound to Pu$^{3+}$ a red-shift would be expected due to charge transfer between the ligand and metal as observed with phenanthroline.$^{35}$

![UV-Vis-nIR spectra of Pu$^{3+}$ in 1 M HCl and salterpyH$_2$ in THF. T = 25 °C; I = not controlled; [Pu$^{3+}$]$_i$ = 1.4 mM; [H$_3$heidi]$_i$ = 1.4n mM (where n = ratio); Titrant = 0.1/0.5 M NaOH.](image)

After two days another spectrum of the Pu$^{3+}$ and salterpyH$_2$ solution was taken. The typical Pu$^{3+}$ spectrum is observed, but there is also the appearance of a band at 930-980 nm (*). This is not a major peak for any oxidation state of aqua coordinated or THF coordinated plutonium (see Table 7-1).$^{18,36}$
Figure 7-8: UV-Vis-nIR spectra of Pu\(^{3+}\) and salterpyH\(_2\) in 1 M HCl over a two day period. T = 25 °C; I = not controlled; [Pu\(^{3+}\)] = 1.4 mM; [H\(_3\)heidi\(_i\)] = 1.4n mM (where n = ratio); Titrant = 0.1/0.5 M NaOH.

A similar band at 939 nm has been reported by Banik et al. in the reaction of alkylated 2,6-ditriazinylpyridine (n-C\(_3\)H\(_7\)-BTP) and Pu\(^{3+}\) after extraction from a 0.1 M HNO\(_3\) and 1.9 M NH\(_4\)NO\(_3\) solution into Kerosene/1-octanol (70:30 v/v). Complexation was demonstrated with a red shift of Pu\(^{3+}\) absorbances with a major [Pu\(^{III}\)(n-C\(_3\)H\(_7\)-BTP)]\(^{3+}\) absorption band at 939 nm compared to that at 900 nm for Pu\(^{3+}\) (Figure 7-9). To further clarify that Pu\(^{3+}\) did not undergo a redox process, the extraction was repeated with trivalent americium. This also showed a distinctive red shift upon complexation to BTP suggestive of an Am\(^{3+}\) complex analogous to the Pu\(^{3+}\) complex. EXAFS spectroscopy was conducted with results establishing 10 ± 1 N atoms in the first coordination shell indicating that it is likely for three n-C\(_3\)H\(_7\)-BTP ligands to be bound to Pu\(^{3+}\) in a [Pu\(^{III}\)(n-C\(_3\)H\(_7\)-BTP)]\(^{3+}\) complex.\(^{27}\)
SalterpyH$_2$ has a N$_3$ cavity similar to that of n-C$_3$H$_7$-BTP in which Pu$^{3+}$ could be located. As the only change from a Pu$^{3+}$ spectra is the presence of a weak band at 940 nm in the presence of salterpyH$_2$ it is possible that a Pu$^{3+}$(salterpy)$^+$ complex is present but in a relatively small concentration.

7.2.4 Speciation of Pu$^{3+}$ with saldien$^{(\text{Et}_2\text{N})_2}\text{H}_2$

Saldien$^{(\text{Et}_2\text{N})_2}\text{H}_2$ was added in aliquots (0.1 equivalents) to a PuCl$_3$ solution in THF. UV-Vis-nIR spectra were recorded after each addition and for 70 minutes after the addition of one equivalent (Figure 7-10). The solution rapidly darkened upon ligand addition from violet to an intense brown colour. Due to intense absorptions at wavelengths below 900 nm it can be suggested that complexation had occurred. These absorptions increased in intensity with increasing ligand concentration; hence, absorbances above 1500 M$^{-1}$cm$^{-1}$ are not shown as they compromise the observation of lower energy bands.

Pu$^{3+}$ has a characteristic spectrum with multiple broad peaks in the visible-nIR region (see Table 7-1). After the addition of 0.5 equivalents of ligand it can be observed that the Pu$^{3+}$ peak at 662 nm shifts slightly to 659 nm (+). The broad Pu$^{3+}$ peak at 750 - 850 nm changes with a narrower peak visible between 810 - 820 nm (*) and there is the appearance of a band at 720 nm (#). These are slight alterations in the spectrum but suggest a change in bonding environment. The more noticeable modification of the Pu$^{3+}$ spectrum is the appearance of a peak at 944 nm. The signal becomes more prominent until one equivalent
of added ligand is reached. The generation of the peak at 944 nm is simultaneous with the changes noted above suggestive of complexation.

The band at 812 nm observed in the presence of saldien(\(\text{Et}_2\text{N}\))\(_2\text{H}_2\) is in a similar position to that observed in the spectrum of the \([\text{Pu}^\text{III}(n\text{-C}_3\text{H}_7\text{-BTP})_3]^3+\) complex where a shoulder is visible on the signal at 795 nm (figure 7-9). The strong absorption band at 944 nm when saldien(\(\text{Et}_2\text{N}\))\(_2\text{H}_2\) is introduced to Pu\(^{3+}\) solution is only slightly shifted to the signal at 939 nm also observed in the spectrum of \([\text{Pu}^\text{III}(n\text{-C}_3\text{H}_7\text{-BTP})_3]^3+\). This leads to the conclusion that a Pu\(^{\text{III}}\)(saldien(\(\text{Et}_2\text{N}\))\(_2\))\(^+\) complex has been formed.

![Figure 7-10: UV-Vis-nIR spectra of Pu\(^{\text{III}}\) and saldien(\(\text{Et}_2\text{N}\))\(_2\)H\(_2\) in THF. T = 25 °C; I = not controlled; [Pu\(^{\text{III}}\)]\(_i\) = 1.4 mM; [saldien(\(\text{Et}_2\text{N}\))\(_2\)H\(_2\)]\(_i\) = 1.4 mM; Titrant = 0.1/0.5 M NaOH.](image)

The increase in absorbance at wavelengths below 500 nm can be attributed to an increased concentration of saldien(\(\text{Et}_2\text{N}\))\(_2\)H\(_2\), which shows a strong absorbance below 400 nm originating from intramolecular \(\pi \rightarrow \pi^*\) transitions within the \(\pi\)-structure. Upon complexation these absorptions red shift as the ligand undergoes charge transfer to the metal. The absorption increase occurs at wavelengths reaching 900 nm suggesting more is occurring in solution than charge transfer; the increase may also be due to Rayleigh scattering of suspended particles.
When the solution is left to stand for 70 minutes, the band at 944 nm decreases in intensity (Figure 7-11). The plutonium complex formed therefore has little solubility with $\varepsilon_{\text{max}(944)}$ reducing from 1100 to 11 M$^{-1}$cm$^{-1}$ over 70 mins as precipitation occurs.

**Figure 7-11:** UV-Vis-nIR spectra of Pu$^{3+}$ and saldien$^{(Et_2N)_2H_2}$ in THF over a 70 minute period. $T = 25^\circ C; I =$ not controlled; $[\text{Pu}^{3+}] = 1.4 \text{ mM; } [\text{saldien}^{(Et_2N)_2H_2}] = 1.4 \text{ mM; Titrant } = 0.1/0.5 \text{ M NaOH.}$

### 7.3 Characterisation of Pu$^{4+}$

The UV-Vis-nIR spectrum of Pu$^{4+}$ in acidic aqueous media has a principal peak at 474 nm which is sharp and narrow with other broader characteristic bands at 542, 658 and 798 nm.$^{29,37}$ All bands except the principal peak are liable to shifting and changes in intensity upon changing HCl concentration as can be seen in Figure 7-12.$^{29}$ Analogous experiments with HNO$_3$ were also provided with shifts equivalent to those observed in HCl media suggesting they are due to changes in H$^+$ concentration not Cl$^-$ or NO$_3^-$.
Pu⁴⁺ is notable for forming oligomers and undergoing disproportionation reactions when not in concentrated acid so reactions involving Pu⁴⁺ are more problematic than the previous experiments attempted with Pu³⁺ (section 7.2).⁶,¹³ Consequently, a strong perchloric acid solution of Pu⁴⁺ was used for complexation studies even with ligands that are only soluble in organic solvents in order to hinder the immediate formation of plutonium colloids upon mixing solutions.

### 7.3.1 Speciation of Pu⁴⁺ with saldien\(^{(Et₂N)₂H₂}\)

The reaction of Pu⁴⁺ with saldien\(^{(Et₂N)₂H₂}\) was conducted by modifying the conditions used by Szigethy et al. who were successful in stabilizing a Pu⁴⁺(maltol)₄ complex (where maltol is the naturally occurring ligand 3-hydroxy-2-methylpyran-4-one) from which the solid state structure was obtained.⁳⁸ A solution of Pu⁴⁺ in 1 M HClO₄ was added to a solution of saldien\(^{(Et₂N)₂H₂}\) in THF to obtain an equimolar solution and UV-Vis-nIR spectra recorded.

After initial mixing, the UV-Vis-nIR spectrum displays high absorption at wavelengths below 600 nm (Figure 7-13); this is likely to be due to charge transfer between ligand and metal. A band at 620 nm (#) forms upon addition along with a shift of the Pu⁴⁺ band in 1 M HClO₄ at 658 to 652 nm (*) and a shift and narrowing of the Pu⁴⁺ band between 725 - 830 nm to 811 nm (+).
The high absorbance below 600 nm, the shift in signals and the emergence of new signals is similar to that displayed in a Pu$^{IV}$($^\text{Aracnac}$)$_4$ complex ($^\text{Aracnac}$ = Ar(3,5-$^\text{Bu}_2$C$_6$H$_3$)NC(Ph)CHC(Ph)O) and in a [Pu(4-6-bis(diphenylphosphinoylmethyl)-dibenzofuran)Cl$_4$].THF complex both formed in THF. Both complexes were also structurally characterised by $^1$H NMR spectroscopy and single crystal XRD confirming complexation. Therefore it is possible a [Pu$^{IV}$saldien$^{(Et_2N)}_2$]$^{2+}$ complex exists in solution.

![Figure 7-13: UV-Vis-nIR spectra of Pu$^{4+}$ and saldien$^{(Et_2N)}_2$H$_2$ in THF. T = 25 °C; I = not controlled; [Pu$^{4+}$] = 1.4 mM; [saldien$^{(Et_2N)}_2$H$_2$] = 1.4 mM; Titrant = 0.1/0.5 M NaOH.](image_url)

After 22 hours, the UV-Vis-nIR spectrum of Pu$^{4+}$ with saldien$^{(Et_2N)}_2$H$_2$ solution had a dramatic change in the spectrum compared to that obtained immediately after mixing with Pu$^{4+}$ peaks no longer visible, but a spectral profile characteristic of Pu$^{3+}$ is observed. The Pu$^{3+}$ spectrum obtained is similar to those in literature (see Table 7-1). As the reduction of Pu$^{4+}$ to Pu$^{3+}$ does not occur in THF solutions, it is presumably caused by the ligand. The reduction of Pu$^{4+}$ to Pu$^{3+}$ has been reported in literature both under hydrothermal conditions and in the presence of hydroxamic acids in nitric acid solution. Cyclic voltammetry of an aqueous solution containing Pu$^{4+}$ and DPTA (diethylenetriaminepentaacetic acid) showed the reversibility of the Pu$^{4+}$/Pu$^{3+}$ couple and demonstrated the presence of a Pu$^{III}$(DPTA)$^2-$ complex. This reduction property has also been observed in other complexes such as Pu(EDTA)(OH)$^+$.33
As saldien\(^{(Et_2N)_2}\)H\(_2\) has a large \(\pi\)-framework, when complexed it may be able to donate electrons to the metal driving the reduction. In contrast to conventional Pu\(^{3+}\) spectra there is a peak at 944 nm in the presence of ligand (Figure 7-13). This band is in the same location as the band observed in the reaction with Pu\(^{3+}\) in section 7.2.4 and relates to the band observed in the [Pu\(^{III}\)(n-C\(_3\)H\(_7\)-BTP)\(_3\)]\(^{3+}\) complex (Figure 7-3 suggesting the band is due to the presence of a [Pu\(^{III}\)saldien\(^{(Et_2N)_2}\)]\(^{+}\) complex.

### 7.4 Characterisation of PuO\(_2\)\(^{2+}\)

PuO\(_2\)\(^{2+}\) has all organic ligand complexation in the equatorial plane. Organic complexes of PuO\(_2\)\(^{2+}\) are generally more soluble than Pu\(^{3+}\) and Pu\(^{4+}\) counterparts, but due to the charge being spread over the O=Pu=O unit as opposed to the metal alone the charge density is smaller and so generally form thermodynamically less stable complexes.\(^1\) The absorption spectrum of aquated PuO\(_2\)\(^{2+}\) displays a prominent band at 831nm with two smaller bands associated with PuO\(_2\)\(^{2+}\) between 930 and 1000 nm.\(^{18,29,44}\)

#### 7.4.1 Speciation of PuO\(_2\)\(^{2+}\) with salterpyH\(_2\)

A solution of salterpyH\(_2\) was added in aliquots to a PuO\(_2\)\(^{2+}\) solution in THF (0.4 equivalents initially followed by 0.2 equivalents until a total of one equivalent was reached). UV-Vis-nIR spectra were recorded after each addition and for 24 hours after complete addition.

Upon the addition of salterpyH\(_2\) to PuO\(_2\)\(^{2+}\), there is an appearance of a shoulder at 844 nm. This band is red shifted by 14 nm in comparison to the characteristic PuO\(_2\)\(^{2+}\) band at 830 nm (Figure 7-14) suggesting a complex had formed.\(^{45}\) The decrease of the PuO\(_2\)\(^{2+}\) band at 830 nm synchronised with the increase of a band at higher wavelengths (840 nm) has been reported for several PuO\(_2\)\(^{2+}\) complexes including Pu\(^{VI}\)O\(_2\)(TMMA)\(^{-}\) (TMMA = N,N,N',N'-tetramethylmalonamide),\(^{45}\) acetato complexes\(^{44}\) and plutonium(VI) pertechnetates\(^{46}\) implying the formation a Pu\(^{VI}\)O\(_2\)(salterpy) complex.
Figure 7-14: UV-Vis-nIR spectra of PuO$_2^{2+}$ and salterpyH$_2$ in THF. $T = 25 \degree C$; $I$ = not controlled; 
$[\text{Pu}^{3+}]_i = 1.4 \text{ mM}$; $[\text{salterpyH}_2]_i = 1.4n \text{ mM}$ (where $n$ = ratio); 
Titrant = 0.1/0.5 M NaOH.

Although the PuO$_2^{2+}$ band at 831 nm shows a reduction in absorption upon addition of salterpyH$_2$ the band at 844 nm does not increase as might be expected for a 1:1 species.$^{46}$ This could be due to weak complexation effects between plutonyl and salterpyH$_2$ similar to those reported when complexed to TMMA$^{45}$ or may suggest the formation of a 1:2 complex.

Spectra recorded over a 24 hour period (Figure 7-15) display a reduction of both plutonium bands within the 825 - 860 nm region. There is also the presence of some precipitate implying that the complex is insoluble. Two weeks after the addition a larger quantity of precipitate was present; a UV-Vis-nIR spectrum was run on the agitated solution. In this spectrum, the profile showed no evidence of PuO$_2^{2+}$ bands, nor any characteristic bands that correspond to other plutonium oxidation states in aqueous or THF solutions (see Table 7-1). There is however, a noticeable band at 942 nm. Assignment of this band to a particular oxidation state is difficult because other characteristic bands may be hidden in the high base line.

This absorbance is in a similar range to the band observed in the titration of Pu$^{3+}$ with salterpyH$_2$ (Figure 7-8) and $[\text{Pu}(n-$C$_3$H$_7$BTP)$_3]^{3+}$ (Figure 7-9),$^{27}$ suggesting the reduction
of PuO$_2^{2+}$ over a two week period to Pu$^{3+}$. Results suggest the formation of a [Pu$^{3+}$saltdien$^{(Et_2N)_2}$]+ complex.

To further aid in species determination, the PuO$_2^{2+}$ and salterpyH$_2$ reaction was repeated but scaled up fourfold. After one hour a brown precipitate/suspension was formed which is shown in Figure 7-16. The supernatant was removed and the precipitate filtered and washed with THF. The solid was dissolved in pyridine and left to crystallise by slow evaporation and vapour diffusion with diethyl ether, THF, ethanol, methanol or acetonitrile (Figure 7-16). After six weeks, crystals were apparent in the vapour diffusion vial with diethyl ether along with precipitate. However, there was limited access to instrumentation because of operational restrictions at the time of the visit preventing further examination of both crystals and precipitate.
7.4.2 Speciation of PuO$_2^{2+}$ with saldien$^{(Et_2N)_2H_2}$

Saldien$^{(Et_2N)_2H_2}$ was introduced to a THF solution of PuO$_2^{2+}$ in aliquots of 0.2 equivalents until one equivalent was attained. UV-Vis-nIR spectra were recorded after each addition and at 24 hours after complete addition.

Upon addition of saldien$^{(Et_2N)_2H_2}$ the plutonium solution darkened, which is suggestive of complexation. The UV-Vis-nIR spectra (Figure 7-17) shows that as saldien$^{(Et_2N)_2H_2}$ is introduced, a band at 847 nm immediately appears. Simultaneously the intensity of the major PuO$_2^{2+}$ band at 831 nm reduces. There are also alterations at higher wavelengths with the band at 950 nm diminishing into baseline and the band at 984 nm shifting to 994 nm. All of these differences imply the formation of a new PuO$_2^{2+}$ complex and the decrease of “free” PuO$_2^{2+}$ concentration in solution.
When the UV-Vis-nIR spectra of the [Pu\textsuperscript{VI}O\textsubscript{2}Cl\textsubscript{2}(Ph\textsubscript{3}PO)\textsubscript{2}] is compared to that of [Pu\textsuperscript{VI}O\textsubscript{2}Cl\textsubscript{2}(thf)\textsubscript{2}]\textsuperscript{2+} a shoulder on the characteristic PuO\textsubscript{2}\textsuperscript{2+} band at 860 nm is observed. Characterisation of the complexes with multinuclear NMR, IR and UV-Vis-nIR spectroscopies and single crystal XRD have confirmed the structural differences between the complexes.\textsuperscript{47} These reported bands complement those observed in the reaction of PuO\textsubscript{2}\textsuperscript{2+} with saldien\textsuperscript{(Et\textsubscript{2}N)\textsubscript{2}H\textsubscript{2}} implying the formation of a Pu\textsuperscript{VI}O\textsubscript{2}(saldien\textsuperscript{(Et\textsubscript{2}N)\textsubscript{2}}) complex.

The band at 847 nm (complex PuO\textsubscript{2}\textsuperscript{2+} peak) is more prominent than the band detected with salterpyH\textsubscript{2} indicating that more PuO\textsubscript{2}\textsuperscript{2+} was complexed by (saldien\textsuperscript{(Et\textsubscript{2}N)\textsubscript{2}})\textsuperscript{2-}. As little “free” PuO\textsubscript{2}\textsuperscript{2+} is observed after the addition of 1 equivalent of saldien\textsuperscript{(Et\textsubscript{2}N)\textsubscript{2}H\textsubscript{2}}, a 1:1 (M:L) complex is implied. It is likely that (saldien\textsuperscript{(Et\textsubscript{2}N)\textsubscript{2}})\textsuperscript{2-} binds in a pentatentate manner through the N\textsubscript{3}O\textsubscript{2} cavity forming a charge neutral complex compared to the 1:2 (M:L) species suggested in complexation with salterpy\textsuperscript{2-} which would bind through two phenolic oxygen atoms.

However, the soluble Pu\textsuperscript{VI}O\textsubscript{2}(saldien\textsuperscript{(Et\textsubscript{2}N)\textsubscript{2}}) species was not long lived; overnight scans were able to monitor the decrease in intensity of bands (Figure 7-18). After two hours there is an appreciable decrease in soluble PuO\textsubscript{2}\textsuperscript{2+} concentration (52.7 % reduction); within six hours the solubility of the complex drops significantly.
hours both PuO$_2$$^{2+}$ bands had blended into the baseline. The UV-Vis-nIR spectrum shows no evidence of PuO$_2$$^{2+}$ in solution after 10 hours, but a precipitate had formed.

The UV-Vis-nIR of the agitated solution displays a prominent band at 944 nm which, as the precipitate settles, is reduced into baseline. The agitated spectrum has no clear typical features usually associated with any plutonium oxidation state in THF, but does complement the band observed in the reaction between Pu$^{3+}$ and saldien$^{(Et_2N)_2}H_2$ suggesting a similar complex is formed.

![Figure 7-18: UV-Vis-nIR spectra of PuO$_2$$^{2+}$ and saldien$^{(Et_2N)_2}H_2$ in THF over an 18 hour period (top); solution of PuO$_2$$^{2+}$ with saldien$^{(Et_2N)_2}H_2$ immediately after titration (bottom left), solution of PuO$_2$$^{2+}$ with saldien$^{(Et_2N)_2}H_2$ after 18 hours (bottom right). $T = 25$ °C; $I$ = not controlled; [Pu$^{3+}$]$_i$ = 1.4 mM; [saldien$^{(Et_2N)_2}H_2$]$_i$ = 1.4n mM (where n = ratio); Titrant = 0.1/0.5 M NaOH.](image)
The reduction of metal ions by ligands has been reported on numerous occasions not only in relation to the actinides (e.g. PuO$_2^{2+}$ to Pu$^{3+}$ on reaction with organic ligands containing amine and oxime$^{15,16}$ and NpO$_2^{2+}$ to NpO$_2^{+}$ upon complexation to saldien$^{(\text{Et}_2\text{N})_2\text{H}_2}$ but also with lanthanides (e.g. the reduction of Ln(III) to Ln(II) with pseudo-macrocyclic ligands$^{48}$) and the d-block (e.g. Mn, Co, Fe and Ni$^{49,50}$). Reducing ligands are often used to stabilise low oxidation states and as such many low oxidation state starting materials contain halides.$^{36,51}$

Further investigation was warranted so the reaction was repeated on a larger scale (Figure 7-19) with the resulting solution a dark brown colour. Crystallization was attempted using slow evaporation and vapour diffusion techniques. Unfortunately crystallization attempts were unsuccessful resembling the results of similar experiments with neptunium ions.$^{34}$

![Picture of PuO$_2^{2+}$ stock solution (left) and solution one hour after reaction of PuO$_2^{2+}$ with (saldien$^{(\text{Et}_2\text{N})_2\text{H}_2}$ (right).]

**Figure 7-19: PuO$_2^{2+}$ stock solution (left) and solution one hour after reaction of PuO$_2^{2+}$ with (saldien$^{(\text{Et}_2\text{N})_2\text{H}_2$.**

### 7.5 Summary

Simple amine and carboxylic acid molecules showed differing success rates when combined with plutonium. There was no indication of complexation when H$_3$heidi was reacted with Pu$^{3+}$. UV-Vis-nIR spectroscopy indicated the formation of a Pu$^{3+}$ complex with 5Me-HXTAH$_2^{2-}$ which could either be monomeric or bridge multiple Pu$^{3+}$ ions. The increased number of ligands complexed to plutonium hence increased number of coordination sites compared to the thorium complex (Na$_5$[Th$_3$(μ$_3$-O)(5Me-HXTA)$_3$].12H$_2$O) reported at pH 4.3$^{32}$ can be rationalised by the increased ionic radius of
Pu$^{3+}$ (1.16 Å)$^{52}$ compared to Th$^{4+}$ (1.05 Å)$^{12}$ and thus an increased coordination number is required to satisfy the coordination sphere.

The pseudo-macrocyclic ligands investigated showed varying levels of complexation. Using UV-Vis-nIR spectroscopy a shoulder on the major PuO$_2^{2+}$ peak was observed when reacted with salterpyH$_2$ in THF. The “free” PuO$_2^{2+}$ band was observed after the addition of one equivalent of salterpyH$_2$ indicating that the ligand did not complex to all plutonium in solution suggesting the formation of a 1:2 PuO$_2^{2+}$:satpy$^{2-}$ complex. This complex was stable in solution for two weeks before a precipitate formed and UV-Vis-nIR spectrum displayed a band at 944 nm. However, when salterpyH$_2$ was added to a Pu$^{3+}$ solution in THF, no evidence of complexation was observed with no change in the UV-Vis-nIR spectrum.

Complexation of PuO$_2^{2+}$ by saldien$^{(Et_2N)_2}H_2$ was observed using UV-Vis-nIR spectroscopy. A decrease of the main solvent coordinated PuO$_2^{2+}$ band at 832 nm and an increase of a shoulder at 846 nm were observed. As there is little “free” PuO$_2^{2+}$ remaining in solution, the formation of an equimolar complex [Pu$^{VI}_2$O$_2$(saldien$^{(Et_2N)_2}$)] was implied. Within 24 hours a precipitate formed with the appearance of a band at 944 nm. The reaction of saldien$^{(Et_2N)_2}H_2$ with Pu$^{3+}$ in THF generated UV-Vis-nIR spectra in which wavelengths below 900 nm had high intensity of absorption masking characteristic oxidation state bands. Upon the addition of saldien$^{(Et_2N)_2}H_2$ a band at 944 nm emerged with increasing intensity with increasing ligand concentration. When saldien$^{(Et_2N)_2}H_2$ is reacted with Pu$^{4+}$ some minor changes are seen compared to the aquated Pu$^{4+}$ spectrum. Within 24 hours the Pu$^{4+}$ is reduced to Pu$^{3+}$ with a small peak at 944 nm.

Reactions of saldien$^{(Et_2N)_2}H_2$ with all oxidation states of plutonium display a band at 944 nm after a maximum of two weeks. The reaction of salterpyH$_2$ with PuO$_2^{2+}$ also displayed a band at 944 nm. This band has been reported for the Pu$^{III}_3$(n-C$_3$H$_7$-BTP)$^{3+}$ complex and as such implies the band at 944 nm is due to the presence of Pu$^{3+}$ complex. If this is the case, it has been shown that pseudo-macrocyclic ligands have the ability to reduce plutonium from a +6 oxidation state to +3 to form [Pu$^{III}_3$L]$^+$ complexes where L = salterpy$^{2-}$ or (saldien$^{(Et_2N)_2}$)$^{2-}$. Further analysis is required to confirm this.

7.6 References

# Conclusions and Future Work

## 8.1 Conclusions

The aqueous speciation of Th\(^{4+}\), U\(^{4+}\) and UO\(_2^{2+}\) with and without the presence of small organic ligands has been investigated with a summary of complexation and calculated formation constants shown in Table 8-1.

<table>
<thead>
<tr>
<th>Organic ligand</th>
<th>Metal</th>
<th>Th(^{4+})</th>
<th>U(^{4+})</th>
<th>UO(_2^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Complexation (M,L,H)/(M:L)</td>
<td>Calculated formation constant</td>
<td>Complexation (M,L,H)/(M:L)</td>
<td>Calculated formation constant</td>
</tr>
<tr>
<td>H(_3)thme</td>
<td>1,0,0</td>
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<td>1,0,0</td>
<td>0</td>
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<tr>
<td></td>
<td>1,0,-1</td>
<td>-4.09 ± 0.4</td>
<td>1,0,-1</td>
<td>2.50 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>1,0,-2</td>
<td>-7.88 ± 0.4</td>
<td>1,0,-2</td>
<td>-1.28 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>2,0,-2</td>
<td>-4.54 ± 0.4</td>
<td>1,0,-3</td>
<td>-6.745 ± 0.2</td>
</tr>
<tr>
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<td>-23.17 ± 0.4</td>
<td>1,0,-4</td>
<td>-11.12 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>4,0,-8</td>
<td>-18.62 ± 0.4</td>
<td>6,0,-15</td>
<td>-8.70 ± 0.2</td>
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<tr>
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<td>6,0,-15</td>
<td>-36.76 ± 0.4</td>
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<td></td>
</tr>
<tr>
<td>H(_3)tea</td>
<td>negligible</td>
<td>-</td>
<td>negligible</td>
<td>-</td>
</tr>
<tr>
<td>H(_3)bic</td>
<td>1:3 monodentate</td>
<td>-</td>
<td>1:3 monodentate</td>
<td>-</td>
</tr>
<tr>
<td>H(_3)heidi</td>
<td>1:2 tridentate</td>
<td>-</td>
<td>1:1 tridentate</td>
<td>-</td>
</tr>
<tr>
<td>H(_3)NTA</td>
<td>1:2 tridentate</td>
<td>1:1 tridentate</td>
<td>-</td>
<td>1:1 tridentate</td>
</tr>
<tr>
<td></td>
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<td>11.95 ± 0.4</td>
<td>15.41 ± 0.7</td>
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<td>1,1,-1</td>
<td>24.90 ± 0.7</td>
<td>15.19 ± 0.4</td>
<td></td>
</tr>
<tr>
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<td>1,2,0</td>
<td>15.19 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)ADA</td>
<td>1:2 tridentate</td>
<td>1:1 sparingly soluble</td>
<td>-</td>
<td>1:1 tridentate</td>
</tr>
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<td></td>
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<td>7.40 ± 0.7</td>
<td>19.29 ± 0.7</td>
<td>6.92 ± 0.8</td>
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<td>5.77 ± 0.7</td>
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<tr>
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<td>1:1 tridentate</td>
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<td>1:1 tridentate</td>
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</tr>
<tr>
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<td>1,1,0</td>
<td>22.56 ± 1.5</td>
<td>13.95 ± 1.5</td>
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</tr>
<tr>
<td></td>
<td>2,1,-1</td>
<td>6.92 ± 1.5</td>
<td>13.95 ± 1.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 8-1: Calculated formation constants and observed complexation of selected actinides with and without small organic ligands in aqueous solution.
Chapter 3 details the solution state characterisation of the organic ligands: \(H_3\text{thme}\), \(H_3\text{tea}\), \(H_3\text{bic}\), \(H_3\text{heidi}\), \(H_3\text{NTA}\), \(H_2\text{ADA}\) and \(H_3\text{cit}\). pKa values of 8.27 ± 0.1 (\(H_3\text{tea}\)), 2.46 and 8.36 ± 0.22 (\(H_3\text{bic}\)), 2.22 and 8.53 ± 0.9 (\(H_3\text{heidi}\)), 1.90, 2.37 and 9.19 ± 0.2 (\(H_3\text{NTA}\)), 2.24 and 6.59 ± 0.3 (\(H_2\text{ADA}\)), 2.68, 4.10 and 5.29 ± 0.2 (\(H_3\text{cit}\)) were determined by fitting potentiometric titrations in the Hyperquad software suite.

Work in chapters 4, 5 and 6 details the determination of the formation constants for aqueous hydrolysis species of \(\text{Th}^{4+}\), \(\text{U}^{4+}\) and \(\text{UO}_2^{2+}\) (Table 8-1). The values determined for \(\text{U}^{4+}\) are less reliable than the others due its tendency to form colloidal species.

The work has shown that the ligands \(H_3\text{thme}\) and \(H_3\text{tea}\) complex in insignificant quantities to \(\text{Th}^{4+}\) or \(\text{UO}_2^{2+}\) under the conditions studied. The binding sites in these ligands comprise of alcohol and amine functional groups showing that for the actinides studied under the conditions used in this thesis alcohol based ligands are not strong complexants; this may have important implications for storage pond chemistry.

The complexation of \(H_3\text{bic}\) to \(\text{Th}^{4+}\) and \(\text{U}^{4+}\) in aqueous solutions observed the formation of a 1:3 (M:L) species with \(\text{Th}^{4+}\) and \(\text{U}^{3+}\) in solutions at pH < 6.2 and < 11.8 respectively. Whereas with \(\text{UO}_2^{2+}\) a 1:2 (M:L) speciation was observed in solutions at pH < 5.7. Fewer \(H_3\text{bic}\) molecules complex to \(\text{UO}_2^{2+}\) as bonding is only in the equatorial plane. In all cases, complexation with the ligand was monodentate through the carboxylate function demonstrating the importance of a carboxylate group in actinide binding as this is the only difference between \(H_3\text{tea}\) and \(H_3\text{bic}\).

\(H_3\text{heidi}\) has two carboxylate functions making it more carboxylate rich than \(H_3\text{bic}\). This ligand formed a 1:2 (M:L) complex with \(\text{Th}^{4+}\) at pH < 11. With \(\text{U}^{4+}\) and \(\text{UO}_2^{2+}\) a 1:1 (M:L) complex formed at pH < 11 and pH < 10 respectively, when the ligand is in a twofold excess. Potentiometric titrations, \(^1\text{H}\) NMR and UV-Vis spectroscopy show that the ligand binds in a tridentate fashion through the carboxylates and the central nitrogen moiety. This reinforces the importance of the carboxylate function in the ligand when considering its potential to bind to actinides.

A 1:1 and 1:2 (M:L) complexation of \(H_3\text{NTA}\) to \(\text{Th}^{4+}\) was observed at pH < 10 and 1:1 (M:L) complexation to \(\text{U}^{4+}\) at pH < 5. In \(\text{U}^{4+}\) spectra between pH 5 – 10, ligands are released into the solution suggesting that the \(\text{U}^{4+}\) is hydrolysing and polymerisation is occurring. The precipitation of uranium hydroxide species occurs at pH 10.5 and above. For \(\text{UO}_2^{2+}\) solutions, a 1:1 (M:L) complex was identified at pH < 7 in equimolar solutions.
and at pH < 10 in solutions containing excess ligand. Formation constants were calculated for the Th⁴⁺, UO₂²⁺ complexes in Hyperquad using potentiometric data (Table 8-1).

In comparison to H₃NTA, H₂ADA replaces a carboxylate group with an amide group. Experiments with Th⁴⁺ show that a 1:2 (M:L) complex is formed at pD < 7 with the ligand bound in a tridentate fashion through the central nitrogen and two carboxylate moieties whereas between pH 7 – 9.5 the ligand is bound in a monodentate fashion through a carboxylate moiety. In the case of UO₂²⁺ a 1:2 (M:L) complex was formed at pH < 10 with the ligand bound tridentate though the central nitrogen and two carboxylate moieties. However, with U⁴⁺ immediate precipitation was observed. Formation constants for the 1:1 and 1:2 (M:L) Th⁴⁺ complexes were calculated in Hyperquad using potentiometric data (Table 8-1).

H₃cit contains an alcohol and three carboxylate moieties providing more multi-metal binding modes. In aqueous solutions of Th⁴⁺ and U⁴⁺, a 1:1 (M:L) speciation was observed at pH < 11.8 and pH < 9 respectively, however, denticity could not be established. In U⁴⁺ solution between pH 9 - 13 the formation of soluble polymeric species was observed. Studies show that both 1:1 and 1:2 (M:L) complexes were formed with UO₂²⁺ at pH < 13. Formation constants for the 1:1 and 1:2 UO₂²⁺ complexes and resulting hydrolysis species were calculated in Hyperquad using potentiometric data (Table 8-4).

The work presented in this thesis found gaps in the LLNL, Hatches-20 and SIT databases which are regularly used for predictions of actinides in the nuclear industries. Only the SIT database predicted complexation of U⁴⁺ to H₃NTA. Whereas for Th⁴⁺, U⁴⁺ and UO₂²⁺ with H₃cit, the SIT and LLNL databases were unable to predict complexation; this was done in PHREEQC using the Hatches-20 database. Therefore, the Hatches-20, SIT and LLNL databases need continually updating with current data to provide accurate predictions.

Solutions state studies between Pu³⁺ and H₃heidi showed weak interactions, however with 5Me-HXTAH₄ new bands were observed in the UV-Vis spectra confirming that complexation had occurred. This demonstrates that 5Me-HXTAH₄ is a better ligand than H₃heidi for complexing Pu³⁺ under the conditions studied.

The appearance of a band at ~945 nm in the UV-Vis showed that complexation of Pu³⁺ by salterpyH₂ occurs only after two days whereas, with saldiene(Et₂N)₂H₂ complexation is instant. New bands were observed in the spectra of Pu⁴⁺ and saldiene(Et₂N)₂H₂ solutions suggesting complexation. However, this was short-lived with plutonium being reduced to
“free” Pu\(^{3+}\) within 24 hrs. Reactions of PuO\(_2\)\(^{2+}\) with salterpyH\(_2\) and saldiene\(^{(Et_2N)_2}H\(_2\) showed complexation with new bands appearing initially at 840 and 860 nm respectively. In the PuO\(_2\)\(^{2+}\) salterpyH\(_2\) solution a further band at 942 nm appeared after 2 weeks and in the PuO\(_2\)\(^{2+}\) saldiene\(^{(Et_2N)_2}H\(_2\) solution at 944 nm after 18 hrs. Bands at \sim 945 nm are observed in spectra of Pu\(^{3+}\) and PuO\(_2\)\(^{2+}\) solutions containing salterpyH\(_2\) and saldiene\(^{(Et_2N)_2}H\(_2\) which have been ascribed to a Pu(L\(^{+}\) species.

The work in this thesis has shown that the solution speciation of the actinide ions are extremely complex and that the presence of organic species complicates this speciation further. Whilst full characterisation of solution speciation is not possible at this time some general conclusions can be drawn. Simple polyol ligands seem to be unimportant in solution state binding under the wide range of conditions studies here, however once carboxylate and amine functionalities are included in the ligands, complexation and hence a change in speciation is observed. This will have important consequences for understanding the solution state chemistry of the fuel storage ponds.

### 8.2 Future work

Further characterisation of the soluble species needs to be conducted using \(^{15}\)N NMR spectroscopy to confirm complexation through amine moieties and EXAFS to determine coordination number and hence inner coordination sphere of the species. If these methods proved polymerisation and cluster formation within the solutions analysis using scanning electron microscopy would allow the determination of size and formation of colloids/clusters. Although solid precipitates were collected, further analysis including powder XRD, Raman spectroscopy, EXAFS and TGA are required to identify their speciation.

Repeats of potentiometric titrations along with the analysis of solutions at various concentrations and ionic strengths would validate calculated formation constants and allow accurate calculations of constants at multiple ionic strengths. Experiments at multiple pressures and temperatures would also be beneficial allowing more variance of experimental conditions to “real-life” conditions.

Conformation of complexation with plutonium could be better assessed using multinuclear NMR spectroscopy. Crystals were grown from a Pu\(^{VI}\)O\(_2\)–(salterpy) solution leading to the possibility of single crystal XRD analysis to determination complexation modes. Analysis
of solid precipitates by IR/Raman Spectroscopy would also obtain data for the possible complexes formed.